HALFSANDWICH TUNGSTEN COMPLEXES WITH A SILANOL-FUNCTIONALIZED CYCLOPENTADIENYL LIGAND

- SYNTHESIS AND REACTIVITY -

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Diese Arbeit ist meinen Eltern gewidmet.

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ANNOTATIONS

♦ The following work is subdivided into seven separated chapters.

♦ High-ranked, arabic numerals in angular brackets refer to the references at the end of each chapter.

♦ High-ranked, arabic numerals refer to footnotes at the bottom of the text.

♦ Numbers in bold type refer to synthesized and characterized compounds.

♦ Capitel letters in bold type refer to synthesized intermediates.

♦ Arabic numerals in round brackets refer to equations and reaction mechanisms.

♦ Following abbreviations are used:

Ar	=	aryl
t-Bu	=	*tert*-butyl
i-Bu	=	*iso*-butyl
Cp	=	η^5-cyclopentadienyl
C_5Me_4	=	η^5-tetramethylcyclopentadienyl
d	=	day
DMD	=	dimethyldioxirane
DME	=	dimethoxyethane
dppm	=	1,2-bis(diphenyl)phosphino-methane
e.g.	=	for example
E	=	element
Et	=	ethyl
Fc	=	ferrocenyl
h	=	hour
L	=	ligand
LDA	=	lithiumdi-*iso*propylamide
M	=	metal

MAS	=	magic angle spinning
m	=	*meta*
min.	=	minute
Me	=	methyl
NMR	=	nuclear magnetic resonance
n	=	*neo*
o	=	*ortho*
p	=	*para*
PE	=	petrolether (50 – 70)
i-Pr	=	*iso*-propyl
Ph	=	phenyl
R	=	substituent
sec.	=	secondary
tert.	=	tertiary
TMEDA	=	tetramethylethylendiamine
THF	=	tetrahydrofuran
VACP	=	variable amplitude cross polarization
vs.	=	versus
X	=	halide

LIST OF PUBLICATIONS

1. "Bis-metallated Silanols and Siloxanes"
    M. Vögler, H. Bera, M. Nieger, W. Malisch, 1st European Silicon Days München **2001**.

2. "Synthesis and Reactivity of Functionalized Silylated Cyclopentadienyl Metal Complexes of the Chromium Group"
    H. Bera, A. Sohns, W. Malisch, 1st European Silicon Days (München **2001**), Abstract P 63.

3. "Tungsten-silanols with η^5-Cyclopentadienyl-Spacer"
    H. Bera, W. Malisch, 2nd European Silicon Days (München **2003**), Abstract P 99.

4. "Halfsandwich Complexes of Iron and Tungsten with Silanol-functionalized Cyclopentadienyl Ligand"
    A. Sohns, H. Bera, D. Schumacher, W. Malisch, in *Organosilicon Chemistry: From Molecules to Materials*, Vol. V (Hrsg.: N. Auner, J. Weis), VCH, Weinheim **2003**, S. 486.

5. "Transition Metal Fragment-substituted Silanols of Iron and Tungsten – Synthesis, Structure, and Condensation Reactions"
    W. Malisch, M. Hofmann, M. Vögler, D. Schumacher, A. Sohns, H. Bera, H. Jehle, in *Silicon Chemistry – From the Atoms to Extended Systems*, (Hrsg.: P. Jutzi, U. Schubert), VCH, Weinheim **2003**, S. 348.

6. "Halfsandwich Complexes of Tungsten with Silyl-functionalized Cyclopentadienyl Ligand"
    H. Bera, A. Sohns, W. Malisch, in *Organosilicon Chemistry: From Molecules to Materials*, Vol. VI (Hrsg.: N. Auner, J. Weis), VCH, Weinheim **2004**, *submitted*.

7. "Metal- and Cyclopentadienyl-bound Silanol Groups in Tungsten Complexes"
H. Bera, S. Schmitzer, D. Schumacher, W. Malisch, in *Organosilicon Chemistry: From Molecules to Materials*, Vol. VI (Hrsg.: N. Auner, J. Weis), VCH, Weinheim **2004**, *submitted*.

8. "Synthesis and Reactivity of Halfsandwich Tungsten Hydrido and Chloro Complexes with η^5-Cyclopentadienyl-bound Silanol Function"
H. Bera, A. Sohns, W. Malisch, *Eur. J. Inorg. Chem.*, *in preparation*.

INTRODUCTION

The attachment of homogeneous transition metal catalysts to insoluble supports offers the opportunity of extending their usefulness particularly with regard to industrial applications. Consequently, there has been considerable interest in this area over the last few decades [1-15]. The heterogenation offers the possibility to combine the most advantageous properties of both homogenous and heterogenous systems [1-3, 6, 7, 9, 13-19]. As support system for organometallic catalysts, both organic and inorganic support materials offer specific advantages. Organic polymers, such as cross-linked polystyrenes, provide a fairly well-defined enviroment for organometallic species attached to their surface; silica gel surfaces on the other hand, while less exactly characterized in terms of their structure and reactivity offer distinct advantages in chemical inertness, thermal stability and easy separation from the reaction mixture.

Transition metal substituted siloxanes represent attractive model compounds for catalytically active transition metal complexes anchored on silica surfaces [20-23]. They offer an opportunity to determine the reaction mechanisms of heterogenous catalyzed reactions on a molecular level in order to improve the selectivity, activity and lifetime of a heterogenous catalyst. As a consequence many of those model compounds have been synthesized in the last few years often starting from stable organosilanetriols [24-28] or incompletely condensed silsesquioxanes [29-36] which can react with various metal complexes resulting in the formation of metallo-siloxanes with the structural unit $L_nM-O-Si$, i.e. a silanolate ligand sphere around the transition metal center.

ORGANOSILANOLS

It is rooted in their important role as intermediates in the technical synthesis of silicones, that organosilanols of the general type $R_{4-n}Si(OH)_n$ (R = alkyl, aryl; n =1-3) have been the subject of extensive studies concerning intermolecular condensation of these species to give polysiloxanes [37]. This tendency rises with temperature and

the number of OH groups as well as with decreasing steric demand of the organic substituents. Therefore, the isolation especially of silanediols or silanetriols has been achieved preferentially with bulky organic ligands and by using special reaction conditions [38].

For example, the group of *Roesky* synthesized a series of silanetriols ArN(SiMe$_3$)-Si(OH)$_3$ [39] (Ar = 2,6-Me$_2$-C$_6$H$_3$, 2,6-*i*-Pr$_2$-C$_6$H$_3$, 2,4,6-Me$_3$-C$_6$H$_2$, 2-*i*-Pr-6-Me-C$_6$H$_3$) and 2,4,6-*t*-Bu$_3$C$_6$H$_2$-O-Si(OH)$_3$ [40] with sterical very demanding amino- and alkoxysubstitutents at the silicon atom. More recently, the silanetriol 2,6-*i*-Pr$_2$-C$_6$H$_3$-N(SiMe$_2$-*i*-Pr)Si(OH)$_3$ was synthesized and even structurally investigated [41].

Jutzi et al. were able to generate the cyclopentadienyl-substituted organo silantriols C$_5$Me$_5$Si(OH)$_3$ [42a], [C$_5$H$_4$(SiMe$_3$)]-Si(OH)$_3$ [42b] and 9-methyl-flouren-9-yl-silanetriol [42c].

The for condensation sensitive organo silanetriols PhSi(OH)$_3$ [43,44], ThexSi(OH)$_3$ (Thex = 1,1,2-trimethylpropyl) [44], *t*-BuSi(OH)$_3$ [45] and Cy-Si(OH)$_3$ [46] are longer known and their stability is rooted only in sterical aspects. In contrast, the tricobaltnonacarbonyl-methylidine-substituted silanetriol Co$_3$(CO)$_9$C-Si(OH)$_3$ [47] is very stable and was first in 1977 by *Seyferth* et al. described.

The group of *Corriu* succeeded in the synthesis of bis(bihydroxymethlysilyl)benzene [48a] and of bis(trihydroxysilyl)benzene [48b], the first molecular compound containing two Si(OH)$_3$ units.

METALLO-SILANOLS

Another approach to transition metal substituted siloxanes involves the synthesis of metallo-silanols of the general type L$_n$M-Si(R)$_{3-n}$(OH)$_n$ (n = 1-3) and their extensive condensation with chlorosilanes giving acces to metallo-siloxanes with a direct metal-silicon bond.

In context with our studies on the reactivity of functionalized silicon transition metal complexes [49], we have established a new type of silanol containing a transition metal fragment directly bonded to silicon. These metallo-silanols are characterized by a remarkably high stability towards self-condensation due to the electron releasing effect of the metal fragment reducing dramatically the acidity of the Si-OH proton.

This property allows the isolation of a number of transition metal substituted silanols [50], mainly of the chromium and iron group including examples with stereogenic metal and silicon atoms [51] and even of metallo-silanediols [52] and -silanetriols [53].

Synthetic Procedures

Two routes proved to be most efficient for the generation of metallo-silanols: the hydrolysis of metallo-chlorosilanes in the presence of an auxiliary base and the oxofunctionalization of metallo-hydridosilanes with the oxygen transfer agent dimethyldioxirane [54].

$$L_nM \!-\! Si(R)_{3-x}Cl_x \xrightarrow[- n \, [Et_3NH]Cl]{+ \, n \, H_2O, \, + \, n \, Et_3N} L_nM \!-\! Si(R)_{3-x}(OH)_x \xleftarrow[- \, n]{+ \, n} L_nM \!-\! Si(R)_{3-x}H_x$$

$x = 1\text{-}3$ $L_nM = C_5R'_5(OC)_2Fe/Ru$ (R' = H, Me) R = Me, Ph, o-Tol
$Cp(OC)(Ph_3P)Fe$
$C_5R'_5(OC)_2(Me_3P)Mo/W$ (R' = H, Me)
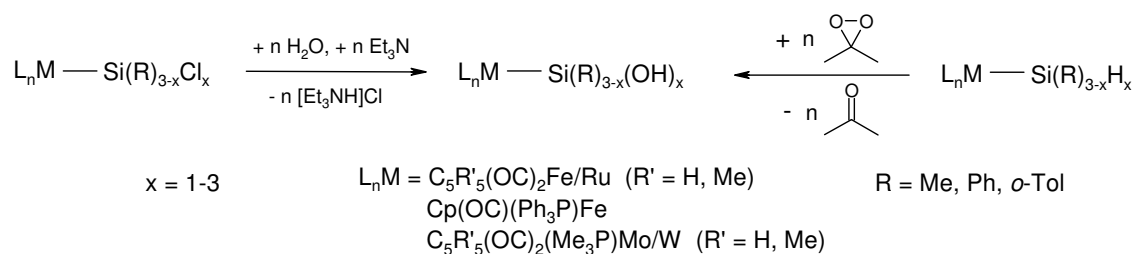
Electrophilic oxygen insertion is especially productive for metallo-silanes with electron rich Si-H bonds provided by metal fragments of high donor capacity. This situation is given in the case of phosphane-substituted metal fragments, like $Cp(OC)(RPh_2P)Fe$ [R = Ph, N(H)C*MePhH]. In this context, even the diastereomerically pure ferrio-silanol $Cp(OC)(Ph_3P)Fe\text{-}SiMePhOH$ [51] and the enantiomerically pure ferrio-silanediol $Cp(OC)[HMePhC*NMePh_2P]Fe\text{-}SiPh(OH)_2$ [55] have been isolated. For these systems the hydrolysis of the analogous metallo-chlorosilanes fails due to insufficient electrophilicity of silicon. In context with the oxygenation procedure, a catalytic method has been developed using urea/hydrogen peroxide adduct in the presence of $MeReO_3$ [56]. For example, the tungsten-silanetriol **2** is provided in a better yield by this method than by using dimethyldioxirane [57].

1   **2**
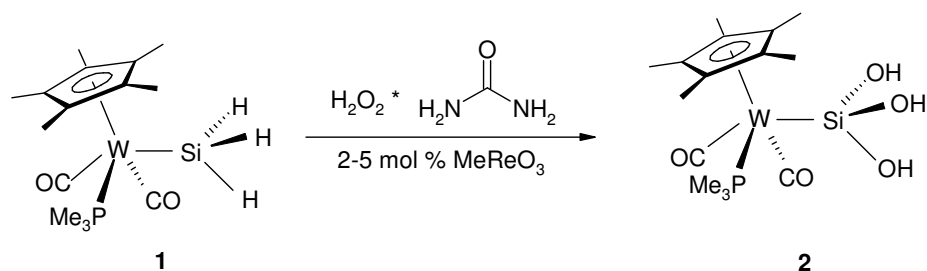
Other procedures involve the selective, hydrolytic cleavage of the Co-Si unit in heterodinuclear complexes of the type $(OC)_4Co\text{-}SiR_2\text{-}Fe(CO)_2Cp$, obtained from $Cp(OC)_2Fe\text{-}SiR_2H$ and $Co_2(CO)_8$. In this case, the H/OH-exchange at silicon can even be performed with catalytical amounts of $Co_2(CO)_8$ [58].

3   **4**   **5**
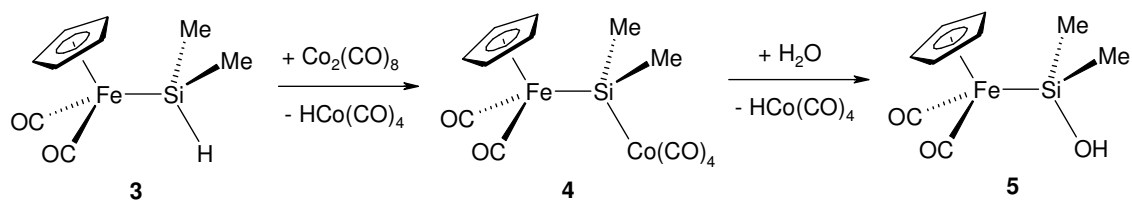
Condensation Reactions to Metallo-siloxanes and -heterosiloxanes

The metallo-silanols with a M-Si bond are characterized by a high stability towards self-condensation, for example the phosphane-substituted ferrio-silanetriol $Cp(OC)(Ph_3P)Fe\text{-}Si(OH)_3$ is recovered unchanged after heating to 60 °C for 5 d in THF. In the case of the ferrio-silanol **5**, a "β-H elimination" of the Si-OH proton is observed, leading to the formation of a metal hydride complex and, formally, dimethyl silanone, which is converted into hexamethyl cyclotrisiloxane.

5
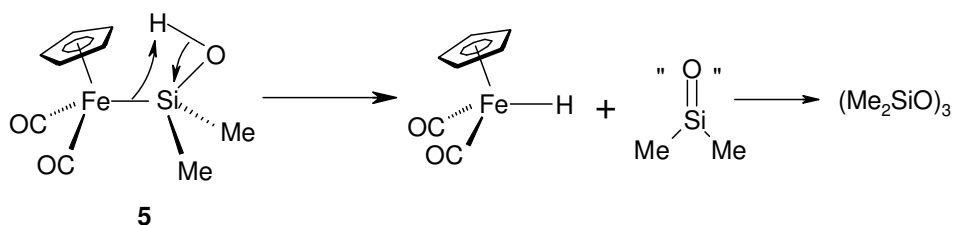
However, the facile isolation of metallo-silanols allows controlled condensation reactions with organochlorosilanes in the presence of an auxiliary base leading to transition metal substituted oligosiloxanes which can be considered as model compounds for silica-immobilized catalytic systems.

The facile isolation of metallo-silanols allows controlled condensation reactions with organochlorosilanes like chlorodimethylsilane, which lead in the presence of an auxiliary base to transition metal substituted oligosiloxanes [59-61]. These species can be considered as model compounds for silica-immobilized catalytic systems.

$$L_nM \text{---} Si(Me)_{3-x}(OH)_x \xrightarrow[\text{- x [Et}_3\text{NH]Cl}]{\text{+ x Me}_2\text{Si(H)Cl, + x Et}_3\text{N}} L_nM \text{---} Si(Me)_{3-x}(OSiMe_2H)_x$$

$$L_nM = Cp(OC)_2Fe, C_5Me_5(OC)_2(Me_3P)Mo/W; \ x = 1-3$$
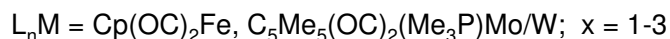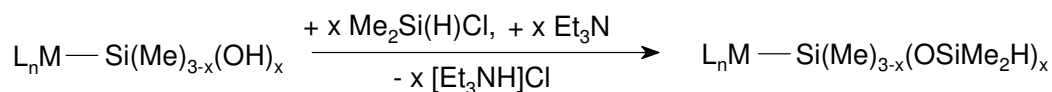
Especially the SiH-functionalized metallo-siloxanes exhibit high synthetical potential due to oxidative addition to electronically unsaturated metal centres giving easy access to Si-O-Si-bridged dinuclear metal complexes, like **6a,b** and **7** [59,61].
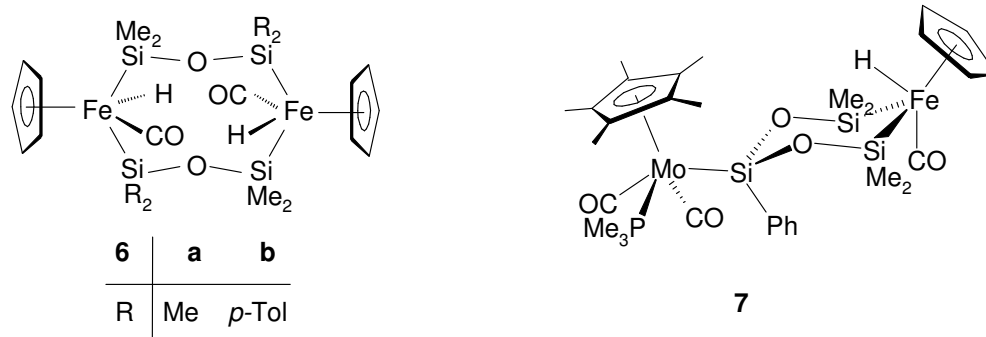
6	a	b
R	Me	p-Tol

7

The preparation of group 13 heterosiloxanes (E = Al, Ga, In) has become an increasing field of research concerning catalytically active zeolithes, e.g. gallium containing zeolithes for the dehydrogenation and dehydrocyclization of alkanes [62-65].

The ferrio-silanols Cp(OC)$_2$Fe-SiMeR'OH (R = Me, Ph), although characterized by a lowered acidity compared to organosilanols, react with trialkylalanes, -gallanes and -indanes to yield the transition metal fragment-substituted heterosiloxanes **8a-d** via elimination of alkane [66]. Molecular-weight determination of **8a,b** shows the presence of dimers in solution, deriving from an intermolecular interaction of the *Lewis*-acidic group 13 element and the *Lewis*-basic oxygen atom of the Si-O unit. In the case of the derivatives **8c,d** with stereogenic silicon atom, the aggregation to dimers can easily be determined by NMR spectroscopy due to the formation of diastereomers. In addition, the dimeric structure is confirmed by X-ray analysis of **8a,b,d** for the solid state [67].

8	a	b	c	d	e	f
E	In	Ga	Al	Ga	Ga	In
R	Me	Me	Ph	Ph	OH	OH

9
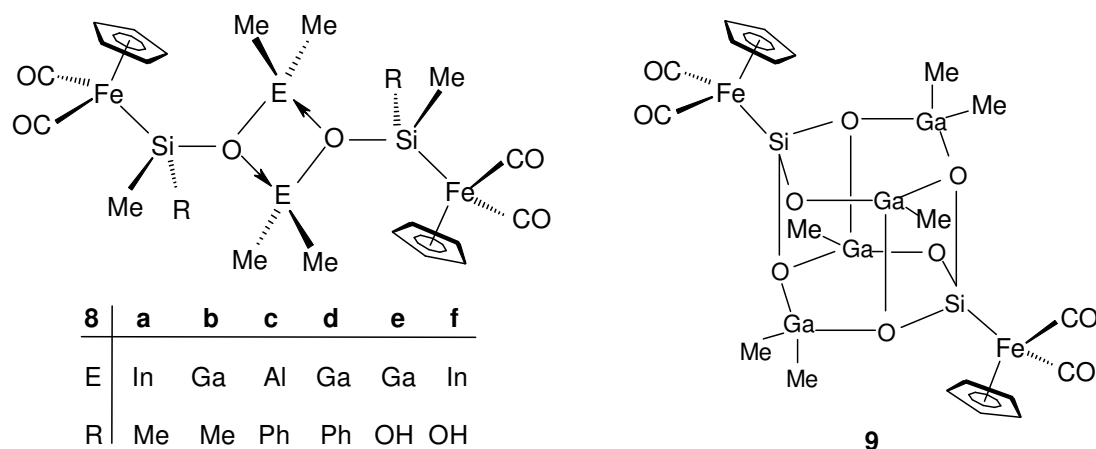
These results clearly indicate, that an increased O-E-π-interaction (E = In, Ga), induced by the Cp(OC)$_2$Fe fragment at the silicon, is not sufficient to suppress dimerization.

The reaction of the ferrio-silanediol Cp(OC)$_2$Fe-SiMe(OH)$_2$ with trimethylgallane and –indane, respectively, results in the formation of the heterosiloxanols **8e,f**. Only one OH function of the ferrio-silanediol is transformed, independent of the amount of trimethylgallane or –indane used, the same finding is valid for the reaction of the ferrio-silanetriol Cp(OC)$_2$Fe-Si(OH)$_3$ with trimethylgallane. In *n*-hexane at room temperature the ferrio-heterosiloxanediol Cp(OC)$_2$Fe-Si(OH)$_2$-OGaMe$_3$ is initially formed. However, in the presence of two equivalents of THF and more severe reaction conditions (65 °C) the drum-shaped heterosiloxane **9** with iron-substituted

silicon atoms is produced [68]. In this reaction, THF acts as a donor to stabilize the formed intermediates and to guarantee a controlled condensation procedure [69].

Metallo-silanols proved also to be synthetically valuable in context with the generation of SiO-bridged polynuclear complexes. Especially the Et_3N-assisted condensation reactions with cyclopentadienyl titanium- and zirconium chlorides results in nearly quantitative conversions due to the oxophilic nature of the group 4 metals. Even permetalated derivatives like **10** with a SiO_3 bridge and **11** with three tungsten-siloxy ligands at one titanium center are easily accesible by this way.

10

11
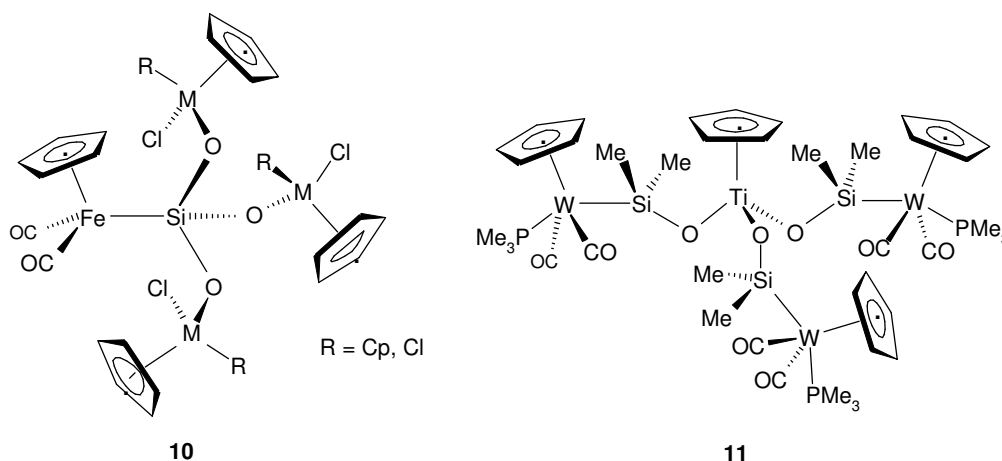
BIS(METALLO)-SILANOLS AND -SILOXANES

The "transition metal effect", that means, the stabilizing effect of the metal fragment on silanol units, can be raised considerably by attaching two transition metal fragments to the same silicon atom.

The synthesis of bis(metallo)-silanols starts with the homo- and hetero-bismetalated silanes **12** and **13**, respectively, which are easily prepared from the monometalated silanes $Cp(OC)_2Fe-Si(H)Cl_2$ and $Cp(OC)_2(Me_3P)W-SiMe(H)Cl$ via substitution reaction employing the strongly nucleophilic metalate reagent $Na[Fe(CO)_2Cp]$.
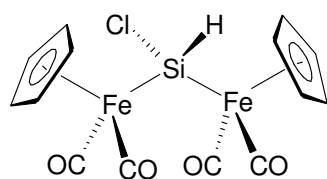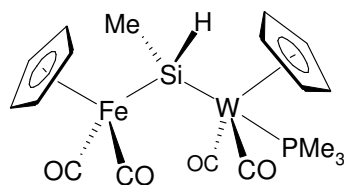
12   **13**

The bis(ferrio)-silanols **14** and **15**, representing extremely rare examples combining a OH and H or Cl function at silicon, respectively [70], are both accessible from the bis(ferrio)-chlorosilane **12** making use of the two complementary synthetic routes hydrolysis and oxygenation [71]. Et_3N-assisted hydrolysis of **12** yields the corresponding SiH-functional bis(ferrio)-silanol **14**, the bis(metallo)-chlorosilanol **15** can be prepared by treating **12** with dimethyldioxirane. However, despite of the two iron substituents, **15** rapidly decomposes at room temperature.

14   **15**
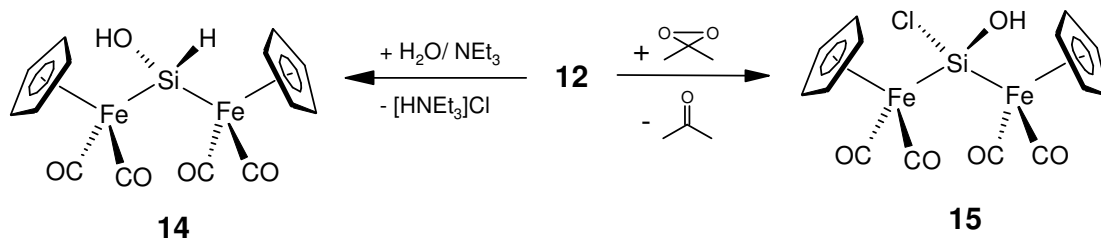
Analogously to the synthesis of **15**, the bis(ferrio)-silanediol **16** is obtained from $[Cp(OC)_2Fe]_2SiH_2$ [72] under standard conditions in acetone at -78 °C in good yield. The oxofunctionalization of an Si-H bond using dimethyldioxirane also proved to be successful for the synthesis of the first hetero-bismetalated silanol **17**, obtained from **13** [71].
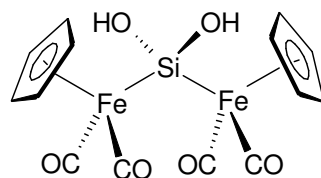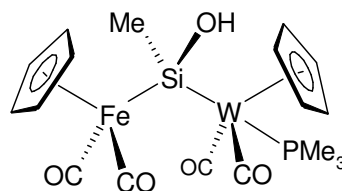
16   **17**

The transition-metal substituted silanols **14**, **16** and **17** show the expected reduced tendency towards self condensation. However, upon treatment with Me$_2$Si(H)Cl in the presence of Et$_3$N, they can be converted into the corresponding bis(metallo)-siloxanes **18a,b** and **19**, useful for further modifications involving the Si-H function [71].

18	a	b
X	H	OSiMe$_2$H
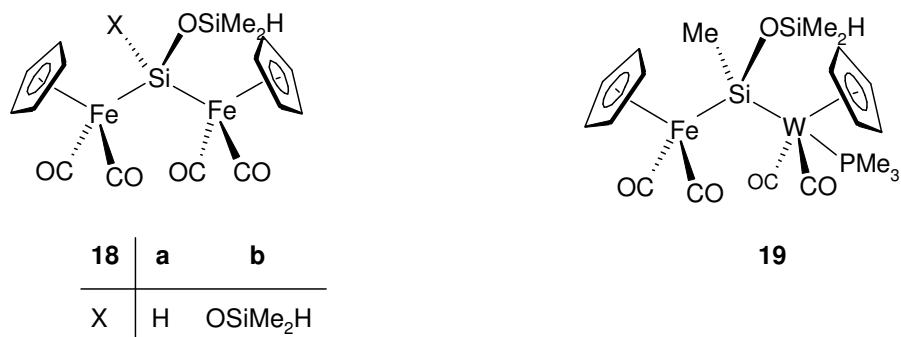
THE TRANSITION METAL EFFECT

Metallo-disilanes L$_n$M-SiX$_2$-SiX$_3$ (X = H, Cl) represent interesting model compounds for the study of the "transition metal effect" since these species contain a transition metal substituted as well as a metal free Si-X unit in the same molecule. In this context, the Et$_3$N-assisted hydrolysis of the ferrio-pentachlorodisilane **21a** yields exclusively the ferriodichloro-trihydroxy-disilane **20**, demonstrating the reduced activity for nucleophilic attack at the silicon in α-position to the transition metal atom [73,74].

21	a	b	c
-o	H	H	Me
X	Cl	H	H

22	a	b
-o	H	Me

a) X = Cl   b) X = H
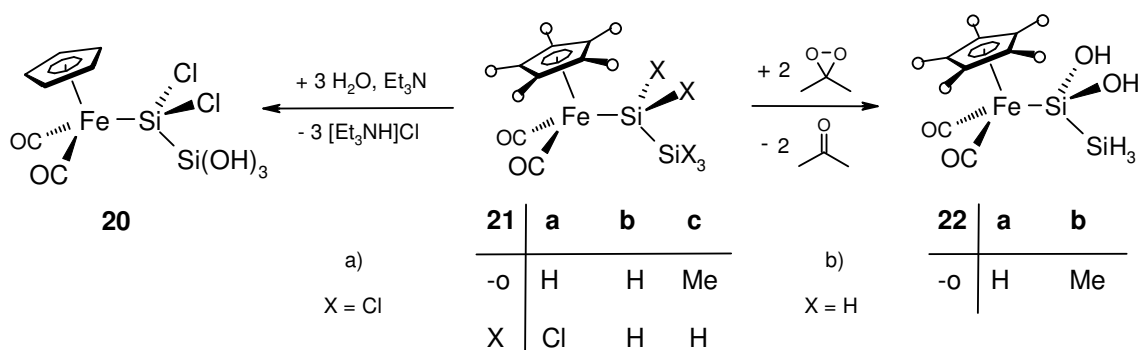
On the other hand, the oxygenation of the ferrio-pentahydridodisilanes **21b,c** with dimethyldioxirane results in the formation of the ferrio-dihydroxydisilanes **22a,b**, which reveals the strong activation of the α-SiH$_2$ unit for electrophilic oxygenation by dimethyldioxirane [73,74].

These regiospecific hydroxylation reactions guarantee the accessibility of new types of Si-H- and Si-Cl-functional metallo-disilanols by simple reaction steps provided by the influence of the transition metal fragment.

A regiospecific hydroxylation can also be performed with the bis(ferrio)-disiloxane **18a**. Again due to the strong influence of the neighbouring transition metal fragments the α-silicon differs considerably both in chemical and spectroscopic properties from the "normal" γ-silicon. This aspect can be used for the regioselective oxygenation of the α-Si-H function resulting in the formation of the bis(ferrio)-disiloxanol **23**, which can be isolated in excellent yield. The exclusive formation of **23** shows that electrophilic attack of dimethyldioxirane at the metal-activated α-Si-H bond is strongly favored [75].
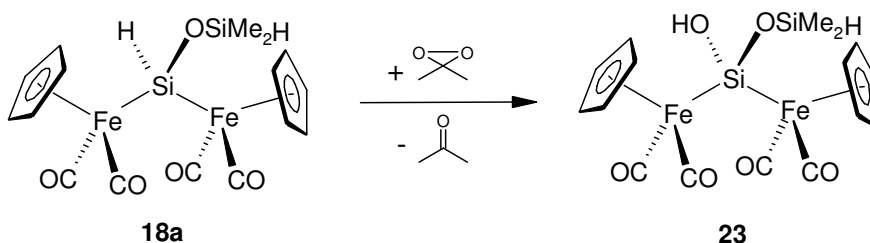
The γ-Si-H moiety remains unaffected even when an excess of dimethyldioxirane is employed. The examples of **18a** and **21a-c** demonstrate impressively how the regioselectivity of the hydrolysis and oxygenation of metallo-silanes and metallo-siloxanes, respectively, can be determined by transition metal substituents.

METALLO-SILANOLS WITH THE SILICON AND THE METAL SEPARATED BY A SPACER GROUP

Due to the great condensation stability of metallo-silanols with M-Si bond it is not possible to obtain any metal fragment substituted polysiloxanes via controlled self-condensation reactions, a consequence of the direct influence of the transition metal fragment on the silanol unit. Therefore, it seemed reasonable to decrease this stabilizing effect by separation of the metal and the silanol group. In this context, we have been used in a first approach a methylene group or a η^5-cyclopentadienyl unit as suitable spacer groups.

$$L_nM - X - \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}} - OH \qquad X = CH_2, \eta^5\text{-}C_5H_4$$
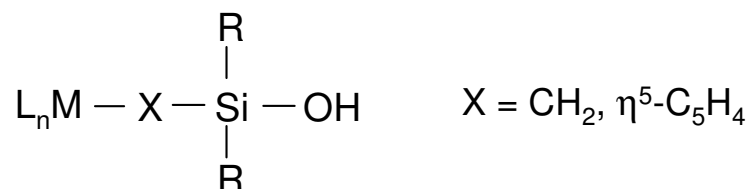
These systems promise a higher tendency for self-condensation compared to those with a direct metal silicon bond, an essential prerequisite to obtain access to polynuclear metal-fragment substituted oligo- and polysiloxanes.

Ironmethyl- and Tungstenmethyl-diorganosilanols

In more recent studies [76], we were looking for metallo-silanols, in which the stabilizing effect of the transition metal group is decreased in order to get access to metal-substituted oligo- and polysiloxanes via controlled self-condensation reactions. In this context, we have synthesized the metallomethyl-silanols **24-26** in which the metal and the silanol group are separated by a methylene spacer group. **24-26** have either been generated by Et_3N-assisted hydrolysis of Si-Cl-functionalized precursors or by oxofunctionalization of the corresponding Si-H-functional metallomethyl-silanes with dimethyldioxirane.

24	a	b	c
-o	H	H	Me
R	Me	Ph	Me

25	a	b
L	CO	Me$_3$P
R	Ph	Me

26	a	b
R	Me	Ph
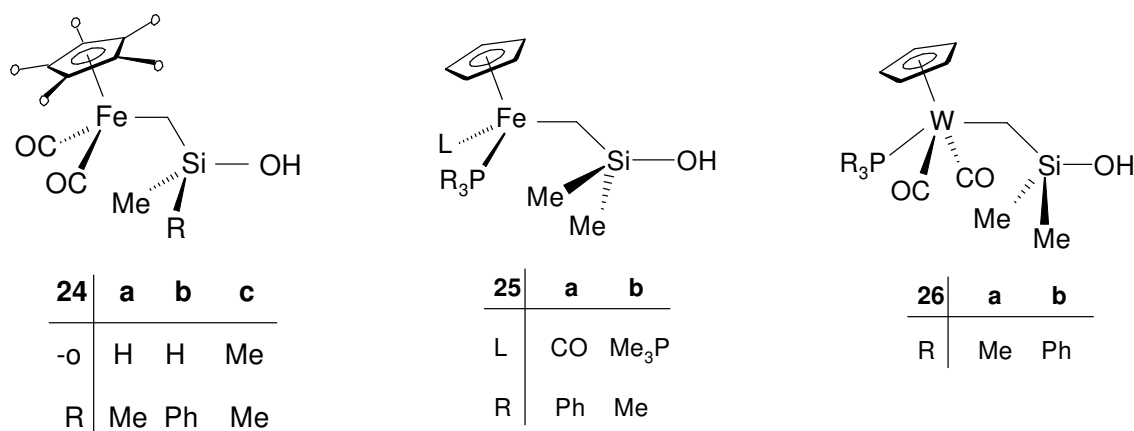
The introduction of the phosphine ligand at the tungsten center is necessary to guarantee sufficient stability of the W-C bond. In contrast to the synthesis of the ferriomethyl-silanols C$_5$R$_5$(OC)$_2$Fe-CH$_2$-SiMeROH, in the case of the tungsten derivatives the oxygenation method is more favourable due to the lability of the chlorofunctional precursors towards decomposition.

Ferriomethyl-disiloxanes and –heterosiloxanes

The ferriomethyl-silanol Cp(OC)$_2$Fe-CH$_2$-SiMe$_2$OH (**24a**), which can be considered as a derivative of trimethylsilanol with a methyl hydrogen substituted by the Cp(OC)$_2$Fe fragment, exhibits an enhanced reactivity towards self-condensation compared to the analogous Fe-Si system. As a consequence, at room temperature, **24a** shows slow self-condensation leading to the 1,3-(bisferriomethyl)-disiloxane **27a**. C$_5$R$_5$(OC)$_2$Fe-CH$_2$-SiMeR'OH [R = H, R' = Ph (**24b**); R = R' = Me (**24c**)] are stable with respect to this process due to steric (**24b**) or electronic (**24c**) factors.

The disiloxane **27a** is in addition obtained by the reaction of the silanol **24a** with the ferriomethyl-chlorosilane Cp(OC)$_2$Fe-CH$_2$-SiMe$_2$Cl in the presence of Et$_3$N. The disiloxanes **27b,c** with only one iron fragment are analogously available using the organochlorosilanes Me(R)Si(H)Cl (R = Me, *p*-Tol).

27	a	b	c
R	Me	Me	*p*-Tol
R'	CH₂Fe(CO)₂Cp	H	H

28	a	b	c
M	Ti	Zr	Zr
X	Cl	Cl	OSiMe₂CH₂Fe(CO)₂Cp
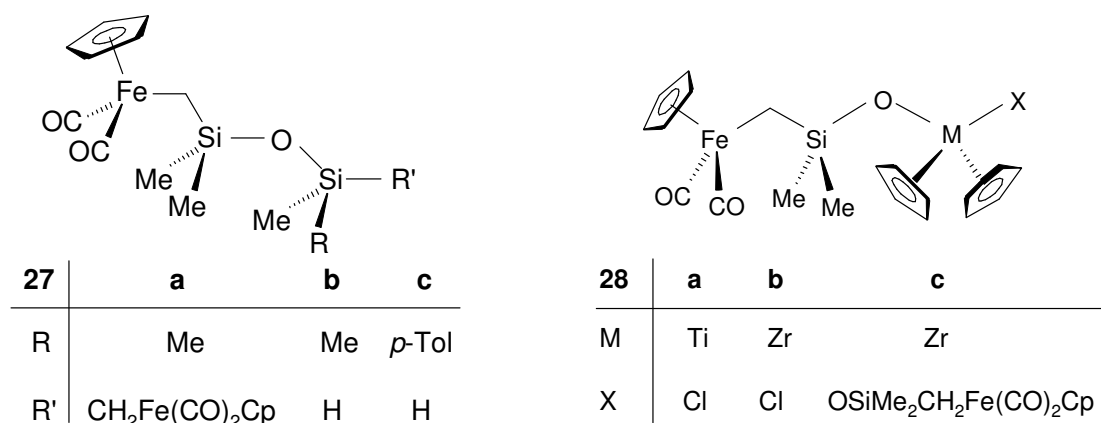
The Si-OH function of ferriomethyl-diorganosilanols is also suitable for condensation reactions with group 4 metal chlorides, as proved for Cp(OC)₂Fe-CH₂-SiMe₂OH (**24a**). The Et₃N-assisted reaction of **24a** with titanocene or zirconocene dichloride offers an easy access to the bismetalated heterosiloxanes **28a,b**. Further condensation of **28b** with the ferriomethyl-silanol **24a** to give the trinuclear species **28c** is achieved almost quantitatively [77].

Ferriomethyl-silanediols and –silanetriols

The synthesis of the silanediol **29a** and silanetriol **30** can be accomplished either by the oxygenation or the hydrolysis method starting from Cp(OC)₂Fe-CH₂-SiRH₂ (R = Me, H) [78] or the chlorofunctional ferriomethyl-silanes Cp(OC)₂Fe-CH₂-SiRCl₂ (R = Me, Cl) [79].

29	a	b
L	CO	PPh₃

30

31	a	b	c
L	CO	PPh₃	CO
n	2	2	3

13
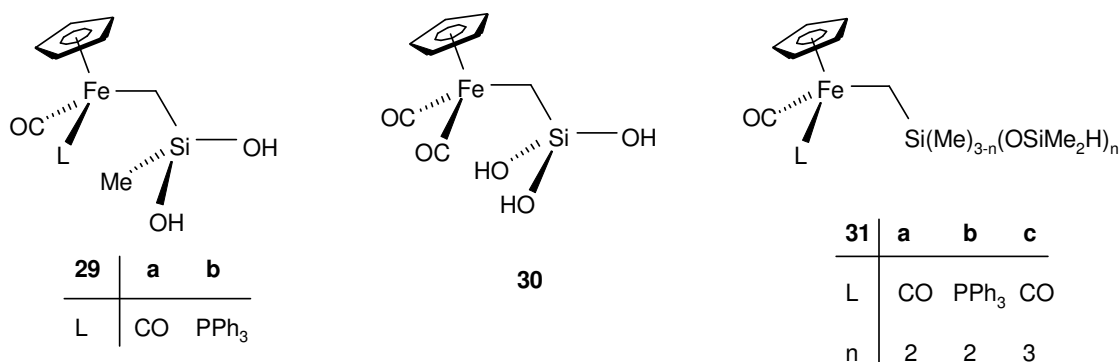
Additional access to the silanetriol **30** is offered by the hydrolysis of the ferriomethyl-trimethoxysilane $Cp(OC)_2Fe-CH_2-Si(OMe)_3$ with an excess of water in the presence of acetic acid.

However, at room temperature, the reactivity of **29a** and **30** in solution is significantly enhanced giving rise to the formation of complex product mixtures, presumably due to self-condensation.

A greater stability towards self-condensation is observed for the phosphane-substituted ferriomethyl-silanediol **29b**, which can be obtained by Et_3N-assisted hydrolysis of the corresponding ferriomethyl-dichlorosilane.

The condensation reaction of **29a,b** and **30** with dimethylchlorosilane in the presence of triethylamine proceeds in a controlled manner yielding the ferriomethyl-tri- and -tetrasiloxanes **31a-c,** respectively, in good yields [78].

Photochemical Reactions of Ironmethyl-siloxanes

The Si-H functions of the ferriomethyl-siloxanes **31a-c** offer the possibility for further functionalization reactions, for example, photochemical treatment inducing CO-elimination and subsequent reaction steps leading to rearrangement of the siloxane backbone.

In the case of the ferriomethyl-tri- and -tetrasiloxanes **31a,c** irradiation with UV-light in benzene results in the formation of the six-membered cyclo(ferra)-trisiloxanes **32a,b** [79].

32a, which bears two methyl groups at the γ-silicon atom, is isolated as a single compound, whereas **32b** is obtained as mixture of two isomers in a ratio of about 60:40, deriving from the relative positions of the substituents at the iron atom and the γ-silicon atom to each other.
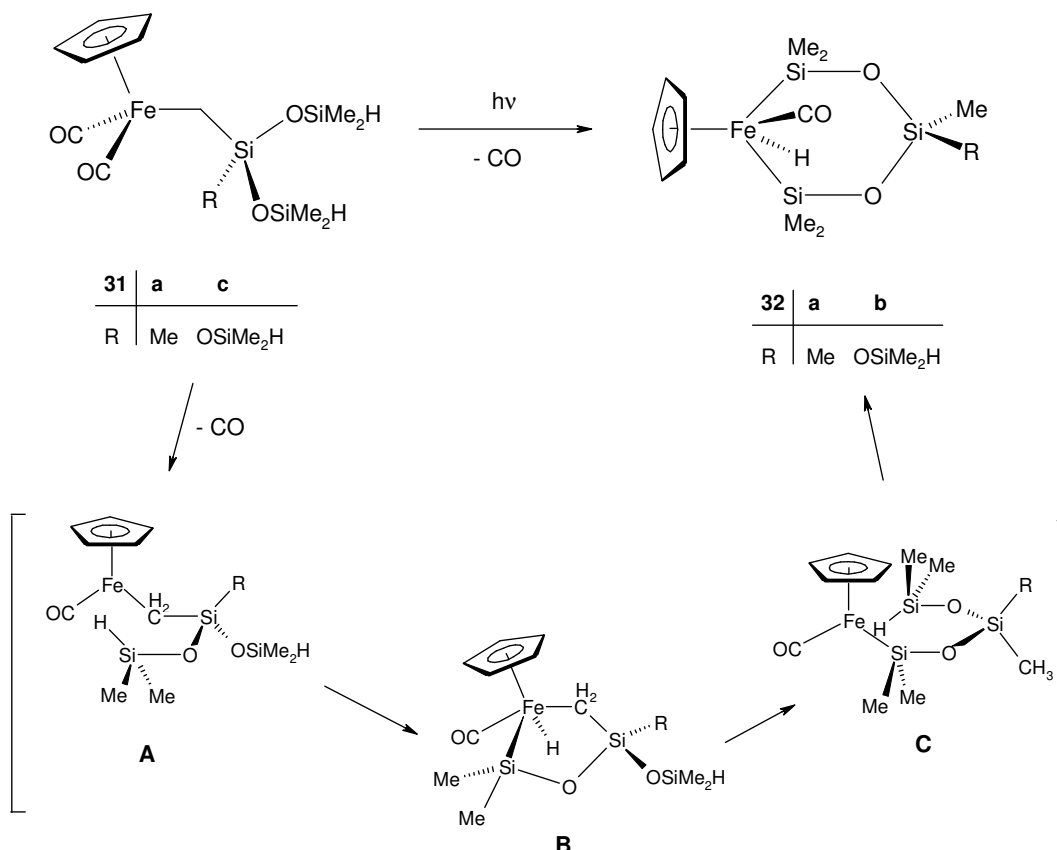
Mechanistically, this reaction involves an initial CO elimination of **31a,c** upon UV-irradiation leading to the 16 valence electron species **A**, which is stabilized by an intramolecular oxidative addition reaction of one of the terminal Si-H units to the iron center. The resulting five-membered ring **B** is transformed via a reductive elimination of the iron bound hydrogen and methylene unit into **C**, giving rise to the formation of a new Si-Me group. **C** is stabilized again by an oxidative addition reaction of the remaining Si-H function to the iron center leading to the formation of **32a,b**.

Metallo-silanols with a η^5-C$_5$H$_5$ Spacer Unit

A further attractive possiblity to decrease the "transition metal effect" on the silanol unit can be realized in metallo-silanols with the η^5-cyclopentadienyl ligand serving as spacer group between the metal fragment and the silanol unit. Such an arrangement also promises higher reactivity with respect to condensation reactions as mentioned

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above and should additionally help to suppress undesirable decomposition reactions involving "β-hydrogen abstraction" from the Si-OH group, observed for ferriosilanols of the type Cp(OC)$_2$FeSiRR'OH (R, R' = alkyl, aryl). Furthermore, it allows broad access to silanol-functionalized halfsandwich complexes without limitation of the ligand sphere around the metal center.

Surprisingly, only a few examples of metallo-silanols of this type can be found in literature like for example the metal-metal-bonded {[Mo(CO)$_3$]$_2$[μ-η^5:η^5-(C$_5$H$_3$)(SiMe$_2$OH)SiMe$_2$(C$_5$H$_4$)]} (*Mo-Mo*) [80], as the first one, reported by *Royo*.

The synthesis of **34** as an example of this special type of metallo-silanols, starts most efficiently with an appropriate silyl metal complex, like Cp(OC)$_2$Fe-SiMe$_2$R (R= H, OMe). With lithium di-*iso*propyl amide an anionic shift of the silyl group from the iron to the cyclopentadienyl unit can be induced, leading to the metalates **33a,b**. Methylation with methyl iodide produces the neutral methyl iron complexes (C$_5$H$_4$SiMe$_2$R)(OC)$_2$Fe-Me (R = H, OMe), which can be converted either, for R = H, by the Co$_2$(CO)$_8$ method, or, for R = OMe, by hydrolysis in the presence of acetic acid, into the corresponding silanol **34** [76,81].

33	a	b
R	H	OMe
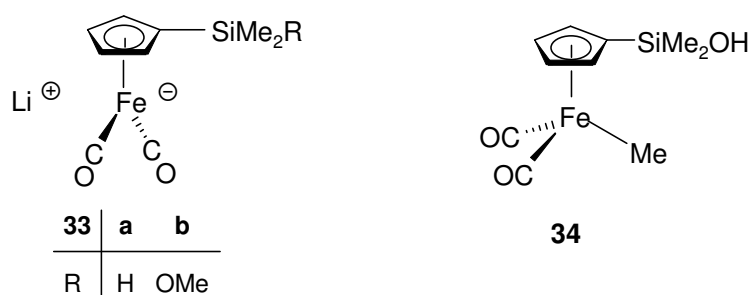
The following seven chapters will present the results made by preparative investigations concerning the synthesis and reactivity, especially the condensation behavior as well as the structural characterization of a series of these novel metallo-silanols containing tungsten as the transition metal.

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Chapter I

SYNTHESIS AND REACTIVITY OF HALFSANDWICH TUNGSTEN COMPLEXES, [HOMe$_2$Si(η^5-C$_5$R$_4$)](OC)$_3$WR'(R = H, Me; R'= H, Cl, Me), WITH A η^5-CYCLOPENTADIENYL-BOUND SILANOL FUNCTION

SUMMARY

Novel halfsandwich tungsten complexes with a η^5-cyclopentadienyl-bound silanol function of the general formula $[HOMe_2Si(\eta^5\text{-}C_5R_4)](OC)_3WR'$ (R = H, Me; R' = H, Cl, Me) have been prepared. Silyl-functionalization of the cyclopentadienyl ligand is achieved by two pathways. One is applying a base-induced silyl shift of the tungsten-silanes $CpL(OC)_2WSiMe_2H$ [L = CO (**1a**), PMe$_3$ (**1b**)] resulting in the formation of the cyclopentadienyl-functionalized lithium tungsten salt $Li\{W[(\eta^5\text{-}C_5H_4)SiMe_2H]L(CO)_2\}$ [L = CO (**2a**), PMe$_3$ (**2b**)]. The other one deals with the regioselective reaction of the dilithiated tungsten complex $Li[W(\eta^5\text{-}LiC_5H_4)(CO)_3]$ (**4**) with $Me_2Si(H)Cl$, giving **2a**, too. **4** is obtained from $Cp(OC)_3WH$ (**3**) by the treatment with two equivalents of nBuLi. The tungsten complex $[ClMe_2Si(\eta^5\text{-}C_5Me_4)](OC)_3WH$ (**9b**), with a tetramethyl-substituted cyclopentadienyl ring is synthesized by reaction of $ClMe_2SiC_5Me_4H$ (**8b**) with $(MeCN)_3W(CO)_3$ in refluxing THF. Oxofunctionalization of the Si-H-bond of $[HMe_2Si(\eta^5\text{-}C_5H_4)](OC)_3WH$ (**5**) is achieved by use of dimethyldioxirane and yields the tungsten-silanol $[HOMe_2Si(\eta^5\text{-}C_5H_4)](OC)_3WH$ (**11**). Alternatively, the treatment of the tungsten-silane **5** with $Co_2(CO)_8$ and subsequent hydrolysis also leads to **11** via the hetero-dinuclear complex $[(OC)_4CoMe_2Si(\eta^5\text{-}C_5H_4)](OC)_3WH$ (**12**). The Si-Cl-functionalized **9a,b** and **10a,b** are hydrolyzed in the presence of the auxiliary base NEt_3 to afford the novel tungsten-silanols $[HOMe_2Si(\eta^5\text{-}C_5R_4)](OC)_3WR'$ [R = H, R'= H, Cl (**11, 13a**); R = Me, R' = H, Cl (**13b,c**)]. All these new compounds have been identified IR- and NMR-spectroscopically and in the case of **13c** in addition by X-ray diffraction analysis. Furthermore, the reactivity of the silanols concerning co-condensation and their behaviour towards nBuLi have been investigated.

INTRODUCTION

The condensation of organosilanols can be considered as the basic reaction in the synthesis of siloxanes and silicones. This process can be suppressed by bulky organic groups, which in some cases offers access even to stable silanediols $R_2Si(OH)_2$ and silanetriols $RSi(OH)_3$ (e.g. R = $C_5H_4SiMe_3$) [1, 2]. Apart from the sterical aspect, another kind of stabilization is achieved by use of metal fragments as silicon substituents in silanols of the general type L_nM-$SiR_{3-n}(OH)_n$ (n = 1-3) [3-14] (Fig. 1, type **I**). In this case the metal fragment acts as a strong electron releasing group, inhibiting self-condensation, which affords even stable metallo-silanediols L_nM-$Si(R)(OH)_2$ [13, 15-18] and metallo-silanetriols L_nM-$Si(OH)_3$ [17, 19]. According to this crucial property, metallo-silanols have been used as precursors for the synthesis of well-defined metallo-siloxanes, representing attractive model compounds for transition metal complexes anchored on silica surfaces. In a confirmation of our interest recent investigations have been extended to metallo-silanols having the Si-OH unit separated from the metal fragment by an organic group, which should lead to an increased tendency towards self-condensation, compared to the M-SiOH derivatives.

$$L_nM\text{---}SiR_2OH \qquad L_nM\text{---}CH_2\text{---}SiR_2OH \qquad L_nM$$

I **II** **III**
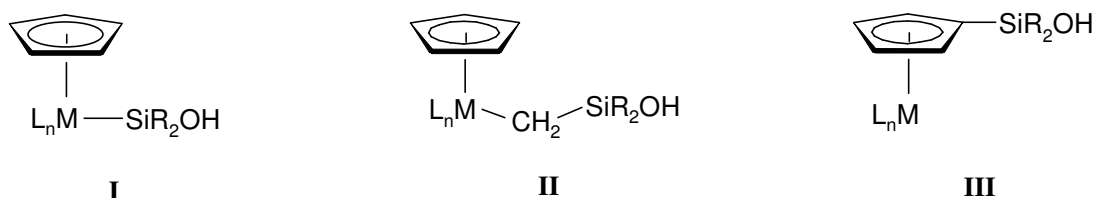
Fig. 1: Classification of different metal fragment-substituted silanols; type **I** has a metal-silicon bond, type **II** contains a methylene group as spacer and type **III** shows the cyclopentadienyl ligand being located between the metal and the silicon atom.

In a first approach metallo-silanols of the type **II**, containing a CH_2-spacer, have been synthesized and structurally characterized [20, 21]. A further attractive possiblity to decrease the "transition metal effect" on the silanol function can be realized in metallo-silanols with the η^5-cyclopentadienyl ligand serving as a spacer group between the metal fragment and the silanol unit (type **III**). Such an arrangement also

promises higher reactivity with respect to condensation reactions and should additionally suppress undesirable decomposition reactions like "β-hydrogen abstraction" from the Si-OH group, observed for ferrio-silanols of the type $Cp(OC)_2FeSiR_2OH$ (R = alkyl, aryl). Furthermore, it offers broad access to silanol-functionalized halfsandwich complexes without limitation of the ligand sphere around the metal center.

Surprisingly, only few examples of metallo-silanols of type **III** are found in literature, including the dinuclear metal-metal-bonded molybdenum complex $\{[\mu\text{-}\eta^5\text{:}\eta^5\text{-}HOMe_2Si(C_5H_3)SiMe_2(C_5H_4)][Mo(CO)_3]_2\}$ (*Mo-Mo*), reported by *Royo* and the iron complexes $[HOMe_2Si(C_5H_4)](OC)_2FeR$ (R = Me, SiMe_3) prepared in our group [22-26]. This paper describes the synthesis of a series of novel tungsten-silanols of the type **III** with the general formula $[HOMe_2Si(\eta^5\text{-}C_5R_4)](OC)_3WR'$ (R = H, Me; R' = H, Cl, Me) and first results concerning the reactivity, as well as the first structural characterization of a tungsten complex with cyclopentadienyl-bound silanol group.

RESULTS AND DISCUSSION

Dimethylsilyl-cyclopentadienyl Tungsten Complexes (5, 6a-c). Due to the fact that it is impossible to introduce a silanol group directly at the cyclopentadienyl ligand of a halfsandwich complex, the main task implies the preparation of appropriate precursors, which allow the generation of a silanol species. Two established methods have been proved to be most efficient for the generation of metallo-silanols: the reaction of metallo-hydridosilanes using mainly the oxygen transfer agent dimethyldioxirane and the hydrolysis of metallo-chlorosilanes in the presence of an auxiliary base. Following these concepts, the functionalization of the cycopentadienyl ligand with Si-H- and Si-Cl functions has been undertaken.

Encouraged by former studies, concerning base-induced silyl shifts in halfsandwich iron complexes, reactions of tungsten-silanes with a strong base, initiating such a silatropic rearrangement, have been investigated as an straightforward route to silylcylclopentadienyl tungsten complexes [25, 27].

Treatment of the tungsten-silanes **1a,b** with LiN(iPr)$_2$ (LDA), nBuLi or tBuLi, respectively, under various conditions[1], induces in all cases the expected silatropic rearrangement, presumably via the primarily formed lithiocyclopentadienyl complexes (LiC$_5$H$_4$)L(OC)$_2$WSiMe$_2$H (L = CO, PMe$_3$) (**A**) to give the lithium tungsten salts Li{W[(C$_5$H$_4$)SiMe$_2$H]L(CO)$_2$} [L = CO (**2a**), PMe$_3$ (**2b**)] characterized by a silylated cyclopentadienyl-ring and a tungsten-centered anion (Scheme 1).

The lithium tungstates **2a,b** are identified by IR- and NMR-spectroscopy with the latter method indicating 6 - 35 % loss of the silyl group during the reactions. After the migration reaction, the ^{1}H-NMR spectrum displays two multiplets for the cyclopentadienyl protons instead of a singulet (**1a**) or doublet (**1b**) of the starting material. In all cases the use of LDA delivers better results than nBuLi, which is in accordance with the observations of base-induced germyl-, stannyl- and plumbyl migrations [28]. It seems that a certain sterical requirement of the base is necessary to diminish nucleophilic attack on the silicon atom, initiating W-Si bond cleavage, or on the carbonyl carbon atom resulting in minor formation of carbene complexes as noted

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[1] E.g. in the solvents PE, Et$_2$O and THF, changed reaction times from 30 minutes to two hours or different reaction temperatures ranging from –78 to 25 °C.

by *Dean* and *Graham* [29]. The lowest yield of **2b** is obtained by the treatment of **1b** with *t*BuLi at 25 °C, leading to extensive decomposition of the starting material. In general, a more controlled shift reaction is observed for the tricarbonyl-substituted tungsten-silane **1a**, compared to **1b**. Reasons for the higher migration tendency of **1a** are the weaker W-Si bond, the higher acidity of the cyclopentadienyl protons and the better stabilization of the tungsten anion of **2a**.
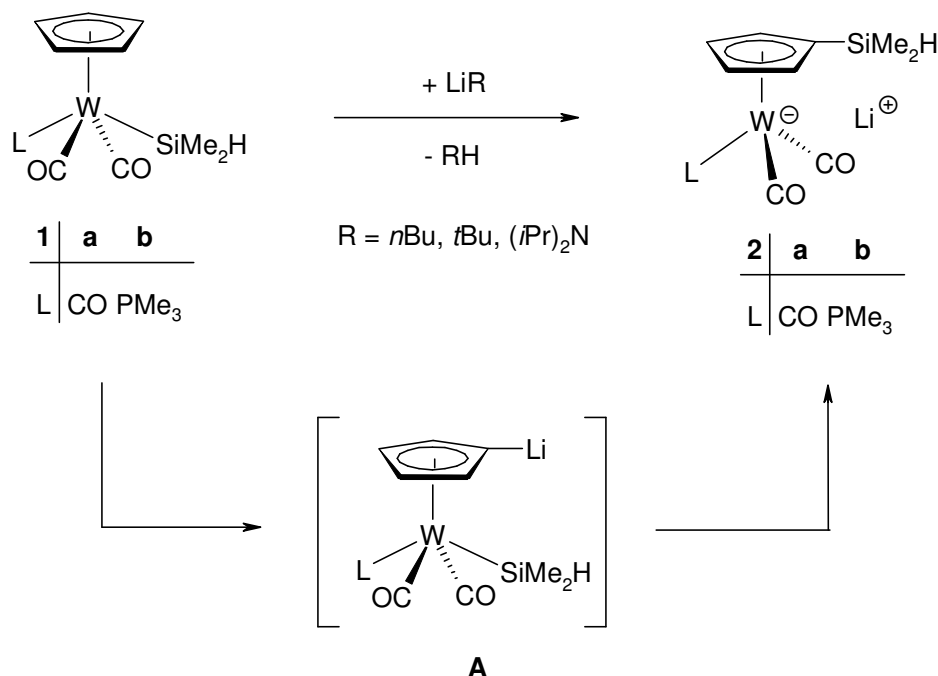
Scheme 1: Base-induced metal-to-cyclopentadienyl ligand silatropic rearrangement of the tungsten-silanes **1a,b**.

These results are in good accordance with the investigations concerning the first example for this type of migration reaction, reported by *Dean* and *Graham* in 1977 for Cp(OC)$_3$M(GePh$_3$) (M = Mo, W) [29] and the silyl shifts in η^5-cyclopentadienyl-containing silyl complexes of rhenium [30, 31], iron [27, 32-34] and osmium [35].

A more direct approach to tungsten complexes, silylated at the cyclopentadienyl ligand is given by the reaction of the dilithiated complex Li[W(LiC$_5$H$_4$)(CO)$_3$] (**4**) with

organo chlorosilanes. **4** is obtainable from Cp(OC)$_3$WH (**3**) by the treatment with two equivalents nBuLi (Scheme 2), according to the method of *Shafiq* et al.[36].

The dilithiation of **3** in THF proceeds cleanly and leads after about half an hour to a yellow precipitation consisting of **4**. The reaction is finished after four hours at room temperature. In contrast to *Shafiq`s* work, **4** is isolated for the first time as yellowgreen and very pyrophoric powder in 88 % yield and characterized by IR- and ^{1}H-NMR spectroscopy. **4** is stable at room temperature and can be stored under nitrogen atmosphere at –30 °C for several months without decomposition. The ^{1}H-NMR spectrum in D$_8$-THF exhibits that **4** is stabilized by four THF molecules. All attempts to generate the analogous phosphine-substituted compound Li[W(LiC$_5$H$_4$)(PMe$_3$)(CO)$_2$] by deprotonation with nBuLi, tBuLi or LDA in THF fail.

The introduction of the Me$_2$(H)Si group at the cyclopentadienyl-ring of a tungsten complex can be realized by the reaction of **4**, suspended in THF, with chlorodimethylsilane at –78 °C (Scheme 2). This reaction proceeds regioselectively at the cyclopentadienyl ring and is finished within few minutes, indicated by the dissolution of the former suspended **4**. The reaction results in the quantitative formation of the lithium tungstate Li{W[(C$_5$H$_4$)SiMe$_2$H](CO)$_3$} (**2a**).
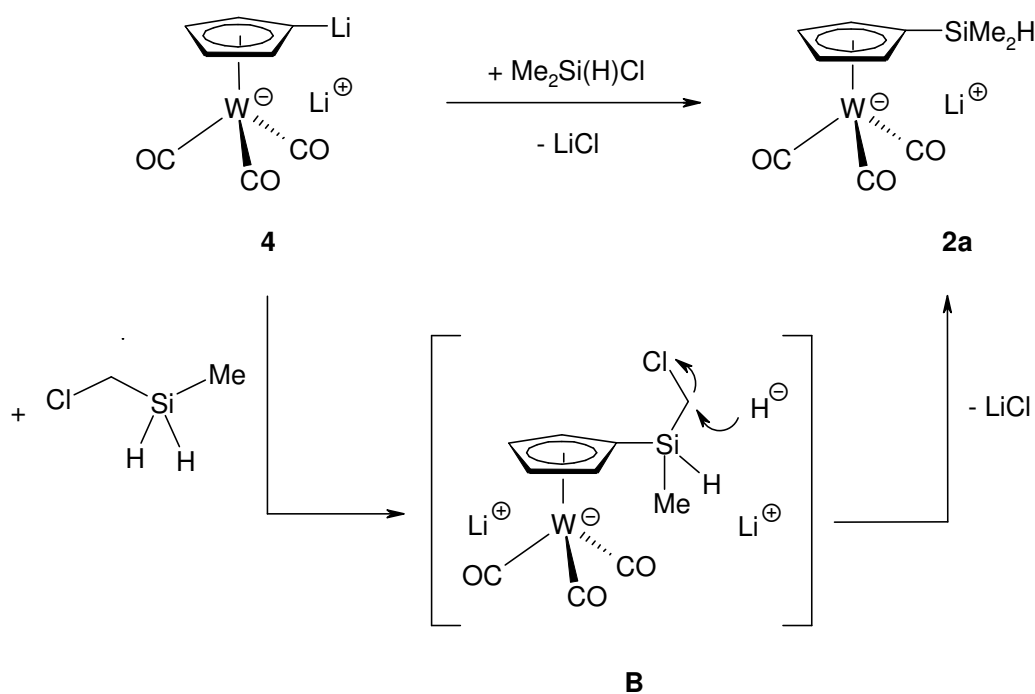
Scheme 2: Two pathways to the lithium metallate **2a** via reaction of the dilithiated complex **4**.

In order to synthesize a tungsten complex containing a methylene spacer unit between the cyclopentadienyl ligand and the silyl group, **4** is reacted with chloromethyl-methylsilane. Surprisingly, instead of the expected complex salt Li{W[(C$_5$H$_4$)CH$_2$SiMe(H)$_2$](CO)$_3$}, the HMe$_2$Si-substituted lithium tungstate **2a** is isolated (Scheme 2). The reaction is carried out in THF at –78 °C and finished after half an hour, giving **2a** in 71 % yield. Obviously, a nucleophilic attack of the lithiated cyclopentadienyl ligand on the silicon atom is preferred under these conditions, leading to hydride elimination in a first step, followed by Cl$^\ominus$/H$^\ominus$-exchange at the carbon atom of **B**. In fact the reaction is chemoselective and no other species are formed.

The lithium tungstates **2a,b** offer easy access to neutral tungsten complexes by salt elimination reaction with diverse electrophilic reagents. Quenching of **2a** with acetic acid leads to the hydrido tungsten complex [HMe$_2$Si(C$_5$H$_4$)](OC)$_3$WH (**5**), while the phosphine derivative **2b** yields the methyl- or silyl-tungsten complexes **6a-c** by reaction with MeI, Me$_2$Si(H)Cl or Me$_3$SiCl (Fig. 2). **5** is obtained as a pale yellow oil with an increased solubility in nonpolar solvents in comparison to **3**. **5** is slightly air-sensitive but can be handled for a short time at air. As known for hydrido tungsten complexes, **3** should be protected from light exposition, when it is stored over longer periods. The complexes **6a-c** are obtained stereospecifically as *trans*-isomers, as it is also valid for analogous C$_5$H$_5$ tungstates. This fact is indicated by the equivalence of the carbonyl ligands in the ^{13}C-NMR spectra, the two multiplets for the cyclopentadienyl ring protons as well as the ^{1}H-NMR singulet for the silicon-bound methyl groups.

6	a	b	c
R	Me	SiMe$_2$H	SiMe$_3$
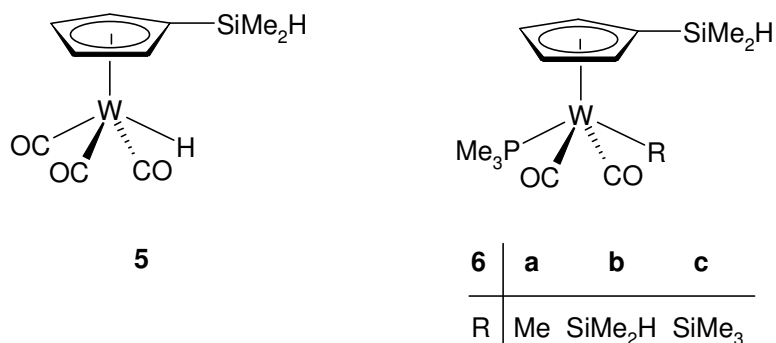
Fig. 2: The neutral silylcyclopentadienyl complexes **5** and **6a-c**, synthesized by the reaction of the lithium tungstates **2a,b** with HOAc, MeI, Me$_2$Si(H)Cl or Me$_3$SiCl, respectively.

Moreover, the ^{1}H-NMR spectra of **5** and **6a-c** in D_6-benzene show virtual triplets evoked by an AA'BB'-spin system for the two inequivalent pairs of cyclopentadienyl ring protons. In the case of the *cis*-isomer an ABCD-spectrum would be excpected for **6a-c**. The W-H hydride resonance of **5** appears at δ = -7.26 ppm, showing [183]W-satellites [^1J(HW) = 36.4 Hz]. The CO-stretching frequencies in the IR spectrum of **5** are detected very close to those for the analogous complex $Cp(OC)_3WH$ and illustrate that the silyl group has nearly no influence on the electronic character of the metal.

An alternative preparation of **5** has been realized by the reaction of $HMe_2SiC_5H_5$ (**7**) with $(MeCN)_3W(CO)_3$ in THF which results after 24 hours in the formation of **5** as the main product. This kind of reaction is literature-known in the cases of non-functionalized cyclopentadiene and involves substitution of the three acetonitrile ligands, with simultaneous ring C-H activation and hydrogen transfer to the metal center [37-40]. However, this synthesis is accompanied by the formation of $Cp(OC)_3WH$ and two others, not identified complexes having both a silyl-substituted cyclopentadienyl ligand (Eq. 1). All attempts to isolate pure **5** from the reaction mixture failed.
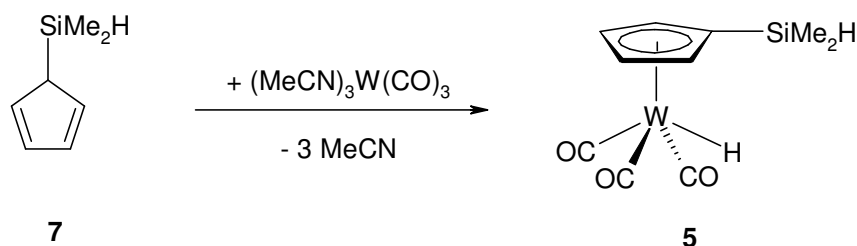
Eq. 1: Synthesis of the silyl-functionalized tungsten hydrido complexe **5**.

Gladysz and *Baya* proved that it is possible to lithiate rhenium- [41, 42] and osmium [35] hydrido halfsandwich complexes at the cyclopentadienyl ring and investigated the subsequent reactions with diverse electrophilic reagents to give $[Me(C_5H_4)](ON)(Ph_3P)ReH$ and $[R(C_5H_4)](Ph_3Ge)(iPr_3P)OsH_2$ (R = Me, *n*Bu and *s*Bu). Furthermore, it was shown that the hydride complex $Cp(Ph_3P)(ON)ReH$ is first lithiated at the cyclopentadienyl ring at −78 °C and rearranges at −32 °C via

hydrogen migration to give the lithium salt Li[ReCp(PPh$_3$)(NO)], characterized by a rhenium-centered negative charge.

Consequently, the kinetic abstraction of the less acidic proton of the cyclopentadienyl ligand in Cp(OC)$_3$WH (**3**) (ca. pK_a ~30 vs. ~8) [36] at –78 °C has been tried in order to generate also a cyclopentadienyl-lithiated hydrido species {(LiC$_5$H$_4$)(OC)$_3$WH}. The reaction of **3** with LDA in THF at –78 °C and followed by the treatment with Me$_2$Si(H)Cl results however in the formation of a product mixture, consisting of the starting material **3** and the tungsten-silane Cp(OC)$_3$WSiMe$_2$H (in a ratio of ca. 2:3). No silyl cyclopentadienyl tungsten species is observed. Since Cp(OC)$_3$WSiMe$_2$H is obtainable from the lithium tungsten salt Li[WCp(CO)$_3$] [43, 44], the question whether this salt is generated directly by W-H deprotonation or via fast hydrogen migration from primarily formed (LiC$_5$H$_4$)(OC)$_3$WH remains open.

Chlorodimethylsilyl-cyclopentadienyl Tungsten Complexes (9a,b and 10a,b). In order to get the chlorosilyl-derivatives, suitable for the silanol synthesis by hydrolysis, the reactions of the chlorodimethylsilyl-functionalized cyclopentadienes **8a,b** with (MeCN)$_3$W(CO)$_3$ have been investigated, as well as SiH-/SiCl-transformation concerning **5**.

The synthesis of [ClMe$_2$Si(C$_5$R$_4$)](OC)$_3$WH [R = H (**9a**), Me (**9b**)] is realized by reaction of the chlorodimethylsilyl-functionalized cyclopentadienes **8a,b** with (MeCN)$_3$W(CO)$_3$ in refluxing THF (Eq. 2). In contrast to the literature [24] we observed that it is necessary to extend the reaction time for **9a** from 3 to 18 hours to get a complete conversion of the starting material while the reaction of **8b** is finished after 25 hours to give the tungsten hydrido complex [ClMe$_2$Si(C$_5$Me$_4$)](OC)$_3$WH (**9b**) in almost quantitative yield. **9a** is obtained as a dark red and high viscous oil in 86 % yield showing good solubility in aliphatic solvents, while the tetramethyl-derivative **9b** is obtained as greenbrown solid. **9b** dissolves readily in petrolether, benzene, diethylether, methylene chloride or THF, respectively. **9b** is more stable against water than **9a** and can be stored without decomposition for several months under nitrogen atmosphere.

In the case of **9a**, the ^{1}H- and ^{13}C-NMR values agree with the literature data and the ^{29}Si-NMR resonance is detected at 17.35 ppm.

8	a	b
o-	H	Me

9	a	b
o-	H	Me
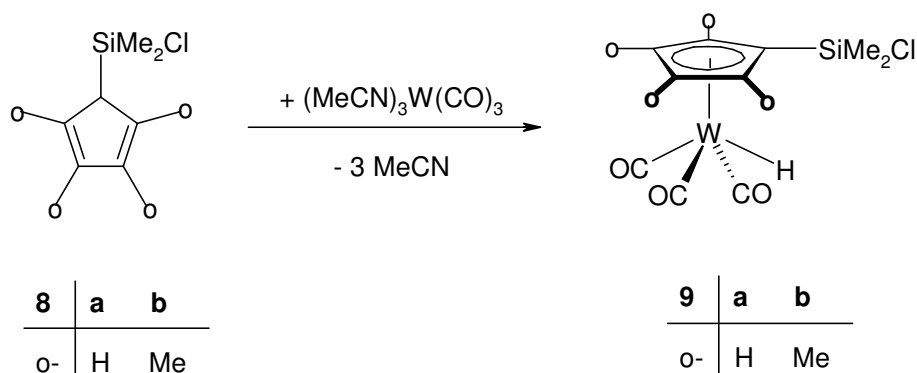
Eq. 2: Synthesis of the chlorodimethylsilyl-functionalized tungsten hydrido complexes **9a,b**.

Chlorination of the cyclopentadienyl-bound Si-H function of **5** succeeds with an equimolar amount of $PdCl_2$ in benzene. However, under these conditions the W-H function of **5** is chlorinated additionally to give the literature-known chloro tungsten complex $[ClMe_2Si(C_5H_4)](OC)_3WCl$ (**10a**) [24] (Scheme 3). The reaction progress can be monitored by IR-spectroscopy indicating the end of the reaction by the dissappearence of the $\tilde{\nu}$ (SiH) absorptions at 2118 cm^{-1}. **10a** is obtained as an orange, very moisture and air sensitive solid which has to be handled and stored under rigorously dry and anaerobic conditions.

The metathetical H/Cl-replacement at the tungsten center, also leading to **10a**, can be realized when a diethylether solution of **9a** is treated with a great excess of CCl_4 and the reaction mixture is stirred over a period of three days. Applying this method, established for $Cp(OC)_3MH$ (M = Mo, W) [45], **10a** is generated in 95 % yield. $[ClMe_2Si(C_5Me_4)](OC)_3WCl$ (**10b**) is analogously synthesized and obtained as a brown solid in 87 % yield (Scheme 3). **10b** is less moisture and air sensitive than **9a** and can be even handled for short time at air.
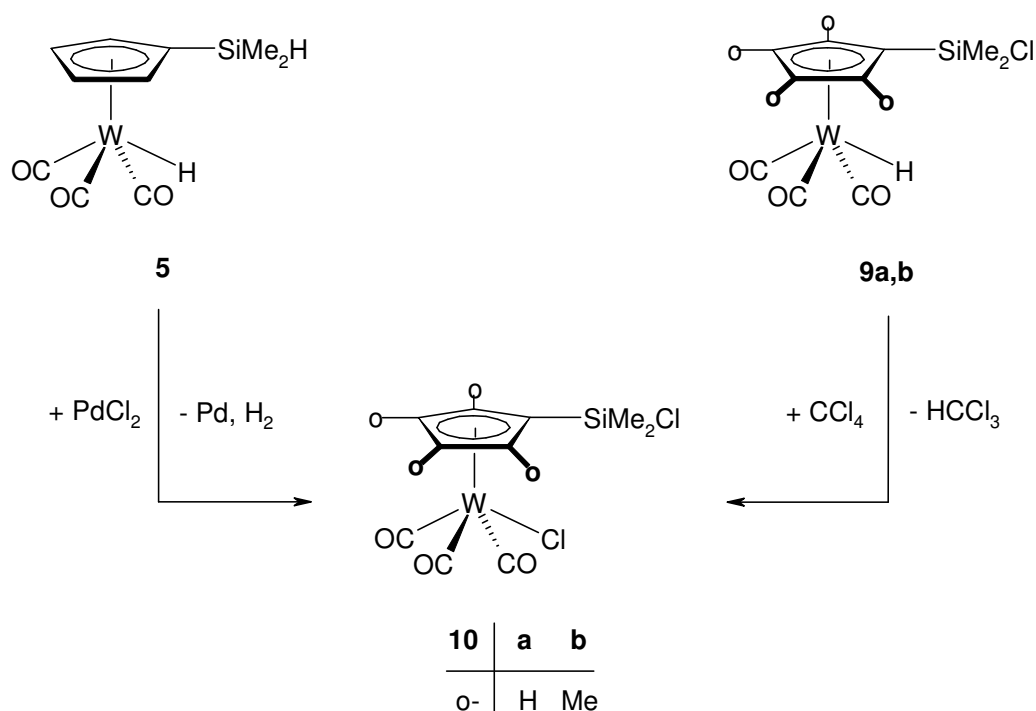
Scheme 3: Chlorination reactions of the tungsten complexes **5** and **9a,b**.

Hydroxydimethylsilyl-cyclopentadienyl Tungsten Complexes (11, 13a-c).
A direct access to **11** involves the reaction with the oxygenation reagent dimethyldioxirane (DMD) which proved to be an efficient method for the generation of $C_5R_5(OC)_2(R'_3P)W$-substituted silanols (R = H, Me; R' = Me, Ph) from tungsten-silanes with an electron rich Si-H function [46-48].

Smooth oxygenation of **5** with DMD in acetone occurs at about 0 °C. However, the synthesis of $[HOMe_2Si(C_5H_4)](OC)_3WH$ (**11**) is accompanied by the formation of a small amount of an unknown byproduct (Scheme 4).

In the case of the tungstenmethyl-counterparts $Cp(OC)_2(R_3P)WCH_2SiMe_2H$ (R = Me, Ph) [20] the same reaction temperatures are necessary for the conversion to the corresponding tungstenmethyl-silanols. In contrast, the DMD oxygenation of $Cp(OC)_2(Me_3P)WSiMe_2H$ with a metal-bound silyl group into the silanol $Cp(OC)_2(Me_3P)WSiMe_2OH$ proceeds quantitively at −78 °C within 15 min [49].

Another pathway for silanol formation involves the successive treatment of the tungsten-silane **5** with $Co_2(CO)_8$ and water. In the first step, the hetero-dinuclear

complex $[(OC)_4CoMe_2Si(C_5H_4)](OC)_3WH$ (**12**) is formed. Due to the weak Co-Si bond of **12**, the hydrolysis at 25 °C in THF affords analytically pure the tungsten-silanol **11** (Scheme 4).
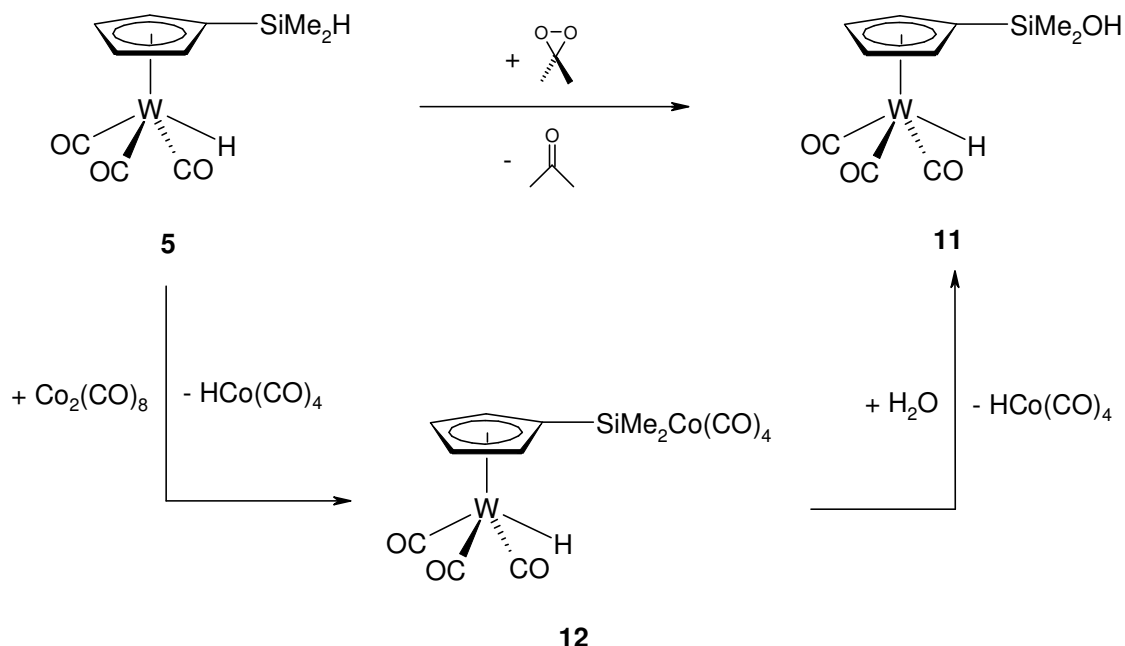
Scheme 4: Two methods applied for the transformation of a Si-H- into a Si-OH function.

As the most efficient route for the synthesis of silanols, the hydrolysis of the tungsten-chlorosilanes **9a,b, 10a,b** in the presence of NEt_3 as auxiliary base at room temperature has been applied, leading directly after about 30 min to the formation of the corresponding tungsten-silanols **11** and **13a**-**c** in yields up to 90 % (Eq. 3). In order to obtain the silanol $[HOMe_2Si(C_5H_4)](OC)_3WH$ (**11**) analytically pure, it is necessary to add acetic acid after hydrolysis. Obviously, the tungsten hydride **9a** is deprotonated partially by NEt_3, indicated by the formation of a pale orange precipitate, observed immediately after the addition of NEt_3. As a consequence, the complex tungsten anion has to be reprotonated after hydrolysis.

	9a	10a	9b	10b
o-	H	H	Me	Me
R	H	Cl	H	Cl

	11	13a	b	c
o-	H	H	Me	Me
R	H	Cl	H	Cl
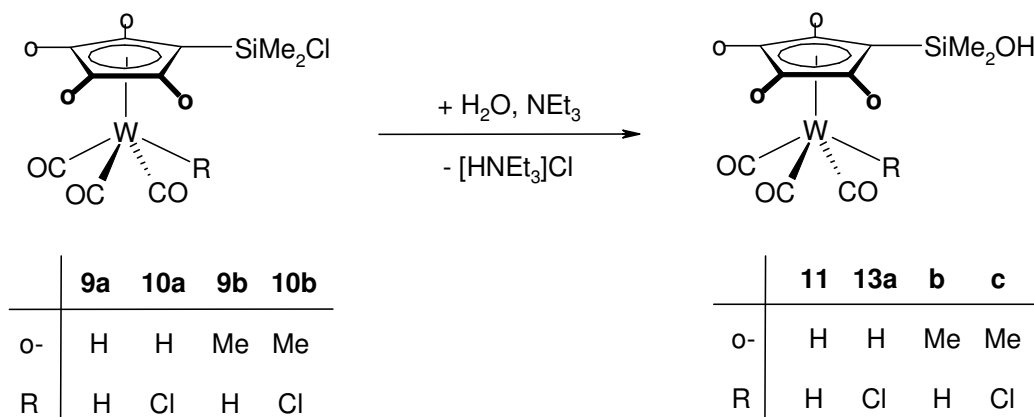
Eq. 3: Synthesis of the tungsten-silanols **11** and **13a-c**.

In the case of the chloro tungsten complex **10a**, the hydrolysis at –60 °C over the period of 25 min affords the tungsten-silanol $[HOMe_2Si(C_5H_4)](OC)_3WCl$ (**13a**) but together with small amounts of $Cp(OC)_3WCl$ (ca. 5 %). Rising the reaction temperature to 0 °C and extending the reaction time to 40 min gives the tungsten-disiloxane $O\{[Me_2Si(C_5H_4)](OC)_3WCl\}_2$ (**14**) (Fig. 3) in 69 % yield accompanied by the tungsten chloride $Cp(OC)_3WCl$ (25 %). These results illustrate an interesting influence of the σ-bonded chlorine atom which evokes a condensation behavior of the tungsten-silanol **13a** which is almost comparable to ordinary organosilanols.

14
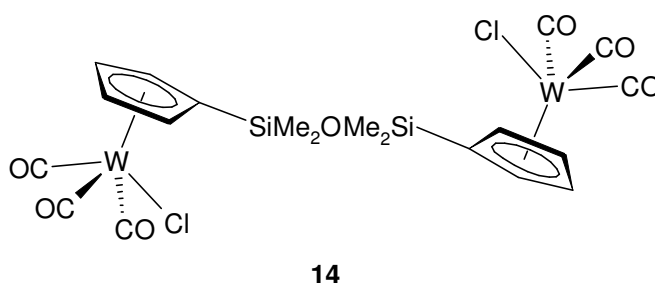
Fig. 3: Dinuclear disiloxane-bridged tungsten chloro complex **14**.

In contrast to this finding, the reactions of **9b** and **10b** take a clean course and affords exclusively the stable tungsten-silanols $[HOMe_2Si(C_5Me_4)](OC)_3WR$ [R = H (**13b**), Cl (**13c**)], indicating that the tetramethyl substitution of the cyclopentadienyl

ligand decrease the condensation tendency. This feature allows even to obtain suitable single crystals of **13c** after evaporation of a saturated benzene solution over the period of few weeks.

The tungsten-silanols are crystalline pale yellow (**11**), orange (**13a,c**) and brown (**13b**) solids, isolated in good yields from 70 to 89 %. **11** and **13a** show a low solubility in nonpolar solvents, increasing in the case of the tetramethyl-substituted derivatives **13b,c**. **11** and **13a-c** can be handled for a short time at air and stored for several months under nitrogen atmosphere.

The ^{29}Si-NMR resonances of **11** and **13a-c** lie very close between 4.31 (**13a**) and 6.34 (**13c**) ppm. The ^{29}Si-NMR resonance of the tungsten-disiloxane **14** is significantly shifted to higher field (-0.50 ppm) in relation to the silanol **13a** which is a typical feature for disiloxanes. All the ^{29}Si-NMR values reveal a minor influence of the transition metal fragment on the silicon atom at the cyclopentadienyl ring. In the case of **11** the signal at 4.70 ppm is shifted approximately 19 ppm to higher field in comparison to its counterpart Cp(OC)$_2$(Ph$_3$P)W-CH$_2$-SiMe$_2$OH with a methylene spacer (23.43 ppm) [20] and nearly 45 ppm compared with Cp(OC)$_2$(Ph$_3$P)W-SiMe$_2$OH (49.6 ppm) [49].

The insignificant difference of about 2 ppm in the ^{29}Si-NMR values of **13a** and **13c** indicates that the increased stability of **13c** towards self-condensation is exclusively caused by the sterical requirement of the cyclopentadienyl-bound methyl groups.

*Structure determination of [HOMe$_2$Si(C$_5$Me$_4$)](OC)$_3$WCl (**13c**)*

The result of the X-ray diffraction analysis of the silanol **13c** confirms the proposed structure and is depicted in figure 4.

The unit cell contains two separate molecules of **13c**, showing no intermolecular interaction. The molecular structure of **13c** shows a pseudo-tetragonal pyramidal piano stool arrangement of the ligands at the central tungsten atom with the cyclopentadienyl ligand in the apical position, typical for complexes of the type (η^5-C$_5$H$_5$)(OC)$_3$MX (M = Cr, Mo, W; X = Cl, Br, I). The values of the tungsten chlorine and the tungsten-carbonyl carbon bond [W2-Cl3 2.489(3), W2-C9 1.993(13), W2-C23 1.993(9) and W2-C30 2.110(13) Å] are very close to the structural parameters of Cp(OC)$_3$WCl [50]. The angles between these ligands forming the basis, also lie in the

normal range for this coordination pattern, a finding which illustrates that the silyl-substitution of the cyclopentadienyl ring has almost no influence on this part of the structure.
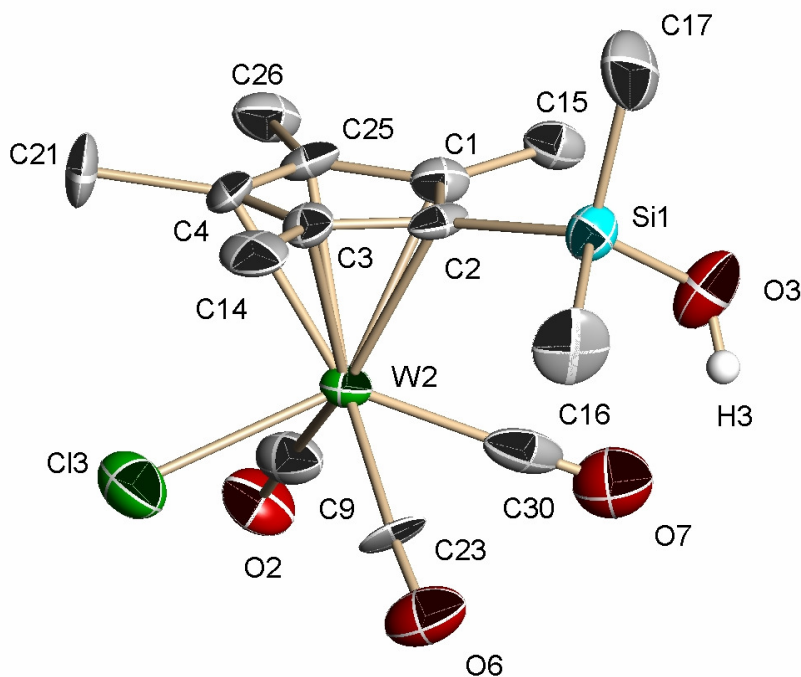
Fig. 4: Depicted molecular structure of $[HOMe_2Si(C_5Me_4)](OC)_3WCl$ (**13c**) in the solid state with the atom-numbering scheme. Thermal ellipsoids are drawn at the 50 % probability level and the hydrogen atoms have been omitted for the sake of clarity except the silanol hydrogen atom H3.

Selected bond lengths [Å], bond and torsion angles [°]: Si1-C2 1.908(10), Si1-C17 1.807(15), Si1-C16 1.907(11), Si1-O3 1.622(9), O3-Si1-C17 111.1(7), O3-Si1-C16 108.7(6), C17-Si1-C16 109.1(7), O3-Si1-C2 107.6(5), C17-Si1-C2 107.7(6), C16-Si1-C2 112.5(6), Si1-C2-W2 126.3(5), C25-C1-C2-Si1 -170.4(8), C17-Si1-C2-C1 81.9(10), C16-Si1-C2-C1 -157.7(9), O3-Si1-C2-C1 -38.0(10), C15-C1-C2-C3 170.7(11), C26-C25-C1-C15 6.9(18).

The Si1-C2 bond length of 1.908(10) Å is very similar to those of the silicon methyl groups [Si1-C16 1.907(11), Si1-C17 1.807(15) Å]. As expected, the silicon atom reveals a tetrahedral arrangement of the substituents with angles between 107.6(5)°

(C17-Si1-C2) and 112.5(6)° (C16-Si1-C2). The silicon-oxygen bond distance of 1.622(9) Å (Si1-O3) lies in the literature-known range for metallo-silanols [13, 21, 51].

The cyclopentadienyl-bound silyl- and methyl groups are bent out of the plane spanned by the cyclopentadienyl ring [C25-C1-C2-Si1 -170.4(8)°; C15-C1-C2-C3 170.7(11)° and C26-C25-C1-C15 6.9(18)°]. The methyl group containing C17 stands almost vertical above the mentioned plane as demonstrated by the torsion angle of 81.9(10)° (C17-Si1-C2-C1). The methyl group of C16 is located below this plane within the quadrant of a carbonyl ligand. This arrangement might be responsible for the fact that no hydrogen bonding between the silanol groups is observed. For some diorgano-metallo-silanols such arrangements are found, which prefer hydrogen-bonded dimeric [$C_5Me_5(OC)_2FeSiMe_2OH$ [51] and $C_5Me_5(OC)_2RuSi(o\text{-}Tol)_2OH$ [13]] or discrete tetrameric units like in the case of the (ferriomethyl)-silanols $C_5R_5(OC)_2FeCH_2SiMeR'OH$ (R = H, Me; R' = Me, Ph) [21].

Reactivity of the Tungsten-silanols 11 and 13b. The deprotonation of metallo-silanols of the general formula $L_nM\text{-}SiR_2OH$ leads to the corresponding lithium silanolates $L_nM\text{-}SiR_2OLi$, which were structurally characterized only in the case of the iridium complex [$(Et_3P)_2Ir(H)(Cl)(Si\mathit{i}Pr_2OLi)]_2$ [52, 53]. Former studies have shown that most halfsandwich metallo-lithiumsilanolates are instable and decompose to the lithium metalate $Li[ML_n]$ and the cyclic trisiloxane $(Me_2SiO)_3$ [54]. The tungsten-silanoles presented in this paper offer the possibility to generate stable silanolates, since the silyl group is separated from the metal center, which should prevent such a fragmentation. In addition, the tungsten-silanol **13b** contains two acidic hydrogen functions capable for deprotonation.

Actually, when the tungsten-silanol **13b** is treated with nBuLi in PE, a beige precipitate is obtained which is identified as the lithium tungstate Li{W[$(C_5H_4)SiMe_2OH](CO)_3$} (**15**) by ^{1}H- and ^{29}Si-NMR spectroscopy (Scheme 5).

The pyrophoric lithium tungstate **15**, isolated quantitively, reacts with an excess of MeI to give the pale orange crystalline tungsten methyl complex **16** in a moderate yield of 51 %.

According to this finding, the W-H bond has to be regarded as the most acidic unit in **13b**.

Furthermore, the reaction of **13b** with two equivalents of *n*BuLi at ambient temperature allows the generating of the double lithiated complex **17** with a negatively charged tungsten center and the targeted silanolate function (Scheme 5). The ^{1}H-NMR spectrum of **17** reveals Li-coordinated THF molecules. The reaction of **17** with an excess of MeI gives the tungsten methyl complex **18**, containing a methoxysilyl group at the cyclopentadienyl ligand as the chemical proof for the existence of a LiOSi unit.
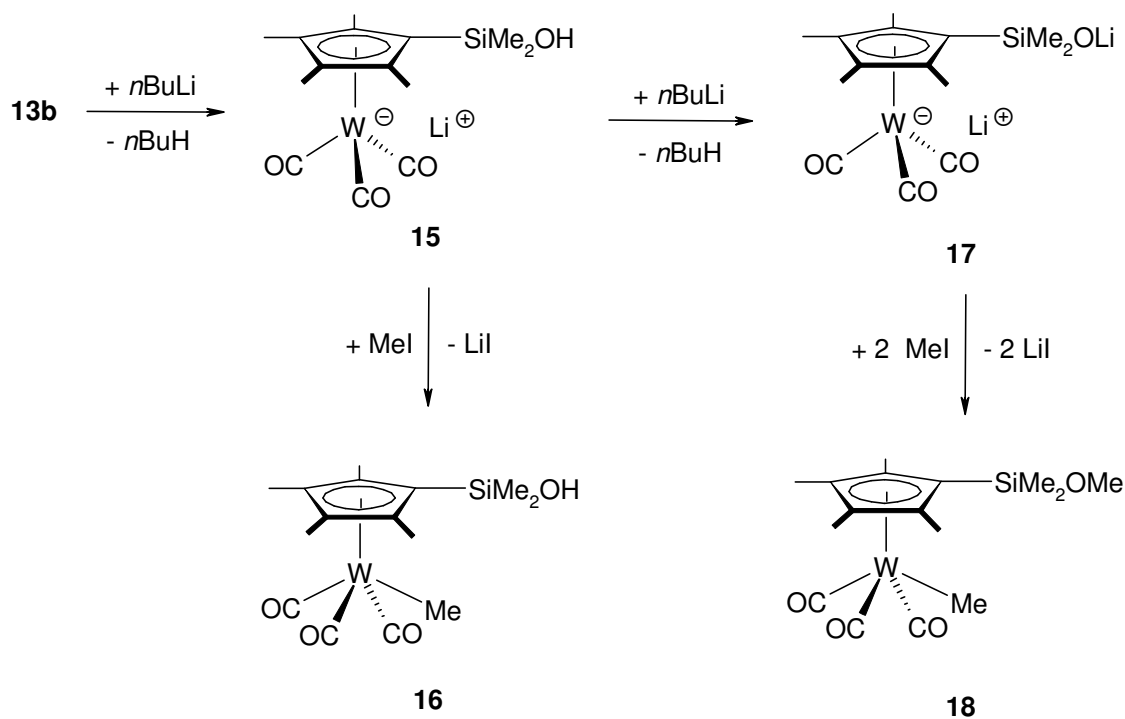
Scheme 5: Reactivity of **13b** towards one and two equivalents of *n*BuLi.

Due to the reasonable stability of the tungsten-silanols **11** and **13b,c** it is possible to perform a controlled co-condensation with organochlorosilanes which can also serve as a chemical proof for a Si-bonded hydroxyl group. In this context, the tungsten-silanol **11** is reacted with chlorodimethylsilane leading after half an hour in the presence of NEt$_3$ to the formation of the tungsten-disiloxane [HMe$_2$SiOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WH (**19**) (Eq. 4). **19** is isolated in an almost quantitive yield (95 %) as a pale beige oil with a high solubility in nonpolar solvents like PE. In comparison, the analogous reaction of its counterparts Cp(OC)$_2$(Ph$_3$P)W-CH$_2$-SiMe$_2$OH and Cp(OC)$_2$(Ph$_3$P)W-SiMe$_2$OH takes two and three days, respectively.

This fact demonstrates the high reactivity of tungsten-silanols with a cyclopentadienyl spacer. The ^{29}Si-NMR signal of the cyclopentadienyl-bound silyl group appears at -1.55 ppm, approximately 5 ppm shifted to higher field in comparison to **11**, which is in agreement with the known properties of metallomethyl-silanols [17].
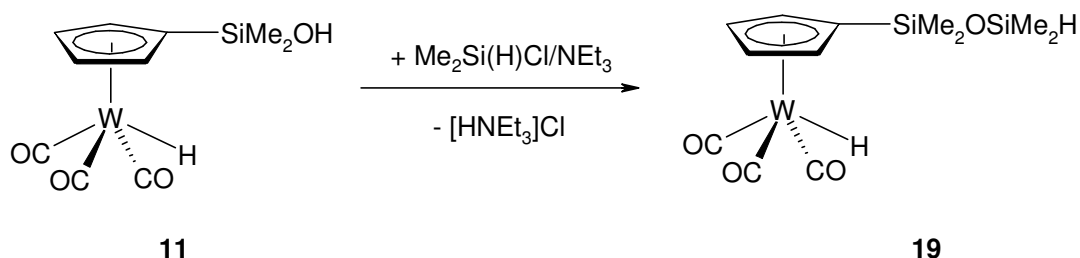
Eq. 4: Co-condensation of the silanol **11** with $Me_2Si(H)Cl$.

Recent work has shown that the properties of ferrio-silanols allow the preparation of metal-fragment substituted heterosiloxanes of group 13 via alkane elimination [55]. The analogous reaction of **13b** with the trialkyl-*iso*butylalane *i*Bu$_3$Al gives the expected dimeric tungsten-alumosiloxane {[*i*Bu$_2$AlOMe$_2$Si(C$_5$Me$_4$)](OC)$_3$WH}$_2$ (**20**) and *iso*butane (Eq. 5).

20 is obtained in 58 % yield as a pale beige solid after two hours reaction time and shows good solubility in nonpolar solvents.

The ^{29}Si-NMR resonance of **20** (7.19 ppm) appears very close to that of the corresponding tungsten-silanol **13b** which seems to be a typical feature for this kind of compounds [55].
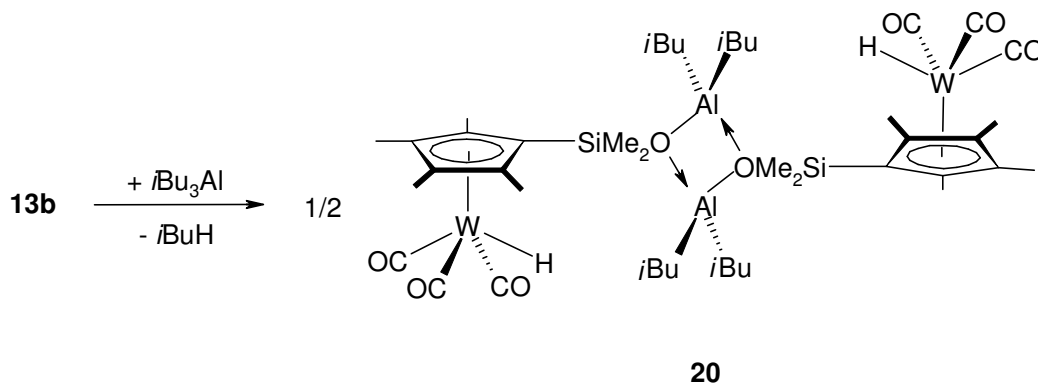
Eq. 5: Synthesis of {[*i*Bu$_2$AlOMe$_2$Si(C$_5$Me$_4$)](OC)$_3$WH}$_2$ (**20**) via butane elimination.

CONCLUSION

This paper presents two new elegant ways for the introduction of a silyl group at the cyclopentadienyl ring of tungsten complexes, e.g. by base-induced silyl shift and via regiospecific silylation of the dilithiated complex Li[W(LiC$_5$H$_4$)(CO)$_3$]. Furthermore, halfsandwich tungsten complexes with η^5-cyclopentadienyl-fixed silanol function are accessible by hydrolysis of the chlorosilyl precursors or in the case of tungsten complexes with a cyclopentadienyl-bound Si-H function via H/Co(CO)$_4$-exchange followed by hydrolytic cleavage of the labile Si-Co bond. The type of metal fragment-substituted silanols represented in this paper, is characterized by an enhanced reactivity with respect to self-condensation leading to the formation of disiloxanes, compared to the tungstenmethyl- and tungsten-silanols Cp(OC)$_2$(Ph$_3$P)W-CH$_2$-SiMe$_2$OH and Cp(OC)$_2$(Ph$_3$P)W-SiMe$_2$OH. Moreover, the reactivity of the SiOH function is high enough to perform controlled reactions with chlorosilanes or trialkylalanes in order to generate novel transition metal-containing siloxanes and heterosiloxanes.

Current work deals with the investigation of tungsten methyl complexes with η^5-cyclopentadienyl-fixed silanol function and the variation of the organo groups attached to the silicon atom in order to comprehend their influence on the stability and reactivity in condensation processes.

EXPERIMENTAL SECTION

General Remarks: All operations were performed under an atmosphere of purified and dried nitrogen using Schlenk-type techniques. Solvents were dried according to conventional procedures, distilled and saturated with N_2 prior to use. - NMR: Jeol Lambda 300 (300.4 MHz, 75.5 MHz, and 59.6 MHz for ^1H, ^{13}C, and ^{29}Si, respectively). [D_6]-benzene as a solvent: $\delta_H = 7.15$, $\delta_C = 128.0$; for ^{29}Si rel. to TMS external. - IR: Perkin-Elmer 283 grating spectrometer. - Melting points: Differential thermo analysis (Du Pont 9000 Thermal Analysis System). - Elemental analyses were performed in the laboratories of the *Institut für Anorganische Chemie der Universität Würzburg*. - Starting materials were prepared according to literature procedures: DMD [46, 47], $(MeCN)_3W(CO)_3$ [56], $Cp(OC)_3WSiMe_2H$ (**1a**) [44], $Cp(Me_3P)(OC)_2WSiMe_2H$ (**1b**) [57], $Cp(OC)_3WH$ (**3**) [58], $HMe_2SiC_5H_5$ (**7**) [59], $ClMe_2SiC_5H_5$ (**8a**) [60] and $[ClMe_2Si(C_5H_4)](OC)_3WH$ (**9a**) [24]. The reagents $Me_2Si(H)Cl$, Me_3SiCl and $ClMe_2SiC_5Me_4H$ (**8b**), $Co_2(CO)_8$ were purchased from commercial sources and $Me_2Si(H)Cl$ distilled prior use.

1) Li{W[(C₅H₄)SiMe₂H](CO)₃} (2a)

Lithium[tricarbonyl(η^5-dimethylsilylcyclopentadienyl)tungstate]

To a solution of 350 mg (0.89 mmol) of $Cp(OC)_3WSiMe_2H$ (**1a**) in 20 ml PE were 0.54 ml (1.07 mmol) LDA (2 M, cyclohexane/ethylbenzene/THF-solution) added at 0 °C. The solution was stirred for 15 min at this temperature and for additional 15 min at 25 °C, while precipitating of a brown solid (**2a**) was observed. This precipitate was filtered off, washed with PE and dried in vacuo giving a pale beige and pyrophoric powder. - **^{1}H-NMR** (300.4 MHz, D_6-Acetone): $\delta = 5.12 - 5.06$ (m, 2 H, H_4C_5), $5.05 - 5.03$ (m, 2 H, H_4C_5), 4.41 [sept, $^3J(HSiCH) = 3.7$ Hz, 1 H, SiH], 0.20 [d, $^3J(HCSiH) = 3.7$ Hz, 6 H, H_3CSi] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C_6D_6): $\delta = 227.23$ [s, $^1J(CW) = 201.3$ Hz, CO], 98.43 (s, C_5H_4), 97.40 [s, $^1J(CW) = 3.7$ Hz, C_5H_4], 90.23 [s, $^1J(CW) = 3.7$ Hz, C_5H_4], 2.69 (s, CH_2Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): $\delta = -20.37$ (s)

ppm. - **IR** (THF): $\tilde{\nu}$ (SiH) = 2089 (w) cm^{-1}; $\tilde{\nu}$ (CO) = 1889 (s), 1803 (s), 1719 (vs) cm^{-1}. - C$_{10}$H$_{11}$LiO$_3$SiW (398.07).

*2) Li{W[(C$_5$H$_4$)SiMe$_2$H](PMe$_3$)(CO)$_2$} (**2b**)*

Lithium[dicarbonyl(η^5-dimethylsilylcyclopentadienyl)(trimethylphosphino)tungstate]

To a solution of 570 mg (1.29 mmol) of Cp(Me$_3$P)(OC)$_2$WSiMe$_2$H (**1b**) in 20 ml Et$_2$O, 0.91 ml (18.1 mmol) of LDA (2 M, cyclohexane/ethylbenzene/THF-solution) were added at -78 ℃. The solution was stirred for 30 min at this temperature, then allowed to warm up to room temperature and stirred for further 1.5 h at this temperature, while precipitating of a yellow solid (**2b**) was observed. The precipitate was filtered off, washed with PE and dried in vacuo giving a yellow and pyrophoric powder. - **^{1}H-NMR** (300.4 MHz, D$_8$-THF): δ = 4.86 − 4.83 (m, 2 H, H$_4$C$_5$), 4.82 − 4.78 (m, 2 H, H$_4$C$_5$), 4.42 [sept, ^3J(HSiCH) = 3.3 Hz, 1 H, SiH], 1.50 [d, ^2J(HCP) = 7.5 Hz, 9 H, H$_3$CP], 0.20 [d, ^3J(HCSiH) = 3.3 Hz, 6 H, H$_3$CSi] ppm. - **^{31}P{^{1}H}-NMR**: (121.5 MHz, D$_8$-THF): δ = -13.14 [s, ^1J(PW) = 461.7 Hz, PW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, D$_8$-THF): δ = 236.66 [d, ^2J(CWP) = 5.7 Hz, ^1J(CW) = 209.3 Hz, CO], 97.43 (s, C$_5$H$_4$), 96.30 [s, ^1J(CW) = 3.8 Hz, C$_5$H$_4$], 89.93 [s, ^1J(CW) = 3.8 Hz, C$_5$H$_4$], 27.89 [d, ^1J(CP) = 26.8 Hz, CH$_3$P], -0.67 (s, CH$_2$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, D$_8$-THF): δ = -21.87 (s) ppm.- **IR** (THF): $\tilde{\nu}$ (SiH) = 2118 (w) cm^{-1}; $\tilde{\nu}$ (CO) = 1783 (vs), 1649 (vs) cm^{-1}. - C$_{12}$H$_{20}$LiO$_2$PSiW (446.13).

*3) Li{W(LiC$_5$H$_4$)(CO)$_3$} x 4 THF (**4**)*

Lithium[tricarbonyl(η^5-lithiocyclopentadienyl)tungstate]

A solution of 4.04 g (12.1 mmol) **3** in 10 ml THF was treated with 22.2 ml (36.3 mmol) *n*BuLi (1.6 M, hexane-solution) at 0 ℃. After 15 min the cooling bath was removed and the solution stirred for four hours at room temperature. A yellow precipitate of **4** was observed after half an hour. The precipitate was filtered off, washed twice with small portions of THF and with PE. Finally it was dried in vacuo, giving a pyrophoric

powder. Yield 6.79 g (88 %). Yellowgreen solid. - **^{1}H-NMR** (300.4 MHz, D$_8$-THF): δ = 5.08 (m, 4 H, H$_4$C$_5$), 3.70 - 3.60 (m, 4 H, THF), 1.85 - 1.75 (m, 4 H, THF) ppm. - **IR** (THF): $\tilde{\nu}$(CO) = 1900 (s), 1802 (s), 1716 (vs) cm^{-1}. - C$_{24}$H$_{36}$Li$_2$O$_7$W (634.33).

4) Li{W[(C$_5$H$_4$)SiMe$_2$H](CO)$_3$} (2a) from reaction of 4 with Me$_2$Si(H)Cl

A suspension of 2.75 g (4.34 mmol) of **4** in 10 ml THF was treated with 0.41 g (4.34 mmol, 0.47 ml) Me$_2$Si(H)Cl at −78 °C over a period of half an hour. Immediately after addition of the silane all the precipitate of **4** dissolved. The solution was allowed to warm up to room temperature. Then all volatiles were removed in vacuo, giving a greasy residue. Washing with PE and drying in vacuo resulted in a pale yellow and pyrophoric powder. Yield 1.69 g (98 %). Pale yellow solid.

5) Li{W[(C$_5$H$_4$)SiMe$_2$H](CO)$_3$} (2a) from reaction of 4 with ClCH$_2$SiMeH$_2$

Analogous to 4) from 1.38 g (2.18 mmol) of **4** and 23 mg (2.18 mmol) ClCH$_2$SiMeH$_2$ in 10 ml THF. Yield 590 mg (68 %). Pale yellow solid.

6) [HMe$_2$Si(C$_5$H$_4$)](OC)$_3$WH (5)

Tricarbonyl[η^5-(dimethylsilyl)-cyclopentadienyl]hydridotungsten(II)

To a suspension of 1.89 g (4.35 mmol) of tungstate **2a** in 20 ml PE, 0.49 ml (8.68 mmol) of acetic acid were added and stirred for one hour in the absence of light. Insoluble material was removed by filtration through a celite pad and the filtrate evaporated to dryness in vacuo. Yield 1.40 g (82 %). Pale yellow oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.83 − 4.80 (m, 2 H, H$_4$C$_5$), 4.77 − 4.74 (m, 2 H, H$_4$C$_5$), 4.40 [sept, ^{3}J(HSiCH) = 3.6 Hz, 1 H, SiH], 0.06 [d, ^{3}J(HCSiH) = 3.6 Hz, 6 H, H$_3$CSi], -7.26 [s, ^{1}J(HW) = 36.4 Hz, 1 H, HW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 217.28 (s, CO), 94.64 (s, C$_5$H$_4$), 93.68 [s, ^{1}J(CW) = 4.8 Hz, C$_5$H$_4$], 92.83 [s, ^{1}J(CW) = 4.2 Hz, C$_5$H$_4$], -3.00 [s, ^{1}J(CSi) = 1.4 Hz, CH$_3$Si] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ =

-20.43 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (SiH) = 2118 (w) cm^{-1}; $\tilde{\nu}$ (CO) = 2017 (vs), 1924 (vs) cm^{-1}. – Anal. calc. for $C_{10}H_{12}O_3SiW$ (392.13): C 30.63, H 3.08; found C 31.13, H 3.02.

*7) [HMe$_2$Si(C$_5$H$_4$)](Me$_3$P)(OC)$_2$WMe (**6a**)*

Dicarbonyl[η^5-(dimethylsilyl)-cyclopentadienyl](trimethylphosphino)methyltungsten(II)

To a suspension of 570 mg (1.27 mmol) of tungstate **2b** in 20 ml cyclohexane, 0.1 ml (1.67 mmol) MeI were added and stirred over night. Insoluble material was removed by filtration through a celite pad and the filtrate, containing **6a**, evaporated to dryness in vacuo. The crude residue was washed with 5 ml PE at −78 °C. Yield 456 mg (79 %). Yellow solid. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.74 - 4.72 (m, 2 H, H$_4$C$_5$), 4.68 [sept, ^3J(HSiCH) = 3.7 Hz, 1 H, HSiC$_5$H$_4$], 4.27 − 4.25 (m, 2 H, H$_4$C$_5$), 1.12 [d, ^3J(HCP) = 9.2 Hz, 9 H, H$_3$CP], 0.74 [d, ^3J(HCWP) = 3.3 Hz, 3 H, H$_3$CW], 0.25 [d, ^3J(HCSiH) = 3.7 Hz, 6 H, H$_3$CSiC$_5$H$_4$] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 251.21 [d, ^2J(CWP) = 19.2 Hz, ^1J(CW) = 135.2 Hz, CO], 97.43 (s, C$_5$H$_4$), 96.30 (s, C$_5$H$_4$), 89.93 [s, ^1J(CW) = 3.8 Hz, C$_5$H$_4$], 16.48 [d, ^1J(CP) = 30.1 Hz, CH$_3$P], -2.67 (s, CH$_3$SiC$_5$H$_4$), -22.19 [d, ^2J(CWP) = 19.2 Hz, CH$_3$W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -20.44 (s) ppm. - **^{31}P{^{1}H}-NMR** (121.5 MHz, C$_6$D$_6$): δ = -19.26 [s, ^1J(PW) = 233.3 Hz, PCH$_3$] ppm. - **IR** (PE): $\tilde{\nu}$ (SiH) = 2127 (w), 2049; $\tilde{\nu}$ (CO) = 1924 (vs), 1836 (vs) cm^{-1}. - C$_{13}$H$_{23}$O$_2$PSiW (454.24).

*8) [HMe$_2$Si(C$_5$H$_4$)](Me$_3$P)(OC)$_2$WSiMe$_2$H (**6b**)*

Dicarbonyl[η^5-(dimethylsilyl)-cyclopentadienyl](trimethylphosphino)-dimethylsilyl-tungsten(II)

Analogous to 7) from 1.07 g (2.41 mmol) of **2b** and 0.65 mg (6.80 mmol, 0.74 ml) Me$_2$Si(H)Cl in 20 ml cyclohexane over a period of 36 hours. Yield 840 mg (70 %). Yellow solid. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 5.26 [sept, ^3J(HSiCH) = 3.7 Hz, 1 H, HSiW], 4.73 - 4.70 (m, 2 H, H$_4$C$_5$), 4.62 − 4.59 (m, 2 H, H$_4$C$_5$), 4.52 [sept, ^3J(HSiCH) = 3.7 Hz, 1 H, HSiC$_5$H$_4$], 1.16 [d, ^3J(HCP) = 9.4 Hz, 9 H, H$_3$CP], 0.92 [d, ^3J(HCSiH) =

3.7 Hz, 6 H, H$_3$CSiW], 0.22 [d, ^{3}J(HCSiH) = 3.7 Hz, 6 H, H$_3$CSiC$_5$H$_4$] ppm. - ^{13}C{^{1}H}-**NMR** (75.5 MHz, C$_6$D$_6$): δ = 224.21 [d, ^{2}J(CWP) = 17.2 Hz, CO], 95.43 (s, C$_5$H$_4$), 95.30 (s, C$_5$H$_4$), 88.93 [s, ^{1}J(CW) = 3.8 Hz, C$_5$H$_4$], 21.8 [d, ^{1}J(CP) = 34.1 Hz, CH$_3$P], 2.19 (s, CH$_3$SiW), -2.67 (s, CH$_3$SiC$_5$H$_4$) ppm. - ^{29}Si{^{1}H}-**NMR** (59.6 MHz, C$_6$D$_6$): δ = 0.02 [d, ^{2}J(SiWP) = 14.3 Hz, SiW], -20.86 (s, SiC$_5$H$_4$) ppm. - ^{31}P{^{1}H}-**NMR** (121.5 MHz, C$_6$D$_6$): δ = -14.70 [s, ^{1}J(PW) = 283.8 Hz, PCH$_3$] ppm. - **IR** (PE): $\tilde{\nu}$(SiH) = 2121 (w), 2049 (w) cm^{-1}; $\tilde{\nu}$(CO) = 1904 (vs), 1832 (vs) cm^{-1}. - C$_{14}$H$_{27}$O$_2$PSi$_2$W (498.35).

*9) [HMe$_2$Si(C$_5$H$_4$)](Me$_3$P)(OC)$_2$WSiMe$_3$ (**6c**)*

Dicarbonyl[η^5-(dimethylsilyl)-cyclopentadienyl](trimethylphosphino)-trimethylsilyl-tungsten(II)

Analogous to 7) from 370 mg (0.83 mmol) of **2b** and 35 mg (3.20 mmol, 0.40 ml) Me$_3$SiCl in 20 ml cyclohexane after a period of 36 hours. Yield 332 mg (78 %). Yellow solid. - ^{1}**H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.74 -4.72 (m, 2 H, H$_4$C$_5$), 4.63 – 4.61 (m, 2 H, H$_4$C$_5$), 4.49 [sept, ^{3}J(HSiCH) = 3.7 Hz, 1 H, HSiC$_5$H$_4$], 1.17 [d, ^{3}J(HCP) = 9.2 Hz, 9 H, H$_3$CP], 0.82 (s, 9 H, H$_3$CSiW), 0.20 [d, ^{3}J(HCSiH) = 3.7 Hz, 6 H, H$_3$CSiC$_5$H$_4$] ppm. - ^{13}C{^{1}H}-**NMR** (75.5 MHz, C$_6$D$_6$): δ = 223.77 [d, ^{2}J(CWP) = 17.3 Hz, CO], 94.77 (s, C$_5$H$_4$), 96.66 (s, C$_5$H$_4$), 89.93 [s, ^{1}J(CW) = 3.7 Hz, C$_5$H$_4$], 22.3 [d, ^{1}J(CP) = 34.0 Hz, CH$_3$P], 2.88 (s, CH$_3$SiW), -2.98 (s, CH$_3$SiC$_5$H$_4$) ppm. - ^{29}Si{^{1}H}-**NMR** (59.6 MHz, C$_6$D$_6$): δ = 17.13 [d, ^{2}J(SiWP) = 13.4 Hz, SiW], -20.72 (s, SiC$_5$H$_4$) ppm. - ^{31}P{^{1}H}-**NMR** (121.5 MHz, C$_6$D$_6$): δ = -13.24 [s, ^{1}J(PW) = 283.1 Hz, PCH$_3$] ppm. - **IR** (cyclohexane): $\tilde{\nu}$(SiH) = 2114 (w) cm^{-1}; $\tilde{\nu}$(CO) = 1939 (vs), 1854 (vs) cm^{-1}. - C$_{15}$H$_{29}$O$_2$PSi$_2$W (512.37).

*10) [HMe$_2$Si(C$_5$H$_4$)](OC)$_3$WH (**5**) by reaction of HMe$_2$SiC$_5$H$_5$ (**7**) with (MeCN)$_3$W(CO)$_3$*

A solution of 3.30 g (26.7 mmol) of HMe$_2$SiC$_5$H$_5$ (**7**) and 10.54 g (26.7 mmol) (MeCN)$_3$W(CO)$_3$ in 60 ml THF was refluxed over a period of 24 hours in the dark until all (MeCN)$_3$W(CO)$_3$ had reacted. All volatiles were removed in vacuo giving a brown oil which was washed with PE at –78 °C. Yield 9.53 g (91 %). Brown oil.

*11) [ClMe$_2$Si(C$_5$H$_4$)](OC)$_3$WH (**9a**)*

Tricarbonyl[η^5-(chlorodimethylsilyl)-cyclopentadienyl]hydridotungsten(II)

Analogous to 10) from 4.08 g (25.7 mmol) of ClMe$_2$SiC$_5$H$_5$ (**8a**) and 10.0 g (25.7 mmol) (MeCN)$_3$W(CO)$_3$ in 100 ml THF over a period of 18 hours under light exclusion until all (MeCN)$_3$W(CO)$_3$ was used up. After cooling all volatiles were removed in vacuo giving a brown residue which was extracted with 8 x 20 ml PE. The extracts were combined and filtered through a celite path. The filtrate was evaporated to dryness and the crude product washed with 5 ml PE at –78 °C. Yield 9.46 g (86 %). Dark red oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.72 – 4.69 (m, 4 H, H$_4$C$_5$), 0.34 (s, 6 H, H$_3$CSi), -7.35 [s, ^{1}J(HW) = 36.4 Hz, 1 H, HW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 216.45 (s, CO), 93.97 [s, ^{1}J(CW) = 5.2 Hz, *ipso*-C$_5$H$_4$], 93.51 [s, ^{1}J(CW) = 3.8 Hz, C$_5$H$_4$], 92.83 [s, ^{1}J(CW) = 4.8 Hz, C$_5$H$_4$], 2.40 [s, ^{1}J(CSi) = 61.7 Hz, CH$_3$Si] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 17.35 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2027 (s), 1938 (vs) cm^{-1}. – Anal. calc. for C$_{10}$H$_{11}$ClO$_3$SiW (426.57): C 28.14, H 2.57; found C 28.69, H 2.88.

*12) [ClMe$_2$Si(C$_5$Me$_4$)](OC)$_3$WH (**9b**)*

Tricarbonyl[η^5-(chlorodimethylsilyl)-tetramethylcyclopentadienyl]hydridotungsten(II)

Analogous to 10) from 5.00 g (23.3 mmol) of ClMe$_2$SiC$_5$Me$_4$H (**8b**) and 9.10 g (23.3 mmol) (MeCN)$_3$W(CO)$_3$ in 50 ml THF after 24 hours in the absence of light. All the volatiles were removed in vacuo giving a solid. Yield 11.1 g (98 %). Greenbrown solid. M.p. 39 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 1.88 (s, 6 H, H$_3$CC$_5$), 1.60 (s, 6 H, H$_3$CC$_5$), 0.60 (s, 6 H, H$_3$CSi), -6.72 [s, ^{1}J(HW) = 38.8 Hz, 1 H, HW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 219.79 (s, CO), 197.03 (s, CO), 110.95 [s, ^{1}J(CW) = 4.5 Hz, $\underline{C}_5$Me$_4$], 108.27 [s, ^{1}J(CW) = 6.6 Hz, $\underline{C}_5$Me$_4$], 87.57 [s, ^{1}J(CW) = 4.8 Hz, *ipso*-$\underline{C}_5$Me$_4$], 13.50 (s, $\underline{C}$H$_3$C$_5$), 10.99 (s, $\underline{C}$H$_3$C$_5$), 5.75 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 18.49 (s) ppm. - **IR** (Et$_2$O): $\tilde{\nu}$ (CO) = 2013 (vs), 1924 (vs) cm^{-1}. – Anal. calc. for C$_{14}$H$_{23}$ClO$_3$SiW (486.72): C 34.55, H 4.76; found C 34.10, H 3.90.

*13) [ClMe$_2$Si(C$_5$H$_4$)](OC)$_3$WCl (**10a**) by reaction of **5** with PdCl$_2$*

Tricarbonylchloro[η^5-(chlorodimethylsilyl)-cyclopentadienyl]tungsten(II)

To a solution of 300 mg (0.77 mmol) of **5** in 5 ml benzene 142 mg (0.80 mmol) of PdCl$_2$ were added. The mixture was stirred for three days until any observed gas formation ended. The solvent was removed in vacuo and the residue extracted with 30 ml PE. Insoluble material was filtered off by use of a celite pad. The obtained filtrate was evaporated to dryness in vacuo. Yield 344 mg (97 %). Orange solid. M.p. 38 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.67 – 4.65 (m, 2 H, H$_4$C$_5$), 4.56 – 4.54 (m, 2 H, H$_4$C$_5$), 0.41 (s, 6 H, H$_3$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 229.51 (s, *cis*-CO), 214.21 (s, *trans*-CO), 103.01 [s, ^{1}J(CW) = 4.2 Hz, C$_5$H$_4$], 94.77 [s, ^{1}J(CW) = 4.0 Hz, C$_5$H$_4$], 93.18 [s, ^{1}J(CW) = 3.9 Hz, *ipso*-C$_5$H$_4$], 2.71 [s, ^{1}J(CSi) = 69.5 Hz, CH$_3$Si] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 18.22 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2050 (s), 1969 (vs), 1955 (s) cm^{-1}. – Anal. calc. for C$_{10}$H$_{10}$Cl$_2$O$_3$SiW (486.72): C 26.05, H 2.19; found C 26.47, H 2.26.

*14) [ClMe$_2$Si(C$_5$H$_4$)](OC)$_3$WCl (**10a**) by reaction of **9a** with CCl$_4$*

A solution of 3.09 g (7.24 mmol) of **9a** in 20 ml Et$_2$O was treated with 6 ml CCl$_4$ and stirred for three days at room temperature. All volatiles were removed in vacuo and the crude product was washed four times each with 5 ml portions of PE at –78 °C. Yield: 3.16 g (95 %). Orange solid.

*15) [ClMe$_2$Si(C$_5$Me$_4$)](OC)$_3$WCl (**10b**)*

Tricarbonylchloro[η^5-(chlorodimethylsilyl)-tetramethylcyclopentadienyl]tungsten(II)

1.97 g (4.06 mmol) of the tungsten-chlorosilane **9b** were dissolved in 15 ml Et$_2$O and treated with an excess of 6 ml CCl$_4$ over a period of three days. When the IR spectrum shows no more **9b** all volatiles were removed in vacuo and the crude

residue was washed twice with 7 ml PE at –78 °C. Yield 1.82 g (87 %). Orangebrown solid. M.p. 52 °C. - **^{1}H-NMR** (300.4 MHz, C_6D_6): δ = 1.69 (s, 6 H, H_3CC_5), 1.39 (s, 6 H, H_3CC_5), 0.56 (s, 6 H, H_3CSi) ppm. - **$^{13}C\{^1H\}$-NMR** (75.5 MHz, C_6D_6): δ = 234.69 (s, CO), 218.30 [s, $^1J(CW)$ = 153.8 Hz, CO], 116.90 [s, $^1J(CW)$ = 6.2 Hz, $\underline{C}_5Me_4$], 109.80 [s, $^1J(CW)$ = 4.5 Hz, $\underline{C}_5Me_4$], 89.07 [s, $^1J(CW)$ = 4.8 Hz, ipso-$\underline{C}_5Me_4$], 13.31 (s, $\underline{C}H_3C_5$), 10.09 (s, $\underline{C}H_3C_5$), 5.02 (s, CH_3Si) ppm. - **$^{29}Si\{^1H\}$-NMR** (59.6 MHz, C_6D_6): δ = 19.90 (s) ppm. - **IR** (Et_2O): $\tilde{\nu}$ (CO) = 2036 (s), 1958 (vs), 1937 (s) cm^{-1}. – Anal. calc. for $C_{14}H_{18}Cl_2O_3SiW$ (517.14): C 32.52, H 3.51; found C 31.56, H 3.41.

*16) [HOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WH (**11**) by oxygenation of **5** with dimethyldioxirane (DMD)*

Tricarbonyl[η^5-(hydroxydimethylsilyl)-cyclopentadienyl]hydridotungsten(II)

To a solution of 200 mg (0.51 mmol) of **5** in 7 ml acetone, 6.78 ml (0.61 mmol) of a 0.09 M solution of dimethyldioxirane in acetone were added at 0 °C and stirred for four hours at this temperature. All volatiles were removed in vacuo and the crude residue washed twice, each with 5 ml PE at –78 °C. Yield 139 mg (67 %). Pale yellow solid.

*17) [(OC)$_4$CoMe$_2$Si(C$_5$H$_4$)](OC)$_3$WH (**12**)*

Tricarbonyl[η^5-(tetracarbonylcobalto)-(dimethylsilyl)-cyclopentadienyl]hydrido-tungsten(II)

970 mg (2.47 mmol) of **5** were dissolved in 10 ml Et_2O and treated with 420 mg (1.23 mmol) of $Co_2(CO)_8$. The reaction mixture was stirred for four hours at roomtemperature. The solvent was removed in vacuo and the residue was extracted with 40 ml PE. Insoluble material was filtered off by use of a celite pad. The filtrate was evaporated to dryness in vacuo and washed with 5 ml PE at –78 °C. Yield 1.06 g (76 %). Dark brown and sticky solid. - **^{1}H-NMR** (300.4 MHz, C_6D_6): δ = 4.79 – 4.73 (m, 4 H, H_4C_5), 0.17 (s, 6 H, H_3CSi) ppm. - **$^{29}Si\{^1H\}$-NMR** (59.6 MHz, C_6D_6): δ = -2.32

(s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2063 (s), 2055 (s), 2025 (w), 1939 (s) cm^{-1}. – $C_{14}H_{11}CoO_7SiW$ (562.10).

18) [HOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WH (11) by hydrolysis of 12

To a solution of 1.06 g (1.89 mmol) of **12** in 10 ml THF were added 0.3 ml water. The solution was stirred over a period of four hours and the volatiles removed in vacuo. The crude residue was washed two times, each with 4 ml PE at –78 °C. Yield 6.87 mg (89 %). Pale yellow solid.

19) [HOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WH (11) by hydrolysis of 9a

970 mg (2.27 mmol) of the tungsten-chlorosilane **9a** were dissolved in 10 ml Et$_2$O and treated with 81.8 mg (0.08 ml, 4.54 mmol) NEt$_3$ and 0.1 ml water. Precipitation of a white solid was observed immediately after addition of water. The suspension was stirred for one hour. Finally, 0.3 ml of acetic acid were added and stirred for a further hour. Then, Na$_2$SO$_4$ was added for drying. All insoluble material was filtered off by use of a celite pad. The filtrate was evaporated to dryness in vacuo and washed twice, each with 5 ml PE at –78 °C. Yield 650 mg (70 %). Pale yellow solid. M.p. 47 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.78 - 4.74 (m, 4 H, H$_4$C$_5$), 2.37 (s, 1 H, HOSi), 0.17 (s, 6 H, H$_3$CSi), -7.26 [s, ^{1}J(HW) = 35.7 Hz, HW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 219.66 (s, CO), 197.83 (s, CO), 110.95 [s, ^{1}J(CW) = 3.8 Hz, C$_5$H$_4$], 108.67 [s, ^{1}J(CW) = 3.8 Hz, C$_5$H$_4$], 87.57 (s, *ipso*-C$_5$H$_4$), 1.11 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 4.70 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2020 (s), 1934 (vs) cm^{-1}. – Anal. calc. for C$_{10}$H$_{12}$O$_4$SiW (408.13): C 29.43, H 2.96; found C 28.80, H 2.95.

*20) [HOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WCl (**13a**)*

Tricarbonylchloro[η^5-(hydroxydimethylsilyl)-cyclopentadienyl]tungsten(II)

Analogous to 19) from 0.70 g (1.52 mmol) of **10a**, 0.1 ml of NEt$_3$ and 0.1 ml of water at –60 °C over a period of 25 min and without final addition of HOAc. The crude residue was washed with 4 ml PE at 0 °C. Yield 545 mg (81 %). Orange solid. M.p. 56 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.93 - 4.92 (m, 2 H, H$_4$C$_5$), 4.62 - 4.61 (m, 2 H, H$_4$C$_5$), 2.32 (s, 1 H, HOSi), 0.23 (s, 6 H, H$_3$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 230.62 (s, CO), 215.40 [s, ^{1}J(CW) = 155.9 Hz, CO], 101.47 [s, ^{1}J(CW) = 4.7 Hz, C$_5$H$_4$), 97.60 (s, *ipso*-C$_5$H$_4$), 93.75 [s, ^{1}J(CW) = 4.8 Hz, C$_5$H$_4$] 0.00 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 4.31 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2048 (s), 1968 (vs), 1951 (s) cm^{-1}. – Anal. calc. for C$_{10}$H$_{11}$ClO$_4$SiW (442.57): C 27.14, H 2.51; found C 27.80, H 2.85.

*21) [HOMe$_2$Si(C$_5$Me$_4$)](OC)$_3$WH (**13b**)*

Tricarbonyl[η^5-(hydroxydimethylsilyl)-tetramethylcyclopentadienyl]hydridotungsten(II)

Analogous to 20) from 533 mg (1.10 mmol) of **9b**, 0.1 ml of NEt$_3$ and 0.1 ml of water in 20 ml Et$_2$O over a period of 45 min. The crude residue was washed with 4 ml PE at –78 °C. Yield 409 mg (80 %). Pale brown solid. M.p. 53 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 1.96 (s, 6 H, H$_3$CC$_5$), 1.73 (s, 1 H, HOSi), 1.71 (s, 6 H, H$_3$CC$_5$), 0.31 (s, 6 H, H$_3$CSi), -6.66 [s, ^{1}J(HW) = 38.5 Hz, 1 H, HW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 220.89 (s, CO), 197.02 (s, CO), 110.20 [s, ^{1}J(CW) = 4.1 Hz, C̲$_5$Me$_4$], 108.34 [s, ^{1}J(CW) = 6.6 Hz, C̲$_5$Me$_4$], 91.81 [s, ^{1}J(CW) = 5.9 Hz, *ipso*-C̲$_5$Me$_4$], 13.38 (s, C̲H$_3$C$_5$), 11.06 (s, C̲H$_3$C$_5$), 3.26 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 5.99 (s) ppm. - **IR** (Et$_2$O): $\tilde{\nu}$ (CO) = 2011 (vs), 1922 (vs) cm^{-1}. – Anal. calc. for C$_{14}$H$_{20}$O$_4$SiW (464.25): C 36.22, H 4.34; found C 35.44, H 4.28.

*22) [HOMe$_2$Si(C$_5$Me$_4$)](OC)$_3$WCl (**13c**)*

Tricarbonylchloro[η^5-(hydroxydimethylsilyl)-tetramethylcyclopentadienyl]tungsten(II)

Analogous to 20) from 160 mg (0.31 mmol) of **10b**, 0.3 ml of NEt$_3$ and 0.3 ml of water in a solvent mixture consisting of 12 ml Et$_2$O and 3 ml benzene at 0 °C over a period of 30 min. The crude residue was washed with 4 ml PE at –78 °C. Yield 138 mg (89 %). Orange solid. M.p. 62 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 2.92 (s, 1 H, HOSi), 1.73 (s, 6 H, H$_3$CC$_5$), 1.45 (s, 6 H, H$_3$CC$_5$), 0.31 (s, 6 H, H$_3$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 235.07 (s, CO), 219.57 40 [s, ^{1}J(CW) = 154.1 Hz, CO], 117.37 [s, ^{1}J(CW) = 6.6 Hz, $\underline{C}$$_5Me_4$], 109.11 [s, ^{1}J(CW) = 4.5 Hz, $\underline{C}$$_5Me_4$], 91.70 [s, ^{1}J(CW) = 5.8 Hz, ipso-$\underline{C}$$_5Me_4$], 13.18 (s, $\underline{C}$H$_3$C$_5$), 10.19 (s, $\underline{C}$H$_3$C$_5$), 2.94 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 6.34 (s) ppm. - **IR** (Et$_2$O): $\tilde{\nu}$(CO) = 2034 (s), 1952 (vs), 1922 (s) cm^{-1}. – Anal. calc. for C$_{14}$H$_{19}$ClO$_4$SiW (498.69): C 33.72, H 3.84; found C 33.94, H 3.95.

*23) O{[Me$_2$Si(C$_5$H$_4$)](OC)$_3$WCl}$_2$ (**14**)*

1,3-Bis[tricarbonyl(η^5-cyclopentadienyl)chloro-tungsten(II)]-μ-1,1,3,3-tetramethyl-disiloxane

Analogous to 20) from 1.94 g (4.21 mmol) of **10a**, 1.16 ml of NEt$_3$ and 0.5 ml of water at –0 °C over a period of 40 min. The crude residue was washed four times, each with 4 ml PE at 25 °C. Yield 1.26 g (69 %). Orange solid. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.82 - 4.81 (m, 2 H, H$_4$C$_5$), 4.79 - 4.78 (m, 2 H, H$_4$C$_5$), 0.23 (s, 6 H, H$_3$CSi), ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 230.61 (s, CO), 215.33 [s, ^{1}J(CW) = 155.9 Hz, CO], 101.78 [s, ^{1}J(CW) = 4.7 Hz, C$_5$H$_4$], 97.66 (s, ipso-C$_5$H$_4$), 93.00 [s, ^{1}J(CW) = 4.8 Hz, C$_5$H$_4$], 0.17 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -0.50 (s) ppm. - **IR** (PE): $\tilde{\nu}$(CO) = 2048 (s), 1969 (vs), 1954 (s) cm^{-1}. – Anal. calc. for C$_{20}$H$_{20}$Cl$_2$O$_7$Si$_2$W$_2$ (867.15): C 27.70, H 2.32; found C 27.84, H 2.55.

*24) Li{W[(C$_5$Me$_4$)SiMe$_2$OH](CO)$_3$} (**15**)*

Lithium{tricarbonyl[η^5-hydroxydimethylsilyl-tetramethylcyclopentadienyl]}tungstate

A solution of 190 mg (0.41 mmol) of [HOMe$_2$Si(C$_5$Me$_4$)](OC)$_3$WH (**13b**) in 5 ml PE was treated with 0.28 ml (0.45 mmol) of a 1.6 M *n*butyllithium solution (in hexane) at 25 °C. After addition of the base a precipitation (**15**) was observed immediately. The suspension was stirred for three hours at this temperature and then all insoluble material was filtered off by use of a celite pad. The solvent was removed and the residue washed twice with PE. The lithium tungstate was dried in vacuo, giving a pyrophoric powder. Yield 191 mg (99 %). Pale beige solid. - **^{1}H-NMR** (300.4 MHz, CD$_3$CN): δ = 2.67 (bs, 1 H, HOSi), 2.13 [s, 6 H, (H$_3$C)$_4$C$_5$], 2.06 [s, 6 H, (H$_3$C)$_4$C$_5$], 0.31 [s, 6 H, (H$_3$C)$_2$Si], ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 5.00 (s) ppm. - **IR** (CH$_2$Cl$_2$): $\tilde{\nu}$ (CO) = 1942 (s), 1880 (s) cm^{-1}. – C$_{14}$H$_{19}$LiO$_4$SiW (470.18).

*25) [HOMe$_2$Si(C$_5$Me$_4$)](OC)$_3$WMe (**16**)*

Tricarbonyl[η^5-(hydroxydimethylsilyl)-tetramethylcyclopentadienyl]methyltungsten(II)

210 mg (0.45 mmol) of Li{W[(C$_5$Me$_4$)SiMe$_2$OH](CO)$_3$} (**15**) were suspended in 20 ml PE and treated with 0.08 ml (1.28 mmol) MeI at room temperature. After stirring over night all insoluble material was filtered off by use of a celite pad. The solvent was removed in vacuo and the residue washed with PE at –78 °C. Yield 110 mg (51 %). Yellow solid. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 3.25 (s, 1 H, HOSi), 1.80 (s, 6 H, H$_3$CC$_5$), 1.47 (s, 6 H, H$_3$CC$_5$), 0.36 (s, H$_3$CW), 0.28 (s, 6 H, H$_3$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 220.77 (s, CO), 197.52 (s, CO), 110.57 [s, ^1J(CW) = 4.3 Hz, $\underline{C}_5$Me$_4$], 108.78 [s, ^1J(CW) = 6.5 Hz, $\underline{C}_5$Me$_4$], 92.25 [s, ^1J(CW) = 5.8 Hz, *ipso*-$\underline{C}_5$Me$_4$], 13.57 (s, $\underline{C}$H$_3$C$_5$), 11.23 (s, $\underline{C}$H$_3$C$_5$), 3.55 (s, CH$_3$Si), -34.62 [s, ^1J(CW) = 27.4 Hz, CH$_3$W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 5.71 (s) ppm. - **IR** (Et$_2$O): $\tilde{\nu}$ (CO) = 2025 (vs), 1947 (s) cm^{-1}. – C$_{15}$H$_{22}$O$_4$SiW (478.27).

26) Li{W[(C$_5$Me$_4$)SiMe$_2$OLi](CO)$_3$} (17)

Lithium{tricarbonyl[η^5-(dimethyl-lithiumsilanolate)-tetramethylcyclopentadienyl]}-tungstate

A solution of 140 mg (0.30 mmol) of [HOMe$_2$Si(C$_5$Me$_4$)](OC)$_3$WH (**13b**) in 7 ml THF was treated with 0.56 ml (0.90 mmol) of a 1.6 M *n*butyllithium solution (in hexane) at room temperature and stirred for five hours. All volatiles were removed in vacuo and the solid was washed twice, each with 5 ml PE. Finally, the product was dried in vacuo, giving a pyrophoric powder. Yield 123 mg (87 %). Greenbrown solid. - **^{1}H-NMR** (300.4 MHz, CD$_3$CN): δ = 2.12 (s, 6 H, H$_3$CC$_5$), 2.05 (s, 6 H, H$_3$CC$_5$), 0.30 (s, 6 H, H$_3$CSi), ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -4.32 (s) ppm. - **IR** (CH$_3$CN): $\tilde{\nu}$(CO) = 1880 (s), 1762 (s) cm^{-1}. – C$_{14}$H$_{18}$Li$_2$O$_4$SiW (470.18).

27) [MeOMe$_2$Si(C$_5$Me$_4$)](OC)$_3$WMe (18)

Tricarbonyl[η^5-(methoxydimethylsilyl)-tetramethylcyclopentadienyl]methyltungsten(II)

165 mg (0.26 mmol) of **17** were dissolved in 5 ml THF and 0.05 ml (0.96 mmol) of MeI added. This solution was stirred for one day at room temperature. The solvent was removed in vacuo and the product extracted with 40 ml PE. Insoluble material was filtered off by use of a celite pad. The extract was evaporated to dryness giving **18** which was washed with PE at –78 °C. Yield 92 mg (72 %). Yellow solid. M.p.: 44 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 3.25 (s, 3 H, H$_3$CO), 1.82 (s, 6 H, H$_3$CC$_5$), 1.48 (s, 6 H, H$_3$CC$_5$), 0.37 [s, ^2J(HCW) = 3.6 Hz, 3 H, H$_3$CW], 0.29 (s, 6 H, H$_3$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 231.44 (s, CO), 218.43 (s, CO), 108.40 [s, ^1J(CW) = 4.4 Hz, C̲$_5$Me$_4$], 106.62 [s, ^1J(CW) = 6.6 Hz, C̲$_5$Me$_4$], 94.05 [s, ^1J(CW) = 5.8 Hz, *ipso*-C̲$_5$Me$_4$], 67.54 (s, CH$_3$O), 12.98 (s, C̲H$_3$C$_5$), 11.11 (s, C̲H$_3$C$_5$), -0.49 (s, CH$_3$Si), -34.32 [s, ^1J(CW) = 27.0 Hz, CH$_3$W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 9,52 (s) ppm. - **IR** (PE): $\tilde{\nu}$(CO) = 2008 (s), 1921 (vs) cm^{-1}. – Anal. calc. for C$_{16}$H$_{24}$O$_4$SiW (492.30): C 39.04, H 4.91, found: C 40.02, H 5.20.

*28) [HMe₂SiOMe₂Si(C₅H₄)](OC)₃WH (**19**)*

Tricarbonyl[η^5-(1,1,3,3-tetramethyl-disiloxano)-cyclopentadienyl]hydridotungsten(II)

A diethylether solution (5 ml) containing 180 mg (0.44 mmol) of **11** was treated with 0.1 ml of NEt₃ und 0.1 ml of Me₂Si(H)Cl. After 2 h reaction time the solvent was removed in vacuo and the residue extracted with 20 ml PE. Filtration and evaporation led to **19**. Yield: 187 mg (0.39 mmol, 95 %). Pale beige oil. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 4.88 [sept, ^3J(HSiCH) = 2.8 Hz, 1 H, HSi], 4.72 - 4.71 (m, 2 H, H₄C₅), 4.60 - 4.58 (m, 2 H, H₄C₅), 0.02 (s, 6 H, HCSiC₅H₄), 0.10 [d, ^3J(HCSiH) = 2.8 Hz, 6 H, H₃CSi], -7.26 [s, ^1J(HW) = 35.7 Hz, HW] ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C₆D₆): δ = 219.66 (s, CO), 197.87 [s, ^1J(CW) = 156.1 Hz, CO], 97.52 [s, ^1J(CSi) = 64.1 Hz, ^1J(CW) = 4.8 Hz, C₅H₄], 96.01 [s, ^1J(CW) = 4.1 Hz, C₅H₄], 95.64 [s, ^1J(CW) = 4.8 Hz, C₅H₄), 0.93 [s, ^1J(CSi) = 55.2 Hz, CH₃SiC₅H₄], 0.74 [s, ^1J(CSi) = 56.4 Hz, CH₃SiH] ppm. - **²⁹Si{¹H}-NMR** (59.6 MHz, C₆D₆): δ = -1.55 (s, SiC₅H₄), -4.76 (s, SiH) ppm. - **IR** (PE): $\tilde{\nu}$(SiH) = 2125 (m), $\tilde{\nu}$(CO) = 2018 (s), 1929 (vs) cm^{-1}. - Anal. Calc. for C₁₂H₁₈O₄Si₂W (466.29): C 30.91, H, 3.89; found: C 31.54, H 4.30.

*29) {[iBu₂AlOMe₂Si(C₅Me₄)](OC)₃WH}₂ (**20**)*

Bis{tricarbonyl[η^5-(1,3-di-*iso*-butylalanyl-1,3-dimethylsiloxy)-cyclopentadienyl]-hydridotungsten(II)}

A solution of 320 mg (0.69 mmol) of [HOMe₂Si(C₅Me₄)](OC)₃WH (**13b**) in 40 ml PE was treated with 0.69 ml (0.69 mmol) of *i*Bu₃Al (1 M, in hexane) at −78 °C. The solution was allowed to warm up to room temperature within two hours. All volatiles were removed in vacuo and the residue washed with PE at −78 °C. Yield: 242 mg (58 %). Pale beige solid. M.p.: 39 °C. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 2.10 (s, 6 H, CH₃C₅), 1.77 (non, 1 H, HC(CH₃)₂), 1.78 (s, 6 H, CH₃C₅), 0.96 (d, ^3J(HCCH) = 6.6 Hz, 12 H, (CH₃)₂CH), 0.72 (s, 6 H, CH₃Si), 0.02 [d, ^3J(HCCH) = 7.2 Hz, 2 H, H₂CCH(CH₃)₂], -6.71 [s, ^1J(HW) = 39.4 Hz, 1 H, HW] ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C₆D₆): δ = 220.77 (s, CO), 197.52 (s, CO), 111.65 [s, ^1J(CW) = 5.6 Hz, CC₄(CH₃)₄], 108.72 (s, ^1J(CW) = 6.6 Hz, C₅(CH₃)₄), 89.50 [s, ^1J(CW) = 5.9 Hz, SiCC₄(CH₃)₄],

28.65 (s, ($\underline{C}H_3$)$_2$CH), 25.65 (s, (CH$_3$)$_2\underline{C}$H), 24.79 (s, CH$\underline{C}H_2$Al), 14.37 (s, C$_5$($\underline{C}H_3$)$_4$), 11.20 (s, C$_5$($\underline{C}H_3$)$_4$), 4.77 (s, (CH$_3$)$_2$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 7.19 ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2015 (m), 1928 (s) cm^{-1}. – Anal. calc. for Al$_2$C$_{44}$H$_{74}$O$_8$Si$_2$W$_2$ (1208.90): C 43.72, H 6.17; found: C 43.42, H 6.00.

*Crystal data for [HOMe$_2$Si(C$_5$Me$_4$)](OC)$_3$WCl (**13c**)*

The data were collected from shockcooled crystals on a BRUKER SMART-APEX diffractometer with D8 goniometer (graphite-monochromated Mo - K$_\alpha$ radiation (λ = 0.71073 Å), equipped with a low temperature device in omega-scan mode at 173(2) K [61]. The data were integrated with SAINT [61] and an empirical absorption correction [62] was applied. The structure was solved by direct methods (SHELXS-97) [63] and refined by full-matrix least squares methods against F^2 (SHELXL-97) [64]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of the hydrogen atoms were calculated by an idealized geometry.

mol formula	C$_{14}$H$_{19}$ClO$_4$SiW
mol wt	498.68
wavelength (Å)	0.71073
temp (K)	173(2)
cryst size (mm)	0.3 x 0.2 x 0.15
cryst syst	triclinic
space group	P1
a (Å)	7.3932(18)
b (Å)	10.167(3)
c (Å)	11.644(3)
α (°)	98.418(4)

β (°)	94.699(4)
γ (°)	98.307(4)
vol (Å^3), Z	851.9(4)
ρ (calcd) (Mgm^{-3})	1.944
F(000)	480
μ (mm^{-1})	7.017
θ range for data collecn (deg)	1.78 - 25.03
no. of rflns collected	12231
no. of indep reflns	5889
abs cor.	empirical
no. of data/restraints /params	5889 / 3 / 393
goodness of fit on F^2	1.057
R1^a	0.0209
wR2^b	0.0481
largest diff peak and hole (eÅ^{-3})	0.528 and -0.565

R1 = $\Sigma||F_0| - |F_c||/\Sigma|F_0|$ for reflections with $I > 2\sigma(I)$. wR2 = $[\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_0^2)/3$ and a and b are constants set by the program.

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Chapter II

HALFSANDWICH TUNGSTEN METHYL COMPLEXES WITH A η^5-CYCLOPENTADIENYL-BOUND SILANOL FUNCTION

SUMMARY

Novel halfsandwich tungsten complexes with a η^5-cyclopentadienyl-bound silanol group of the general formula $[HOR_2Si(\eta^5\text{-}C_5H_4)](OC)_3WMe$ [R = Me, Ph, iPr (**13a-c**)] have been prepared. The silyl group at the cyclopentadienyl ring is introduced by metallation with nBuLi and following reaction with the dialkylchlorosilanes RR'Si(H)Cl [R, R' = Me, iPr, Ph, (**5a-d**)] to afford the tungsten-silanes $[HRR'Si(\eta^5\text{-}C_5H_4)](OC)_3WMe$ [R, R' = Me, Ph, iPr (**6a-d**)]. The Chlorination of the cyclopentadienyl-bound Si-H functions of **6a-d** is realized by reaction with $PdCl_2$. As a result the tungsten-chlorosilanes $[ClR_2Si(\eta^5\text{-}C_5H_4)](OC)_3WMe$ [R = Me (**3a**), Ph (**3b**), iPr (**7**)], suitable for hydrolysis, are obtained. In the case of **6c** the reaction leads also to the formation of the tungsten-chloride $[Cli$Pr_2Si(\eta^5\text{-}C_5H_4)](OC)_3WCl$ (**8**) and the dimeric complex $\{[Cli$Pr_2Si(\eta^5\text{-}C_5H_4)](OC)_3W\}_2$ ($W\text{-}W$) (**9**). There is an alternative synthesis for pure **7** via the dilithiated species $Li[W(LiC_5H_4)(CO)_3]$ (**11**), which is generated by the treatment of $Cp(OC)_3WH$ (**10**) with two equivalents of nBuli. **11** allows a regioselective reaction with dichlorodiisopropylsilane (**2c**), giving $Li\{W[Cli$Pr_2Si(\eta^5\text{-}C_5H_4)](CO)_3\}$ (**12**). Finally, **12** is converted to **7** by use of an excess of MeI. The hydrolysis of **3a,b**, **7** and **9** in the presence of NEt_3 affords the corresponding tungsten-silanols $[HOR_2Si(\eta^5\text{-}C_5H_4)](OC)_3WMe$ [R = Me, Ph, iPr (**13a-c**)] and the bis-silanol $\{[HOi$Pr_2Si(\eta^5\text{-}C_5H_4)](OC)_3W\}_2$ ($W\text{-}W$) (**14**) which are stable with respect to self-condensation. The chemical behaviour of these novel silanols have been investigated. For example, the self-condensation of **13a** gives $O\{[Me_2Si(\eta^5\text{-}C_5H_4)](OC)_3WMe\}_2$ (**15**) and co-condensation with $Me_2Si(H)Cl$, Me_3SnCl or Cp_2TiCl_2, respectively leads to the formation of the corresponding heterosiloxanes $[HMe_2SiOMe_2Si(\eta^5\text{-}C_5H_4)](OC)_3WMe$ (**17a**), $[Me_3SnOMe_2Si(\eta^5\text{-}C_5H_4)](OC)_3WMe$ (**17b**) and $[Cp_2Ti(ClOMe_2Si(\eta^5\text{-}C_5H_4)](OC)_3WMe$ (**17c**). The reaction of **13a** with nBuLi generates the lithium tungsten-silanolate

[LiOMe$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$WMe (**19**) which is transformed with an excess MeI into [MeOMe$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$WMe (**20**). In the case of Ph$_2$Si[(η^5-C$_5$H$_4$)(OC)$_3$WMe]$_2$ (**4b**), [HPh$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$WMe (**6b**) and {[HO*i*Pr$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$W}$_2$ (*W-W*) (**14**), the results of X-ray diffraction analyses are presented.

INTRODUCTION

Due to their important role as intermediates in the technical synthesis of silicones [1-4] organosilanols have been the subject of extensive studies over several decades [5-12]. Polysiloxanes of the general formula $[R_2SiO]_n$ are interesting polymers for many applications as a consequence of their chemical stability, low toxicity, high gas permeability, and insulating charateristics [1, 3, 4]. For example, this class of inorganic polymers can be found in sealants, contact linses, coatings and a variety of biomedical applications [2]. More recently, the incorporation of transition metals into polymeric structures became attractive, as it may allow the combination of the interesting physical properties of metals with the solubility and processibility of polymers [13-23].

Transition metal silicon compounds of the general formula $L_nM\text{-}SiR_3$ and the electronic effect of transition metal fragments on the reactivity of the silicon atom have attracted great attention in recent years [24-28]. Concerning the synthesis and the reactivity, much interest was focused on Si-OH-functional transition metal complexes due to their remarkable stability towards self-condensation. Consequently, a large number of metallo-silanols of the general type $L_nM\text{-}SiR_{3-m}(OH)_m$ (m = 1-3) [26, 27, 29-58] (Fig. 1, type **I**) have been prepared in the past by various synthetic methods. The compounds of this class serve as valuable precursors for a controlled build-up of metal fragment-substituted siloxanes and -heterosiloxanes [32-34, 58].
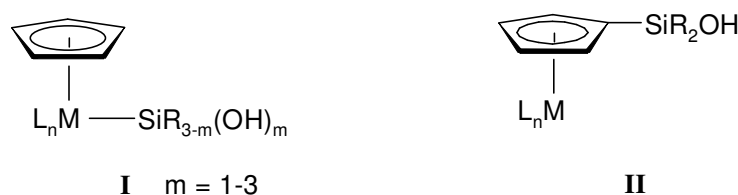
Fig. 1: Different types of metallo-silanols with the metal fragment directly silicon-bound (type **I**) or attached to the η^5-cyclopentadienyl ligand (type **II**).

In context with our ongoing interest concerning the influence of transition metal fragments on the silanol function, we have now turned to species, having the Si-OH

moiety separated from the metal fragment by a spacer group. We expect reduction of the "transition metal effect" on the silanol unit in comparison to "common" metallo-silanols of the type **I**, leading as a consequence to an increased reactivity in condensation processes.

An attractive possibility is offered by use of the η^5-cyclopentadienyl ligand as spacer (type **II**). Such an arrangement offers broad access to silanol-functionalized halfsandwich complexes without limitation of the ligand sphere around the metal center.

However, only few examples of metallo-silanols of this type have been reported to the present day [59-63]. This report deals with the synthesis and reactivity of the novel tungsten-silanols $[HOR_2Si(\eta^5\text{-}C_5H_4)](OC)WMe$ (R = Me, Ph, iPr).

RESULTS AND DISCUSSION

Diorganochlorosilyl- and Diorganosilyl-cyclopentadienyl Tungsten Complexes (3-11). An attractive route to introduce a silyl group at the cyclopentadienyl ligand of a halfsandwich tungsten complex is offered by the direct metallation of the ring ligand with a strong base like *n*BuLi followed by the reaction with electrophilic reagents [64-67]. Therefore, Cp(OC)$_3$WMe (**1**) is treated with *n*BuLi at –78 °C in THF, according to literature procedure [64], generating the cyclopentadienyl-lithiated species **A**. In order to synthesize SiCl-functionalized complexes, suitable for hydrolysis, **A** is reacted *in situ* with an excess of the diorganodichlorosilanes R$_2$SiCl$_2$ [R = Me (**2a**), Ph (**2b**)]. The reactions are performed at –78 °C with additional warmup to room temperature over the period of one hour. Work up affords product mixtures consisting of the targeted chlorosilyl complexes **3a**,**b** and the dinuclear tungsten complexes **4a**,**b**, indicating double substitution of the silicon by the nucleophilic reagent **A** (Scheme 1).

3	**a**	**b**
R	Me	Ph

4	**a**	**b**
R	Me	Ph
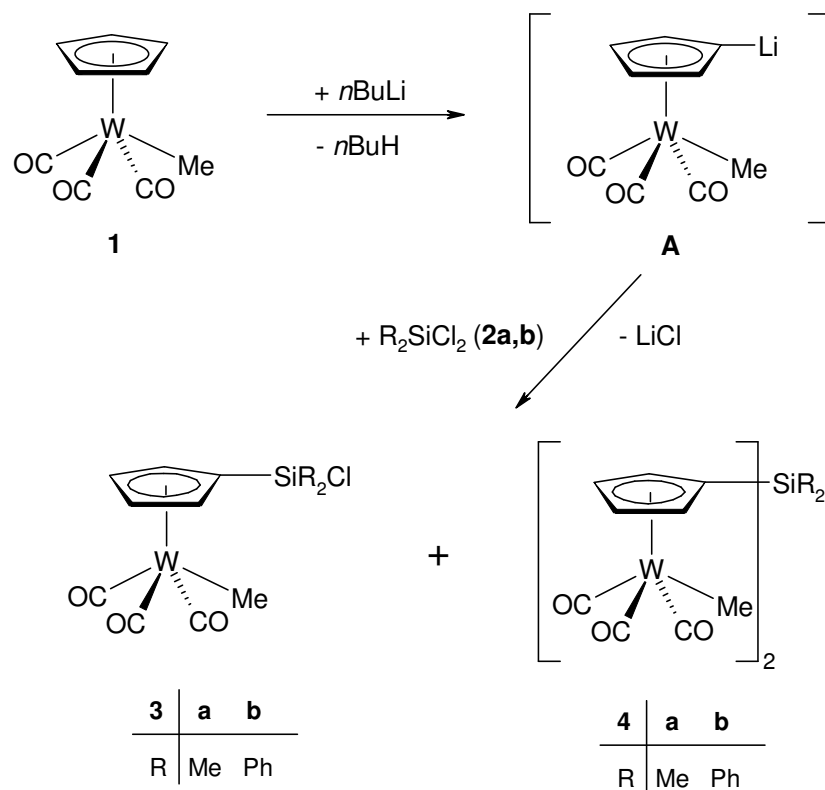
Scheme 1: Synthesis of cyclopentadienyl-silylated tungsten methyl complexes.

Only in the case of the phenyl derivatives **3b** and **4b**, the separation succeeds by repeated fractional crystallization from petrolether.

The fact that this reaction takes place even in the case of the sterical hindered dichlorodiphenylsilane, demonstrates the high reactivity of the tungsten methyl nuclephile **A**.

All attempts to isolate **A** failed and only products of decomposition are observed, even in the presence of stabilizing TMEDA.

In order to establish an alternative access to tungsten complexes with chlorosilyl-functionalized cyclopentadienyl ligand, it has been tried to generate SiH-functionalized complexes which appear promising for subsequent chlorination. The *in situ* reaction of the lithiated species **A** with the dialkylchlorosilanes RR'Si(H)Cl (R, R' = Me, *i*Pr, Ph) [R, R' = Me, Ph, *i*Pr (**5a-d**)] guarantees the monosubstitution and results exclusively in the targeted compounds [HRR'Si(C$_5$H$_4$)](OC)$_3$WMe [R, R' = Me, Ph, *i*Pr (**6a-d**)], which are isolated as yellow oils (**6a,c,d**) and yellowbrown solid (**6b**) in good and even excellent yields from 90 to 99 % (Eq. 1).

5	a	b	c	d
R	Me	Ph	*i*Pr	Me
R'	Me	Ph	iPr	Ph
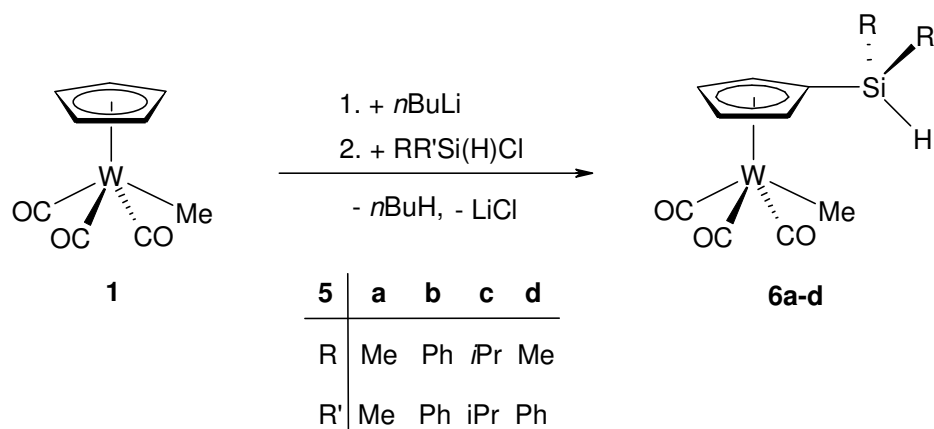
Eq. 1: Synthesis of the tungsten-silanes [HRR'Si(C$_5$H$_4$)](OC)$_3$WMe (**6a-d**).

The silyl group of **6a-d** improves the solubility in solvents like petrolether or diethylether in comparison to **1**.

The ^{1}H-NMR spectra in C$_6$D$_6$ of **6a-c** exhibit two virtual triplets for the two inequivalent pairs of cyclopentadienyl ring protons evoked by an AA`BB`-spin

system, characteristic for a monosubstituted cyclopentadienyl ligand. The ^{1}H-NMR spectrum of the complex [HMePhSi(C$_5$H$_4$)](OC)$_3$WMe (**6d**), characterized by a stereogenic silicon center, shows four multiplets for the four inequivalent cyclopentadienyl ring protons. In the IR-spectra of **6a-d** the $\tilde{\nu}$(SiH) stretching frequencies lie between 2128 (**6c**) and 2147 (**6b**) wavenumbers and indicate a minute influence of the metal fragment in comparison to "common" tungsten-silanes with M-Si moiety, e.g. the tungsten complex Cp(OC)$_3$WSiMe$_2$H [$\tilde{\nu}$(SiH): 2076 cm^{-1}] [27].

Chlorination of the Diorganosilyl-cyclopentadienyl Complexes 6a-c. Synthetical approach to chlorosilylcyclopentadienyl tungsten complexes is achieved by the treatment of the Si-H-functionalized compounds **6a-c** with PdCl$_2$ in benzene [68, 69]. This SiH/SiCl-exchange reaction affords in the cases of the dimethyl- and diphenylsilyl complexes **6a,b** after three days at room temperature cleanly the chlorosilyl complexes **3a,b** (Scheme 2).

6	a	b	c
R	Me	Ph	iPr

3	a	b	7
R	Me	Ph	iPr
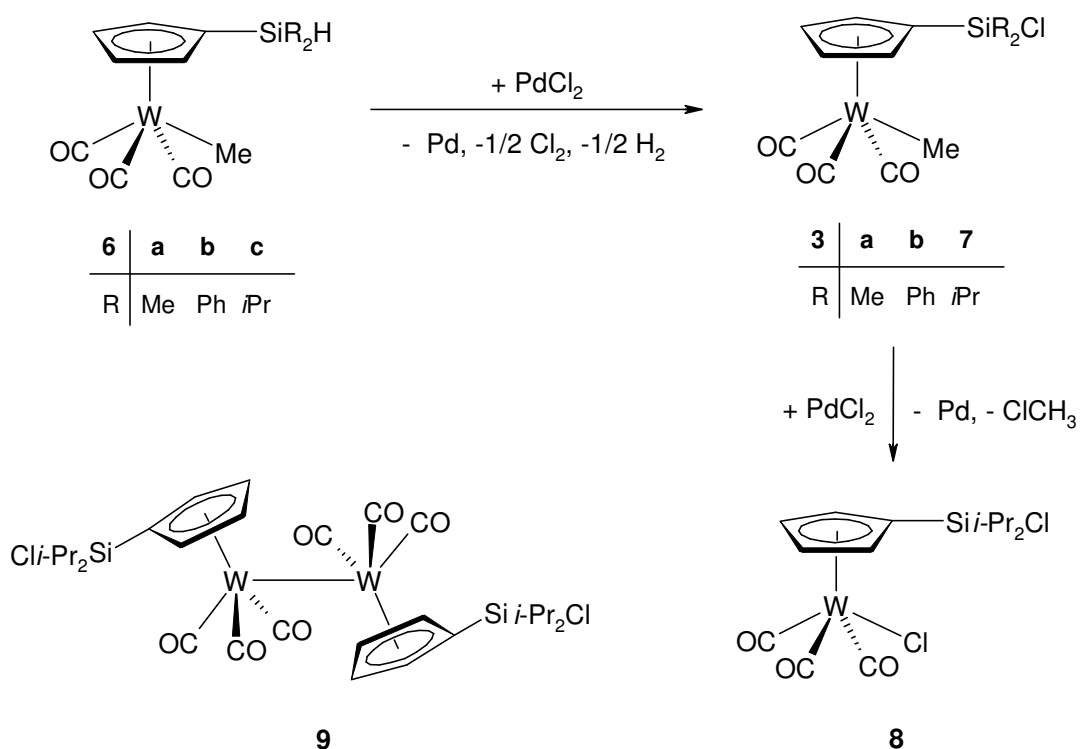
Scheme 2: Chlorination of the tungsten-silanes **6a-c** with PdCl$_2$.

In contrast to this finding, the same reaction conditions applied for the di*iso*propylsilyl derivative **6c**, results unexpectedly in the formation of a product mixture consisting of **7**, the tungsten chloride [Cl*i*Pr$_2$Si(C$_5$H$_4$)](OC)$_3$WCl (**8**) and small amounts of the dinuclear complex {[Cl*i*Pr$_2$Si(C$_5$H$_4$)](OC)$_3$W}$_2$ (*W-W*) (**9**), bearing a tungsten-tungsten bond (Scheme 2). The addition of another equivalent of PdCl$_2$ converts **7** after three days completely into **8**, which can be separated from the small amount of **9** by extraction with PE at 0 °C.

We assume, that the sterical requirement of the *iso*-propyl groups prevents the SiH-function from reaction and the complex product mixture in the case of **6c** arises from a prefered radical cleavage of the W-C-bond generating the 17-electron tungsten radical [Cl*i*Pr$_2$Si(C$_5$H$_4$)](OC)$_3$W·. This radical species stabilizes via chlorine abstraction or dimerization to give **8** and **9**. [1]

It is interesting that the amount of the dimeric **9** is only marginal despite the fact that transition-metal radicals like Cp(OC)$_3$W· prefer stabilization with respect to dimerization. Apparently, the bulky *iso*-propyl groups at the silicon atom prevent such a species from dimerization and therefore the chlorination is favored. For example, it is known that substitution of small ligands with sterically more demanding ones, stabilizes 17-electron metal-centered species [70].

3a,b and **8** are obtained in yields from 78 % (**3b**) to 91 % (**3a**) as yellow oil (**3a**) and yellow or orange solids (**3b**, **8**).

Chlorination with an excess of CCl$_4$ in the presence of a catalytic amount of Pd/C in Et$_2$O, as a cheaper alternative for the H/Cl-exchange, works exclusively in the case of the dimethylsilyl derivative **6a**, to afford after three days at room temperature **3a** in 93 % yield.

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[1] The existence of such organometallic radicals that deviate from the conventional 18-electron rule is nowadays well investigated [71]. It is generally known that among other methods intermediates of the form Cp(OC)$_3$M· (M = Cr, Mo, W) can be readily generated by visible photolysis of the metal-metal bond in precursor dimer complexes [71] but for example in the photolysis of the tungsten methyl monomer Cp(OC)$_3$WMe [generating the solvated intermediate Cp(OC)$_2$WMe] the radical Cp(OC)$_3$W· plays only a minor role [72].

Other attempts to chlorinate **6a** with an excess of CCl_4 or $SnCl_4$ lead only to decomposition products.

The reaction of **6a** with BCl_3 results in the formation of the targeted **3a**, however, in addition the literature-known tungsten choride $[ClMe_2Si(C_5H_4)](OC)_3WCl$ [61] and a few unidentified byproducts have been obtained.

In contrast, the treatment of **6a** with Ph_3CCl leads cleanly to **3a** but the separation of **3a** from the generated Ph_3CH failed.

A clean synthesis of **7** can be realized by the regioselective silylation of the cyclopentadienyl ligand of the dilithiated tungsten complex **11**, which is generated from $Cp(OC_3)WH$ (**10**) by the reaction with two equivalents of nBuLi in THF [73, 74]. The advantage of this method is that it allows the use of a big excess of a dialkyldichlorosilane to avoid double substitution of the silicon. In dichlorodi*iso*-propylsilane suspended **11** dissolves at −78 °C within few minutes, while generation of the lithium tungstate $Li\{W[(C_5H_4)SiiPr_2Cl](CO)_3\}$ (**12**) occurs (Scheme 3).
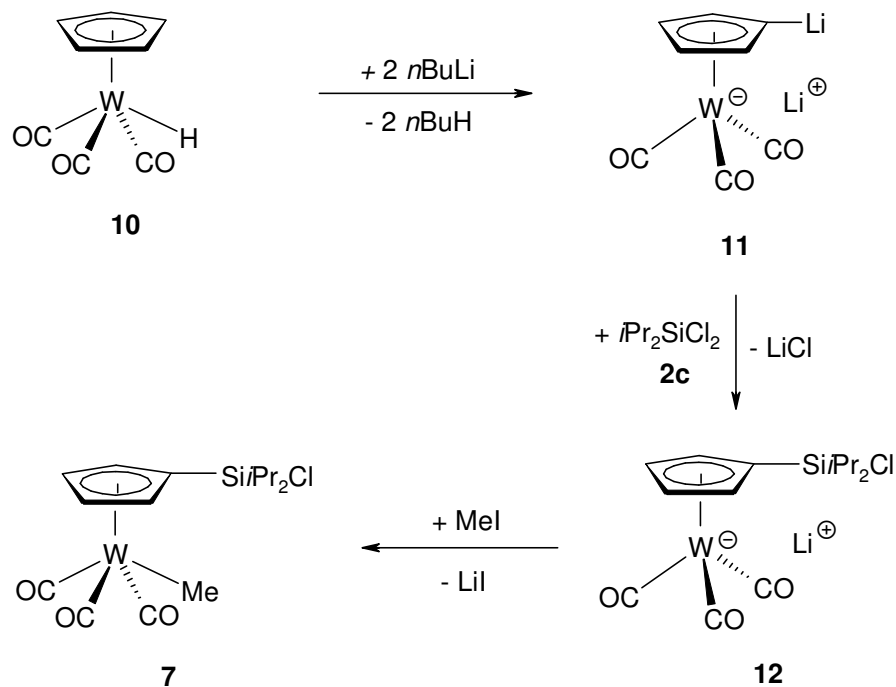
Scheme 3: Alternative synthesis of **7** starting from the dilithiated **11** via the silyl-functionalized lithium metallate **12**.

12 is isolated in 88 % yield as a pale brown powder showing pyrophoric and moisture sensitive properties. In contrast to $Li[WCp(CO)_3]$, **12** is soluble in benzene due to the presence of the silyl group.

The heterogeneous reaction of **12** in PE with MeI forms the methyl tungsten complex **7** in of 91 % yield.

Furthermore, **11** allows quenching with diverse electrophilic reagents leading to an easy introduction of a σ-bonded ligand at the tungsten atom to enable variation of the ligand sphere around the metal center.

Formation of the Hydroxydiorganosilyl-cyclopentadienyl Tungsten Complexes 13a-c and 14. The Si-H-functionalized complexes **6a-d** offer the oxygenation with dimethyldioxirane (DMD) as an established procedure for the synthesis of metallo-silanols [40, 49, 75, 76].

However, the treatment of **6a-c** with DMD in acetone at −78 °C leads to blue solutions, indicating the oxidation of the tungsten. Furthermore, decomposition products of unknown structure are observed.

In contrast to this finding, the oxofunctionalization of the tungstenmethyl-silanes $Cp(OC)_2(R_3P)WCH_2SiMe_2H$ (R = Me, Ph) [51] is successful and confirms the idea of a strongly reduced influence of the metal fragment on the silicon of **6a-c**, indicated by the high values of the $\tilde{\nu}$ (SiH) stretching frequencies, ranging from 2128 (**5c**) to 2147 cm^{-1} (**5b**).

Nevertheless, the Si-H-functionalized tungsten complexes **6a-d** might have synthetical potential, since transition metal complexes with the $[HMe_2Si(C_5H_4)]$-ligand have been used for the hydrosilylation of alkines [77] as well as for oxidative addition at transition metal complexes [78].

In contrast to the oxygenation of the Si-H function with DMD, it is possible to transform **6a** into the corresponding tungsten-silanol by successive treatment with $Co_2(CO)_8$ and water (Scheme 4). The first step gives after four hours in petrolether the intermediate hetero-dinuclear complex $[(OC)_4CoSiMe_2(C_5H_4)](OC)_3WMe$ (**B**). The

most important feature of **B** is the very labile Co-Si bond which can be easily hydrolized. Performance of this reaction in THF results within four hours at room temperature in the formation of the tungsten-silanol $[HOMe_2Si(C_5H_4)](OC)_3WMe$ (**13a**). In the case of **6b,c** no reaction with $Co_2(CO)_8$ at room temperature is observed. It seems that the higher sterical requirements of the *iso*-propyl- and phenyl groups prevent $H/Co(CO)_4$-exchange at the silicon.

3	a	b	7
R	Me	Ph	*i*Pr

13	a	b	c
R	Me	Ph	*i*Pr
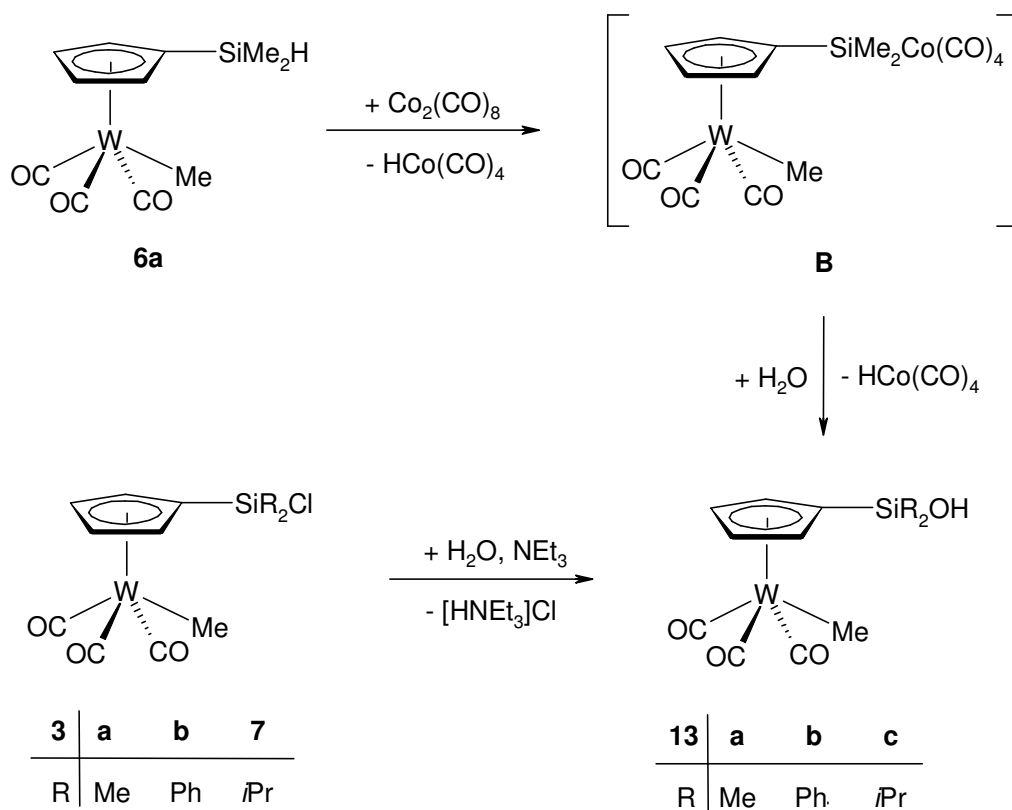
Scheme 4: Generation of the tungsten-silanols $[HOR_2Si(C_5H_4)](OC)_3WMe$ [R = Me, Ph, *i*Pr (**13a-c**)] as well as the alternative synthesis of **13a** via the intermediate hetero-dinuclear complex $[(OC)_4CoSiMe_2(C_5H_4)](OC)_3WMe$ (**B**).

The NEt_3-assisted hydrolysis of the tungsten-chlorosilanes **3a,b 7** and **9** affords the corresponding silanols $[HOR_2Si(C_5H_4)](OC)_3WMe$ [R = Me, Ph, *i*Pr (**13a-c**)] (Scheme 4) and the bis-silanol $\{[HO iPr_2Si(C_5H_4)](OC)_3W\}_2$ (*W-W*) (**14**) with a tungsten-tungsten bond as well (Fig. 2). The reactions are carried out in Et_2O at room temperature and are finished after about half an hour. The tungsten-silanols are

obtained in yields ranging from 78 to 90 %. **13a-c** and **14** are isolated as yellow (**13b**), orange (**13a**, **14**) and red (**13c**) solids with low solubility in aliphatic solvents like petrolether and they show reasonable stability with respect to self-condensation.

14
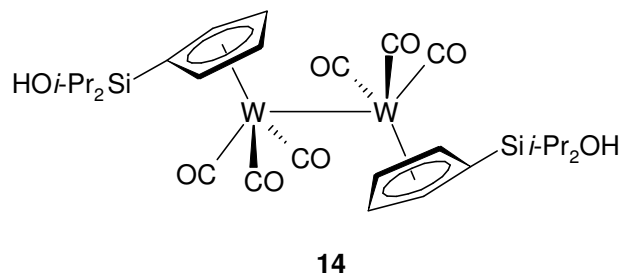
Fig. 2: Tungsten-tungsten-bonded bis-silanol $\{[HOiPr_2Si(\eta^5-C_5H_4)](OC)_3W\}_2$ (*W-W*) (**14**).

The Si-OH resonances in the ^{1}H-NMR spectra ranges from 1.99 (**13b**) to 2.55 ppm (**13a**), which are typical values of tungsten-silanols [40, 49]. The ^{29}Si-NMR resonances are detected close to each other at 4.26 (**14**), 4.70 (**13a**) and 6.02 ppm (**13c**), while the diphenylsilanol-substituted **13b** shows a significantly high field shifted signal at –0.45 ppm.

These ^{29}Si-NMR values reveal by its shifts to higher field the decreased influence of the transition metal fragment on the silicon atom at the cyclopentadienyl ring. For example, in the case of **13a** the signal is shifted approximately 19 ppm to higher field in comparison to the tungstenmethyl-silanol $Cp(OC)_2(Ph_3P)W-CH_2-SiMe_2OH$ (23.43 ppm) [51] and nearly 45 ppm to $Cp(OC)_2(Ph_3P)W-SiMe_2OH$ (49.6 ppm) [40].

Reactivity of the Tungsten-silanol 13a. Despite the fact that the tungsten-silanols **13a-c** and **14** are stable enough for clean isolation, **13a** undergoes self-condensation, if it is kept for a prolonged time in solution. This reaction results after stirring for three weeks in concentrated solutions of THF, CH_2Cl_2 or Et_2O at room temperature in the formation of the tungsten fragment-substituted disiloxane $O\{[Me_2Si(C_5H_4)](OC)_3WMe\}_2$ (**15**) which is obtained in 93 % yield as a yellow powder (Scheme 5).

The dinuclear structure of **15** is finally confirmed by mass spectrscopy. The ^{29}Si-NMR resonance of **15** at δ = −1.58 ppm is about 5 ppm shifted to higher field in comparison to **13a**.

Alternatively, **15** can be synthesized more directyl in 72 % yield by the reaction of two moles of **1** with nBuLi and 1,3-dichlorotetramethyldisiloxane in THF (Scheme 5).
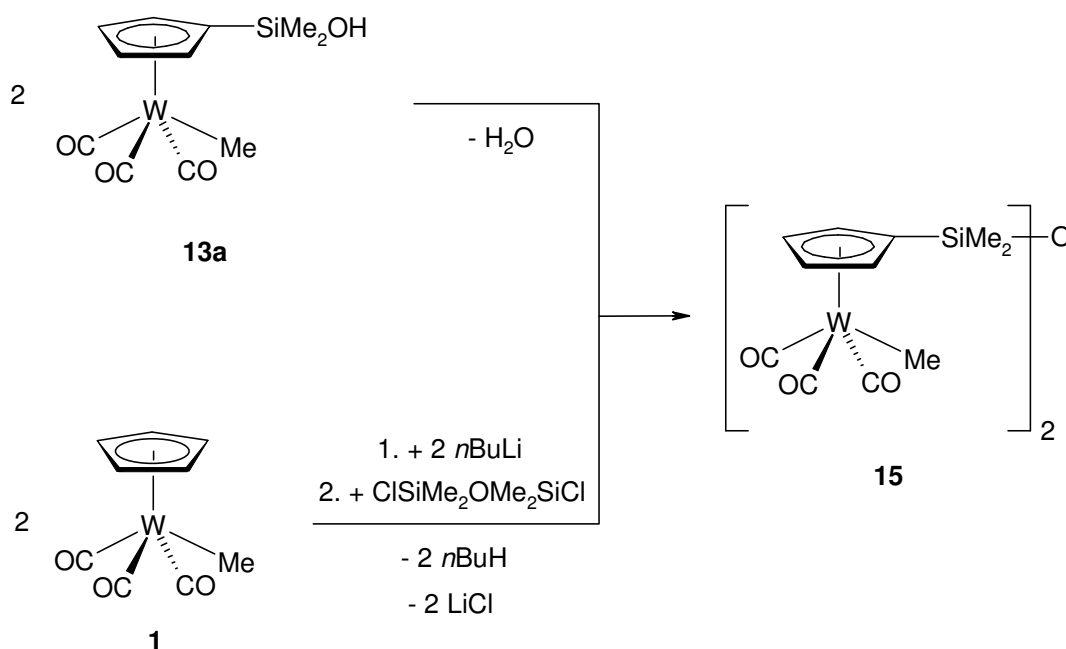
Scheme 5: Two pathways for the synthesis of the metal fragment-substituted disiloxane **15**.

The stability of the tungsten-silanols **13a-c** and **14**, offers the possibility to perform controlled co-condensation reactions with chlorosilanes, chlorostannanes or oxophilic reagents like titanocene dichloride as demonstrated for **13a** (Eq. 2). Additionally, these reactions serve as a chemical proof for the existence of a silanol function. In this context, **13a** is co-condensated with $Me_2Si(H)Cl$ in Et_2O in the presence of NEt_3 as auxiliary base, leading after a reaction time of one hour at ambient temperature to the tungsten-disiloxane $[HMe_2SiOMe_2Si(C_5H_4)](OC)_3WMe$ (**17a**) in an almost quantitive yield (95 %).

The analogous reactions of $Cp(OC)_2(Ph_3P)W-CH_2-SiMe_2OH$ and $Cp(OC)_2(Ph_3P)W-SiMe_2OH$ take two and three days.

Analogously, the co-condensation of **13a** with Me$_3$SnCl or Cp$_2$TiCl$_2$ in Et$_2$O affords the tungsten fragment-substituted heterosiloxanes [Me$_3$SnOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**17b**) and [Cp$_2$Ti(Cl)SiOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**17c**) after one day. The synthesis of **17c** is accompanied by the generation of small amounts of the trinuclear complex Cp$_2$Ti{[OMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe}$_2$.

The siloxane-bridged **17a** is obtained as a high viscous orange oil and **17b** as a yellowbrown solid. Both compounds show a very good solubility in nonpolar solvents even at low temperatures. The siloxy titanocene derivative **17c**, a yellow solid, is purified by repeated fractional crystallization with pentane at −78 °C.

The ^{29}Si-NMR spectra of **17a-c** show the signals at -1.69 (**17a**), 0.57 (**17c**) and -4.08 (**17b**) ppm, being shifted about 4 - 8 ppm to higher field in comparison to **13a**, which is in good accordance with ^{29}Si-NMR data of metallomethyl-silanols [37, 51].

	5a	16a	16b
R	Me$_2$(H)Si	Me$_3$Sn	Cp$_2$Ti(Cl)
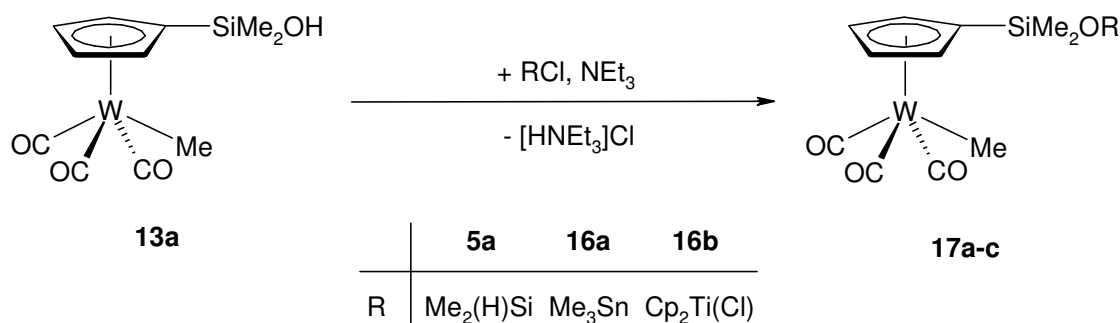
Eq. 2: NEt$_3$-assisted co-condensation reactions of the tungsten-silanol **13a**.

The preparation of group 13 heterosiloxanes (E = Al, Ga, In) has become an increasing field of research, especially with respect to gallium containing zeolithes for the dehydrogenation and dehydrocyclization of alkanes [79-82]. Recent work has shown that the reactivity of ferrio-silanols and ferriomethyl-silanols is high enough to allow the preparation of metal-fragment substituted heterosiloxanes of gallium [50].

The reaction of **13a** with iBu$_3$Al results via isobutane elimination in the formation of the tungsten-alumosiloxane {[iBu$_2$AlOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe}$_2$ (**18**) (Eq. 3). The expected dimeric structure in solution, deriving from an interaction of the Lewis-acidic aluminium and the Lewis-basic oxygen atom of the Si-O unit, is confirmed by molecular-weight determination. The reaction is carried out in PE at room

temperature and is completed after two hours. **18** is isolated in 64 % yield as a pale beige solid with a good solubility in nonpolar solvents.

The ^{29}Si-NMR resonance of **18** (6.75 ppm) is found downfield-shifted in comparison to the co-condensation products **17a-c** and appears very close to that of the starting material **13a** [50].
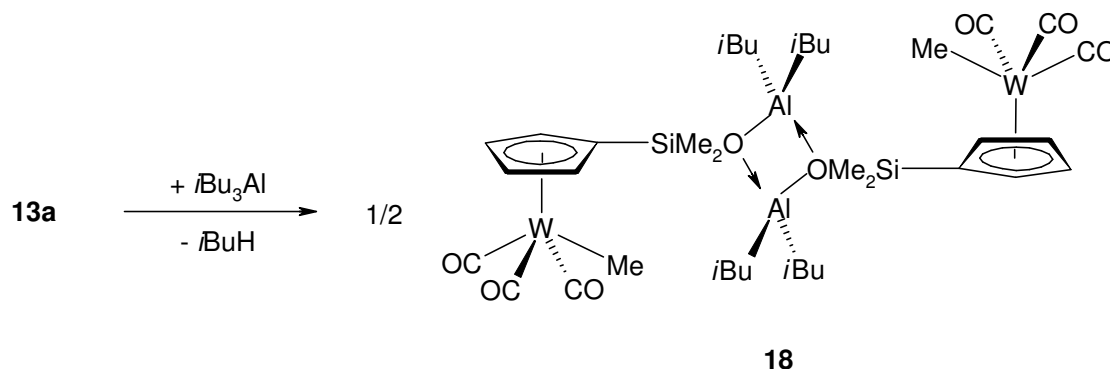
Eq. 3: Synthesis of {[iBu$_2$AlOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe}$_2$ (**18**).

Own studies have shown that most halfsandwich metallo-silanolates of the general formula L$_n$M-SiR$_2$O$^{\ominus}$ are instable and decompose to the L$_n$M$^{\ominus}$-metallate and the cyclotrisiloxane (R$_2$SiO)$_3$. The tungsten-silanoles presented in this paper, offer the possibility to generate stable silanolates because the silyl group and the metal center are separated from each other which should prevent such a rearrangement.

In this context, **13a** is treated with nBuLi in THF, giving the lithium tungsten-silanolate [LiOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**19**), but also some byproducts which are not identified (Scheme 6). The treatment of **19** with MeI in THF results in the formation of [MeOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**20**). The methoxysilyl group of **20** is ^{1}H-NMR-spectroscopically detected at 3.15 ppm. In order to avoid the formation of byproducts, **13a** is alternatively added to a suspension of sodium in THF. However, this reaction leads to the desilylation of **13a** to give Cp(OC)$_3$WMe (**1**) analytically pure.

The methoxysilyl-substituted **20** can be transformed into the corresponding silanol **13a** by the reaction with an excess of aqueous NaOH (0.1 M) in Et$_2$O. This reaction is finished after one week at room temperature.
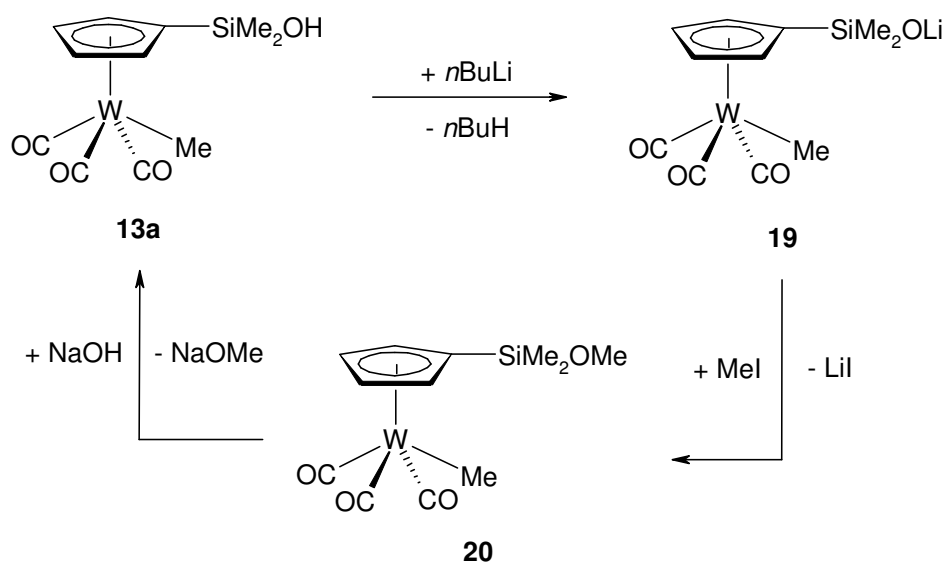
Scheme 6: Reaction cycle which includes the generation of the lithium tungsten-silanolate **19**, its subsequent conversion to a methoxysilyl complex (**20**) and the transformation into the starting silanol **13a**, as well.

X-RAY STRUCTURE DETERMINATIONS

1) $Ph_2Si[(C_5H_4)(OC)_3WMe]_2$ (**4b**)

Yellow crystalline needles of **4b**, suitable for X-ray analysis, are obtained from slow evaporation of a saturated THF-solution at room temperature.
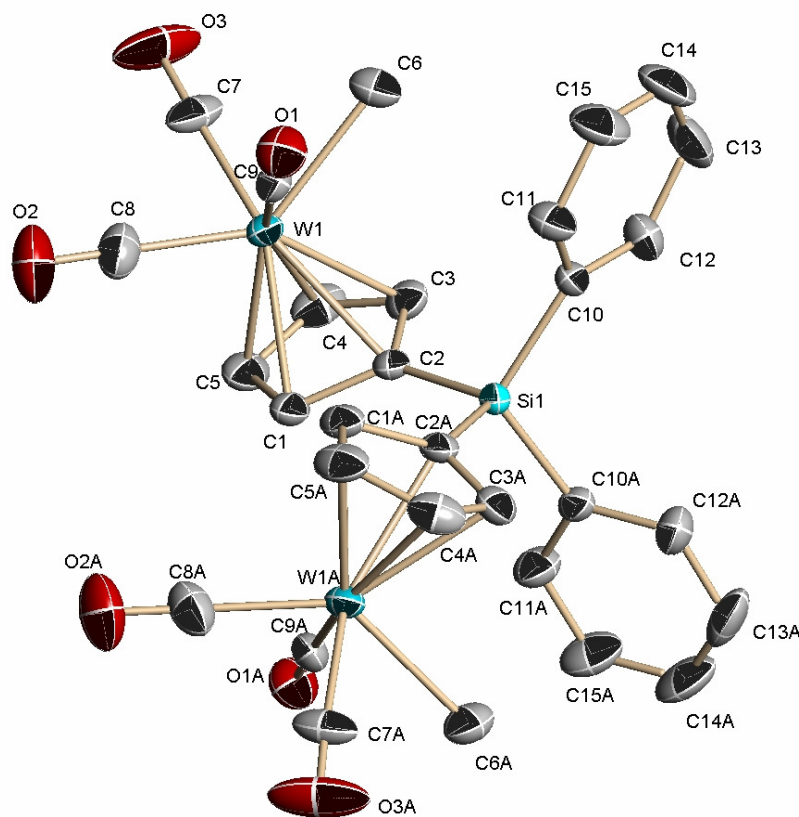
Fig. 3: Depicted molecular structure of $Ph_2Si[(C_5H_4)(OC)_3WMe]_2$ (**4b**) in the solid state with the atom-numbering scheme. Thermal ellipsoids are drawn at the 50 % probability level and the hydrogen atoms have been omitted for the sake of clarity.

Selected bond lengths [Å], bond and torsion angles [°]: W1-C7 1.966(6), W1-C8 1.972(7), W1-C9 1.983(6), W1-C6 2.309(6), Si1-C10 1.863(5), Si1-C2 1.864(5), C1-C5 1.419(8), C1-C2 1.427(7), C3-C4 1.400(8), C3-C2 1.427(8), C5-C4 1.396(9), C10-Si1-C10A 112.2(3), C10-Si1-C2 108.7(2), C2-Si1-C2A 112.702(3), C10-Si1-C2-C3 43.3(5), C4-C3-C2-Si1 169.7(4).

The space group of the molecule is C2/c. The coordination sphere around the tungsten atom can be considered as a pseudo square-pyramid, with the three carbonyl ligands [mean W-C 1.982 Å] and the methyl group [W1-C6 2.309(6) Å] forming the base and the cyclopentadienyl ring at the apical position. These bond distances lie in the range reported in literature for comparable compounds [83]. Due to the silyl substitution, the C-C distances of the cyclopentadienyl ligand are different. The longest bonds are found for C1-C2 [1.427(7) Å] and C2-C3 [1.427(8) Å] including the *ipso*-carbon atom, followed by C1-C5 and C3-C4 with 1.419(8) Å and 1.400(8) Å. The shortest bond length is found between C4 and C5 with 1.396(9) Å. The bond lengths between the silicon and the carbon atoms have very similar values between 1.864(5) Å (Si1-C2) and 1.863(5) Å (Si1-C10). The silicon atom is coordinated tetrahedally which is verified by bond angles between 112.2(3)° (C10-Si1-C10A)°, 108.7(2)° (C10-Si1-C2) and 112.2(3)° (C2-Si1-C2A).

2) [HPh$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**6b**)

The result of the diffraction analysis is presented in figure 4. The crystals of **6b**, suitable for a X-ray structure analysis, are pale yellow and show a characteristic diamond-shaped form.

6b shows the same coordination sphere around the tungsten atom as **4b**, with the three carbonyls [mean W-C 1.982 Å] and the methyl group [W-C 2.301(3) Å] as the basis. The C-C distances in the cyclopentadienyl ligand of **6b** are also different. The largest distances are found for C9-C12 [1.433(4) Å] and C12-C10 [1.436(4) Å] including the *ipso*-carbon atom, followed by C10-C18 and C9-C13 with 1.408(4) Å and 1.420(4) Å. The shortest bond is C13-C18 which amounts to 1.399(4) Å. The bond lengths between the silicon atom Si1 and the carbon atoms of the cyclopentadienyl- and the phenyl substituents systems have nearly identical values of 1.859(3) Å (Si1-C12), 1.862(3) Å (Si1-C24) and 1.875(3) Å (Si1-C8). The silicon atom shows a tetrahedal coordination which is verified by the observed bond angles between 110.00(13)° (C12-Si1-C24), 108.26(12)° (C12-Si1-C8) and 109.70(13)° (C24-Si1-C8). One phenyl group adopts an almost vertical position above the plane

spanned by the cyclopentadienyl ligand, as demonstrated by the torsion angle C8-Si1-C12-C9 of –90.1(2)°. The other phenyl group is located below this plane in a quadrant of the carbonyl ligand (C5-O2).
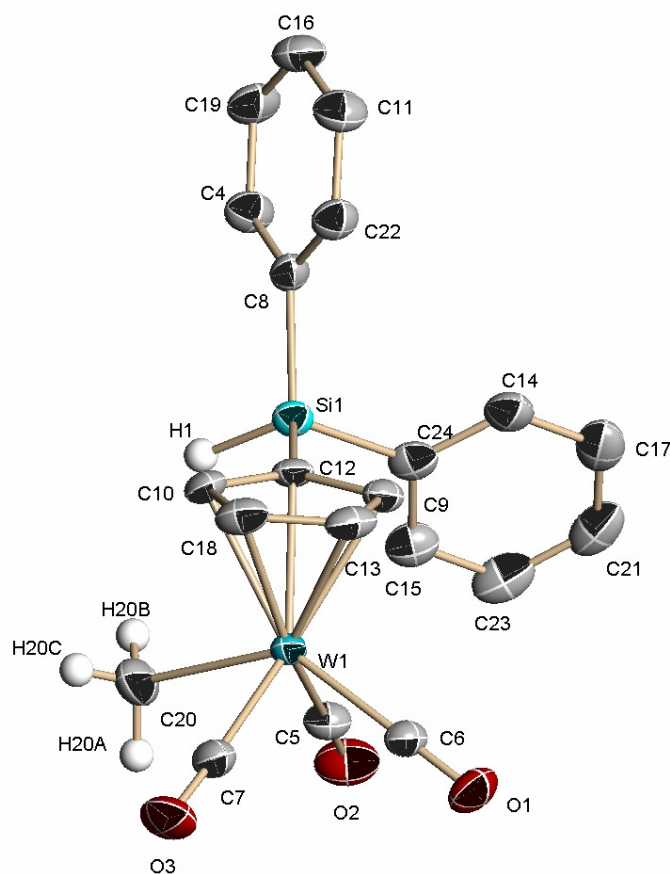
Fig. 4: Molecular structure of [HPh$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**6b**) with the atom-labeling scheme. Thermal ellipsoids are drawn at the 50 % probability level and the hydrogen atoms have been omitted for the sake of clarity except H1 and H20A-C.

Selected bond lengths [Å], bond and torsion angles [°]: W1-C7 1.980(3), W1-C6 1.982(3), W1-C5 1.983(3), W1-C20 2.301(3), Si1-C12 1.859(3), Si1-C24 1.862(3), Si1-C8 1.875(3), C9-C13 1.420(4), C9-C12 1.433(4), C10-C18 1.408(4), C10-C12 1.436(4), C13-C18 1.399(4), C12-Si1-C24 110.00(13), C12-Si1-C8 108.26(12), C24-Si1-C8 109.70(13), C8-Si1-C12-C9 –90.1(2).

3) {[HO*i*Pr$_2$Si(C$_5$H$_4$)](OC)$_3$W}$_2$ (*W-W*) (**14**)

The result of this analysis confirms the proposed dimeric structure of **14** and is depicted in figure 5.

Red crystals of **14** are obtained from slow evaporation of a benzene-saturated solution at room temperature.

14, which to the best of our knowledge is the first structurally characterized dimeric halfsandwich tungsten complex with a cyclopentadienyl-bound silyl group, crystallizes in the triclinic systeme and the space group P-1 (valid for a monomeric [HO*i*Pr$_2$Si(C$_5$H$_4$)](OC)$_3$W-unit). The dimeric molecule has got an inversion center being located in the middle of the tungsten-tungsten bond.

The tungsten complex reveals a pseudo tetragonal pyramidal arrangement of the three carbonyl ligands [mean W-C 1.986 Å] and the second tungsten atom, forming the base while the cyclopentadienyl ring occupies the apical position. The tungsten-tungsten bond length of 3.206(13) Å is very close to that in the parent tungsten complex [(C$_5$H$_5$)(OC)$_3$W]$_2$.(*W-W*) [3.222(1) Å] [84]. There is no significant difference of the W-C carbonyl [W1-C6 1.958(9) Å, W1-C7 1.994(8) Å, W1-C8 1.986(8) Å] and the C-O distances [mean 1.150 Å] to comparable tungsten complexes [83]. As already described for **4b** and **6b**, the C-C bond distances within the cyclopentadienyl ring are different. The shortest one (C3-C4) is found in opposite to C1 [1.384(12) Å] and the largest bond is C1-C2 with a value of 1.451(10) Å.

The silyl group lies almost in the plane of the cyclopentadienyl ring [Si1-C1-C5-C4 – 173.8(6)]. The C1-Si1 distance amounts to 1.882(8) Å and is very simlilar to Si1-C9 [1.883(8) Å] and Si1-C13 [1.880(9) Å]. The Si1-O4 bond length of 1.644(6) Å lies in the expected range. The silyl group stands above the plane spanned by the cyclopentadienyl ligand proved by the torsion angle C5-C1-Si1-C13 of 75.5(8)°. The orientation of the di*iso*propylsilyl moieties above the equatorial plane of the ring ligand is favoured due to their sterical requirements. The HO-groups adopts a position beneath the cyclopentadienyl ring.

The metal fragments show an *anti*-conformation, best illustrated by the lines described by the W1-C6-O1 and W1A-C6A-O1A atoms which stand exactly parallel to each other but contradictory.
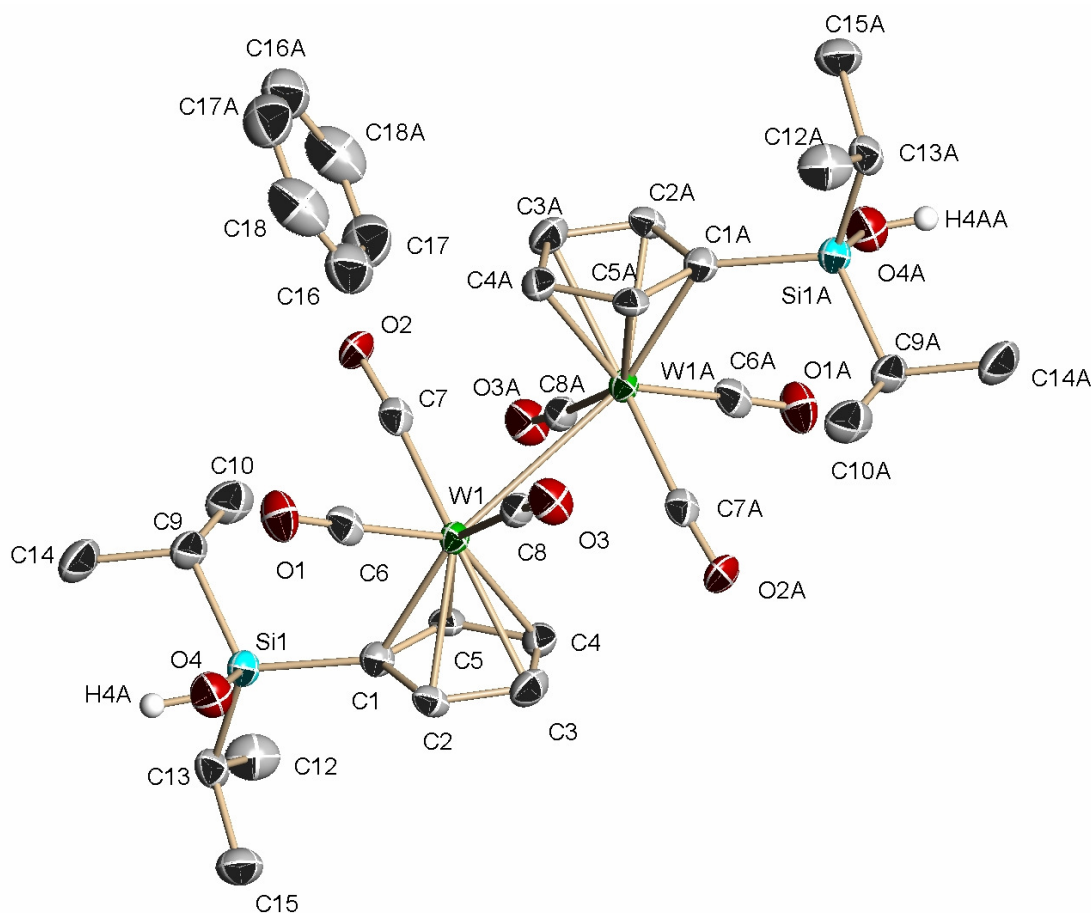
Fig. 5: Molecular structure of {[HO*i*Pr$_2$Si(C$_5$H$_4$)](OC)$_3$W}$_2$ (*W-W*) (**14**) in the solid state illustrating anti-conformation of the both [HO*i*Pr$_2$Si(C$_5$H$_4$)](OC)$_3$W-units. The thermal ellipsoids are drawn at the 50 % probability. The hydrogen atoms have been omitted for clarity except the silanol hydrogen atoms H4A and H4AA.

Selected bond lengths [Å], bond and torsion angles [°]:W1-C6 1.958(9), W1-C7 1.994(8), W1-C8 1.986(8), W1-C1 2.313(8), W1-C2 2.304(8), W1-C3 2.359(8), W1-C4 2.392(8), W1-C5 2.347(8), W1-W1A 3.206(13), C1-C5 1.415(11), C1-C2 1.451(10), C5-C4 1.410(11), C2-C3 1.409(11), C4-C3 1.387(12), C1-Si1 1.882(8), Si1-C9 1.883(8), Si1-C13 1.880(9), Si1-O4 1.644(6), C6-W1-C8 77.6(3), C6-W1-C7 78.8(3), C8-W1-C7 107.2(3), C6-W1-W1A 126.6(2), C1-Si1-O4 101.3(3), O4-Si1-C9 108.8(4), O4-Si1-C13 110.9(4), C1-Si1-C13 110.2(4), C5-C1-Si1-C13 75.5(8).

Crystal Data for **4b, 6b, 14**

	4b)	6b)
mol formula	$C_{30}H_{24}O_6SiW_2$	$C_{21}H_{18}O_3SiW$
mol wt	876.30	530.92
wavelength (Å)	0.71073	0.71073
temp (K)	173(2)	173(2)
cryst size (mm)	0.13 x 0.12 x 0.07	0.20 x 0.20 x 0.10
cryst syst	monoclinic	triclinic
space group	C2/c	P-1
a (Å)	13.260(3)	7.8621(13)
b (Å)	22.957(5)	9.26(14)
c (Å)	11.443(3)	13.762(2)
α (°)	90	98.736(3)
β (°)	124.170(3)	104.970(3)
γ (°)	90	91.008(3)
vol (Å^3), Z	2882.0(12)	955.1(3),
ρ (calcd) (Mgm^{-3})	2.020	1.844
$F(000)$	1656	512
μ (mm^{-1})	8.059	0.723
θ range for data collecn (deg)	2.09 – 25.06	1.55 – 25.52
no. of rflns collected	24231	12590
no. of indep reflns	2566	3556
abs cor.	empirical	empirical
no. of data/restraints /params	2566 / 0 / 178	3556 / 0 / 240
goodness of fit on F^2	1.289	1.081
R1^a	0.0281	0.0165
wR2^b	0.0587	0.0409
largest diff peak and hole (eÅ^{-3})	1.018 and –0.989	0.965 and –0.611

14

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mol formula	$C_{26}H_{32}O_8Si_2W_2$
mol wt	502.29
wavelength (Å)	0.71073
temp (K)	173(2)
cryst size (mm)	0.15 x 0.15 x 0.10
cryst syst	triclinic
space group	P-1
a (Å)	7.607(3)
b (Å)	10.919(4)
c (Å)	12.028(4)
α (°)	64.797(5)
β (°)	86.252(5)
γ (°)	82.457(6)
vol (Å^3), Z	896.1(6)
ρ (calcd) (Mgm^{-3})	1.862
F(000)	488
μ (mm^{-1})	6.528
θ range for data collecn (deg)	1.87 - 25.06
no. of rflns collected	6449
no. of indep reflns	3140
abs cor.	empirical
no. of data/restraints /params	3140 / 0 / 219
goodness of fit on F^2	0.981
R1^a	0.0466
wR2^b	0.0959
largest diff peak and hole (eÅ^{-3})	3.679 and -1.923

R1 = $\Sigma||F_0| - |F_c||/\Sigma|F_0|$ for reflections with $I > 2\sigma(I)$. wR2 = $[\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_0^2)/3$ and a and b are constants set by the program.

CONCLUSION

The results of this paper demonstrate that halfsandwich tungsten complexes with a η^5-cyclopentadienyl-fixed silanol function are good accessible by SiCl/SiOH-exchange of the corresponding tungsten-chlorosilanes. The stability of this type of metal fragment substituted silanols is significantly reduced with respect to self-condensation, compared to tungstenmethyl- and tungsten-silanols [e.g.: $Cp(OC)_2(Ph_3P)W-CH_2-SiMe_2OH$ and $Cp(OC)_2(Ph_3P)W-SiMe_2OH$]. As a consequence, the tungsten-silanol $[HOMe_2Si(C_5H_4)](OC)_3WMe$ (**13a**) undergoes condensation to the disiloxane $O\{[Me_2Si(C_5H_4)](OC)_3WMe\}_2$ (**15**), which is well known from triorganosilanols and allows further the formation of heterosiloxanes in co-condensation reactions.

Apart from that, these compounds can be considered as ideal precursors which are suitable for controlled reactions with organoelemnthalides in order to generate novel transition metal containing siloxanes.

Current work deals with the synthesis and reactivity of such type of tungsten-silanols with a phosphine-substituted tungsten center, serving for investigations about the influence of the phosphine ligand on the silyl unit.

EXPERIMENTAL SECTION

General Remarks: All operations were performed under an atmosphere of purified and dried nitrogen using Schlenk-type techniques. Solvents were dried according to conventional procedures, distilled and saturated with N_2 prior to use. - NMR: Jeol Lambda 300 (300.4 MHz, 75.5 MHz, and 59.6 MHz for ^{1}H, ^{13}C, and ^{29}Si, respectively). [D$_6$]-benzene as a solvent: δ_H = 7.15, δ_C = 128.0; for ^{29}Si rel. to TMS external. - IR: Perkin-Elmer 283 grating spectrometer. - Melting points: Differential thermo analysis (Du Pont 9000 Thermal Analysis System). - Elemental analyses were performed in the laboratories of the *Institut für Anorganische Chemie der Universität Würzburg*. - Starting materials were prepared according to literature procedures: DMD [75, 76, 85], Cp(OC)$_3$WMe (**1**) [86], Cp(OC)$_3$WH (**10**) [87] and [(LiC$_5$H$_4$)(OC)$_3$W]Li (**11**) [73, 74]. Me$_2$SiCl$_2$ (**2a**), Ph$_2$SiCl$_2$ (**2b**), *i*-Pr$_2$SiCl$_2$ (**2c**), Me$_2$Si(H)Cl (**5a**), Ph$_2$Si(H)Cl (**5b**), *i*-Pr$_2$Si(H)Cl (**5c**), MePhSi(H)Cl (**5d**), ClMe$_2$SiOSiMe$_2$Cl, Me$_3$SnCl (**16a**), Cp$_2$TiCl$_2$ (**16b**) and Co$_2$(CO)$_8$ were purchased from commercial sources and the liquid silanes destilled prior use.

1) [ClMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (3a) and Me$_2$Si[(C$_5$H$_4$)(OC)$_3$WMe]$_2$ (4a)

Tricarbonyl[η^5-(chlorodimethylsilyl)-cyclopentadienyl]methyltungsten(II) and

Bis[tricarbonyl(η^5-cyclopentadienyl)-methyltungsten(II)]-dimethylsilane

A THF-solution (15 ml) containing 970 mg (2.79 mmol) of Cp(OC)$_3$WMe (**1**) was treated with 2.07 ml (3.34 mmol, 1.6 M in cyclohexane) of *n*BuLi at –78 °C and stirred for 45 min. During this period the color changed from yellow to deep brown. This solution was added dropwise to 720 mg (0.68 ml, 5.58 mmol) of dichlorodimethylsilane in 15 ml THF at –78 °C. The mixture was allowed to warm up to room temperature over a period of 1 h. Afterwards the solvent was removed in vacuo. The residue was extractet with 50 ml PE. After filtration, the extract was evaporated in vacuo resulting in a brown oily mixture consisting of **3a** and **4a**.

3a)

^{1}H-NMR (300.4 MHz, C_6D_6): δ = 4.58 - 4.56 (m, 2 H, H_4C_5), 4.46 - 4.44 (m, 2 H, H_4C_5), 0.42 [s, ^2J(HCW) = 4.0 Hz, 3 H, H_3CW], 0.33 [s, ^2J(HCSi) = 7.0 Hz, 6 H, H_3CSi] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C_6D_6): δ = 229.08 [s, ^1J(CW) = 132.3 Hz, CO], 215.97 [s, ^1J(CW) = 155.9 Hz, CO], 96.91 [s, ^1J(CW) = 4.1 Hz, C_5H_4], 95.26 [s, ^1J(CW) = 4.5 Hz, C_5H_4), 94.07 [s, ^1J(CSi) = 65.1 Hz, ^1J(CW) = 4.8 Hz, C_5H_4], 2.93 [s, ^1J(CSi) = 14.9 Hz, CH_3Si], -34.20 [s, ^1J(CW) = 26.2 Hz, CH_3W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = 17.70 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2020 (s), 1930 (vs) cm^{-1}. Anal. Calc. for $C_{11}H_{13}ClO_3SiW$ (440.60): C 29.98, H 2.97; found: C 29.57, H 3.13 %.

4a)

^{1}H-NMR (300.4 MHz, C_6D_6): δ = 4.68 - 4.66 (m, 4 H, H_4C_5), 4.49 - 4.47 (m, 4 H, H_4C_5), 0.42 [s, ^2J(HCW) = 3.6 Hz, 6 H, H_3CW], 0.22 (s, 6 H, H_3CSi) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2021 (s), 1932 (vs) cm^{-1}.

2) [ClPh$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (3b) and Ph$_2$Si[(C$_5$H$_4$)(OC)$_3$WMe]$_2$ (4b)

Tricarbonyl[η^5-(chlorodiphenylsilyl)-cyclopentadienyl]methyltungsten(II) and

Bis[tricarbonyl(η^5-cyclopentadienyl)-methyltungsten(II)]-diphenylsilane

Analogous to 1) from 435 mg (0.36 ml, 1.72 mmol) dichlorodiphenylsilane in 15 ml THF and 1.72 mmol of **A** resulting in a oily mixture of **3b** and **4b**.

3b)

^{1}H-NMR (300.4 MHz, C_6D_6): δ = 7.61 - 7.58 (m, 4 H, H_5C_6Si), 7.23 - 7.08 (m, 6 H, H_5C_6Si), 4.75 - 4.66 (m, 2 H, H_4C_5), 4.64 - 4.53 (m, 2 H, H_4C_5), 0.36 [s, ^2J(HCW) = 3.9 Hz, 3 H, H_3CW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C_6D_6): δ = 230.39 [s, ^1J(CW) = 131.8 Hz, CO], 215.64 [s, ^1J(CW) = 156.7 Hz, CO], 134.86, 132.57, 131.37, 128.38 (s, C_6H_5), 105.08 [s, ^1J(CW) = 4.8 Hz, C_5H_4], 96.88 [s, ^1J(CW) = 4.8 Hz, C_5H_4), 93.51 (s, C_5H_4), -33.89 [s, ^1J(CW) = 27.9 Hz, CH_3W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = -0.45 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2022 (s), 1933 (vs) cm^{-1}. Anal. Calc. for $C_{21}H_{17}ClO_3SiW$ (564.75): C 44.66, H 3.03; found: C 45.13, H 3.50 %.

4b)

¹H-NMR (300.4 MHz, C_6D_6): δ = 7.51 - 7.07 (m, 10 H, H_5C_6Si), 4.77 - 4.74 (m, 4 H, H_4C_5), 4.70 - 4.67 (m, 4 H, H_4C_5), 0.20 [s, ^2J(HCW) = 3.4 Hz, 6 H, H_3CW] ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C_6D_6): δ = 228.78 [s, ^1J(CW) = 131.7 Hz, CO], 215.64 [s, ^1J(CW) = 156.9 Hz, CO], 135.95, 132.76, 131.00, 128.47 (s, C_6H_5), 98.43 [s, ^1J(CW) = 4.8 Hz, C_5H_4], 95.88 [s, ^1J(CW) = 4.5 Hz, C_5H_4), 94.07 (s, C_5H_4), -33.62 [s, ^1J(CW) = 28.0 Hz, CH_3W] ppm. - **²⁹Si{¹H}-NMR** (59.6 MHz, C_6D_6): δ = 13.79 (s) ppm. - **IR** (PE): $\tilde{\nu}$(CO) = 2020 (s), 1933 (vs) cm^{-1}. Anal. Calc. for $C_{30}H_{24}O_6SiW_2$ (876.30): C 41.12, H 2.76; found: C 41.59, H 3.02 %.

3) [HMe₂Si(C₅H₄)](OC)₃WMe (6a)

Tricarbonyl[η^5-(dimethylsilyl)-cyclopentadienyl]methyltungsten(II)

To a solution containing 6.18 mmol of lithiated Cp(OC)$_3$WMe (**1**) in 30 ml THF 1.17 mg (1.35 ml, 12.36 mmol) of Me$_2$Si(H)Cl (**5a**) were added *in situ* at −78 °C . During the addition the color changed from brown to yellow. The mixture was stirred for 45 min and allowed to warm up to room temperature within this period. The solvent was removed in vacuo and the residue extracted with 3 x 20 ml PE. After separation from LiCl by filtration the extract was evaporated in vacuo. - Yield: 2.49 g (6.13 mmol, 99 %). - Yellow oil. - **¹H-NMR** (300.4 MHz, C_6D_6): δ = 4.69 - 4.67 (m, 2 H, H_4C_5), 4.50 - 4.48 (m, 2 H, H_4C_5), 4.44 [sept, ^3J(HSiCH) = 3.8 Hz, 1 H, HSi], 0.48 [s, ^2J(HCW) = 3.5 Hz, 3 H, H_3CW], 0.05 [d, ^3J(HCSiH) = 3.8 Hz, 6 H, H_3CSi] ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C_6D_6): δ = 229.85 [s, ^1J(CW) = 131.3 Hz, CO], 216.85 [s, ^1J(CW) = 155.6 Hz, CO], 96.48 [s, ^1J(CW) = 4.8 Hz, C_5H_4], 95.94 [s, ^1J(CW) = 3.8 Hz, C_5H_4), 93.93 [s, ^1J(CSi) = 64.1 Hz, ^1J(CW) = 4.5 Hz, C_5H_4], -3.24 [s, ^1J(CSi) = 53.4 Hz, CH_3Si], -34.34 [s, ^1J(CW) = 28.3 Hz, CH_3W] ppm. - **²⁹Si{¹H}-NMR** (59.6 MHz, C_6D_6): δ = -20.31 (s) ppm. - **IR** (PE): $\tilde{\nu}$(SiH) = 2142 (m), $\tilde{\nu}$(CO) = 2019 (s), 1930 (vs) cm^{-1}. Anal. Calc. for $C_{11}H_{14}O_3SiW$ (406.15): C 32.53, H 3.47; found: C 32.29, H 3.41 %.

*4) [HPh₂Si(C₅H₄)](OC)₃WMe (**6b**)*

Tricarbonyl[η^5-(diphenylsilyl)-cyclopentadienyl]methyltungsten(II)

Analogous to 3) from 4.57 mmol of lithiated Cp(OC)₃WMe (**1**) and 1.29 g (1.15 ml, 5.94 mmol) chlorodiphenylsilane (**5b**) in 30 ml THF. After evaporation of the extract the resulting oil is solidified at −78 °C and washed twice with each 10 ml PE. - Yield: 2.18 g (4.11 mmol, 90 %). - Yellowbrown solid. - M.p: 29 °C. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 7.49 - 6.99 (m, 10 H, H₅C₆Si), 5.50 [s, ^1J(HSi) = 207.5 Hz,1 H, HSi], 4.64 - 4.62 (m, 2 H, H₄C₅), 4.55 - 4.54 (m, 2 H, H₄C₅), 0.34 [s, ^2J(HCW) = 3.3 Hz, 3 H, H₃CW] ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C₆D₆): δ = 229.14 [s, ^1J(CW) = 131.5 Hz, CO], 216.22 [s, ^1J(CW) = 155.9 Hz, CO], 135.67, 134.72, 130.56, 128.52 (s, C₆H₅), 97.51 [s, ^1J(CW) = 4.8 Hz, C₅H₄], 96.52 [s, ^1J(CW) = 3.8 Hz, C₅H₄], 95.88 (s, C₅H₄), -34.23 [s, ^1J(CW) = 27.9 Hz, CH₃W] ppm. - **²⁹Si{¹H}-NMR** (59.6 MHz, C₆D₆): δ = -21.84 (s) ppm. - **IR** (PE): $\tilde{\nu}$(SiH) = 2147 (m), $\tilde{\nu}$(CO) = 2020 (s), 1933 (vs) cm^{-1}. Anal. Calc. for C₂₁H₁₈SiW (530.31): C 47.56, H 3.42; found: C 48.16, H 3.64 %.

*5) [HiPr₂Si(C₅H₄)](OC)₃WMe (**6c**)*

Tricarbonyl[η^5-(di-*iso*-propylsilyl)-cyclopentadienyl]methyltungsten(II)

Analogous to 3) from 4.89 mmol of lithiated Cp(OC)₃WMe (**1**) and 1.47 g (1.69 ml, 9.78 mmol) of chlorodi*iso*propylsilane (**5c**) in 25 ml THF after two hours reaction time. After evaporation of the extract the resulting oil was solidified at −78 °C and washed with 10 ml PE. - Yield: 2.03 g (4.40 mmol, 90 %). - Yellow oil. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 4.77 - 4.75 (m, 2 H, H₄C₅), 4.64 - 4.63 (m, 2 H, H₄C₅), 4.02 - 3.98 (m, 1 H, HSi), 0.98 - 0.94 (m, 14 H, *i*Pr), 0.52 [s, ^2J(HCW) = 3.5 Hz, 3 H, H₃CW] ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C₆D₆): δ = 229.76 [s, ^1J(CW) = 132.0 Hz, CO], 216.66 [s, ^1J(CW) = 155.8 Hz, CO], 97.32 [s, ^1J(CW) = 4.8 Hz, C₅H₄], 95.89 [s, ^1J(CW) = 3.8 Hz, C₅H₄], 90.89 [s, ^1J(CW) = 4.5 Hz, C₅H₄], 19.15, 18.93 (s, (C̲H₃)₂CSi), 11.87 [s, ^1J(CSi) = 55.2 Hz, C̲H(Me₂)Si], -34.06 [s, ^1J(CW) = 28.2 Hz, CH₃W] ppm. - **²⁹Si{¹H}-NMR** (59.6 MHz, C₆D₆): δ = -2.19 (s) ppm. - **IR** (PE): $\tilde{\nu}$(SiH) = 2128 (m), $\tilde{\nu}$(CO) =

2019 (s), 1931 (vs) cm^{-1}. Anal. Calc. for $C_{15}H_{22}O_3SiW$ (462.27): C 38.97, H 4.80; found: C 39.60, H 5.02 %.

*6) [HMePhSi(C$_5$H$_4$)](OC)$_3$WMe (**6d**)*

Tricarbonyl[η^5-(methylphenylsilyl)-cyclopentadienyl]methyltungsten(II)

Analogous to 3) from 2.23 mmol of lithiated Cp(OC)$_3$WMe (**1**) and 0.87 g (5.56 mmol) of chloromethylphenylsilane (**5d**) in 25 ml THF after three hours reaction time. After evaporation of the extract the resulting oil was washed with three times with each 10 ml PE at −78 °C. - Yield: 1.47 g (3.14 mmol, 66 %). - Yellowbrown oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.41 - 7.10 (m, 5 H, H$_5$C$_6$Si), 4.95 [q, ^3J(HSiCH) = 3.8 Hz,1 H, HSi], 4.65 - 4.58 (m, 2 H, H$_4$C$_5$), 4.52 - 4.47 (m, 2 H, H$_4$C$_5$), 0.45 [s, ^2J(HCW) = 3.4 Hz, 3 H, H$_3$CW], 0.33 [d, ^3J(HCSiH) = 3.8 Hz, 3 H, H$_3$CSi] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 228.12 [s, ^1J(CW) = 131.8 Hz, CO], 215.21 [s, ^1J(CW) = 155.8 Hz, CO], 137.48, 133.25, 129.09, 127.06 (s, C$_6$H$_5$), 95.99 [s, ^1J(CW) = 4.7 Hz, C$_5$H$_4$], 95.01 [s, ^1J(CW) = 4.4 Hz, C$_5$H$_4$], 94.98 [s, ^1J(CW) = 4.4 Hz, C$_5$H$_4$], 94.67 [s, ^1J(CW) = 3.6 Hz, C$_5$H$_4$], 90.81 (s, C$_5$H$_4$Si), -6.00 (s, CH$_3$Si), -34.55 [s, ^1J(CW) = 27.8 Hz, CH$_3$W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -21.84 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (SiH) = 2133 (m), $\tilde{\nu}$ (CO) = 2019 (s), 1932 (vs) cm^{-1}. Anal. Calc. for $C_{16}H_{16}O_3SiW$ (468.23): C 41.04, H 3.44; found: C 39.78, H 3.82 %.

*7) [ClMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**3a**) by chlorination of **6a** with PdCl$_2$*

To a solution of 310 mg (0.76 mmol) of **6a** in 10 ml benzene, 142 mg (0.80 mmol) of PdCl$_2$ were added. After stirring for 3 d the solvent was removed in vacuo and the residue extracted with 30 ml PE. Filtration of the extract through a celite pad and following evaporation to dryness led to an yellow oil. Washing with 5 ml PE at −78 °C resulted in **3a**. - Yield: 304 mg (0.69 mmol, 91 %). - Viscous, yellow oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.58 - 4.56 (m, 2 H, H$_4$C$_5$), 4.46 - 4.44 (m, 2 H, H$_4$C$_5$), 0.42 [s, ^2J(HCW) = 4.0 Hz, 3 H, H$_3$CW], 0.33 [s, ^2J(HCSi) = 7.0 Hz, 6 H, H$_3$CSi] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 229.08 [s, ^1J(CW) = 132.3 Hz, CO], 215.97 [s,

^1J(CW) = 155.9 Hz, CO], 96.91 [s, ^1J(CW) = 4.1 Hz, C$_5$H$_4$], 95.26 [s, ^1J(CW) = 4.5 Hz, C$_5$H$_4$), 94.07 [s, ^1J(CSi) = 65.1 Hz, ^1J(CW) = 4.8 Hz, C$_5$H$_4$], 2.93 [s, ^1J(CSi) = 14.9 Hz, CH$_3$Si], -34.20 [s, ^1J(CW) = 26.2 Hz, CH$_3$W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 17.70 (s) ppm. - **IR** (PE): $\tilde{\nu}$(CO) = 2020 (s), 1930 (vs) cm^{-1}. Anal. Calc. for C$_{11}$H$_{13}$O$_3$SiW (440.60): C 29.98, H 2.97; found: C 29.57, H 3.13 %.

*8) [ClPh$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**3b**) by chlorination of **6b** with PdCl$_2$*

Analogous to 7) from 390 mg (0.74 mmol) of **6b** and 130 mg (0.74 mmol) of PdCl$_2$ in 10 ml benzene after three days reaction period at room temperature. - Yield: 330 mg (0.58 mmol, 78 %). - Yellow solid. - M.p: 32 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.61 - 7.58 (m, 4 H, H$_5$C$_6$Si), 7.23 - 7.08 (m, 6 H, H$_5$C$_6$Si), 4.75 - 4.66 (m, 2 H, H$_4$C$_5$), 4.64 - 4.53 (m, 2 H, H$_4$C$_5$), 0.36 [s, ^2J(HCW) = 3.9 Hz, 3 H, H$_3$CW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 230.39 [s, ^1J(CW) = 131.8 Hz, CO], 215.64 [s, ^1J(CW) = 156.7 Hz, CO], 134.86, 132.57, 131.37, 128.38 (s, C$_6$H$_5$), 105.08 [s, ^1J(CW) = 4.8 Hz, C$_5$H$_4$], 96.88 [s, ^1J(CW) = 4.8 Hz, C$_5$H$_4$), 93.51 (s, C$_5$H$_4$), -33.89 [s, ^1J(CW) = 27.9 Hz, CH$_3$W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 11.05 (s) ppm. - **IR** (PE): $\tilde{\nu}$(CO) = 2022 (s), 1933 (vs) cm^{-1}. Anal. Calc. for C$_{21}$H$_{17}$ClO$_3$SiW (564.75): C 44.66, H 3.03; found: C 45.13, H 3.50 %.

*9) [CliPr$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**7**) and [CliPr$_2$Si(C$_5$H$_4$)](OC)$_3$WCl (**8**)*

Tricarbonyl[η^5-(chloro-di-*iso*-propylsilyl)-cyclopentadienyl]methyltungsten(II) and Tricarbonylchloro[η^5-(chloro-di-*iso*-propylsilyl)-cyclopentadienyl]tungsten(II)

Analogous to 7) from 390 mg (0.84 mmol) of **6c** and 160 mg (0.90 mmol) of PdCl$_2$ in 10 ml benzene. PdCl$_2$ was used up after 3 d and a mixture of **7** and **8** and small traces of **9** was observed. A further equivalent of PdCl$_2$ was added and the reaction mixture stirred for another three days at room temperature. The solvent was removed in vacuo and the residue extracted with 30 ml PE. After filtration through a celite pad and evaporation of the extract to dryness, the crude red product was washed twice at

0 °C with each 5 ml PE to give **8**. - Yield: 378 mg (0.73 mmol, 87 %). - Orange solid. - M.p: 42 °C.

(7)

¹H-NMR (300.4 MHz, C_6D_6): δ = 4.68 - 4.62 (m, 4 H, H_4C_5), 0.94 - 0.92 (m, 14 H, *i*Pr), 0.56 [s, ^2J(HCW) = 3.7 Hz, 3 H, H_3CW] ppm. - **IR** (PE): $\tilde{\nu}$(CO) = 2021 (s), 1931 (vs) cm^{-1}.

(8)

¹H-NMR (300.4 MHz, C_6D_6): δ = 4.81 - 4.80 (m, 2 H, H_4C_5), 4.78 - 4.76 (m, 2 H, H_4C_5), 0.96 - 0.93 (m, 14 H, *i*Pr) ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C_6D_6): δ = 229.76 [s, ^1J(CW) = 132.0 Hz, CO], 216.66 [s, ^1J(CW) = 155.8 Hz, CO], 97.32 [s, ^1J(CW) = 4.8 Hz, C_5H_4], 95.89 [s, ^1J(CW) = 3.8 Hz, C_5H_4), 90.89 [s, ^1J(CW) = 4.5 Hz, C_5H_4], 19.15, 18.93 (s, (CH$_3$)$_2$CSi), 11.87 [s, ^1J(CSi) = 55.2 Hz, CH(Me$_2$)Si], -34.06 [s, ^1J(CW) = 28.2 Hz, CH$_3$W] ppm. - **²⁹Si{¹H}-NMR** (59.6 MHz, C_6D_6): δ = 24.13 (s) ppm. - **IR** (PE): $\tilde{\nu}$(CO) = 2052 (s), 1972 (vs), 1956 (s) cm^{-1}. Anal. Calc. for $C_{14}H_{18}Cl_2O_3SiW$ (517.14): C 32.51, H 3.51; found: C 32.23, H 3.53 %.

*10) {[CliPr$_2$Si(C$_5$H$_4$)](OC)$_3$W}$_2$ (W-W) (**9**)*

Bis{tricarbonyl[η^5-(chloro-di-*iso*-propylsilyl)-cyclopentadienyl]-tungsten(II)}

The PE wash layer of **8** was evaporated to dryness giving **9** as a dark orange and high viscous oil. - Yield: 78 mg (0.08 mmol, 9.5 %). - Orange solid. - M.p: 42 °C. - **¹H-NMR** (300.4 MHz, C_6D_6): δ = 4.99 - 4.97 (m, 2 H, H_4C_5), 4.88 - 4.87 (m, 2 H, H_4C_5), 0.97 - 0.94 (m, 14 H, *i*Pr) ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C_6D_6): δ = 232.88 [s, ^1J(CW) = 132.5 Hz, CO], 218.67 [s, ^1J(CW) = 155.9 Hz, CO], 99.45 [s, ^1J(CW) = 4.9 Hz, C_5H_4], 97.49 [s, ^1J(CW) = 3.8 Hz, C_5H_4), 93.77 [s, ^1J(CW) = 4.6 Hz, C_5H_4], 20.25, 19.94 (s, (CH$_3$)$_2$CSi), 12.03 [s, ^1J(CSi) = 55.3 Hz, CH(Me$_2$)Si] ppm. - **²⁹Si{¹H}-NMR** (59.6 MHz, C_6D_6): δ = 24.56 (s) ppm. - **IR** (CH$_2$Cl$_2$): $\tilde{\nu}$(CO) = 1961 (s), 1908 (s) cm^{-1}. Anal. Calc. for $C_{28}H_{36}Cl_2O_6Si_2W_2$ (963.37): C 34.91, H 3.77; found: C 34.27, H 3.53 %.

11) Li{W[(C₅H₄)SiiPr₂Cl](CO)₃} (12)

Lithium{tricarbonyl[η⁵-(di-*iso*-propylsilyl)-cyclopentadienyl]tungstate}

580 mg (0.91 mmol) of **11** were suspended in 1 ml *i*Pr₂SiCl₂ at room temperature leading to a deep dark mixture which was stirred for 4 h. The silane was removed in vacuo and the residue washed 10 times each with 2 ml PE giving a pale brown and pyrophoric powder. - Yield: 390 mg (0.80 mmol, 88 %). - **¹H-NMR** (300.4 MHz, C_6D_6): δ = 4.84 - 4.83 (m, 2 H, H_4C_5), 4.71 - 4.69 (m, 2 H, H_4C_5), 0.94 - 0.91 (m, 14 H, *i*Pr) ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C_6D_6): δ = 231.54 [s, ^1J(CW) = 132.3 Hz, CO], 219.07 [s, ^1J(CW) = 155.7 Hz, CO], 98.58 [s, ^1J(CW) = 4.8 Hz, C_5H_4], 96.48 [s, ^1J(CW) = 3.8 Hz, C_5H_4), 93.22 [s, ^1J(CW) = 4.4 Hz, C_5H_4], 20.26, 19.99 (s, ($\underline{C}H_3$)₂CSi), 12.06 [s, ^1J(CSi) = 55.7 Hz, $\underline{C}H(Me_2)$Si] ppm. - **²⁹Si{¹H}-NMR** (59.6 MHz, C_6D_6): δ = 24.65 (s) ppm. - **IR** (THF): $\tilde{\nu}$ (CO) = 1899 (s), 1780 (vs), 1740 (vs) cm⁻¹. $C_{14}H_{18}ClLiO_3SiW$ (488.63).

12) [CliPr₂Si(C₅H₄)](OC)₃WMe (7)

To a suspension of 390 mg (0.80 mmol) of **12** in a solvent mixture of 20 ml PE and 10 ml benzene were 0.09 ml (1.50 mmol) of MeI added. The mixture was stirred for 18 hours at room temperature. The yellow solution, containing **7**, was separated from LiI by filtration over celite and the filtrate evaporated to dryness. The crude product was washed with 5 ml PE at 78 °C giving an orange powder. - Yield: 363 mg (0.73 mmol, 91 %). - M.p: 35 °C. - **¹H-NMR** (300.4 MHz, C_6D_6): δ = 4.68 - 4.62 (m, 4 H, H_4C_5), 0.94 - 0.92 (m, 14 H, *i*Pr), 0.56 [s, ^2J(HCW) = 3.7 Hz, 3 H, H_3CW] ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C_6D_6): δ = 229.56 [s, ^1J(CW) = 132.7 Hz, CO], 216.04 [s, ^1J(CW) = 155.3 Hz, CO], 95.56 [s, ^1J(CW) = 4.7 Hz, C_5H_4], 94.68 [s, ^1J(CW) = 3.7 Hz, C_5H_4), 90.89 [s, ^1J(CW) = 4.3 Hz, C_5H_4], 18.25, 18.93 (s, ($\underline{C}H_3$)₂CSi), 11.99 [s, ^1J(CSi) = 55.4 Hz, $\underline{C}H(Me_2)$Si], -34.34 [s, ^1J(CW) = 28.3 Hz, CH₃W] ppm. - **²⁹Si{¹H}-NMR** (59.6 MHz, C_6D_6): δ = 23.99 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2021 (s), 1931 (vs) cm⁻¹. Anal. Calc. for $C_{15}H_{21}ClO_3SiW$ (496.72): C 36.27, H 4.26; found: C 36.23, H 4.53 %.

*13) [HOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**13a**)*

Tricarbonyl[η^5-(hydroxydimethylsilyl)-cyclopentadienyl]tungsten(II)methyl

a) by reaction of **6a** with Co$_2$(CO)$_8$ and H$_2$O

250 mg (0.62 mmol) of **6a** were suspended in 10 ml PE. During addition of 212 mg Co$_2$(CO)$_8$ the colour of the reaction mixture changed from yellow to dark brown and was stirred for 4 h at room temperature. The solvent was removed in vacuo and the residue dissolved in 10 ml THF. 0.4 ml water were added and the reaction mixture was stirred for further 4 h. Then the solvent was removed in vacuo and the residue washed 5 times each with 3 ml PE at 0 °C leading to a pale yellow powder. - Yield: 226 mg (0.54 mmol, 87 %).

b) by hydrolysis of [ClMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**3a**)

180 mg (0.41 mmol) of **3a** were dissolved in 10 ml diethylether. 0.1 ml NEt$_3$ and 0.1 ml water were added and the reaction mixture was stirred for 30 min. The solution was dried over Na$_2$SO$_4$ and filtered through a celite pad. The evaporation to dryness and washing with PE at 0 °C led to pure **13a**. - Yield: 156 mg (0.37 mmol, 90 %). - Slight orange solid. - M.p: 38 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.65 - 4.64 (m, 2 H, H$_4$C$_5$), 4.55 - 4.54 (m, 2 H, H$_4$C$_5$), 2.55 (bs, 1 H, HOSi), 0.50 [s, ^2J(HCW) = 3.8 Hz, 3 H, H$_3$CW], 0.11 (s, 6 H, H$_3$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 230.08 [s, ^1J(CW) = 131.3 Hz, CO], 216.99 [s, ^1J(CW) = 155.6 Hz, CO], 97.33 (s, C$_5$H$_4$), 96.05 [s, ^1J(CW) = 4.1 Hz, C$_5$H$_4$), 95.67 [s, ^1J(CW) = 4.8 Hz, C$_5$H$_4$] 0.54 (s, CH$_3$Si), -34.36 [s, ^1J(CW) = 27.9 Hz, CH$_3$W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 4.70 (s) ppm. - **IR** (PE): $\tilde{\nu}$(CO) = 2014 (s), 1923 (vs) cm^{-1}. Anal. Calc. for C$_{11}$H$_{14}$O$_4$SiW (422.15): C 31.29, H 3.34; found: C 30.68, H 3.25 %.

*14) [HOPh$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**13b**)*

Tricarbonyl[η^5-(hydroxydiphenylsilyl)-cyclopentadienyl]methyltungsten(II)

Analogous to 13b) from 390 mg (0.74 mmol) of **3b** and 0.4 ml of water in 10 ml Et$_2$O over a period of 2 h. - Yield: 368 mg (0.67 mmol, 91 %). - Yellow solid. - M.p: 56 ℃. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.61 - 7.58 (m, 4 H, H$_5$C$_6$Si), 7.23 - 7.08 (m, 6 H, H$_5$C$_6$Si), 4.75 - 4.66 (m, 2 H, H$_4$C$_5$), 4.64 - 4.53 (m, 2 H, H$_4$C$_5$), 1.99 (s, 1 H, HOSi), 0.36 [s, ^{2}*J*(HCW) = 3.9 Hz, 3 H, H$_3$CW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 230.39 [s, ^{1}*J*(CW) = 131.8 Hz, CO], 215.64 [s, ^{1}*J*(CW) = 156.7 Hz, CO], 134.86, 132.57, 131.37, 128.38 (s, C$_6$H$_5$), 105.08 [s, ^{1}*J*(CW) = 4.8 Hz, C$_5$H$_4$], 96.88 [s, ^{1}*J*(CW) = 4.8 Hz, C$_5$H$_4$), 93.51 (s, C$_5$H$_4$), -33.89 [s, ^{1}*J*(CW) = 27.9 Hz, CH$_3$W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -0.45 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2019 (s), 1933 (vs) cm^{-1}. Anal. Calc. for C$_{21}$H$_{18}$O$_4$SiW (546.31): C 46.17, H 3.32; found: C 45.83, H 3.45 %.

*15) [HOiPr$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**13c**)*

Tricarbonyl[η^5-(hydroxydi-*iso*-propylsilyl)-cyclopentadienyl]methyltungsten(II)

Analogous to 13b) from 330 mg (0.66 mmol) of **7** and 0.4 ml of water in 20 ml Et$_2$O after a reaction time of one hour. - Yield: 287 mg (0.60 mmol, 91 %). - Red solid. - M.p: 66 ℃. - **^{1}H-NMR** (300.4 MHz, CDCl$_3$): δ = 5.57 - 5.56 (m, 2 H, H$_4$C$_5$), 5.25 - 5.24 (m, 2 H, H$_4$C$_5$), 2.22 (s, 1 H, HOSi), 1.09 - 1.00 (m, 14 H, *i*Pr), 0.42 [s, ^{2}*J*(HCW) = 3.5 Hz, 3 H, H$_3$CW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 235.58 [s, ^{1}*J*(CW) = 132.7 Hz, CO], 219.22 [s, ^{1}*J*(CW) = 155.3 Hz, CO], 95.74 [s, ^{1}*J*(CW) = 4.4 Hz, C$_5$H$_4$], 94.60 [s, ^{1}*J*(CW) = 3.6 Hz, C$_5$H$_4$), 92.69 [s, ^{1}*J*(CW) = 4.3 Hz, C$_5$H$_4$], 16.52, 16.37 (s, (C̲H$_3$)$_2$CSi), 12.74 [s, ^{1}*J*(CSi) = 55.5 Hz, C̲H(Me$_2$)Si], -32.32 [s, ^{1}*J*(CW) = 28.4 Hz, CH$_3$W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 6.02 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2022 (s), 1932 (vs) cm^{-1}. Anal. Calc. for C$_{15}$H$_{22}$O$_4$SiW (478.27): C 37.67, H 4.64; found: C 36.23, H 4.53 %.

16) {[HOiPr$_2$Si(C$_5$H$_4$)](OC)$_3$W}$_2$ (W-W) (14)

Bis{tricarbonyl[η^5-(hydroxy-di-*iso*-propylsilyl)-cyclopentadienyl]-tungsten(II)}

Analogous to 13b) from 62 mg (0.06 mmol) of **9** and 0.05 ml of water in 20 ml Et$_2$O after a reaction time of one hour. - Yield: 54 mg (0.05 mmol, 83 %). - Red solid. - M.p: 53 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 5.20 - 5.18 (m, 2 H, H$_4$C$_5$), 5.11 - 5.09 (m, 2 H, H$_4$C$_5$), 2.16 (s, 1 H, HOSi), 1.03 - 0.96 (m, 14 H, *i*Pr) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 231.55 [s, ^{1}*J*(CW) = 132.6 Hz, CO], 217.26 [s, ^{1}*J*(CW) = 155.5 Hz, CO], 94.41 [s, ^{1}*J*(CW) = 4.4 Hz, C$_5$H$_4$], 92.79 [s, ^{1}*J*(CW) = 3.5 Hz, C$_5$H$_4$), 91.61 [s, ^{1}*J*(CW) = 4.2 Hz, C$_5$H$_4$], 18.02, 17.89 (s, (C̲H$_3$)$_2$CSi), 14.55 [s, ^{1}*J*(CSi) = 55.2 Hz, C̲H(Me$_2$)Si] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 6.02 (s) ppm. - **IR** (PE): ṽ(CO) = 1951 (vs), 1906 (s) cm^{-1}. Anal. Calc. for C$_{28}$H$_{38}$O$_8$SiW (926.47): C 36.30, H 4.13; found: C 36.75, H 4.51 %.

17) O{[Me$_2$Si(C$_5$H$_4$)](OC)$_3$WMe}$_2$ (15)

1,3-Bis[tricarbonyl(η^5-cyclopentadienyl)methyl-tungsten(II)]-1,1,3,3-tetramethyl-disiloxane

a) by condensation of [HOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**13a**)

A solution of 190 mg (0.44 mmol) of **13a** in 5 ml THF were stirred for three weeks at room temperature. The solvent was dried over Na$_2$SO$_4$ and the mixture stirred for 30 min. Na$_2$SO$_4$ was filtered off and the solvent was removed in vacuo. The residue washed twice with each 4 ml PE at –78 °C resulting in a yellow solid. - Yield: 91 mg (0.20 mmol, 93 %). - Yellow solid. - M.p: 72 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.72 - 4.71 (m, 4 H, H$_4$C$_5$), 4.57 - 4.56 (m, 4 H, H$_4$C$_5$), 0.48 [s, ^{2}*J*(HCW) = 3.8 Hz, 6 H, H$_3$CW], 0.17 (s, 12 H, H$_3$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 229.92 [s, ^{1}*J*(CW) = 133.4 Hz, CO], 216.75 [s, ^{1}*J*(CW) = 155.8 Hz, CO], 97.18 (s, ipso-C of C$_5$H$_4$), 96.05 [s, ^{1}*J*(CW) = 4.1 Hz, C$_5$H$_4$), 95.67 [s, ^{1}*J*(CW) = 4.8 Hz, C$_5$H$_4$] 1.06 (s, CH$_3$Si), -34.28 [s, ^{1}*J*(CW) = 28.0 Hz, CH$_3$W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$):

δ = -1.58 (s) ppm. - **IR** (PE): $\tilde{v}$ (CO) = 2015 (s), 1925 (vs) cm^{-1}. – MS (EI): m/e [%] 826 (M$^+$). Anal. Calc. for C$_{22}$H$_{26}$O$_7$Si$_2$W$_2$ (826.32): C 31.98, H 3.17; found: C 31.69, H 3.32 %.

b) by reaction of Cp(OC)$_3$WMe (**1**) with nBuLi and ClMe$_2$SiOSiMe$_2$Cl

Analogous to 3) with 660 mg (1.90 mmol) of **1**, 1.41 ml (2.28 mmol) of nBuLi (1.6 M, hexane solution) and 193 mg (0.18 ml, 0.95 mmol) of ClMe$_2$SiOSiMe$_2$Cl resulting in a yellow solid. - Yield: 738 mg (0.89 mmol, 94 %).

18) [HMe$_2$SiOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (17a)

Tricarbonyl[η^5-(1,1,3,3-tetramethyl-disiloxano)-cyclopentadienyl]methyltungsten(II)

A diethylether solution (5 ml) containing 180 mg (0.41 mmol) of **13a** was treated with 0.1 ml of NEt$_3$ und 0.1 ml of Me$_2$Si(H)Cl (**5a**). After a reaction time of two hours the diethylether was removed in vacuo and the residue extracted with 10 ml PE. Final filtration through a celite pad and evaporation to dryness led to **17a**. - Yield: 187 mg (0.39 mmol, 95 %). - Orange oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.88 [sept, ^{3}J(HSiCH) = 2.8 Hz, 1 H, HSi], 4.72 - 4.71 (m, 2 H, H$_4$C$_5$), 4.60 - 4.58 (m, 2 H, H$_4$C$_5$), 0.49 [s, ^{2}J(HCW) = 3.5 Hz, 3 H, H$_3$CW], 0.02 (s, 6 H, HCSiC$_5$H$_4$), 0.10 [d, ^{3}J(HCSiH) = 2.8 Hz, 6 H, H$_3$CSi] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 229.97 [s, ^{1}J(CW) = 133.7 Hz, CO], 216.87 [s, ^{1}J(CW) = 156.1 Hz, CO], 97.52 [s, ^{1}J(CSi) = 64.1 Hz, ^{1}J(CW) = 4.8 Hz, C$_5$H$_4$], 96.01 [s, ^{1}J(CW) = 4.1 Hz, C$_5$H$_4$], 95.64 [s, ^{1}J(CW) = 4.8 Hz, C$_5$H$_4$), 0.93 [s, ^{1}J(CSi) = 55.2 Hz, CH$_3$SiC$_5$H$_4$], 0.74 [s, ^{1}J(CSi) = 56.4 Hz, CH$_3$SiH], -34.38 [s, ^{1}J(CW) = 27.9 Hz, CH$_3$W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -1.69 (s, SiC$_5$H$_4$), -4.76 (s, SiH) ppm. - **IR** (PE): $\tilde{v}$ (SiH) = 2125 (m), $\tilde{v}$ (CO) = 2018 (s), 1929 (vs) cm^{-1}. Anal. Calc. for C$_{13}$H$_{20}$O$_4$Si$_2$W (480.30): C 32.51, H 4.19; found: C 33.54, H 4.30 %.

*19) [Me₃SnOMe₂Si(C₅H₄)](OC)₃WMe (**17b**)*

Tricarbonyl[η^5-(trimethylstanna-dimethylsiloxano)-cyclopentadienyl]methyltungsten(II)

A solution of 200 mg (0.47 mmol) of **13a** in 35 ml Et₂O was treated with 94 mg (0.47 mmol) of Me₃SnCl (**16a**) in the presence of 0.4 ml NEt₃ and stirred over a period of 24 h at room temperature. The precipitate of [HNEt₃]Cl was filtered off and the filtrate evaporated to dryness giving **17b** as solid. - Yield: 200 mg (0.34 mmol, 72 %). - Yellowbrown solid. - M.p: 75 °C. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 4.77 - 4.75 (m, 2 H, H₄C₅), 4.68 - 4.67 (m, 2 H, H₄C₅), 0.56 [s, ^2J(HCW) = 3.6 Hz, 3 H, H₃CW], 0.26 [s, ^2J(HCSn) = 52.6, 55.0 Hz, 9 H, H₃CSn], 0.18 (s, 6 H, H₃CSi) ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C₆D₆): δ = 233.70 [s, ^1J(CW) = 133.5 Hz, CO], 220.57 [s, ^1J(CW) = 155.6 Hz, CO], 104.26 [s, ^1J(CW) = 4.7, *ipso*C₅H₄], 98.67 [s, ^1J(CW) = 4.7 Hz, C₅H₄], 98.44 [s, ^1J(CW) = 4.8 Hz, C₅H₄), 5.63 (s, CH₃Si), 0.00 [s, ^1J(CSn) = 387.3, 405.2 Hz, CH₃Sn], -34.45 [s, ^1J(CW) = 27.8 Hz, CH₃W] ppm. - **²⁹Si{¹H}-NMR** (59.6 MHz, C₆D₆): δ = -4.08 (s) ppm. - **IR** (CH₂Cl₂): $\tilde{\nu}$(CO) = 2011 (s), 1915 (s) cm⁻¹. Anal. Calc. for C₁₄H₂₂O₄SiSnW (584.97): C 28.75, H 3.79; found: C 28.54, H 4.11 %.

*20) [Cp₂(Cl)TiOMe₂Si(C₅H₄)](OC)₃WMe (**17c**)*

Tricarbonyl{η^5-[(chloro-dicyclopentadienyl-titanio)dimethyl-siloxy]-cyclopentadienyl}-methyltungsten(II)

A solution of 200 mg (0.47 mmol) of **13a** in a solvent mixture of 15 ml Et₂O and 5 ml benzene was treated with 0.3 ml NEt₃ and 118 mg (0.47 mmol) Cp₂TiCl₂ (**16b**) The reaction mixture was stirred for one day at room temperature, while the colour changed from red to yellow. The precipitate of [HNEt₃]Cl was filtered off and the filtrate evaporated to dryness. The residue was dissloved in 5 ml CH₂Cl₂ and treated with PE at –78 °C to precipitate **17c**. Washing with PE at –78 °C gave **16c** as a powder. - Yield: 183 mg (0.29 mmol, 55 %). - Yellow solid. - M.p: 78 °C. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 5.84 (s, 10 H, H₅C₅Ti), 4.77 - 4.72 (m, 4 H, H₄C₅), 0.55 [s, ^2J(HCW) = 3.8 Hz, 3 H, H₃CW], 0.30 (s, 6 H, H₃CSi) ppm. - **¹³C{¹H}-NMR** (75.5 MHz,

C$_6$D$_6$): δ = 231.02 [s, ^1J(CW) = 131.2 Hz, CO], 216.76 [s, ^1J(CW) = 155.5 Hz, CO], 116.86 (s, C$_5$H$_5$Ti), 99.02 (s, C$_5$H$_4$), 95.39 [s, ^1J(CW) = 4.4 Hz, C$_5$H$_4$), 94.87 [s, ^1J(CW) = 4.7 Hz, C$_5$H$_4$] 0.53 (s, CH$_3$Si), -33.34 [s, ^1J(CW) = 28.8 Hz, CH$_3$W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 0.57 (s) ppm. - **IR** (CH$_2$Cl$_2$): $\tilde{\nu}$ (CO) = 2012 (s), 1916 (vs) cm^{-1}. Anal. Calc. for C$_{21}$H$_{23}$ClO$_4$SiTiW (634.68): C 39.74, H 3.65; found: C 39.68, H 3.35 %.

*21) {[iBu$_2$AlOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe}$_2$ (**18**)*

Bis{tricarbonyl[η^5-(1,3-di-*iso*-butylalanyl-1,3-dimethylsiloxy)-cyclopentadienyl]-methyltungsten(II)}

To a suspension of 320 mg (0.69 mmol) of **13a** in 40 ml PE, were given at −78 °C 0.69 ml (0.69 mmol) of *i*Bu$_3$Al (1 M, in hexane). The reaction mixture was allowed to warm up to room temperature within 2 h. All volatiles were removed in vacuo and the crude product was washed with 4 ml PE at −78 °C and finally dried in vacuo giving **18** as pale beige solid. - Yield: 248 mg (0.22 mmol, 64 %). - Pale beige solid. - M.p: 65 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.76 - 4.75 (m, 4 H, H$_4$C$_5$), 4.65 - 4.64 (m, 4 H, H$_4$C$_5$), 2.10 [non, ^3J(HCCH) = 6.4 Hz, 4 H, HC(CH$_3$)$_2$], 1.31 [d, ^3J(HCCH) = 6.4 Hz, 24 H, (H$_3$C)$_2$CH], 0.53 [s, ^2J(HCW) = 3.5 Hz, 6 H, H$_3$CW], 0.46 [d, ^3J(HCCH) = 6.4 Hz, 8 H, H$_2$CAl] 0.30 (s, 12 H, H$_3$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 230.52 [s, ^1J(CW) = 131.5 Hz, CO], 214.74 [s, ^1J(CW) = 155.6 Hz, CO], 98.12 (s, C$_5$H$_4$), 95.44 [s, ^1J(CW) = 4.5 Hz, C$_5$H$_4$), 94.97 [s, ^1J(CW) = 4.7 Hz, C$_5$H$_4$] 29.05 [s, (CH$_3$)$_2$CH], 26.35 [s, (CH$_3$)$_2$CH], 25.15 (s, CH$_2$Al), 0.73 (s, CH$_3$Si), -33.32 [s, ^1J(CW) = 29.8 Hz, CH$_3$W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 6.75 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2020 (s), 1929 (vs) cm^{-1}. Anal. Calc. for C$_{38}$H$_{62}$Al$_2$O$_8$Si$_2$W$_2$ (1124.74): C 40.58, H 5.56; found: C 39.68, H 5.35 %.

*22) [LiOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**19**)*

Tricarbonyl[η^5-(dimethyl-lithiumsilanolate)-cyclopentadienyl]methyltungsten(II)

To a solution of 90 mg (0.21 mmol) of **13a** in 5 ml THF, 0.20 ml (0.32 mmol) of *n*BuLi were added and stirred for 18 h at room temperature. The solvent was removed in vacuo and the residue was washed twice with each 4 ml PE resulting in a brown solid. - Yield: 91 mg (0.21 mmol, 97 %). - Brown solid. - **^{1}H-NMR** (300.4 MHz, D$_8$-THF): δ = 4.99 - 4.98 (m, 2 H, H$_4$C$_5$), 4.73 - 4.72 (m, 2 H, H$_4$C$_5$), 0.59 [s, ^{2}*J*(HCW) = 3.9 Hz, 3 H, H$_3$CW], 0.21 (s, 6 H, H$_3$CSi) ppm. - **IR** (THF): $\tilde{\nu}$ (CO) = 2012 (s), 1921 (vs) cm^{-1}. C$_{11}$H$_{14}$O$_4$SiW (428.10)

*23) [MeOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**20**)*

Tricarbonyl[η^5-(methoxy-dimethylsilyl)-cyclopentadienyl]methyltungsten(II)

A solution of 88 mg (0.20 mmol) of **19** in 5 ml THF was treated with 0.02 ml (0.32 mmol) of MeI and the reaction mixture stirred for 18 h at room temperature. After reaction all volatiles were removed in vacuo and the residue extracted with 20 ml PE. The extract was filtered through a celite pad and then evaporated to dryness giving **20** as yellow solid. - Yield: 72 mg (0.16 mmol, 82 %). - Yellow solid. - M.p: 78 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.68 - 4.67 (m, 2 H, H$_4$C$_5$), 4.55 - 4.54 (m, 2 H, H$_4$C$_5$), 3.15 (s, 3 H, H$_3$COSi), 0.49 [s, ^{2}*J*(HCW) = 3.6 Hz, 3 H, H$_3$CW], 0.16 (s, 6 H, H$_3$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 230.07 [s, ^{1}*J*(CW) = 131.3 Hz, CO], 217.00 [s, ^{1}*J*(CW) = 155.6 Hz, CO], 96.38 [s, ^{1}*J*(CW) = 4.7 Hz, C$_5$H$_4$), 95.98 [s, ^{1}*J*(CW) = 4.5 Hz, C$_5$H$_4$] 92.32 (s, C$_5$H$_4$), 50.49 (s, CH$_3$OSi), 1.53 (s, CH$_3$Si), -33.78 [s, ^{1}*J*(CW) = 27.5 Hz, CH$_3$W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 7.22 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2020 (s), 1925 (vs) cm^{-1}. Anal. Calc. for C$_{12}$H$_{16}$O$_4$SiW (436.19): C 33.04, H 3.70; found: C 33.68, H 3.35 %.

*24) [HOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**13a**) by reaction of **20** with aqueous NaOH (0.1 M)*

A solution of 72 mg (0.16 mmol) of **20** in 10 ml Et$_2$0 was treated with 0.5 ml of aqueous NaOH (0.1 M) and stirred for one week at room temperature. All insoluble material was filtered off and the filtrate was evaporated to dryness. The crude product was washed with 2 ml PE at 0 °C. - Yield: 69 mg (87 %). - Pale yellow solid.

Crystal analyses

The data were collected from shockcooled crystals on a BRUKER SMART-APEX diffractometer with D8 goniometer (graphite-monochromated Mo- K$_\alpha$ radiation (λ = 0.71073 Å) equipped with a low temperature device in omega-scan mode at 173(2) K [88]. The data was integrated with SAINT [88] and an empirical absorption correction [89] was applied. The structure was solved by direct methods (SHELXS-97) [90] and refined by full-matrix least squares methods against F^2 (SHELXL-97) [91]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of the hydrogen atoms were calculated by an idealized geometry.

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Chapter III

PHOSPHINE-SUBSTITUTED TUNGSTEN COMPLEXES WITH A η^5-CYCLOPENTADIENYL-BOUND SILANOL FUNCTION

Keywords: Tungsten / Halfsandwich complexes / Metallo-silanols / Phosphines

SUMMARY

The reactions of the tungsten hydrido complexes [XMe$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$WH (**1a,b**), containing a silyl-functionalized cyclopentadienyl ligand, with PMe$_3$ lead to [XMe$_2$Si(η^5-C$_5$H$_4$)](OC)$_2$(Me$_3$P)WH [X = H (**2a**), Cl (**2b**)], which are obtained as a mixture of *cis/trans*-isomers. The UV-irradiation of [ClMe$_2$Si(η^5-C$_5$R$_4$)](OC)$_3$WCl [R = H (**3a**), Me (**3b**)] or [Cl*i*Pr$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$WCl (**3c**) in the presence of PPh$_3$ results in the formation of the chiral *cis*-products [ClMe$_2$Si(η^5-C$_5$R$_4$)](OC)$_2$(Ph$_3$P)WCl [R = H (**4a**), Me (**4b**)] and [Cl*i*Pr$_2$Si(η^5-C$_5$H$_4$)](OC)$_2$(Ph$_3$P)WCl (**4c**). The treatment of **3a** with Ph$_2$PCH$_2$PPh$_2$ (dppm) and UV-light, gives the tungsten complex [ClMe$_2$Si(η^5-C$_5$H$_4$)](OC)(η^2-dppm)WCl (**6**), containing a chelating phosphine ligand. The hydrolysis of the complexes with cyclopentadienyl-bonded Si-Cl-function (**2b, 4a-c** and **6**) generates the corresponding silanols **7a-c**, **8** and **9**, which are stable with respect to self-condensation. The controlled co-condensation of these silanols is realized with Me$_2$Si(H)Cl, Me$_3$SnCl and even with complex **2b** to give the following tungsten-disiloxanes [HMe$_2$SiOMe$_2$Si(η^5-C$_5$R$_4$)](OC)$_2$(Ph$_3$P)WCl [R = H (**10a**), Me (**10b**)], O{[Me$_2$Si(η^5-C$_5$H$_4$)](OC)$_2$(Me$_3$P)WH}$_2$ (**11**), [HMe$_2$SiOMe$_2$Si(η^5-C$_5$H$_4$)](OC)(η^2-dppm)WCl (**13a**) and the stanna-heterosiloxane [Me$_3$SnOMe$_2$Si(η^5-C$_5$H$_4$)](OC)(η^2-dppm)WCl (**13b**), respectively. The new compounds have been identified IR- and NMR-spectroscopically and, in the case of **7c**, **8** and **11**, by X-ray diffraction analyses.

INTRODUCTION

Metallo-silanols containing a metal-silicon bond, represent a special type of silanols, which are characterized by a remarkable high stability with respect to self-condensation, evoked by the strong electron-releasing effect of the metal fragment. This crucial property is even valid for metal-derivatized silanediols L_nM-$SiR(OH)_2$ [1-5] and silanetriols L_nM-$Si(OH)_3$ [3, 6], which are synthetically useful for the generation of well-defined metallasiloxanes and heterosiloxanes by controlled co-condensation processes with chlorosilanes, chlorostannanes, transitionmetal halides and trialkyl compounds of group 13 elements. Furthermore these special silanols represent attractive model compounds for transition metal complexes anchored on silica surfaces.

Further development of the class of metallo-silanols involves now derivatives having the Si-OH moiety separated from the metal fragment by an organic group in order to reduce the "transition metal effect" on the silanol unit which should increase the reactivity in condensation processes.

Recent investigations have shown that halfsandwich iron-, molybdenum-, tungsten- and zirconium-silanols with the η^5-cyclopentadienyl ligand serving as a spacer between the metal and the silanol unit (Fig.1) are stable enough for isolation and exhibit indeed higher reactivity in condensation reactions [7-11].

$$L_nM = ZrCl_3, (OC)_2FeMe,$$
$$(OC)_3MoR\ (R = H, Cl),$$
$$(OC)_3WR\ (R = H, Cl)$$
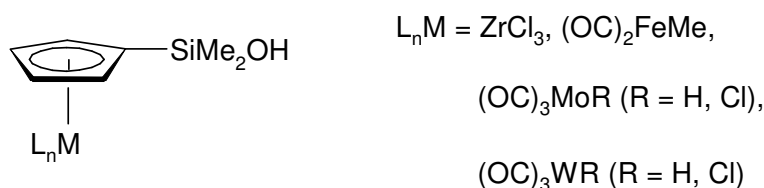
Fig.1: Metallo-silanols with a SiOH-functionalized η^5-cyclopentadienyl ligand.

Tungsten complexes synthesized in this context, are characterized by three carbonyl ligands and a σ-bonded hydrogen, chlorine or methyl group. Extension of this work is now focused on the synthesis of tungsten complexes containing a silanol group at the cyclopentadienyl ligand and the carbonyl groups partially substituted by tertiary

phosphines or bis-diphenylphosphino-methane (dppm), as well as their condensation properties.

RESULTS AND DISCUSSION

Introduction of the Phosphine Ligands. The addition of PMe_3 to solutions of the tungsten hydrides $[XMe_2Si(C_5H_4)](OC)_3WH$ [X = H (**1a**), Cl (**1b**)], dissolved in PE, results at room temperature in the displacement of one CO ligand and in the formation of the PMe_3-substitution products $[XMe_2Si(C_5H_4)](OC)_2(Me_3P)WH$ [X = H (**2a**), Cl (**2b**)] (Eq. 1). The ligand exchange reactions proceed quantitively within two days and evoke a change of the consistency of the starting material, illustrated by the fact that the tungsten hydrides **1a,b** are oils while the phosphine-substituted complexes **2a,b** are obtained as pale yellow solids with a reduced solubility in solvents like PE or Et_2O.
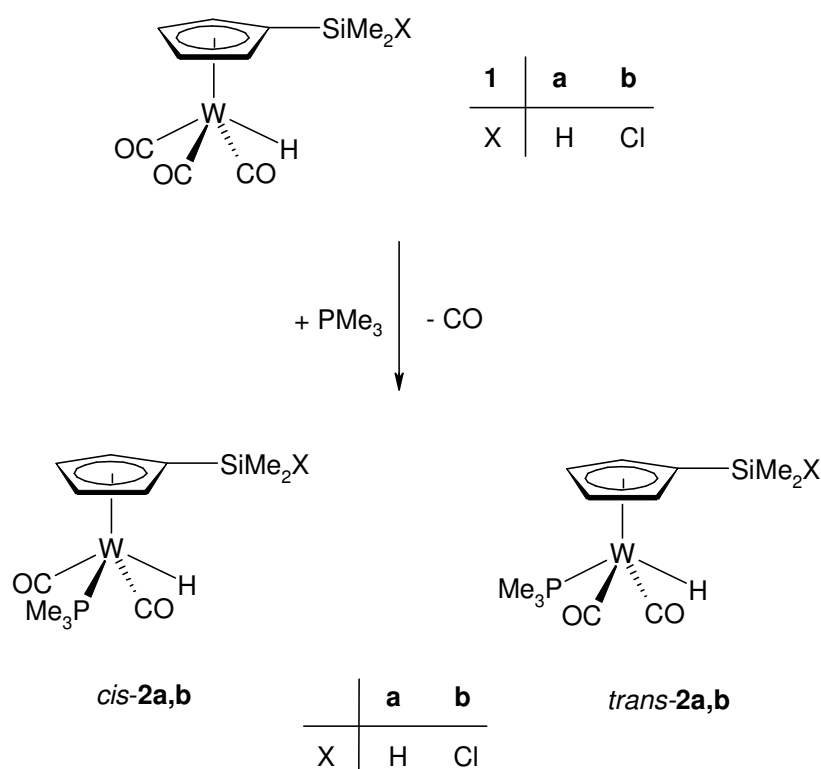
Eq. 1: Synthesis of the CO/PMe_3-exchange products *cis*- and *trans*-$[XMe_2Si(C_5H_4)](OC)_2(Me_3P)WH$ [X = H, Cl (**2a,b**)].

The ^{1}H- and ^{31}P-NMR spectra of **2a,b** indicate a 1:1-mixture of the *cis-* and *trans-* isomers which is in agreement with the finding for Cp(OC)$_2$(Me$_3$P)MH (M = Mo, W) [12].

In contrast to these results, it is not possible to introduce PMe$_3$ or PPh$_3$ cleanly into [ClMe$_2$Si(C$_5$Me$_4$)](OC)$_3$WH [13] or PPh$_3$ in [HMe$_2$Si(C$_5$H$_4$)](OC)$_3$WH (**1a**) [13]. The PMe$_3$-substitution reaction results in a mixture of several phosphine-containing compounds of unknown composition while PPh$_3$ evokes decomposition of **1a** leading to an undefined grey powder.

The reactions of the tungsten chlorides **3a-c** with PPh$_3$ are carried out in benzene under UV-irradiation for about four hours at ambient temperature and result stereoselectively in the formation of the chiral *cis-*isomers of [ClMe$_2$Si(η^5-C$_5$R$_4$)](OC)$_2$(Ph$_3$P)WCl [R = H, Me (**4a,b**)] and [CliPr$_2$Si(η^5-C$_5$H$_4$)](OC)$_2$(Ph$_3$P)WCl (**4c**) which are isolated very clean as orange (**4a,b**) and red (**4c**) crystalline solids in high yields up to 95 % (**4a**) (Eq. 2).

4a-c show a low solubility in diethylether but dissolve readily in benzene or chloroform. The triphenylphosphine-substitution of **4a** reduces strongly the moisture sensibility and allows as a consequence air exposition for minutes in contrast to **3a**.

	a	**b**	**c**
o-	H	Me	H
R	Me	Me	iPr
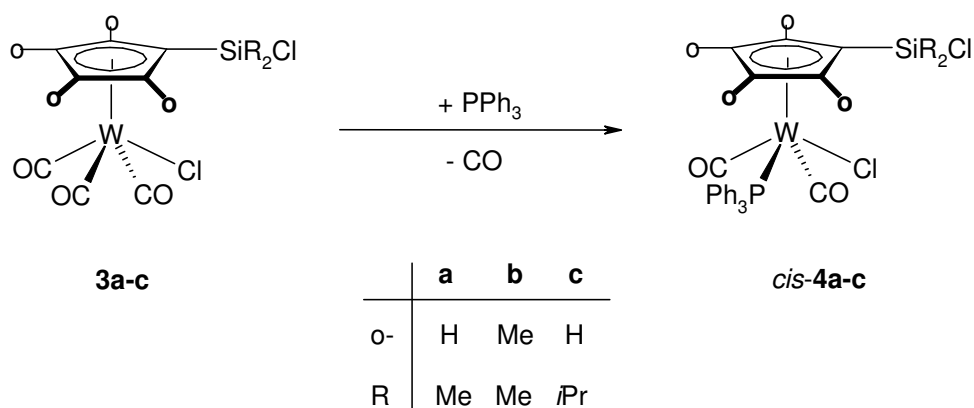
Eq. 2: Chiral CO/PPh$_3$-substitution products.

As a consequence of the tungsten stereo center, the four cyclopentadienyl ring protons (**4a,c**) or methyl groups (**4b**) are inequivalent giving four multiplets (**4a,c**) or singulets (**4b**) in the ^{1}H-NMR spectra. Furthermore, the silicon-bound diastereotopic methyl groups of **4a,b** appear as two singulets, separated by 0.11 (**4a**) or 0.01 ppm (**4b**). In the ^{31}P-NMR spectra of **4a-c** the singulets appear in a narrow range [22.49 (**4a**), 22.80 (**4c**) and 23.88 (**4b**) ppm], each accompanied by ^{183}W-satellites evoked by a ^1J(PW) coupling [267.3 Hz (**4a**), 270.1 (**4b**) and 272.2 Hz (**4c**)].

The synthesis of a phosphine-chelated tungsten complexe is accomplished by UV-light irradiation of **3a** and bis-diphenylphosphino-methane (dppm) in benzene at room temperature. The ^{31}P-NMR spectroscopic control of the reaction reveals after 20 hours the formation of a η^1-phosphine-bonded complex (*cis*-**5**) showing the expected *cis*-arrangement of the chlorine and the phosphine ligand at the tungsten center together with the targeted chelate complex [ClMe$_2$Si(C$_5$H$_4$)](OC)(η^2-dppm)WCl (**6**) (Scheme 1).
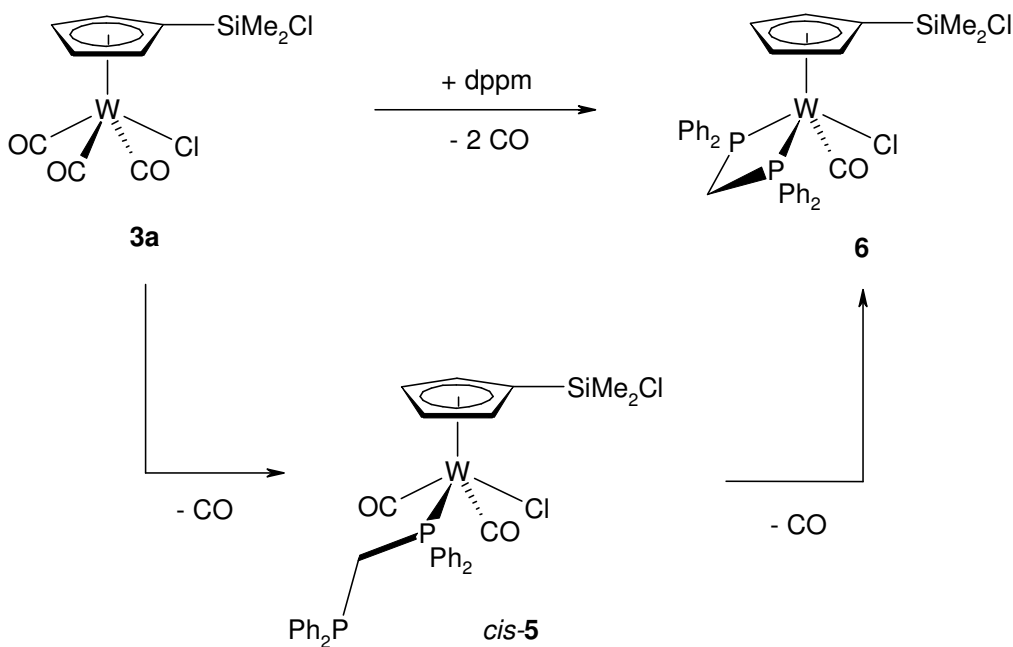
Scheme 1: Introduction of dppm in the tungsten chloride **3a**.

After irradiation of the reaction mixture for additional 24 hours, **3a** and *cis*-**5** have been completely converted into **6** which is obtained in 91 % yield as an orange solid. Analogous to **2c**, the introduced phosphine ligand evokes an increased stability of **6** towards air and moisture in comparison to **1c**. As a result, **6** can be handled for short time at air without decomposition. **6** shows nearly the same solubility towards solvents like diethylether, benzene and chloroform like **4a-c**.

Similar to the chiral *cis*-**4a-c**, the cyclopentadienyl ring protons of **6** are inequivalent and four multiplets are observed in the ^{1}H-NMR spectrum and the signals for the diastereotopic methyl groups attached to the silicon atom appears as two singulets with a difference of 0.25 ppm.

According to conditions, which are identical to that for the formation of the parent complexes $Cp(OC)_2(Me_3P)MH$ (M = Mo, W) [12], $Cp(OC)_2(Ph_3P)MX$ (M = Mo, W; X = Cl, Br, I) [14, 15], for all these reactions the silyl group attached to the cyclopentadienyl ring has no influence on the stereochemistry.

Synthesis of the Phosphine-substituted Tungsten-silanols 7a-c, 8 and 9.

The phosphine-substituted complexes **2b, 4a-c** and **6**, with the SiCl-functionalized cyclopentadienyl ligand can be transformed directly into the corresponding silanols by hydrolysis in the presence of NEt_3 as auxiliary base. The reaction is finished after half an hour and results in the formation of the tungsten-silanols **7a-c**, **8** and **9**, which are obtained in yields of 74 – 83 % (Fig. 2). In all cases the hydrolysis proceed cleanly and no self-condensation products are observed indicating high stability of this type of tungsten-silanols. **7a-c**, **8** and **9** are microcrystalline yellow (**7a**) and orange (**7b,c**, **8**, **9**) solids and show a limited solubility in nonpolar solvents which improves significantly for the tetramethyl-substituted **7c**. **7a-c**, **8** and **9** dissolve readily in benzene or chloroform and can be handled for short time at air and stored for several months under an N_2-atmosphere without decompostion.

The silanol proton resonances are detected in the range expected for tungsten-silanols [16, 17] at 2.06 ppm for **7a** and between 3.67 and 4.09 ppm for the tungsten chlorides (**7b,c, 8** and **9**). The sharp signals of **7b,c, 8** and **9** indicates limited intermolecular hydrogen bonding in solution. The values of the ^{29}Si-NMR resonances

of **7a,b, 8** and **9** (4.39 - 5.39 ppm) lie within narrow bounds while that of **7c** amounts to 7.89 ppm. Obviously the methyl-substitution at the cyclopentadienyl ring has more influence on the ^{29}Si-chemical shift than the OC/R$_3$P-exchange at the metal center.

2	**b**	**4a**	**4b**
o-	H	H	Me
R	H	Cl	Cl
R'	Me	Ph	Ph

7	**a**	**b**	**c**
o-	H	H	Me
R	H	Cl	Cl
R'	Me	Ph	Ph
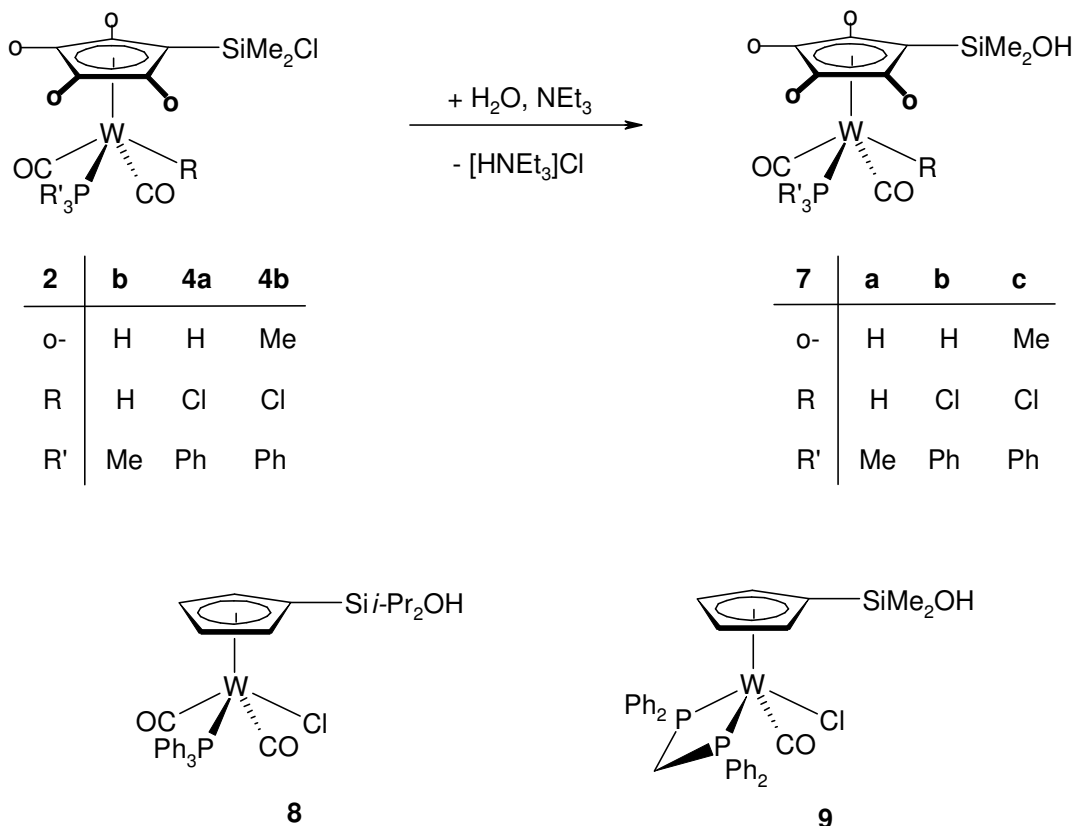
Fig. 2: Series of phosphine-substituted tungsten complexes with a silanol-functionalized η^5-cyclopentadienyl ligand.

*X-ray structure determinations of the silanols **7c** and **8***

The structures of the silanols [HOMe$_2$Si(C$_5$Me$_4$)](OC)$_2$(Ph$_3$P)WCl (**7c**) and [HO*i*Pr$_2$Si(C$_5$H$_4$)](OC)$_2$(Ph$_3$P)WCl (**8**) are confirmed by the results of X-ray diffraction analyses and depicted in figure 3 and 4 as well as in the following table.

Orange crystals of **7c** and **8**, suitable for X-ray analysis, have been obtained from slow evaporation of saturated dichloromethane- (**7c**) and benzene solutions (**8**) at room temperature.

The molecular structure of **7c** consists of four molecules per unit cell and reveals a tetragonal monopyramidal arrangement of the cyclopentadienyl-, chloro-, triphenylphosphan- and the *cis*-orientated carbonyl ligands at the tungsten atom (Fig. 3).
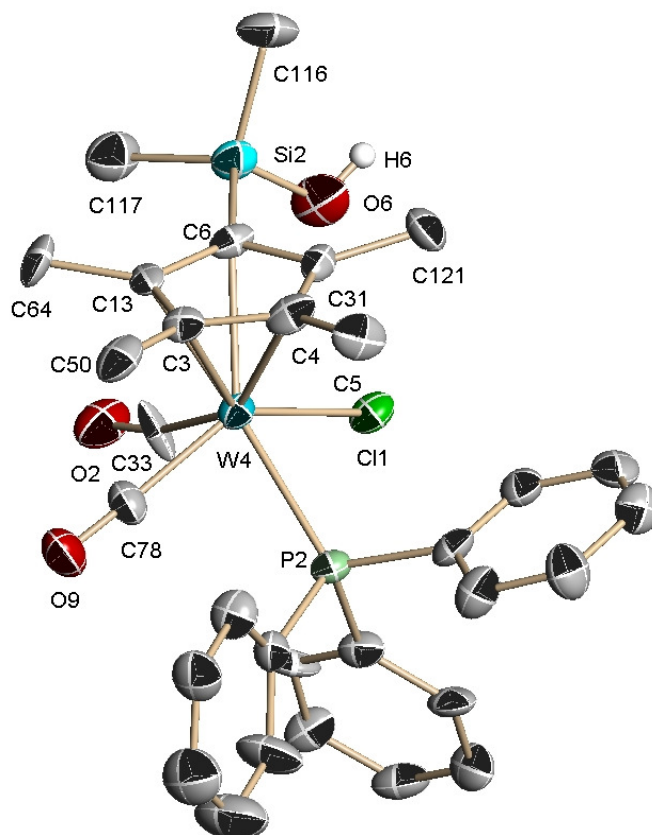
Fig. 3: Molecular structure of [HOMe$_2$Si(C$_5$Me$_4$)](OC)$_2$(Ph$_3$P)WCl (**7c**) with the atomic labeling scheme. Ellipsoids are drawn at the 50 % probability level, and the hydrogen atoms have been omitted for the sake of clarity except the silanol hydrogen atom H6.

Selected bond lengths [Å], bond and torsion angles [°]: W4-C33 1.980(16), W4-C78 1.985(18), W4-Cl1 2.515(4), W4-P2 2.527(4), Si2-O6 1.639(13), Si2-C117 1.850(2), Si2-C116 1.862(19), Si2-C6 1.887(16), C33-W4-C78 74.8(7), C33-W4-Cl1 78.8(6), C78-W4-P2 77.8(5), Cl1-W4-P2 78.66(13), O6-Si2-C117 107.9(9), O6-Si2-C116 108.5(9), C117-Si2-C116 108.5(9), O6-Si2-C6 109.7(7), C117-Si2-C6 113.6(9), C116-Si2-C6 108.4(8), O6-Si2-C6-C31 52.8(15), C117-Si2-C6-C31 173.6(13), C116-Si2-C6-C31 -65.6(15), Si2-C6-C31-C4 172.4(11).

As expected, **8** reveals the same ligand substitution pattern (Fig. 4), concerning the cyclopentadienyl-, chloro-, triphenylphosphan- and the carbonyl ligands. The angles between the ligands at the basis as well as their bond distances lie in the expected range [18-23].

Due to the silyl substition at the cyclopentadienyl ligand and the chiral metal center of **7c** and **8**, the C-C bond distances of the cyclopentadienyl ring are different. For example, in the case of **8** the longest bond is found between C24 and C25 and amounts to 1.449(8) Å, the shortest lies between C22 and C23 with 1.395(8) Å.

A crucial feature of both molecular structures is the silicon atom being located slightly above the plane defined by the cyclopentadienyl ring, as documented by the torsion angles of 172.4(11)° (Si2-C6-C31-C4) (**7c**) and 178.3(4)° (Si1-C24-C23-C22) (**8**). The values of the Si-C bond distances of 1.850(2) (Si2-C117), 1.862(19) (Si2-C116) and 1.887(16) (Si2-C6) Å lie in the literature-known range [24], as well as the silicon oxygen distance of 1.639(13) Å (Si2-O6), which is typical for metallo-silanols [4, 13, 18, 25]. These findings are also valid for **8** as illustrated by the values 1.878(6) (Si1-C24), 1.878(7) (Si1-C29) and 1.879(8) Å (Si1-C26) for the silicon-carbon bond and 1.636(6) Å for the silicon oxygen bond distance Si1-O3.

The silicon atoms of **7c** and **8** are characterized by a tetrahedral substituent environment, revealing bond angles with values close to the ideal tetraeder angle [26].

It is rooted in sterical requirements that one of the two *iso*propyl groups of **8** is located above the cyclopentadienyl ligand which is illustrated by a torsion angle of –69.3(5)° (C29-Si1-C24-C23), while the other one is lying beneath this plane [C26-Si1-C24-C25: -16.5(6)°]. As a result, the hydroxy group with its lower sterical requirements is turned towards the chloro ligand indicated by the torsion angle of 45.7(6)° (O3-Si1-C24-C23).

The silanol unit of **7c** is placed beneath the plane of the cyclopentadienyl ligand in the same manner. These arrangements of **7c** and **8** might be responsible for the fact that no intermolecular interaction between the silanol groups via hydrogen bridges are found. Furthermore, **7c** and **8** are characterized by nearly the same W-Cl- and W-P bond distances [W4-Cl1: 2.515(4) Å, W4-P2: 2.527(4) Å (**7c**); W1-Cl1: 2.518(17) Å, W1-P1: 2.507(17) Å (**8**)].
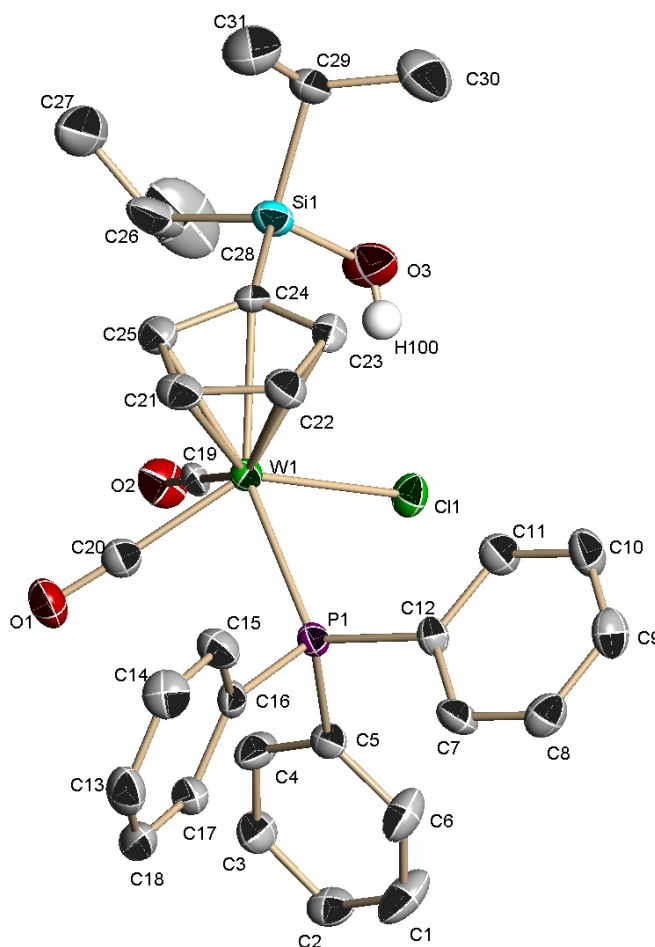
Fig. 4: Depicted molecular structure of [HO*i*Pr$_2$Si(C$_5$H$_4$)](OC)$_2$(Ph$_3$P)WCl (**8**) and its atom-labeling scheme. Thermal ellipsoids are drawn at the 50 % probability. The hydrogen atoms have been omitted except the silanol hydrogen atom H100.

Selected bond lengths [Å], bond and torsion angles [°]: W1-C19 1.963(6), W1-C20 1.975(6), W1-C25 2.273(6), W1-C21 2.303(6), W1-C24 2.314(5), W1-C23 2.381(5), W1-C22 2.384(6), W1-P1 2.507(17), W1-Cl1 2.518(17), Si1-O3 1.636(6), Si1-C24 1.878(6), Si1-C29 1.878(7), Si1-C26 1.879(8), C24-C23 1.439(8), C24-C25 1.449(8), C25-C21 1.413(9), C21-C22 1.411(9), C22-C23 1.395(8), Si1-C24-W1 122.5(3), O3-Si1-C24 107.7(3), O3-Si1-C29 106.1(3), C24-Si1-C29 109.6(3), O3-Si1-C26 111.7(4), C24-Si1-C26 110.1(3), C29-Si1-C26 111.4(3), O3-Si1-C24-C23 45.7(6), C29-Si1-C24-C23 –69.3(5), C26-Si1-C24-C25 –16.5(6), Si1-C24-C23-C22 178.3(4).

The constitution of **8** in the solid state is determined by two types of hydrogen bonds (Fig. 5): The interaction between a carbonyl oxygen (O2) and a cyclopentadienyl

hydrogen (H22) and the contact of a silanol oxygen (O3) with a phenyl hydrogen (H13) of a triphenylphosphine ligand forming formally a tetrameric unit. In both cases the distances can be classified as weak hydrogen bonds according to the values of 2.755(2) (O2···H22) and 2.685(3) Å (O3···H13).
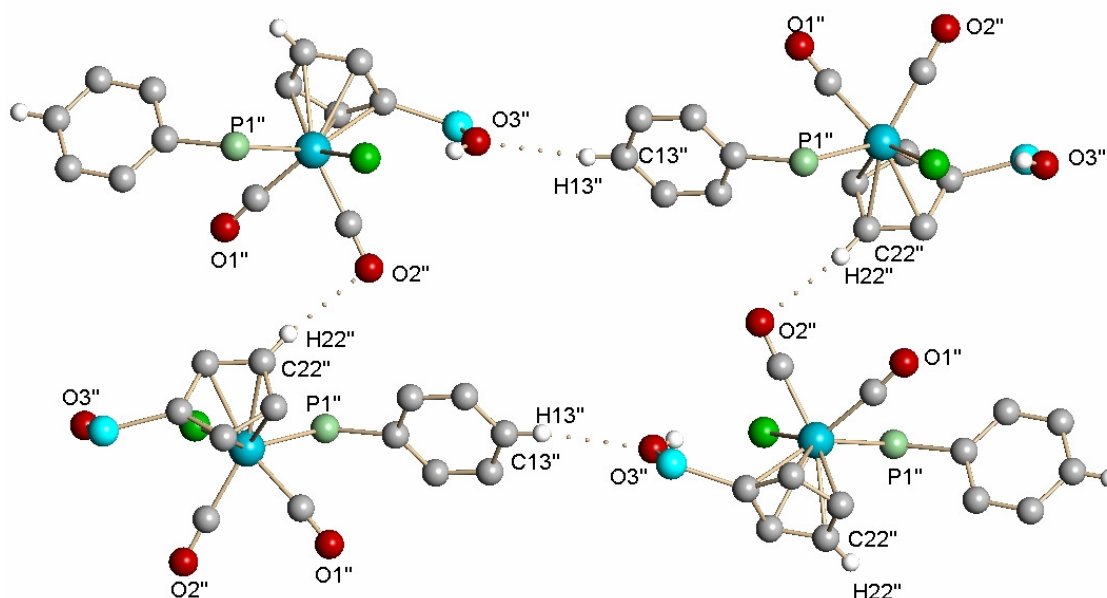
Fig. 5: Two types of intermolecular hydrogen bonds of **8** in the solid state.

*Table of crystal data for the compounds **7c** and **8***

	7c	**8**
mol formula	$C_{31}H_{34}ClO_3PSiW$	$C_{31}H_{34}ClO_3PSiW$
mol wt	732.94	732.94
wavelength (Å)	0.71073	0.71073
temp (K)	173(2)	173(2)
cryst size (mm)	0.20 x 0.2 x 0.25	0.10 x 0.15 x 0.13
cryst syst	triclinic	monoclinic
space group	P1	P2(1)/n

a (Å)	15.119(8)	7.935(3)
b (Å)	16.899(9)	14.605(6)
c (Å)	23.587(12)	25.784(11)
α (°)	90.023(9)	90
β (°)	96.941(9)	91.303(7)
γ (°)	90.009(10)	90
vol (Å^3), Z	5982(5)	2987(2)
ρ (calcd) (Mgm^{-3})	1.628	1.630
F(000)	2912	1456
μ (mm^{-1})	4.075	4.080
θ range for data collecn (deg)	0.87 – 23.32	1.60 - 25.20
no. of rflns collected	49267	35.204
no. of indep reflns	17092	5367
abs cor.	empirical	empirical
no. of data/restraints /params	17092 / 0 / 1373	5367 / 0 / 357
goodness of fit on F^2	1.280	1.199
R1^a	0.0739	0.0379
wR2^b	0.1738	0.0850
largest diff peak and hole (eÅ^{-3})	3.090 and −1.414	2.535 and −0.646

R1 = $\Sigma||F_0| - |F_c||/\Sigma|F_0|$ for reflections with $I > 2\sigma(I)$. wR2 = $[\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_0^2)/3$ and a and b are constants set by the program.

Reactivity of the Phosphine-substituted Tungsten-silanols 7a-c and 9.
The silanols **7a-c** show the typical reactivity of metallo-silanols concerning the co-condensation with organochlorosilanes. In first experiments, NEt$_3$-assisted co-condensations of **7b,c** with chlorodimethylsilane is accomplished, leading to the formation of the corresponding SiH-functionalized disiloxanes [HMe$_2$SiOMe$_2$Si(C$_5$R$_4$)](OC)$_2$(Ph$_3$P)WCl [R = H (**10a**), Me (**10b**)] (Scheme 2).

10a,**b** are isolated after reaction periods of three (**10a**) and four (**10b**) hours as orange solids in 92 (**10a**) and 72 % (**10b**) yield.

Furthermore, it is possible to co-condensate the silanol **7a** with the metal-substituted chlorosilane [ClMe$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WH (**2b**). After five days reaction time the dinuclear tungsten-disiloxane O{[Me$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WH}$_2$ (**11**) is isolated in a yield of 98 % as a pale yellow solid (Scheme 2).

7	a	b	c
o-	H	H	Me
R	H	Cl	Cl
R'	Me	Ph	Ph

+ Me$_2$Si(H)Cl, NEt$_3$ - [HNEt$_3$]Cl

+ **2b**, NEt$_3$ - [HNEt$_3$]Cl

10	a	b
o-	H	Me

11
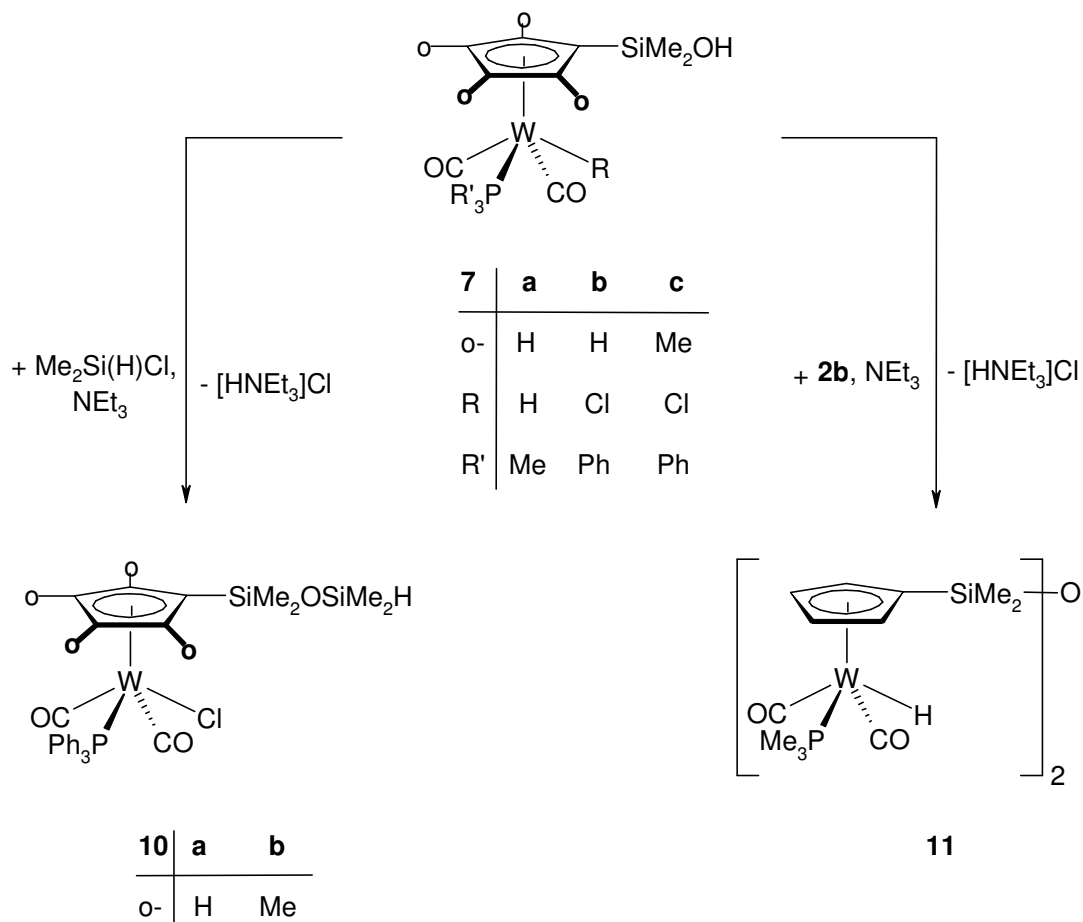
Scheme 2: Co-condensation of the silanols **7a-c** with SiCl-functionalized organo- and metallo-silanes.

10a,**b** and **11** show an increasing solubility in the sequence petrolether < diethylether << benzene ~ chloroform and they can be stored at –20 °C under a nitrogen atmosphere for several months without any decomposition.

Compared to the silanols **7a-c**, the ^{29}Si-NMR resonances of the directly cyclopentadienyl-bound silicon atoms of **10a,b** and **11** are significantly shifted about 6 ppm to higher field, which is in good accordance with the δ([29]Si) values of triorganosilanols and the corresponding disiloxanes [27]. The signals for the H-substituted silicon atoms of **10a,b** are detected at δ = –5.31 (**10a**) and –9.84 (**10b**) ppm.

X-ray structure determination of the dinuclear tungsten-disiloxane 11

Final verification of the structure of O{[Me$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WH}$_2$ (**11**) is achieved from a X-ray crystallographic study, whose result is presented in figure 6 and the following table. Suitable yellow single crystals of **11** are obtained from a saturated solution of **11** in benzene at room temperature.
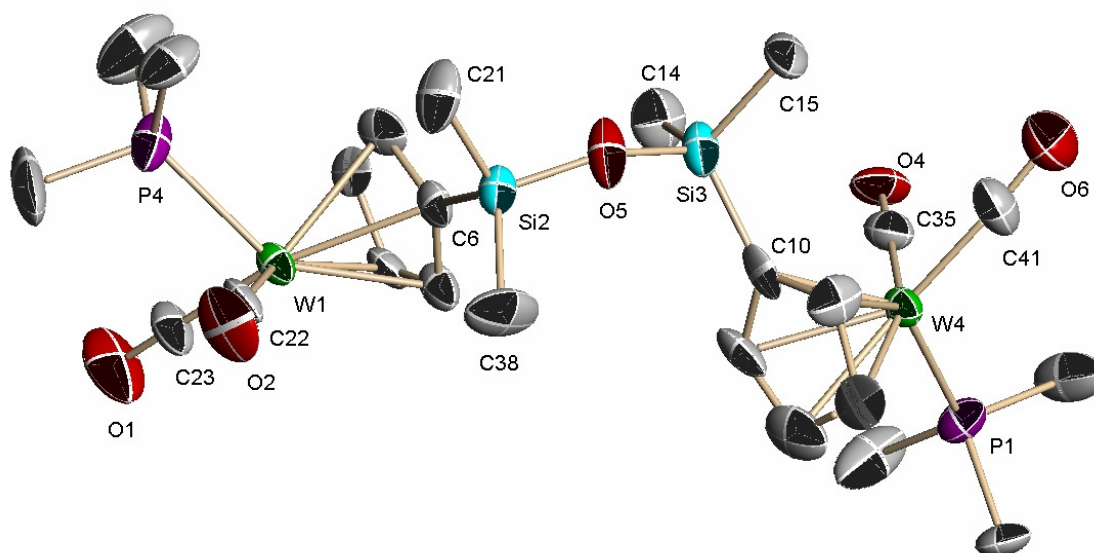
Fig. 6: Molecular structure of O{[Me$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WH}$_2$ (**11**) including the atomic labeling scheme. Ellipsoids are drawn at the 50 % probability level, and the hydrogen atoms have been omitted for clarity.

Selected bond lengths [Å], bond and torsion angles [°]: W1-C22 1.92(2), W1-C23 1.942(19), W1-P4 2.433(5), W4-C35 1.93(2), W4-C41 1.93(2), W4-P1 2.407(5), Si2-

O5 1.617(14), Si2-C21 1.83(2), Si2-C38 1.84(2), Si2-C6 1.859(18), Si3-O5 1.638(14), Si3-C10 1.86(2), Si3-C15 1.863(19), Si3-C14 1.87(2), Si2-O5-Si3 149.1(9), C22-W1-C23 99.9(8), C22-W1-P4 81.6(6), C23-W1-P4 83.5(6), C35-W4-C41 81.2(8), C35-W4-P1 79.0(6), C41-W4-P1 111.8(7), O5-Si2-C21 107.2(9), O5-Si2-C38 108.9(11), C21-Si2-C38 112.6(13), O5-Si2-C6 107.5(7), C21-Si2-C6 111.6(9), C38-Si2-C6 108.9(10), O5-Si3-C10 107.4(8), O5-Si3-C15 107.1(8), C10-Si3-C15 108.7(9), O5-Si3-C14 109.4(9), C10-Si3-C14 111.5(9), C15-Si3-C14 112.5(11), Si2-C6-C5-C44 -175.8(12), C37-C9-C10-Si3 -174.6(13), O5-Si2-C6-C7 -88.7(16), O5-Si3-C10-C9 90.5(15).

The crystal structure consists of two identical molecules of **11** per unit cell, showing no intermolecular interactions.

The hydride ligands at both tungsten atoms are not located, but are obviously positioned differently at the both tungsten atoms of one molecule namely *cis* to P1 and *trans* to P4 (Fig. 7). This assumption is supported by the angles spanned by the carbonyl and phosphine ligand and the two carbonyls which amounts to 111.8(7) (C41-W4-P1) and 99.9(8) Å (C22-W1-C23). The second value is silmilar to that one found in the *trans*-substituted tungsten complex Cp(OC)$_2$(PTA)WH (PTA = 1,3,5-triaza-7-phosphaadamantane) [102.8(5) Å] [28]. In contrast to **11**, the tungsten hydrido complex Cp(OC)$_2$(Me$_3$P)WH [29] was shown to crystallize selectively *cis* but no further informations concerning bond lenghts and -angles were mentioned. The phosphor tungsten bond distances W1-P4 and W4-P1 of 2.433(5) and 2.407(5) Å lie in the expected range [28].

The disiloxane angle Si2-O5-Si3 amounts to 149.1(9)°, and is about 9° smaller than in the open-chained metal fragment-substituted disiloxanes O{HOSi[(C$_5$H$_4$)FeCp]$_2$}$_2$ [157.1(3)°] [30] and Cp(OC)$_2$FeSiCl$_2$OSiCl$_3$ [159.2(2)°] [31]. The common oxygen O5 of the disiloxane bridge connecting the both metal fragments, is orientated almost vertical to the planes being defined by the cyclopentadienyl rings as it is illustrated by the torshion angles of -88.7(16)° (O5-Si2-C6-C7) and 90.5(15)° (O5-Si3-C10-C9).

If the line defined by the Si2-Si3 atoms is regarded as an imagined axis, the silicon-bound methyl rests and the metal fragments as well, take up a "*gauche*"-like conformation.
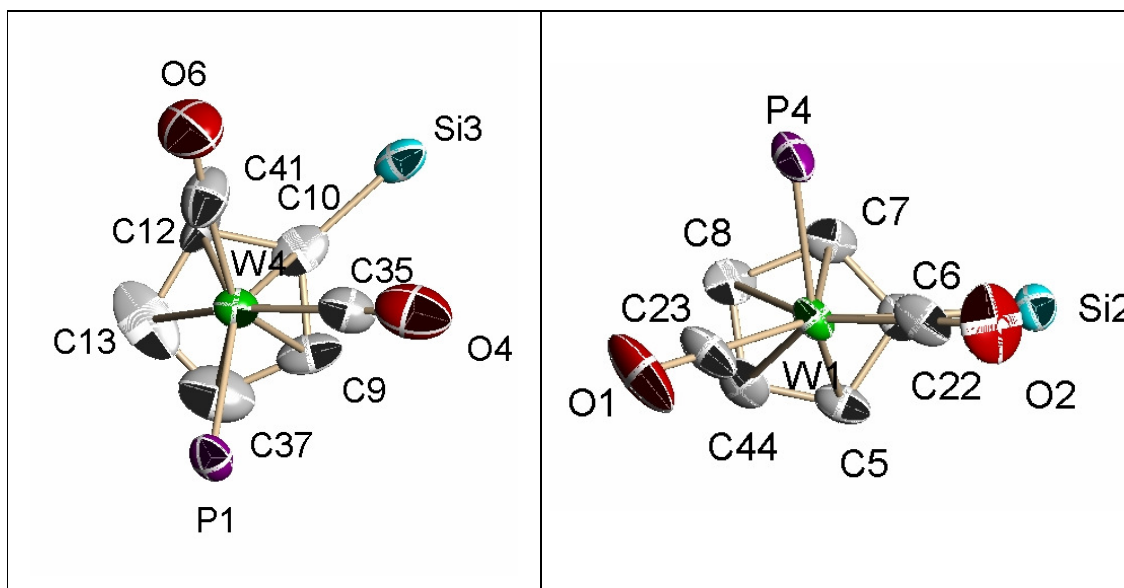
Fig. 7: View of the both differently substituted tungsten atoms of the dinuclear **11**, illustrating *cis-* and *trans*-substitution of W4 (left side) and W1 (right side) concerning the hydrido and phosphine ligands.

*Table of crystal data for the compound **11***

mol formula	$C_{26}H_{40}O_7P_2Si_2W_2$
mol wt	950.42
wavelength (Å)	0.71073
temp (K)	173(2)
cryst size (mm)	0.10 x 0.2 x 0.15
cryst syst	triclinic
space group	P1
a (Å)	6.967(2)
b (Å)	16.309(5)
c (Å)	28.648(8)
α (°)	89.357(5)
β (°)	87.815(5)

γ (°)	82.095(5)
vol (Å^3), Z	3221(16)
ρ (calcd) (Mgm^{-3})	1.840
F(000)	1712
μ (mm^{-1})	7.338
θ range for data collecn (deg)	1.26 – 25.15
no. of rflns collected	62513
no. of indep reflns	11498
abs cor.	empirical
no. of data/restraints /params	11498 / 0 / 579
goodness of fit on F^2	1.365
R1[a]	0.1052
wR2[b]	0.1768
largest diff peak and hole (eÅ^{-3})	2.825 and –3.257

R1 = $\Sigma||F_0| - |F_c||/\Sigma|F_0|$ for reflections with $I > 2\sigma(I)$. wR2 = $[\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_0^2)/3$ and a and b are constants set by the program.

In analogous manner to **7a-c**, the dppm-substituted silanol **9** is co-condensated with chlorodimethylsilane (**12a**) and chlorotrimethylstannane (**12b**), respectively in the presence of NEt$_3$ (Scheme 3). This procedure affords the Si-H-functionalized disiloxane [HMe$_2$SiOMe$_2$Si(C$_5$H$_4$)](OC)(dppm)WCl (**13a**) and the stanna-heterosiloxane [Me$_3$SnOMe$_2$Si(C$_5$H$_4$)](OC)(dppm)WCl (**13b**). The reactions are finished after one (**13a**) and three (**13b**) days. Both co-condensation products are obtained as orange microcrystalline solids in yields of 74 (**13a**) and 62 % (**13b**).
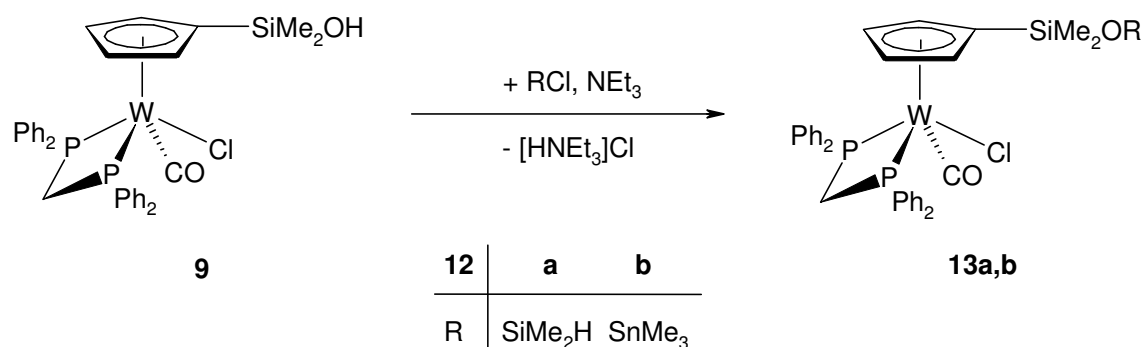
Scheme 3: Co-condensation reactions of silanol **9** leading to tungsten-disiloxane **13a** and the stanna hetero disiloxane **13b**.

The ^{29}Si-NMR resonances of **13a,b** are shifted to higher field [δ = 1.64 (**13a**) and –0.20 ppm (**13b**)] in comparison to the silanol **9**.

CONCLUSION

This paper deals with the synthesis and reactivity of novel phosphine-substituted halfsandwich tungsten complexes with a silanol-functionalized cyclopentadienyl ligand, as well as their structural analyses.

The preparative route to these compounds includes first the introduction of the triorganophosphine ligand, followed by the transformation of the Si-Cl group into a silanol function. The electron-releasing effect of the metal fragment on the silicon atom is reduced compared to tungsten-silanols with directly metal-bonded Si-OH moiety but despite, the silanols are stable enough with respect to self-condensation which allow isolation and co-condensation. Additionally, the introduced phosphine ligands reduce the moisture sensibility of the SiCl-functionalized precursor complexes and allow even air exposition for a short time in the range of minutes in contrast to the starting material with tricarbonyl substitution pattern which decompose within few seconds.

Further investigation is currently directed towards halfsandwich tungsten derivatives, containing both a cyclopentadienyl- and metal-bound silanol group. This type of complexes should give access to branched transition metal fragment substituted oligosiloxanes which can be regarded as model compounds for catalytic systems immobilized on a silica surface.

EXPERIMENTAL SECTION

General Remarks: All operations were performed under an atmosphere of purified and dried nitrogen using Schlenk-type techniques. Solvents were dried according to conventional procedures, distilled and saturated with N_2 prior to use. - NMR: Jeol Lambda 300 (300.4 MHz, 75.5 MHz, and 59.6 MHz for ^{1}H, ^{13}C, and ^{29}Si, respectively). [D$_6$]-benzene as a solvent: δ_H = 7.15, δ_C = 128.0; for ^{29}Si rel. to TMS external. - IR: Perkin-Elmer 283 grating spectrometer. - Melting points: Differential thermo analysis (Du Pont 9000 Thermal Analysis System). - Elemental analyses were performed in the laboratories of the *Institut für Anorganische Chemie der Universität Würzburg*. - Starting materials were prepared according to literature procedures: PMe$_3$ [32], [XMe$_2$Si(C$_5$H$_4$)](OC)$_3$WH [X = H (**1a**), Cl (**1b**)] [13], [ClMe$_2$Si(C$_5$R$_4$)](OC)$_3$WCl [R = H (**3a**), Me (**3b**)] [13] and [Cl*i*Pr$_2$Si(C$_5$H$_4$)](OC)$_3$WCl (**3c**) [33]. The reagents NEt$_3$, PPh$_3$, dppm, Me$_2$Si(H)Cl (**12a**), Me$_3$SnCl (**12b**), were purchased from commercial sources and the liquids destilled prior use.

*1) [HMe$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WH (**2a**)*

Dicarbonyl[η^5-(dimethylsilyl)-cyclopentadienyl]hydrido(trimethylphosphino)tungsten(II)

To a solution of 1.40 g (3.57 mmol) of [HMe$_2$Si(C$_5$H$_4$)](OC)$_3$WH (**1a**) in 10 ml PE, 1.52 g (20.0 mmol) of PMe$_3$ were added. The reaction mixture was stirred at room temperature over the period of 12 hours under light exclusion. The volatiles were removed in vacuo leading to a yellow oil. The crude product was washed with 4 ml PE at 0 °C resulting in a solid. Yield: 1.57 g (3.57 mmol, quant.). Pale yellow solid. M.p.: 40 °C. - *trans*-**2a**: - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.96 (bs, 4 H, H$_4$C$_5$), 4.62 (bs, 1 H, HSi), 1.20 [d, ^2J(HCP) = 9.3 Hz, 9 H, H$_3$CP], 0.26 [d, ^3J(HCSiH) = 3.6 Hz, 6 H, H$_3$CSi], -7.99 [d, ^1J(HW) = 49.3 Hz, ^2J(HWP) = 68.8 Hz, 1 H, HW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 224.06 [d, ^2J(CP) = 15.5 Hz, CO], 92.28 (s, C$_5$H$_4$), 91.13 (s, C$_5$H$_4$), 89.16 (s, C$_5$H$_4$), 25.47 [d, ^1J(CP) = 35.5 Hz, CH$_3$P], -2.41 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -20.74 (s) ppm. - **^{31}P{^{1}H}-NMR** (121.5 MHz,

C_6D_6): δ = -17.24 [s, $^1J(PW)$ = 255.9 Hz, PCH$_3$] ppm. - **IR** (Et$_2$O): $\tilde{\nu}$ (SiH) = 2115.1 (w) cm^{-1}; $\tilde{\nu}$ (CO) = 1941.7 (vs), 1857.2 (vs) cm^{-1}. - *cis*-**2a**: - ^{1}**H-NMR** (300.4 MHz, C_6D_6): δ = 4.78 (bs, 4 H, H$_4$C$_5$), 4.62 (bs, 1 H, HSi), 1.20 [d, $^2J(PH)$ = 9.3 Hz, 9 H, H$_3$CP], 0.26 [d, $^3J(HCSiH)$ = 3.6 Hz, 6 H, H$_3$CSi], -7.18 [d, $^1J(HW)$ = 49.3 Hz, $^2J(HWP)$ = 23.7 Hz, 1 H, HW] ppm. - ^{13}**C{^{1}H}-NMR** (75.5 MHz, C_6D_6): δ = 92.45 (s, C$_5$H$_4$), 91.43 (s, C$_5$H$_4$), 90.67 (s, C$_5$H$_4$), 22.40 [d, $^1J(P-C)$ = 33.4 Hz, CH$_3$P], -2.41 (s, CH$_3$Si) ppm. - ^{29}**Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = -20.51 (s) ppm. - ^{31}**P{^{1}H}-NMR** (121.5 MHz, C_6D_6): δ = -19.56 [s, $^1J(PW)$ = 281.6 Hz, PCH$_3$] ppm. - **IR** (PE): $\tilde{\nu}$ (SiH) = 2115.1 (w) cm^{-1}; $\tilde{\nu}$ (CO) = 1941.7 (vs), 1857.2 (vs) cm^{-1}. - Anal. calc. for $C_{12}H_{21}O_2SiPW$ (440.19): C 32.74, H 4.81; found: C 32.67; H 4.78.

2) [ClMe$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WH (*2b*)

Dicarbonyl[η^5-(chlorodimethylsilyl)-cyclopentadienyl]hydrido(trimethylphosphino)-tungsten(II)

Analogous to 1) from 880 mg (2.06 mmol) of [ClMe$_2$Si(C$_5$H$_4$)](OC)$_3$WH (**1b**) and 1.0 ml (10.0 mmol) of PMe$_3$ in 20 ml PE after 24 hours at room temperature. Yield: 0.96 g (2.02 mmol, 98 %). Pale yellow solid. M.p.: 44 °C. - ^{1}**H-NMR** (300.4 MHz, C_6D_6): δ = 5.00 – 4.60 (m, 4 H, H$_4$C$_5$), 1.08 [d, $^2J(HCP)$ = 9.3 Hz, 9 H, H$_3$CP], 0.62, 0.61 (s, 6 H, H$_3$CSi), -7.08 (*cis*) [d, $^1J(HW)$ = 49.2 Hz, $^2J(HWP)$ = 23.7 Hz, 1 H, HW], -7.96 (*trans*) [d, $^1J(HW)$ = 49.4 Hz, $^2J(HWP)$ = 68.6 Hz, 1 H, HW] ppm. - ^{13}**C{^{1}H}-NMR** (75.5 MHz, C_6D_6): δ = 224.06 [d, $^2J(CP)$ = 15.5 Hz, CO], 92.45, 92.28, 91.43, 91.13 (s, C$_5$H$_4$), 90.67, 89.16 (s, *ipso*-C$_5$H$_4$), 25.67 [d, $^1J(CP)$ = 35.4 Hz, CH$_3$P], 22.39 [d, $^1J(CP)$ = 33.0 Hz, CH$_3$P], 3.38, 3.09, 1.25 (s, CH$_3$Si) ppm. - ^{29}**Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = 17.20, 17.19 (s) ppm. - ^{31}**P{^{1}H}-NMR** (121.5 MHz, C_6D_6): δ = -17.46 [s, $^1J(PW)$ = 255.8 Hz, *trans*-PCH$_3$], -19.67 [s, $^1J(PW)$ = 281.3 Hz, *cis*-PCH$_3$] ppm. - **IR** (Et$_2$O): $\tilde{\nu}$ (CO) = 1942.4 (vs), 1858.7 (vs) cm^{-1}. - Anal. calc. for $C_{12}H_{20}ClO_2PSiW$ (474.65): C 30.37, H 4.25; found: C 30.77; H 4.09.

*3) [ClMe₂Si(C₅H₄)](OC)₂(Ph₃P)WCl (**4a**)*

Dicarbonylchloro[η⁵-(chlorodimethylsilyl)-cyclopentadienyl](triphenylphosphino)-tungsten(II)

A solution of 400 mg (0.87 mmol) of [ClMe$_2$Si(C$_5$H$_4$)](OC)$_3$WCl (**3a**) and 227 mg (0.87 mmol) of PPh$_3$ in 7 ml benzene was irradiated over a period of 3.5 hours. After reaction the solvent was removed in vacuo and the crude orange residue was washed three times with each 4 ml PE at 0 °C. Yield: 580 mg (0.83 mmol, 95 %). Orange solid. M.p.: 67 °C. - **¹H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.56 - 7.48, 7.03 - 6.97 (m, 15 H, H$_5$C$_6$P), 5.66 - 5.68 (m, 1 H, H$_4$C$_5$), 5.59 - 5.57 (m, 1 H, H$_4$C$_5$), 4.64 - 4.62 (m, 1 H, H$_4$C$_5$), 4.54 - 4.53 (m, 1 H, H$_4$C$_5$), 0.69, 0.58 (s, 6 H, H$_3$CSi) ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 247.95 [d, ^2J(CWP) = 21.4 Hz, *cis*-CO], 236.80 [d, ^2J(CWP) = 6.9 Hz, *trans*-CO], 134.84 [d, ^1J(CP) = 47.2 Hz, *ipso*-C$_6$H$_5$], 134.38 [d, ^3J(CCCP) = 10.0 Hz, *meta*-C$_6$H$_5$], 130.55 [d, ^4J(CCCCP) = 2.4 Hz, *para*-C$_6$H$_5$], 128.59 [d, ^2J(CCP) = 10.0 Hz, *ortho*-C$_6$H$_5$], 117.33 (s, C$_5$H$_4$Si), 107.45 (s, C$_5$H$_4$Si), 102.49 (s, *ipso*-C$_5$H$_4$Si), 91.03 (s, C$_5$H$_4$Si), 89.60 (s, C$_5$H$_4$Si), 1.12, 0.54 (s, CH$_3$Si) ppm. - **²⁹Si{¹H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 26.00 (s) ppm. - **³¹P{¹H}-NMR**: (121.5 MHz, C$_6$D$_6$): δ = 22.49 [s, ^1J(PW) = 267.3 Hz, PW] ppm. - **IR** (THF): $\tilde{\nu}$ (CO) = 1965 (vs) 1888 (m) cm⁻¹. - Anal. calc. for C$_{27}$H$_{25}$Cl$_2$PO$_2$SiW (695.30): C 46.64, H 3.62; found: C 47.24, H 3.97.

*4) [ClMe₂Si(C₅Me₄)](OC)₂(Ph₃P)WCl (**4b**)*

Dicarbonylchloro[η⁵-(chlorodimethylsilyl)-tetramethylcyclopentadienyl]-(triphenylphosphino)tungsten(II)

Analogous to 3) from 140 mg (0.31 mmol) of [ClMe$_2$Si(C$_5$Me$_4$)](OC)$_3$WCl (**3b**) and 81 mg (0.31 mmol) of PPh$_3$ in 5 ml benzene after four hours. The crude product was washed five times each with 2 ml PE at –60 °C. Yield: 212 mg (0.28 mmol, 91 %). Orange solid. M.p.: 81 °C. - **¹H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.53 - 7.47, 7.03 - 6.96 (m, 15 H, H$_5$C$_6$P), 1.98, 1.95 1.29 and 1.21 (s, 3 H, H$_3$CC$_5$), 0.84, 0.83 (s, 6 H, H$_3$CSi) ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 250.75 [d, ^2J(CWP) = 18.5 Hz,

cis-CO], 237.99 [d, ^2J(CWP) = 7.3 Hz, *trans*-CO], 135.85 [d, ^1J(CP) = 47.4 Hz, *ipso*-C$_6$H$_5$], 132.28 [d, ^3J(CCCP) = 10.1 Hz, *meta*-C$_6$H$_5$], 130.95 [d, ^4J(CCCCP) = 2.4 Hz, *para*-C$_6$H$_5$], 128.69 [d, ^2J(CCP) = 9.0 Hz, *ortho*-C$_6$H$_5$], 124.96, 116.15 (s, H$_3$C$\underline{C}_5$), 102.80 [d, ^2J(CWP) = 1.2 Hz, H$_3$C$\underline{C}_5$], 102.26 (s, H$_3$C$\underline{C}_5$), 86.60 [d, ^2J(CWP) = 5.9 Hz, *ipso*-H$_3$C$\underline{C}_5$], 13.99, 13.56, 11.00 and 10.65 (s, H$_3$$\underline{C}C_5$), 3.25, 3.23 (s, CH$_3$Si) ppm. - ^{29}**Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 23.00 (s) ppm. - ^{31}**P{^{1}H}-NMR**: (121.5 MHz, C$_6$D$_6$): δ = 22.43 [s, ^1J(PW) = 272.1 Hz, PW] ppm. - **IR** (Et$_2$O): $\tilde{\nu}$ (CO) = 1947 (vs), 1870 (m) cm^{-1}. - Anal. calc. for C$_{31}$H$_{33}$Cl$_2$O$_2$PSiW (695.30): C 49.55, H 4.43; found: C 48.39, H 4.54.

5) [Cl*i*Pr$_2$Si(C$_5$H$_4$)](OC)$_2$(Ph$_3$P)WCl (**4c**)

Dicarbonylchloro[η^5-(chlorodi*iso*propylsilyl)-cyclopentadienyl](triphenylphosphino)-tungsten(II)

Analogous to 3) from 100 mg (0.19 mmol) of [Cl*i*Pr$_2$Si(C$_5$H$_4$)](OC)$_3$WCl (**3c**) and 50 mg (0.19 mmol) of PPh$_3$ in 5 ml benzene after four hours. Yield: 128 mg (0.17 mmol, 94 %). Brown solid. M.p: 76 °C. - ^{1}**H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.62 - 7.56, 7.03 - 6.99 (m, 15 H, H$_5$C$_6$P), 5.82 - 5.81 (m, 1 H, H$_4$C$_5$), 5.71 - 5.70 (m, 1 H, H$_4$C$_5$), 4.79 - 4.78 (m, 1 H, H$_4$C$_5$), 4.74 - 4.73 (m, 1 H, H$_4$C$_5$), 1.58 [sept, ^3J(HCCH) = 7.2 Hz, 1 H, HC(CH$_3$)$_2$Si], 1.40 [sept, ^3J(HCCH) = 6.8 Hz, 1 H, HC(CH$_3$)$_2$Si], 1.17, 1.15 [d, ^3J(HCCH) = 7.2 Hz, 6 H, H$_3$CCSi], 1.02, 1.00 [d, ^3J(HCCH) = 6.8 Hz, 6 H, H$_3$CCSi] ppm. - ^{13}**C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 247.95 [d, ^2J(CWP) = 21.4 Hz, *cis*-CO], 236.80 [d, ^2J(CWP) = 6.9 Hz, *trans*-CO], 134.84 [d, ^1J(CP) = 47.2 Hz, *ipso*-C$_6$H$_5$], 134.38 [d, ^3J(CCCP) = 10.0 Hz, *meta*-C$_6$H$_5$], 130.55 [d, ^4J(CCCCP) = 2.4 Hz, *para*-C$_6$H$_5$], 128.59 [d, ^2J(CCP) = 10.0 Hz, *ortho*-C$_6$H$_5$], 117.33 (s, C$_5$H$_4$Si), 107.45 (s, C$_5$H$_4$Si), 102.49 (s, *ipso*-C$_5$H$_4$Si), 91.03 (s, C$_5$H$_4$Si), 89.60 (s, C$_5$H$_4$Si), 17.97, 17.82 (s, $\underline{C}$H(CH$_3$)$_2$Si), 17.75, 17.65 (s, ($\underline{C}$H$_3$)$_2$CHSi) ppm. - ^{29}**Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 25.62 (s) ppm. - ^{31}**P{^{1}H}-NMR**: (121.5 MHz, C$_6$D$_6$): δ = 22.80 [s, ^1J(PW) = 272.2 Hz, PW] ppm. - **IR** (THF): $\tilde{\nu}$ (CO) = 1963 (vs) 1869 (m) cm^{-1}. Anal. Calc. for C$_{31}$H$_{33}$Cl$_2$PO$_2$SiW (751.42): C 49.55, H 4.43; found: C 49.71, H 4.50.

*6) [ClMe$_2$Si(C$_5$H$_4$)](OC)(η^2-dppm)WCl (**6**)*

Carbonylchloro[η^5-(chlorodimethylsilyl)-cyclopentadienyl](η^2-bis-diphenylphosphino-methane)tungsten(II)

Analogous to 3) from 650 mg (1.52 mmol) of **3a** and 584 mg (1.52 mmol) of dppm in 15 ml benzene over a period of 24 hours. The crude product was washed three times with each 4 ml PE. Yield: 1.09 g (1.38 mmol, 91 %). Orange solid. M.p.: 71 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.80 - 6.70 (m, 20 H, H$_5$C$_6$P), 5.48 (s, 1 H, H$_4$C$_5$), 5.39 (s, 1 H, H$_4$C$_5$), 4.96 – 4.87 (m, 2 H, H$_4$C$_5$), 4.18 [dt, ^{2}J(HCH) = 15.2 Hz, ^{2}J(PCH) = 10.0 Hz, 1 H, H$_2$C], 3.74 [dt, ^{2}J(HCH) = 15.2 Hz, ^{2}J(PCH) = 10.7 Hz, 1 H, H$_2$C], 1.12, 0.89 (s, 6 H, H$_3$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 229.10 [d, ^{2}J(CWP) = 14.2 Hz, CO], 138.00 – 128.21 (phenyl-C), 117.94, 114.83, 91.88, 90.95 (s, C$_5$H$_4$), 90.30 [d, ^{2}J(CWP) = 1.8 Hz, C$_5$H$_4$], 44.7 [t, ^{1}J(CP) = 27.5 Hz, CH$_2$], 21.30, 12.87 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 20.8 (s) ppm. - **^{31}P{^{1}H}-NMR**: (121.5 MHz, C$_6$D$_6$): δ = -3.27 [d, ^{1}J(WP) = 183.5 Hz, ^{2}J(PCP) = 32.8 Hz], -16.78 [d, ^{1}J(WP) = 261.2 Hz, ^{2}J(PCP) = 32.8 Hz] ppm. - **IR** (THF): $\tilde{\nu}$ (CO) = 1761 (vs) cm^{-1}. - Anal. calc. for C$_{33}$H$_{32}$Cl$_2$OP$_2$SiW (789.41): C 50.21, H 4.09; found: C 49.93, H 4.08.

*[ClMe$_2$Si(C$_5$H$_4$)](OC)$_2$(η^1-dppm)WCl (cis-**5**)*

cis-Dicarbonylchloro[η^5-(chlorodimethylsilyl)-cyclopentadienyl](η^2-bis-diphenyl-phosphino-methane)tungsten(II)

^{31}P{^{1}H}-NMR: (121.5 MHz, CDCl$_3$): δ = 11.40 [d, ^{1}J(PW) = 266.1 Hz, ^{2}J(PCP) = 74.1 Hz, WPPh$_2$], -26.48 [d, ^{2}J(PCP) = 74.1 Hz, PPh$_2$] ppm.

*7) [HOMe₂Si(C₅H₄)](OC)₂(Me₃P)WH (**7a**)*

Dicarbonyl[η⁵-(hydroxydimethylsilyl)-cyclopentadienyl]hydrido(trimethylphosphino)-tungsten(II)

To a solution of 1.06 g (2.23 mmol) of **2b** and 82 mg (0.08 ml, 4.54 mmol) of NEt₃ in 40 ml Et₂O, 0.2 ml water were added. The reaction mixture was stirred for one hour at room temperature while a white precipitate of [HNEt₃]Cl was observed. Then, the supension was dried over Na₂SO₄ and the insoluble material was filtered off by use of a celite pad. The filtrate was evaporated to dryness in vacuo and the crude residue washed twice, with each 4 ml PE. Yield: 814 mg (1.78 mmol, 80 %). Pale yellow solid. M.p.: 47 °C. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 4.99 – 4.70 (m, 4 H, H₄C₅), 2.06 (s, 1 H, HOSi), 1.12 [d, ²J(HCP) = 9.0 Hz, 9 H, H₃CP], 0.35 (bs, 6 H, H₃CSi), -7.18 (*cis*) [d, ¹J(HW) = 48.8 Hz, ²J(HCP) = 25.8 Hz, HW], -8.00 (*trans*) [d, ¹J(HW) = 49.4 Hz, ²J(HCP) = 69.7 Hz, HW] ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C₆D₆): δ = 221.16 [d, ²J(CP) = 15.5 Hz, CO], 91.04, 90.28, 89.67, 88.65, 88.60, 88.54 (s, C₅H₄), 88.11, 88.00 (s, *ipso*-C₅H₄), 24.17 [d, ¹J(CP) = 35.2 Hz, CH₃P], 21.29 [d, ¹J(P-C) = 33.5 Hz, CH₃P], -0.49, -0.52, -0.62 (s, CH₃Si) ppm. - **²⁹Si{¹H}-NMR** (59.6 MHz, C₆D₆): δ = 4.93 (s) ppm. - **³¹P{¹H}-NMR** (121.5 MHz, C₆D₆): δ = -18.34 [s, ¹J(PW) = 255.7 Hz, *trans*-PCH₃], -20.55 [s, ¹J(PW) = 281.6 Hz, *cis*-PCH₃] ppm. - **IR** (Et₂O): ṽ (CO) = 1935.4 (vs), 1863.9 (vs) cm⁻¹. - Anal. calc. for C₁₂H₂₁O₃PSiW (456.21): C 31.59, H 4.64; found: C 31.24, H 4.39.

*8) [HOMe₂Si(C₅H₄)](OC)₂(Ph₃P)WCl (**7b**)*

Dicarbonylchloro[η⁵-(hydroxydimethylsilyl)-cyclopentadienyl](triphenylphosphino)-tungsten(II)

Analogous to 7) from 370 mg (0.53 mmol) of **4a** and 41 mg (0.04 ml, 2.27 mmol) of NEt₃ and 0.1 ml water in 20 ml Et₂O after a period of 30 minutes. The crude product was washed three times with each 3 ml PE at 0 °C. Yield: 280 mg (0.41 mmol, 77 %). Orange solid. M.p.: 61 °C. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 7.55 - 7.48, 7.02 - 7.00 (m, 15 H, H₅C₆P), 5.82 - 5.81 (m, 1 H, H₄C₅), 5.46 - 5.44 (m, 1 H, H₄C₅), 4.73 - 4.72

(m, 1 H, H_4C_5), 4.32 - 4.30 (m, 1 H, H_4C_5), 3.70 (s, 1 H, HOSi), 0.44, 0.39 (s, 6 H, H_3CSi) ppm. - **$^{13}C\{^1H\}$-NMR** (75.5 MHz, C_6D_6): δ = 247.80 [d, $^2J(CWP)$ = 20.7 Hz, *cis*-CO], 237.14 [d, $^2J(CWP)$ = 7.2 Hz, *trans*-CO], 134.54 [d, $^1J(CP)$ = 46.6 Hz, *ipso*-C_6H_5], 134.29 [d, $^1J(CP)$ = 10.0 Hz, *meta*-C_6H_5], 130.53 [d, $^3J(CCCP)$ = 2.4 Hz, *para*-C_6H_5], 128.56 [d, $^2J(CCP)$ = 9.9 Hz, *otho*-C_6H_5], 116.01 (s, C_5H_4), 103.84 (s, C_5H_4), 95.32 [d, $^2J(CWP)$ = 3.8 Hz, C_5H_4], 87.35 [d, $^2J(CWP)$ = 1.0 Hz, *ipso*-C_5H_4], 86.483 [s, $^1J(CW)$ = 4.8 Hz, C_5H_4], 2.45, 2.44 (s, CH_3Si) ppm. - **$^{29}Si\{^1H\}$-NMR** (59.6 MHz, C_6D_6): δ = 5.22 (s) ppm. - **$^{31}P\{^1H\}$-NMR**: (121.5 MHz, C_6D_6): δ = 24.13 [s, $^1J(PW)$ = 268.5 Hz, PW] ppm. - **IR** (Et_2O): $\tilde{\nu}$ (CO) = 1962 (vs), 1877 (m) cm^{-1}. - Anal. calc. for $C_{27}H_{26}ClO_3PSiW$ (676.86): C 47.91, H 3.87; found: C 47.61, H 4.07.

*9) [HOMe$_2$Si(C$_5$Me$_4$)](OC)$_2$(Ph$_3$P)WCl (**7c**)*

Dicarbonylchloro[η^5-(hydroxydimethylsilyl)-tetramethylcyclopentadienyl]-(triphenylphosphino)tungsten(II)

Analogous to 7) from 1.50 g (2.00 mmol) of **4b** and 410 mg (0.40 ml, 22.7 mmol) of NEt_3 and 0.3 ml water in 10 ml Et_2O and 5 ml benzene after a period of 30 minutes. The crude product was washed three times each with 5 ml PE at 0 °C. Yield: 1.08 g (1.48 mmol, 74 %). Orange solid. M.p.: 50 °C. - **^{1}H-NMR** (300.4 MHz, C_6D_6): δ = 7.53 - 7.46, 7.04 - 6.88 (m, 15 H, H_5C_6P), 4.09 (s, HOSi), 2.00 (s, 3 H, H_3CC_5), 1.94 (s, 3 H, H_3CC_5), 1.40 (s, 3 H, H_3CC_5), 1.20 (s, 3 H, H_3CC_5), 0.65 (s, 3 H, H_3CSi), 0.46 (s, 3 H, H_3CSi) ppm. - **$^{13}C\{^1H\}$-NMR** (75.5 MHz, C_6D_6): δ = 250.30 [d, $^2J(CWP)$ = 18.6 Hz, *cis*-CO], 237.80 [d, $^2J(CWP)$ = 7.2 Hz, *trans*-CO], 134.40 [d, $^1J(CP)$ = 40.0 Hz, *ipso*-C_6H_5], 132.40 [d, $^3J(CCCP)$ = 9.7 Hz, *meta*-C_6H_5], 130.35 [d, $^4J(CCCCP)$ = 2.0 Hz, *para*-C_6H_5], 128.3 [d, $^2J(CCP)$ = 9.0 Hz, *ortho*-C_6H_5], 124.96, 116.15 (s, $H_3C\underline{C}_5$), 102.80 [d, $^2J(CWP)$ = 0.7 Hz, $H_3C\underline{C}_5$], 102.20 (s, $H_3C\underline{C}_5$), 86.50 [d, $^2J(CWP)$ = 5.2 Hz, *ipso*-$H_3C\underline{C}_5$], 13.84, 13.12, 10.78 and 10.55 (s, $H_3C\underline{C}_5$), 3.25, 3.23 (s, CH_3Si) ppm. - **$^{29}Si\{^1H\}$-NMR** (59.6 MHz, C_6D_6): δ = 7.89 (s) ppm. - **$^{31}P\{^1H\}$-NMR**: (121.5 MHz, C_6D_6): δ = 23.88 [s, $^1J(PW)$ = 270.9 Hz, PW] ppm. - **IR** (Et_2O): $\tilde{\nu}$ (CO) = 1948 (vs) 1870 (m) cm^{-1}. - Anal. calc. for $C_{31}H_{33}Cl_2O_2PSiW$ (695.30): C 49.55, H 4.43; found: C 48.39, H 4.54.

*10) [HOiPr₂Si(C₅H₄)](OC)₂(Ph₃P)WCl (**8**)*

Dicarbonylchloro[η^5-(hydroxydi*iso*propylsilyl)-cyclopentadienyl](triphenylphosphino)-
tungsten(II)

Analogous to 7) from 150 mg (0.22 mmol) of **4c**, 0.2 ml of NEt₃ and 0.2 ml of water in 10 ml Et₂O after a period of 30 minutes. The resulting crude residue was washed three times with each 5 ml PE at room temperature. Yield: 140 mg (0.19 mmol, 87 %). Orange solid. M.p: 145 ℃. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 7.55 - 7.48, 7.01 - 6.98 (m, 15 H, H₅C₆P), 5.99 - 5.97 (m, 1 H, H₄C₅), 5.52 - 5.48 (m, 1 H, H₄C₅), 4.98 - 4.96 (m, 1 H, H₄C₅), 4.40 - 4.37 (m, 1 H, H₄C₅), 3.71 (s, 1 H, HOSi), 1.43, 1.17 [h, ^3J(HCCH₃) = 7.3 Hz, 2 H, HCSi], 1.30, 1.28, 1.21, 1.20, 1.15, 1.12 [d, ^3J(H₃CCH) = 7.3 Hz, 12 H, H₃CCSi) ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C₆D₆): δ = 247.90 [d, ^2J(CWP) = 20.7 Hz, *cis*-CO], 236.80 [d, ^2J(CWP) = 6.9 Hz, *trans*-CO], 134.44 [d, ^1J(CP) = 47.2 Hz, *ipso*-C₆H₅], 134.29 [d, ^3J(CCCP) = 10.0 Hz, *meta*-C₆H₅], 130.54 [d, ^4J(CCCCP) = 2.4 Hz, *para*-C₆H₅], 128.57 [d, ^2J(CCP) = 10.1 Hz, *ortho*-C₆H₅], 117.31 (s, C₅H₄Si), 102.58 (s, C₅H₄Si), 93.48 [d, ^2J(CWP) = 3.9 Hz, *ipso*-C₅H₄Si], 88.31 [d, ^2J(CWP) = 1.1 Hz, C₅H₄Si], 86.25 [s, ^1J(CW) = 4.5 Hz, C₅H₄Si], 18.23, 17.99 (s, CH(CH₃)₂Si), 17.88, 17.83 (s, (CH₃)₂CHSi) ppm. - **²⁹Si{¹H}-NMR** (59.6 MHz, C₆D₆): δ = 4.39 [d, ^3J(SiCWP) = 0.9 Hz] ppm. - **³¹P{¹H}-NMR**: (121.5 MHz, C₆D₆): δ = 24.00 [s, ^1J(PW) = 268.5 Hz, PW, ^3J(PSi) = 9.7 Hz, PSi] ppm. - **IR** (THF): $\tilde{\nu}$ (CO) = 1964 (vs), 1889 (m) cm⁻¹. Anal. Calc. for C₃₁H₃₄ClPO₃SiW (732.98): C 50.80, H 4.68; found: C 49.71, H 4.50.

*11) [HOMe₂Si(C₅H₄)](OC)₂(η^2-dppm)WCl (**9**)*

Carbonylchloro[η^5-(hydroxydimethylsilyl)-cyclopentadienyl](η^2-bis-diphenylphosphino-
methane)tungsten(II)

Analogous to 7) from 1.20 g (1.52 mmol) of **6** and 410 mg (0.40 ml, 22.7 mmol) of NEt₃ and 0.3 ml water in 20 ml Et₂O and 5 ml benzene over a period of 30 minutes. The crude product was washed three times with each 5 ml PE at 0 ℃. Yield: 867 mg

(1.12 mmol, 74 %). Orange solid. M.p.: 80 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 8.06 - 6.65 (m, 20 H, H$_5$C$_6$P), 5.43 - 5.40 (m, 1 H, H$_4$C$_5$), 5.39 - 5.28 (m, 1 H, H$_4$C$_5$), 5.15 - 5.11 (m, 1 H, H$_4$C$_5$), 4.90 - 4.88 (m, 1 H, H$_4$C$_5$), 4.20 - 4.07 (m, 1 H, H$_2$C), 3.90 [ddd, ^2J(HCH) = 9.0 Hz, ^2J(PCH) = 2.6 Hz, ^2J(PCH) = 2.0 Hz, 1 H, H$_2$C], 3.67 (s, HOSi), 0.71 (s, 3 H, H$_3$CSi), 0.54 (s, 3 H, H$_3$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, CDCl$_3$): δ = 228.90 [d, ^2J(CWP) = 14.1 Hz, CO], 132.00 - 126.92 (phenyl-C), 113.92, 92.02, 91.20, 90.62 (s, C$_5$H$_4$), 85.44 [d, ^2J(CWP) = 2.3 Hz, C$_5$H$_4$], 32.99 [t, ^1J(CP) = 25.4 Hz, CH$_2$], 21.21, 12.93 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 5.39 (s) ppm. - **^{31}P{^{1}H}-NMR**: (121.5 MHz, C$_6$D$_6$): δ = -2.72 [d, ^1J(WP) = 187.5 Hz, ^2J(PCP) = 34.0 Hz], -15.01 [d, ^1J(WP) = 247.9 Hz, ^2J(PCP) = 34.0 Hz] ppm. - **IR** (CH$_2$Cl$_2$): $\tilde{\nu}$(CO) = 1830 (vs) cm^{-1}. - Anal. calc. for C$_{33}$H$_{33}$ClO$_2$P$_2$SiW (770.96): C 51.41, H 4.31; found: C 50.93, H 4.08.

*12) [HMe$_2$SiOMe$_2$Si(C$_5$H$_4$)](OC)$_2$(Ph$_3$P)WCl (**10a**)*

Dicarbonylchloro[η^5-(1,1,3,3-tetramethyl-disiloxano)-cyclopentadienyl]-(triphenylphosphino)tungsten(II)

Analogous to 7) from 80 mg (0.41 mmol) of **7b** and 0.1 ml of NEt$_3$ and 0.1 ml of Me$_2$Si(H)Cl in a solvent mixture of 10 ml Et$_2$O and 3 ml benzene over a period of 30 minutes at room temperature. The crude product was washed three times each with 5 ml PE at –30 °C. Yield: 81 mg (0.10 mmol, 92 %). Orange solid. M.p.: 56 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.62 - 7.55, 7.04 - 7.00 (m, 15 H, H$_5$C$_6$P), 5.80 - 5.78 (m, 1 H, H$_4$C$_5$), 5.74 - 5.70 (m, 1 H, H$_4$C$_5$), 4.96 [sept, ^3J(HSiCH) = 2.8 Hz, 1 H, HSi], 4.88 - 4.83 (m, 1 H, H$_4$C$_5$), 4.60 - 4.56 (m, 1 H, H$_4$C$_5$), 0.45 (s, 3 H, H$_3$CSiC$_5$), 0.41 (s, 3 H, H$_3$CSiC$_5$), 0.14 (s, 3 H, H$_3$CSiH), 0.13 (s, 3 H, H$_3$CSiH) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 247.80 [d, ^2J(CWP) = 20.7 Hz, *cis*-CO], 237.14 [d, ^2J(CWP) = 7.2 Hz, *trans*-CO], 134.54 [d, ^1J(CP) = 46.6 Hz, *ipso*-C$_6$H$_5$], 134.29 [d, ^1J(CP) = 10.0 Hz, *meta*-C$_6$H$_5$], 130.53 [d, ^3J(CCCP) = 2.4 Hz, *para*-C$_6$H$_5$], 128.56 [d, ^2J(CCP) = 9.9 Hz, *otho*-C$_6$H$_5$], 116.01 (s, C$_5$H$_4$), 103.84 (s, C$_5$H$_4$), 95.32 [d, ^2J(CWP) = 3.8 Hz, C$_5$H$_4$], 87.35 [d, ^2J(CWP) = 1.0 Hz, *ipso*-C$_5$H$_4$], 86.483 [s, ^1J(CW) = 4.8 Hz, C$_5$H$_4$], 2.45, 2.44 (s, CH$_3$SiC$_5$), 0.74 (s, CH$_3$SiH) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -0.60 (s, SiC$_5$), -5.31 (s, SiH) ppm. - **^{31}P{^{1}H}-NMR**: (121.5 MHz, C$_6$D$_6$): δ = 23.32 [s,

^1J(PW) = 268.5 Hz, PW] ppm. - **IR** (Et$_2$O): $\tilde{\nu}$ (SiH) = 2125 (m), $\tilde{\nu}$ (CO) = 1963 (vs), 1885 (m) cm^{-1}. - Anal. calc. for C$_{29}$H$_{32}$ClO$_3$PSi$_2$W (735.02): C 47.39, H 4.39; found: C 47.63, H 4.16.

*13) [HMe$_2$SiOMe$_2$Si(C$_5$Me$_4$)](OC)$_2$(Ph$_3$P)WCl (**10b**)*

Dicarbonylchloro[η^5-(1,1,3,3-tetramethyl-disiloxano)-tetramethylcyclopentadienyl]-(triphenylphosphino)tungsten(II)

Analogous to 7) from 90 mg (1.29 mmol) of **7c** and 0.2 ml of NEt$_3$ and 0.2 ml of Me$_2$Si(H)Cl in a solvent mixture of 10 ml Et$_2$O and 3 ml benzene over a period of 1.5 hours. The crude product was washed two times with each 5 ml PE at –78 °C. Yield: 735 mg (0.93 mmol, 72 %). Pale orange solid. M.p.: 47 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.59 - 7.54, 7.02 - 7.00 (m, 15 H, H$_5$C$_6$P), 5.04 [sept, ^3J(HSiCH) = 2.7 Hz, 1 H, HSi], 2.07 (s, 3 H, H$_3$CC$_5$), 2.01 (s, 3 H, H$_3$CC$_5$), 1.45 (s, 3 H, H$_3$CC$_5$), 1.29 (s, 3 H, H$_3$CC$_5$), 0.58 (s, 3 H, H$_3$CSiC$_5$), 0.51 (s, 3 H, H$_3$CSiC$_5$), 0.21 (s, 3 H, H$_3$CSiH), 0.20 (s, 3 H, H$_3$CSiH) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 247.80 [d, ^2J(CWP) = 20.7 Hz, *cis*-CO], 237.14 [d, ^2J(CWP) = 7.2 Hz, *trans*-CO], 134.54 [d, ^1J(CP) = 46.6 Hz, *ipso*-C$_6$H$_5$], 134.29 [d, ^1J(CP) = 10.0 Hz, *meta*-C$_6$H$_5$], 130.53 [d, ^3J(CCCP) = 2.4 Hz, *para*-C$_6$H$_5$], 128.56 [d, ^2J(CCP) = 9.9 Hz, *otho*-C$_6$H$_5$], 116.01 (s, H$_3$C$\underline{C}_5$), 103.84 (s, H$_3$C$\underline{C}_5$), 95.32 [d, ^2J(CWP) = 3.8 Hz, H$_3$C$\underline{C}_5$], 87.35 [d, ^2J(CWP) = 1.0 Hz, *ipso*-H$_3$C$\underline{C}_5$], 86.483 [s, ^1J(CW) = 4.8 Hz, H$_3$C$\underline{C}_5$], 13.77, 13.32, 10.79 and 10.65 (s, H$_3$$\underline{C}C_5$), 4.45, 2.44 (s, CH$_3SiC_5$), 0.74 (s, CH$_3$SiH), 0.23 (s, CH$_3$SiH) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 1.49 (s, SiC$_5$), -9.84 (s, SiH) ppm. - **^{31}P{^{1}H}-NMR**: (121.5 MHz, C$_6$D$_6$): δ = 23.41 [s, ^1J(PW) = 268.6 Hz, PW] ppm. - **IR** (PE): $\tilde{\nu}$ (SiH) = 2136 (m), $\tilde{\nu}$ (CO) = 1949 (vs), 1886 (m) cm^{-1}. - Anal. calc. for C$_{33}$H$_{40}$ClO$_3$PSi$_2$W (791.13): C 50.10, H 5.10; found: C 50.07, H 5.01.

*14) O{[Me$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WH}$_2$ (**11**)*

1,3-Bis[dicarbonyl(η^5-cyclopentadienyl)hydrido(trimethylphosphino)tungsten(II)]-1,1,3,3-tetramethyl-disiloxane

Analogous to 7) from 440 mg (0.96 mmol) of **7a** and 0.2 ml of NEt$_3$ and 456 mg (0.96 mmol) of **2b** in 20 ml Et$_2$O over a period of five days. The crude product was washed two times with each 5 ml. Yield: 841 mg (0.94 mmol, 98 %). Pale yellow solid. M.p.: 51 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 5.09 - 5.08 (m, 1 H, H$_4$C$_5$), 4.92 - 4.90 (m, 1 H, H$_4$C$_5$), 4.89 - 4.87 (m, 1 H, H$_4$C$_5$), 4.76 - 4.74 (m, 1 H, H$_4$C$_5$), 1.15 [d, ^{2}J(HCP) = 9.0 Hz, H$_3$CP], 0.48 (s, H$_3$CSi), -7.09 [d, ^{1}J(HW) = 49.3 Hz, ^{2}J(HWP) = 23.7 Hz, HW (*cis*)], -7.99 [d, ^{1}J(HW) = 49.0 Hz, ^{2}J(HWP) = 68.5 Hz, HW (*trans*)] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 224.10 [d, ^{2}J(CWP) = 14.8 Hz, CO], 94.61, 92.47, 91.55, 89.96, 89.03 (m, C$_5$H$_4$), 25.42 [d, ^{1}J(CP) = 33.4 Hz, CH$_3$P (*trans*)], 22.44 [d, ^{1}J(CP) = 31.4 Hz, CH$_3$P (*cis*)], 1.55, 1.54 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -2.42, -2.44 (s) ppm. - **^{31}P{^{1}H}-NMR**: (121.5 MHz, C$_6$D$_6$): δ = -17.2 [s, ^{1}J(PW) = 255.2 Hz, PW (*trans*)], -19.6 [s, ^{1}J(PW) = 282.0 Hz, PW (*cis*)] ppm. - **IR** (THF): $\tilde{\nu}$(CO) = 1939 (vs), 1856 (m) cm^{-1}. - Anal. calc. for C$_{24}$H$_{40}$O$_5$P$_2$Si$_2$W$_2$ (894.40): C 32.23, H 4.51; found: C 30.77, H 4.09.

*15) [HMe$_2$SiOMe$_2$Si(C$_5$H$_4$)](OC)$_2$(η^2-dppm)WCl (**13a**)*

Carbonylchloro[η^5-(1,1,3,3-tetramethyl-disiloxano)-cyclopentadienyl](η^2-bis-diphenylphosphino-methane)tungsten(II)

Analogous to 7) from 180 mg (0.23 mmol) of **9** and 205 mg (0.20 ml, 11.4 mmol) of NEt$_3$ and 0.4 ml Me$_2$Si(H)Cl (**12a**) in a solvent mixture of 10 ml Et$_2$O and 10 ml benzene over a period of one day. The crude product was washed three times with each 5 ml PE. Yield: 143 mg (0.17 mmol, 74 %). Pale orange solid. M.p.: 62 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.69 - 6.69 (m, 20 H, H$_5$C$_6$P), 5.44 - 5.41 (m, 1 H, H$_4$C$_5$), 5.37 - 5.28 (m, 1 H, H$_4$C$_5$), 5.16 - 5.12 (m, 1 H, H$_4$C$_5$), 5.07 [sept, ^{3}J(HSiCH) = 2.4 Hz, 1 H, HSi], 4.91 - 4.90 (m, 1 H, H$_4$C$_5$), 4.18 - 4.08 (m, 1 H, H$_2$C), 3.89 [ddd,

^2J(HCH) = 9.1 Hz, ^2J(PCH) = 2.7 Hz, ^2J(PCH) = 2.0 Hz, 1 H, H$_2$C], 0.90 (s, 3 H, H$_3$CSiC$_5$), 0.73 (s, 3 H, H$_3$CSiC$_5$), 0.23 (s, 3 H, H$_3$CSiH), 0.21 (s, 3 H, H$_3$CSiH) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, CDCl$_3$): δ = 227.90 [d, ^2J(CWP) = 14.1 Hz, CO], 134.00 - 126.42 (phenyl-C), 114.42, 93.02, 91.70, 90.67 (s, C$_5$H$_4$), 85.44 [d, ^2J(CWP) = 2.7 Hz, C$_5$H$_4$], 32.99 [t, ^1J(CP) = 25.2 Hz, CH$_2$], 21.22, 12.92 (s, $\underline{C}$H$_3$SiC$_5$), 2.02, 0.57 (s, CH$_3$SiH) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 1.64 (s, SiC$_5$), -6.74 (s, SiH) ppm. - **^{31}P{^{1}H}-NMR**: (121.5 MHz, C$_6$D$_6$): δ = -2.24 [d, ^1J(WP) = 183.5 Hz, ^2J(PCP) = 31.6 Hz], -16.43 [d, ^1J(WP) = 281.2 Hz, ^2J(PCP) = 31.6 Hz] ppm. - **IR** (CH$_2$Cl$_2$): $\tilde{\nu}$ (SiH) = 2131 (m), $\tilde{\nu}$ (CO) = 1831 (vs) cm^{-1}. - Anal. calc. for C$_{35}$H$_{39}$ClO$_2$P$_2$Si$_2$W (829.19): C 52.62, H 4.78; found: C 51.63, H 4.71.

*16) [Me$_3$SnOMe$_2$Si(C$_5$H$_4$)](OC)$_2$(η^2-dppm)WCl (**13b**)*

Carbonylchloro[η^5-(trimethylstanna-dimethylsiloxano)-cyclopentadienyl](η^2-bis-diphenylphosphino-methane)tungsten(II)

Analogous to 7) from 100 mg (0.13 mmol) of **9** and 205 mg (0.20 ml, 11.4 mmol) of NEt$_3$ and 78 mg (0.39 mmol) Me$_3$SnCl (**12b**) in 20 ml benzene over a period of three days. The crude product was washed two times with each 5 ml PE. Yield: 75 mg (0.08 mmol, 62 %). Pale orange solid. M.p.: 71 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.57 - 6.85 (m, 20 H, H$_5$C$_6$P), 5.56 - 5.51 (m, 1 H, H$_4$C$_5$), 5.40 - 5.32 (m, 1 H, H$_4$C$_5$), 5.26 - 5.22 (m, 1 H, H$_4$C$_5$), 4.95 - 4.91 (m, 1 H, H$_4$C$_5$), 4.19 - 4.10 (m, 1 H, H$_2$C), 3.84 [ddd, ^2J(HCH) = 9.0 Hz, ^2J(PCH) = 2.6 Hz, ^2J(PCH) = 2.0 Hz, 1 H, H$_2$C], 0.93 (s, 3 H, H$_3$CSi), 0.73 (s, 3 H, H$_3$CSi), 0.32 (s, 3 H, H$_3$CSn) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, CDCl$_3$): δ = 227.70 [d, ^2J(CWP) = 14.1 Hz, CO], 134.12 - 126.32 (phenyl-C), 115.42, 94.02, 91.60, 90.55 (s, C$_5$H$_4$), 85.32 [d, ^2J(CWP) = 2.8 Hz, C$_5$H$_4$], 32.77 [t, ^1J(CP) = 25.5 Hz, CH$_2$], 22.07, 13.32 (s, $\underline{C}$H$_3$SiC$_5$), 4.02, (s, CH$_3$Sn) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -0.20 (s) ppm. - **^{31}P{^{1}H}-NMR**: (121.5 MHz, C$_6$D$_6$): δ = -1.78 [d, ^1J(WP) = 186.6 Hz, ^2J(PCP) = 32.6 Hz], -15.60 [d, ^1J(WP) = 280.2 Hz, ^2J(PCP) = 32.6 Hz] ppm. - **IR** (CH$_2$Cl$_2$): $\tilde{\nu}$ (CO) = 1856 (vs) cm^{-1}. - Anal. calc. for C$_{36}$H$_{41}$ClO$_2$P$_2$SiSnW (933.77): C 46.31, H 4.43; found: C 46.78, H 4.06.

Tab. 1: ^{1}H- and ^{29}Si-NMR values of silanols

	^{1}H (HOSi)	^{29}Si	
7a	1.64	4.93	ppm
7b	3.77	5.22	ppm
7c	4.09	7.89	ppm
8	3.71	4.39	ppm
9	3.67	5.39	ppm

Tab. 2: ^{29}Si-NMR values of disiloxanes

	^{29}Si (SiC_5H_4)	
10a	-0.60	ppm
10b	1.49	ppm
11	-2.42	ppm
13a	1.64	ppm
13b	-0.20	ppm

X-ray diffraction analyses data

The data were collected from shockcooled crystals on a BRUKER SMART-APEX diffractometer with D8 goniometer (graphite-monochromated Mo - K$_\alpha$ radiation (λ = 0.71073 Å) equipped with a low temperature device in omega-scan mode at 173(2) K [34]. The data was integrated with SAINT [32] and an empirical absorption correction [35] was applied. The structure was solved by direct methods (SHELXS-97) [36] and refined by full-matrix least squares methods against F^2 (SHELXL-97) [37]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of the hydrogen atoms were calculated by an idealized geometry.

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Chapter IV

HALFSANDWICH TUNGSTEN COMPLEXES WITH METAL- AND η^5-CYCLOPENTADIENYL-BOUND FUNCTIONAL SILYL GROUPS

SUMMARY

The double silyl-functionalized tungsten complexes [HR$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$WSiR$_2$H [R = Me (**3a**); Ph (**3b**)] have been synthesized by reaction of the dilithiated compound Li[W(η^5-C$_5$H$_4$Li)(CO)$_3$] (**1**) with two equivalents of ClSiR$_2$H (R = Me, Ph). Modified reaction conditions lead to a mixture of **3b** and the binuclear Ph$_2$Si-bridged Ph$_2$Si[(η^5-C$_5$H$_4$)(OC)$_3$WSiPh$_2$H]$_2$ (**5**). It is possible to change the substitution pattern by successive conversion of **1** with different organochlorosilanes like illustrated by the synthesis of [HMe$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$WSiMe$_3$ (**6**) which takes course via the lithium tungsten anion Li{W[(η^5-C$_5$H$_4$)SiMe$_2$H](CO)$_3$} (**2**). Formation of [HMe$_2$Si(η^5-C$_5$H$_4$)](OC)$_2$(Me$_3$P)WSiMe$_2$H (**9**) is achieved by deprotonation of [HMe$_2$Si(η^5-C$_5$H$_4$)](OC)$_2$(Me$_3$P)WH (**7**) with *n*BuLi and reaction of the resulting lithium tungstate Li{W[(η^5-C$_5$H$_4$)SiMe$_2$H](PMe$_3$)(CO)$_2$} (**8**) with Me$_2$Si(H)Cl. Hydrolysis of [HMe$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$WSiMe$_2$Cl (**11a**) and [ClPh$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$WSiPh$_2$Cl (**12**) gives the corresponding silanols [HMe$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$WSiMe$_2$OH (**13**) and [HOPh$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$WSiPh$_2$Cl (**16**) which are stable with respect to self-condensation. [HMe$_2$Si(η^5-C$_5$H$_4$)](OC)$_2$(Me$_3$P)WSiMe$_2$OH (**14**) is synthesized by oxofunctionalization of the tungsten-silane [HMe$_2$Si(η^5-C$_5$H$_4$)](OC)$_2$(Me$_3$P)WSiMe$_2$H (**9**) with dimethyldioxirane (DMD). **14** is stable with respect to self-condensation and give, when treated with DMD, the bis-silanol [HOMe$_2$Si(η^5-C$_5$H$_4$)](OC)$_2$(Me$_3$P)WSiMe$_2$OH (**A**) which undergoes rapid intramolecular condensation leading to the novel disiloxane-bridged [(η^5-C$_5$H$_4$)SiMe$_2$O-η^1-SiMe$_2$](OC)$_2$(Me$_3$P)W (**15**). The synthesized compounds have been characterized by IR- and NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si and ^{31}P), as well as in the case of **15** by X-ray analysis whose result is depicted and discussed.

INTRODUCTION

There has been a great deal of interest in the synthesis and reactions of silyl-functionalized metal complexes, $L_nM\text{-}SiR_2X$ [1-13]. Such compounds have attracted attention as precursors mainly due to their important role as intermediates in hydrosilylation reactions and further more to metal fragment-substituted silanols [14, 15] which are easily accessible via hydrolysis of metallo-chlorosilanes [16], by oxygenation of metallo-silanes with dimethyldioxirane (DMD) [17] or the catalytic system urea-hydrogenperoxide in the presence of catalytic amounts of methylrheniumtrioxide (MTO/UHP) [18], provided that the starting material contains a stable metal-silicon bond. The outstanding feature of metallo-silanols is their strongly reduced tendency towards self-condensation compared with organosilanols. This property makes them useful precursors towards controlled and base-assisted condensation with diverse organoelement halides, to build up special siloxane- and heterosiloxane ligands at the transition metal center [18-20]. We have recently shown that even silanol groups attached at the cyclopentadienyl ligand of tungsten and iron halfsandwich complexes are stable with respect to self-condensation [14, 21, 22]. In an extention of this research about metal fragment-substituted silanols, we have now focused our interest on the synthesis of complexes bearing both a metal- and a cyclopentadienyl-bound silanol function (**III**), which can be regarded as a formal hybrid of metallo-silanols (**I**) and metal complexes with a cyclopentadienyl-fixed silanol group (**II**) (Fig. 1).
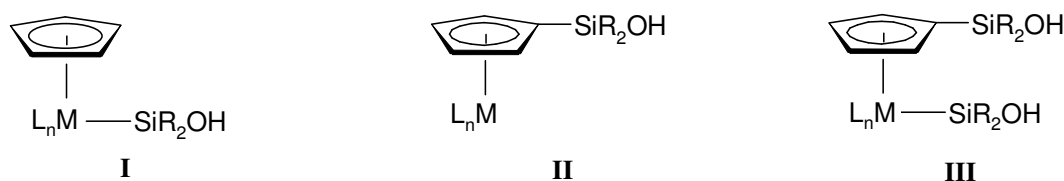

Fig. 1: Classification of metal fragment-substituted silanols: "Common" metallo-silanol (**I**), metal complex containing cyclopentadienyl-bound silanol group (**II**) and formal hybrid of both (**III**).

The literature knows only a few examples of complexes characterized by such a double silyl-subsitution pattern having rhenium, iron and ruthenium as the central

atoms. These compounds are generated in common by rearrangements involving metal-to-carbon silatropic shift, e.g. $[\mu\text{-}\eta^1\text{-}SiMe_2Me_2Si(\eta^5\text{-}C_5H_4)]Re(NO)(PPh_3)$ and $[R_3Si(\eta^5\text{-}C_5H_4)](OC)_2FeSiR_3'$ [R_3 = Me_3, Me_2Ph; R_3' = Me_3, $Me(H)Cl$] [23-26] or by metathesis of the Si-Si- and Fe-Fe/Ru-Ru bonds of the complexes $[\mu\text{-}(Me_2Si)(\eta^5\text{-}C_5R_4)]_2[Ru(CO)(\mu\text{-}CO)]_2$ leading to $[\mu\text{-}(\eta^5\text{-}C_5R_4)Me_2SiM(CO)_2]_2$ (R = H, Me; M = Fe, Ru) [27-30].

In this report we present a complete novel approach to this type of complexes with a metal- and a cyclopentadienyl-bound silyl function by use of appropriate tungsten complexes. Furthermore we describe the experiments for the conversion into silanols and the results concernig the behaviour with regard to self-condensation.

RESULTS AND DISCUSSION

Double Silyl-functionalization of Halfsandwich Tungsten Complexes. An attractive route to introduce two silyl groups at the cycopentadienyl ligand and at the metal center is offered by the reaction of the double lithiated tungsten complex Li[W(C$_5$H$_4$Li)(CO)$_3$] (**1**) with organochlorosilanes. **1** is generated by reaction of the tungsten hydrido complex Cp(OC)$_3$WH with two equivalents of nBuLi [31]. As recently shown, it is possible to silylate **1** regioselectively at the cyclopentadienyl ligand by treatment with one equivalent of chlorodimethylsilane (**2a**) in THF at −78 °C leading to the lithium tungsten salt Li{W[(C$_5$H$_4$)SiMe$_2$H](CO)$_3$} (**4**) [32] (Scheme 1).

3	**a**	**b**
R	Me	Ph
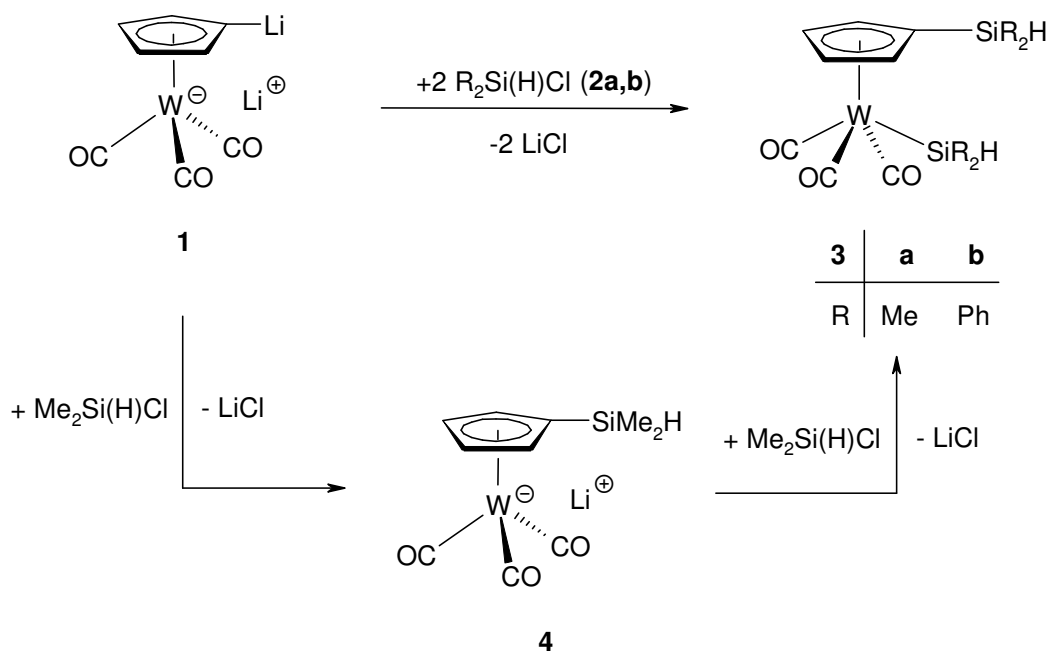
Scheme 1: Double silyl-functionalization of the dilithiated tungsten complex **1**, which takes course via the lithium silyl-cyclopentadienyl tungstate Li{W[(C$_5$H$_4$)SiMe$_2$H](CO)$_3$} (**4**).

Double silylation of **1** with two equivalents of the same organochlorosilane in one step is realized by use of dimethyl- and diphenylchlorosilane (**2a,b**) under heterogeneous conditions in cyclohexane, a commonly applied method for the synthesis of silicon transition metal complexes [33]. After addition of the chlorosilanes

the suspension of **1** gets immediately clear, indicating beginning reaction. As a result, the double silyl-functionalized tungsten complexes $[HR_2Si(C_5H_4)](OC)_3WSiR_2H$ [R = Me (**3a**), Ph (**3b**)] are generated after four hours (**3a**) and five days (**3b**) stirring at room temperature (Fig. 2). **3a** is obtained as a dark red oil in 91 % yield and **3b** as a brown solid in 56 % yield. The longer reaction time and the lower yield of **3b** is rooted in the higher sterical requirements of diphenylchlorosilane in relation to its methyl-counterpart. **3a**,**b** show a reasonable solubility in aliphatic and aromatic solvents.

Interestingly, nearly the same reaction of **1** with diphenylchlorosilane, when performed in a 5:1-cyclohexane/benzene solvent mixture, leads also to the formation of **3b** but together with equimolar amounts of the dinuclear Ph_2Si-bridged tungsten complex $Ph_2Si[(C_5H_4)(OC)_3WSiPh_2H]_2$ (**5**) (Fig. 2). [1]

Accordingly, under these conditions hydride substitution at the silyl function of the primary generated $Li\{W[(C_5H_4)SiPh_2H](CO)_3\}$ - the HPh_2Si-analogue to the lithium tungsten salt **4** - occurs by the dilithiated **1**. Probably, this reaction creates the Ph_2Si-bridged lithium tungsten salt $Li_2\{[W(CO)_3(C_5H_4)]_2SiPh_2\}$ which then undergoes W-Si bond formation with chlorodiphenylsilane. The complexes **3b** and **5** can be separated by fractional crystallization due to the low solubility of **5** in PE or Et_2O compared with **3b**. **5** is obtained as grey powder which dissolves readily in benzene or chloroform.

The silyl groups of **3a,b** are in crucial different electronic situations and can be easily distinguished in the IR spectra by the $\tilde{\nu}$ (SiH) values of 2127.9 (**3a**) and 2148.3 cm^{-1} (**3b**) for the cyclopentadienyl-bound Si-H functions while those of the metal silyl unit appear at 2077.2 (**3a**) and 2080.3 cm^{-1} (**3b**).

The ^{1}H-NMR spectra show the $\underline{H}$Si-C$_5$H$_4$ resonances at 4.42 (**3a**) and 5.51 ppm (**3b**) highfield-shifted in relation to the resonances of the HSi-W signals at 4.97 (**3a**) and 5.96 ppm (**3b**). Additionally, the ^{29}Si-NMR resonance of the tungsten-bonded silicon atom of **3a** at -20.43 is shifted about 18 ppm to downfield compared with the cyclopentadienyl-bound silicon (-2.63 ppm).

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[1] This result illustrate the potential of this reaction for the synthesis of bridged biscyclopentadienyl dinuclear complexes which allow a systematic approach to models for the study of the interactions between two metal reaction sites in proximity to each other, if the two metals are additionally fixed for instance by a bisphosphine like dppe. They can be considered to represent the simplest model of metal surfaces and should have the potential, through cooperativity of the metal centers, to effect unique transformations of simple organic substrates not possible by singel metal centers [34-38].

In contrast to many complexes with a monosubstituted cyclopentadienyl ligand, showing two separate multiplets of a AA'BB'-spin system for the four ring protons, in the case of **3a** they overlap in the range from 4.70 to 4.67 ppm.
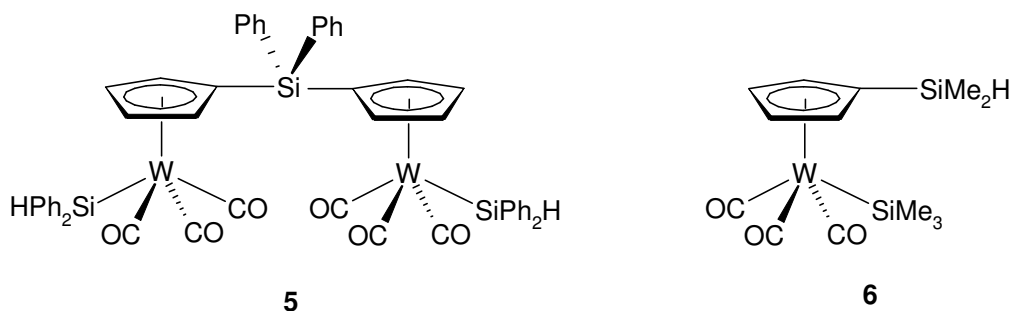

Fig. 2: Dinuclear Ph$_2$Si-bridged tungsten complex **5** and mononuclear tungsten complex **6** bearing both different silyl groups at the metal and the cyclopentadienyl ligand.

Due to the different reactivity of the anionic centers in **1**, a regioselective reaction with different organochlorosilanes in two separated steps is possible. The first step has been already demonstrated in scheme 1. The resulting lithium metalate **4** is then reacted with bromotrimethylsilane leading to the formation of the neutral trimethylsilyl tungsten complex [HMe$_2$Si(C$_5$H$_4$)](OC)$_3$WSiMe$_3$ (**6**) (Fig. 2). This heterogeneous alkali salt elimination is a common procedure for the synthesis of silyl transition metal compounds [7, 13, 33, 39-44], which offers furthemore reaction with various electrophilic reagents like HOAc, MeI, Me$_3$SnCl or Ph$_2$PCl. **6** is generated after 18 hours stirring at room temperature and is obtained in 76 % as red oil showing a good solubility in benzene, Et$_2$O or even PE.

No difference to the synthesis of the cyclopentadienyl analogue Cp(OC)$_3$WSiMe$_3$ [33] is observed concerning the chemical course of the reaction.

In order to synthesize a PMe$_3$-substituted analogue of **3a**, the tungsten hydrido complex [HMe$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WH (**7**) [45] is deprotonated with *n*BuLi generating quantitively the lithium tungstate Li{W[(C$_5$H$_4$)SiMe$_2$H](PMe$_3$)(CO)$_2$} (**8**) as yellow and pyrophoric powder (Scheme 2). The treatment of **8** with chlorodimethylsilane affords after stirring for 36 hours in cyclohexane at ambient

temperature the neutral silyl tungsten complex [HMe$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WSiMe$_2$H (**8**) [22] which is obtained as a pale brown microcrystalline solid in 70 % yield.

SiMe$_2$H

+ *n*BuLi

− *n*BuH

Me$_3$P H
OC CO

7

SiMe$_2$H

W$^{\ominus}$ Li$^{\oplus}$

Me$_3$P CO
CO

8

+ Me$_2$Si(H)Cl − LiCl

SiMe$_2$H

W

Me$_3$P SiMe$_2$H
OC CO

9
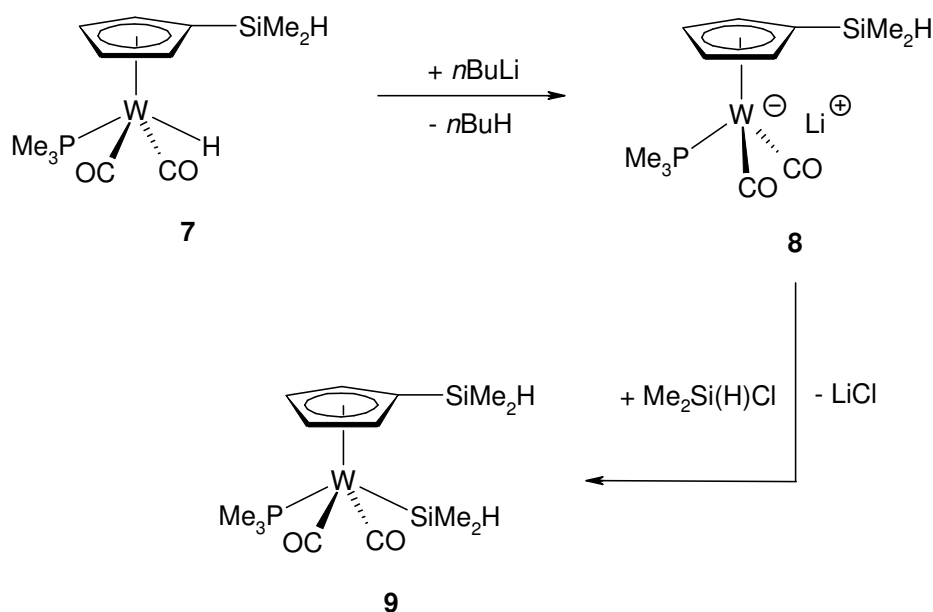
Scheme 2: Two-step synthesis of [HMe$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WSiMe$_2$H (**9**).

9 is generated exclusively as *trans*-isomer, indicated very well by a single resonance at 224.21 ppm for the both carbonyl ligands in the ^{13}C-NMR spectrum. The ^{31}P-signal appears at −14.70 ppm. Like in the case of **3a** illustrated, the both silyl groups can be distinguished in the IR spectrum by the $\tilde{\nu}$ (SiH) sretching frequencies of 2121.7 and 2049.8 cm^{-1} for the cyclopentadienyl- and metal-bound Si-H functions. In addition, the hydrido signal of the the cyclopentadienyl-bound silicon atom appears in the ^{1}H-NMR spectrum as septet while the tungsten-bound silyl group shows a septet of doublets pattern due to coupling with the Si-methyl groups and the phosphorus atom [^3J(PWSiH) = 0.9 Hz]. A crucial characteristic of **9** is the different electronic situation of the silicon atoms, which allows regioselective derivatization of the Si-H functions.

Derivatization of the Si-H Functions of 3a,b and 9. The following reactions are performed in order to generate suitable precursors for the synthesis of silanols (Scheme 3). One possibility deals with the treatment of the Si-H functions with

$Co_2(CO)_8$ since recent work has shown that the resulting Si-Co bond is very sensitive towards water which evokes Si-Co bond cleavage leading to the formation of a silanol unit [21, 32, 46, 47]. The reaction of **3a** with a stoichiometric amount of $Co_2(CO)_8$ gives the known tungsten hydrido complex $[(OC)_4CoMe_2Si(C_5H_4)](OC)_3WH$ (**10**) [32] by prefered cleavage of the W-Si bond followed by W-H unit generation instead of the targeted trinuclear complex $[(OC)_4CoMe_2Si(C_5H_4)(OC)_3WSiMe_2Co(CO)_4$. We assume cleavage of the W-Si bond by $HCo(CO)_4$, formed in the metallation step and expect the resulting Co-Si compound $HSiMe_2$-$Co(CO)_4$ as the second product which could not be identified due to decomposition under the reaction conditions.

The reaction of $[HR_2Si(C_5H_4](OC)_3WSiR_2H$ [R = Me (**3a**), Ph (**3b**)] with an excess of CCl_4 in petrolether (**3a**) or diethylether and catalytical amounts of Pd/C (**3b**) results in the formation of the tungsten-chlorosilane $[HR_2Si(C_5H_4](OC)_3WSiR_2Cl$ [R = Me (**11a**), Ph (**11b**)] (Scheme 3).

3	a	b	9
R	Me	Ph	Me
L	CO	CO	PMe₃

11	a	b	c
R	Me	Ph	Me
L	CO	CO	PMe₃
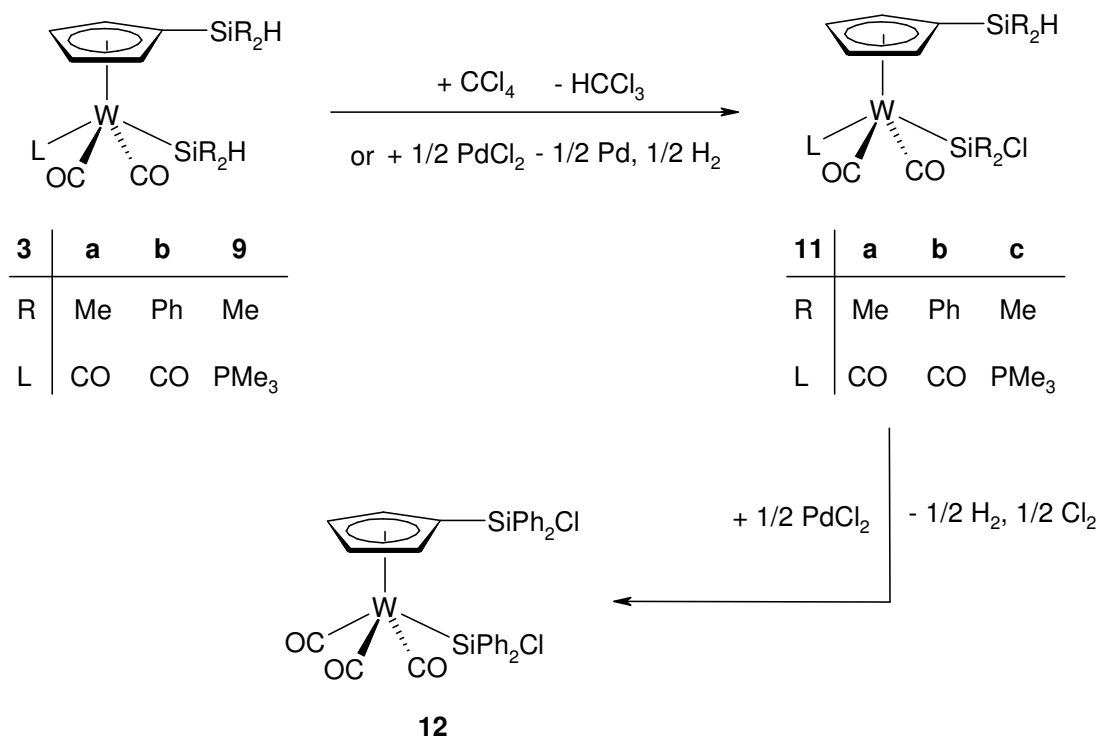
**Scheme 3:** Regioselective SiH/SiCl-exchange reactions of **3a,b** and **9**.

Thess conversions are regioselective and only the tungsten-bound Si-H groups are chlorinated. **11a** is isolated after two hours stirring at room temperature in high yield

of 93 % as a red oil while the reaction of **3b** takes 18 hours yielding **11b** as brown solid in 91 % yield.

The same conditions applied for the chlorination of **9** are not successful. However, PdCl$_2$ converts **9**, dissolved in benzene, into the corresponding tungsten-chlorosilane [HMe$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WSiMe$_2$Cl (**11c**) (Scheme 3). Like in the case of **11a** only the metal-bound Si-H function is affected. The reaction is finished after two days and **11c** is isolated in 85 % yield. In contrast to the tricarbonyl derivative **11a**, the PMe$_3$-substituted tungsten-chlorosilane **11c** is a solid with a reduced solubility in solvents like PE or Et$_2$O.

Chlorination of the cyclopentadienyl-bonded Si-H function of **11b** with PdCl$_2$ leads after three days in benzene at room temperature to the formation of the double Si-Cl-functionalized complex [ClPh$_2$Si(C$_5$H$_4$)](OC)$_3$WSiPh$_2$Cl (**12**) which is obtained as a pale bown solid in 93 % yield (Scheme 3).

Synthesis of the Tungsten-silanols and -disiloxanes 13-18. The NEt$_3$-assisted hydrolysis of **11a** in Et$_2$O at -40 °C affords cleanly the corresponding tungsten-silanol [HMe$_2$Si(C$_5$H$_4$)](OC)$_3$WSiMe$_2$OH (**13**) in 70 % yield (Eq. 1). Performance of the reaction at such low temperatures is necessary since carrying out at room temperature evokes cleavage of the W-Si bond in large quantity.
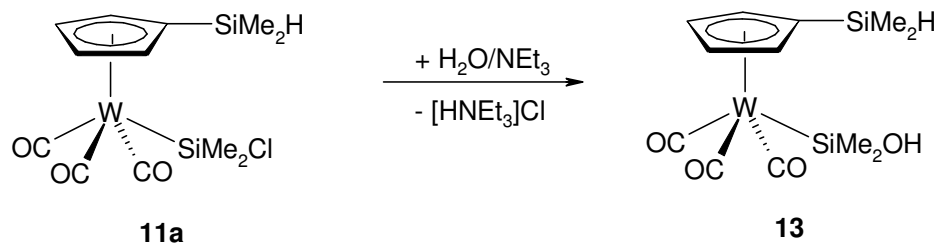
Eq. 1: Synthesis of the tricarbonyl tungsten-silanol **13**.

13 dissolves very well in all common aliphatic and aromatic solvents, even in petrolether at low temperature in contrast to ordinary tungsten-silanols which has to be referred to the presence of a cyclopentadienyl-bonded HMe$_2$Si unit. **13** is obtained

as dark red oil. The ^{29}Si-NMR resonance of the Si-OH unit is detected at 48.23 ppm and lies in the typical range for tungsten-silanols [18].

A reasonable synthetic approach to a tungsten complex bearing both a metal- and a cyclopentadienyl-fixed silanol group is given by the stepwise oxygenation of the double Si-H-functionalized complex **9** with DMD. A crucial charateristic of **9** is the different electronic character of the Si-H units, which allows a successive transformation into silanol groups. The reaction of **9** with one equivalent of DMD at –78 °C in acetone occurs regioselectively at the more hydridic tungsten-bonded Si-H group to give the tungsten-silanol [HMe$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WSiMe$_2$OH (**14**), isolated in 71 % yield as a pale yellow solid (Scheme 4). The ^{29}Si-NMR resonance of the Si-OH moiety is found at 49.87 ppm, very close to the values of the known tungsten-silanols Cp(OC)$_2$(R$_3$P)WSiMe$_2$OH [R = Me, Ph (50.09, 49.60 ppm)] and Cp*(OC)$_2$(Me$_3$P)WSiMe$_2$OH (51.50 ppm) [18, 48].
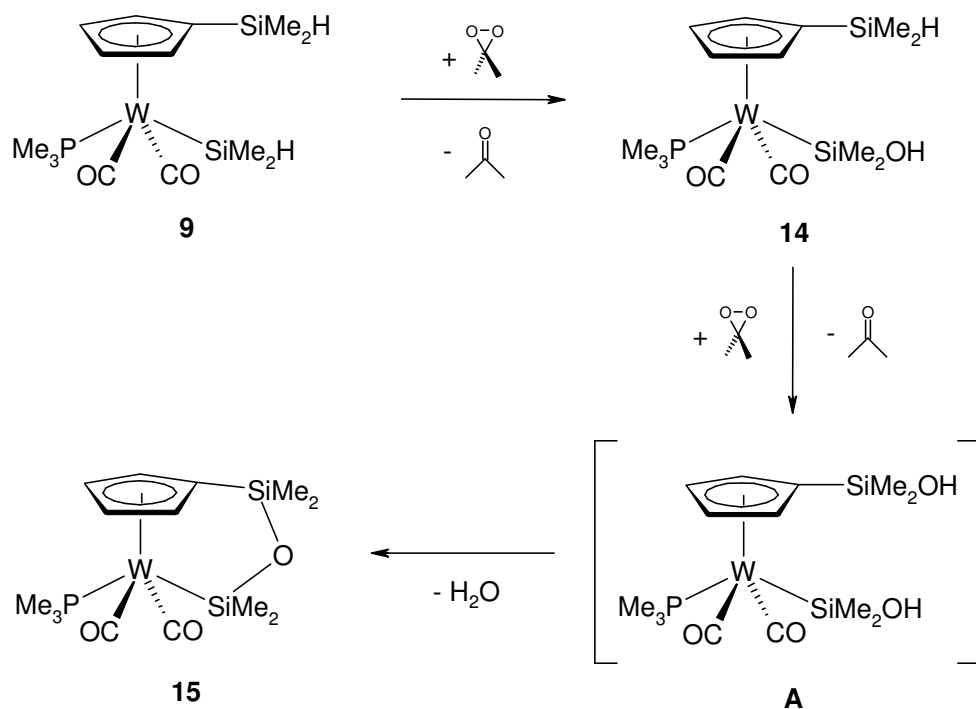
Scheme 4: Successive oxygenation of the both Si-H functions of **9** by use of DMD, leading via an instable bis-silanol species (**A**) to the formation of the disiloxane-bridged tungsten complex **15**.

Treatment of **14** with a further equivalent of DMD presumably leads to the short-lived bis-silanol **A**. However, this intermediate undergoes immediately intramolecular condensation resulting in the formation of $[(\eta^5\text{-}C_5H_4)SiMe_2O\text{-}\eta^1\text{-}SiMe_2](OC)_2(Me_3P)W$ (**15**), bearing a disiloxane unit connecting the cyclopentadienyl ligand with the metal center (Scheme 4). **15** is obtained in 58 % yield as an ocher solid. The ^{29}Si-NMR resonance at 44.38 ppm is characteristic for a tungsten-bonded silicon atom while the cyclopentadienyl-fixed silicon appears at 4.93 ppm.

15 is also generated, when **11c** is treated with an equimolar amount of DMD in acetone at −78 °C, obviously via the instable tungsten-chlorosilane $[HOMe_2Si(C_5H_4)](OC)_2(Me_3P)WSiMe_2Cl$ (**B**), with a cyclopentadienyl-fixed silanol unit, which shows fast intramolecular condensation (Scheme 5).
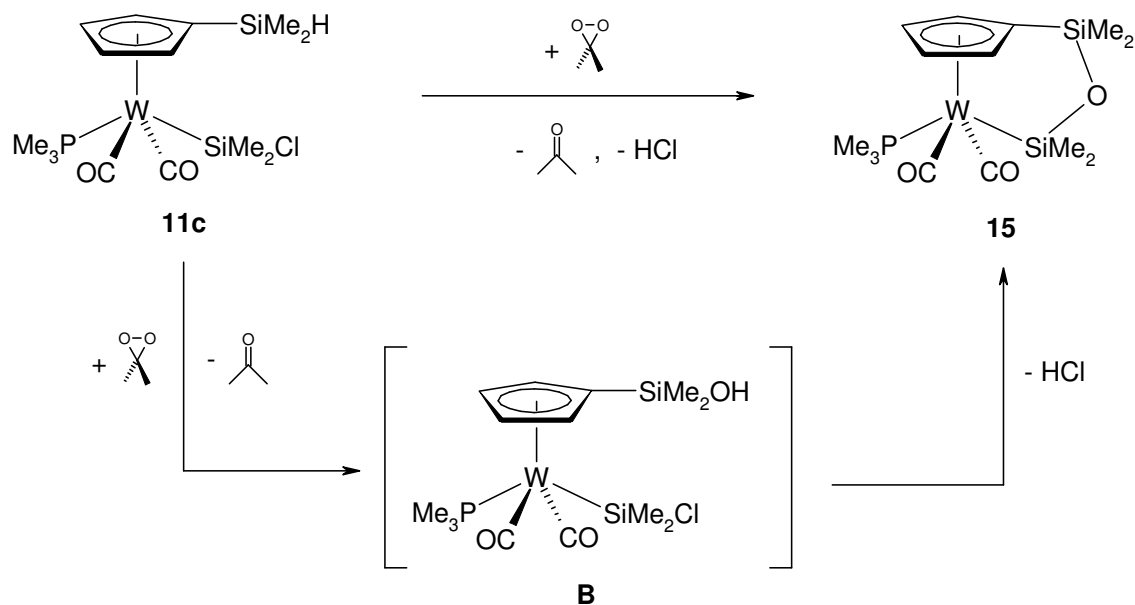
Scheme 5: The alternative synthesis of **15**, starting from a tungsten-chlorosilane (**11c**), takes course via the instable $[HOMe_2Si(C_5H_4)](OC)_2(Me_3P)WSiMe_2Cl$-species (**B**).

Regioselective NEt_3-assisted hydrolysis of **12** occurs at the cyclopentadienyl-bound chlorosilyl group within half of an hour when the reaction is performed at room temperature leading to the formation of $[HOPh_2Si(C_5H_4)](OC)_3WSiPh_2Cl$ (**16**)

(Scheme 6), bearing a silanol group at the cyclopentadienyl ligand. The silanol **16** is isolated analytically pure as a pale orange solid in 87 % yield and is stable with respect to self-condensation as it is known for the tungsten methyl analogue [HOPh₂Si(C₅H₄)](OC)₃WMe [47].

The ^{29}Si-NMR resonance of the cyclopentadienyl-bound silyl group of **16** appears at -0.44 ppm and is about 14 ppm shifted to higher field in comparison to that of **12** (14.86 ppm) while the resonance of the W-Si unit remains almost unchanged.

However, **16** shows some significant changes in benzene after some days. The ^{1}H-NMR spectrum reveals the loss of the Si-OH function, indicating complete conversion to **17**, the product of the intramolecular condensation of the Si-OH- and Si-Cl function (Scheme 6). Intermolecular condensation leading to double disiloxane-bridged dinuclear tungsten complexes can not excluded since further characterization of **17** fails due to rapid decomposition of **17** in solution, resulting in several unknown compounds.

In addition, attempts to generate a tungsten complex with metal- and cyclopentadienyl-bound Si-OH function by further hydrolysis of **16** fails and lead also to decompostion.
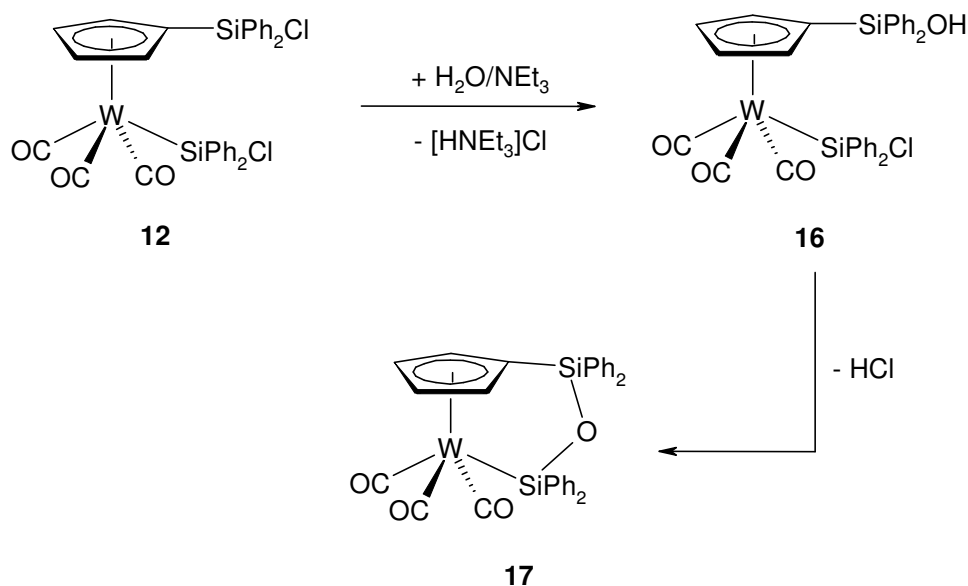
Scheme 6: Synthesis of [HOPh₂Si(C₅H₄)](OC)₃WSiPh₂Cl (**16**) and subsequent intramolecular ring-closure to **17**.

The reaction of **5** with the oxygenation reagent DMD [17, 49, 50] in acetone yields the expected diphenylsilyl-bridged Ph$_2$Si[(C$_5$H$_4$)(OC)$_3$WSiPh$_2$OH]$_2$ (**18**) which is characterized by two tungsten-bound silanol functions in one molecule (Fig. 3). However, the ^{1}H-NMR spectrum of **18** reveals additionally several other by-products, presumably evoked by the cleavage of the W-Si bond and following conversion into a tungsten hydrido complex.

18
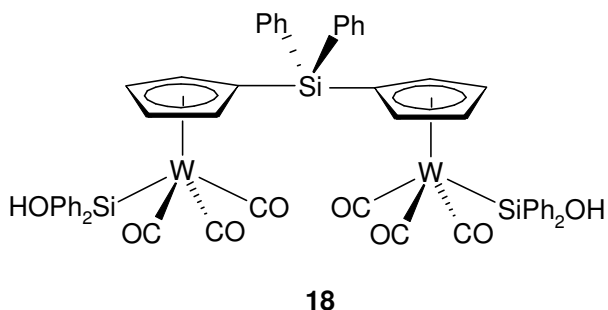
Fig. 3: Dinuclear tungsten-silanol Ph$_2$Si[(C$_5$H$_4$)(OC)$_3$WSiPh$_2$OH]$_2$ (**18**) bearing a bridging Ph$_2$Si-unit.

*X-ray diffraction analysis of [(η^5-C$_5$H$_4$)SiMe$_2$O-η^1-SiMe$_2$](OC)$_2$(Me$_3$P)W (**15**)*

Suitable crystals of **15** for a single crystal X-ray analysis are obtained from a saturated benzene solution at room temperature. The result of this analysis confirms the proposed structure of **15** and is depicted in figure 4.

The tungsten complex reveals a pseudo-tetragonal pyramidal arrangement of the ligands at the tungsten atom with the cyclopentadienyl ligand in the apical position. The two carbonyl ligands are found in a *trans*-arrangement as well as the phosphine- and the silyl ligand.

The disiloxane angle amounts to 125.21(16)°, which is more than 30° smaller than in the open-chained metal fragment-substituted disiloxanes O{HOSi[(C$_5$H$_4$)FeCp]$_2$}$_2$ [157.1(3)°] [51] and Cp(OC)$_2$FeSiCl$_2$OSiCl$_3$ [159.2(2)°] [5]. The Si1-O1- and Si2-O1 bond distances of 1.631(3) and 1.672(3) Å are almost similiar to those observed in hexamethyldisiloxane [52]. The angle spanned by the opposite phosphine- and silyl ligand of 135.85(4)° (P1-W1-Si2) is enlarged compared to the hydrosilyl complexes

Cp*(OC)$_2$(Me$_3$P)WSi(H)$_2$R [R = H, Me; 124.2(5) and 126.72(9)°] [53] and illustrates a degree of ring strain within the five-membered ring.

The tungsten phosphorus and tungsten silicon bond distances [W1-Si2 2.5896(11) and W1-P1 2.4297(10) Å] lie in the expected range for such tungsten-substituted silanes [e.g. 2.559(2) and 2.434(1) Å for Cp*(OC)$_2$(Me$_3$P)WSi(H)$_2$Me [53]].
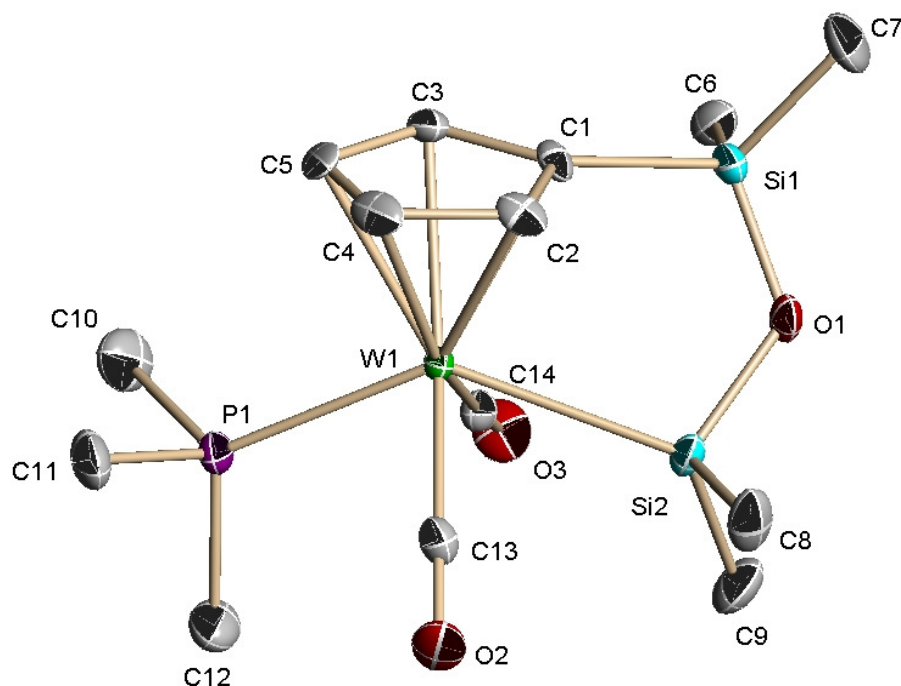
Fig. 4: View of the molecular structure of [(η^5-C$_5$H$_4$)SiMe$_2$O-η^1-SiMe$_2$](OC)$_2$(Me$_3$P)W (**15**) with the atom labeling scheme. Ellipsoids are drawn at the 50 % probality level, and the hydrogen atoms have been omitted for the sake of clarity.

Selected bond lengths [Å], bond and torsion angles [°]: W1-C13 1.945(4), W1-C14 1.935(4), W1-P1 2.4297(10), W1-Si2 2.5896(11), C1-Si1 1.869(4), Si1-O1 1.631(3), Si2-O1 1.672(3), Si1-O1-Si2 125.21(16), O1-Si2-W1 104.94(10), O1-Si1-C1 105.23(16), P1-W1-Si2 135.85(4), Si1-O1-Si2-W1 0.3(2), C1-Si1-O1-Si2 21.7(3), C4-C2-C1-Si1 -171.32(29).

The most characteristic structural feature of **15** is the five-membered ring consisting of the C1, W1, Si2, O2 and Si1 atoms, which adopts an envelope conformation. The

atoms W1, Si2, O2 and Si1 are defining one plane while the carbon atom C1 is bent out of it, illustrated by the torsion angle of 21.7(3)° (C1-Si1-O1-Si2) (Fig. 5).
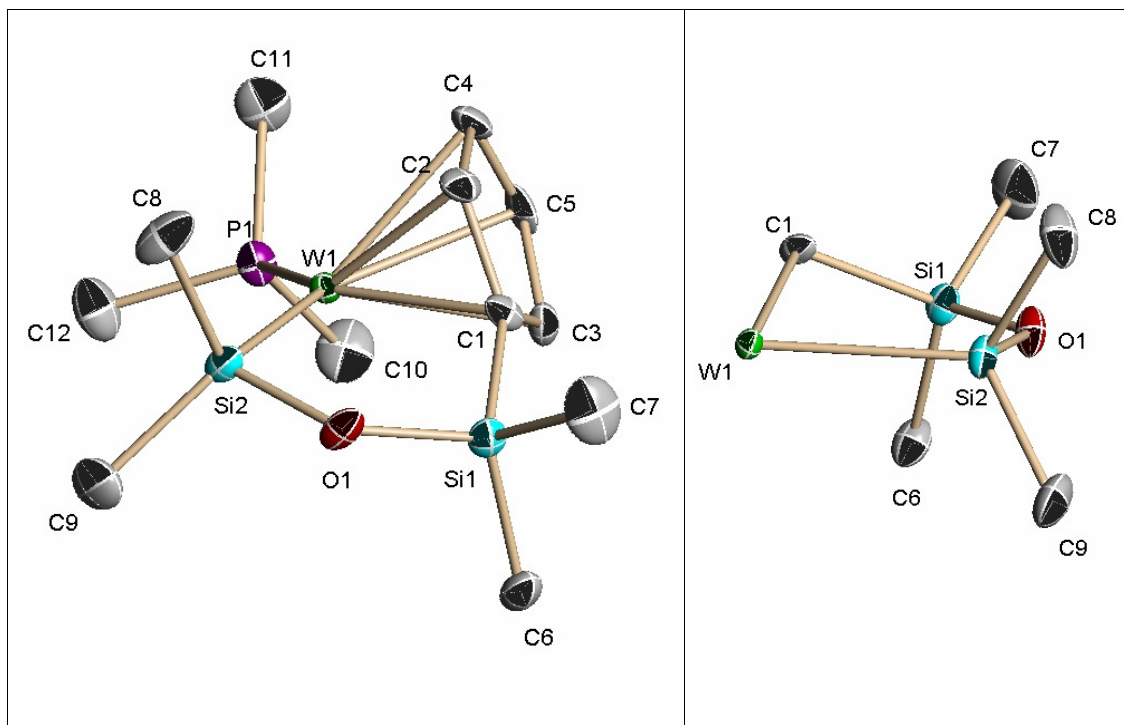
Fig. 5: View on the siloxane unit and envelope conformation of the five-membered ring found in compound **15**, viewed in the absence of the carbonyls (left side) and the ancillary atoms (right side) for the sake of clarity.

Crystal Data for Compound **15**

mol formula	$C_{14}H_{25}O_3PSi_2W$
mol wt	512.34
wavelength (Å)	0.71073
temp (K)	173(2)
cryst size (mm)	0.2 x 0.2 x 0.15
cryst syst	monoclinic
space group	P2(1)/n (No. 14)
a (Å)	9.7357(8)
b (Å)	12.965(2)

c (Á)	15.678(3)
α (°)	90(9)
β (°)	106.756(3)
γ (°)	90(10)
vol (Á^3), Z	1894.9(5)
ρ (calcd) (Mgm^{-3})	1.796
F(000)	1000
μ (mm^{-1})	6.313
θ range for data collecn (deg)	2.08 - 27.56
no. of rflns collected	15779
no. of indep reflns	4267
abs cor.	empirical
no. of data/restraints /params	4267 / 0 / 198
goodness of fit on F^2	0.986
R1^a	0.0739
wR2^b	0.1738
largest diff peak and hole (eÁ$^{-3}$)	3.090 and -1.414

R1 = $\Sigma||F_0| - |F_c||/\Sigma|F_0|$ for reflections with $I > 2\sigma(I)$. wR2 = $[\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_0^2)/3$ and a and b are constants set by the program.

CONCLUSION

The results of this paper demonstrate that we established a new elegant way for the introduction of two silyl groups into tungsten halfsandwich complexes by use of the dilithiated $Li[W(C_5H_4Li)(CO)_3]$ (**1**) which enables also a successive treatment with different chlorodiorganosilanes. The electronic situations of the silicon atoms differs from each other and allows regioselective reaction courses. Despite the fact that tungsten-silanols and tungsten complexes with cyclopentadienyl-bound silanol group are stable with respect to self-condensation, the hybridic bis-silanol $[HOMe_2Si(C_5H_4)](OC)_2(Me_3P)WSiMe_2OH$ (**A**) shows unexpected a strong tendency of intramolecular condensation. This behavior could not be suppressed even by use of bulky organorests at the silicon atom as demonstrated in the case of $[HOPh_2Si(C_5H_4)](OC)_3WSiPh_2Cl$ (**16**).

EXPERIMENTAL SECTION

General Remarks: All operations were performed under an atmosphere of purified and dried nitrogen using Schlenk-type techniques. Solvents were dried according to conventional procedures, distilled and saturated with N_2 prior to use. - NMR: Jeol Lambda 300 (300.4 MHz, 75.5 MHz, and 59.6 MHz for ^1H, ^{13}C, and ^{29}Si, respectively). [D_6]-benzene as a solvent: δ_H = 7.15, δ_C = 128.0; for ^{29}Si rel. to TMS external. - IR: Perkin-Elmer 283 grating spectrometer. - Melting points: Differential thermo analysis (Du Pont 9000 Thermal Analysis System). - Elemental analyses were performed in the laboratories of the *Institut für Anorganische Chemie der Universität Würzburg*. - Starting materials were prepared according to literature procedures: DMD [49, 50], $Cp(OC)_3WH$ (**1**) [54], $Li\{W[(C_5H_4)SiMe_2H](CO)_3\}$ (**5**) [32], $[HMe_2Si(C_5H_4)](OC)_2(Me_3P)WH$ (**7**) [45]. The reagents $Me_2Si(H)Cl$ (**2a**), $Ph_2Si(H)Cl$ (**2b**), Me_3SiBr, $PdCl_2$ and $Co_2(CO)_8$ were purchased from commercial sources. The chlorosilanes were destilled and the $PdCl_2$ were heated at 150 °C over four hours prior use.

*1) [HMe$_2$Si(C$_5$H$_4$)](OC)$_3$WSiMe$_2$H (**3a**)*

Tricarbonyl[η^5-(dimethylsilyl)-cyclopentadienyl](dimethylsilyl)tungsten(II)

To a suspension of 2.32 g (3.66 mmol) of **1** in 20 ml cyclohexane were added 1.38 g (14.6 mmol, 1.59 ml) $Me_2Si(H)Cl$ (**2a**) while the precipitate dissolves. After stirring for four hours at room temperature all volatiles were removed in vacuo resulting in an oil. Yield: 1.50 g (91 %). Dark red oil. - **^{1}H-NMR** (300.4 MHz, C_6D_6): δ = 4.97 [sept, ^3J(HSiCH) = 3.7 Hz, 1 H, HSiW], 4.71 – 4.66 (m, 4 H, H_4C_5), 4.42 [sept, ^3J(HSiCH) = 3.7 Hz, 1 H, $\underline{H}SiC_5H_4$], 0.67 [d, ^3J(HCSiH) = 3.7 Hz, 6 H, H_3CSiW], 0.07 [d, ^3J(HCSiH) = 3.7 Hz, 6 H, $\underline{H}_3CSiC_5H_4$] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C_6D_6): δ = 216.06 (s, CO), 94.88 [s, ^1J(CW) = 4.8 Hz, C_5H_4], 94.65 (s, C_5H_4), 94.47 (s, C_5H_4), 1.63 (s, CH_3SiW), -3.11 (s, $\underline{C}H_3SiC_5H_4$) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = -2.63 (s, SiW), -20.43 (s, SiC_5H_4) ppm. - **IR** (PE): $\tilde{\nu}$ (SiH) = 2127.9 (w), 2077.2 (w) cm^{-1};

$\tilde{\nu}$ (CO) = 2024.9 (vs), 2002.7 (vs), 1937.3 (vs), 1927.0 (vs), 1906.3 (vs) cm^{-1}. – Anal. calc. for $C_{12}H_{18}O_3Si_2W$ (450.28): C 32.01, H 4.03; found:C 31.24, H 3.56.

*2) [HPh$_2$Si(C$_5$H$_4$)](OC)$_3$WSiPh$_2$H (**3b**)*

Tricarbonyl[η^5-(diphenylsilyl)-cyclopentadienyl](diphenylsilyl)tungsten(II)

Analogous to 1) from 1.72 g (2.71 mmol) of **1** and 1.19 g (5.42 mmol, 1.05 ml) Ph$_2$Si(H)Cl (**3b**) in 40 ml cyclohexane over a period of five days. Yield: 1.06 g (56 %). Brown solid. M.p. 70 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.77 - 7.73 [m, 8 H, H$_5$C$_6$Si], 7.49 - 7.42 [m, 12 H, H$_5$C$_6$Si], 5.96 (s, 1 H, HSiW), 5.51 (s, 1 H, $\underline{H}$SiC$_5$H$_4$), 4.75 - 4.71 (m, 4 H, H$_4$C$_5$) ppm. -**^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 218.25 [s, ^{1}J(CW) = 147.1 Hz, *trans*-CO], 215.75 [s, ^{1}J(CW) = 152.0 Hz, *cis*-CO], 135.75, 135.63, 134.70, 130.64, 129.31, 128.55. 128.31, 128.17 (s, C$_6$H$_5$), 97.01 [s, ^{1}J(CW) = 4.8 Hz, C$_5$H$_4$], 96.30 [s, ^{1}J(CW) = 3.8 Hz, C$_5$H$_4$], 94.93 [s, ^{1}J(CW) = 4.8 Hz, *ipso*-C$_5$H$_4$] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -18.76 (s, SiW), -22.25 (s, SiC$_5$H$_4$) ppm. - **IR** (PE): $\tilde{\nu}$ (SiH) = 2148.3 (w), 2080.3 (w) cm^{-1}; $\tilde{\nu}$ (CO) = 2007.4 (vs), 1934.9 (vs), 1912.9 (vs) cm^{-1}. - Anal. calc. for $C_{32}H_{26}O_3Si_2W$ (698.58): C 55.02, H 3.75; found:C 55.10, H 3.59.

*3) Ph$_2$Si[(C$_5$H$_4$)(OC)$_3$WSiPh$_2$H]$_2$ (**5**)*

Bis[tricarbonyl(η^5-cyclopentadienyl)(diphenylsilyl)-tungsten(II)]-diphenylsilane

Analogous to 1) from 4.63 g (7.30 mmol) of **1** and 4.24 ml (21.90 mmol) Ph$_2$Si(H)Cl (**3b**) in 100 ml cyclohexane and 20 ml benzene over a period of five days. After evaporation of the solvens the crude oily residue was washed several times with each 5 ml PE resulting in pure **5**. Yield: 2.04 g (46 %). Grey solid. M.p. 72 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.78 - 7.72, 7.53 - 7.47, 7.24 - 7.15 [m, 30 H, H$_5$C$_6$Si], 5.98 (s, 1 H, HSiW), 4.90 - 4.83 (m, 4 H, H$_4$C$_5$) ppm. -**^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 217.75 [s, ^{1}J(CW) = 143.1 Hz, *trans*-CO], 216.11 [s, ^{1}J(CW) = 152.1 Hz, *cis*-CO], 137.82, 134.49, 134.40, 134.34, 131.27, 129.28. 128.09, 127.95 (s, C$_6$H$_5$),

96.39 [s, $^1J(CW)$ = 4.8 Hz, C_5H_4], 95.11 [s, $^1J(CW)$ = 3.9 Hz, C_5H_4], 92.47 [s, $^1J(CW)$ = 4.7 Hz, $ipso$-C_5H_4] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = 2.63 (s, SiC_5H_4), -20.11 (s, SiW) ppm. - **IR** ($HCCl_3$): $\tilde{\nu}$ (SiH) = 2079.5 (w) cm^{-1}; $\tilde{\nu}$ (CO) = 2009.2 (vs), 1935.8 (vs), 1915.2 (vs) cm^{-1}. - Anal. calc. for $C_{52}H_{40}O_6Si_3W_2$ (1212.84): C 51.50, H 3.32; found: C 51.35, H 3.71.

*4) [HMe$_2$Si(C$_5$H$_4$)](OC)$_3$WSiMe$_3$ (**6**)*

Tricarbonyl[η^5-(dimethylsilyl)-cyclopentadienyl](trimethylsilyl)tungsten(II)

To a suspension of 1.32 g (3.32 mmol) of **4** in 20 ml cyclohexane were added 2.04 g (13.3 mmol) Me$_3$SiBr while the precipitate dissolves. After stirring over a period of 18 hours at room temperature all volatiles were removed in vacuo resulting in a dark red oil. Finally washing with 3 ml PE at –78 °C led to pure **6**. Yield: 1.17 g (76 %). Red oil. - **^{1}H-NMR** (300.4 MHz, C_6D_6): δ = 4.70 – 4.64 (m, 4 H, H_4C_5), 4.44 [sept, $^3J(HSiCH)$ = 3.6 Hz, 1 H, $\underline{H}SiC_5H_4$], 0.62 (s, 9 H, H_3CSiW], 0.06 [d, $^3J(HCSiH)$ = 3.6 Hz, 6 H, $\underline{H}_3CSiC_5H_4$] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C_6D_6): δ = 220.06 (s, CO), 95.57 [s, $^1J(CW)$ = 4.8 Hz, C_5H_4], 94.75 (s, C_5H_4), 92.47 (s, C_5H_4), 2.83 (s, CH_3SiW), -3.00 (s, $\underline{C}H_3SiC_5H_4$) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = 7.23 (s, SiW), -20.10 (s, SiC_5H_4) ppm. - **IR** (cyclohexane): $\tilde{\nu}$ (SiH) = 2130.7 (w) cm^{-1}; $\tilde{\nu}$ (CO) = 2000.9 (vs), 1921.3 (m), 1899.3 (vs) cm^{-1}. - Anal. calc. for $C_{13}H_{20}O_3Si_2W$ (464.32): C 33.63, H 4.34; found: C 33.25, H 4.11.

*5) [HMe$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WSiMe$_2$H (**9**)*

Dicarbonyl[η^5-(dimethylsilyl)-cyclopentadienyl](trimethylphosphino)-dimethylsilyl-tungsten(II)

To a solution of 1.50 g (3.41 mmol) of **7** in 25 ml PE were added dropwise 2.50 ml (4.09 mmol) *n*-BuLi (1.6 M in *n*-hexane) at 0 °C while precipitation of a pale yellow solid (**8**) begun and this mixture was stirred over 15 min. at this temperature. After that, the icebath was removed and a further hour stirred at room temperature. The

solid was filtered off, washed two times with each 10 ml PE and dried in vacuo. Then, **8** was suspended in 20 ml cyclohexane and treated with 0.65 g (6.80 mmol, 0.74 ml) $Me_2Si(H)Cl$ (**2a**). The resulting mixture was stirred at room temperature over 36 hours. The white precipitate was filtered off through a celite path and washed several times with further cyclohexane. The obtained filtrate was evaporated to dryness and the crude residue was washed three times with each 5 ml PE at –30 °C resulting in **9**. Yield: 1.20 g (70 %). Pale yellow solid. M.p. 48 °C. - **^{1}H-NMR** (300.4 MHz, C_6D_6): δ = 5.26 [sept, ^3J(HSiCH) = 3.7 Hz, 1 H, HSiW], 4.73 -4.70 (m, 2 H, H_4C_5), 4.62 – 4.59 (m, 2 H, H_4C_5), 4.52 [sept, ^3J(HSiCH) = 3.7 Hz, 1 H, $\underline{H}SiC_5H_4$], 1.16 [d, ^2J(HCP) = 9.4 Hz, 9 H, H_3CP], 0.92 [d, ^3J(HCSiH) = 3.7 Hz, 6 H, H_3CSiW], 0.22 [d, ^3J(HCSiH) = 3.7 Hz, 6 H, $\underline{H}_3CSiC_5H_4$] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C_6D_6): δ = 224.21 [d, ^2J(CWP) = 17.2 Hz, CO], 95.43 (s, C_5H_4), 95.30 (s, C_5H_4), 88.93 [s, ^1J(CW) = 3.8 Hz, C_5H_4], 21.8 [d, ^1J(CP) = 34.1 Hz, CH_3P], 2.19 (s, CH_3SiW), -2.67 (s, $\underline{C}H_3SiC_5H_4$) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = 0.02 [d, ^2J(SiWP) = 14.3 Hz, SiW], -20.86 (s, SiC_5H_4) ppm. - **^{31}P{^{1}H}-NMR** (121.5 MHz, C_6D_6): δ = -14.70 [s, ^1J(PW) = 283.8 Hz, PCH_3] ppm. - **IR** (PE): $\tilde{\nu}$ (SiH) = 2121.7 (w), 2049.8 (w) cm^{-1}; $\tilde{\nu}$ (CO) = 1904.0 (vs), 1832.7 (vs) cm^{-1}. - Anal. calc. for $C_{14}H_{27}O_2PSi_2W$ (498.35): C 33.74, H 5.46; found: C 33.42, H 5.19.

*6) [(OC)$_4$CoMe$_2$Si(C$_5$H$_4$)](OC)$_3$WH (**10**)*

Tricarbonyl[η^5-(tetracarbonylcobalto)-(dimethylsilyl)-cyclopentadienyl]hydrido-tungsten(II)

245 mg (0.54 mmol) of **3a** were dissolved in 10 ml PE and treated with 93 mg (0.27 mmol) of $Co_2(CO)_8$ and stirred over a period of 18 hours at room temperature while formation of gas was observed. The solvent was removed in vacuo and the crude residue washed with 5 ml PE at –78 °C. - **^{1}H-NMR** (300.4 MHz, C_6D_6): δ = 4.79 – 4.73 (m, 4 H, H_4C_5), 0.17 (s, 6 H, H_3CSi) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = -2.32 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2063 (s), 2055 (s), 2025 (w), 1939 (s) cm^{-1}.

*7) [HMe$_2$Si(C$_5$H$_4$)](OC)$_3$WSiMe$_2$Cl (**11a**)*

Tricarbonyl[η^5-(dimethylsilyl)-cyclopentadienyl](chlorodimethylsilyl)tungsten(II)

To a solution of 0.50 g (1.10 mmol) of **3a** in 7 ml PE were added dropwise 0.68 g (4.44 mmol, 0.43 ml) CCl$_4$ at room temperature and this mixture stirred over a period of two hours. Then, all volatiles were removed in vacuo and the crude residue was washed with 4 ml PE at –78 °C. Yield: 0.50 g (93 %). Red oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.93 – 4.90 (m, 2 H, H$_4$C$_5$), 4.76 – 4.73 (m, 2 H, H$_4$C$_5$), 4.38 [sept, ^{3}J(HSiCH) = 3.7 Hz, 1 H, HSiC$_5$H$_4$], 0.97 (s, 6 H, H$_3$CSiW), 0.01 [d, ^{3}J(HCSiH) = 3.7 Hz, 6 H, H$_3$CSiC$_5$H$_4$] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 216.79 (s, CO), 96.53 [s, ^{1}J(CW) = 4.1 Hz, C$_5$H$_4$], 95.71 [s, ^{1}J(CW) = 4.8 Hz, C$_5$H$_4$], 94.91 (s, C$_5$H$_4$), 11.22 (s, CH$_3$SiW), -3.16 (s, CH$_3$SiC$_5$H$_4$) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 60.55 (s, SiW), -20.01 (s, SiC$_5$H$_4$) ppm. - **IR** (PE): $\tilde{\nu}$(SiH) = 2139.6 (w) cm^{-1}, $\tilde{\nu}$(CO) = 2011.8 (vs), 1940.0 (vs), 1912.0 (vs) cm^{-1}. - Anal. calc. for C$_{12}$H$_{17}$ClO$_3$Si$_2$W (484.72): C 29.73, H 3.53; found: C 29.58, H 3.28.

*8) [HPh$_2$Si(C$_5$H$_4$)](OC)$_3$WSiPh$_2$Cl (**11b**)*

Tricarbonyl[η^5-(diphenylsilyl)-cyclopentadienyl](chlorodiphenylsilyl)tungsten(II)

To a solution of 890 mg (1.27 mmol) of **3b** in 10 ml Et$_2$O were added 5 ml CCl$_4$ and 50 mg Pd/C and the obtained mixture was stirred over a period of 18 hours at room temperature. Then, insoluble material was filtered off through a celite path and the filtrate was evaporated to dryness. The crude residue was washed two times each with 4 ml PE and final drying in vacuo gave **11b**. Yield: 847 mg (91 %). Brown solid. M.p. 89 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.88 - 7.83, 7.42 - 7.39, 7.15 – 7.07 [m, 20 H, H$_5$C$_6$Si], 5.41 (s, 1 H, HSiC$_5$H$_4$), 4.97 - 4.93 (m, 2 H, H$_4$C$_5$), 4.86 - 4.82 (m, 2 H, H$_4$C$_5$) ppm. -**^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 218.24 [s, ^{1}J(CW) = 147.6 Hz, *trans*-CO], 215.63 [s, ^{1}J(CW) = 152.6 Hz, *cis*-CO], 135.52, 134.89, 132.30, 130.71, 129.82, 128.58. 128.08, 127.68 (s, C$_6$H$_5$), 98.01 [s, ^{1}J(CW) = 4.2 Hz, C$_5$H$_4$], 97.54 [s, ^{1}J(CW) = 4.1 Hz, C$_5$H$_4$], 91.46 [s, ^{1}J(CW) = 4.2 Hz, *ipso*-C$_5$H$_4$] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 48.13 (s, SiW), -21.89 (s, SiC$_5$H$_4$) ppm. - **IR** (Et$_2$O): $\tilde{\nu}$(SiH) =

2143.5 (w) cm^{-1}; $\tilde{\nu}$ (CO) = 2016.1 (vs), 1945.9 (s), 1920.7 (vs) cm^{-1}. - Anal. calc. for C$_{32}$H$_{25}$ClO$_3$Si$_2$W (733.02): C 52.43, H 3.44; found: C 52.27, H 3.72.

9) [HMe$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WSiMe$_2$Cl (11c)

Dicarbonyl[η^5-(dimethylsilyl)-cyclopentadienyl](trimethylphosphino)-chlorodimethyl-silyl-tungsten(II)

A solution of 0.28 g (0.55 mmol) of **9** in 10 ml benzene was treated with 0.05 g (0.28 mmol) PdCl$_2$ and stirred over a period of 44 hours. The solvent was removed in vacuo and the crude residue was extracted with 10 ml PE and 10 ml Et$_2$O. The extract was evaporated to dryness and the resulting residue was washed with 3 ml PE at –30 °C and finally drying in vacuo gave **11c**. Yield: 0.25 g (85 %). Yellow solid. M.p. 66 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.81 - 4.78 (m, 4 H, H$_4$C$_5$), 4.46 [sept, ^3J(HSiCH) = 3.6 Hz, 1 H, HSiC$_5$H$_4$], 1.23 (s, 6 H, H$_3$CSiW), 1.07 [d, ^3J(HCP) = 9.6 Hz, 9 H, H$_3$CP], 0.21 [d, ^3J(HSiCH) = 3.6 Hz, 6 H, H$_3$CSiC$_5$H$_4$] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 224.81 [d, ^2J(PWC) = 18.6 Hz, CO], 97.10 (d, C$_5$H$_4$), 96.49 (s, C$_5$H$_4$), 90.11 [s, ^1J(CW) = 3.3 Hz, C$_5$H$_4$], 21.04 [d, ^1J(CP) = 34.9 Hz, CH$_3$P], 11.89 (s, CH$_3$SiW), -2.52 (s, CH$_3$SiC$_5$H$_4$) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 68.65 [d, ^2J(SiWP) = 14.7 Hz, SiW], -20.79 (s, SiC$_5$H$_4$) ppm. - **^{31}P{^{1}H}-NMR** (121.5 MHz, C$_6$D$_6$): δ = -14.67 [s, ^1J(PW) = 262.4 Hz, PCH$_3$] ppm. - **IR** (PE): $\tilde{\nu}$ (SiH) = 2124.6 (w) cm^{-1}; $\tilde{\nu}$ (CO) = 1915.9 (vs), 1841.4 (vs) cm^{-1}. - Anal. calc. for C$_{14}$H$_{26}$ClO$_2$PSi$_2$W (532.81): C 31.56, H 4.92; found: C 31.56, H 4.92.

10) [ClPh$_2$Si(C$_5$H$_4$)](OC)$_3$WSiPh$_2$Cl (12)

Tricarbonyl[η^5-(chlorodiphenylsilyl)-cyclopentadienyl](chlorodiphenylsilyl)tungsten(II)

To a solution of 711 mg (0.97 mmol) of **11b** in 20 ml benzene were added 53 mg PdCl$_2$ and the resulting mixture was stirred over a period of three days at room temperature. Then, insoluble material was filtered off through a celite path and the filtrate was evaporated to dryness. The crude residue was washed with 10 ml PE at

–78 °C and final drying in vacuo gave **12**. Yield: 692 mg (93 %). Pale brown solid. M.p. 91 °C. - **^{1}H-NMR** (300.4 MHz, C_6D_6): δ = 7.90 - 7.81, 7.50 - 7.46, 7.11 - 7.00 [m, 20 H, H_5C_6Si], 5.04 - 4.99 (m, 2 H, H_4C_5), 4.90 - 4.86 (m, 2 H, H_4C_5) ppm. -**^{13}C{^{1}H}-NMR** (75.5 MHz, C_6D_6): δ = 218.67 [s, ^1J(CW) = 147.5 Hz, *trans*-CO], 215.89 [s, ^1J(CW) = 152.4 Hz, *cis*-CO], 136.12, 135.09, 132.44, 130.98, 129.80, 128.78. 127.99, 127.35 (s, C_6H_5), 98.45 [s, ^1J(CW) = 4.8 Hz, C_5H_4], 97.76 [s, ^1J(CW) = 4.8 Hz, C_5H_4], 91.66 [s, ^1J(CW) = 3.8 Hz, *ipso*-C_5H_4] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = 47.75 (s, SiW), 14.86 (s, SiC_5H_4) ppm. - **IR** (Et_2O): $\tilde{\nu}$ (CO) = 2013.9 (s), 1962.2 (vs), 1913.1 (s) cm^{-1}. - Anal. calc. for $C_{32}H_{24}Cl_2O_3Si_2W$ (767.47): C 50.08, H 3.15; found: C 50.29, H 3.58.

*11) [HMe$_2$Si(C$_5$H$_4$)](OC)$_3$WSiMe$_2$OH (**13**)*

Tricarbonyl[η^5-(dimethylsilyl)-cyclopentadienyl](hydroxydimethylsilyl)tungsten(II)

To a solution of 220 mg (0.45 mmol) **11a** in 20 ml Et_2O were added 10.8 mg (0.60 mmol, 0.02 ml) H_2O and 0.17 g (1.82 mmol, 0.23 ml) NEt_3 while a wite solid began to precipitate. The reaction mixture was stirred for 45 min. and then dried by use of Na_2SO_4. All insoluble material was filtered off and the obtained filtrate was evaporated to dryness giving an oil. The crude product was washed with 2 ml PE at – 30 °C and finally dried in vacuo. Yield: 150 mg (70 %). Red oil. - **^{1}H-NMR** (300.4 MHz, C_6D_6): δ = 4.90 – 4.87 (m, 2 H, H_4C_5), 4.74 - 4.70 (m, 2 H, H_4C_5), 4.37 [sept, ^3J(HSiCH) = 3.6 Hz, 1 H, $\underline{H}SiC_5H_4$], 2.65 (s, 1 H, HOSi), 0.98 (s, 6 H, H_3CSiW), 0.01 [d, ^3J(HCSiH) = 3.6 Hz, 6 H, $\underline{H}_3CSiC_5H_4$] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C_6D_6): δ = 216.16 (s, CO), 96.53 (s, C_5H_4), 95.70 [s, ^1J(CW) = 4.8 Hz, C_5H_4], 93.63 (s, C_5H_4), 11.21 (s, CH_3SiW), -3.17 (s, $\underline{C}H_3SiC_5H_4$) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): 48.23 (s, SiW), -20.17 (s, SiC_5H_4) ppm. - **IR** (PE): $\tilde{\nu}$ (SiH) = 2130.0 (w) cm^{-1}; $\tilde{\nu}$ (CO) = 2011.7 (vs), 1939.0 (vs), 1911.8 (vs) cm^{-1}. - Anal. calc. for $C_{12}H_{18}O_4Si_2W$ (466.27): C 30.91, H 3.89; found: C 30.28, H 3.47.

*12) [HMe$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WSiMe$_2$OH (**14**)*

Dicarbonyl[η^5-(dimethylsilyl)-cyclopentadienyl](trimethylphosphino)-hydroxydimethyl-silyl-tungsten(II)

A solution of 210 mg (0.41 mmol) of **9** was treated with 5.44 ml of (0.49 mmol) DMD (0.09 M in acetone) in 5 ml acetone at −78 °C. The mixture was allowed to warm up to room temperature over four hours. All volatiles were removed in vacuo resulting in a crude solid which was washed with 2 ml PE at room temperature. Yield: 150 mg (71 %). Pale yellow solid. M.p. 50 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.79 (s, 4 H, H$_4$C$_5$), 4.48 [sept, ^3J(HSiCH) = 3.7 Hz, 1 H, HSi], 2.38 (s, 1 H, HOSi), 1.15 [d, ^2J(HCP) = 9.2 Hz, 9 H, H$_3$CP], 0.99 (s, 6 H, H$_3$CSiW), 0.20 [d, ^3J(HCSiH) = 3.7 Hz, 6 H, H$_3$CSiC$_5$H$_4$] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 224.21 [d, ^2J(CWP) = 17.2 Hz, CO], 95.46 - 95.39 (d, C$_5$H$_4$), 95.30 (s, C$_5$H$_4$), 88.93 (s, C$_5$H$_4$), 21.80 [d, ^1J(CP) = 34.1 Hz, CH$_3$P], 2.19 (s, CH$_3$SiW), -2.67 (s, CH$_3$SiH) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): 49.87 [d, ^2J(SiWP) = 13.2 Hz, SiW], -20.83 (s, SiC$_5$H$_4$) ppm. - **^{31}P{^{1}H}-NMR** (121.5 MHz, C$_6$D$_6$): δ = -14.00 [s, ^1J(PW) = 281.9 Hz, PCH$_3$] ppm. - **IR** (PE): $\tilde{\nu}$(SiH) = 2125.3 (w) cm^{-1}; $\tilde{\nu}$(CO) = 1898.9 (vs), 1825.7 (vs) cm^{-1}. - Anal. calc. for C$_{14}$H$_{27}$O$_3$PSi$_2$W (514.34): C 32.69, H 5.29; found: C 31.93, H 4.84.

*13) (η^5-C$_5$H$_4$-SiMe$_2$O-η^1-SiMe$_2$)(OC)$_2$(Me$_3$P)W (**15**) by reaction of*
*   [HMe$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WSiMe$_2$OH (**14**) with DMD*

Dicarbonyl[η^5-cyclopentadienyl-(η^1-1,1,3,3-tetramethylsiloxy)](trimethylphosphino)-tungsten(II)

Analgous to 12) from 150 mg (0.29 mmol) of **14** and 5.44 ml (0.49 mmol) DMD (0.09 M in acetone) in 5 ml acetone resulting in a crude solid which was washed with 2 ml PE at room temperature. Yield: 86 mg (58 %). Pale ocher solid. M.p. 58 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 5.04 − 5.00 (m, 2 H, H$_4$C$_5$), 4.64 − 4.59 (m, 2 H, H$_4$C$_5$), 1.13 (s, 6 H, H$_3$CSiW), 1.12 [d, ^3J(HCP) = 8.4 Hz, 9 H, H$_3$CP], 0.35 (s, 6 H, H$_3$CSiC$_5$H$_4$) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 224.28 [d, ^2J(CWP) = 16.9 Hz, CO], 92.14 (d, C$_5$H$_4$), 91.97 [s, ^1J(CW) = 2.7 Hz, C$_5$H$_4$], 21.55 [d, ^1J(PC) = 33.8

Hz, CH$_3$P], 9.53 (s, CH$_3$SiW), -0.35 (s, $\underline{C}$H$_3$SiC$_5$H$_4$) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): 44.38 [d, ^2J(SiWP) = 14.2 Hz, SiW], 4.93 (s, SiC$_5$H$_4$) ppm. - **^{31}P{^{1}H}-NMR** (121.5 MHz, C$_6$D$_6$): δ = -14.03 [s, ^1J(PW) = 267.3 Hz, PCH$_3$] ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 1905.3 (vs), 1834.0 (vs) cm^{-1}. - Anal. calc. for C$_{14}$H$_{25}$O$_3$PSi$_2$W (512.32): C 32.82, H 4.92; found: C 31.81, H 5.16.

14) (η^5-C$_5$H$_4$-SiMe$_2$O-η^1-SiMe$_2$)(OC)$_2$(Me$_3$P)W (**15**) by reaction of
   [HMe$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WSiMe$_2$Cl (**11c**) with DMD

Analgous to 12) from 250 mg (0.47 mmol) of **11c** and 6.22 ml (0.56 mmol) DMD (0.09 M in acetone) in 5 ml acetone resulting in a crude solid which was washed with 2 ml PE at room temperature. Yield: 157 mg (65 %).

15) [HOPh$_2$Si(C$_5$H$_4$)](OC)$_3$WSiPh$_2$Cl (**16**)

Tricarbonyl[η^5-(hydroxydiphenylsilyl)-cyclopentadienyl](chlorodiphenylsilyl)-tungsten(II)

Analogous to 11) from 520 mg (6.78 mmol) of **12**, 0.2 ml water and 0.2 ml NEt$_3$ in 20 ml Et$_2$O over a period of 30 min. at room temperature. The crude orange product was washed two times each with 4 ml PE at –30 °C and finally dried in vacuo. Yield: 652 mg (87 %). Pale orange solid. M.p. 33 °C (decomp.). - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.88 - 7.84, 7.54 - 7.50, 7.16 - 7.08 [m, 20 H, H$_5$C$_6$Si], 5.05 - 4.96 (m, 4 H, H$_4$C$_5$), 2.25 (s, 1 H, HOSi) ppm. -**^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 218.05 [s, ^1J(CW) = 147.0 Hz, *trans*-CO], 215.59 [s, ^1J(CW) = 152.1 Hz, *cis*-CO], 135.52, 134.99, 132.68, 130.68, 129.20, 128.68. 127.90, 127.30 (s, C$_6$H$_5$), 97.65 [s, ^1J(CW) = 4.8 Hz, C$_5$H$_4$], 97.06 [s, ^1J(CW) = 4.8 Hz, C$_5$H$_4$], 91.86 [s, ^1J(CW) = 3.8 Hz, *ipso*-C$_5$H$_4$] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 47.43 (s, SiW), -0.44 (s, SiC$_5$H$_4$) ppm. - **IR** (Et$_2$O): $\tilde{\nu}$ (CO) = 2015.4 (s), 1960.8 (vs), 1944.7 (s), 1915.1 (vs) cm^{-1}. - Anal. calc. for C$_{32}$H$_{25}$ClO$_4$Si$_2$W (749.02): C 51.31, H 3.36; found: C 51.29, H 3.45.

*16) (η^5-C$_5$H$_4$-SiPh$_2$O-η^1-SiPh$_2$)(OC)$_3$W (**17**)*

Tricarbonyl[η^5-cyclopentadienyl-(η^1-1,1,3,3-tetraphenylsiloxy)]tungsten(II)

^{1}H-NMR (300.4 MHz, C$_6$D$_6$): δ = 7.95 - 7.59, 7.18 - 7.06 [m, 20 H, H$_5$C$_6$Si], 5.18 – 5.07 (m, 2 H, H$_4$C$_5$), 5.03 – 5.00 (m, 2 H, H$_4$C$_5$) ppm.

*17) Ph$_2$Si[(C$_5$H$_4$)(OC)$_3$WSiPh$_2$OH]$_2$ (**18**)*

Bis[tricarbonyl(η^5-cyclopentadienyl)(hydroxydiphenylsilyl)-tungsten(II)]-diphenylsilane

Analogous to 12) from 201 mg (1.66 mmol) of **5** in 10 ml acetone and 10.88 ml (4.90 mmol) of DMD (0.09 M in acetone) at −78 °C. The reaction mixture was allowed to warm up slowly to room temperature during a period of four hours. After evaporation of all volatiles the crude residue was washed several times with each 2 ml PE at −30 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.88 - 7.79, 7.63 - 7.57, 7.34 - 7.25 [m, 30 H, H$_5$C$_6$Si], 5.16 – 5.14 (m, 2 H, H$_4$C$_5$), 5.01 - 4.99 (m, 2 H, H$_4$C$_5$), 3.08 (s, 2 H, HOSi) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 2.78 (s, SiC$_5$H$_4$), 44.56 (s, SiW) ppm. - **IR** (HCCl$_3$): $\widetilde{\nu}$ (CO) = 2015.2 (vs), 1965.5 (vs), 1914.4 (vs) cm^{-1}.

*X-ray analysis of (η^5-C$_5$H$_4$-SiMe$_2$O-η^1-SiMe$_2$)(OC)$_2$(Me$_3$P)W (**15**)*

The data were collected from shockcooled crystals on a BRUKER SMART-APEX diffractometer with D8 goniometer (graphite-monochromated Mo - K$_\alpha$ radiation (λ = 0.71073 Å) equipped with a low temperature device in omega-scan mode at 173(2) K [55]. The data was integrated with SAINT [56] and an empirical absorption correction [56] was applied. The structure was solved by direct methods (SHELXS-97) [57] and refined by full-matrix least squares methods against F^2 (SHELXL-97) [58]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of the hydrogen atoms were calculated by an idealized geometry.

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Chapter V

TUNGSTEN COMPLEXES CONTAINING A η^5-CYCLOPENTADIENYL-BOUND ALKOXYSILYL-GROUP

AND

NOVEL *ANSA*-COMPLEXES FROM DIANIONIC TUNGSTEN PRECURSORS

SUMMARY

Novel tungsten methyl complexes with alkoxysilyl-functionalized cyclopentadienyl ligand of the type $[(MeO)_nMe_{3-n}Si(\eta^5\text{-}C_5H_4)](OC)_3WMe$ [n = 1-3 (**6a-c**)] have been prepared by reaction of the dilithiated $Li[W(\eta^5\text{-}C_5H_4Li)(OC)_3]$ (**3**) with the methoxysilanes $Me_{4-n}Si(OMe)_n$ [n = 1 - 3 (**4a-c**)]. The reaction proceeds via the lithium tungsten anions $Li\{W(CO)_3[(\eta^5\text{-}C_5H_4)SiMe_{3-n}(OMe)_n]\}$ [n = 1 - 3 (**5a-c**)] and includes final treatment with methyliodide. The same reaction with two equivalents of **3** with $Si(OMe)_4$ (**4c**) leads to the formation of the dinuclear tungsten methyl complex $(MeO)_2Si[(\eta^5\text{-}C_5H_4)(OC)_3WMe]_2$ (**8**). If functional silanes like halogenalkylalkoxysilanes are used, synthetical approach to novel *ansa*-complexes containing a lateral silylalkyl bridge between the cyclopentadienyl ligand and the tungsten atom of the type $[\eta^1\text{-}(CH)_{n+1}(MeO)_nMe_{2-n}Si(\eta^5\text{-}C_5H_4)](OC)_3W$ [n = 0 - 2 (**14a-16**)] is given. The compounds **15, 16** and **8**, containing one and two methoxy groups can be converted into the corresponding silanol $[\eta^1\text{-}(CH_2)_2(HO)MeSi(\eta^5\text{-}C_5H_4)](OC)_3W$ (**19**) and even into the silanediols $[\eta^1\text{-}(CH)_3(HO)_2Si(\eta^5\text{-}C_5H_4)](OC)_3W$ (**20**) and $(HO)_2Si[(\eta^5\text{-}C_5H_4)(OC)_3WMe]_2$ (**21**) by reaction with aqueous NaOH. In addition, a tungsten-bound siloxane polymer (**23**) is prepared by a sol-gel process from $Cp(OC)_3W(CH_2)_3Si(OMe)_3$ (**17**) and $Si(OMe)_4$ leading to a xerogel.

INTRODUCTION

The attachment of homogeneous transition metal catalysts to insoluble supports offers the opportunity of extending their usefulness particularly with regard to industrial applications. Consequently, there has been considerable interest in this area over the last few decades [1-15]. The heterogenation offers the possibility to combine the most advantageous properties of both homogeneous and heterogeneous systems [1-3, 6, 7, 9, 13-19]. As support system for organometallic catalysts, organic as well as inorganic materials have been used each offering specific advantages. Organic polymers, such as cross-linked polystyrenes, provide a fairly well-defined enviroment for organometallic species attached to their surface: Silica gel surfaces on the other hand, while less exactly characterized in terms of their structure and reactivity offer distinct advantages in chemical inertness, thermal stability and easy separation from the reaction mixture. Organofunctionalized polysiloxanes prepared by a sol-gel procedure [20-22] represent a class of supports intermediate between those of an organic and inorganic nature, and have received renewed and detailed attention quite recently [4, 23-27]. One of the possibilities of heterogenization of transition metal complexes by using organic or inorganic supports is their coordination via a cyclopentadienyl anchoring ligand having alkoxysilyl groups. In this case, linkage on a support like silica can be realized by condensation leading to the formation of Si-O-Si units, as shown for the dimeric iron complex in figure 1 [28].
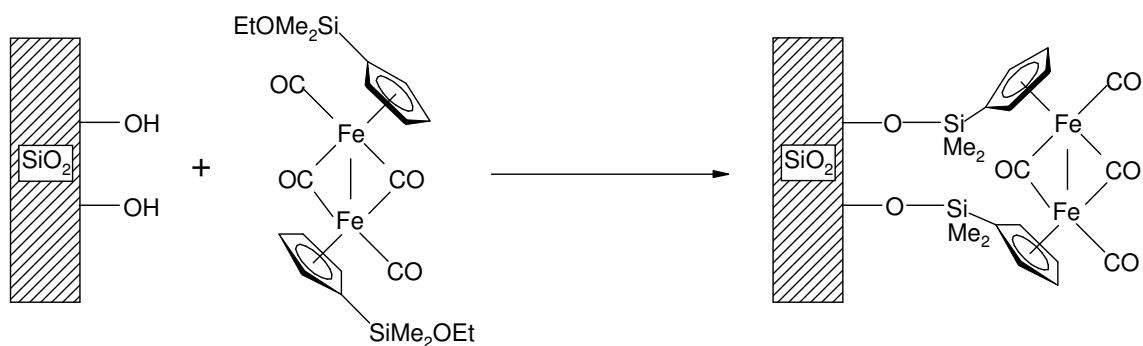

Fig. 1: Immobilization of dimeric iron complex on a silica surface

In the literature only few complexes bearing such a suitable substitution pattern at the cyclopentadienyl ligand are described, among these the dinuclear ruthenium complex $\{\mu\text{-}\eta^5\text{:}\eta^5\text{-}[MeOMe_2Si(C_5H_3)SiMe_2(C_5H_4)]\}Ru_2(CO)_4$ [29] or the cymantrenyl derivatives $[(ROMe_2Si)_n(C_5X_{5-n})]Mn(CO)_3$ (n = 1, 2; X = H, Cl, Br; R = alkyl) [30], should be mentioned, although these complexes were not used for investigations on supports. In contrast, the titanium complexes $[EtOMe_2Si(C_5H_4)]CpTiCl_2$ and $[EtOMe_2Si(C_5H_4)]_2TiCl_2$ have been attached to silica under mild conditions and reduced to afford active hydrogenation catalysts [31]. Silica-support has also been realized for the cobalt derivatives $[(EtO)_nMe_{3-n}Si(C_5H_4)]Co(CO)_2$ (n = 1, 3) which were found to be a catalyst for olefin hydroformylation reactions [28]. In the case of the manganese complex $[MeOMe_2Si(C_5H_4)]Mn(CO)_3$ a single crystal silicon wafer was used as support. This established system served for investigations of photoinduced ligand substitution processes [30, 32].

Important for the following work is the report of *Herrmann* et al. which describes the lithiation of the manganese complex $Cp(OC)_3Mn$ at the cyclopentadienyl ligand with *n*BuLi and the following treatment of the resulting species with $Si(OEt)_4$. The product of this reaction is the triethoxysilyl-functionalized manganese complex $[(EtO)_3Si(C_5H_3)Me](OC)_3Mn$ which was converted into the corresponding silatrane $\{N[(CH_2)_2O]_3Si(C_5H_3)Me\}(OC)_3Mn$ in order to serve for investigations due to their potential as material for applications in non-linear optics (NLO) [33].

The only reported alkoxysilyl-containing halfsandwich complexes of the chromium triad are $[PhOMe_2Si(C_5H_4)](OC)_3MMe$ and $1,4\text{-}C_6H_4\text{-}\{[OMe_2Si(C_5H_4)](OC)_3MMe\}_2$ (M = Mo, W) [34], which were not further inverstigated. In contrast, the chromium zero-valent arene complex $[(EtO)_3Si(C_6H_5)](OC)_3Cr$ was attached on silica [35] or used to create nano-sized chromium clusters in an inorganic-organic xerogels [36, 37]. These amorphous materials are prepared from molecular building blocks using sol-gel chemistry, a mild method for the formation of inorganic oxide linkages. $[(EtO)_3Si(C_6H_5)](OC)_3Cr$ was also co-polymerized with $Si(OMe)_4$ in a sol-gel process, leading to a hydrogenation reactive polymer catalyst. Its activity persisted throughout several cycles, and its significance lies in the recycling feasibility of the catalyst [38].

Our investigations are concentrated on the generation of model compounds containing tungsten as metal center, that represent promising precursors for the anchoring on silica supports.

In this report we present a suitable approach to such tungsten complexes characterized by a cyclopentadienyl-bound alkoxysilyl function and to new *ansa*-type tungsten complexes including their structural determination, as well as experiments concerning the conversion into silanols and tungsten fragment-containing polysiloxanes.

RESULTS AND DISCUSSION

Alkoxysilyl-functionalization of Halfsandwich Tungsten Complexes. In order to introduce the trimethoxysilyl group at the cyclopentadienyl ring, the tungsten methyl complex **1** is treated with *n*BuLi in THF at −78 °C. The resulting lithiated complex $(LiC_5H_4)(OC)_3WMe$ is reacted *in situ* with an excess of tetramethoxysilane by warming up of the reaction mixture to room temperature. After five days a mixture consisting of the targeted complex $[(MeO)_3Si(C_5H_4)](OC)_3WMe$ (**2**) (32 %) and the starting compound **1** is obtained (Eq. 1). Attempts to separate **2** by fractional crystallization in petrolether failed.
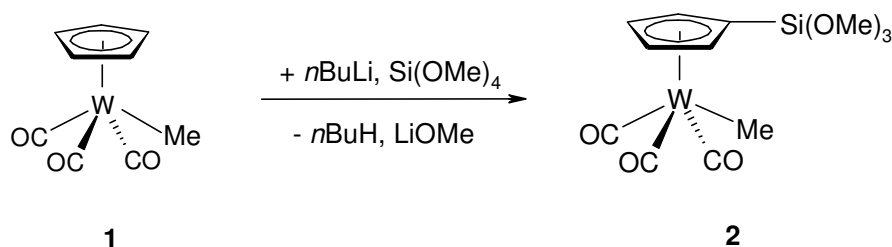
Eq. 1: Synthesis of $[(MeO)_3Si(C_5H_4)](OC)_3WMe$ (**2**) via *in situ*-formed $(LiC_5H_4)(OC)_3WMe$-species.

As recently shown, an attractive route to introduce functional silyl groups at the cyclopentadienyl ligand is offered by reaction of the double lithiated tungsten complex $Li[W(C_5H_4Li)(CO)_3]$ (**3**), characterized by a more nucleophilic behaviour compared to $(LiC_5H_4)(OC)_3WMe$, with chlorodiorganosilanes [39-41]. The reactions of **3** with $Me_{4-n}Si(OMe)_n$ (**4a-c**) are carried out in THF at room temperature and lead after 18 hours reaction time to the lithium methoxysilylcyclopentadienyl tungsten salts **5a-c** (Scheme 1), obtained as beige, pyrophoric powders. The treatment of **5a-c**, suspended in petrolether with an excess of methyliodide or acetic acid in petrolether results heterogeneously in the formation of the neutral alkoxysilyl-functionalized complexes $[(MeO)_nMe_{3-n}Si(C_5H_4)](OC)_3WR$ [n = 1 - 3, R = Me (**6a-c**); n = 3, R = H (**2**)], which are isolated in good yields (78 – 84 %) as orange (**6c**) and yellow (**2, 6a,b**) solids. **2, 6a-c** show increasing solubility in the row PE < Et₂O << benzene ~

chlorform, are stable at room temperature and can be stored under nitrogen atmosphere at -30 °C over months.
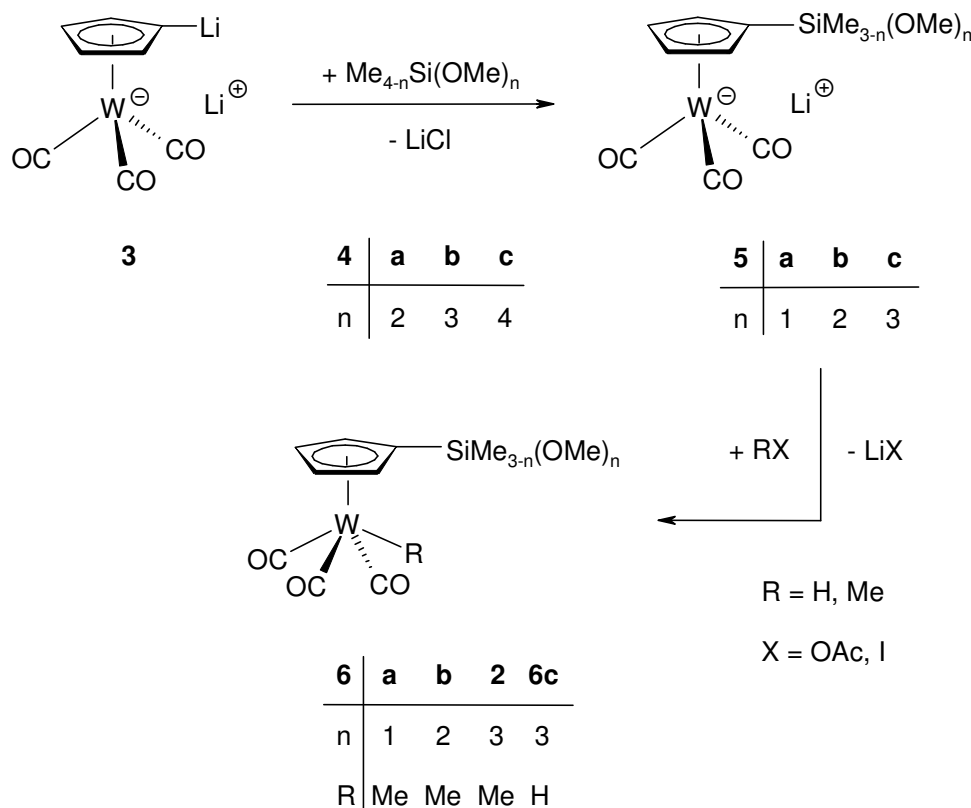
Scheme 1: Alkoxysilyl-functionalization of the η^5-cyclopentadienyl ligand of a halfsandwich tungsten complex.

For **2, 6a,b**, the ^{29}Si{^{1}H}-NMR resonance is shifted more to higher field as the number of methoxy groups attached to the silicon atom increases. This fact is illustrated by the values of 7.22 (**6a**), -16.08 (**6b**) and -56.01 (**2**) ppm (^{29}Si-NMR values of alkoxysilyl complexes are summed up in table 1 in the experimental section). The value of the monomethoxy-**6a** is very similar to that of the reported phenoxysilyl halfsandwich complexes [PhOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe and 1,4-C$_6$H$_4$-{[OMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe}$_2$, whose resonances are found at 6.90 and 7.05 ppm [34]. Complexes **2** and **6c**, bearing a trimethoxysilyl group, exhibit ^{29}Si-resonances, which are shifted approximately 10 ppm high-field in comparison to ferrocene complexes showing the same substitution pattern at the cyclopentadienyl ligand - the only

examples for which ^{29}Si-NMR values have been determined {e.g. [(MeO)$_3$Si(C$_5$H$_4$)]$_2$Fe: -45.70 ppm} [42]. The ^{1}H-NMR spectra in C$_6$D$_6$ of **2**, **6a-c** exhibit a virtuel triplett evoked by an AA'BB'-spin system for the two inequivalent pairs of cyclopentadienyl ring protons, characteristic for a monosubstituted cyclopentadienyl ligand. The $\tilde{\nu}$ (CO) wave numbers of **2, 6a,b** are in the expected range for terminal carbonyl ligands of methyl tungsten complexes.

The 2:1-stoichiometric reaction of **3** with Si(OMe)$_4$ (**4c**) in THF results after four days stirring at room temperature in the formation of the dilithium ditungsten salt **7** which is isolated as a pale beige solid, showing the expected pyrophoric feature for a tungstate. **7** enables the generation of neutral species containing two metal fragments attached to one silicon atom via the η^5-cyclopentadienyl ligand (Scheme 2). The heterogeneous conversion of **7** in cyclohexane with an excess of methyliodide affords after two hours stirring at ambient temperature the dinuclear complex (MeO)$_2$Si[(C$_5$H$_4$)(OC)$_3$WMe]$_2$ (**8**) in 76 % yield.
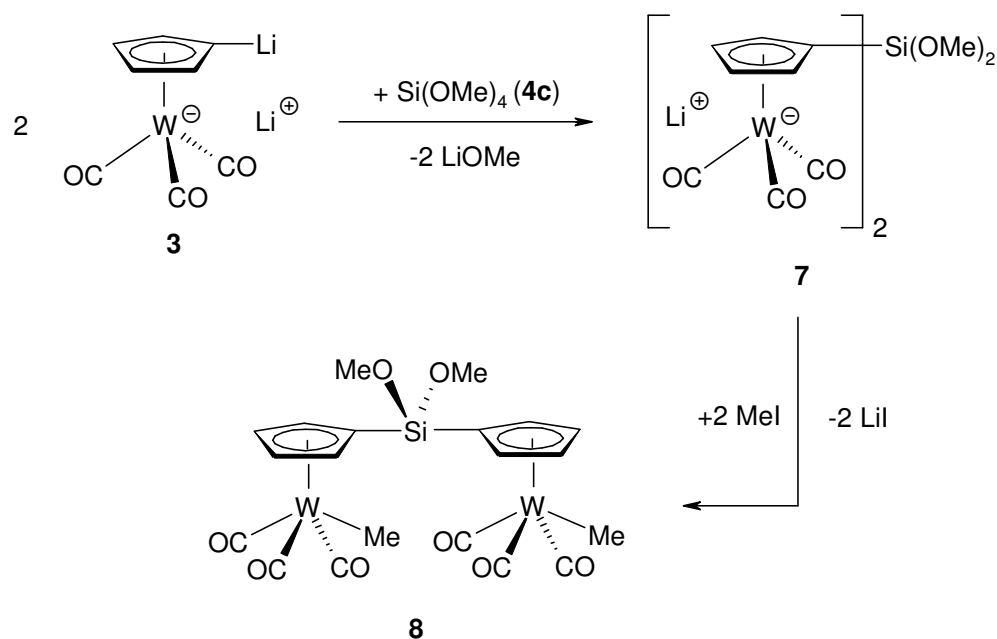
Scheme 2: Synthesis of a tungsten complex containing two metal fragments bridged by a (MeO)$_2$Si-unit via dilithium ditungstate (**7**).

8 shows a good solubility in benzene and chloroform and is isolated as yellow solid which can be handled at air for a short time. The $^{29}Si\{^1H\}$-NMR resonance of **8** is found at –32.90 ppm and differs strongly from that of the dimethoxysilyl-substituted mononuclear complex **6b** (^{29}Si: -16.08 ppm).

8 can serve as starting material for the synthesis of trinuclear MeOSi-bridged complexes by treatment of it with a further equivalent of **3**. Such complexes with two or maybe even three metal fragments are interesting for investigations in heterogenization chemistry because the linkage of such systems could guarantee a high metal density on a support or in a polysiloxane formed via sol-gel process.

Reaction of the type outlined in scheme 1 or 2 is also usable to realize introduction of a (MeO)$_2$Si-functionalized tether with a phosphino group, suitable for subsequent coordination at the tungsten center. Upon treatment of the dilithiated complex **3** with (2-diphenylphosphino)-ethyltrimethoxysilane (**9**) in THF creates after three days at ambient temperature the lithium tungstate Li{W(CO)$_3$[(C$_5$H$_4$)Si(MeO)$_2$(CH$_2$)$_2$PPh$_2$]} (**10**) (Scheme 3) [1]. The pyrophoric **10** is obtained in high yield of 91 % as a crystalline orange solid.

The structure of **10** is confirmed by ^1H- and $^{31}P\{^1H\}$-NMR spectroscopy with the ^{31}P-NMR resonance appearing at –10.44 ppm. The formation of the *ansa*-complex [η^1-PPh$_2$(CH$_2$)$_2$(MeO)$_2$Si(η^5-C$_5$H$_4$)](OC)$_2$WH (**12**) is initiated by the addition of acetic acid to a suspension of **10** in PE and occurs via the tungsten hydrido complex **11** which bears a non-coordinated phosphino group. **11** is generated as an intermediate and undergoes rapidly ring closure, indicated by CO-bubbling out of the reaction mixture which starts immediately after the addition of the acid. This process is finished after 18 hours and gives a mixture of *cis*- and *trans*-substituted isomers in a ratio of about 40:60, illustrated by doubling of the W-H- and W-P resonances in the ^1H- and $^{31}P\{^1H\}$-NMR spectra. The compound **12** is obtained as beige solid in just moderate

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[1] First attempts involve the treatment of Cp(OC)$_3$WMe with *n*BuLi, followed by addition of (2-diphenylphosphino)-ethyltrimethoxysilane, similar to the reaction referred to equation 1. However, the *in situ*-generated (LiC$_5$H$_4$)(OC)$_3$WMe is not reactive enough for methoxy substitution and after three hours reaction time only starting material has been isolated.

yield of 41 % due to decomposition, indicated by a dark brown precipitate formed during the reaction.
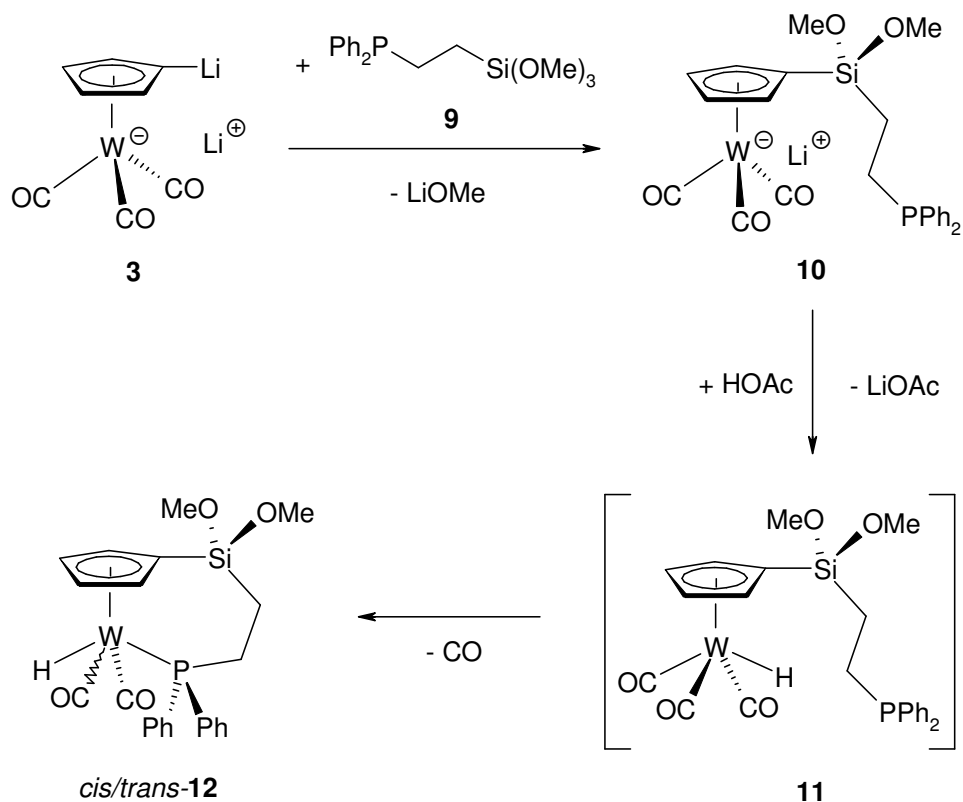
Scheme 3: Synthesis of an *ansa*-complex with a chelating silylalkylphosphine bridge between the cyclopentadienyl ligand and the tungsten center (**12**).

12 opens a synthetical approach to halfsandwich tungsten complexes bearing both alkoxysilyl- and silanol groups in the same molecule, which is topic of current investigations. In sol-gel processes it should be possible to co-condensate the silanol group in order to formate new arrangements of metal fragement-substituted polysiloxanes while the cyclopentadienyl-bound alkoxysilyl function is serving as the co-reagent. Silanol formation might be achieved by deprotonation of **12** and following reaction of the generated lithium tungstate with functional chlorosilanes and final conversion to a tungsten-silanol by hydrolysis or use of dimethyldioxirane as it was already described for $Cp(R_3P)(OC)_2WSiMe_2OH$ (R = Me, Ph) [43].

The dilithium tungsten salt **3** can be used in a surprisingly easy manner to synthesize *ansa*-type complexes bearing a lateral silylalkyl bridge between the cyclopentadienyl ligand and the tungsten atom. The synthetic approach to these novel type of *ansa*-complexes involves the reaction **3** with a stoichiometric amount of an haloalkylalkoxysilanes (**13a-e**) at –78 °C in THF. After the addition of the silane, the suspended **3** dissolved immediately and the solution has been allowed to warm up afterwards to room temperature. When **3** is reacted over the period of three hours with the bifunctional (chloromethyl)-*iso*propoxydimethylsilane (**13a**), (2-chloroethyl)-dimethoxymethylsilane (**13d**) or (3-iodopropyl)-trimethoxysilane (**13e**), respectively the conversion proceeds regioselectively and lead cleanly to the novel *ansa*-compounds $[\eta^1\text{-}(CH)_{n+1}(MeO)_n Me_{2-n}Si(\eta^5\text{-}C_5H_4)](OC)_3W$ (n = 0 - 2), bearing an intramolecular ring including one (**14a**), two (**15**) or three (**16**) carbon atoms between the tungsten and the silicon atom (Scheme 4).

13	a	b	c
n	1	2	3
R	*i*Pr	Et	Me

14	a	b	c
R	Me	Me	OMe
R'	Me	OEt	OMe
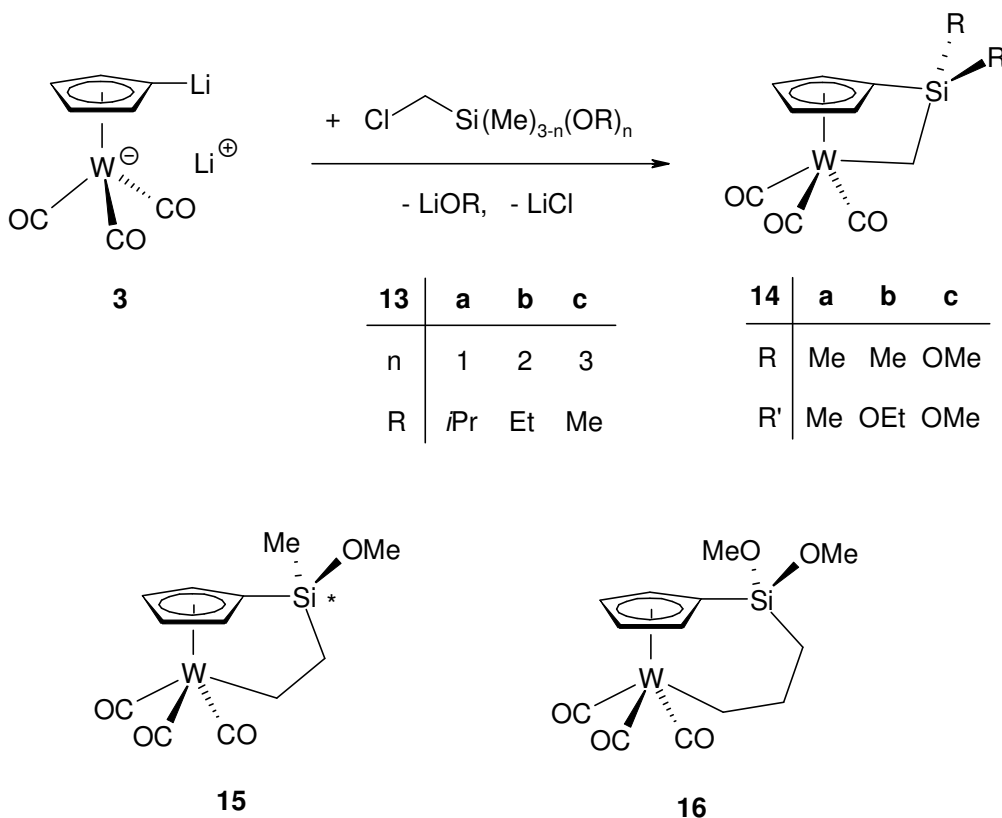
Scheme 4: Synthesis of *ansa*-type complexes containing a silylalkyl bridge between the tungsten atom and the η^5-cyclopentadienyl ligand. This fundamental method allows variation of the chainlength as well as the number of alkoxy groups being attached to the silicon.

These compounds are obtained in good yields (70 – 81 %) as yellow (**14a, 16**) and red (**15**) solids which are all stable at room temperature and can be handled at air for short time. The complex **14a** shows even after weeks of air exposition no signs of decomposition and is stable towards water over the period of some days even in the presence of acetic acid. These features differs strongly from the ethyl-chelated $[\eta^1\text{-}$ $CH_2CH_2(\eta^5\text{-}C_5H_4)](OC)_3W$ derivative, which is very moisture sensitive and thermally unstable [44].

The analogous reaction of **3** with (chloromethyl)-diethoxymethylsilane (**13b**) and (chloromethyl)-trimethoxysilane (**13c**), but with prolonged period of 18 hours, also gives the expected *ansa*-type compounds **14b**,**c**. However, the targeted **14b**,**c** are not obtained as the main products (Fig. 2). In the first reaction an oil is obtained consisting of **14b** in about 20 % yield and a further cyclopentadienyl-substituted compound of unknown structure without a stereo center in a ratio of ca. 60:40. The second reaction leads to only very small amounts (less than 10 %) of **14c** (Fig. 2) accompanied by some others unknown neutral and ionic side-products. An isolation of pure **14c** from this product mixture failed.

These findings shows that the increasing amount of alkoxy groups at the silicon atom of the chloromethyl-alkoxysilane leads to a preferrence of side-reactions and as a consequence reduces the yield of the desired *ansa*-complexes.

The reaction of **3** with the disiloxane $(ClCH_2Me_2Si)_2O$ results unexpectedly very clean in the formation of **14a**. Apparently via cleavage of the Si-O-Si-unit induced by a preferred attack of **3** at the silicon instead of halogenide substitution. The applied 2:1-stoichiometric ratio of **3** and the disiloxane emerged from the intention to synthesize the disiloxane-bridged $Li_2\{\{W(CO)_3[(C_5H_4)CH_2SiMe_2]\}_2O\}$-species which contains a spacing methylene unit between the cyclopentadienyl ligand and the silyl group.

The proposed structures of **14a** - **16** are proved spectroscopically (^{1}H-, ^{13}C- and ^{31}Si-NMR, MS, IR) and in the case of **14a** and **16** by x-ray diffraction analyses, as well. The ^{1}H-NMR spectra of **14a** and **16** show two multiplets corresponding to an AA'BB'-spin system observed for the substituted cyclopentadienyl ring, and demonstrate the C_S symmetry of the distorted four legged piano stool structure of these compounds. The spectrum of **15** reveals four multiplets for the cyclopentadienyl ligand evoked by the stereo center at the silicon atom, which is also responsible for the existence of two signals in the ^{13}C\{^{1}H\}-NMR spectrum for the diastereotopic carbonyl ligands *cis*

to the bridging group. A special spectroscopic feature of the metallacycle **14a** is the unusual high-field resonance at -61.05 ppm for the CH_2-carbon atom in the $^{13}C\{^1H\}$-NMR spectrum and which is almost similar to the value of $[\eta^1\text{-}CH_2CH_2(\eta^5\text{-}C_5H_4)](OC)_3W$ (δ = -61.7 ppm). For the related 1-sila-3-metallacyclobutane $[\eta^1\text{-}CH_2SiMe_2(\eta^5\text{-}C_5H_4)](OC)_2Fe$ a $^{13}C\{^1H\}$-NMR chemical shift of -53 ppm was found, indicating significant influence of the metal on the chemical shift. But in contrast to **14a**, the iron complex is only stable in solution for several hours and demands replacement of the methyl groups by more bulky groups (e.g. *n*-butyl) to increase the thermal stability [45]. The methylene bridge of **14a** shows two pairs of satellites resonances caused by ^{29}Si- and ^{183}W-atoms with the coupling constants $^1J(CSi)$ of 52.1 and $^1J(CW)$ of 21.0 Hz. The $^{29}Si\{^1H\}$-NMR resonances are detected at -12.18 (**14a**), 7.10 (**15**) and -15.26 (**16**) ppm, respectively. The values of **16** and **15** lie very close to those of the dimethoxysilyl- and monomethoxysilyl complexes **6b** (-16.08 ppm) and **6a** (7.22 ppm) (see Tab. 1). The $\tilde{\nu}$ (CO) wave numbers in the complexes **14-16** are found in the expected range for terminal carbonyl ligands of alkyl-substituted tungsten complexes.

The following reaction is performed in order to synthesize the *ansa*-complex **16** by an inverse ring closure. For this purpose, the required 3-trimethoxysilyl-propyl-functionalized tungsten complex $Cp(OC)_3W(CH_2)_3Si(OMe)_3$ (**18**) is synthesized by reaction of the lithium tungstate $Li[W(CO)_3Cp]$ (**17**) with (3-iodopropyl)-trimethoxysilane (Scheme 5).

After stirring over a period of five hours in DME at room temperature, **18** is obtained in 73 % yield as pale yellow and air-stable solid which shows a good solubility in solvents like PE or Et_2O.

However, the lithiation of **18** with *n*BuLi in THF at -78 °C doesn`t lead to the formation of **16** but instead to a mixture consisting of three compounds. Two of them are ^{1}H-NMR spectrsocopically identified as the starting complex **18** and $Cp(OC)_3W(CH_2)_3Si(OMe)_2n$Bu while the third one is unknown at this time. None of the observed compounds show the for **16** expected two multiplets for the ring protons characteristic for mono-substituted cyclopentadienyl ligands. It seems that under these conditions the methoxy substitution at the silicon is more preferred than the deprotonation of the cyclopentadienyl ring.
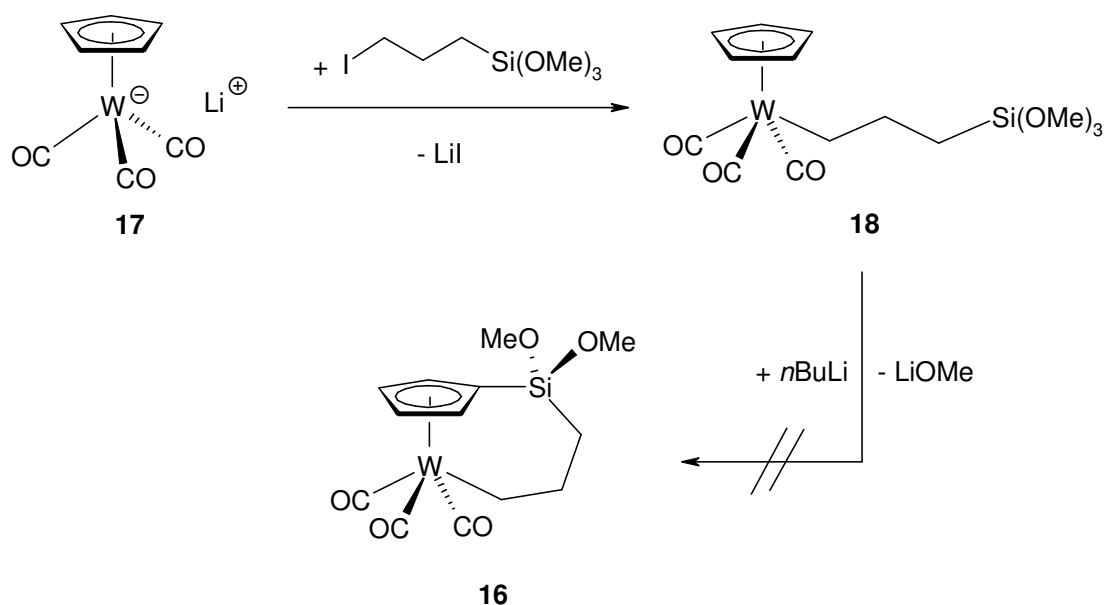
Scheme 5: Alternative attempt for the synthesis of **16** by an inverse ring closure

Reactivity of Alkoxysilyl-functionalized Tungsten Complexes. As recently shown it is possible to transform a cyclopentadienyl-bound methoxysilyl group of a tungsten complex into the corresponding silanol by use of aqueous sodium hydroxide in diethylether [40]. Such a reaction leads in the case of the *ansa*-complex **15** after one week to the corresponding silanol $[\eta^1\text{-(CH}_2)_2\text{(HO)MeSi}(\eta^5\text{-C}_5\text{H}_4)](\text{OC})_3\text{W}$ (**19**) (Eq. 2). Compared to the methoxysilyl compound **15**, the $^{29}\text{Si\{H\}}$-NMR signal of the silicon atom of **19** (δ = 5.01 ppm) is shifted ca. 2.1 ppm to higher field, which is in good accordance with the findings concerning other tungsten complexes with cyclopentadienyl-bound silanol group [39-41, 46].
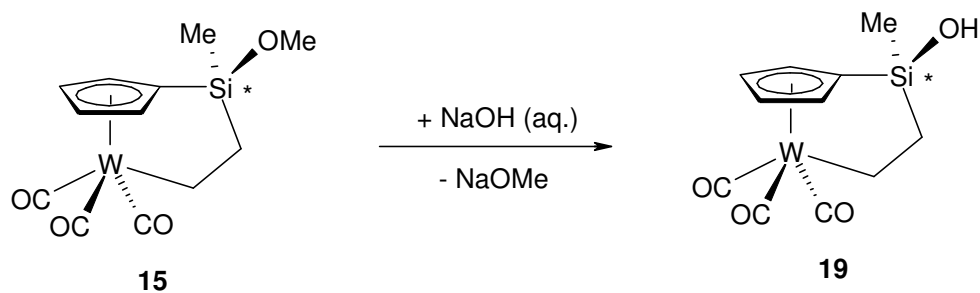
Eq. 2: Synthesis of the silanol-functionalized *ansa*-tungsten complex **19**.

The same reaction conditions allow even the conversion of **16** into the corresponding silanediol $[\eta^1\text{-}(CH_2)_3(HO)_2Si(\eta^5\text{-}C_5H_4)](OC)_3W$ (**20**) when the reaction period is extended to two weeks (Fig. 2). Interestingly, the $Si(OMe)_2$-bridged **8** undergoes also clean transformation to the silanediol $(HO)_2Si[(\eta^5\text{-}C_5H_4)(OC)_3WMe]_2$ (**21**). Both silandiols - the first examples of halfsandwich complexes bearing cyclopentadienyl-bound silanediol functions - show no condensation involving the HO-Si groups neither in solution nor in the solid state. The only reported complexes containing an $Si(OH)_2$ moiety at the cyclopentadienyl ring are of the ferrocenyl-type (e.g. $[(HO)_2MeSi(C_5H_4)]FeCp$ or $(HO)_2Si[(C_5H_4)FeCp]_2)$, which were shown to be stable also in the case of small organo groups attached to the silicon atom [47-50]. **20** and **21** are obtained as beige (**20**) and yellow (**21**) solids showing a good solubility in acetone or chloroform.

20   **21**
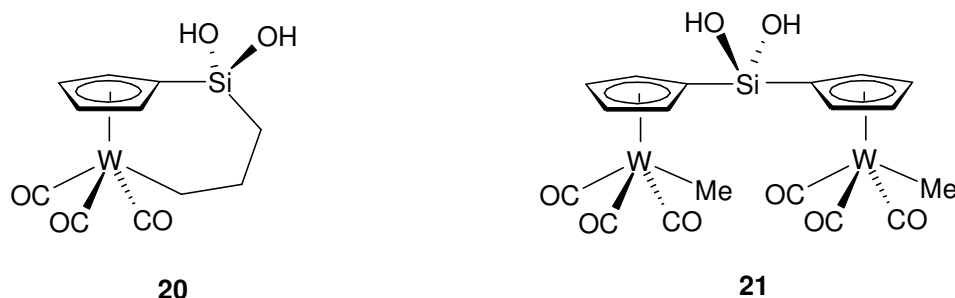
Fig. 2: Complexes **20** and **21** with silanediol groups being attached to the cyclopentadienyl ligand deriving from the $Si(OMe)_2$-precursors **16** and **8**.

The ^{1}H-NMR resonance for the protons of the silandiol group is observed at 2.88 ppm for **20** (D_6-acetone) and at 2.30 ppm for **21** (D_6-benzene). The ^{29}Si-NMR resonances are found at -20.08 (**20**, D_6-acetone) and at -34.35 ppm (**21**, D_6-benzene), very strongly highfield-shifted in relation to common tungsten-silanediols (^{29}Si-NMR: 44.8 and 50.5 ppm for $(C_5R_5)(OC)_2(Me_3P)WSiMe(OH)_2$, R = H, Me). The ^{29}Si-NMR resonance for **20** is about 4 ppm highfield-shifted in comparison to the ferrocenyl-silanediol $[(HO)_2MeSi(C_5H_4)]FeCp$ [^{29}Si-NMR (D_6-DMSO): -16.5 ppm] and about 9 ppm for **21** to the related silanediol-bridged dinuclear ferrocenyl complex $(HO)_2Si[(C_5H_4)FeCp]_2$ [^{29}Si-NMR (D_6-DMSO): -25.1 ppm] [49, 50].

The structure of silanediol **20** is confirmed by NMR- and mass-spectroscopy, while the chemical proof of the existence of the silanediol **21** is given by the transformation into the corresponding trisiloxane $(HMe_2SiO)_2Si[(C_5H_4)(OC)_3WMe]_2$ (**22**) by use of an excess of $Me_2Si(H)Cl$ in the presence of NEt_3 (Eq. 3).
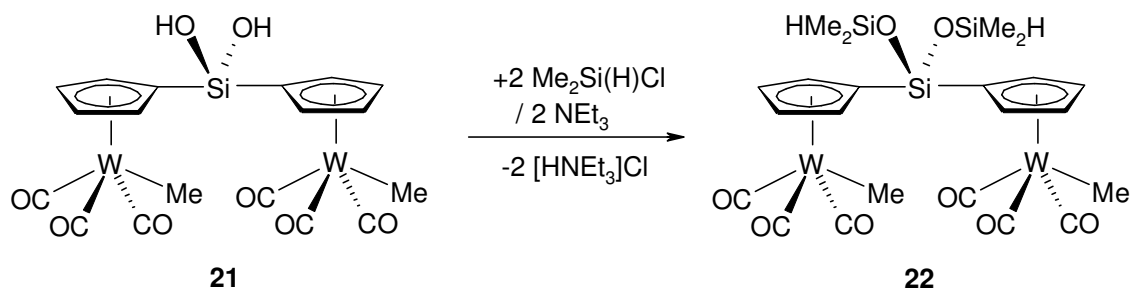
Eq. 3. Chemical proof of the existence of the $(HO)_2Si$-function by transformation into the corresponding trisiloxane **22** by use of $Me_2Si(H)Cl$.

In a first experiment it was tried to build up a metal fragment-substituted polysiloxane by a simple sol-gel process. The heterogenization of the tungsten complex **18** is realized by co-polymerization with an excess of $Si(OMe)_4$ in a 6:1-THF/MeOH solvent mixture, in the presence of excess water and catalytical amounts of $(nBu)_2Sn(OAc)_2$ [51] (Eq. 4). The ratio of **18** and co-reagent is 1:4 and the reaction has been stirred over the period of one week at room temperature. After work up the polysiloxane **23** is obtained as pale brown solid material which is in contrast to **18** not soluble in benzene, chloroform or even acetone.
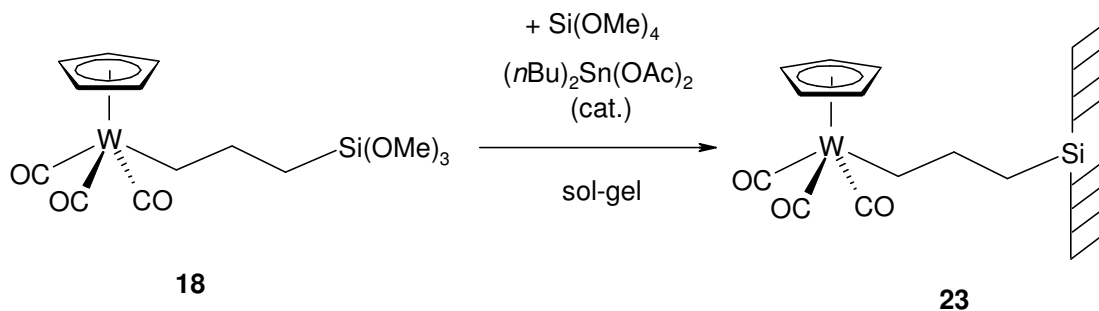
Eq. 4: Formation of the sol-gel tungsten complex-substituted polysiloxane **23**.

For this reason solid state ^{29}Si- and ^{13}C-MAS NMR investigations have been recorded. The ^{13}C-VACP/MAS NMR spectrum reveals a broad signal at 92.44 ppm, characteristic for the area of metal-coordinated cyclopentadienyl ligands, indicating that the polysiloxane apparently contains the complex tungsten fragment. The ^{29}Si-CP/MAS NMR spectrum gives information about the condensation degree, revealing that the metal-incorporated material contains only T^2- [Cp(OC)$_3$W-(CH$_2$)$_3$Si(OMe)(OSi)$_2$] and T^3- [Cp(OC)$_3$W(CH$_2$)$_3$Si(OSi)$_3$] substructures (in the ratio of ca. 2:3) which is indicated by the broad signals at -61 and -68 ppm. The metal fragment-substituted polysiloxane **23** is very stable at room temperature and can be handled for long time under air-exposition.

X-ray Diffraction Analyses. The molecular structures of $[\eta^1\text{-CH}_2\text{Me}_2\text{Si}(\eta^5\text{-}$ $\text{C}_5\text{H}_4)](\text{OC})_3\text{W}$ (**14a**) and $[\eta^1\text{-(CH}_2)_3(\text{MeO})_2\text{Si}(\eta^5\text{-C}_5\text{H}_4)](\text{OC})_3\text{W}$ (**16**), which to the best of our knowledge are the first structurally characterized tungsten *ansa*-complexes containing a silicon-carbon bridge, are confirmed by X-ray diffraction studies (Figure 3 - 6). Yellow crystals of **14a** and **16**, suitable for X-ray analysis, are obtained in both cases from saturated benzene solutions at room temperature.
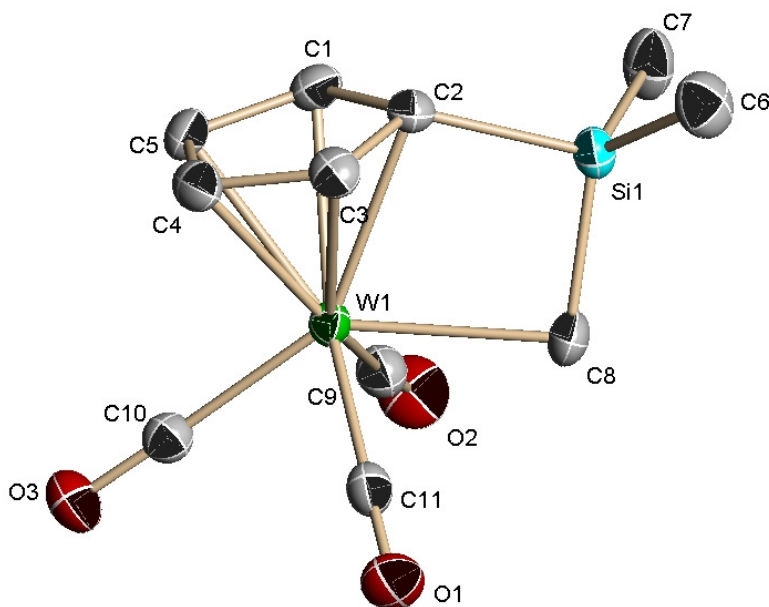
Fig. 3: Molecular structure of $[\eta^1\text{-CH}_2\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{H}_4)](\text{OC})_3\text{W}$ (**14a**) with the atomic labeling scheme. Ellipsoids are drawn at the 50 % probability level, and the hydrogen atoms have been omitted for the sake of clarity.

Selected bond lengths [Å], bond and torsion angles [°]: W1-C8 2.353(3), W1-C9 1.984(3), W1-C10 2.003(3), W1-C11 1.977(3), C2-Si1 1.877(3), Si1-C8 1.855(3), Si1-C7 1.860(3), Si1-C6 1.858(3), C11-W1-C8 74.38(11), C9-W1-C8 76.75(11), C11-W1-C10 79.80(11), C9-W1-C10 81.31(11), C10-W1-C8 140.16(10), C11-W1-C9 104.89(11), C8-Si1-C6 115.80(15), C8-Si1-C7 112.49(15), C6-Si1-C7 111.30(16), Si1-C2-W1 94.54(11), C8-Si1-C2 96.26(12), C6-Si1-C2 111.15(15), C7-Si1-C2 108.76(13), Si-C8-W1 94.65(11), Cp$_Z$-C2-Si1 152.8, W1-C8-Si1-C2 11.42(13), C4-C3-C2-Si1 −147.06(21).

The ligands of **14a** and **16** are disposed in a distorted four-legged piano stool fashion similiar to that established for analogous tricarbonyl cyclopentadienyl group 6 metal complexes [52-56]. The angles between contiguous ligands range from 72.7(2) to 79.1(2)° (**16**) and from 74.38(11) to 81.31(11)° (**14a**), characteristic for this type of structure. The W-C(sp^3) bond distances amounts to 2.341(6) (W1-C9) (**16**) and 2.353(3) Å (W1-C8) (**14a**) and are slightly longer than those of ordinary tungsten methyl complexes [2.293(9) – 2.309(6) Å [34, 40, 57]] but lie in the range for reported alkyl groups bound to a d^4-tungsten center [58, 59] and are very close to that of the ethyl-chelated derivative [η^1-CH$_2$CH$_2$(η^5-C$_5$H$_4$)](OC)$_3$W [2.36(1) Å] [44]. The angle between the *trans*-positioned alkyl- and carbonyl ligands of 131.5(2)° (C7-W1-C9) of **16** is very similar to reported ones of tungsten methyl complexes [34, 40, 57-59]. In contrast, the analogous angle in **14a** is enlarged to 140.16(10)° (C10-W1-C8) but does not reach the value of 147.7(4)° found in [η^1-CH$_2$CH$_2$(η^5-C$_5$H$_4$)](OC)$_3$W.

The structure-determining four-membered ring W1-C8-Si1-C2 in **14a** shows a butterfly geometry with a torsion angle of 11.42(13)° (Fig. 4). For the silicon a tetrahedral arrangement with carbon-silicon bond lengths in the normal range from 1.855(3) Å (C2-Si1) to 1.877(3) Å (Si1-C8) is found. The angles within the four-membered ring indicate a degree of ring strain for this unusual structural arrangement and lie between 72.66(9)° (C2-W1-C8) and 96.26(12)° (C8-Si1-C2) which differ significantly from the values for normal tetrahedral angles. Consequently, a slight enlargment of the exocyclic C-Si-C angle to 111.3(16)° is observed.
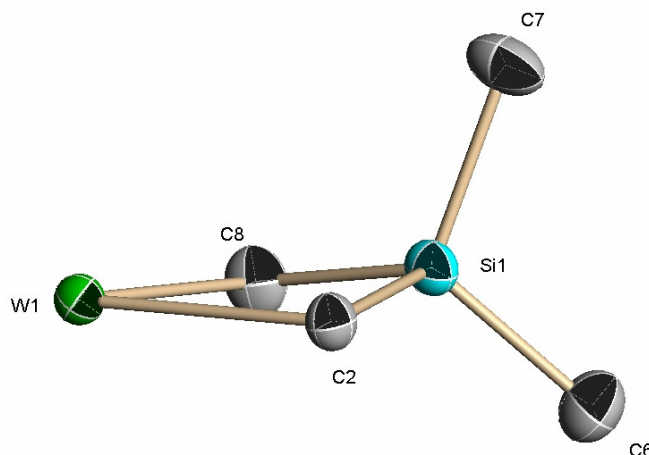
Fig. 4: Butterfly geometry of the four-membered ring of the 1-sila-3-metallacyclobutane **14a**.

In the *ansa*-complex **14a** the silicon atom is strongly bent beneath the cyclopentadienyl plane, illustrated by the torsion angle of −147.06(21)° (C4-C3-C2-Si1), which is large in comparison to that of **16** [Si1-C4-C5-C1 -174.5(3)] (Fig. 5).
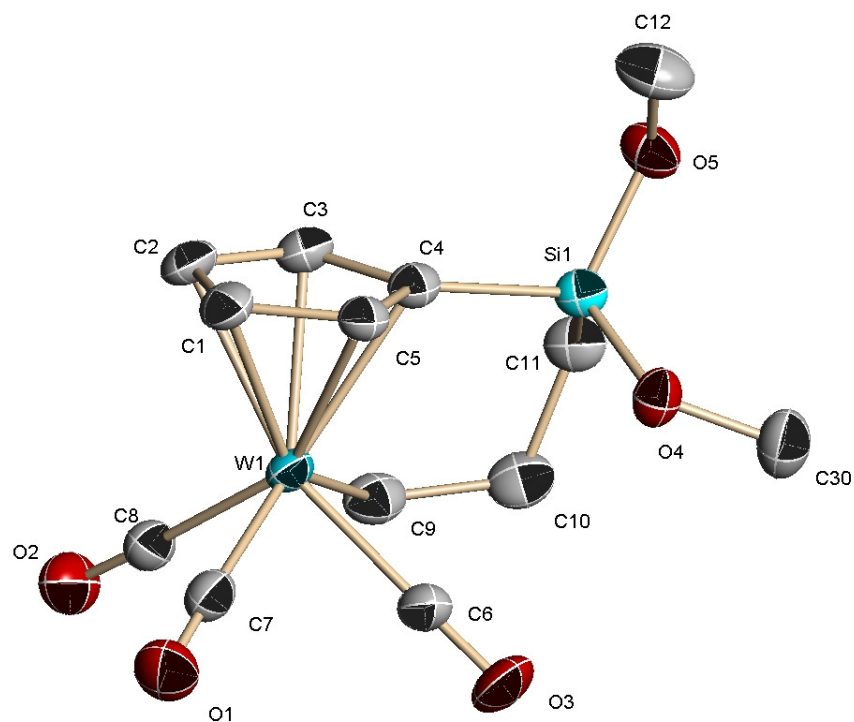
Fig. 5: View of the molecular structure of $[\eta^1\text{-}(CH_2)_3(MeO)_2Si(\eta^5\text{-}C_5H_4)](OC)_3W$ (**16**) with the atom-numbering scheme. Ellipsoids are drawn at the 50 % probability level, and the hydrogen atoms have been omitted for the sake of clarity.

Selected bond lengths [Å], bond and torsion angles [°]: W1-C8 1.980(5), W1-C6 1.983(5), W1-C7 1.987(5), W1-C9 2.341(6), Si1-O4 1.630(3), Si1-O5 1.631(3), Si1-C4 1.846(5), Si1-C11 1.850(5), C9-C10 1.534(8), C11-C10 1.522(7), C8-W1-C6 106.5(2), C8-W1-C7 79.1(2), C6-W1-C7 76.75(19), C8-W1-C9 72.7(2), C6-W1-C9 74.7(2), C7-W1-C9 131.5(2), O4-Si1-O5 111.6(2), O4-Si1-C4 105.03(19), O5-Si1-C4 111.11(19), O4-Si1-C11 112.8(2), O5-Si1-C11 106.7(2), C4-Si1-C11 109.6(2), C10-C9-W1 120.5(4), C10-C11-Si1 114.2(3), C11-C10-C9 116.6(4), Si1-C4-C5-C1 -174.5(3), C9-W1-C4-Si1 -40.0(3), C4-Si1-C11-C10 -63.3(4).

The *ansa*-complex **16** contains a six-membered ring which adopts a chair-like conformation formed by the atoms W1, C4, Si1, C11, C10, and C9 (Fig. 6). C4, Si1, C10 and C9 lie nearly in one plane, while W1 and C11 are located above and beneath this plane, illustrated by the torsion angles of -40.0(3)° (C9-W1-C4-Si1) and -63.3(4) (C4-Si1-C11-C10).
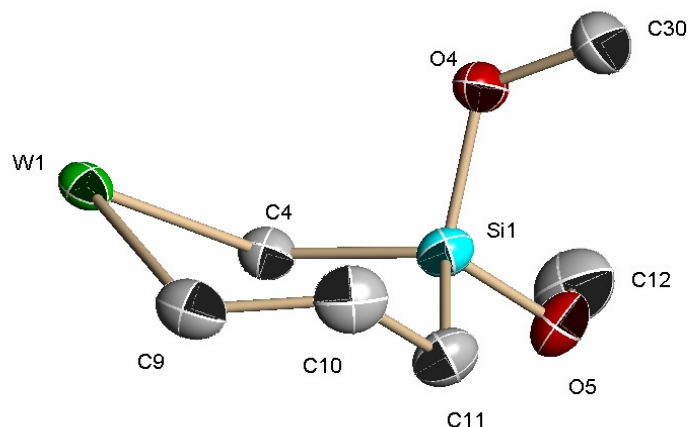
Fig. 6: Chair-like conformation of the six-membered ring found in compound **16**, viewed in the absence of some ancillary atoms for clarity.

Crystal Data for Compounds **14a** and **16**

	16)	14a)
mol formula	$C_{13}H_{16}O_5SiW$	$C_{11}H_{12}O_3SiW$
mol wt	464.20	404.15
wavelength (Å)	0.71073	0.71073
temp (K)	173(2)	173(2)
cryst size (mm)	0.3 x 0.2 x 0.157	0.30 x 0.25 x 0.25
cryst syst	triclinic	monoclinic
space group	P1	P2(1)/c
a (Å)	7.9821(8)	6.6756(16)
b (Å)	10.0363(11)	13.068(3)
c (Å)	10.4003(11)	14.617(3)

α (°)	96.090(2)	90.0(0)
β (°)	108.005(10)	100.676(4)
γ (°)	103.664(2)	90.0(0)
vol (Å^3), Z	755.35(14)	1253.0(5)
ρ (calcd) (Mgm^{-3})	2.041	2.124
F(000)	444	760
μ (mm^{-1})	7.740	9.303
θ range for data collecn (deg)	2.10 – 25.06	2.11 – 27.50
no. of rflns collected	9868	24036
no. of indep reflns	2632	2858
abs cor.	empirical	empirical
no. of data/restraints /params	2632 / 0 / 183	2858 / 0 / 147
goodness of fit on F^2	1.082	1.086
R1[a]	0.0276	0.0209
wR2[b]	0.0703	0.0481
largest diff peak and hole (eÅ^{-3})	1.925 and −1.157	0.741 and −0.855

R1 = $\Sigma||F_0| - |F_c||/\Sigma|F_0|$ for reflections with $I > 2\sigma(I)$. wR2 = $[\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_0^2)/3$ and a and b are constants set by the program.

CONCLUSION

A new and convenient method for the preparation of tungsten complexes with alkoxysilyl group attached to the cyclopentadienyl ligand has been established. It enables the functionalization with silyl groups containing one, two or even three alkoxy moieties and furthermore the formation of $(MeO)_2Si$-bridged dinuclear tungsten complexes. The same strategy gives also access to a novel kind of *ansa*-complexes with a lateral silylalkyl bridge connecting the cyclopentadienyl ring and the tungsten center. It is possible to vary easily the bridging element for example by use of phosphino groups. All synthesized compounds show a high stability which make them easy to handle. The alkoxy groups allow the conversion into the corresponding silanols and even silanediols and they enable additionally condensation reactions of sol-gel type with the co-reagent tetramethoxysilane leading to novel metal fragment-subsituted polysiloxanes.

EXPERIMENTAL SECTION

General Remarks: All operations were performed under an atmosphere of purified and dried nitrogen using Schlenk-type techniques. Solvents were dried according to conventional procedures, distilled and saturated with N_2 prior to use. - NMR: Jeol Lambda 300 (300.4 MHz, 75.5 MHz, and 59.6 MHz for ^{1}H, ^{13}C, and ^{29}Si, respectively). [D_6]-benzene as a solvent: $\delta_H = 7.15$, $\delta_C = 128.0$; for ^{29}Si rel. to TMS external. - IR: Perkin-Elmer 283 grating spectrometer. - Melting points: Differential thermo analysis (Du Pont 9000 Thermal Analysis System). - Elemental analyses were performed in the laboratories of the *Institut für Anorganische Chemie der Universität Würzburg*. - Starting materials were prepared according to literature procedures: Cp(OC)$_3$WMe (**1**) [60], Li[W(LiC$_5$H$_4$)(CO)$_3$] (**3**) [39, 61], Li[WCp(CO)$_3$] (**17**) [62]. The reagents *n*BuLi and (*n*Bu)$_2$Sn(OAc)$_2$ were purchased from commercial source and not further purified. All used silanes were purchased from commercial sources, too and distilled prior use. The synthesis of (MeO)$_2$Si(CH$_2$)$_2$PPh$_2$ (**9**) is described under 20).

Table 1. ^{29}Si-NMR values of alkoxysilyl-substituted complexes

Entry	Si(OR)	Si(OR)$_2$	Si(OR)$_3$	ppm
1			**2** (Me)	-56.01
2	**6a** (Me)			7.22
3		**6b** (Me)		-16.08
4			**6c** (Me)	-51.02
5		**8** (Me)		-32.90
6		**12** (Me)		-14.90
7	**15** (Me)			7.10
8		**16** (Me)		-15.26
9			**18** (Me)	-42.80

1) [(MeO)₃Si(C₅H₄)](OC)₃WMe (2) by reaction of 1 with nBuLi and Si(OMe)₄

Tricarbonyl[η^5-(trimethoxysilyl)-cyclopentadienyl]methyltungsten(II)

To a solution of 0.30 g (0.86 mmol) of **1** in 5 ml THF were added at −78 °C 0.69 ml (1.12 mmol) of *n*BuLi while the color changes from yellow to dark brown over the period of 45 min. Then, 131 mg (0.86 mmol) of Si(OMe)₄ (**4c**) were added and the reaction mixture was allowed to warm up to room temperature over two hours and additionally stirred up to five days. All volatiles were removed in vacuo and the product was extracted with PE out of the residue. The filtered and combined extracts were evaporated to dryness leading to a yellow solid. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 4.86 − 4.85 (m, 2 H, H₄C₅), 4.76 − 4.75 (m, 2 H, H₄C₅), 3.40 (s, 9 H, H₃CO), 0.57 [s, ²*J* (HCW) = 3.6 Hz, H₃CW] ppm.

2) Li{W[MeOMe₂Si(C₅H₄)](CO)₃} (5a)

Lithium{tricarbonyl[η^5-(methoxydimethylsilyl)-cyclopentadienyl]tungstate}

A suspension of 2.34 g (3.69 mmol) of **3** in 10 ml THF was treated with 1.03 ml (7.38 mmol) of Me₂Si(OMe)₂ (**4a**) at room temperature and stirred for 18 hours. All volatiles were removed in vacuo and the crude product was washed three times with each 5 ml PE leading to a pyrophoric powder. Yield: 1.30 g (82 %). Beige solid. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 5.37 − 5.35 (m, 2 H, H₄C₅), 5.34 − 5.32 (m, 2 H, H₄C₅), 3.40 (s, 3 H, H₃CO), 0.44 (s, 6 H, H₃CSi) ppm. - **IR** (THF): $\tilde{\nu}$ (CO) = 1889 (s), 1803 (s), 1719 (vs) cm⁻¹. – C₁₁H₁₃LiO₄SiW (428.10).

3) Li{W[(MeO)₂MeSi(C₅H₄)](CO)₃} (5b)

Lithium{tricarbonyl[η^5-(dimethoxymethylsilyl)-cyclopentadienyl]tungstate}

Analogous to 2) from 1.20 g (1.89 mmol) of **3** and 0.54 ml (3.78 mmol) of MeSi(OMe)₃ (**4b**) in 10 ml THF over the period of 18 hours. Yield: 730 mg (87 %).

Beige solid. - ^{1}**H-NMR** (300.4 MHz, C_6D_6): δ = 5.40 – 5.37 (m, 2 H, H_4C_5), 5.35 – 5.33 (m, 2 H, H_4C_5), 3.60 (s, 6 H, H_3CO), 0.48 (s, 3 H, H_3CSi) ppm. - **IR** (THF): $\tilde{\nu}$ (CO) = 1892 (s), 1806 (s), 1723 (vs) cm^{-1}. – $C_{11}H_{13}LiO_4SiW$ (444.10).

*4) Li{W[(MeO)$_3$Si(C$_5$H$_4$)](CO)$_3$} (**5c**)*

Lithium{tricarbonyl[η^5-(trimethoxysilyl)-cyclopentadienyl]tungstate}

Analogous to 2) from 0.77 g (1.21 mmol) of **3** and 0.36 ml (2.42 mmol) of $Si(OMe)_4$ (**4c**) in 10 ml THF over the period of 18 hours. Yield: 445 mg (80 %). Beige solid. - ^{1}**H-NMR** (300.4 MHz, C_6D_6): δ = 4.99 – 4.91 (m, 4 H, H_4C_5), 3.27 (s, 9 H, H_3CO) ppm. - **IR** (THF): $\tilde{\nu}$ (CO) = 1893 (s), 1808 (s), 1724 (vs) cm^{-1}. – $C_{11}H_{13}LiO_6SiW$ (460.10).

*5) [MeOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**6a**)*

Tricarbonyl[η^5-(methoxydimethylsilyl)-cyclopentadienyl]methyltungsten(II)

A suspension of 890 mg (2.08 mmol) of **5a** in 20 ml PE was treated with 0.24 ml (4.00 mmol) of MeI and stirred for two hours at room temperature. All insoluble material was filtered off through a celite path and the filtrate was evaporated to dryness. The crude product was washed with 3 ml PE at –78 ℃ and finally dried in vacuo. Yield: 717 mg (79 %). Yellow solid. M.p.: 55 ℃. - ^{1}**H-NMR** (300.4 MHz, C_6D_6): δ = 4.72 – 4.71 (m, 2 H, H_4C_5), 4.58 – 4.57 (m, 2 H, H_4C_5), 3.16 (s, 3 H, H_3CO), 0.47 [s, ^2J (HCW) = 3.5 Hz, H_3CW], 0.17 (s, 6 H, H_3CSi) ppm. - ^{13}**C{^{1}H}-NMR** (75.5 MHz, C_6D_6): δ = 230.07 (s, CO), 217.00 (s, CO), 96.38 [s, ^1J(CW) = 4.7 Hz, C_5H_4], 95.98 [s, ^1J(CW) = 4.7 Hz, C_5H_4], 92.33 [s, ^1J(CW) = 4.2 Hz, *ipso*-C of C_5H_4], 50.49 (s, CH_3OSi), -1.74 [s, ^1J(CSi) = 1.4 Hz, CH_3Si], -34.55 [s, ^1J(CW) = 6.5 Hz, CW] ppm. - ^{29}**Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = 7.22 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2025 (s), 1927 (vs) cm^{-1}. – Anal. calc. for $C_{12}H_{16}O_4SiW$ (436.19): C 33.04, H 3.70; found: C 33.13, H 3.22.

*6) [(MeO)$_2$MeSi(C$_5$H$_4$)](OC)$_3$WMe (**6b**)*

Tricarbonyl[η^5-(dimethoxymethylsilyl)-cyclopentadienyl]methyltungsten(II)

Analogous to 5) from 1.03 g (2.14 mmol) of **5b** and 0.30 ml (4.17 mmol) of MeI in 20 ml PE over the period of two hours. Yield: 755 mg (78 %). Yellow solid. M.p.: 58 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.71 − 4.70 (m, 2 H, H$_4$C$_5$), 4.67 − 4.66 (m, 2 H, H$_4$C$_5$), 3.27 (s, 6 H, H$_3$CO), 0.53 [s, ^{2}J (HCW) = 3.6 Hz, H$_3$CW], 0.23 (s, 3 H, H$_3$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 230.05 (s, CO), 217.00 (s, CO), 96.42 [s, ^{1}J(CW) = 4.5 Hz, C$_5$H$_4$], 96.20 [s, ^{1}J(CW) = 4.5 Hz, C$_5$H$_4$], 92.33 [s, ^{1}J(CW) = 4.1 Hz, *ipso*-C of C$_5$H$_4$], 48.96 (s, CH$_3$OSi), -4.63 [s, ^{1}J(CSi) = 1.5 Hz, CH$_3$Si], -34.00 [s, ^{1}J(CW) = 9.8 Hz, CW] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -16.08 (s) ppm. - **IR** (PE): $\tilde{v}$ (CO) = 2026 (s), 1926 (vs) cm^{-1}. – Anal. calc. for C$_{12}$H$_{16}$O$_5$SiW (452.19): C 31.87, H 3.57; found: C 31.23, H 3.55.

*7) [(MeO)$_3$Si(C$_5$H$_4$)](OC)$_3$WMe (**2**)*

Tricarbonyl[η^5-(trimethoxysilyl)-cyclopentadienyl]methyltungsten(II)

Analogous to 5) from 1.03 g (2.14 mmol) of **5c** and 0.30 ml (4.17 mmol) of MeI in 20 ml PE over the period of two hours. Yield: 755 mg (78 %). Yellow solid. M.p.: 62 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.86 − 4.85 (m, 2 H, H$_4$C$_5$), 4.76 − 4.75 (m, 2 H, H$_4$C$_5$), 3.40 (s, 9 H, H$_3$CO), 0.57 [s, ^{2}J (HCW) = 3.6 Hz, H$_3$CW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, CDCl$_3$): δ = 228.26 [s, ^{1}J(CW) = 135.9 Hz, CO], 215.18 [s, ^{1}J(CW) = 155.0 Hz, CO], 95.60 [s, ^{1}J(CW) = 4.5 Hz, C$_5$H$_4$], 94.96 [s, ^{1}J(CW) = 4.6 Hz, C$_5$H$_4$], 86.37 [s, ^{1}J(CW) = 4.0 Hz, *ipso*-C of C$_5$H$_4$], 50.22 (s, CH$_3$OSi), -34.12 [s, ^{1}J(CW) = 9.8 Hz, CW] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, CDCl$_3$): δ = -56.01 (s) ppm. - **IR** (PE): $\tilde{v}$ (CO) = 2022 (s), 1923 (vs) cm^{-1}. – Anal. calc. for C$_{12}$H$_{16}$O$_6$SiW (468.19): C 30.78, H 3.44; found: C 31.03, H 3.33.

*8) [(MeO)₃Si(C₅H₄)](OC)₃WH (**6c**)*

Tricarbonyl[η^5-(trimethoxysilyl)-cyclopentadienyl]hydridotungsten(II)

Analogous to 5) from 0.72 g (1.47 mmol) of **5c** and 0.30 ml of HOAc in 20 ml PE over the period of two hours under light exclusion. Yield: 561 mg (84 %). Orange solid. M.p.: 53 °C. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 5.01 – 4.99 (m, 2 H, H₄C₅), 4.72 – 4.71 (m, 2 H, H₄C₅), 3.40 (s, 9 H, H₃CO), -7.22 [s, ^1J (HW) = 36.9 Hz, HW] ppm. - **¹³C{¹H}-NMR** (75.5 MHz, CDCl₃): δ = 219.66 (s, CO), 197.83 (s, CO), 110.95 [s, ^1J(CW) = 3.8 Hz, C₅H₄], 108.67 [s, ^1J(CW) = 3.8 Hz, C₅H₄], 87.57 (s, *ipso*-C₅H₄), 59.52 (s, CH₃OSi), 1.11 (s, CH₃Si) ppm. - **²⁹Si{¹H}-NMR** (59.6 MHz, CDCl₃): δ = -51.02 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2020 (s), 1934 (vs) cm^{-1}. – Anal. calc. for C₁₁H₁₄O₆SiW (454.16): C 29.09, H 3.11; found: C 30.03, H 3.13.

*9) Li₂{(MeO)₂Si[(C₅H₄)(OC)₃W]₂} (**7**)*

Dilithium{bis[tricarbonyl(η^5-cyclopentadienyl)dimethoxysilyl-tungstate]}

Analogous to 2) from 630 mg (0.99 mmol) of **3** and 0.07 ml (0.50 mmol) Si(OMe)₄ (**4c**) in 10 ml THF over the period of four days. Yield: 547 mg (72 %). Pale beige pyrophoric solid. - **¹H-NMR** (300.4 MHz, CD₃CN): δ = 5.27 – 5.25 (m, 4 H, H₄C₅), 5.15 – 5.13 (m, 4 H, H₄C₅), 3.53 (s, 6 H, H₃CO) ppm. - **IR** (THF): $\tilde{\nu}$ (CO) = 1890 (s), 1805 (s), 1721 (vs) cm^{-1}. – C₁₈H₁₄Li₂O₈SiW₂ (767.97).

*10) (MeO)₂Si[(C₅H₄)(OC)₃WMe]₂ (**8**)*

Bis[tricarbonyl(η^5-cyclopentadienyl)-tungsten(II)methyl]-dimethoxysilane

Analogous to 5) from 499 mg (0.65 mmol) of **7** and 0.40 ml (5.19 mmol) of MeI in 20 ml cyclohexane over the period of two hours. Yield: 387 mg (76 %). Yellow solid. M.p.: 81 °C. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 4.75 – 4.73 (m, 4 H, H₄C₅), 4.69 – 4.67

(m, 4 H, H$_4$C$_5$), 3.36 (s, 6 H, H$_3$CO), 0.50 [s, ^2J (HCW) = 3.7 Hz, H$_3$CW] ppm. -
^{13}C{^{1}H}-NMR (75.5 MHz, CDCl$_3$): δ = 228.36 [s, ^1J(CW) = 135.9 Hz, CO], 213.18 [s,
^1J(CW) = 155.0 Hz, CO], 95.77 [s, ^1J(CW) = 4.5 Hz, C$_5$H$_4$], 94.61 [s, ^1J(CW) = 4.6 Hz,
C$_5$H$_4$], 86.32 [s, ^1J(CW) = 4.0 Hz, *ipso*-C of C$_5$H$_4$], 50.11 (s, CH$_3$OSi), -34.45 [s,
^1J(CW) = 9.8 Hz, CW] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -32.90 (s) ppm. -
IR (cyclohexane): $\tilde{\nu}$ (CO) = 2022 (s), 1923 (vs) cm^{-1}. – Anal. calc. for C$_{20}$H$_{20}$O$_8$SiW$_2$
(784.16): C 30.63, H 2.57; found: C 30.19, H 2.59.

*11) (MeO)$_2$Si(CH$_2$)$_2$PPh$_2$ (**9**)*

(2-Dimethoxysilyl)-ethyl-diphenylphosphine

A mixture of 1.48 g (9.89 mmol) of vinyltrimethoxysilane and 1.86 g (9.98 mmol) of
diphenylphosphine in 5 ml benzene was irradiated with UV-light over the period of 50
hours. All volatiles were removed in vacuo giving a colorless oil. Yield 2.52 g (76 %).
Colorless oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.46 − 7.41 (m, 4 H, H$_5$C$_6$), 7.08 −
7.00 (m, 6 H, H$_5$C$_6$), 3.35 (s, 9 H, H$_3$CO), 2.31 − 2.22 (m, 2 H, H$_2$CP), 0.91 − 0.82 (m,
2 H, H$_2$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 139.70 [d, ^3J(CCCP) = 15.6
Hz, C$_6$H$_5$], 134.39 [d, ^1J(CP) = 28.7 Hz, C$_6$H$_5$], 133.25 [d, ^2J(CCP) = 18.5 Hz, C$_5$H$_4$],
128.85 [d, ^4J(CCCCP) = 6.5 Hz, C$_5$H$_4$], 50.38 (s, CH$_3$), 21.20 [d, ^1J(CP) = 14.5 Hz,
CH$_2$P], 5.83 [d, ^2J(CCP) = 12.7 Hz, CH$_2$Si] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ
= -43.27 (s) ppm. - **^{31}P{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -10.63 (s) ppm. – Anal. calc.
for C$_{17}$H$_{23}$O$_3$PSi (334.43): C 61.06, H 6.93; found: C 61.27, H 6.86.

*12) Li{W[(C$_5$H$_4$)Si(OMe)$_2$(CH$_2$)$_2$PPh$_2$](CO)$_3$} (**10**)*

Lithium{tricarbonyl{η^5-[2-(diphenylphosphino)ethyl-dimethoxysilyl]-cyclopentadienyl}-
tungstate}

Analogous to 2) from 0.66 g (1.04 mmol) of **3** and 696 mg (2.08 mmol) of
(MeO)$_2$Si(CH$_2$)$_2$PPh$_2$ (**9**) in 10 ml THF over the period of 36 hours resutlting in an
pyrophoric solid matter. Yield 818 mg (91 %). Orange solid. - **^{1}H-NMR** (300.4 MHz,

CD$_3$CN): δ = 7.10 – 7.04 (m, 4 H, H$_5$C$_6$), 7.00 – 6.95 (m, 6 H, H$_5$C$_6$), 4.83 – 4.82 (m, 2 H, H$_4$C$_5$), 4.78 – 4.76 (m, 2 H, H$_4$C$_5$), 3.10 (s, 6 H, H$_3$CO), 1.84 – 1.81 (m, 2 H, H$_2$CP), 0.43 – 0.34 (m, 2 H, H$_2$CSi) ppm. - **^{31}P{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -10.44 (s) ppm. – C$_{24}$H$_{24}$LiO$_5$PSiW (642.30).

*13) cis-/trans-[η^1-PPh$_2$(CH$_2$)$_2$(MeO)$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$WH (**12**)*

Tricarbonyl{η^1-[2-(diphenylphosphino)ethyl-dimethoxysilyl]-η^5-cyclopentadienyl}-hydridotungsten(II)

A suspension of 818 mg (1.00 mmol) of 16 was treated with 1 ml HOAc and stirred for 18 hours under exclusion of light. Immediately after addition of the acid gas formation started. After finished reaction all volatiles were removed in vacuo and the residue was extracted with 50 ml benzene. The combined extracts were filtered through a celite path and evaporated to dryness. The crude product was washed three times with each 3 ml PE and dried finally in vacuo. Yield 249 mg (41 %). Beige solid. - **^{1}H-NMR** (300.4 MHz, CDCl$_3$): δ = 7.63 – 7.51 (m, 8 H, H$_5$C$_6$), 7.43 – 7.20 (m, 12 H, H$_5$C$_6$), 5.55 – 5.42 (m, 8 H, H$_4$C$_5$), 3.44, 4.41, 3.34 (s, 12 H, H$_3$CO), 2.45 – 2.32 (m, 4 H, H$_2$CP), 0.97 – 0.91 (m, 4 H, H$_2$CSi), -7.28 (*cis*) [d, ^{1}*J*(HW) = 48.2 Hz, ^{2}*J*(HCP) = 23.8 Hz, 1 H, HW], -7.76 (*trans*) [d, ^{1}*J*(HW) = 46.4 Hz, ^{2}*J*(HCP) = 66.6 Hz, 1 H, HW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, CDCl$_3$): δ = 237.95 [d, ^{2}*J*(CWP) = 21.4 Hz, *cis*-CO], 233.95 [d, ^{2}*J*(CWP) = 17.4 Hz, *cis*-CO], 226.80 [d, ^{2}*J*(CWP) = 6.9 Hz, *trans*-CO], 134.84 - 128.59 (d, C$_6$H$_5$), 117.33 - 87.60 (s, d, C$_5$H$_4$Si), 51.34, 50.38, 49.00 (s, CH$_3$O), 28.68 [d, ^{1}*J*(CP) = 16.5 Hz, CH$_2$P], 21.66 [d, ^{1}*J*(CP) = 14.6 Hz, CH$_2$P], 19.79 [d, ^{2}*J*(CCP) = 13.7 Hz, CH$_2$Si], 13.11 [d, ^{2}*J*(CCP) = 12.2 Hz, CH$_2$Si] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, CDCl$_3$): δ = -14.90 (s) ppm. - **^{31}P{^{1}H}-NMR** (59.6 MHz, CDCl$_3$): δ = 30.74 [s, ^{1}*J*(PW) = 248.8 Hz, *trans*-PCH$_3$], 29.26 [s, ^{1}*J*(PW) = 271.3 Hz, *cis*-PCH$_3$] ppm. - **IR** (CCl$_2$H$_2$): $\tilde{\nu}$ (CO) = 1942.4 (vs), 1858.7 (vs) cm^{-1}. – Anal. calc. for C$_{23}$H$_{25}$O$_4$PSiW (608.36): C 45.41, H 4.14; found: C 44.88, H 3.82.

*14) [η^1-CH$_2$Me$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$W (**14a**)*

Tricarbonyl[η^1-methylene-(dimethylsilyl)-η^5-cyclopentadienyl]tungsten(II)

A suspension of 760 mg (1.20 mmol) of **3** in 10 ml THF was cooled to −78 °C and treated with 200 mg (1.20 mmol) of (chloromethyl)-*iso*propoxy-dimethylsilane (**13a**) while dissolving of the precipitate occurred. The reaction mixture was allowed to warm up slowly to room temperature over the period of four hours. After that all volatiles were removed in vacuo and the obtained residue was extracted with 20 ml portions of PE until the extracts were colorless. The combined extracts were filtered through a celite path and then evaporated to dryness. The crude product was washed with 4 ml PE at −78 °C and finally dried in vacuo. Yield: 475 mg (98 %). Yellow solid. M.p.: 91 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.93 - 4.91 (m, 2 H, H$_4$C$_5$), 4.59 - 4.58 (m, 2 H, H$_4$C$_5$), -0.05 [s, ^{2}J(HCSi) = 6.6 Hz, 6 H, H$_3$CSi], -1.02 [s, (^{2}J(HCW) = 27.0 Hz, 2 H, H$_2$CW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 228.52 (s, CO), 216.89 [s, ^{1}J(CW) = 160.3 Hz, CO], 94.08 [s, ^{1}J(CW) = 7.2 Hz, C$_5$H$_4$], 91.90 (s, C$_5$H$_4$), 82.89 (s, C$_5$H$_4$Si), -1.00 [s, ^{1}J(CSi) = 52.4 Hz, CH$_3$Si), -61.05 [s, ^{1}J(CSi) = 52.1 Hz, ^{1}J(CW) = 21.0 Hz, CH$_2$W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -12.18 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2016 (s), 1938 (s), 1927 (vs) cm^{-1}. - **MS** (EI): m/e [%] 404 (M$^+$) [38], 376 (- CO) [12], 348 (-2 CO) [18]. – Anal. calc. for C$_{11}$H$_{12}$O$_3$SiW (404.15): C 32.69, H 2.99; found: C 33.20, H 3.02.

*15) [η^1-CH$_2$Me$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$W (**13**) by reaction of **3** with [ClCH$_2$SiMe$_2$]$_2$O*

Analogous to 14) from 420 mg (0.67 mmol) of **3** and 81 mg (0.35 mmol) of [ClCH$_2$SiMe$_2$]$_2$O in 10 ml THF. Yield: 216 mg (80 %). Yellow solid.

*16) [η¹-CH₂(EtO)MeSi(η⁵-C₅H₄)](OC)₃W (**14b**)*

Tricarbonyl[η¹-methylene-(ethoxymethylsilyl)-η⁵-cyclopentadienyl]tungsten(II)

Analogous to 14) from 2.17 g (3.42 mmol) of **3** and 0.63 g (0.63 ml, 0.35 mmol) of (chloromethyl)-diethoxymethylsilane (**13b**) in 10 ml THF. Yield: 297 mg (20 %). Yellow solid. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 5.07 - 5.05 (m, 1 H, H₄C₅), 4.89 - 4.87 (m, 1 H, H₄C₅), 4.65 - 4.63 (m, 1 H, H₄C₅), 4.43 - 4.41 (m, 1 H, H₄C₅), 3.61, 3.62 [q, ^3J(HCCH) = 6.9 Hz, 2 H, H₂CO], 1.17 [t, ^3J(HCCH) = 6.9 Hz, 3 H, H̲₃CCH₂], 0.09 [s, ^2J(HCSi) = 6.6 Hz, 3 H, H₃CSi], -0.53, -0.54 [s, ^2J(HCW) = 28.0 Hz, 2 H, H₂CW] ppm. – C₁₂H₁₄O₄SiW (434.18).

*17) [η¹-CH₂(MeO)₂Si(η⁵-C₅H₄)](OC)₃W (**14c**)*

Tricarbonyl[η¹-methylene-(dimethoxysilyl)-η⁵-cyclopentadienyl]tungsten(II)

Analogous to 14) from 3.94 g (6.21 mmol) of **3** and 1.06 g (0.94 ml, 6.21 mmol) of (chloromethyl)-trimethoxysilane (**13c**) in 10 ml THF. Yellow oil. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 4.82 - 4.81 (m, 4 H, H₄C₅), 3.49 (s, 6 H, H₃CO), -0.12 [s, ^2J(HCW) = 27.2 Hz, 3 H, H₃CW] ppm. – C₁₁H₁₂O₅SiW (436.15).

*18) [η¹-(CH₂)₂(MeO)MeSi(η⁵-C₅H₄)](OC)₃W (**15**)*

Tricarbonyl[η¹-ethyl-(methoxymethylsilyl)-η⁵-cyclopentadienyl]tungsten(II)

Analogous to 14) from 1.00 g (1.58 mmol) of **3** and 267 mg (1.58 mmol) of (2-chloroethyl)-dimethoxymethylsilane (**13d**) in 10 ml THF. Yield: 480 mg (70 %). Red solid. M.p.: 58 °C. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 5.44 - 5.42 (m, 1 H, H₄C₅), 5.06 - 5.01 (m, 1 H, H₄C₅), 4.55 - 4.53 (m, 1 H, H₄C₅), 4.51 - 4.49 (m, 1 H, H₄C₅), 3.16 (s, 3 H, H₃COSi), 2.20 - 2.07 (m, 2 H, H₂CCH₂), 1.96 - 1.84 (m, 2 H, H₂CCH₂), -0.01 [s, ^1J(HCSi) = 3.5 Hz, 3 H, H₃CSi] ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C₆D₆): δ = 228.59 (s, *trans*-CO), 216.90, 216.71 (s, *cis*-CO), 95.30 [s, ^1J(CW) = 5.4 Hz, C₅H₄], 94.92 [s,

^1J(CW) = 5.1 Hz, C$_5$H$_4$], 88.56 [s, ^1J(CW) = 3.3 Hz, C$_5$H$_4$], 87.91 [s, ^1J(CW) = 3.6 Hz, C$_5$H$_4$] 87.08 (s, *ipso*-C of C$_5$H$_4$Si), 49.29 (s, CH$_3$O), 31.08 [s, ^1J(CSi) = 5.1 Hz, CH$_2$Si], -13.73 [s, ^1J(CW) = 28.0 Hz, CH$_2$W] ppm. - ^{29}**Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 7.10 (s) ppm. - **IR** (PE): $\tilde{\nu}$(CO) = 2016 (s), 1926 (vs) cm^{-1}. – Anal. calc. for C$_{12}$H$_{14}$O$_4$SiW (434.18): C 33.20, H 3.25; found: C 33.76, H 2.78.

19) [η^1-(CH$_2$)$_3$(MeO)$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$W (16)

Tricarbonyl[η^1-*n*-propyl-(dimethoxysilyl)-η^5-cyclopentadienyl]tungsten(II)

Analogous to 14) from 2.30 g (3.63 mmol) of **3** in THF and 1.05 g (0.71 ml, 3.63 mmol) of (3-iodopropyl)-trimethoxysilane (**13e**) over the period of four hours. Yield: 1.28 g (76 %). Yellow solid. M.p.: 50 °C. - ^{1}**H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.76 - 4.75 (m, 2 H, H$_4$C$_5$), 4.60 - 4.59 (m, 2 H, H$_4$C$_5$), 3.30 (s, 6 H, H$_3$COSi) 2.42 - 2.34 (m, 2 H, H$_2$CCH$_2$Si) 1.92 - 1.88 (m, 2 H, H$_2$CSi) 0.62 - 0.56 (m, 2 H, H$_2$CW) ppm. - ^{13}**C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 229.05 (s, CO), 217.29 [s, ^1J(CW) = 160.9 Hz, CO], 95.97 [s, ^1J(CW) = 5.5 Hz, C$_5$H$_4$], 94.07 (s, C$_5$H$_4$), 85.68 (s, *ipso*-C of C$_5$H$_4$Si), 50.12 (s, CH$_3$O), 29.31 (s, CH$_2$CH$_2$Si), 12.05 [s, ^1J(CSi) = 7.2 Hz, CH$_2$Si], -6.39 [s, ^1J(CW) = 30.7 Hz, CH$_2$W] ppm. - ^{29}**Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -15.26 (s) ppm. - **IR** (PE): $\tilde{\nu}$(CO) = 2016 (s), 1929 (vs) cm^{-1}. – **MS** (EI): m/e [%] 464 (M$^+$), 436 (- CO) [33], 406 (-2 CO) [48]. – Anal. calc. for C$_{13}$H$_{16}$O$_5$SiW (464.20): C 33.64, H 3.47; found: C 32.80, H 3.54.

20) Cp(OC)$_3$W(CH$_2$)$_3$Si(OMe)$_3$ (18)

{[3-Tricarbonyl(η^5-cyclopentadienyl)tungsten(II)]-propyl}trimethoxysilane

A solution of 941 mg (2.77 mmol) of **17** in 10 ml DME was treated with 2.90 g (2.08 ml, 10.0 mmol) of (3-iodopropyl)-trimethoxysilane (**13e**) and the reaction mixture was stirred at room temperature over the period of five hours. After that the solvent was removed in vacuo and the obtained residue was extracted with 40 ml PE until the extracts were colorless. The combined extracts were filtered through a celite path

and then evaporated to dryness. The crude product was washed three times each with 4 ml PE at −78 °C and finally dried in vacuo. Yield: 1.00 g (73 %). Yellow solid. M.p.: 138 °C. - **^{1}H-NMR** (300.4 MHz, C_6D_6): δ = 4.47 (s, 5 H, H_5C_5), 3.49 (s, 9 H, H_3CO) 1.94 - 1.83 (m, 2 H, $\underline{H}_2CCH_2Si$) 1.65 - 1.59 (m, 2 H, H_2CSi) 0.91 - 0.86 (m, 2 H, H_2CW) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C_6D_6): δ = 229.73 (s, CO), 218.17 [s, ^1J(CW) = 161.0 Hz, CO], 91.29 [s, ^1J(CW) = 4.5 Hz, C_5H_4], 50.27 (s, CH_3O), 30.58 (s, $\underline{C}H_2CH_2Si$), 17.16 [s, ^1J(CSi) = 5.9 Hz, CH_2Si], -5.71 [s, ^1J(CW) = 28.6 Hz, CH_2W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = -42.80 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2016 (s), 1925 (vs) cm^{-1}. – Anal. calc. for $C_{14}H_{20}O_6SiW$ (496.24): C 33.89, H 4.06; found: C 32.84, H 3.58.

*21) [η^1-(CH$_2$)$_3$(MeO)$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$W (**16**) attempted by reaction of **18** with nBuLi*

A solution of 130 mg (0.26 mmol) of **18** in 5 ml THF was treated at −78 °C with 0.16 ml (0.26 mmol) of *n*BuLi (1.6 M, hexane solution) while a slight change of the color from yellow to orange occurred. The reaction mixture was allowed to warm up slowly over the period of three hours. Then, all volatiles were removed in vacuo and the residue was extracted with PE until the extracts were colorless. The combined extracts were filtered through a celite path and then evaporated to dryness. The crude product was washed three times each with 4 ml PE at −78 °C and finally dried in vacuo. Yellow oil.

*22) [η^1-(CH$_2$)$_2$(HO)MeSi(η^5-C$_5$H$_4$)](OC)$_3$W (**19**)*

Tricarbonyl[η^1-ethyl-(hydroxymethylsilyl)-η^5-cyclopentadienyl]tungsten(II)

A solution consisting of 480 mg (1.11 mmol) of **15** and 0.5 ml aqueous NaOH in 20 ml Et_2O was stirred over the period of one week at room temperature. All insoluble material was filtered off and the filtrate was evaporated to dryness. The crude product was washed with 2 ml PE at 0 °C. Yield: 448 mg (96 %). Red solid. M.p.: 69 °C. - **^{1}H-NMR** (300.4 MHz, C_6D_6): δ = 5.42 - 5.40 (m, 1 H, H_4C_5), 5.05 - 5.00 (m, 1 H, H_4C_5), 4.54 - 4.52 (m, 1 H, H_4C_5), 4.51 - 4.49 (m, 1 H, H_4C_5), 3.12 (s, 3 H, H_3COSi), 2.40 (s,

1 H, HOSi), 2.18 - 2.06 (m, 2 H, H_2CCH_2), 1.90 - 1.82 (m, 2 H, H_2CCH_2), 0.00 [s, $^1J(HCSi)$ = 3.7 Hz, 3 H, H_3CSi] ppm. - $^{13}C\{^1H\}$-**NMR** (75.5 MHz, C_6D_6): δ = 228.23 (s, *trans*-CO), 216.50, 214.74 (s, *cis*-CO), 95.20 [s, $^1J(CW)$ = 5.4 Hz, C_5H_4], 95.02 [s, $^1J(CW)$ = 5.5 Hz, C_5H_4], 88.23 [s, $^1J(CW)$ = 3.5 Hz, C_5H_4], 87.71 [s, $^1J(CW)$ = 3.5 Hz, C_5H_4] 87.48 (s, *ipso*-C of C_5H_4Si), 49.09 (s, CH_3O), 31.45 [s, $^1J(CSi)$ = 5.4 Hz, CH_2Si], -13.53 [s, $^1J(CW)$ = 28.2 Hz, CH_2W] ppm. - $^{29}Si\{^1H\}$-**NMR** (59.6 MHz, C_6D_6): δ = 5.01 (s) ppm. - **IR** (CCl_2H_2): $\tilde{\nu}$ (CO) = 2015 (s), 1927 (vs) cm^{-1}. – Anal. calc. for $C_{11}H_{12}O_4SiW$ (420.15): C 31.45, H 2.88; found: C 32.76, H 2.79.

*23) $[\eta^1$-$(CH_2)_3(HO)_2Si(\eta^5$-$C_5H_4)](OC)_3W$ (**20**)*

Tricarbonyl[η^1-*n*-propyl-(dihydroxysilyl)-η^5-cyclopentadienyl]tungsten(II)

Analogous to 22) from 152 mg (3.27 mmol) of **16** and 0.60 ml of aqueous NaOH in 20 ml Et_2O over the period of two weeks. Yield: 105 mg (74 %). Beige solid. M.p.: 180 °C. - ^1H-**NMR** (300.4 MHz, D_6-acetone): δ = 5.74 - 5.72 (m, 2 H, H_4C_5), 5.57 - 5.56 (m, 2 H, H_4C_5), 2.88 (s, 2 H, HOSi) 2.36 - 2.25 (m, 2 H, $\underline{H}_2CCH_2Si$) 1.89 - 1.85 (m, 2 H, H_2CSi) 0.67 - 0.62 (m, 2 H, H_2CW) ppm. - $^{13}C\{^1H\}$-**NMR** (75.5 MHz, D_6-acetone): δ = 232.25 (s, CO), 219.79 [s, $^1J(CW)$ = 162.5 Hz, CO], 97.50 [s, $^1J(CW)$ = 3.9 Hz, C_5H_4], 95.74 [s, $^1J(CW)$ = 4.5 Hz, C_5H_4], 93.50 (s, *ipso*-C of C_5H_4Si), 32.701 (s, $\underline{C}H_2CH_2Si$), 16.91 (s, CH_2Si), -4.93 [s, $^1J(CW)$ = 30.5 Hz, CH_2W] ppm. - $^{29}Si\{^1H\}$-**NMR** (59.6 MHz, D_6-acetone): δ = -20.08 (s) ppm. - **IR** (THF): $\tilde{\nu}$ (CO) = 2019 (s), 1935 (vs) cm^{-1}. – **MS** (EI): m/e [%] 436 (M$^+$), 408 (- CO) [22], 380 (-2 CO) [88]. – Anal. calc. for $C_{11}H_{12}O_5SiW$ (436.15): C 30.29, H 2.77; found: C 29.43, H 2.96.

*24) $(HO)_2Si[(C_5H_4)(OC)_3WMe]_2$ (**21**)*

Bis[tricarbonyl(η^5-cyclopentadienyl)-tungsten(II)methyl]-dihydroxysilane

Analogous to 22) from 311 mg (0.40 mmol) of **8** and 0.5 ml of aqueous NaOH in 20 ml Et_2O over the period of two weeks. Yield: 281 mg (93 %). Yellow solid. M.p.: 93 °C. - ^1H-**NMR** (300.4 MHz, C_6D_6): δ = 4.80 – 4.78 (m, 4 H, H_4C_5), 4.67 – 4.65 (m, 4 H,

H$_4$C$_5$), 2.52 (s, 2 H, HOSi), 0.49 [s, ^2J (HCW) = 3.5 Hz, H$_3$CW] ppm. - ^{13}C{^{1}H}-NMR (75.5 MHz, CDCl$_3$): δ = 226.76 [s, ^1J(CW) = 136.6 Hz, CO], 216.32 [s, ^1J(CW) = 156.6 Hz, CO], 96.82 [s, ^1J(CW) = 4.2 Hz, C$_5$H$_4$], 94.79 [s, ^1J(CW) = 4.1 Hz, C$_5$H$_4$], 84.98 [s, ^1J(CW) = 3.8 Hz, *ipso*-C of C$_5$H$_4$], -34.65 [s, ^1J(CW) = 9.5 Hz, CW] ppm. - ^{29}Si{^{1}H}-NMR (59.6 MHz, C$_6$D$_6$): δ = -34.35 (s) ppm. - IR (CHCl$_3$): $\tilde{\nu}$ (CO) = 2024 (s), 1924 (vs) cm^{-1}. – Anal. calc. for C$_{18}$H$_{16}$O$_8$SiW$_2$ (756.10): C 28.59, H 2.13; found: C 29.19, H 2.39.

*25) (HMe$_2$SiO)$_2$Si[(C$_5$H$_4$)(OC)$_3$WMe]$_2$ (**22**)*

1,3-Bis[tricarbonyl(η^5-cyclopentadienyl)-tungsten(II)methyl]-1,3-dimethyl-disiloxane

A solution of 149 mg (0.20 mmol) of **21** and 0.4 ml NEt$_3$ in 5 ml Et$_2$O and 5 ml benzene was treated with 0.3 ml Me$_2$Si(H)Cl and stirred over the period of 18 hours. All insoluble material was filtered of through a celite path and the filtrated was evaporated to dryness in vacuo. Yield: 141 mg (81 %). Orange solid. - ^{1}H-NMR (300.4 MHz, C$_6$D$_6$): δ = 4.82 – 4.79 (m, 4 H, H$_4$C$_5$), 4.74 – 4.72 (m, 4 H, H$_4$C$_5$), 4.30 [sept, ^3J(HSiCH) = 6.2 Hz, 2 H, HSi], 0.48 [s, ^2J (HCW) = 3.6 Hz, H$_3$CW], 0.21 [d, ^3J(HCSiH) = 6.2 Hz, 12 H, H$_3$C] ppm. - ^{13}C{^{1}H}-NMR (75.5 MHz, CDCl$_3$): δ = 227.85 [s, ^1J(CW) = 134.9 Hz, CO], 214.48 [s, ^1J(CW) = 156.0 Hz, CO], 96.25 [s, ^1J(CW) = 4.3 Hz, C$_5$H$_4$], 93.51 [s, ^1J(CW) = 4.4 Hz, C$_5$H$_4$], 88.22 [s, ^1J(CW) = 4.1 Hz, *ipso*-C of C$_5$H$_4$], 0.90 (s, CSiH), -34.67 [s, ^1J(CW) = 9.5 Hz, CW] ppm. - IR (CHCl$_3$): $\tilde{\nu}$ (SiH) = 2145 cm^{-1}; $\tilde{\nu}$ (CO) = 2026 (s), 1924 (vs) cm^{-1}. – C$_{22}$H$_{28}$O$_8$Si3W$_2$ (872.42).

*26) Sol-gel polysiloxane (**23**) from Cp(OC)$_3$W(CH$_2$)$_3$Si(OMe)$_3$ (**18**) and Si(OMe)$_4$ (**4c**)*

A solution of 0.36 ml (2.42 mmol) of Si(OMe)$_4$ (**4c**) in a solvent mixture of 1 ml MeOH and 6 ml THF was treated with 0.4 ml of water and 0.1 ml of (*n*Bu)$_2$Sn(OAc)$_2$ and stirred for four hours at room temperature. Then, 301 mg (0.61 mmol) of **18** were added and the resutling mixture stirred for one week. All volatiles were removed in vacuo and the obtained crude product was washed with 6 ml benzene, 4 ml Et$_2$O and 4 ml PE and finally dried in vacuo. Yield: 500 mg. Beige solid. - ^{13}C VACP/MAS-NMR

(100.6 MHz): δ = 230 (CO), 217 (CO), 92.4 (Cp), 27.3 (s, $\underline{C}H_2CH_2Si$), 16.8 (CH_2Si), -7.1 (CH_2W) ppm. - **^{29}Si CP/MAS-NMR** (79.5 MHz): δ = -61 (T^2), -68 (T^3), -103 (Q^3), -112 (Q^4) ppm.

Crystal analyses

The data were collected from shockcooled crystals on a BRUKER SMART-APEX diffractometer with D8 goniometer (graphite-monochromated Mo - K$_\alpha$ radiation (λ = 0.71073 Å) equipped with a low temperature device in omega-scan mode at 173(2) K [62]. The data was integrated with SAINT [63] and an empirical absorption correction [64] was applied. The structure was solved by direct methods (SHELXS-97) [65] and refined by full-matrix least squares methods against F^2 (SHELXL-97) [66]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of the hydrogen atoms were calculated by an idealized geometry.

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Chapter VI

HALFSANDWICH TUNGSTEN COMPLEXES WITH A SILANEDIOL-FUNCTIONALIZED η^5-CYCLOPENTADIENYL LIGAND

- SYNTHESIS OF THE STABLE SILANEDIOL [(HO)$_2$*t*BuSi(η^5-C$_5$H$_4$)](OC)$_3$WMe -

SUMMARY

The reaction of $Cl_2MeSiC_5H_5$ (**1**) with $(MeCN)_3W(CO)_3$ results in the formation of $[Cl_2MeSi(\eta^5\text{-}C_5H_4)](OC)_3WH$ (**2**), suitable for hydrolysis, which is then converted into the tungsten chloride $[Cl_2MeSi(\eta^5\text{-}C_5H_4)](OC)_3WCl$ (**3**) by treatment with CCl_4. **2** and **3** undergo CO/PR_3-exchange (R = Me, Ph) resulting in the formation of the phosphine-substituted tungsten complexes $[Cl_2MeSi(\eta^5\text{-}C_5H_4)](OC)_2(Me_3P)WH$ (**4a**) and $[Cl_2MeSi(\eta^5\text{-}C_5H_4)](OC)_2(Ph_3P)WCl$ (**4b**). Another approach to $SiCl_2$-functionalized tungsten complexes is given by the succesive reaction of $Cp(OC)_3WMe$ (**5**) with nBuLi, followed by $MeSiCl_3$, yielding $[Cl_2MeSi(\eta^5\text{-}C_5H_4)](OC)_3WMe$ (**6**). Introduction of a *tert*-butyldichlorosilyl group into the cyclopentadienyl ring is achieved when the dilithiated $Li[W(\eta^5\text{-}LiC_5H_4)(CO)_3]$ (**7**) is reacted with tBuSiCl_3 to give the lithium tungstate $Li\{W[(\eta^5\text{-}C_5H_4)Sit\text{BuCl}_2](CO)_3\}$ (**8**). Final salt elimination of **8** with MeI affords the neutral $[Cl_2t\text{BuSi}(\eta^5\text{-}C_5H_4)](OC)_3WMe$ (**9**). The hydrolyses of the $RSiCl_2$-precursors proceed cleanly only in the case of **9** (R = tBu) and afford the pure silanediol $[(HO)_2t\text{BuSi}(\eta^5\text{-}C_5H_4)](OC)_3WMe$ (**10b**) which is stable with respect to self-condensation. The co-condensation of **10b** with an excess of $Me_2Si(H)Cl$ gives the multifunctionalized tungsten-trisiloxane $[(HMe_2SiO)_2t\text{BuSi}(\eta^5\text{-}C_5H_4)](OC)_3WMe$ (**11**).

INTRODUCTION

The incorporation of transition elements into polymeric structures is attractive, as it may allow the combination of the interesting physical properties of metals with the solubility and processibility of polymers [1-11]. Polysiloxanes, $[R_2SiO]_n$, are appealing polymers for many applications as a consequence of their chemical stability, low toxicity, high gas permeability, and insulating charateristics [12-14]. For example, this class of inorganic polymers can be found in sealants, contact linses, coatings, and a variety of biomedical applications [15].

The condensation of organosilanols can be viewed as the basis in the synthesis of siloxanes and silicones. This process can be suppressed by bulky organic groups, which in some cases offers access even to stable silanediols $R_2Si(OH)_2$ and silanetriols $RSi(OH)_3$ [e.g. $R = C_5H_4(SiMe_3)$] [16, 17]. Apart from the sterical aspect, another kind of stabilization is achieved by use of metal fragments as substituent in silanols of the general type $L_nM\text{-}SiR_{3-n}(OH)_n$ (n = 1-3) [18-29] (Fig. 1, Type **I**), where the metal fragment acts as strong electron releasing group. Due to this property of the metal fragment the acidity of the Si-OH function and the tendency towards self-condensation are strongly reduced. This situation offers even the possibility of isolating metal-derivatived silanediols $L_nM\text{-}SiR(OH)_2$ [28, 30-33] and silanetriols $L_nM\text{-}Si(OH)_3$ [32, 34], which are synthetical useful for the generation of well-defined metallo-siloxanes by controlled co-condensation processes and represent attractive model compounds for transition metal complexes anchored on silica surfaces.
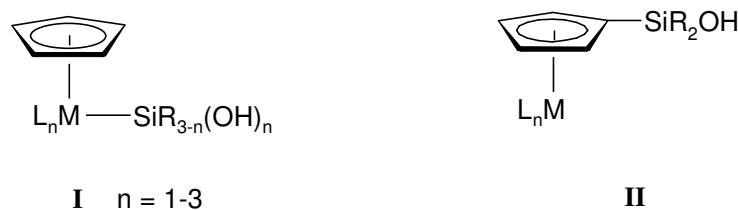

$$L_nM \longrightarrow SiR_{3-n}(OH)_n$$

I   n = 1-3

$$SiR_2OH$$

$$L_nM$$

II

Fig. 1: Different types of silanols containing metal fragments.

It is rooted in the high stability of metallo-silanols of type **I**, that recent interest has turned now to silanols having the Si-OH moiety separated from the metal fragment by an alkyl group in order to reduce the "transition metal effect" on the silanol unit and to enhance the reactivity in condensation processes. As recently shown it is possible to functionalize the cyclopentadienyl ligand with silanol groups (Type **II**), which are often stable with respect to self-condesation [35-39].

Nevertheless, apart from $[\eta^1\text{-}(CH_2)_3(HO)_2Si[(\eta^5\text{-}C_5H_4)](OC)_3W$ and the dinuclear silandiol $(HO)_2Si[(\eta^5\text{-}C_5H_4)](OC)_3WMe]_2$ by our group (Fig. 2) [40], no attempts so far have been made to generate or isolate any halfsandwich metal complexes bearing a silanediol group at the cyclopentadienyl ligand, which can be regarded as promising precursors for the formation of unusual arrangements of metal-functionalized polysiloxanes.

Further complexes containing an $Si(OH)_2$ unit at the cyclopentadienyl ring are realized in context with ferrocene derivatives, which were shown to be stable enough, even in the case of small organo groups at the silicon atom, to be structurally characterized by X-ray diffraction analyses revealing fascinating hydrogen-bonded arrangements in the solid state structure [41-44] (Fig. 2).
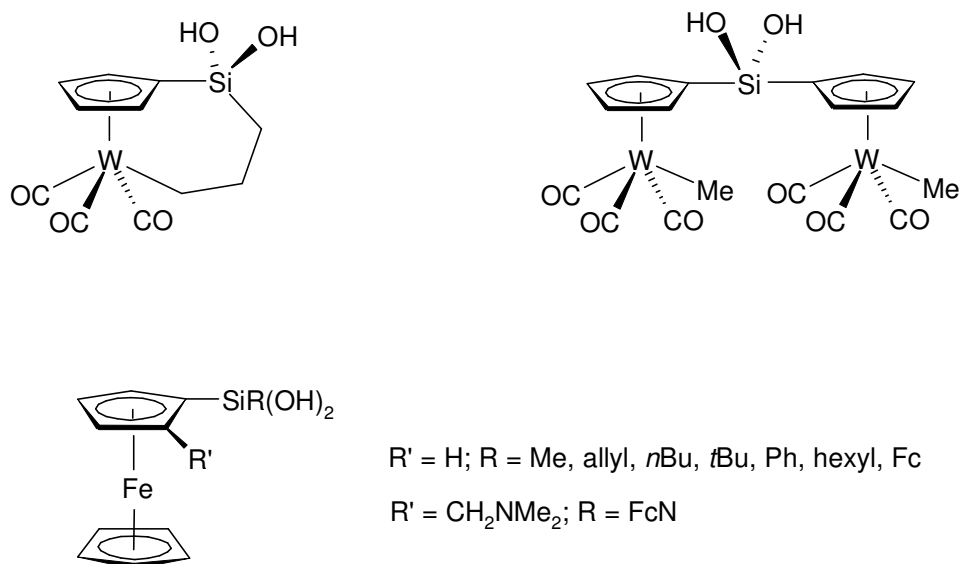

R' = H; R = Me, allyl, *n*Bu, *t*Bu, Ph, hexyl, Fc

R' = CH$_2$NMe$_2$; R = FcN

Fig. 2: Halfsandwich tungsten fragment- and ferrocenyl-containing silanediols.

This report deals with the synthesis of halfsandwich tungsten-silanediols and the conversion into the corresponding silanetrisiloxane as well. Additionally, some alternative strategies for the introduction of an organodichlorosilyl group at the cyclopentadienyl ligand, suitable for hydrolysis are discussed.

RESULTS AND DISCUSSION

Organodichloro-η^5-cyclopentadienyl Tungsten Complexes. Due to the fact that it is not possible to introduce directly a silanediol group into the cyclopentadienyl ligand of a halfsandwich tungsten complex, suitable precursors which allow the conversion into the corresponding silanediol have to be established. A direct access involves the reaction of $Cl_2MeSiC_5H_5$ (**1**) with $(MeCN)_3W(CO)_3$ in refluxing THF which is finished after 18 hours and results in the formation of the hydrido complex $[Cl_2MeSi(C_5H_4)](OC)_3WH$ (**2**) (Scheme 1). The reaction involves substitution of the three acetonitrile ligands, with simultaneous ring C-H activation and hydrogen transfer to the metal center [45-48] and was already realized for the diorganochloro analogue $[ClMe_2Si(C_5H_4)](OC)_3WH$ [38, 49]. The tungsten-dichlorosilane **2** is obtained in good yield of 76 % as a red and high viscous oil which shows good solubility in petrolether, benzene, diethylether, methylene chloride or THF. **2** is moisture sensitive but can be stored without decomposition for several months under nitrogen atmosphere.
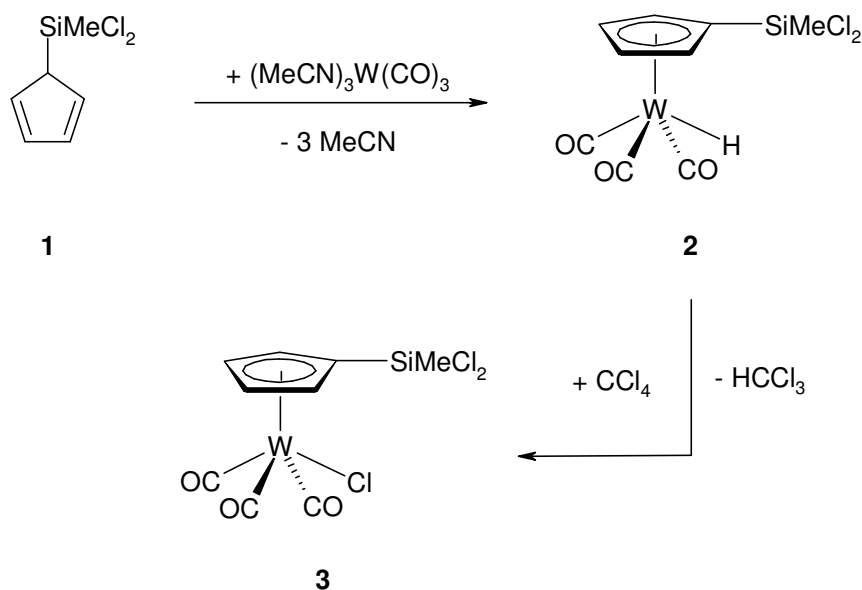
Scheme 1: Preparation of tungsten hydrido and chloro complexes containing a $MeSiCl_2$-function at the cyclopentadienyl ligand.

Metathetical H/Cl-replacement at tungsten is realized when an diethylether solution of **2** is treated with a high excess of CCl_4 and the reaction mixture stirred over four days at ambient temperature. As a result, the tungsten chloride $[Cl_2MeSi(C_5H_4)](OC)_3WCl$ (**3**) (Scheme 1) is isolated in a good yield of 82 % as a dark orange solid which shows a raised moisture sensitivity in comparison to **2**.

The ^{1}H-NMR spectra of **2** and **3** in D_6-benzene show virtuel triplets evoked by an AA'BB'-spin system for the two inequivalent pairs of cyclopentadienyl ring protons. The W-H hydride resonance of **2** appears at δ = -7.34 ppm and is accompanied by ^{183}W-satellites [^1J(HW) = 36.3 Hz]. The ^{29}Si-NMR resonances are detected at 17.35 (**2**) and 17.14 (**3**) ppm and lie in the range reported for the dichlorosilyl ferrocene derivative $CpFe[(C_5H_4)SiMeCl_2]$ (^{29}Si-NMR: δ = 22.3 ppm) [50]. The $\tilde{\nu}$ (CO) absorption bands of **2** and **3** are detected very close to those of the analogous $Cp(OC)_3WR$ (R = H, Cl) and illustrate that the silyl group have nearly no influence on the electronic situation at the metal.

As recently shown it is possible to vary the ligand sphere at the metal center of tungsten complexes with a SiH- or SiCl-functionalized cyclopentadienyl ligand by carbonyl-phosphine exchange [51]. These manipulations leads to a raised electron density at the tungsten atom which is partially transferred to the silicon. As a consequence the silanediol group should be stabilized with respect to self-condensation.

Addition of PMe_3 to a solution of **2** in PE results cleanly after two days in the displacement of one CO ligand and the formation of $[Cl_2MeSi(C_5H_4)](OC)_2(Me_3P)WH$ (**4a**) in high yield of 93 % (Eq. 1). **4a** is obtained as pale yellow solid which show an reduced solubility in solvents like PE or Et_2O in comparison to **2**.

Analogous reaction of **3** with PPh_3 is realized when the reaction is carried out in benzene under UV-irradiation over the period of about four hours at room temperature to give stereospecifically *cis*-$[Cl_2MeSi(C_5H_4)](OC)_2(Ph_3P)WCl$ (**4b**) (Eq. 1). **4** is isolated as a microcrystalline orange solid in high yield of 95 % and dissolves readily in common aliphatic and aromatic solvents. The phosphine-substitution of **4b**

reduces significantly the moisture sensibility in comparison to **3** and allows air exposition for several minutes.
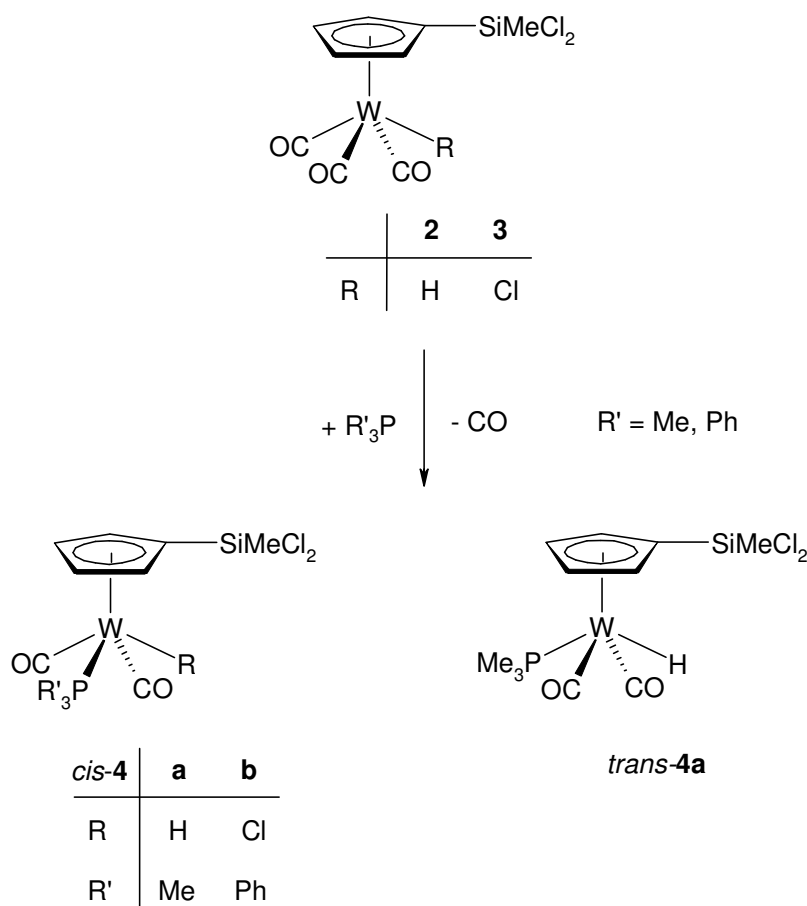
**Eq. 1:** CO/PR'$_3$-exchange products deriving from the tungsten complexes **2** and **3**.

The NMR spectra of **4a** indicate the formation of the *cis-* and the *trans-*isomer, e.g. illustrated by two ^{31}P-NMR signals at -19.11 (*trans*) and -21.60 (*cis*) ppm and doubling of the hydrido resonance in the ^{1}H-NMR spectrum. The ratio of the isomers is ^{1}H-NMR-spectroscopically determined and amounts to 55:45 (*trans/cis*) which is very similar to that of Cp(OC)$_2$(Me$_3$P)MH (M = Mo, W) [52], reflecting that the dichlorosilyl group attached to the cyclopentadienyl ligand has nearly no influence on the isomer ratio.

In the ^{31}P-NMR spectrum of **4b** appears a singulet at 21.99 ppm, showing [183]W-satellites [^1J(PW) = 268.2 Hz] which lie in the expected range. As a consequence of

the stereogenic metal center, all four ring protons are inequivalent and four multiplets are observed in the ^{1}H-NMR spectra.

In general, no significant differences concerning reaction time and stereochemistry in relation to the well-established C_5H_5 derivatives $Cp(OC)_2(Me_3P)MH$ (M = Mo, W) [52], $Cp(OC)_2(Ph_3P)MX$ (M = Mo, W; X = Cl, Br, I) [53, 54] or the monochlorosilyl-cyclopentadienyl tungsten complexes $[XMe_2Si(C_5H_4)](OC)_2(R'_3P)WR$ (X = H, Cl; R' = Me, Ph; R = H, Cl) [51] are observed.

An attractive route to introduce a dichlorosilyl group at the cyclopentadienyl unit of a halfsandwich tungsten complex is offered by the direct metalation of the ring ligand with a strong base like nBuLi followed by the reaction with organochlorosilanes. For example it is possible to lithiate the methyl tungsten complex $Cp(OC)_3WMe$ with nBuLi at −78 °C in THF to generate the $(LiC_5H_4)(OC)_3WMe$-species which can be treated *in situ* with electrophilic reagents like chlorosilanes [55], chlorophosphanes [56] or CO_2 [57] and as recently demonstrated by our own work, also with diorganochlorosilanes affording the tungsten complexes $[HR_2Si(C_5H_4)](OC)_3WMe$ (R = Me, iPr, Ph) [58]. According to this method, the tungsten methyl complex $Cp(OC)_3WMe$ (**5**) is treated with nBuLi at −78 °C in THF to generate the cyclopentadienyl-lithiated intermediate $(LiC_5H_4)(OC)_3WMe$ which is then reacted *in situ* with an excess of $MeSiCl_3$ to avoid multiple substitution of the silane. After two hours the dichlorosilyl-functionalized tungsten complex $[Cl_2MeSi(C_5H_4)](OC)_3WMe$ (**6**) is obtained in 75 % yield as a yellow solid (Eq. 2). The ^{1}H-NMR spectrum shows the expected pattern of an AA'BB'-spin system and the ^{29}Si-NMR resonance lies very close to that of **2** at 17.99 ppm.
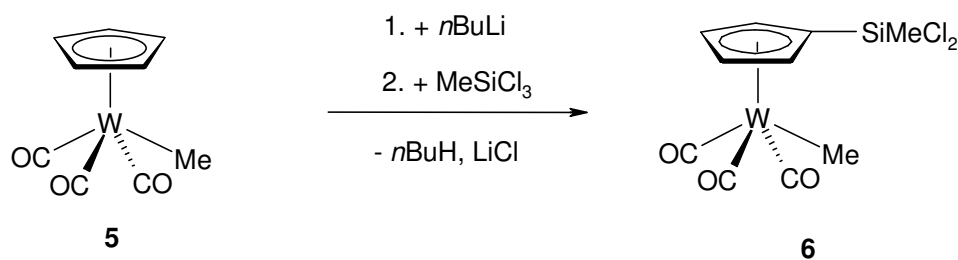
Eq. 2: Synthesis of the tungsten methyl complex **6** containing a $MeSiCl_2$-function attached to the cyclopentadienyl ligand.

Like our previous studies have shown, it is possible to silylate regioselectively the cyclopentadienyl ligand of the dilithiated tungsten complex Li[W(C_5H_4Li)(CO)$_3$] (**7**) which can be synthesized from the tungsten hydrido complex Cp(OC$_3$)WH by metallation with two equivalents of *n*BuLi in THF [49, 59]. This method allows the use of an excess of non-volatile chlorosilane to avoid double substitution, since unreacted silane can be easily separated from the lithium tungsten salt by washing with petrolether. In addition, **7** is charaterized by a higher nucleophilicity than the lithio-species (LiC_5H_4)(OC)$_3$WMe, which shows no reaction with *tert*-butyltrichlorosilane at room temperature (Scheme 2).

Indeed **7**, when suspended in THF, reacts with *tert*-butyltrichlorosilane at room temperature to give after 18 hours the cyclopentadienyl-functionalized lithium tungstate Li{W[(C_5H_4)Si*t*BuCl$_2$](CO)$_3$} (**8**) in 83 % yield (Scheme 2). After washing with petrolether, **8** is isolated as a pale redbrown, pyrophoric and moisture sensitive powder. Final treatment of **8** with MeI in petrolether leads at room temperature to the transformation into the neutral methyl complex [Cl$_2$*t*BuSi(C_5H_4)](OC)$_3$WMe (**9**) in 74 % yield.
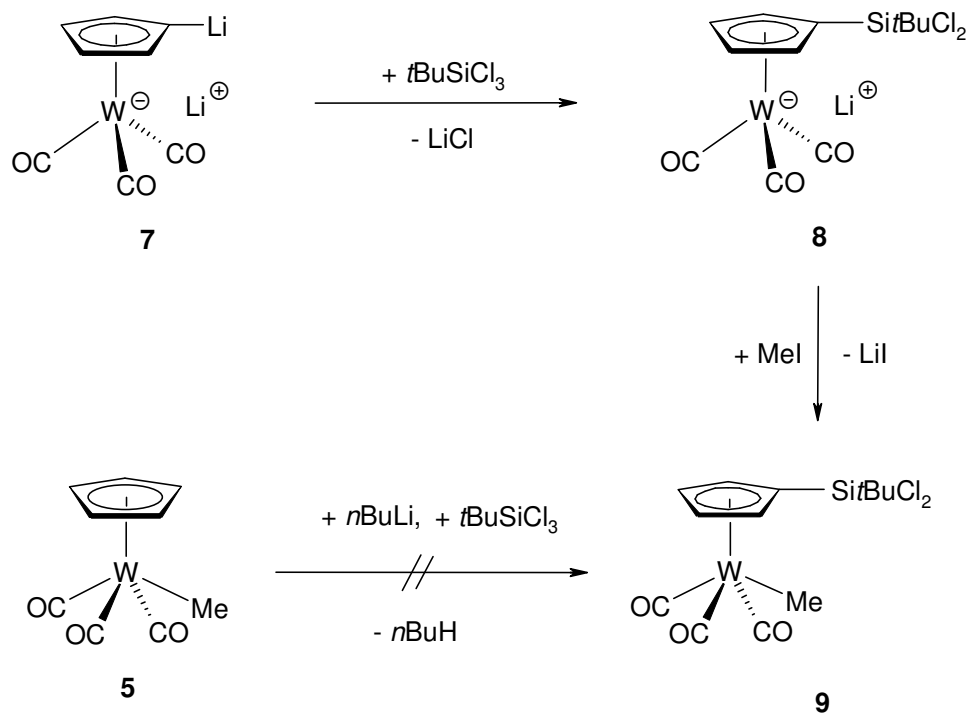

Scheme 2: Two step reaction via the tungstate **8**, necessary for the functionalization with a *tert*-butyl group leading to the neutral tungsten methyl complex **9**.

The ^{29}Si-NMR resonance of **9** is observed at 22.72 ppm and is slightly shifted to lower field in relation to the tungsten complexes **2-4a,b** and about 8 ppm to higher field compared to the ferrocene complex FcSitBuCl$_2$ (^{29}Si-NMR: 30.4 ppm) [42].

Formation of Tungsten-silandiols (10a-c) by Hydrolysis. The most efficient approach to silandiols is given by the hydrolysis of the organodichlorosilyl precursors in the presence of NEt$_3$ as an auxiliary base. However, only in the case **9**, this reaction affords cleanly the novel tungsten complex [(HO)$_2$$t$BuSi(C$_5H_4$)](OC)$_3$WMe (**10b**) containing a cyclopentadienyl-bound silanediol group (Eq. 3).

After 45 min. stirring in a solvent mixture of diethylether and benzene at room temperature the corresponding tungsten-silanediol **10b** is obtained in 89 % yield as a red crystalline solid showing an increased solubility in aromatic solvents compared to metallo-silanediols with M-Si bond [28, 30-33]. No condensation is observed for **10b**, neither in solution nor in the solid state. This behaviour can be referred to the bulkiness of the *tert*-butyl group preventing intermolecular interaction of the Si(OH)$_2$ groups.

	6	**9**	**4b**
R	Me	tBu	Me
R'	Me	Me	Cl
L	CO	CO	PPh$_3$

10	**a**	**b**	**c**
R	Me	tBu	Me
R'	Me	Me	Cl
L	CO	CO	PPh$_3$
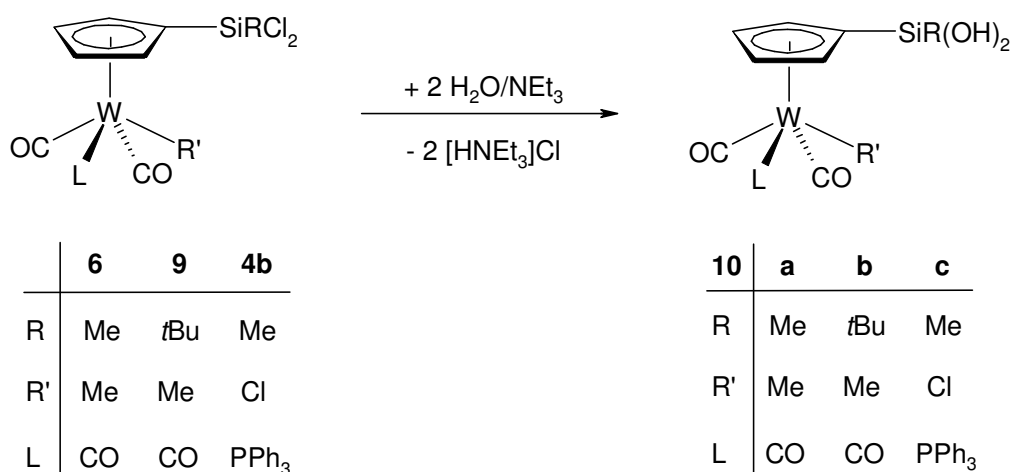
Eq. 3: Hydrolysis of the RSiCl$_2$-precursors **4b**, **6** and **9** leading to only one pure and stable silanediol (**10b**).

The ^{29}Si-NMR resonance of **10b** is located at −18.1 ppm (C$_6$D$_6$), strongly highfield-shifted in relation to tungsten-silanediols [^{29}Si-NMR: δ = 44.8 and 50.5 ppm for (C$_5$R$_5$)(OC)$_2$(Me$_3$P)WSiMe(OH)$_2$, R = H, Me] but close to the value of the ferrocenyl-silanediol [(HO)$_2$tBuSi(C$_5$H$_4$)]FeCp [^{29}Si-NMR (CDCl$_3$): δ = -9.8 ppm] [42].

In the case of the tungsten methyl complex **6**, the reaction in diethylether at room temperature over the period of one hour leads to the formation of the corresponding silanediol [(HO)$_2$MeSi(C$_5$H$_4$)](OC)$_3$WMe (**10a**) (Eq. 3), indicated by the ^{1}H-NMR resonance at 2.85 ppm for the silanediol group. However, this hydrolysis is accompanied by the formation of several unknown by-products, presumably generated by self-condensation of the Si(OH)$_2$ group.

The hydrolysis of **4b**, performed at 0 °C in a 2:1-diethylether/benzene solvent mixture gives the corresponding silanediol [(HO)$_2$MeSi(C$_5$H$_4$)](Ph$_3$P)(OC)$_2$WCl (**10c**) (Eq. 3). However, the reaction involves generation of a rising amount of unknown by-products and free PPh$_3$, indicating extensive decomposition of **10c**.

The hydrolyses of the dichlorosilyl compounds [Cl$_2$MeSi(C$_5$H$_4$)](OC)$_3$WH (**2**) and [Cl$_2$MeSi(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WH (**4a**) are carried out in diethylether, also in the presence of NEt$_3$. The reaction of **2** is performed at −40 °C over the period of 45 minutes and doesn`t yield the desired silanediol [(HO)$_2$MeSi(C$_5$H$_4$)](OC)$_3$WH analytical pure.

Instead broad signals for the cyclopentadienyl ring, the methyl and for the hydrido protons are observed in the ^{1}H-NMR spectrum, indicating uncontrolled self-condensation of the silanediol. An almost similar result is obtained by the hydrolysis of **4a** under identical conditions, leading in this case to a yellow smudgy solid. The ^{1}H- and ^{31}P-NMR spectra shows broad signals and reveales additionally the loss of the coordinated PMe$_3$ ligand.

The tungsten-silanediol **10b** allow specially designed synthesis of siloxanes bearing functionality. In this context, **10b** is treated in diethylether with an excess of Me$_2$Si(H)Cl to give at ambient temperature in the presence of NEt$_3$ after four hours

the multifunctionalized tungsten-trisiloxane [(HMe₂SiO)₂tBuSi(C₅H₄)](OC)₃WMe (**11**) (Eq. 4), crystallized from PE at 0 °C, in 83 % yield.
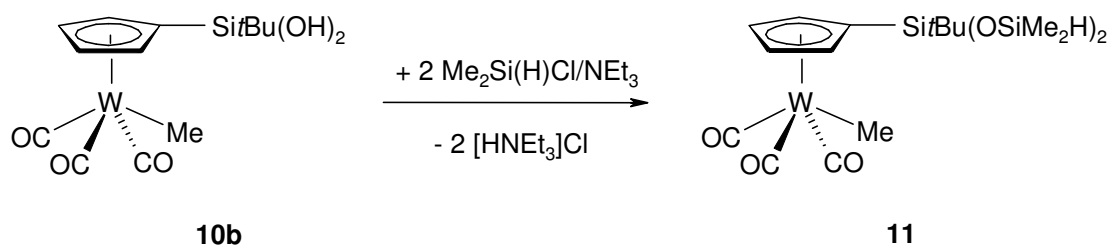
Eq. 4: Chemical proof of the existence of silanediol **10b** by transformation into the corresponding trisiloxane by use of Me₂Si(H)Cl.

11, the first example of a mononuclear metal complex containing a cyclopentadienyl-bound branched trisiloxane, is isolated as a red microcrystalline powder, showing good solubility in nonpolar solvents.

CONCLUSION

The findings of this report demonstrate that halfsandwich tungsten complexes with η^5-cyclopentadienyl-fixed dichlorosilyl function are good accessible by reaction of MeSiCl$_2$-substituted cyclopentadienes with (MeCN)$_3$W(CO)$_3$, by one-pot reaction of Cp(OC)$_3$WMe with nBuLi and MeSiCl$_3$ or upon treatment of the dilithated Li[W(LiC$_5$H$_4$)(CO)$_3$] with organodichlorosilanes and MeI via a Cl$_2$RSi-substituted lithium tungstate. Such precursor complexes can be modified at the tungsten center without any complications. The transition metal effect and the stability of this type of metal fragment-substituted silandiols are strongly reduced, compared to the tungstenmethyl- and tungsten-silandiols containing a methylene spacer or bearing the Si(OH)$_2$ unit directly at the transition metal atom [28, 30-33, 60]. As a consequence, the compounds with methyl groups at the silicon atom are not obtained analytically pure and only the sterical hindered *tert*-butyl-substituted tungsten-silandiol **10b** allows isolation and characterization. **10b** undergoes controlled co-condensation to a metal fragment-containing trisiloxane and will probably allow the formation of heterosiloxanes with a series of element- and metal chlorides.

EXPERIMENTAL SECTION

General Remarks: All operations were performed under an atmosphere of purified and dried nitrogen using Schlenk-type techniques. Solvents were dried according to conventional procedures, distilled and saturated with N_2 prior to use. - NMR: Jeol Lambda 300 (300.4 MHz, 75.5 MHz, and 59.6 MHz for ^{1}H, ^{13}C, and ^{29}Si, respectively). [D$_6$]-benzene as a solvent: δ_H = 7.15, δ_C = 128.0; for ^{29}Si rel. to TMS external. - IR: Perkin-Elmer 283 grating spectrometer. - Melting points: Differential thermo analysis (Du Pont 9000 Thermal Analysis System). - Elemental analyses were performed in the laboratories of the *Institut für Anorganische Chemie der Universität Würzburg*. - Starting materials were prepared according to literature procedures: Cl$_2$MeSiC$_5$H$_5$ (**1**) [61], (MeCN)$_3$W(CO)$_3$ [62], PMe$_3$ [63], Cp(OC)$_3$WMe (**5**) [64] and Li[W(LiC$_5$H$_4$)(CO)$_3$] (**7**) [49, 59]. The reagents *n*BuLi, NEt$_3$, PPh$_3$, *t*BuSiCl$_3$, Me$_2$Si(H)Cl and CCl$_4$ were purchased from commercial sources and the liquids distilled prior use except *n*BuLi.

*1) [Cl$_2$MeSi(C$_5$H$_4$)](OC)$_3$WH (**2**)*

Tricarbonyl[η^5-(dichloromethylsilyl)-cyclopentadienyl]hydridotungsten(II)

A solution of 3.40 g (18.9 mmol) of **1** and 5.87 g (15.0 mmol) of (MeCN)$_3$W(CO)$_3$ in 80 ml THF were refluxed under light exclusion over the period of 18 hours. Then, all volatiles were removed in vacuo and the crude residue was extracted with 8 x 20 ml PE. The extracts were combined and filtered through a celite path. The solvent was removed in vacuo and the crude product was washed two times with each 5 ml PE at –78 °C and finally dried in vacuo. Yield 5.10 g (76 %). Dark red oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.74 – 4.73 (m, 2 H, H$_4$C$_5$), 4.63 – 4.61 (m, 2 H, H$_4$C$_5$), 0.57 (s, 3 H, H$_3$CSi), -7.34 [s, ^{1}J(HW) = 36.3 Hz, 1 H, HW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 216.15 (s, CO), 93.27 [s, ^{1}J(CW) = 4.8 Hz, C$_5$H$_4$], 91.33 [s, ^{1}J(CW) = 3.8 Hz, C$_5$H$_4$], 90.04 [s, ^{1}J(CW) = 4.2 Hz, *ipso*-C$_5$H$_4$], 4.71 [s, ^{1}J(CSi) = 72.5 Hz, CH$_3$Si] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 15.78 (s) ppm. - **IR** (pentane): $\tilde{\nu}$ (CO) = 2031

(s), 1942 (vs) cm^{-1}. – Anal. calc. for C$_9$H$_8$Cl$_2$O$_3$SiW (447.00): C 24.18, H 1.80; found: C 24.34, H 1.71.

2) [Cl$_2$MeSi(C$_5$H$_4$)](OC)$_3$WCl (**3**)

Tricarbonylchloro[η^5-(dichloromethylsilyl)-cyclopentadienyl]tungsten(II)

A solution of 1.13 g (2.54 mmol) of **2** in 20 ml Et$_2$O was treated with 6 ml of CCl$_4$ and stirred over the period of four days at room temperature. All volatiles were removed in vacuo and the crude product was washed two times with each 5 ml portions of PE at –78 °C. Yield: 1.00 g (82 %). Dark orange solid. M.p. 48 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.68 – 4.66 (m, 2 H, H$_4$C$_5$), 4.49 – 4.47 (m, 2 H, H$_4$C$_5$), 0.72 (s, 3 H, H$_3$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 229.51 (s, *cis*-CO), 214.21 (s, *trans*-CO), 103.01 [s, ^{1}J(CW) = 4.2 Hz, C$_5$H$_4$], 94.77 [s, ^{1}J(CW) = 4.0 Hz, C$_5$H$_4$], 93.18 [s, ^{1}J(CW) = 3.9 Hz, *ipso*-C$_5$H$_4$], 5.71 [s, ^{1}J(CSi) = 69.5 Hz, CH$_3$Si] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 17.14 (s) ppm. - **IR** (Et$_2$O): $\tilde{\nu}$ (CO) = 2048 (s), 1963 (vs), 1957 (s) cm^{-1}. – Anal. calc. for C$_9$H$_7$Cl$_3$O$_3$SiW (481.45): C 22.45, H 1.47; found: C 22.47, H 1.86.

3) [Cl$_2$MeSi(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WH (**4a**)

Dicarbonyl[η^5-(dichloromethylsilyl)-cyclopentadienyl]hydrido(trimethylphosphino)-tungsten(II)

To a solution of 700 mg (1.57 mmol) of **2** in 20 ml PE, were added 1.4 ml of PMe$_3$ and the reaction mixture stirred over a period of two days under exclusion of light. All volatiles were removed in vacuo leading to an oil. The crude product was washed with 4 ml PE at 0 °C and finally dried in vacuo. Yield: 739 mg (95 %). Pale yellow solid. M.p.: 53 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.97 – 4.58 (m, 4 H, H$_4$C$_5$), 1.01 [d, ^{2}J(HCP) = 9.6 Hz, 9 H, H$_3$CP], 0.56, 0.55 (s, 3 H, H$_3$CSi), -7.28 (*cis*) [d, ^{1}J(HW) = 49.6 Hz, ^{2}J(HCP) = 24.4 Hz, 1 H, HW], -8.09 (*trans*) [d, ^{1}J(HW) = 49.3 Hz, ^{2}J(HCP) = 68.3 Hz, 1 H, HW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 224.46 [d, ^{2}J(CP) =

15.6 Hz, CO], 92.75, 92.48, 91.47, 91.33 (s, C_5H_4), 90.77, 89.44 (s, *ipso*-C_5H_4), 25.68 [d, ^1J(CP) = 35.3 Hz, CH_3P], 22.39 [d, ^1J(PC) = 33.2 Hz, CH_3P], 4.68, 4.09, 3.95 (s, CH_3Si) ppm. - ^{29}**Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = 16.13, 16.12 (s) ppm. - ^{31}**P{^{1}H}-NMR** (121.5 MHz, C_6D_6): δ = -19.11 [s, ^1J(PW) = 256.2 Hz, *trans*-PCH_3], -21.60 [s, ^1J(PW) = 281.0 Hz, *cis*-PCH_3] ppm. - **IR** (Et_2O): $\tilde{\nu}$ (CO) = 1943.4 (vs), 1859.6 (vs) cm^{-1}. - Anal. calc. for $C_{11}H_{17}Cl_2O_2PSiW$ (495.07): C 26.69, H 3.46; found: C 26.77, H 3.59.

*4) [Cl$_2$MeSi(C$_5$H$_4$)](OC)$_2$(Ph$_3$P)WCl (**4b**)*

Dicarbonylchloro[η^5-(dichloromethylsilyl)-cyclopentadienyl](triphenylphosphino)-tungsten(II)

A solution of 1.00 g (2.08 mmol) of **3** and 545 mg (2.08 mmol) of PPh_3 in 15 ml benzene was UV-irradiated (Quarz lamp TQ 718, 700 W, Hanau) over a period of 4 hours. After reaction the solvent was removed in vacuo and the crude orange residue was washed two times with each 4 ml PE at -78 °C. Yield: 1.40 g (1.96 mmol, 94 %). Orange solid. M.p.: 56 °C. - ^{1}**H-NMR** (300.4 MHz, C_6D_6): δ = 7.61 - 7.42, 7.00 - 6.91 (m, 15 H, H_5C_6P), 5.62 - 5.58 (m, 1 H, H_4C_5), 5.51 - 5.46 (m, 1 H, H_4C_5), 4.70 - 4.64 (m, 1 H, H_4C_5), 4.60 - 4.55 (m, 1 H, H_4C_5), 0.97 (s, 3 H, H_3CSi) ppm. - ^{13}**C{^{1}H}-NMR** (75.5 MHz, C_6D_6): δ = 247.95 [d, ^2J(CWP) = 21.4 Hz, *cis*-CO], 236.80 [d, ^2J(CWP) = 6.9 Hz, *trans*-CO], 134.84 [d, ^1J(CP) = 47.2 Hz, *ipso*-C_6H_5], 134.38 [d, ^3J(CCCP) = 10.0 Hz, *meta*-C_6H_5], 130.55 [d, ^4J(CCCCP) = 2.4 Hz, *para*-C_6H_5], 128.59 [d, ^2J(CCP) = 10.0 Hz, *ortho*-C_6H_5], 117.33 (s, C_5H_4Si), 107.45 (s, C_5H_4Si), 102.49 (s, *ipso*-C_5H_4Si), 91.03 (s, C_5H_4Si), 89.60 (s, C_5H_4Si), 4.98 (s, CH_3Si) ppm. - ^{29}**Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = 20.00 (s) ppm. - ^{31}**P{^{1}H}-NMR**: (121.5 MHz, C_6D_6): δ = 21.98 [s, ^1J(PW) = 268.2 Hz, PW] ppm. - **IR** ($CHCl_3$): $\tilde{\nu}$ (CO) = 1967 (vs), 1889 (m) cm^{-1}. - Anal. calc. for $C_{26}H_{22}Cl_3O_2PSiW$ (715.73): C 43.63, H 3.10; found: C 44.37, H 3.00.

*5) [Cl$_2$MeSi(C$_5$H$_4$)](OC)$_3$WMe (**6**)*

Tricarbonyl[η^5-(dichloromethylsilyl)-cyclopentadienyl]methyltungsten(II)

A THF-solution (10 ml) containing 240 mg (0.69 mmol) of Cp(OC)$_3$WMe (**5**) was treated with 0.62 ml (0.97 mmol, 1.6 M in cyclohexane) of *n*BuLi at −78 °C and stirred for 45 min. During this period the color changed from yellow to deep brown. To 3.82 g (3 ml, 0.03 mmol) of MeSiCl$_3$ in 15 ml THF were added dropwise at −78 °C the starting THF-solution. The mixture was allowed to warm up to room temperature over the period of 1.5 h and the solvent removed in vacuo. The residue was extracted with 40 ml PE. After filtration the extract was evaporated in vacuo resulting in **6**. Yield: 239 mg (75 %). Yellow solid. M.p.: 59 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.51 - 4.45 (m, 4 H, H$_4$C$_5$), 0.57 [s, ^{2}*J*(HSi) = 7.0 Hz, 3 H, H$_3$CSi], 0.41 [s, ^{2}*J*(HCW) = 4.0 Hz, 3 H, H$_3$CW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 229.08 [s, ^{1}*J*(CW) = 132.3 Hz, CO], 215.97 [s, ^{1}*J*(CW) = 155.9 Hz, CO], 96.91 [s, ^{1}*J*(CW) = 4.1 Hz, C$_5$H$_4$], 95.26 [s, ^{1}*J*(CW) = 4.5 Hz, C$_5$H$_4$), 94.07 [s, ^{1}*J*(CSi) = 65.1 Hz, ^{1}*J*(CW) = 4.8 Hz, C$_5$H$_4$], 2.93 [s, ^{1}*J*(CSi) = 14.9 Hz, CH$_3$Si], -34.20 [s, ^{1}*J*(CW) = 26.2 Hz, CH$_3$W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 17.99 (s) ppm. - **IR** (PE): $\tilde{v}$ (CO) = 2020 (s), 1930 (vs) cm^{-1}. - Anal. calc. for C$_{10}$H$_{10}$Cl$_2$O$_3$SiW (461.03): C 26.05, H 2.19; found: C 26.57, H 2.13.

*6) Li{W[(C$_5$H$_4$)SitBuCl$_2$](CO)$_3$} (**8**)*

Lithium{tricarbonyl[η^5-(*tert*-butyl-dichlorosilyl)-cyclopentadienyl]tungstate}

A suspension of 590 mg (0.93 mmol) of Li[W(LiC$_5$H$_4$)(CO)$_3$] (**7**) in 1 ml THF was treated with 191 mg (1 mmol) of MeSiCl$_3$ at room temperature and the reaction mixture stirred over the period of 18 hours. The solvent was removed in vacuo and the crude residue was washed six times with 4 ml portions of PE leading to a pale redbrown and pyrophoric powder after drying in vacuo. Yield: 380 mg (83 %). Pale redbrown solid. - **^{1}H-NMR** (300.4 MHz, CD$_3$CN): δ = 5.31 - 5.29 (m, 2 H, H$_4$C$_5$), 5.24 - 5.22 (m, 2 H, H$_4$C$_5$), 1.12 (s, 9 H, H$_3$CSi) ppm. - **IR** (THF): $\tilde{v}$ (CO) = 1889 (s), 1805 (s), 1720 (vs) cm^{-1}. C$_{12}$H$_{13}$Cl$_2$LiO$_3$SiW (495.02).

*7) [Cl₂tBuSi(C₅H₄)](OC)₃WMe (**9**)*

Tricarbonyl[η^5-(*tert*-butyl-dichlorosilyl)-cyclopentadienyl]methyltungsten(II)

380 mg (0.77 mmol) of **8** were suspended in a solvent mixture of 20 ml PE and 10 ml benzene and then treated with 0.4 ml of MeI. The reaction mixture was then stirred over 20 hours at room temperature. All insoluble material was filtered off by use of a celite path and the resulting filtrate was evaporated to dryness. The crude product was washed with 4 ml PE at −78 °C. Final drying in vacuo led to a solid consisting of **9**. Yield: 287 mg (74 %). Orange solid. M.p.: 91 °C. - **¹H-NMR** (300.4 MHz, C_6D_6): δ = 5.58 − 5.54 (m, 4 H, H_4C_5), 0.82 (s, 9 H, H_3CSi), 0.55 [s, ^2J(HCW) = 3.8 Hz, 3 H, H_3CW] ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C_6D_6): δ = 229.02 [s, ^1J(CW) = 132.0 Hz, CO], 214.47 [s, ^1J(CW) = 152.2 Hz, CO], 95.36 [s, ^1J(CW) = 4.4 Hz, C_5H_4], 95.24 [s, ^1J(CW) = 4.0 Hz, C_5H_4), 92.72 [s, ^1J(CW) = 3.3 Hz, *ipso*-C of C_5H_4], 23.14 [s, ^1J(CSi) = 15.7 Hz, CH_3Si], -33.45 [s, ^1J(CW) = 25.1 Hz, CH_3W] ppm. - **²⁹Si{¹H}-NMR** (59.6 MHz, C_6D_6): δ = 22.72 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2021 (s), 1933 (vs) cm⁻¹. - Anal. calc. for $C_{13}H_{16}Cl_2O_3SiW$ (503.11): C 31.04, H 3.21; found: C 30.57, H 3.13.

*8) [(HO)₂MeSi(C₅H₄)](OC)₃WMe (**10a**)*

Tricarbonyl[η^5-(dihydroxymethylsilyl)-cyclopentadienyl]methyltungsten(II)

A solution of 220 mg (0.46 mmol) of **6** and 0.3 ml of NEt_3 in 10 ml Et_2O was treated with 0.3 ml of water at room temperature. The reaction mixture was stirred over the period of one hour at this temperature. Then, the reaction mixture was dried over Na_2SO_4 and all insoluble material was filtered off through a celite path and the filtrate evaporated to dryness. The crude product was washed with 4 ml PE at −78 °C and finally dried in vacuo. - **¹H-NMR** (300.4 MHz, C_6D_6): δ = 4.80 − 4.76 (m, 4 H, H_4C_5), 2.85 (bs, 2 H, HOSi), 0.45 [s, ^2J(HCW) = 3.7 Hz, 3 H, H_3CW], 0.25 (s, 3 H, H_3CSi) ppm. $C_{10}H_{12}O_5SiW$ (414.14).

*9) [(HO)$_2$tBuSi(C$_5$H$_4$)](OC)$_3$WMe (**10b**)*

Tricarbonyl[η^5-(*tert*-butyl-dihydroxysilyl)-cyclopentadienyl]methyltungsten(II)

Analogous to 8) from 202 mg (3.80 mmol) of **9** and 0.3 ml of NEt$_3$ and 0.4 ml of water in a solvent mixture of 20 ml Et$_2$O and 10 ml benzene at room temperature over the period of 45 min. Yield: 158 mg (89 %). Red solid. M.p.: 71 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.75 – 4.74 (m, 2 H, H$_4$C$_5$), 4.65 – 4.63 (m, 2 H, H$_4$C$_5$), 2.30 (s, 2 H, HOSi), 0.91 (s, 9 H, H$_3$CSi), 0.56 [s, ^{2}J(HCW) = 3.5 Hz, 3 H, H$_3$CW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 231.12 [s, ^{1}J(CW) = 132.5 Hz, CO], 215.45 [s, ^{1}J(CW) = 152.6 Hz, CO], 97.46 [s, ^{1}J(CW) = 4.5 Hz, C$_5$H$_4$], 96.41 [s, ^{1}J(CW) = 4.2 Hz, C$_5$H$_4$), 94.44 [s, ^{1}J(CW) = 3.8 Hz, *ipso*-C of C$_5$H$_4$], 25.97 [s, ^{1}J(CSi) = 16.0 Hz, CH$_3$Si], -32.31 [s, ^{1}J(CW) = 25.6 Hz, CH$_3$W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = - 18.1 (s) ppm. - **IR** (Et$_2$O): $\tilde{\nu}$ (CO) = 2024 (s), 1935 (vs) cm^{-1}. - Anal. calc. for C$_{13}$H$_{18}$O$_5$SiW (466.22): C 33.49, H 3.89; found: C 33.11, H 4.26.

*10) [(HO)$_2$MeSi(C$_5$H$_4$)](Ph$_3$P)(OC)$_2$WCl (**10c**)*

Dicarbonylchloro[η^5-(dihydroxymethylsilyl)-cyclopentadienyl](triphenylphosphino)-tungsten(II)

Analogous to 8) from 440 mg (0.61 mmol) of **4b** and 0.6 ml of NEt$_3$ and 0.6 ml of water in a solvent mixture of 20 ml Et$_2$O and 10 ml benzene at 0 °C over the period of 30 min. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.82 – 7.53, 7.10 – 6.90 (m, 15 H, phenyl), 4.97 – 4.95 (m, 1 H, H$_4$C$_5$), 4.77 – 4.75 (m, 1 H, H$_4$C$_5$), 4.55 – 4.53 (m, 1 H, H$_4$C$_5$), 4.07 – 4.05 (m, 1 H, H$_4$C$_5$), 2.44 (s, 2 H, HOSi), 0.80, 0.54 (s, 3 H, H$_3$CSi) ppm. - **^{31}P{^{1}H}-NMR** (121.5 MHz, C$_6$D$_6$): δ = 28.01 [s, ^{1}J(PW) = 268.8 Hz, PW] ppm. C$_{26}$H$_{24}$ClO$_4$PSiW (678.84).

*11) Hydrolysis of [Cl$_2$MeSi(C$_5$H$_4$)](OC)$_3$WH (**2**)*

Analogous to 8) from 250 mg (5.59 mmol) of **2** and 0.3 ml of NEt$_3$ in 10 ml Et$_2$O and 0.2 ml of water at –40 °C for 45 min. at this temperature. Then, 0.2 ml of HOAc was added and then dried over Na$_2$SO$_4$. All insoluble material was filtered off through a celite path and the filtrate evaporated to dryness. The crude product was washed with 4 ml PE at –78 °C and finally dried in vacuo. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 5.60 – 4.88 (m, 4 H, H$_4$C$_5$), 0.64 – 0.56 (s, 3 H, H$_3$CSi), -6.93 - -7.12 (s, 1 H, HW) ppm. C$_9$H$_{10}$O$_5$SiW (410.11).

*12) Hydrolysis of [Cl$_2$MeSi(C$_5$H$_4$)](Me$_3$P)(OC)$_2$WH (**4a**)*

Analogous to 8) from 370 mg (7.47 mmol) of **4a** and 0.5 ml of NEt$_3$ and 0.5 ml of water in 5 ml Et$_2$O at room temperature leading to a smudgy solid. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 5.21 – 4.81 (m, 4 H, H$_4$C$_5$), 1.20 (s, 9 H, H$_3$CP), 0.72 – 0.62 (s, 3 H, H$_3$CSi), -6.98 - -7.24, -7.80 - -7.99 (s, 1 H, HW) ppm. - **^{31}P{^{1}H}-NMR** (121.5 MHz, C$_6$D$_6$): δ = -18.04 (s, *trans*-PCH$_3$), -20.70 (s, *cis*-PCH$_3$) ppm. C$_{11}$H$_{19}$O$_4$PSiW (458.18).

*13) [(HMe$_2$SiO)$_2$tBuSi(C$_5$H$_4$)](OC)$_3$WMe (**11**)*

Tricarbonyl{η^5-[*tert*-butyl-bis(dimethylsiloxy)silyl]-cyclopentadienyl}methyltungsten(II)

Analogous to 8) from 122 mg (2.62 mmol) of **10b** and 0.3 ml of NEt$_3$ and 0.4 ml of Me$_2$Si(H)Cl in 10 ml Et$_2$O at room temperature over the period of 18 hours. Yield: 127 mg (83 %). Red solid. M.p.: 51 °C. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 5.07 [sept, ^{3}J(HSiCH) = 2.8 Hz, 2 H, HSi], 4.78 – 4.73 (m, 4 H, H$_4$C$_5$), 0.90 (s, 9 H, H$_3$CSi), 0.59 [s, ^{2}J(HCW) = 3.9 Hz, 3 H, H$_3$CW], 0.26 [d, ^{3}J(HCSiH) = 2.8 Hz, 12 H, H$_3$CSi] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 238.12 [s, ^{1}J(CW) = 132.3 Hz, CO], 215.35 [s, ^{1}J(CW) = 153.3 Hz, CO], 96.77 [s, ^{1}J(CW) = 4.1 Hz, C$_5$H$_4$], 96.17 [s, ^{1}J(CW) = 4.0 Hz, C$_5$H$_4$), 93.22 [s, ^{1}J(CW) = 3.9 Hz, *ipso*-C of C$_5$H$_4$], 24.31 [s, ^{1}J(CSi) = 16.1 Hz, CH$_3$Si], -0.47 (s, CH$_3$Si), -33.44 [s, ^{1}J(CW) = 25.3 Hz, CH$_3$W] ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -34.88 (s, Si*t*Bu), -21.4 (s, SiMe$_2$) ppm. - **IR** (Et$_2$O): $\tilde{\nu}$ (CO) =

2024 (s), 1936 (vs) cm^{-1}. - Anal. calc. for C$_{17}$H$_{30}$O$_5$Si$_3$W (582.53): C 35.05, H 5.19; found: C 35.11, H 5.26.

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Chapter VII

NOVEL MOLYBDENUM AND TUNGSTEN HALFSANDWICH COMPLEXES WITH AN ALKOXYSILYLALKYL-FUNCTIONALIZED η^5-CYCLOPENTADIENYL LIGAND

- SYNTHESIS OF THE DISILOXANE-BRIDGED BIS-TUNGSTEN-SILANOL $\{HOMe_2SiW(PMe_3)(CO)_2[(\eta^5-C_5H_4)(CH_2)_3Me_2Si]\}_2O$ -
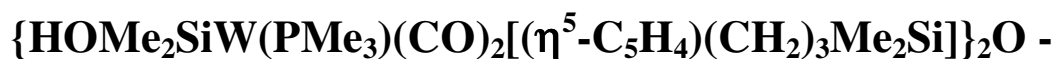
SUMMARY

The reaction of the silylated cyclopentadiene $Cp(CH_2)_3Si(OMe)Me_2$ (**4a**) with $(MeCN)_3W(CO)_3$ leads to the formation of the tungsten hydrido complex $[MeOMe_2Si(CH_2)_3(\eta^5-C_5H_4)](OC)_3WH$ (**5c**) with an methoxysilylpropyl-substituted cyclopentadienyl-ligand. An alternative access to this type of compound is given by the reaction of $Cp(CH_2)_3Si(OMe)_nMe_{3-n}$ [n = 1 - 3 (**4a-c**)] with NaH and $M(CO)_6$ (M = Mo, W), generating the sodium metallates $Na\{M[(\eta^5-C_5H_4)Si(CH_2)_3(MeO)_nMe_{3-n}](CO)_3\}$ [n = 1 - 3, M = Mo, W (**6c-g**)] which are protonated with HOAc to give $[(MeO)_nMe_{3-n}Si(CH_2)_3(\eta^5-C_5H_4)](OC)_3MH$ [n = 1 - 3, M = Mo, W (**5c-f**)]. The alkyl derivatives $[(MeO)_nMe_{3-n}Si(CH_2)_3(\eta^5-C_5H_4)](OC)_3WR$ [R = Me, n = 1 (**8a**); R = Me, n = 3 (**8b**); R = $(CH_2)_3Si(OMe)_2Me$, n = 2 (**8c**)] are generated by the analogous reaction of the sodium tungstates **6c,e,g** with MeI or $(OMe)_2MeSi(CH_2)_3I$. HMe_2Si-functionalization of the tungsten center is accomplished by the deprotonation of **5c** with nBuLi, leading to the lithium tungsten anion $Li\{W[(\eta^5-C_5H_4)Si(CH_2)_3Me_2(MeO)](CO)_3\}$ (**6c**), which is treated with $Me_2Si(H)Cl$ to give $[MeOMe_2Si(CH_2)_3(\eta^5-C_5H_4)](OC)_3WSiMe_2H$ (**10**). Acetic acid-assisted hydrolysis of $[ROMe_2Si(CH_2)_n(\eta^5-C_5H_4)](OC)_3WH$ [(n = 1, R = Et (**5b**), n = 3, R = Me (**5c**)] forms the disiloxane-bridged $\{HW(CO)_3[(\eta^5-C_5H_4)(CH_2)_nMe_2Si-]\}_2$-O [(n = 1 (**12b**), 3 (**12c**)], via the corresponding silanols $[HOMe_2Si(CH_2)_n(\eta^5-C_5H_4)](OC)_3WH$ [(n = 1 (**11b**), 3 (**11c**)]. **12b,c** undergo CO/PMe_3-exchange resulting in the formation of the tungsten complexes $\{HW(PMe_3)(CO)_2[(\eta^5-C_5H_4)(CH_2)_nMe_2Si]\}_2O$ [(n = 1 (**14a**), 3 (**14b**)], which are transformed into the tungsten-silylated species $\{HMe_2SiW(PMe_3)(CO)_2[(\eta^5-C_5H_4)(CH_2)_nMe_2Si]\}_2O$ [(n = 1 (**16a**), 3 (**16b**)] by deprotonation of **14a,b** with nBuLi, followed by the reaction with $Me_2Si(H)Cl$. The treatment of **16b** with dimethyldioxirane yields the novel disiloxane-bridged dinuclear bis-tungsten-silanol $\{HOMe_2SiW(PMe_3)(CO)_2[(\eta^5-C_5H_4)(CH_2)_3Me_2Si]\}_2O$ (**18**).

INTRODUCTION

The preparation of catalysts by immobilizing active transition metal fragments on solid supports such as inorganic surfaces, organic polymers and related materials attracts widespread attention, because heterogenation of homogeneous metal catalysts offers the possibility to combine the most advantageous properties of both homogeneous and heterogeneous systems [1-13]. Organofunctionalized polysiloxanes prepared by a sol-gel procedure [14-16] represent a class of supports intermediate between those of an organic and inorganic nature, and have received renewed and detailed attention quite recently [17-22]. An established method is the modfication of the metal complexes with suitable ligands capable for anchoring on the support surface (Scheme 1).
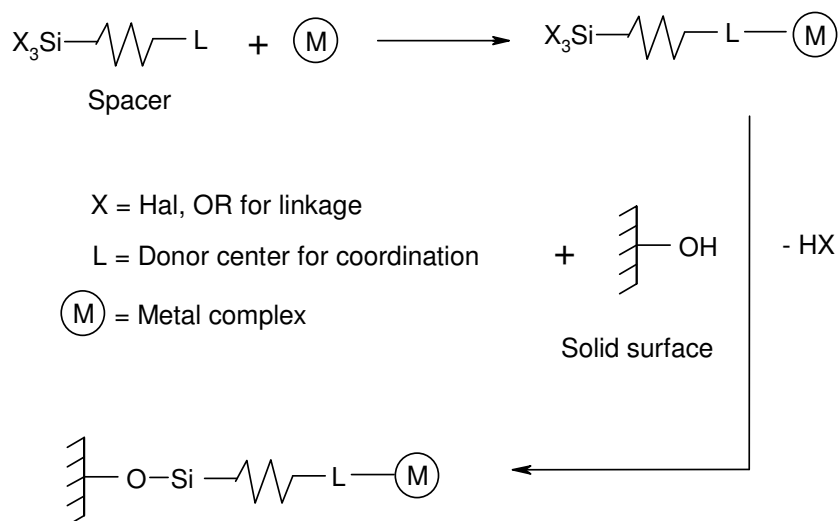
Scheme 1: Immobilization of metal complexes on solid supports.

Numerous studies have been focused on phosphines and amines as ligands for anchoring catalysts [11, 23]. It is therefore surprising that cyclopentadienyls have only marginally been applied as anchoring ligands, although a great number of

organometallic compounds contain cyclopentadienyl as ligand [9, 24-26]. However, recently there is growing interest in the development of catalysts based on functionalized cyclopentadienyl ligands which is rooted in the strong η^5-coordination to the metal, which promises longer lifetime for the catalyst. Furthermore, it allows broad access to cyclopentadienyl-functionalized halfsandwich complexes without limitation of the ligand sphere around the metal center. Suitable units for the attachment on a solid like silica are alkoxysilyl groups, which in principle can be fixed in three different modes to halfsandwich complexes (Fig. 1 and 2). An obvious possibility is to introduce the alkoxysilyl group directly at the cyclopentadienyl ligand of a halfsandwich complex (Type **I**) which can be modified by an alkylidene spacer between these both moieties (Type **II**).
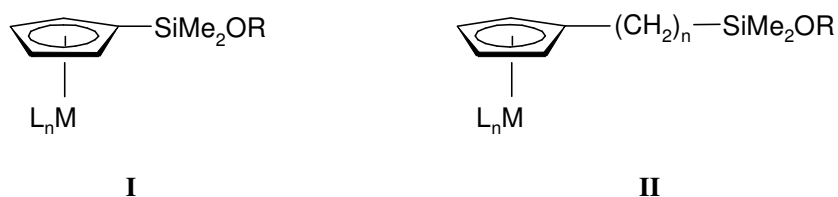

| **I** | **II** |

Fig. 1: Types of halfsandwich complexes with differently alkoxysilyl-functionalized η^5-cyclopentadienyl ligand.

Complexes with directly cyclopentadienyl-bound alkoxysilyl group (Type **I**) have been realized in the case of the ironmethyl complex $[MeOMe_2Si(C_5H_4)](OC)_2FeMe$ [27] and the manganese compound $[MeOMe_2Si(C_5H_4)](OC)_3Mn$, the latter has been anchored on a single crystal silicon wafer for investigations of photoinduced ligand substitution processes [28, 29]. The only reported halfsandwich complexes of the chromium triad are $[PhOMe_2Si(C_5H_4)](OC)_3MMe$ and $1,4\text{-}C_6H_4\text{-}\{[OMe_2Si(C_5H_4)](OC)_3MMe\}_2$ (M = Mo, W) [30].

Furthermore, a few halfsandwich complexes containing alkoxysilylalkyl groups at the cyclopentadienyl ring of the type **II** have been already synthesized. For example the cyclo-octadiene rhodium complex $[(MeO)_3Si(CH_2)_3(C_5H_4)]Rh(COD)$, characterized by a propylidene unit between the cyclopentadienyl ligand and the silicium atom has

been shown to be an efficient catalyst for alkyne cyclotrimerization [9] and the silica-supported $[(MeO)_3Si(CH_2)_3(C_5H_4)]_2TiCl_2$ titanium complex has been used after reduction with butyllithium, as an efficient and selective catalyst for hydrogenation of alk-1-enes [9]. Polysiloxane-bound cyclopentadienyl metal complexes prepared by sol-gel method were reported only in the case of a polysiloxane-bound ferrocene [31]. However, in literature there are some catalytically active sol-gel siloxane polymers described in which a rhodium- [32, 33], titanium- [34], ruthenium- [35] and iridium [35] fragment is connected to the polysiloxane via a cyclopentadienylalkyl-unit. Incorporation of them into porous polysiloxanes has been realized by sol-gel processes and leads to new matter with catalytic activity. The advantages of easy recycling and resistance towards leaching was proved in several reaction cycles as well.

In addition, to type **I** and **II** related complexes containing an alkylidene spacer between the metal and the silicon atom (Type **III**) are known and have been realized in the case of the iron and tungsten complexes $Cp(OC)(L)Fe(CH_2)_nSi(OR)_3$ (L = CO, PPh$_3$; n = 1, 3; R = Me, Et) and $Cp(OC)_2(L)W(CH_2)_nSi(OMe)_3$ (L = PPh$_3$, n = 1 [36]; L = CO, n = 3 [37]).
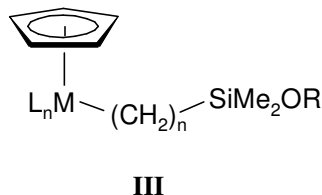

III

Fig. 2: Metalloalkyl-substituted alkoxysilanes classified as type **III**.

Our interest now is mainly focused on the generation of model compounds of the type **II** that represent promising precursors for the immobilization of metal fragments on silica surfaces or for the synthesis of sol-gel polysiloxanes containing halfsandwich metal complexes.

In this paper we report full details on the synthesis and the chemical behaviour of a series of new molybdenum- and tungsten complexes bearing an alkoxysilylalkyl-functionalized cyclopentadienyl ligand.

The following examples exhibit the possibilities of variation of the spacer chainlength between the cyclopentadienyl-ligand and the silicon moiety as well as the number of alkoxy groups being attached to the silicon, appropriate for hydrolysis. Besides, the introduction of a silyl group at the metal is described which allows the formation of highly branched metal fragment-substituted polysiloxanes.

RESULTS AND DISCUSSION

Hydrido-, Alkyl-, Chloro- and Silyl Complexes with an Alkoxysilylalkyl-functionalized Cyclopentadienyl Ligand

A straightforward approach to the targeted compounds is given by the alkoxysilylalkyl-functionalization of cyclopentadiene, followed by metallation with molybdenum or tungsten.

In order to synthesize an alkoxysilyl-functionalized cyclopentadienyl-ligand with a CH_2-spacer, (chlormethyl)ethoxydimethylsilane (**1**) is treated with NaCp in THF over a period of two hours at room temperature leading to a pale yellow oil consisting of $CpCH_2SiMe(OEt)$ (**2**) (Eq. 1). **2** is obtained as a mixture of two vinyl- and one allyl isomers in the ratio of about 1:1:0.4, as it is known for the related $CpCH_2Si(OEt)_3$ species [24]. This finding is clearly demonstrated by three ^{29}Si-NMR signals found at 12.60, 11.96 and 10.31 ppm.
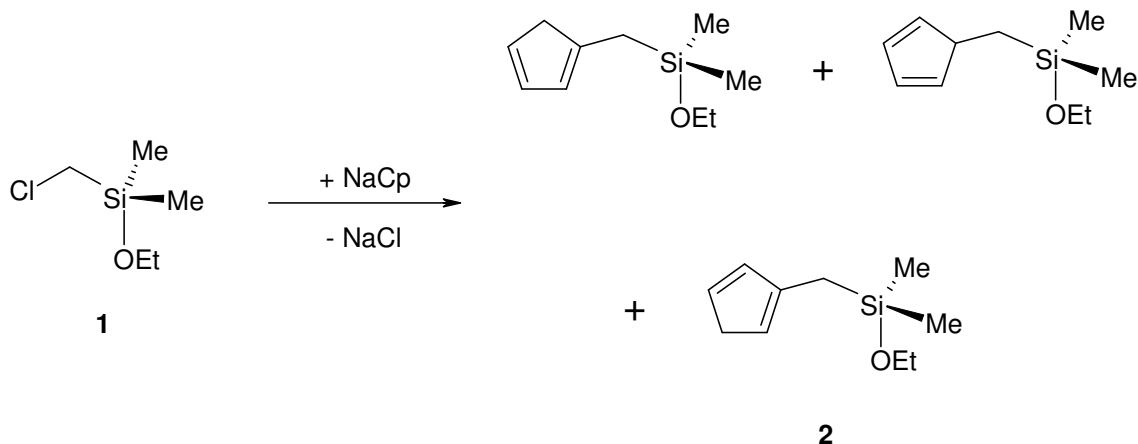

Eq. 1: Synthesis of ligand (**2**) with a spacering methylene unit.

Analogous reaction of the (3-iodo-propyl)alkoxysilanes **3a**,**b** with NaCp in THF generates after two hours at room temperature the silyl-propylcyclopentadienes **4a,b** in good yields of 90 (**4a**) and 75 % (**4b**) according to equation 2. Use of the iodo

compounds **3a,b** improves the only moderate yields of about 50 % achieved in the case of the chloro derivatives [9] and shortens the reaction times as well.

4a,b are obtained as mixtures of two vinyl isomers in the ratio of about 1:1. The ^{29}Si-NMR resonances are detected at 17.88 and 17.83 ppm (**4a**) and at −2.53 and −2.61 ppm, respectively (**4b**).

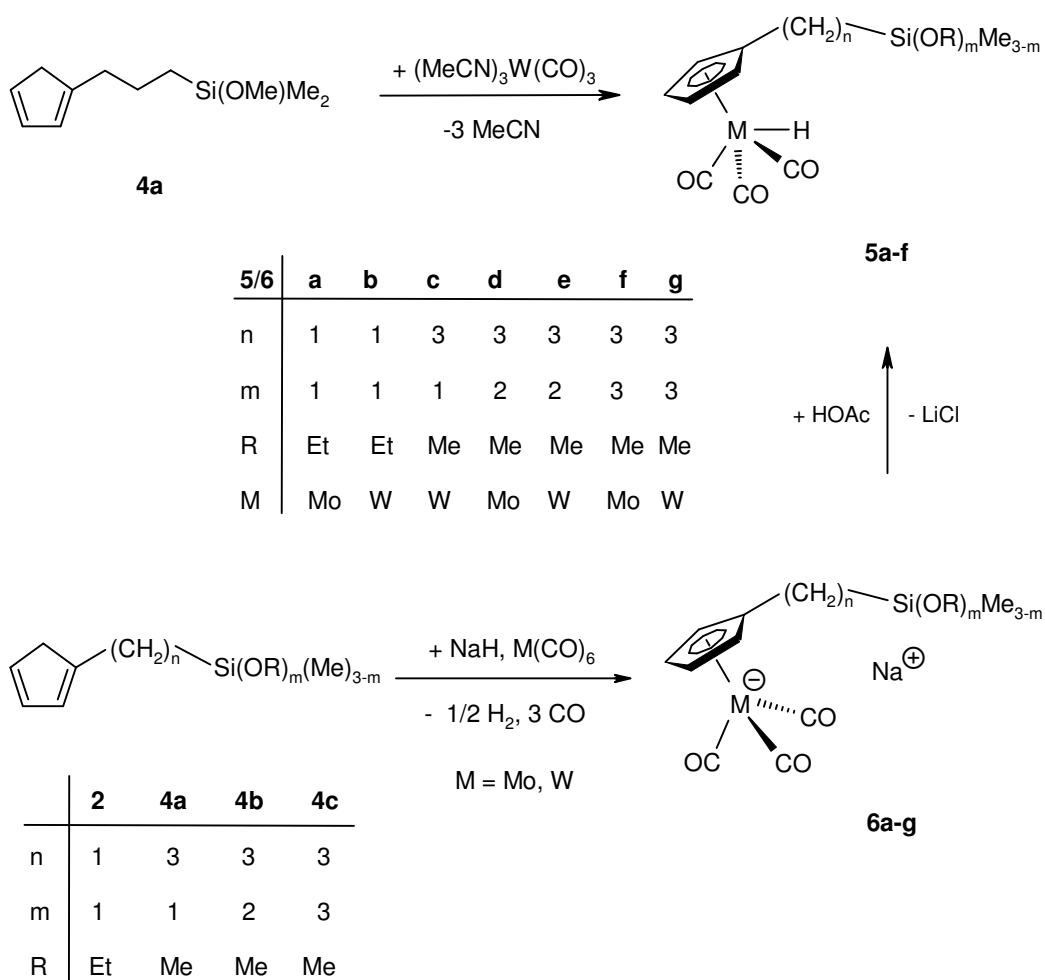| 3	a	b
m	1	2

4	a	b
m	1	2
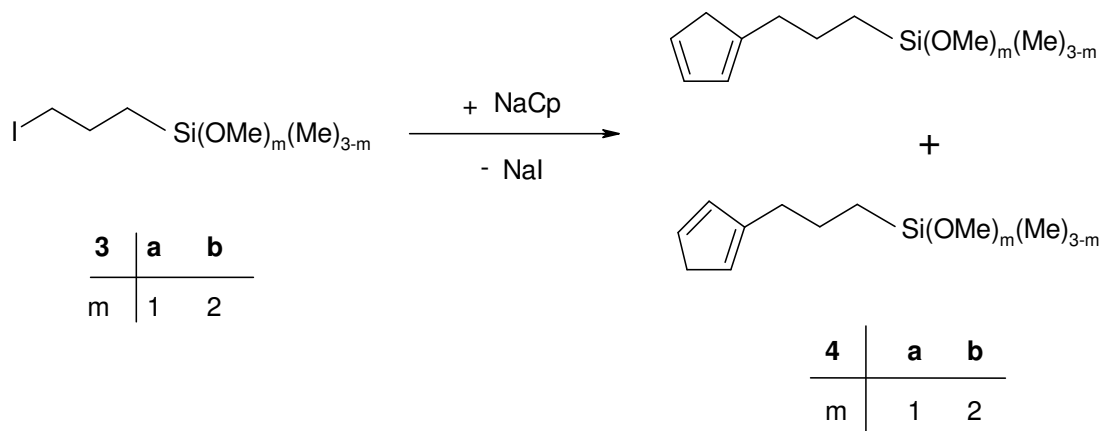
Eq. 2: Ligand synthesis of **4a,b** containing a propylene unit.

Coordination of the methoxysilyl-functionalized cyclopentadiene units with a transition metal can be realized in two different ways (Scheme 2). One route deals with the treatment of the cyclopentadiene Cp(CH$_2$)$_3$SiMe$_2$OMe (**4a**) with (MeCN)$_3$W(CO)$_3$ in refluxing THF and results after three days in the formation of the tungsten hydrido complex [MeOMe$_2$Si(CH$_2$)$_3$(C$_5$H$_4$)](OC)$_3$WH (**5c**). The reaction time is considerably longer in comparison to the analogous reaction with cyclopentadiene which takes usually 20 hours. **5c** is obtained in good yield of 75 % as a red and viscous oil.

The second access is given by an one-pot reaction which includes the deprotonation of the functionalized cyclopentadiens **2** and **4a-c** with sodiumhydride in THF or DME, followed by *in situ* reaction of the resulting sodium cyclopentadienide with molybdenum- or tungstenhexacarbonyl to give the pyrophoric sodium metallates **6a-g**. Treatment of **6a-g** with acetic acid affords the molybdenum- and tungsten hydrides **5a-f** (Scheme 2) in yields ranging from 42 (**5b**) to 76 % (**5d**). **5a-f** are obtained as

yellow and red oils which dissolve readily in most common aliphatic and aromatic solvents. **5a-f** are stable at room temperature and can be stored under nitrogen atmosphere under light exclusion at -30 °C for several months without any signs of decomposition.

The hydrido signals of the molybdenum complexes appear in the ^{1}H-NMR spectra in the range of -5.24 (**5a**) and -5.38 ppm (**5d**), for the tungsten complexes **5b,c**,**e** between δ = -6.88 (**5b**) and -7.03 ppm (**5e**), showing ^{183}W-satellite resonances with ^1J(HW) coupling of about 37 Hz.

5/6	a	b	c	d	e	f	g
n	1	1	3	3	3	3	3
m	1	1	1	2	2	3	3
R	Et	Et	Me	Me	Me	Me	Me
M	Mo	W	W	Mo	W	Mo	W

	2	4a	4b	4c
n	1	3	3	3
m	1	1	2	3
R	Et	Me	Me	Me

Scheme 2: Two different syntheses of molybdenum- and tungsten hydrido complexes with an alkoxysilylalkyl-functionalized cyclopentadienyl ligand.

Alkylation of the lithium metallates **6c**,**e**,**g** is accomplished by the reaction with methyliodide or (3-iodopropyl)-dimethoxymethylsilane in PE which affords the alkyl complexes [(MeO)$_n$Me$_{3-n}$Si(CH$_2$)$_3$(C$_5$H$_4$)](OC)$_3$WR [n = 1, R = Me (**8a**); n = 3, R = Me (**8b**); n = 2, R = (CH$_2$)$_3$Si(OMe)$_2$Me (**8c**)] (Scheme 3). **8a-c**, readily soluble in most common organic solvents, can be stored for months under nitrogen atmosphere at -30 °C and handled for a short time at air without decomposition.
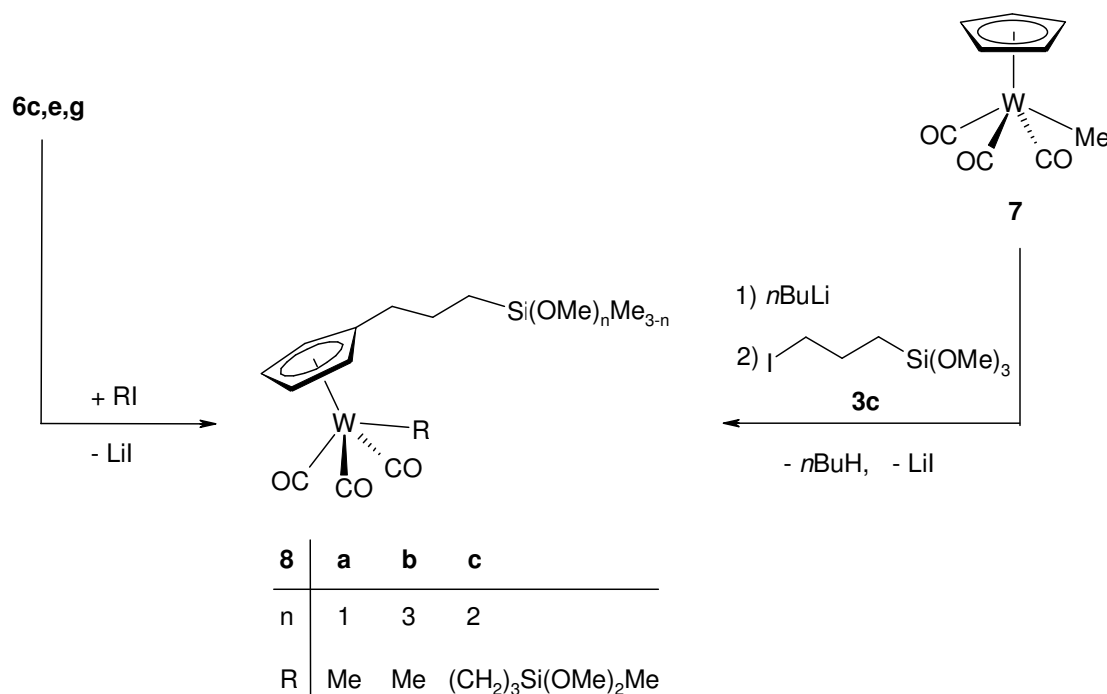
Scheme 3: Synthesis of the alkylated tungsten complexes **8a-c** starting from the tungsten anions **6c**,**e**,**g** and the attempt for the synthesis of **8b** by *in situ* reaction of the lithiated (LiC$_5$H$_4$)(OC)$_3$WMe-species (**A**).

In order to establish an attractive alternative route for the synthesis of **8b**, the introduction of the alkylsilyl group at the cyclopentadienyl unit has been tried by lithiation of the cyclopentadienyl ligand with *n*BuLi and following *in situ* reaction with halogenalkylsilanes (Scheme 3). According to literature methods [38, 39] the tungsten methyl complex Cp(OC)$_3$WMe (**7**) is treated with *n*BuLi at -78 °C in THF which

generates the cyclopentadienyl-lithiated $(LiC_5H_4)(OC)_3WMe$-species (**A**). The *In situ* treatment of **A** with (3-iodopropyl)-trimethoxysilane (**3c**) leads to **8b** but only in very small amounts (13 %). Mainly the starting material **7** and **3c** is observed. Further attempts to raise the yield of **8b** by higher reaction temperature or prolonged reaction time did not succeed.

The ^{1}H-NMR-spectra in C_6D_6 of all these cyclopentadienyl-functionalized compounds exhibit two virtuel triplets evoked by an AA'BB'-spin system for the two inequivalent pairs of cyclopentadienyl ring protons, characteristic for monosubstituted cyclopentadienyl ligands. These multiplet resonances lie in the range of 4.39 and 4.81 ppm.

The ^{29}Si-NMR spectra of the ethoxysilyl-substituted complexes **5a,b** which bear a methylene spacer show chemical shifts at 11.41 (**5a**) and 12.23 ppm (**5b**).

The ^{29}Si-NMR resonances of the trimethoxysilyl groups of the complexes **5f** and **8b** appear at -42.98 and -43.10 ppm, very similar to that of the literature-known halfsandwich iron compound $\{[(MeO)_3Si(CH_2)_4(C_5Me_4)]Fe\}_2$ (δ = -45.40 ppm) [40]. Silicon atoms substituted with two methoxy groups have resonances in the range from -3.01 to -3.29 ppm (**5d** and **8c**) whereas those containing only one MeO group appear at 17.57 (**8a**) and 17.67 ppm (**5c**). All these ^{29}Si-NMR values lie very close to that ones of the non-coordinated cyclopentadienes and reflect a negligible influence of the transition metal on this parameters.

The molybdenum and tungsten hydrido complexes **5a-d** can be easily transformed with tetrachloromethane into the corresponding chloro complexes (**9a-d**) (Eq. 3). The radical reaction proceeds cleanly and **9a-d** are obtained after one hour reaction time in PE at room temperature as yellow and red oils in yields between 71 and 94 %. The reaction course can be monitored by IR spectroscopy because the wave numbers of the carbonyl resonances shift to higher values during the substitution as it is well known for the common C_5H_5 analogues [41-43].

As a consequence of the H/Cl-exchange the solubility of the tungsten chlorides **9a-d** is reduced in comparison to the starting materials.

	a	b	c	d
n	1	3	3	3
m	1	2	2	3
R	Et	Me	Me	Me
M	Mo	Mo	W	Mo
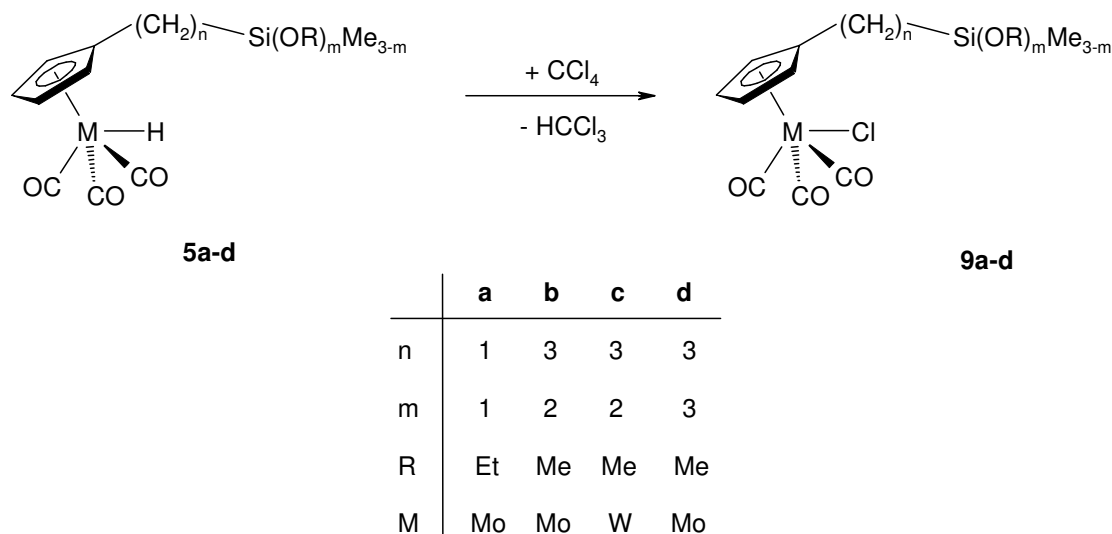
Eq. 3: H/Cl-exchange of **5a-d** achieved by use of an excess of CCl_4.

The introduction of a silyl group at the metal center is accomplished by the deprotonation of the tungsten hydrido complex **5c** with *n*BuLi in PE, leading after two hours reaction time at ambient temperature to the lithium tungsten salt Li{W[(C_5H_4)(CH_2)$_3$SiMe$_2$OMe](CO)$_3$} (**6c**), which is isolated as yellow pyrophoric powder. Final treatment of **6c**, suspended in cyclohexane, with chlordimethylsilane gives after 18 hours at room temperature the double silyl-functionalized tungsten complex [MeOMe$_2$Si(CH_2)$_3$(C_5H_4)](OC)$_3$WSiMe$_2$H (**10**) in very good yields (92 %) as a red oil (Eq. 4). The solubility of **10** in nonpolar solvents is raised in relation to **5c**. The nearly identical ^{29}Si-NMR shift values of 17.67 (**5c**) and 17.53 ppm (**19**), detected for the MeOMe$_2$Si group, underline the notion of a strongly reduced transition metal influence on the cyclopentadienylpropyl-bound silyl function. The signal for the metal-bound silicon atom of the ^{29}Si-NMR spectrum is found at –2.37 ppm which lies very close to those of the related [HMe$_2$Si(C_5H_4)](OC)$_3$WSiMe$_2$H, showing its resonance at –2.63 ppm [44]. The values for the methoxy groups are

nearly the same in the ^{1}H-NMR spectra of **5c** and **10** and appear at 3.24 (**5c**) and 3.25 ppm (**10**).
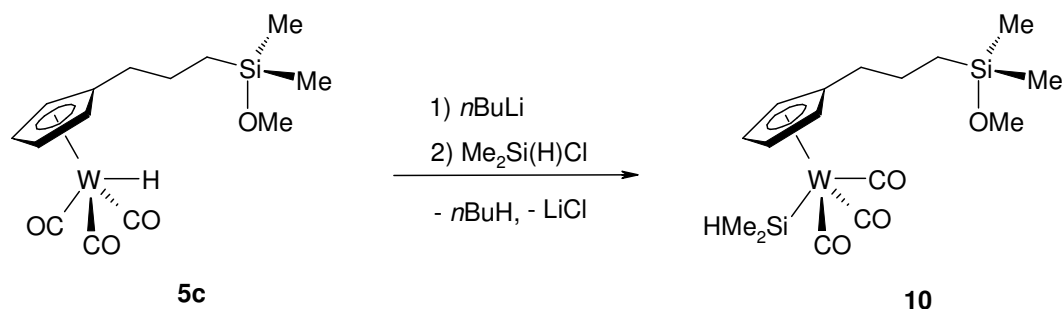
Eq. 4: Two-step synthesis of the double silyl-functionalized tungsten complex **10**.

Disiloxane-bridged Dinuclear Halfsandwich Complexes of Molybdenum and Tungsten

In order to generate the corresponding silanols, **5a-c** and **8b** are treated with water and acetic acid at room temperature in THF. However, the hydrolyses under these conditions can not be stopped at the stage of the silanols **11a-d** due to rapid subsequent self-condensation, leading to the formation of the metal fragment-substituted disiloxanes **12a-d**, characterized by M-H- and M-Me moieties (M = Mo, W) (Scheme 4).

This behaviour is comparable to that of ordinary organosilanols and prevents the generated silanols **11a-d** from isolation. **12a-d** are obtained in yields up to 94 % (**12b,d**) as dark yellow and red oils which are characterized by a high viscosity. They dissolve readily in all common organic solvents, can be handled for short time at air and allow storage at –30 °C for several months under nitrogen atmosphere.

12a-d evoke a highfield shift of the ^{29}Si-NMR resonance of about 10 ppm referred to starting **5a-c** and **8b**. The values of **12a-d** lie in the range from 5.54 (**12c**) to 7.50

ppm (**12d**) which is in agreement with those of the palladium- and platin-substituted disiloxanes $\{Cl_2M[(C_5Me_4)(CH_2)_3SiMe_2]\}_2O$ (M = Pd, Pt) (7.6 and 7.7 ppm) [40].
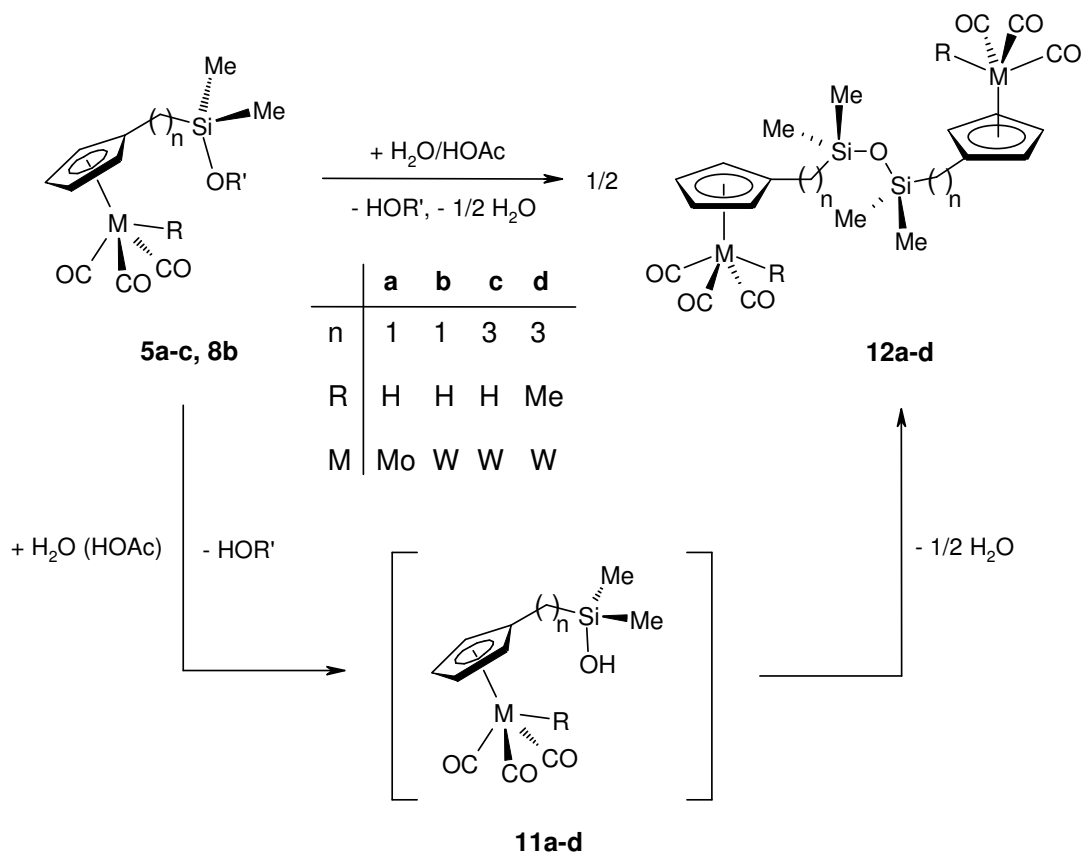
Scheme 4: The reaction of **5a-c** and **8b** with water in the presence of acetic acid leads via the silanole stage (**11a-d**) to metal-substituted disiloxanes **12a-d**.

The possibility of H/Cl-exchange concerning the metal fragment-substituted disiloxanes with a hydrido function is demonstrated by the reaction of **12c** with CCl_4. This conversion leads after three days in PE at room temperature to the formation of the disiloxane-bridged ditungsten chloride $\{ClW(CO)_3[(C_5H_4)(CH_2)_3Me_2Si]\}_2O$ (**13**), isolated as a dark red oil in 94 % yield (Fig. 3).

Further modification of the metal centers of the tungsten-disiloxanes **12a,b** and **13** has been investigated by carbonyl/phosphine-substitution with trimethyl- (**12a,b**) or triphenylphosphine (**13**) according to figure 3.

The substitution products {HW(PMe$_3$)(CO)$_2$[(C$_5$H$_4$)(CH$_2$)$_n$Me$_2$Si]}$_2$O [(n = 1 (**14a**), 3 (**14b**)], yielded after 24 hours in PE at room temperature are isolated as orange oils in moderate and good yields of 52 and 89 %. **14a,b** contain metal fragments with either *cis-* or *trans-*positioned CO ligands at the tungsten centers in a ratio of about 45:55. As a consequence, besides the dominating isomer combining *cis-* and *trans-*substituted metal centers, also isomers showing *cis/cis-* or *trans/trans-*combination are observed in small amounts.

The irradiation of **13** and two equivalents of PPh$_3$ with UV-light over the period of three hours at ambient temperature in benzene affords the dinuclear PPh$_3$-substituted tungsten chloride {ClW(PPh$_3$)(CO)$_2$[(C$_5$H$_4$)(CH$_2$)$_n$Me$_2$Si]}$_2$O (**14c**) (Fig. 3), isolated as a crystalline orange material in 86 % yield. The air stable **14c** can be stored for several months under nitrogen atmosphere without decomposition and dissolves readily in common aromatic solvents. The introduction of the triphenylphosphine ligand occurs stereospecifically *cis* to the chlorine ligand, creating a stereogenic tungsten center. As a result, **14c** is obtained as a mixture of three stereo isomers consisting of one enantiomerically related pair of isomers (*R,R* / *S,S*) and the *meso*-form (*R,S*).
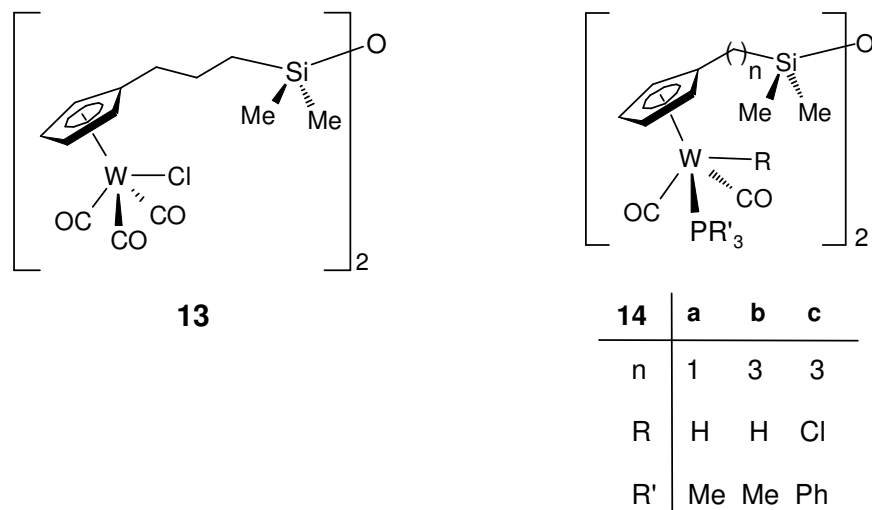

14	a	b	c
n	1	3	3
R	H	H	Cl
R'	Me	Me	Ph

Fig. 3: Chlorination product of WH/WCl-exchange of **12c** and PR$_3$'-substituted **14a-c** deriving from **12a,b** and **13**.

The tungsten-disiloxanes **14a,b** can be transformed into the dinuclear dilithium ditungsten dianions **15a,b** by treatment with two equivalents *n*BuLi in PE at room temperature (Scheme 5). **15a,b** show the for lithium tungstates typical pyrophoric behavior and are stable at room temperature.

Under heterogeneous conditions in cyclohexane react **15a,b** with two equivalents of chlorodimethylsilane to afford the disiloxane-brigded dinuclear bis-tungsten-silanes {HMe$_2$SiW(PMe$_3$)(CO)$_2$[(C$_5$H$_4$)(CH$_2$)$_n$Me$_2$Si]}$_2$O [n = 1 (**16a**), n = 3 (**16b**)] in good yields of 79 (**16a**) and 97 % (**16b**). The introduction of the silyl group proceeds stereoselectively *trans* to the Me$_3$P ligand.

	a	b
n	1	3
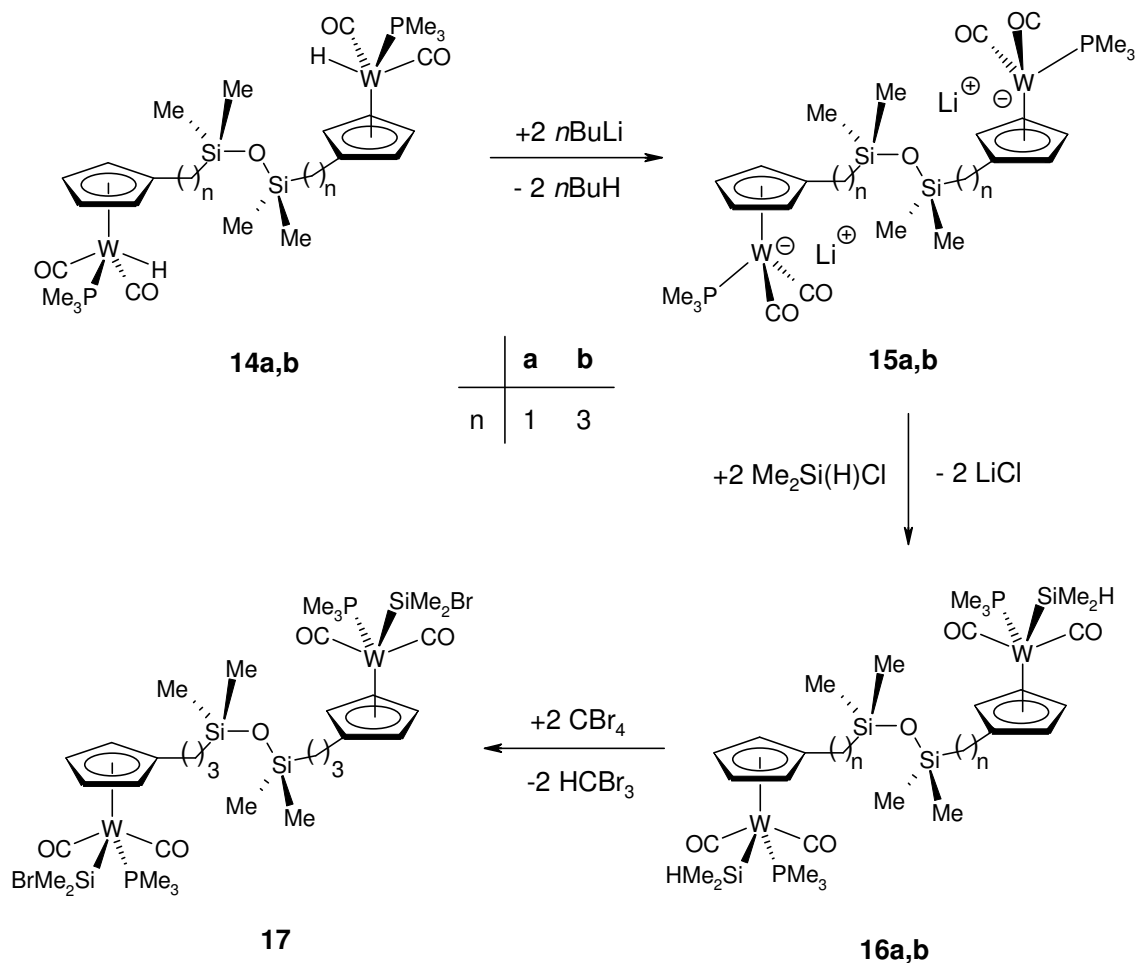
Scheme 5: Synthesis of suitable precursors (**16a,b** and **17**) for the synthesis of dinuclear bis-tungsten-silanols.

Derivatization of the Si-H function is realized by the reaction of **16b** with tetrabromomethane in toluene. Among $HCBr_3$-formation, **17**, characterized by a Si-Br bond suitable for hydrolysis, is obtained after three hours in PE in 68 % yield as a moisture sensitive brown oil.

The ^{31}P-NMR resonances appear at -14.40 (**16a**) and -14.34 ppm (**16b**). The ^{29}Si-NMR signals for the metal-bound silicon atoms are detected at 1.01 (**16a**) and 0.41 ppm (**16b**), both as doublets with a ^2J(SiWP) coupling constant of about 17 Hz. These findings are in agreement with the values found for the related mononuclear silyl tungsten complexes $Cp(Me_3P)(OC)_2WSiMe_2H$ [$\delta(^{29}Si)$ = 0.18 ppm] [45] and $[HMe_2Si(C_5H_4)](Me_3P)(OC)_2WSiMe_2H$ [$\delta(^{29}Si)$ = 0.02 ppm] [44].

The Si-H- and Si-Br-functionalized complexes **16b** and **17** offer an attractive access to the corresponding silanols. One method deals with the use of dimethyldioxirane (DMD) and is well know for the introduction of an oxygen-atom into a metal-fixed Si-H bond [46-48]. As expected, the oxygenation of **16b** with two equivalents of DMD in acetone at -78 °C leads to the formation of the dinuclear tungsten-bis-silanol $\{HOMe_2SiW(PMe_3)(CO)_2[(C_5H_4)(CH_2)_3Me_2Si]\}_2O$ (**18**) in 52 % yield (Scheme 6).

Alternatively, **18** is generated by the NEt_3-assisted hydrolysis of **17** in Et_2O after three hours (Scheme 6). **18**, isolated as brown solid in 75 % yield, shows the typical features of a metallo-silanol with respect to self-condensation.

The ^{29}Si-NMR resonance of the Si-OH group is found at 51.28 ppm and thus displays the expected characteristic low-field shift for tungsten-silanols [e.g. $Cp(Me_3P)(OC)_2WSiMe_2OH$ (δ = 50.09 ppm)] [45, 47].

The derivatization of **18** is realized by the co-condensation with two equivalents of dichlorodimethylsilane in the presence of triethylamine according to scheme 6. After one hour stirring in diethylether at ambient temperature the disiloxane-bridged tungsten-disiloxane $\{HMe_2SiOMe_2SiW(PMe_3)(CO)_2[(C_5H_4)(CH_2)_3Me_2Si]\}_2O$ (**19**) is obtained in 90 % yield. The condensation reaction is accompanied by a ^{29}Si-NMR highfield shift of the tungsten-bound silicon atom which amounts to about 7 ppm

[δ(**19**) = 45.72 ppm]. **19** is isolated as a high viscous brown oil which dissolves readily in common aliphatic and aromatic solvents.
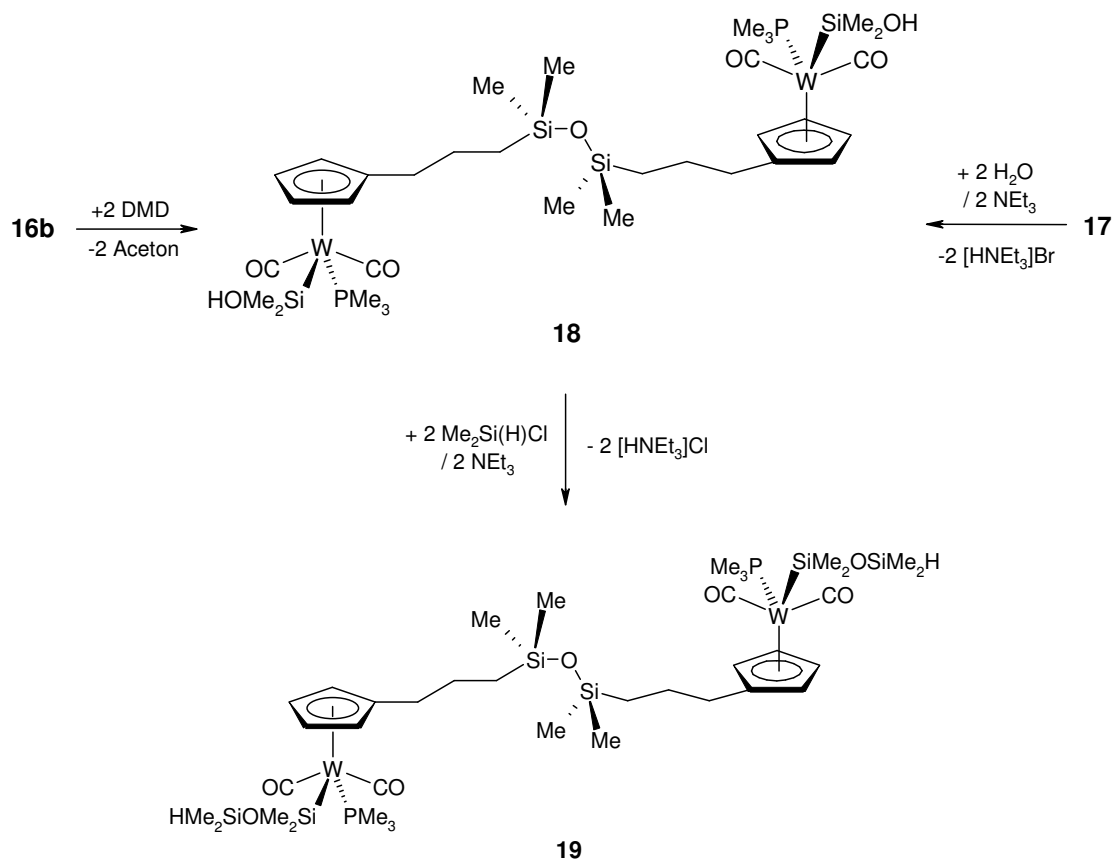
Scheme 6: Two pathways applied for the conversion of **16b** and **17** into the dinuclear tungsten-silanol **18** and its co-condensation to the disiloxane-bridged dinuclear tungsten-disiloxane **19**.

CONCLUSION

The molybdenum- and tungsten halfsandwich complexes with an alkoxysilyl-functionalized cyclopentadienyl ligand, presented in this paper, proved to be easily synthesized and open furthermore the functionalization of the metal center before and after co-condensation of the alkoxysilyl groups. Lots of standard reactions for non-cyclopentadienyl-functionalized molybdenum- and tungsten halfsandwich complexes can be carried out without complications. The electron-releasing effect of the metal fragment on the silicon atom is disappeared in comparison to tungsten-silanols with directly metal-bonded Si-OH moiety. This fact evokes a high reactivity of the silanol group leading to short reaction times in condensation processes. As a result, we regard these species as ideal compounds for the formation of highly-branched metal fragment-substituted oligo- and polysiloxanes.

Consequently, further investigations are currently being directed towards the heterogenation of halfsandwich tungsten complexes by simple sol-gel processes by demand on the methoxysilyl groups. First experiments have already shown that co-polymerization of the tungsten complex $Cp(OC)_3W(CH_2)_3Si(OMe)_3$ with the co-reagent $Si(OMe)_4$ results in the formation of the corresponding metal fragment-substituted polysiloxane [37].

EXPERIMENTAL SECTION

General Remarks: All operations were performed under an atmosphere of purified and dried nitrogen using Schlenk-type techniques. Solvents were dried according to conventional procedures, distilled and saturated with N_2 prior to use. - NMR: Jeol Lambda 300 (300.4 MHz, 75.5 MHz, and 59.6 MHz for ^{1}H, ^{13}C, and ^{29}Si, respectively). [D$_6$]-benzene as a solvent: δ_H = 7.15, δ_C = 128.0; for ^{29}Si rel. to TMS external. - IR: Perkin-Elmer 283 grating spectrometer. - Melting points: Differential thermo analysis (Du Pont 9000 Thermal Analysis System). - Elemental analyses were performed in the laboratories of the *Institut für Anorganische Chemie der Universität Würzburg*. - Starting materials were prepared according to literature procedures: $I(CH_2)_3Si(OMe)_n(Me)_{3-n}$ [n = 1-3 (**3a-c**)] [9], $Cp(CH_2)_3Si(OMe)_3$ (**4c**) [9], $(MeCN)_3W(CO)_3$ [49], $Cp(OC)_3WMe$ (**7**) [50], PMe_3 [51], Dimethyldioxirane [52, 53]. $ClCH_2SiMe_2OEt$ (**1**), NEt_3, PPh_3, CCl_4 and $Me_2Si(H)Cl$ were obtained commercially and destilled prior to use.

1. Cp(CH$_2$)SiMe$_2$OEt (*2*)

(Cyclopentadienylmethyl)ethoxydimethylsilane

10.8 g (164 mmol) of CpH were added to a suspension of 3.94 g (164 mmol) of NaH in 60 ml THF at 0 °C and the reaction mixture stirred for 4 h. The mixture was treated with 25.0 g (164 mmol) of (chlormethyl)ethoxydimethylsilane (**1**) and refluxed for 6 h. After cooling, the solvent was removed under vacuo and PE added to the residue, followed by filtration of the NaCl. The solvent was removed under vacuo, and the crude product got destilled (35 - 45 °C, 0.05 Torr). Yield: 5.80 g (19 %). Yellow liquid. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 5.50 - 6.68 (m, 10 H, Vinyl-CpH), 3.59 - 3.37 (m, 6 H, $\underline{H}_2$CCH$_3$), 2.87 - 2.68 (m, 5 H, Allyl-CpH), 1.92 - 1.86 (m, 6 H, H$_2$CSi), 1.12 - 1.03

(m, 9 H, $\underline{H}_3CCH_2$), 0.13 - 0.03 (m, 18 H, H_3CSi) ppm. - **$^{13}C\{^1H\}$-NMR** (75.5 MHz, C_6D_6): δ = 147.88, 145.51, 142.82, 136.64, 133.47, 133.30, 129.23, 127.78, 126.53, 126.00, 125.53, 124.81 (s, Vinyl-CpC), 58.37 (s, CH_2O), 58.32, 45.57, 41.64 (s, Allyl-CpC), 21.73, 21.47, 20.53 (s, CH_2Si), 18.79 (s, $\underline{C}H_3CH_2O$), -1.99, -2.00, -2.09 (s, CH_3Si) ppm. - **$^{29}Si\{^1H\}$-NMR** (59.6 MHz, C_6D_6): δ = 12.60, 11.96, 10.31 (s) ppm.

$C_{10}H_{18}OSi$ (182.34)	Calcd.: C 65.87	H 9.95
	Found: C 66.00	H 9.89

2. Cp(CH₂)₃SiMe₂OMe (*4a*)

*2. Cp(CH$_2$)$_3$SiMe$_2$OMe (**4a**)*

(3-Cyclopentadienyl)propylmethoxydimethylsilane

A solution of 15.5 g (59.9 mmol) of (3-iodopropyl)methoxydimethylsilane in 30 ml THF was treated dropwise with a suspension of NaCp in 10 ml THF and stirred for 2 h at room temperature. All volatiles were removed in vacuo and five times extracted with 20 ml PE. The combined extracts were evaporated in vacuo leaving **4a** as yellow oily liquid. Yield: 10.6 g (90 %). - **^{1}H-NMR** (300.4 MHz, C_6D_6): δ = 6.95 - 5.50 (m, 4 H, H_4C_5), 3.24 (s, 3 H, H_3CO), 2.85 - 2.67 (m, 2 H, $H_2CC=C$), 2.42 - 2.31 (m, 2 H, H_2CCp), 1.70 - 1.50 (m, 2 H, CH_2), 0.63 - 0.51 (m, 2 H, H_2CSi), 0.04 (s, 6 H, H_3CSi) ppm. - **$^{13}C\{^1H\}$-NMR** (75.5 MHz, C_6D_6): δ = 149.62, 147.29, 135.02, 133.73, 132.81, 130.54, 127.09, 126.29 (s, C_5H_4) 49.98 (s, CH_3O), 43.23, 41.38 (s, $\underline{C}H_2C_5H_4$), 34.68, 33.86 (s, CH_2), 23.92, 23.05 (s, CH_2Si), -2.51, -2.71 (s, CH_3Si) ppm. - **$^{29}Si\{^1H\}$-NMR** (59.6 MHz, C_6D_6): δ = 17.88, 17.83 (s) ppm.

$C_{11}H_{20}OSi$ (196.37)	Calcd.: C 67.28	H 10.27
	Found: C 67.02	H 10.55

3. Cp(CH₂)₃SiMe(OMe)₂ (*4b*)

*3. Cp(CH$_2$)$_3$SiMe(OMe)$_2$ (**4b**)*

(3-Cyclopentadienyl)propyldimethoxymethylsilane

According to *2.* from 19.1 g (69.7 mmol) of (3-iodopropyl)dimethoxymethylsilane in 30 ml THF and 6.10 g (69.7 mmol) of NaCp in 10 ml THF. Yield: 11.1 g (75 %). Yellow-golden liquid. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 6.82 - 5.43 (m, 4 H, H$_4$C$_5$), 3.33 (s, 6 H, H$_3$CO), 2.80 - 2.65 (m, 2 H, H$_2$CC=C), 2.38 - 2.29 (m, 2 H, H$_2$CCp), 1.73 - 1.49 (m, 2 H, CH$_2$), 0.72 - 0.58 (m, 2 H, H$_2$CSi), 0.05 (s, 3 H, H$_3$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 149.62, 147.29, 135.02, 133.73, 132.81, 130.54, 127.09, 126.29 (s, C$_5$H$_4$) 49.98 (s, CH$_3$O), 43.23, 41.38 (s, $\underline{C}$H$_2$C$_5$H$_4$), 34.68, 33.86 (s, CH$_2$), 23.92, 23.05 (s, CH$_2$Si), -2.51, -2.71 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = -2.53, -2.61 (s) ppm.

C$_{11}$H$_{20}$O$_2$Si (212.37)	Calcd.: C 62.21	H 9.49
	Found: C 61.29	H 9.32

4. [EtOMe₂SiCH₂(C₅H₄)](OC)₃MoH (*5a*)

*4. [EtOMe$_2$SiCH$_2$(C$_5$H$_4$)](OC)$_3$MoH (**5a**)*

Tricarbonyl[ethoxydimethylsilyl(η^5-methylcyclopentadienyl)]hydridomolybdenum(II)

2.62 g (14.38 mmol) of (chlormethyl)ethoxydimethylsilane **2** were added to a suspension of 420 mg (17.5 mmol) of NaH in 20 ml THF at 0 °C and stirred for 5 h. This reaction mixture was treated with 3.80 g (14.38 mmol) of Mo(CO)$_6$ and refluxed for 24 h. Finally 1.50 g (25.0 mmol) of HOAc were added and this mixture was stirred for 2 h at room temperature. All volatiles were removed in vacuo and the residue was extracted with PE (5 x 20 ml). The combined extracts were evaporated in vacuo leaving **5a**. Yield: 2.83 g (54 %). Dark red oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.78 - 4.77 (m, 2 H, H$_4$C$_5$), 4.57 - 4.56 (m, 2 H, H$_4$C$_5$), 3.32 [q, ^{3}*J*(HCCH) = 6.6 Hz, 2 H, $\underline{H}_2$CCH$_3$], 1.47 (s, 2 H, H$_2$CSi), 1.00 [t, ^{3}*J*(HCCH) = 6.6 Hz, 3 H, $\underline{H}_3$CCH$_2$], -0.13 (s, 6

H, H$_3$CSi), -5.24 (s, 1 H, HMo) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 228.23 (s, CO), 201.03 (s, CO), 113.55 (s, C-1 of C$_5$H$_4$), 90.05 (s, C$_5$H$_4$), 87.69 (s, C$_5$H$_4$), 58.43 (s, CH$_2$O), 19.68 (s, C̲H$_2$C$_5$H$_4$), 18.63 (s, C̲H$_3$CH$_2$O), -2.61 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 11.41 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2024 (s), 1942 (vs) cm^{-1}.

C$_{13}$H$_{18}$MoO$_4$Si (362.31)   Calcd.: C 43.10   H 5.01

                                                     Found: C 42.40   H 4.79

*5. [EtOMe$_2$SiCH$_2$(C$_5$H$_4$)](OC)$_3$WH (**5b**)*

Tricarbonyl[ethoxydimethylsilyl(η^5-methylcyclopentadienyl)]hydridotungsten(II)

According to *4.* from 0.16 g (6.53 mmol) of NaH, 1.19 g (6.53 mmol) of (chlormethyl)ethoxydimethylsilane **2**, 2.49 g (6.53 mmol) of W(CO)$_6$ and 0.39 g (6.53 mmol) of HOAc in 40 ml DME. Yield: 1.23 g (42 %). Dark yellow oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.80 - 4.76 (m, 2 H, H$_4$C$_5$), 4.55 - 4.50 (m, 2 H, H$_4$C$_5$), 3.31 [q, ^{3}*J*(HCCH) = 6.9 Hz, 2 H, H̲$_2$CCH$_3$], 1.50 (s, 2 H, H$_2$CSi), 1.00 [t, ^{3}*J*(HCCH) = 6.9 Hz, 3 H, H̲$_3$CCH$_2$], -0.15 (s, 6 H, H$_3$CSi), -6.88 [s, ^{1}*J*(HW) = 37.5 Hz, 1 H, HW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 202.23 (s, CO), 191.15 (s, CO), 112.07 (s, C-1 of C$_5$H$_4$), 88.87 (s, C$_5$H$_4$), 85.85 (s, C$_5$H$_4$), 58.46 (s, CH$_2$O), 19.47 (s, C̲H$_2$C$_5$H$_4$), 18.62 (s, C̲H$_3$CH$_2$O), -2.66 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 12.23 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2021 (s), 1983 (w), 1933 (vs) cm^{-1}.

C$_{13}$H$_{18}$O$_4$SiW (450.22)   Calcd.: C 34.68   H 4.03

                                                     Found: C 34.47   H 4.53

*6. [MeOMe$_2$Si(CH$_2$)$_3$(C$_5$H$_4$)](OC)$_3$WH (**5c**)*

Tricarbonyl[(3-methoxydimethylsilyl)propyl(η^5-cyclopentadienyl)]hydridotungsten(II)

2.36 g (12.0 mmol) of (3-cyclopentadienylpropyl)methoxydimethylsilane **4a** were added to a suspension of 4.70 g (12.0 mmol) of (MeCN)$_3$W(CO)$_3$ in 40 ml THF and refluxed for 3 days. The solvent was removed under vacuo and the resulting residue was extracted with PE (3 x 10 ml). The combined extracts were evaporated in vacuo leaving **5c** as a red oil. Yield: 4.02 g (72 %). Red oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.77 - 4.73 (m, 2 H, H$_4$C$_5$), 4.59 - 4.55 (m, 2 H, H$_4$C$_5$), 3.24 (s, 3 H, H$_3$CO), 1.99 [t, ^3J(HCCH) = 7.8 Hz, 2 H, H$_2$CC$_5$H$_4$], 1.33 - 1.25 (m, 2 H, CH$_2$), 0.38 [t, ^3J(HCCH) = 8.1 Hz, 2 H, H$_2$CSi], 0.03 (s, 6 H, H$_3$CSi), -7.02 [s, ^1J(HW) = 37.2 Hz, 1 H, HW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 218.23 (s, CO), 201.15 (s, CO), 114.43 (s, C-1 of C$_5$H$_4$), 89.03 (s, C$_5$H$_4$), 86.62 (s, C$_5$H$_4$), 50.01 (s, CH$_3$O), 32.30 (s, $\underline{C}$H$_2$C$_5$H$_4$), 26.35 (s, CH$_2$), 16.01 (s, CH$_2$Si), -2.65 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 17.67 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2020 (s), 1973 (w), 1929 (vs) cm^{-1}.

C$_{14}$H$_{20}$O$_4$SiW$_1$ (464.25)   Calcd.: C 36.22   H 4.34

                                              Found: C 36.40   H 4.35

*7. [(MeO)$_2$MeSi(CH$_2$)$_3$(C$_5$H$_4$)](OC)$_3$MoH (**5d**)*

Tricarbonyl[(3-dimethoxymethylsilyl)propyl(η^5-cyclopentadienyl)]hydrido-molybdenum(II)

According to *4.* from 0.31 g (12.8 mmol) of NaH, 2.72 g (12.8 mmol) of (3-cyclopentadienylpropyl)dimethoxymethylsilane **4b**, 3.38 g (12.8 mmol) of Mo(CO)$_6$ and 1.50 g (25.0 mmol) of HOAc in 60 ml THF. Yield: 3.80 g (76 %). Dark red oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.78 - 4.75 (m, 2 H, H$_4$C$_5$), 4.61 - 4.55 (m, 2 H, H$_4$C$_5$), 3.32 (s, 6 H, H$_3$CO), 1.95 [t, ^3J(HCCH) = 7.5 Hz, 2 H, H$_2$CC$_5$H$_4$], 1.41 - 1.32

(m, 2 H, CH$_2$), 0.47 [t, ^3J(HCCH) = 8.4 Hz, 2 H, H$_2$CSi], 0.02 (s, 3 H, H$_3$CSi), -5.38 (s, 1 H, HMo) ppm. - ^{13}C{^{1}H}-NMR (75.5 MHz, C$_6$D$_6$): δ = 228.23 (s, CO), 201.05 (s, CO), 116.11 (s, C-1 of C$_5$H$_4$), 90.29 (s, C$_5$H$_4$), 88.31 (s, C$_5$H$_4$), 49.90 (s, CH$_3$O), 32.14 (s, CH$_2$C$_5$H$_4$), 25.84 (s, CH$_2$), 13.35 (s, CH$_2$Si), -5.73 (s, CH$_3$Si) ppm. - ^{29}Si{^{1}H}-NMR (59.6 MHz, C$_6$D$_6$): δ = -3.01 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2026 (s), 1989 (m) 1943 (vs) cm^{-1}.

C$_{14}$H$_{20}$MoO$_5$Si (392.34)   Calcd.: C 42.86   H 5.14

                                             Found: C 42.40   H 4.79

*8. [(MeO)$_2$MeSi(CH$_2$)$_3$(C$_5$H$_4$)](OC)$_3$WH (**5e**)*

Tricarbonyl[(3-dimethoxymethylsilyl)propyl(η^5-cyclopentadienyl)]hydridotungsten(II)

According to *4.* from 0.43 g (17.9 mmol) of NaH, 3.80 g (17.9 mmol) of (3-cyclopentadienylpropyl)dimethoxymethylsilane **4b**, 6.30 g (17.9 mmol) of W(CO)$_6$ and 1.50 g (25.0 mmol) of HOAc in 60 ml DME. Yield: 4.80 g (56 %). Dark yellow oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.74 - 4.70 (m, 2 H, H$_4$C$_5$), 4.55 - 4.50 (m, 2 H, H$_4$C$_5$), 3.33 (s, 6 H, H$_3$CO), 1.98 [t, ^3J(HCCH) = 7.8 Hz, 2 H, H$_2$CC$_5$H$_4$], 1.42 - 1.30 (m, 2 H, CH$_2$), 0.44 [t, ^3J(HCCH) = 8.5 Hz, 2 H, H$_2$CSi], 0.03 (s, 3 H, H$_3$CSi), -7.03 [s, ^1J(HW) = 37.2 Hz, 1 H, HW] ppm. - ^{13}C{^{1}H}-NMR (75.5 MHz, C$_6$D$_6$): δ = 202.23 (s, CO), 191.15 (s, CO), 114.32 (s, C-1 of C$_5$H$_4$), 90.29 (s, C$_5$H$_4$), 86.57 (s, C$_5$H$_4$), 49.92 (s, CH$_3$O), 32.08 (s, CH$_2$C$_5$H$_4$), 25.94 (s, CH$_2$), 13.34 (s, CH$_2$Si), -5.74 (s, CH$_3$Si) ppm. - ^{29}Si{^{1}H}-NMR (59.6 MHz, C$_6$D$_6$): δ = -3.08 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2022 (s), 1983 (m) 1936 (vs) cm^{-1}.

C$_{14}$H$_{20}$O$_5$SiW (480.25)   Calcd.: C 35.01   H 4.20

                                            Found: C 35.31   H 4.18

9. [(MeO)₃Si(CH₂)₃(C₅H₄)](OC)₃MoH (*5f*)

Tricarbonyl[(3-trimethoxysilyl)propyl(η^5-cyclopentadienyl)]hydridomolybdenum(II)

According to *4.* from 0.38 g (16.0 mmol) of NaH, 3.65 g (15.9 mmol) of (3-cyclopentadienylpropyl)trimethoxysilane **4c**, 3.96 g (15.9 mmol) of Mo(CO)₆ and 1.80 g (30.0 mmol) of HOAc in 60 ml THF. Yield: 3.64 g (59 %). Dark red oil. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 4.72 - 4.68 (m, 2 H, H₄C₅), 4.57 - 4.55 (m, 2 H, H₄C₅), 3.42 (s, 9 H, H₃CO), 1.96 [t, ^3J(HCCH) = 7.8 Hz, 2 H, H̲₂CC₅H₄], 1.55 - 1.41 (m, 2 H, CH₂), 0.52 [t, ^3J(HCCH) = 8.1 Hz, 2 H, H₂CSi], -5.31 (s, 1 H, HMo) ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C₆D₆): δ = 228.25 (s, CO), 215.70 (s, CO), 115.95 (s, C-1 of C₅H₄), 90.25 (s, C₅H₄), 88.23 (s, C₅H₄), 50.29 (s, CH₃O), 31.90 (s, C̲H₂C₅H₄), 25.82 (s, CH₂), 9.51 (s, CH₂Si) ppm. - **²⁹Si{¹H}-NMR** (59.6 MHz, C₆D₆): δ = -42.98 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2027 (s), 1984 (s) 1942 (vs) cm⁻¹.

C₁₄H₂₀MoO₆Si (408.33)	Calcd.: C 41.18	H 4.94
	Found: C 41.42	H 5.01

10. [MeOMe₂Si(CH₂)₃(C₅H₄)](OC)₃WMe (*8a*)

Tricarbonyl[(3-methoxydimethylsilyl)propyl(η^5-cyclopentadienyl)]methyltungsten(II)

According to *4.* from 0.91 g (3.79 mmol) of NaH, 670 mg (3.41 mmol) (3-cyclopentadienylpropyl)methoxydimethylsilane **4a**, 1.20 g (3.41 mmol) of W(CO)₆ and 484 mg (3.41 mmol, 0.22 ml) of MeI in 40 ml DME. Yield: 870 mg (53 %). Yellow oil. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 4.51 - 4.49 (m, 2 H, H₄C₅), 4.43 - 4.41 (m, 2 H, H₄C₅), 3.24 (s, 3 H, H₃CO), 1.87 [t, ^3J(HCCH) = 7.7 Hz, 2 H, H̲₂CC₅H₄], 1.34 - 1.25 (m, 2 H, CH₂), 0.48 (s, 3 H, H₃CW), 0.38 [t, ^3J(HCCH) = 7.7 Hz, 2 H, H₂CSi], 0.03 (s, 6 H, H₃CSi) ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C₆D₆): δ = 230.65 (s, CO), 217.66 (s, CO), 114.19 (s, C-1 of C₅H₄), 91.39 (s, C₅H₄), 88.77 (s, C₅H₄), 50.00 (s, CH₃O),

31.72 (s, $\underline{C}H_2C_5H_4$), 25.88 (s, CH_2), 16.08 (s, CH_2Si), -2.64 (s, CH_3Si), -31.79 [t, $^1J(CW)$ = 29.3 Hz, CH_3W] ppm. - ^{29}**Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = 17.57 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2017 (s), 1928 (vs) cm^{-1}.

$C_{15}H_{22}O_4SiW$ (478.27)   Calcd.: C 37.67   H 4.64

                                       Found: C 37.85   H 4.60

*11. [(MeO)$_3$Si(CH$_2$)$_3$(C$_5$H$_4$)](OC)$_3$WMe (**8b**)*

Tricarbonyl[(3-trimethoxysilyl)propyl(η^5-cyclopentadienyl)]methyltungsten(II)

According to *4*. from 0.21 g (8.76 mmol) of Nah, 2.20 g (8.76 mmol) of (3-cyclopentadienylpropyl)trimethoxysilane **4c**, 3.35 g (8.76 mmol) of W(CO)$_6$ and 2.41 g (17.0 mmol) of MeI in 45 ml DME. Yield: 2.76 g (65 %). Dark yellow oil. - ^{1}**H-NMR** (300.4 MHz, C_6D_6): δ = 4.50 - 4.46 (m, 2 H, H_4C_5), 4.42 - 4.39 (m, 2 H, H_4C_5), 3.41 (s, 9 H, H_3CO), 1.89 [t, $^3J(HCCH)$ = 7.8 Hz, 2 H, $\underline{H}_2CC_5H_4$], 1.46 - 1.40 (m, 2 H, CH_2), 0.61 [t, $^3J(HCCH)$ = 7.7 Hz, 2 H, H_2CSi], 0.47 (s, 3 H, H_3CW) ppm. - ^{13}**C{^{1}H}-NMR** (75.5 MHz, C_6D_6): δ = 230.70 (s, CO), 217.74 (s, CO), 114.04 (s, C-1 of C_5H_4), 91.45 (s, C_5H_4), 88.78 (s, C_5H_4), 50.30 (s, CH_3O), 31.21 (s, $\underline{C}H_2C_5H_4$), 25.42 (s, CH_2), 9.45 (s, CH_2Si), -31.88 [t, $^1J(CW)$ = 29.6 Hz, CH_3W] ppm. - ^{29}**Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = -43.10 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2019 (s), 1918 (vs) cm^{-1}.

$C_{15}H_{22}O_6SiW$ (510.27)   Calcd.: C 35.31   H 4.35

                                       Found: C 34.85   H 4.61

12. [(MeO)₂MeSi(CH₂)₃(C₅H₄)](OC)₃W(CH₂)₃SiMe(OMe)₂ (8c)

*12. [(MeO)$_2$MeSi(CH$_2$)$_3$(C$_5$H$_4$)](OC)$_3$W(CH$_2$)$_3$SiMe(OMe)$_2$ (**8c**)*

Tricarbonyl[(3-dimethoxymethylsilyl)propyl(η^5-cyclopentadienyl)][(3-dimethoxy-methylsilyl)propyl]tungsten(II)

According to *4.* from 20.4 mg (0.85 mmol) of NaH, 168 mg (0.79 mmol) of (3-cyclopentadienylpropyl)dimethoxymethylsilane **4b**, 278 mg (0.79 mmol) of W(CO)₆ and 217 mg (0.79 mmol) (3-cyclopentadienylpropyl)dimethoxymethylsilane **4b** in 40 ml DME. Yield: 210 mg (43 %). Orange oil. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 4.72 - 4.69 (m, 1 H, H₄C₅), 4.63 - 4.60 (m, 1 H, H₄C₅), 4.54 (m, 1 H, H₄C₅), 4.48 (m, 1 H, H₄C₅), 3.41 (s, 6 H, H₃CO^W), 3.34 (s, 6 H, H₃CO^Cp), 1.96 [t, ^3J(HCCH) = 7.7 Hz, 2 H, H₂CC₅H₄], 1.59 [t, ^3J(HCCH) = 5.1 Hz, 2 H, H₂CSi^W], 1.41 - 1.30 (m, 2 H, CH₂^Cp), 1.40-1.28 (m, 2 H, CH₂^W), 0.88 [t, ^3J(HCCH) = 7.9 Hz, 2 H, H₂CSi^Cp], 0.46 [t, ^3J(HCCH) = 7.9 Hz, 2 H, H₂CW], 0.16 (s, 3 H, H₃CSi^W), 0.05 (s, 3 H, H₃CSi^Cp) ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C₆D₆): δ = 230.50 (s, CO), 219.39 (s, CO), 191.12 (s, CO), 113.31 (s, C-1 of C₅H₄), 91.66 (s, C₅H₄), 90.08 (s, C₅H₄), 88.99 (s, C₅H₄), 86.57 (s, C₅H₄), 49.91 (s, CH₃O^W), 49.89 (s, CH₃O^Cp), 32.05 (s, CH₂C₅H₄), 30.34 (s, CH₂Si^W), 25.77 (s, CH₂^Cp), 21.45 (s, CH₂^W), 13.36 (s, CH₂Si^Cp), -3.71 (s, CH₂W), -5.14 (s, CH₃Si^W), -5.14 (s, CH₃Si^Cp) ppm. - **²⁹Si{¹H}-NMR** (59.6 MHz, C₆D₆): δ = -3.21 (s, Si^Cp), - 3.29 (s, Si^W) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2022 (s), 2011 (s), 1983 (m) cm⁻¹.

C₂₀H₃₄O₇Si₂W (626.51)	Calcd.: C 38.34	H 5.47
	Found: C 37.49	H 5.17

13. Reaction of Cp(OC)₃WMe (7) with nBuLi and 3-iodopropyltrimethoxysilane (4c)

*13. Reaction of Cp(OC)$_3$WMe (**7**) with nBuLi and 3-iodopropyltrimethoxysilane (**4c**)*

A THF-solution (7 ml) containing 220 mg (0.63 mmol) of Cp(OC)₃WMe (**7**) was treated with 0.61 ml (0.95 mmol, 1.6 M in cyclohexane) of *n*BuLi at -78 °C and stirred for 45 min. During this period the color changed from yellow to deep brown. To this mixture 0.17 ml (0.90 mmol) of **4c** had been rapidly added at -78 °C. The mixture

was allowed to warm up to room temperature over a period of 4 h and the solvent was removed in vacuo. The residue was extractet with 50 ml PE. After filtration the extract was evaporated to dryness resulting in a yellow oil.

14. [EtOMe$_2$SiCH$_2$(C$_5$H$_4$)](OC)$_3$MoCl (*9a*)

Tricarbonylchloro[ethoydimethylsilyl(η^5-methylcyclopentadienyl)]molybdenum(II)

560 mg (1.55 mmol) of [EtOMe$_2$SiCH$_2$(C$_5$H$_4$)](OC)$_3$MoH (**5a**) were dissolved in 10 ml PE and 0.52 g (3.35 mmol) of CCl$_4$ were added. The solution was stirred for 1 h at room temperature. Finally all volatiles were removed in vacuo, and the residue was washed with 4 ml PE at -78 °C. Yield: 580 mg (94 %). Dark red oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.83 - 4.80 (m, 2 H, H$_4$C$_5$), 4.15 - 3.98 (m, 2 H, H$_4$C$_5$), 3.35 [q, ^{3}J(HCCH) = 6.6 Hz, 2 H, H$_2$CCH$_3$], 1.60 (s, 2 H, H$_2$CSi), 1.01 [t, ^{3}J(HCCH) = 6.6 Hz, 3 H, H$_3$CCH$_2$], -0.06 (s, 6 H, H$_3$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 243.58 (s, CO), 224.86 (s, CO), 114.46 (s, C-1 of C$_5$H$_4$), 91.72 (s, C$_5$H$_4$), 85.67 (s, C$_5$H$_4$), 58.54 (s, CH$_2$O), 21.09 (s, CH$_2$C$_5$H$_4$), 18.59 (s, CH$_3$CH$_2$O), -2.10 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 12.37 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2052 (s), 1981 (vs), 1956 (s) cm^{-1}.

C$_{13}$H$_{17}$ClMoO$_4$Si (396.75)   Calcd.: C 39.36   H 4.32

                                        Found: C 39.67   H 4.78

15. [(MeO)$_2$MeSi(CH$_2$)$_3$(C$_5$H$_4$)](OC)$_3$MoCl (*9b*)

Tricarbonylchloro[(3-dimethoymethylsilyl)propyl(η^5-cyclopentadienyl)]molybdenum(II)

430 mg (1.10 mmol) of [(MeO)$_2$MeSi(CH$_2$)$_3$(C$_5$H$_4$)](OC)$_3$MoH (**5b**) were dissolved in 10 ml PE and 0.52 g (3.35 mmol) of CCl$_4$ were added. The solution was stirred for 1

h at room temperature. Finally all volatiles were removed in vacuo, and the residue was washed with 4 ml PE at -78 °C. Yield: 400 mg (85 %). Dark red oil. - **^{1}H-NMR** (300.4 MHz, C_6D_6): δ = 4.76 - 4.71 (m, 2 H, H_4C_5), 4.13 - 4.10 (m, 2 H, H_4C_5), 3.34 (s, 6 H, H_3CO), 2.04 [t, ^3J(HCCH) = 7.8 Hz, 2 H, $\underline{H_2}CC_5H_4$], 1.48 - 1.36 (m, 2 H, CH_2), 0.53 [t, ^3J(HCCH) = 8.7 Hz, 2 H, H_2CSi], 0.07 (s, 3 H, H_3CSi) ppm. - **$^{13}C\{^1H\}$-NMR** (75.5 MHz, C_6D_6): δ = 242.51 (s, CO), 223.78 (s, CO), 115.90 (s, C-1 of C_5H_4), 93.83 (s, C_5H_4), 88.83 (s, C_5H_4), 49.98 (s, CH_3O), 31.99 (s, $\underline{C}H_2C_5H_4$), 23.66 (s, CH_2), 13.57 (s, CH_2Si), -5.63 (s, CH_3Si) ppm. - **$^{29}Si\{^1H\}$-NMR** (59.6 MHz, C_6D_6): δ = -3.15 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2054 (s), 1983 (vs), 1958 (s) cm^{-1}.

$C_{14}H_{19}ClMoO_5Si$ (426.78)	Calcd.: C 39.40	H 4.49
	Found: C 39.60	H 5.02

*16. [(MeO)$_2$MeSi(CH$_2$)$_3$(C$_5$H$_4$)](OC)$_3$WCl (**9c**)*

Tricarbonylchloro[(3-dimethoymethylsilyl)propyl(η^5-cyclopentadienyl)]tungsten(II)

According to *14.* from 700 mg (1.46 mmol) of [(MeO)$_2$MeSi(CH$_2$)$_3$(C$_5$H$_4$)](OC)$_3$WH (**5c**) and 0.52 g (3.35 mmol) of CCl_4 in 10 ml PE. Yield: 530 mg (71 %). Dark orange oil. - **^{1}H-NMR** (300.4 MHz, C_6D_6): δ = 4.87 - 4.83 (m, 2H, H_4C_5), 4.33 - 4.30 (m, 2 H, H_4C_5), 3.34 (s, 6 H, H_3CO), 1.99 [t, ^3J(HCCH) = 7.8 Hz, 2 H, $\underline{H_2}CC_5H_4$], 1.42 - 1.35 (m, 2 H, CH_2), 0.50 [t, ^3J(HCCH) = 8.5 Hz, 2 H, H_2CSi], 0.05 (s, 3 H, H_3CSi) ppm. - **$^{13}C\{^1H\}$-NMR** (75.5 MHz, C_6D_6): δ = 232.76 (s, CO), 217.47 (s, CO), 119.54 (s, C-1 of C_5H_4), 92.24 (s, C_5H_4), 87.41 (s, C_5H_4), 49.97 (s, CH_3O), 32.00 (s, $\underline{C}H_2C_5H_4$), 23.74 (s, CH_2), 13.49 (s, CH_2Si), -5.71 (s, CH_3Si) ppm. - **$^{29}Si\{^1H\}$-NMR** (59.6 MHz, C_6D_6): δ = -3.20 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2047 (s), 1966 (vs), 1945 (s) cm^{-1}.

$C_{14}H_{19}ClO_5SiW$ (514.69)	Calcd.: C 32.67	H 3.72
	Found: C 32.80	H 3.54

*17. [(MeO)₃Si(CH₂)₃(C₅H₄)](OC)₃MoCl (**9d**)*

Tricarbonylchloro[(3-trimethoysilyl)propyl(η^5-cyclopentadienyl)]molybdenum(II)

According to *14.* from 1.20 g (2.94 mmol) of [(MeO)₃Si(CH₂)₃(C₅H₄)](OC)₃MoH (**5d**) and 2.06 g (13.4 mmol) of CCl₄ in 10 ml PE. Yield: 1.21 g (93 %). Dark yellow oil. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 4.73 - 4.70 (m, 2 H, H₄C₅), 4.07 - 4.05 (m, 2 H, H₄C₅), 3.43 (s, 9 H, H₃CO), 2.05 [t, ³*J*(HCCH) = 7.8 Hz, 2 H, H̲₂CC₅H₄], 1.58 - 1.48 (m, 2 H, CH₂), 0.59 [t, ³*J*(HCCH) = 8.1 Hz, 2 H, H₂CSi] ppm. - **¹³C{¹H}-NMR** (75.5 MHz, C₆D₆): δ = 243.86 (s, CO), 225.17 (s, CO), 115.95 (s, C-1 of C₅H₄), 93.82 (s, C₅H₄), 88.90 (s, C₅H₄), 50.36 (s, CH₃O), 31.75 (s, C̲H₂C₅H₄), 23.64 (s, CH₂), 9.62 (s, CH₂Si) ppm. - **²⁹Si{¹H}-NMR** (59.6 MHz, C₆D₆): δ = -43.05 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2054 (s), 1983 (vs), 1958 (s) cm⁻¹.

C₁₄H₁₉ClMoO₆Si (442.78)   Calcd.: C 37.98   H 4.33

                                                 Found: C 37.70   H 4.15

*18. [MeOMe₂Si(CH₂)₃(C₅H₄)](OC)₃WSiMe₂H (**10**)*

Tricarbonyl[(3-methoxydimethylsilyl)propyl(η^5-cyclopentadienyl)](dimethylsilyl)-tungsten(II)

51.2 mg (0.80 mmol) of *n*BuLi (1.6 M *n*BuLi-solution of hexane) were added dropwise to a suspension of 300 mg (0.65 mmol) of [MeOMe₂Si(CH₂)₃(C₅H₄)](OC)₃WH (**5c**) in 10 ml PE and stirred for 2 h at room temperature. The resulting yellow solid was filtered, then wasched with 5 ml PE, and finally transformed in a new flask and suspended in 10 ml cyclohexane. 95.9 mg (0.91 mmol) of Me₂Si(H)Cl were added and stirred for 18 h at room temperature. All volatiles were removed in vacuo, and the residue was extracted with toluol (3 x 10 ml). The combined extracts were evaporated in vacuo and the resulting residue was wasched with 10 ml PE at -78 °C. Yield: 313 mg (92 %). Yellow oil. - **¹H-NMR** (300.4 MHz, C₆D₆): δ = 4.96 [sept,

^3J(HSiCH) = 3.3 Hz, 1 H, HSi], 4.62 - 4.58 (m, 2 H, HCp), 4.49 - 4.45 (m, 2 H, HCp), 3.25 (s, 3 H, H$_3$CO), 2.02 [t, ^3J(HCCH) = 7.8 Hz, 2 H, $\underline{H}_2$CC$_5$H$_4$], 1.38 - 1.25 (m, 2 H, CH$_2$), 0.69 [d, ^3J(HCSiH) = 3.9 Hz, 6 H, ($\underline{H}_3$C)$_2$SiH], 0.38 [t, ^3J(HCCH) = 8.1 Hz, 2 H, H$_2$CSi], 0.04 (s, 6 H, H$_3$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 219.89 (s, CO), 216.76 (s, CO), 113.78 (s, C-1 of C$_5$H$_4$), 90.03 (s, C$_5$H$_4$), 88.42 (s, C$_5$H$_4$), 49.99 (s, CH$_3$O), 31.87 (s, $\underline{C}$H$_2$C$_5$H$_4$), 26.19 (s, CH$_2$), 16.02 (s, CH$_2$Si), 1.59 (s, CH$_3$SiW), -2.65 (s, CH$_3$SiO) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 17.53 (s, SiO), -2.37 (s, SiW) ppm. - **IR** (PE): $\tilde{\nu}$ (SiH) = 2073 (vw); $\tilde{\nu}$ (CO) = 2001 (m), 1935 (vs), 1902 (s) cm^{-1}.

C$_{16}$H$_{26}$O$_4$Si$_2$W (522.40)   Calcd.: C 36.79   H 5.02

                                              Found: C 36.99   H 4.78

19. {HMo(CO)$_3$[(C$_5$H$_4$)(CH$_2$)Me$_2$Si]}$_2$O (**12a**)

1,3-Bis[tricarbonyl(η^5-methylcyclopentadienyl)hydridomolybdenum(II)]-1,1,3,3-tetra-methyl-disiloxane

After addition of 31.1 mg (1.73 mmol) of water and acetic acid to 440 mg (1.21 mmol) of [EtOMe$_2$SiCH$_2$(C$_5$H$_4$)](OC)$_3$MoH (**5a**) in 15 ml THF, the reaction mixture was stirred for 2 d. All volatiles were removed in vacuo, and the residue was washed with 10 ml PE at -78 °C and dried in vacuo. Yield: 335 mg (85 %). Dark red oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.86 - 4.85 (m, 4 H, H$_4$C$_5$), 4.63 - 4.61 (m, 4 H, H$_4$C$_5$), 1.48 (s, 4 H, H$_2$CSi), 0.23 (s, 12 H, H$_3$CSi), -5.25 (s, 2 H, HMo) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 228.25 (s, CO), 201.07 (s, CO), 113.60 (s, C-1 of C$_5$H$_4$), 90.09 (s, C$_5$H$_4$), 87.73 (s, C$_5$H$_4$), 19.70 (s, $\underline{C}$H$_2$C$_5$H$_4$), -0.40 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 5.87 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2023 (s), 1943 (vs) cm^{-1}.

C$_{22}$H$_{26}$Mo$_2$O$_7$Si$_2$ (650.50)   Calcd.: C 40.62   H 4.03

                                              Found: C 39.70   H 4.25

*20. {HW(CO)$_3$[(C$_5$H$_4$)(CH$_2$)Me$_2$Si]}$_2$O (**12b**)*

1,3-Bis[tricarbonyl(η^5-methylcyclopentadienyl)hydridotungsten(II)]-1,1,3,3-tetra-
methyl-disiloxane

According to *19.* from 311 mg (17.3 mmol) of water and acetic acid to 4.02 g (8.66 mmol) of [EtOMe$_2$SiCH$_2$(C$_5$H$_4$)](OC)$_3$WH (**5b**) in 40 ml THF. Yield: 3.58 g (94 %). Dark red oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.81 - 4.77 (m, 4 H, H$_4$C$_5$), 4.59 - 4.55 (m, 4 H, H$_4$C$_5$), 2.03 [t, ^3J(HCCH) = 7.5 Hz, 4 H, $\underline{H}_2$CC$_5$H$_4$], 1.35 - 1.28 (m, 4 H, CH$_2$), 0.41 [t, ^3J(HCCH) = 8.7 Hz, 4 H, H$_2$CSi], 0.10 (s, 12 H, H$_3$CSi), -6.99 [s, ^1J(HW) = 37.6 Hz, 2 H, HW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 218.21 (s, CO), 201.13 (s, CO), 114.47 (s, C-1 of C$_5$H$_4$), 88.98 (s, C$_5$H$_4$), 86.66 (s, C$_5$H$_4$), 32.65 (s, $\underline{C}$H$_2$C$_5$H$_4$), 26.51 (s, CH$_2$), 18.34 (s, CH$_2$Si), 0.42 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 7.47 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2024 (s), 1983 (vs) 1929 (vs) cm^{-1}. - **MS**, *m/e* 826 (M$^+$).

C$_{22}$H$_{26}$O$_7$Si$_2$W (826.32)	Calcd.: C 31.98	H 3.17
	Found: C 31.24	H 3.56

*21. {HW(CO)$_3$[(C$_5$H$_4$)(CH$_2$)$_3$Me$_2$Si]}$_2$O (**12c**)*

1,3-Bis{tricarbonyl[3-(η^5-cyclopentadienyl)propyl]hydridotungsten(II)}-1,1,3,3-
tetramethyl-disiloxane

According to *19.* from 1.10 g (2.44 mmol) of [MeOMe$_2$Si(CH$_2$)$_3$(C$_5$H$_4$)](OC)$_3$WH (**5c**), 110 mg (6.11 mmol) of water and one drop acetic acid in 5 ml THF. Yield: 640 mg (63 %). Dark yellow oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.75 - 4.70 (m, 4 H, H$_4$C$_5$), 4.53 - 4.48 (m, 4 H, H$_4$C$_5$), 1.39 (s, 4 H, H$_2$CSi), -0.14 (s, 12 H, H$_3$CSi), -6.85 [s, ^1J(HW) = 37.6 Hz, 1 H, HW] ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 202.20 (s,

CO), 191.12 (s, CO), 111.89 (s, C-1 of C_5H_4), 88.75 (s, C_5H_4), 85.88 (s, C_5H_4), 20.69 (s, $\underline{C}H_2C_5H_4$), -1.04 (s, CH_3Si) ppm. - **$^{29}Si\{^1H\}$-NMR** (59.6 MHz, C_6D_6): δ = 5.54 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2021 (s), 1917 (vs) cm^{-1}. - **MS**, *m/e* 882 (M$^+$) 826 (-2 CO).

$C_{26}H_{34}O_7Si_2W$ (882.42)	Calcd.: C 35.39	H 3.88
	Found: C 36.44	H 4.30

*22. {MeW(CO)$_3$[(C$_5$H$_4$)(CH$_2$)$_3$Me$_2$Si]}$_2$O (**12d**)*

1,3-Bis{tricarbonyl[3-(η^5-cyclopentadienyl)propyl]methyltungsten(II)}-1,1,3,3-tetramethyl-disiloxane

According to *19.* from 500 mg (1.05 mmol) of [MeOMe$_2$Si(CH$_2$)$_3$(C$_5$H$_4$)](OC)$_3$WMe (**8a**), 110 mg (6.11 mmol) of water and one drop acetic acid in 10 ml THF. Yield: 450.7 mg (94 %). Dark yellow oil. - **^{1}H-NMR** (300.4 MHz, C_6D_6): δ = 4.57 - 4.56 (m, 4 H, H$_4$C$_5$), 4.47 - 4.45 (m, 4 H, H$_4$C$_5$), 1.90 [t, ^3J(HCCH) = 7.8 Hz, 4 H, $\underline{H}_2$CC$_5$H$_4$], 1.39 - 1.27 (m, 4 H, CH$_2$), 0.50 (s, 6 H, H$_3$CW), 0.44 [t, ^3J(HCCH) = 7.8 Hz, 4 H, H$_2$CSi], 0.09 (s, 12 H, H$_3$CSi) ppm. - **$^{13}C\{^1H\}$-NMR** (75.5 MHz, C_6D_6): δ = 230.65 (s, CO), 217.66 (s, CO), 114.12 (s, C-1 of C$_5$H$_4$), 91.36 (s, C$_5$H$_4$), 88.95 (s, C$_5$H$_4$), 31.84 (s, $\underline{C}H_2C_5H_4$), 26.00 (s, CH$_2$), 18.37 (s, CH$_2$Si), 0.42 (s, CH$_3$Si), -31.84 [t, ^1J(CW) = 29.3 Hz, CH$_3$W] ppm. - **$^{29}Si\{^1H\}$-NMR** (59.6 MHz, C_6D_6): δ = 7.50 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2015 (s), 1925 (vs) cm^{-1}.

$C_{28}H_{38}O_7Si_2W_2$ (910.48)	Calcd.: C 36.94	H 4.21
	Found: C 37.35	H 4.44

*23. {ClW(CO)$_3$[(C$_5$H$_4$)(CH$_2$)$_3$Me$_2$Si]}$_2$O (**13**)*

1,3-Bis{dicarbonylchloro[3-(η^5-cyclopentadienyl)propyl]tungsten(II)}-1,1,3,3-tetramethyl-disiloxane

According to *14.* from 440 mg (0.50 mmol) of {ClW(CO)$_3$[(C$_5$H$_4$)(CH$_2$)$_3$Me$_2$Si]}$_2$O (**11b**) and 1.03 g (6.70 mmol, 0.5 ml) of CCl$_4$ in 20 ml PE. Yield: 445 mg (94 %). Darkyellow oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.94 - 4.91 (m, 4 H, H$_4$C$_5$), 4.29 - 4.25 (m, 4 H, H$_4$C$_5$), 2.07 [t, ^3J(HCCH) = 7.7 Hz, 4 H, $\underline{H}_2$CC$_5$H$_4$], 1.44 - 1.36 (m, 4 H, CH$_2$), 0.50 [t, ^3J(HCCH) = 8.8 Hz, 4 H, H$_2$CSi], 0.14 (s, 12 H, H$_3$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 232.65 (s, CO), 217.29 (s, CO), 120.01 (s, C-1 of C$_5$H$_4$), 92.23 (s, C$_5$H$_4$), 86.87 (s, C$_5$H$_4$), 32.33 (s, $\underline{C}$H$_2$C$_5$H$_4$), 24.08 (s, CH$_2$), 18.53 (s, CH$_2$Si), 0.53 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 7.54 (s) ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 2047 (s), 1967 (vs), 1947 (s) cm^{-1}.

C$_{26}$H$_{32}$Cl$_2$O$_7$Si$_2$W$_2$ (951.31)   Calcd.: C 32.83   H 3.39

                                                         Found: C 33.12   H 3.00

*24. {HW(PMe$_3$)(CO)$_2$[(C$_5$H$_4$)(CH$_2$)Me$_2$Si]}$_2$O (**14a**)*

1,3-Bis[dicarbonyl(η^5-methylcyclopentadienyl)hydrido(trimethylphosphino)-tungsten(II)]-1,1,3,3-tetramethyl-disiloxane

A mixture of 840 mg (1.02 mmol) of {HW(CO)$_3$[(C$_5$H$_4$)(CH$_2$)Me$_2$Si]}$_2$O (**12a**), 232 mg (3.04 mmol) of PMe$_3$ and 20 ml PE was stirred for 22 h at room temperature. All volatiles were removed in vacuo, and the residue was washed with 10 ml PE at -78 °C. Yield: 530 mg (52 %). Yellow orange oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 4.95 - 4.73 (m, 8 H, H$_4$C$_5$), 1.78, 1.77 (s, 4 H, H$_2$CSi), 1.26, 1.24 [d, ^2J(PCH) = 5.7 Hz, 18 H, H$_3$CP], -0.03 (s, 12 H, H$_3$CSi), -6.70 (*cis*), -7.56 (*trans*) [d, ^2J(PWH) = 23.7 Hz (*cis*), 70.3 Hz (*trans*), ^1J(HW) = 51.7 Hz (*cis*), 49.6 Hz (*trans*), 2 H, HW] ppm. - **^{13}C{^{1}H}-**

NMR (75.5 MHz, C_6D_6): δ = 226.01 [d, ^2J(CWP) = 15.2 Hz, CO), 108.95, 107.39 (s, C-1 of C_5H_4), 88.03, 86.53 (s, C_5H_4), 85.44, 83.00 (s, C_5H_4), 25.44 [d, ^1J(PC) = 34.8 Hz, CH_3P (*trans*)], 22.45 [d, ^1J(PC) = 34.0 Hz, CH_3P (*cis*)], 22.64, 21.87 (s, $\underline{C}H_2C_5H_4$), 0.00 (s, CH_3Si) ppm. - ^{29}**Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = 5.45 (s) ppm. - ^{31}**P{^{1}H}-NMR**: (121.5 MHz, C_6D_6): δ = -16.20 [s, ^1J(PW) = 255.2 Hz, PMe_3 (*trans*)], -19.0 [s, ^1J(PW) = 279.5 Hz, PMe_3 (*cis*)] ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 1937 (vs), 1853 (vs) cm^{-1}.

$C_{26}H_{44}O_5P_2Si_2W_2$ (922.45)	Calcd.: C 33.85	H 4.81
	Found: C 33.32	H 4.52

25. {HW(PMe$_3$)(CO)$_2$[(C$_5$H$_4$)(CH$_2$)$_3$Me$_2$Si]}$_2$O (14b)

1,3-Bis{dicarbonyl[3-(η^5-cyclopentadienyl)propyl]hydrido(trimethylphosphino)-tungsten(II)}-1,1,3,3-tetramethyl-disiloxane

According to *24.* from 2.36 g (2.67 mmol) of {HW(CO)$_3$[(C$_5$H$_4$)(CH$_2$)$_3$Me$_2$Si]}$_2$O (**12b**) and 810 mg (10.7 mmol) of PMe_3 in 40 ml PE. Yield: 2.33 g (89 %). Orange oil. - ^{1}**H-NMR** (300.4 MHz, C_6D_6): δ = 4.99 - 4.92, 4.90 - 4.85, 4.79 - 4.62 and 4.60 - 4.55 (m, 8 H, H_4C_5), 2.40 - 2.25 (m, 4 H, H_2CCp), 1.55 - 1.48 (m, 4 H, H_2C), 1.26, 1.24 [d, ^2J(PCH) = 8.7 Hz, 18 H, H_3CP], 0.58 - 0.51 (m, 4 H, H_2CSi), 0.13 (s, 12 H, H_3CSi), -6.89 (*cis*), -7.70 (*trans*) [d, ^2J(PWH) = 23.7 Hz (*cis*), 69.1 Hz (*trans*), ^1J(HW) = 51.7 Hz (*cis*), 49.6 Hz (*trans*), 1 H, HW] ppm. - ^{13}**C{^{1}H}-NMR** (75.5 MHz, C_6D_6): δ = 225.46 [d, ^2J(CWP) = 11.4 Hz, CO), 112.02, 110.83 (s, C-1 of C_5H_4), 88.05, 86.42 (s, C_5H_4), 85.99, 83.45 (s, C_5H_4), 34.30, 33.48 (s, CH_2Cp) 27.40, 26.88 (s, CH_2), 25.52 [d, ^1J(PC) = 34.1 Hz, CH_3P (*trans*)], 22.45 [d, ^1J(PC) = 32.4 Hz, CH_3P (*cis*)], 19.00, 18.58 (s, CH_2Si), 0.00 (s, CH_3Si) ppm. - ^{29}**Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = 7.50 (s) ppm. - ^{31}**P{^{1}H}-NMR**: (121.5 MHz, C_6D_6): δ = -16.65 [s, ^1J(PW) = 257.6 Hz, PMe_3 (*trans*)], -19.18 [s, ^1J(PW) = 280.7 Hz, PMe_3 (*cis*)] ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 1939 (vs), 1853 (vs) cm^{-1}.

C$_{30}$H$_{52}$O$_5$P$_2$Si$_2$W$_2$ (978.56)   Calcd.: C 36.82   H 5.36

          Found: C 35.96   H 5.76

*26. {ClW(PPh$_3$)(CO)$_2$[(C$_5$H$_4$)(CH$_2$)$_3$Me$_2$Si]}$_2$O (**14c**)*

1,3-Bis{dicarbonylchloro[3-(η^5-cyclopentadienyl)propyl](triphenylphosphino)-tungsten(II)}-1,1,3,3-tetramethyl-disiloxane

A solution of 150 mg (0.16 mmol) of **13** in 10 ml benzene was irradiated with UV-light (Quarz lamp TQ 718, 700 W, Hanau) for 3 h in the presence of 82.8 mg (0.32 mmol) of PPh$_3$. After evaporation to dryness the resulting residue is washed three times with 10 ml PE at -78 °C. Yield: 185 mg (0.13 mmol, 86 %). Orange solid. M.p: 40 °C (decomp.). - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 7.63 - 7.50 (m, 12 H, *ortho*-H of PPh$_3$), 7.15 - 6.95 (m, 18 H, *meta*- and *para*-H of PPh$_3$), 5.36 - 4.25 (m, 8 H, H$_4$C$_5$), 2.35 - 2.24 (m, 4 H, $\underline{H}_2$CC$_5$H$_4$), 1.60 - 1.50 (m, 4 H, CH$_2$), 0.59 - 0.44 (m, 4 H, H$_2$CSi), 0.14, 0.13 and 0.12 (s, 12 H, H$_3$CSi) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 249.32 [d, ^2J(CWP) = 29.6 Hz, *cis*-CO], 237.01 [d, ^2J(CWP) = 10.3 Hz, *trans*-CO], 134.43 [d, ^1J(CP) = 9.5 Hz, *ipso*-C of PPh$_3$], 130.39 [d, ^2J(CCP) = 2.9 Hz, *ortho*-C of PPh$_3$], 128.50 (s, *meta*-C of PPh$_3$), 128.40 (s, *para*-C of PPh$_3$), 123.22, 123.17 and 123.12 (s, C-1 of C$_5$H$_4$), 99.05, 92.38 and 89.43 (s, C$_5$H$_4$), 87.00, 85.40 and 84.55 (s, C$_5$H$_4$), 32.95, 32.91 and 32.87 (s, $\underline{C}$H$_2$C$_5$H$_4$), 24.82, 24.78 and 24.68 (s, CH$_2$), 18.65, 18.57 and 18.50 (s, CH$_2$Si), 0.62, 0.59 and 0.54 (s, CH$_3$Si) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 7.72, 7.71 and 7.55 (s) ppm. - **^{31}P{^{1}H}-NMR**: (121.5 MHz, C$_6$D$_6$): δ = 24.77, 24.75 and 24.71 [s, ^1J(PW) = 269.7, 269.7 and 270.9 Hz, PW] ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 1962 (vs), 1868 (m) cm^{-1}.

C$_{34}$H$_{62}$Cl$_2$O$_5$P$_2$Si$_2$W$_2$ (1419.88)   Calcd.: C 50.75   H 4.40

          Found: C 51.22   H 4.30

*27. {HMe$_2$SiW(PMe$_3$)(CO)$_2$[(C$_5$H$_4$)(CH$_2$)Me$_2$Si]}$_2$O (**16a**)*

1,3-Bis[dicarbonyl(η^5-methylcyclopentadienyl)(trimethylphosphino)(dimethylsilyl)-tungsten(II)]-1,1,3,3-tetramethyl-disiloxane

According to *18.* from 530 mg (0.57 mmol) of {HW(PMe$_3$)(CO)$_2$[(C$_5$H$_4$)(CH$_2$)Me$_2$Si]}$_2$O (**14a**), 41.6 mg (1.30 mmol) of *n*BuLi in 10 ml PE und 95.9 mg (0.91 mmol) of Me$_2$Si(H)Cl in 10 ml cyclohexane. Yield: 150 mg (79 %). Yellow oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 5.22 [sept-d, ^3J(HSiCH) = 3.5 Hz, ^3J(PWSiH) = 1.3 Hz, 2 H, HSi] 4.72 - 4.68 (m, 4 H, H$_4$C$_5$), 4.63 - 4.58 (m, 4 H, H$_4$C$_5$), 1.79 (s, 4 H, H$_2$CSi), 1.28 [d, ^2J(PCH) = 5.8 Hz, 18 H, H$_3$CP], 0.95 [d, ^3J(HCSiH) = 3.5 Hz, 12 H, (H̲$_3$C)$_2$SiH], -0.02 (s, 12 H, H$_3$CSiO) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 225.58 [d, ^2J(CWP) = 17.2 Hz, CO), 108.44 (s, C-1 of C$_5$H$_4$), 89.10 (s, C$_5$H$_4$), 85.29 (s, C$_5$H$_4$), 22.03 [d, ^1J(PC) = 33.8 Hz, CH$_3$P], 20.53 (s, C̲H$_2$C$_5$H$_4$), 2.24 (s, CH$_3$SiW), 0.00 (s, CH$_3$SiO) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 5.75 (s, SiO), 1.01 [d, ^2J(SiWP) = 17.1, ^1J(SiW) = 39.9 Hz, SiW] ppm. - **^{31}P{^{1}H}-NMR**: (121.5 MHz, C$_6$D$_6$): δ = -14.40 [s, ^1J(PW) = 240.6 Hz, PMe$_3$] ppm. - **IR** (PE): $\tilde{\nu}$(SiH) = 2041 (w); $\tilde{\nu}$(CO) = 1901 (s), 1828 (vs) cm^{-1}.

C$_{30}$H$_{56}$O$_5$P$_2$Si$_4$W$_2$ (1038.77)	Calcd.: C 34.69	H 5.43
	Found: C 34.55	H 5.61

*28. {HMe$_2$SiW(PMe$_3$)(CO)$_2$[(C$_5$H$_4$)(CH$_2$)$_3$Me$_2$Si]}$_2$O (**16b**)*

1,3-Bis{dicarbonyl[3-(η^5-cyclopentadienyl)propyl](trimethylphosphino)(dimethylsilyl)-tungsten(II)}-1,1,3,3-tetramethyl-disiloxane

According to *18.* from 2.15 g (2.20 mmol) of {HW(PMe$_3$)(CO)$_2$[(C$_5$H$_4$)(CH$_2$)$_3$Me$_2$Si]}$_2$O (**14b**), 384 mg (6.00 mmol) of *n*BuLi in 10 ml PE und 0.57 mg (6.00 mmol) of Me$_2$Si(H)Cl in 10 ml cyclohexane. Yield: 2.34 g (97 %). Brown oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 5.26 [sept-d, ^3J(HSiCH) = 3.7 Hz, ^3J(PWSiH) = 1.1 Hz, 2 H, HSi],

4.70 - 4.65 (m, 4 H, H$_4$C$_5$), 4.56 - 4.54 (m, 4 H, H$_4$C$_5$), 2.28 [t, ^3J(HCCH) = 7.7 Hz, 4 H, H$_2$CC$_5$H$_4$], 1.60 - 1.42 (m, 4 H, H$_2$C), 1.24 [d, ^2J(PCH) = 9.2 Hz, 18 H, H$_3$CP], 0.94 [d, ^3J(HCSiH) = 3.7 Hz, 12 H, H$_3$CSiW], 0.58 - 0.50 (m, 4 H, H$_2$CSi), 0.15 (s, 12 H, H$_3$CSiO) ppm. - ^{13}C{^{1}H}-NMR (75.5 MHz, C$_6$D$_6$): δ = 225.05 [d, ^2J(CWP) = 17.3 Hz, CO), 111.99 (s, C-1 of C$_5$H$_4$), 89.50 (s, C$_5$H$_4$), 85.16 (s, C$_5$H$_4$), 32.47 (s, CH$_2$Cp), 26.29 (s, CH$_2$), 21.94 [d, ^1J(PC) = 33.8 Hz, CH$_3$P], 18.61 (s, CH$_2$Si), 2.27 (s, CH$_3$SiW), 0.57 (s, CH$_3$SiO) ppm. - ^{29}Si{^{1}H}-NMR (59.6 MHz, C$_6$D$_6$): δ = 7.57 (s, SiO), 0.41 [d, ^2J(SiWP) = 17.4, ^1J(SiW) = 39.9 Hz, SiW] ppm. - ^{31}P{^{1}H}-NMR: (121.5 MHz, C$_6$D$_6$): δ = -14.34 [s, ^1J(PW) = 283.1 Hz, PMe$_3$] ppm. - IR (PE): $\tilde{\nu}$ (SiH) = 2041 (w); $\tilde{\nu}$ (CO) = 1901 (s), 1827 (vs) cm^{-1}.

C$_{34}$H$_{64}$O$_5$P$_2$Si$_4$W$_2$ (1094.87)   Calcd.: C 37.30   H 5.89

Found: C 37.97   H 6.02

29. {BrMe$_2$SiW(PMe$_3$)(CO)$_2$[(C$_5$H$_4$)(CH$_2$)$_3$Me$_2$Si]}$_2$O (17)

1,3-Bis{dicarbonyl[3-(η^5-cyclopentadienyl)propyl](bromodimethylsilyl)-(trimethylphosphino)tungsten(II)}-1,1,3,3-tetramethyl-disiloxane

450 mg (0.41 mmol) of **16b** in 15 ml toluene were treated with 680 mg (2.05 mmol) of CBr$_4$ and the solution stirred for 3 h at room temperature. The volatiles were removed in vacuo and the residue washed with 10 ml PE at -78 °C and finally dried in vacuo. Yield: 340 mg (68 %). Brown oil. - ^{1}H-NMR (300.4 MHz, C$_6$D$_6$): δ = 4.96 - 4.90 (m, 4 H, H$_4$C$_5$), 4.68 - 4.65 (m, 4 H, H$_4$C$_5$), 2.36 [t, ^3J(HCCH) = 7.5 Hz, 4 H, H$_2$CC$_5$H$_4$], 1.59 - 1.45 (m, 4 H, H$_2$C), 1.39 (s, 12 H, H$_3$CSiW), 1.22 [d, ^2J(PCH) = 9.4 Hz, 18 H, H$_3$CP], 0.59 - 0.52 (m, 4 H, H$_2$CSi), 0.17 (s, 12 H, H$_3$CSiO) ppm. - ^{13}C{^{1}H}-NMR (75.5 MHz, C$_6$D$_6$): δ = 224.83 [d, ^2J(CWP) = 18.9 Hz, CO), 113.53 (s, C-1 of C$_5$H$_4$), 87.35 (s, C$_5$H$_4$), 85.57 (s, C$_5$H$_4$), 31.74 (s, CH$_2$Cp), 25.65 (s, CH$_2$), 20.74 [d, ^1J(PC) = 34.9 Hz, CH$_3$P], 17.74 (s, CH$_2$Si), 11.78 (s, CH$_3$SiW), -0.14 (s, CH$_3$SiO) ppm. - ^{29}Si{^{1}H}-NMR (59.6 MHz, C$_6$D$_6$): δ = 67.98 [d, ^2J(SiWP) = 17.9 Hz, ^1J(SiW) = 65.2 Hz, SiW], 7.59 (s,

SiO) ppm. - **^{31}P{^{1}H}-NMR**: (121.5 MHz, C_6D_6): δ = -14.97 [s, ^1J(PW) = 260.0 Hz, PMe$_3$] ppm. - **IR** (PE): $\tilde{\nu}$ (CO) = 1901 (s), 1827 (vs) cm^{-1}.

$C_{34}H_{62}Br_2O_5P_2Si_4W_2$ (1252.66)   Calcd.: C 32.60   H 4.99

          Found: C 32.97   H 5.02

*30. {HOMe$_2$SiW(PMe$_3$)(CO)$_2$[(C$_5$H$_4$)(CH$_2$)$_3$Me$_2$Si]}$_2$O (**18**) by oxygenation of **16b** with dimethyldioxirane*

1,3-Bis{dicarbonyl[3-(η^5-cyclopentadienyl)propyl][hydroxy(dimethyl)silyl]-(trimethylphosphino)tungsten(II)}-1,1,3,3-tetramethyl-disiloxane

360 mg (0.33 mmol) of {HMe$_2$SiW(PMe$_3$)(CO)$_2$[(C$_5$H$_4$)(CH$_2$)$_3$Me$_2$Si]}$_2$O (**16b**) were solved in 10 ml acetone. 51.8 mg (0.70 mmol) of a 0.09 M dimethyldioxirane solution were added at -78 °C. The reaction mixture was stirred for 1 h while warming up to 25 °C. Then all volatiles were removed in vacuo and the residue washed with 10 ml PE at -78 °C. Yield: 190 mg (52 %). Brown solid. Mp.: 45 °C. - **^{1}H-NMR** (300.4 MHz, C_6D_6): δ = 4.93 - 4.87 (m, 4 H, H$_4$C$_5$), 4.67 - 4.65 (m, 4 H, H$_4$C$_5$), 2.70 (br, 2 H, HOSi), 2.34 [t, ^3J(HCCH) = 7.7 Hz, 4 H, H$_2$CC$_5$H$_4$], 1.60 - 1.48 (m, 4 H, H$_2$C), 1.28 [d, ^2J(PCH) = 9.3 Hz, 18 H, H$_3$CP], 1.05 (s, 12 H, H$_3$CSiW), 0.61 - 0.55 (m, 4 H, H$_2$CSi), 0.17 (s, 12 H, H$_3$CSiO) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C_6D_6): δ = 227.20 [d, ^2J(CWP) = 17.2 Hz, CO), 112.70 (s, C-1 of C$_5$H$_4$), 90.12 (s, C$_5$H$_4$), 85.16 (s, of C$_5$H$_4$), 32.79 (s, CH$_2$Cp), 26.50 (s, CH$_2$), 21.83 [d, ^1J(PC) = 33.8 Hz, CH$_3$P], 18.62 (s, CH$_2$Si), 9.71 (s, CH$_3$SiW), 0.55 (s, CH$_3$SiO) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C_6D_6): δ = 51.28 [d, ^2J(SiWP) = 17.6, ^1J(SiW) = 44.5 Hz, SiW], 7.58 (s, SiO) ppm. - **^{31}P{^{1}H}-NMR**: (121.5 MHz, C_6D_6): δ = -13.77 [s, ^1J(PW) = 280.7 Hz, PMe$_3$] ppm. - **IR** (Toluol): $\tilde{\nu}$ (SiOH) = 3675 (w); $\tilde{\nu}$ (CO) = 1891 (s), 1813 (vs) cm^{-1}.

$C_{34}H_{64}O_7P_2Si_4W_2$ (1126.87)   Calcd.: C 36.24   H 5.72

          Found: C 35.90   H 6.05

*31. {HOMe$_2$SiW(PMe$_3$)(CO)$_2$[(C$_5$H$_4$)(CH$_2$)$_3$Me$_2$Si]}$_2$O (**18**) by hydrolysis of **17***

To a solution of 270 mg (0.22 mmol) of **17** in 10 ml Et$_2$O were added 50.6 mg (0.50 mmol) of NEt$_3$ and 10 mg (0.55 mmol) of H$_2$O. After the mixture had been stirred for 3 h at room temperature, the precipitate of [Et$_3$NH]Br was filtered off and all volatiles were removed in vacuo. The resulting residue was extracted three times with 10 ml benzene and the combined extracts were concentrated to dryness. The resulting **18** was washed with 5 ml PE dried in vacuo. Yield: 186 mg (77 %). Brown solid.

*32. {HMe$_2$SiOMe$_2$SiW(PMe$_3$)(CO)$_2$[(C$_5$H$_4$)(CH$_2$)$_3$Me$_2$Si]}$_2$O (**19**)*

1,3-Bis{dicarbonyl[3-(η^5-cyclopentadienyl)propyl](trimethylphosphino)(1,1,3,3-tetramethyl-disiloxy)-1-tungsten(II)}-1,1,3,3-tetramethyl-disiloxane

To a solution of 110 mg (0.10 mmol) of **18** in 10 ml Et$_2$O were 18.9 mg (0.20 mmol, 0.22 ml) of Me$_2$Si(H)Cl in the presence of 20.0 mg (0.20 mmol, 0.27 ml) of NEt$_3$ added. After the mixture had been stirred for 1 h at room temperature, the precipitate of [Et$_3$NH]Cl was filtered off and all volatiles were removed in vacuo. The brown residue was washed with 5 ml PE at -78 °C and finally dried in vacuo. Yield: 112 mg (90 %). Brown oil. - **^{1}H-NMR** (300.4 MHz, C$_6$D$_6$): δ = 5.26 [sept, ^3J(HSiCH) = 2.8 Hz, 2 H, HSi], 4.90 - 4.83 (m, 4 H, H$_4$C$_5$), 4.67 - 4.63 (m, 4 H, H$_4$C$_5$), 2.35 [t, ^3J(HCCH) = 7.9 Hz, 4 H, H$_2$CC$_5$H$_4$], 1.60 - 1.50 (m, 4 H, H$_2$C), 1.24 [d, ^2J(PCH) = 9.2 Hz, 18 H, H$_3$CP], 1.01 (s, 12 H, H$_3$CSiW), 0.64 - 0.57 (m, 4 H, H$_2$CSi), 0.39 [d, ^3J(HCSiH) = 2.6 Hz, 12 H, H$_3$CSiH], 0.17 (s, 12 H, H$_3$CSiO) ppm. - **^{13}C{^{1}H}-NMR** (75.5 MHz, C$_6$D$_6$): δ = 226.03 [d, ^2J(CWP) = 17.3 Hz, CO], 112.00 (s, C-1 of C$_5$H$_4$), 89.45 (s, C$_5$H$_4$), 84.46 (s, C$_5$H$_4$), 32.79 (s, CH$_2$Cp), 26.20 (s, CH$_2$), 21.69 [d, ^1J(PC) = 33.8 Hz, CH$_3$P], 18.67 (s, CH$_2$Si), 10.15 (s, CH$_3$SiW), 1.35 (s, CH$_3$SiH), 0.54 (s, CH$_3$SiO) ppm. - **^{29}Si{^{1}H}-NMR** (59.6 MHz, C$_6$D$_6$): δ = 45.72 [d, ^2J(SiWP) = 17.0, ^1J(SiW) = 44.5 Hz, SiW], 7.70 (s, SiO), -10.34 (s, SiH) ppm. - **^{31}P{^{1}H}-NMR**: (121.5 MHz, C$_6$D$_6$): δ = -13.87 [s, ^1J(PW) = 278.2 Hz, PMe$_3$] ppm. - **IR** (PE): $\tilde{\nu}$(SiH) = 2114 (w); $\tilde{\nu}$(CO) = 1900 (s), 1827 (vs) cm^{-1}.

$C_{38}H_{76}O_7P_2Si_6W_2$ (1243.18)   Calcd.: C 36.71   H 6.16

Found: C 35.99   H 6.15

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CHAPTER I: SYNTHESIS AND REACTIVITY OF HALFSANDWICH TUNGSTEN HYDRIDO AND CHLORO COMPLEXES WITH A η^5-CYCLOPENTADIENYL-BOUND SILANOL FUNCTION

Treatment of the tungsten-silanes **1a,b** with LiN(iPr)$_2$, nBuLi or tBuLi, respectively induces a silatropic rearrangement via the lithiocyclopentadienyl complex (LiC$_5$H$_4$)L(OC)$_2$WSiMe$_2$H (L = CO, PMe$_3$) which results in the formation of Li{W[(C$_5$H$_4$)SiMe$_2$H]L(CO)$_2$} [L = CO (**2a**), PMe$_3$ (**2b**)]. Alternatively, the reaction of the hydrido complex **3** with two equivalents of nBuLi, leads to the dilithiated compound **4** which reacts regioselectively with dimethylchlorosilane at −78 °C at the cyclopentadienyl ring to give **2a**.
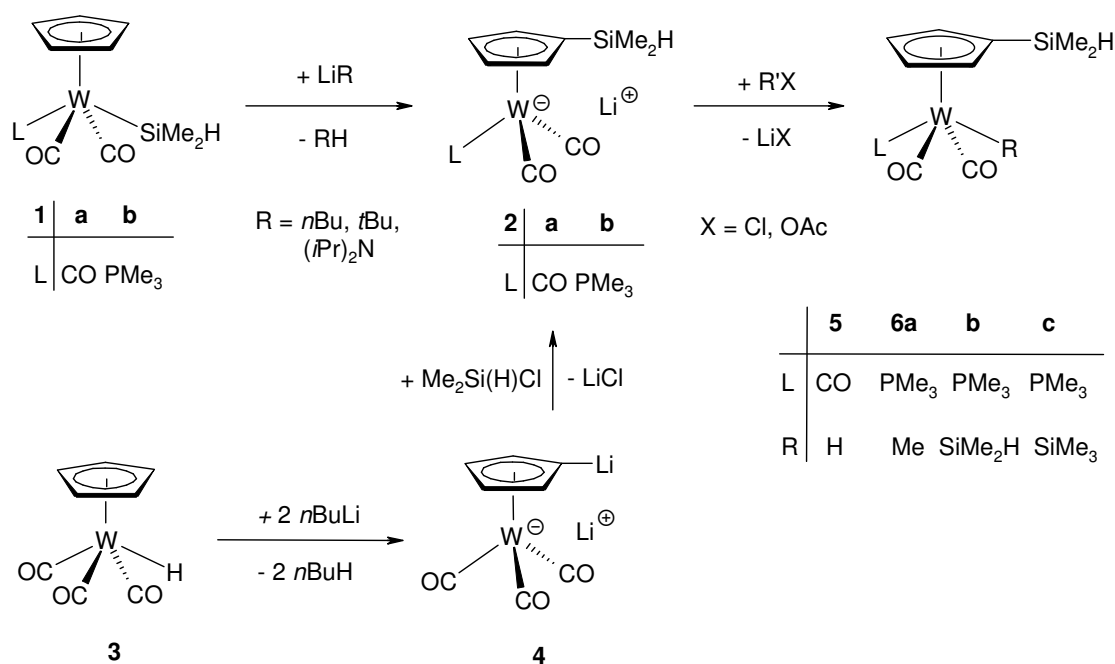
2a,b are transformed into the neutral complexes **5** and **6a-c** by heterogeneous reaction with HOAc, MeI, Me$_2$Si(H)Cl or Me$_3$SiCl, respectively in cyclohexane.

The reaction of the cyclopentadienes HC$_5$R$_4$(SiMe$_2$X) [R = H, Me; X = H, Cl (**7, 8a,b**)] with (MeCN)$_3$W(CO)$_3$ in THF results in the formation of the hydrido- or chlorosilyl-cyclopentadienyl hydrido complexes **5, 9a,b**.

Both hydrido functions are chlorinated, if **5** is treated with one equivalent of PdCl$_2$, giving the tungsten chloride **10a** which can also be generated when **9a** is treated with an excess of CCl$_4$. In the case of **9b** the analogous reaction leads to the expected **10b**.
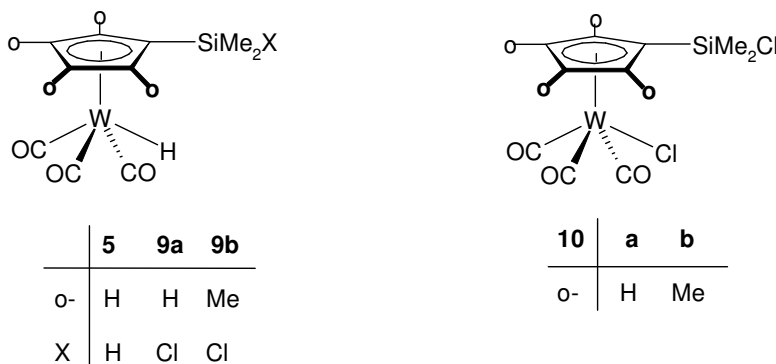
	5	**9a**	**9b**
o-	H	H	Me
X	H	Cl	Cl

10	**a**	**b**
o-	H	Me

The hydrolysis of the tungsten-chlorosilanes **9a,b, 10a,b** in the presence of NEt$_3$ as an auxiliary base affords directly the corresponding tungsten-silanols **11** and **13a**-**c**. Whereas **11** and **13b,c** are stable with respect to self-condensation at room temperature, **13a** converts partially to the corresponding tungsten-disiloxane O{[Me$_2$Si(C$_5$H$_4$)](OC)$_3$WCl}$_2$ (**14**).

	11	**13a**	**b**	**c**
o-	H	H	Me	Me
R	H	Cl	H	Cl

	16	**18**
R	H	Me
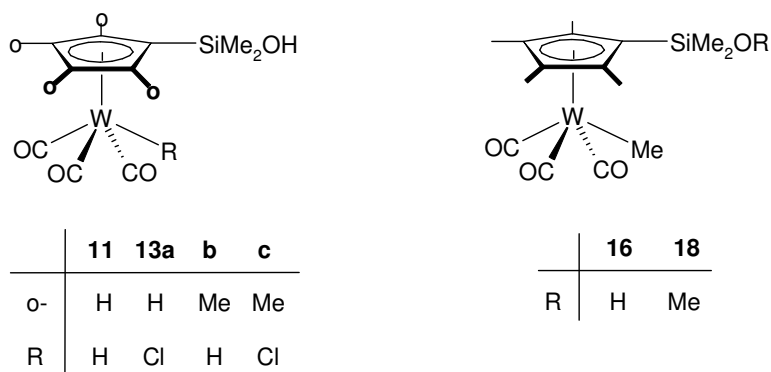
13b can be deprotonated with *n*BuLi regioselectively at the W-H function, yielding the corresponding lithium tungstate Li{W[(C$_5$H$_4$)SiMe$_2$OH](CO)$_3$} which is converted with an excess of MeI into the tungsten methyl complex **16**. With two equivalents of *n*BuLi the formation of the double lithiated Li{W[(C$_5$H$_4$)SiMe$_2$OLi](CO)$_3$}-species is enabled whose treatment with MeI give the double methylated product **18**.

Co-condensation with $Me_2Si(H)Cl$ gives in the case of **11** the tungsten-disiloxane **19** while the reaction of **13b** with iBu_3Al results in the formation of the dimeric tungsten-alumosiloxane **20**, accompanied by *iso*-butane elimination.
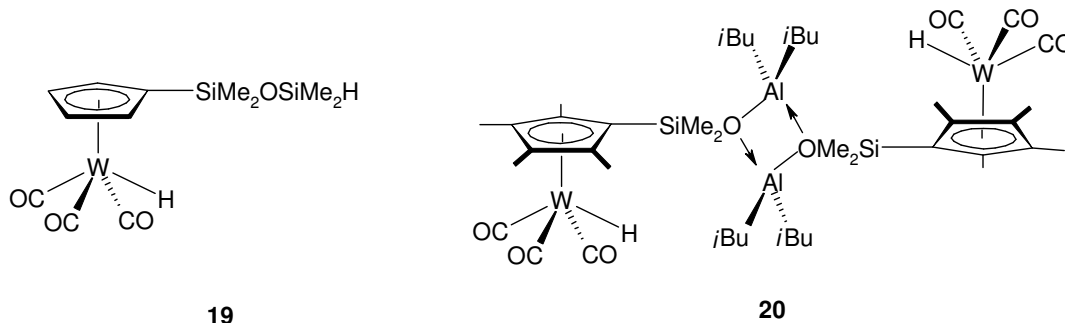
19

20

CHAPTER II: HALFSANDWICH TUNGSTEN METHYL COMPLEXES WITH A η^5-CYCLOPENTADIENYL-BOUND SILANOL FUNCTION

Treatment of $Cp(OC)_3WMe$ (**1**) with *n*BuLi at −78 °C in THF generates the cyclopentadienyl-lithiated $(LiC_5H_4)(OC)_3WMe$-species whose *in situ* reaction with $ClSiRR'H$ [R, R' = Me, Ph, *i*-Pr (**5a-d**)] affords the tungsten-silanes **6a-d**.

1. + *n*BuLi, - *n*BuH
2. + ClSiRR'H, - LiCl

1

5	a	b	c	d
R	Me	Ph	*i*Pr	Me
R'	Me	Ph	*i*Pr	Ph

6a-d
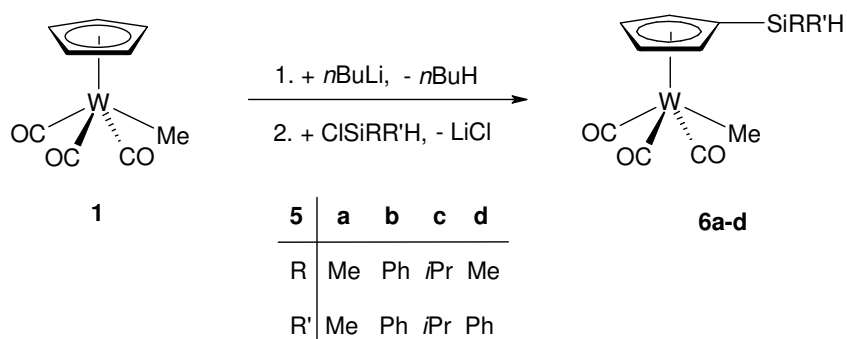
Chlorination to the tungsten-chlorosilanes **3a,b** is realized when **6a-c** are treated with $PdCl_2$ in benzene. However, in the case of **6c** a mixture consisting of **7** and the unexpected tungsten chloro complex **8** is obtained after one equivalent of $PdCl_2$ is used up. Further addition of $PdCl_2$ converts all **6c** and **7** into **8**.

The exclusive synthesis of **7** is achieved by regioselective silylation at the cyclopentadienyl ligand of the dilithiated complex $Li[W(LiC_5H_4)(CO)_3]$ with iPr_2SiCl_2 to

give the lithium tungstate Li{W[(C$_5$H$_4$)SiiPr$_2$H](CO)$_3$} which is converted into **7** with MeI.

3	**a**	**b**	**7**	**8**
R	Me	Ph	iPr	iPr
R'	Me	Me	Me	Cl

13	**a**	**b**	**c**
R	Me	Ph	iPr
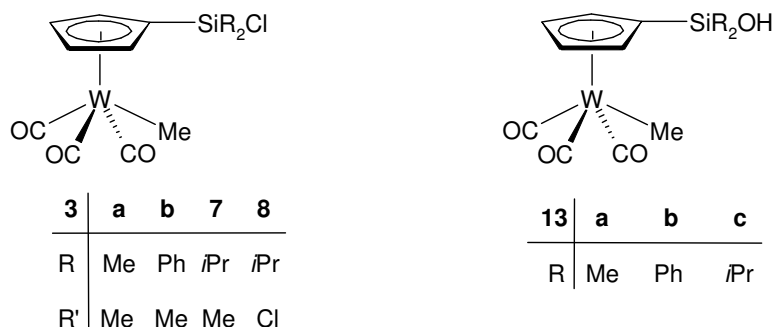
The transformation the Si-H-functionalized **6a** into the corresponding tungsten-silanol **13a** is accomplished upon treatment with Co$_2$(CO)$_8$ via the intermediate hetero-dinuclear complex [(OC)$_4$CoMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**B**), followed by hydrolysis. **3a,b** and **7** are hydrolyzed in the presence of NEt$_3$, resulting in the formation of the pure tungsten-silanols **13a**-**c**.

The reasonable stability of the tungsten-silanol **13a** garantees controlled co-condensation with Me$_2$Si(H)Cl, Me$_3$SnCl and Cp$_2$TiCl$_2$, respectively in the presence of NEt$_3$, leading to the tungsten-disiloxanes and -heterosiloxanes **17a-c**.

17	**a**	**b**	**c**	**20**
R	Me$_2$(H)Si	Me$_3$Sn	Cp$_2$Ti(Cl)	Me

18
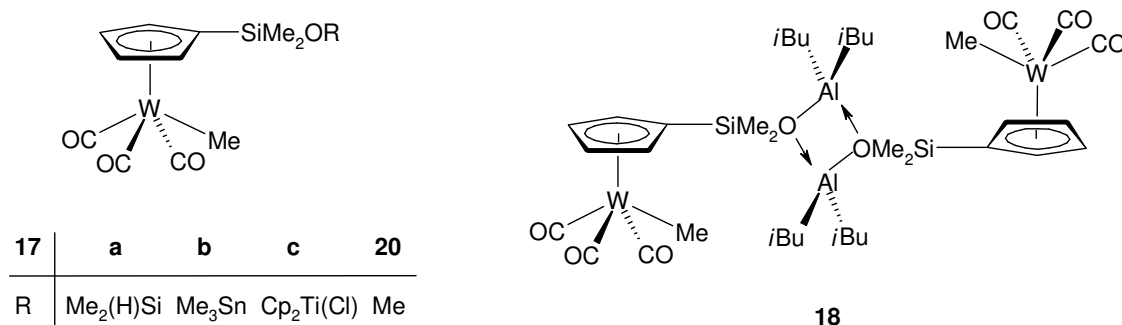
The reaction of **13a** with the trialkylalane iBu$_3$Al results via *iso*-butane elimination in the formation of the dimeric tungsten-alumosiloxane **18**.

The reaction of **13a** with *n*BuLi in THF yields the lithium tungsten-silanolate [LiOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe **19** which allows quenching with MeI to afford **20**, bearing a methoxysilyl group. **20** is converted into the silanol **13a** by reaction with aqueous NaOH in Et$_2$O.

CHAPTER III: PHOSPHINE-SUBSTITUTED TUNGSTEN COMPLEXES WITH A η^5-CYCLOPENTADIENYL-BOUND SILANOL FUNCTION

Addition of PMe_3 to solutions of the tungsten hydrides **1a,b** results in the displacement of one CO ligand to give the ligand exchange products **2a,b** which are isolated as 1:1 mixtures of the *cis-* and *trans-*isomers.

The *cis-*substituted **4a-c** are generated stereoselectively by reaction of the tungsten chlorides **3a-c** with PPh_3.

UV-irradiation of **3a** in the presence of bis-diphenylphosphino-methane (dppm) leads via the η^1-phosphine-bonded $[ClMe_2Si(C_5H_4)](OC)_2(\eta^1$-dppm)WCl-species to the η^2-dppm-chelated complex **6**.

cis-4	a	b	c
o-	H	Me	H
R	Me	Me	*i*Pr

	a	b
X	H	Cl
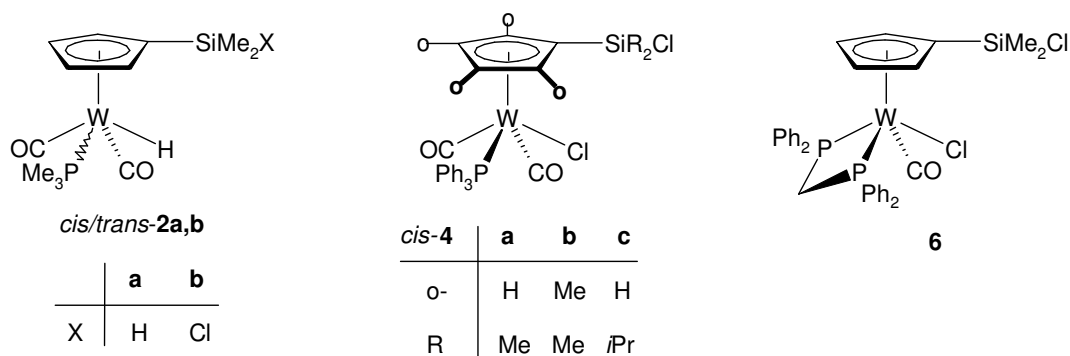
NEt$_3$-assisted hydrolysis of **2b**, **4a-c** and **6** gives the tungsten-silanols **7a-c**, **8** and **9** which show the expected stability towards self-condensation.

7	a	b	c
o-	H	H	Me
R	H	Cl	Cl
R'	Me	Ph	Ph
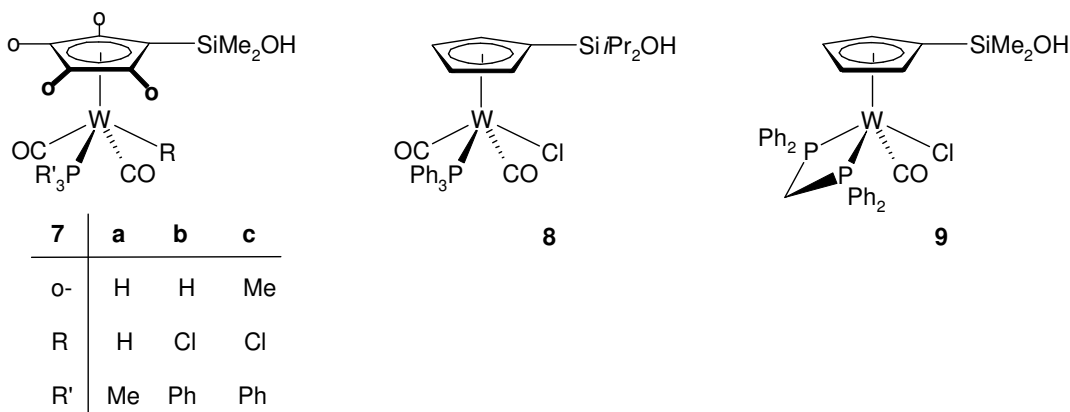
The co-condensation of **7b,c** and **9** with Me$_2$Si(H)Cl affords the metallo-disiloxanes **10a,b** and **13a**, the reaction of **7a** with the chlorosilyl complex **2b** gives the dinuclear tungsten-disiloxane **11** while **9** reacts with Me$_3$SnCl to the stanna-siloxane **13b**.
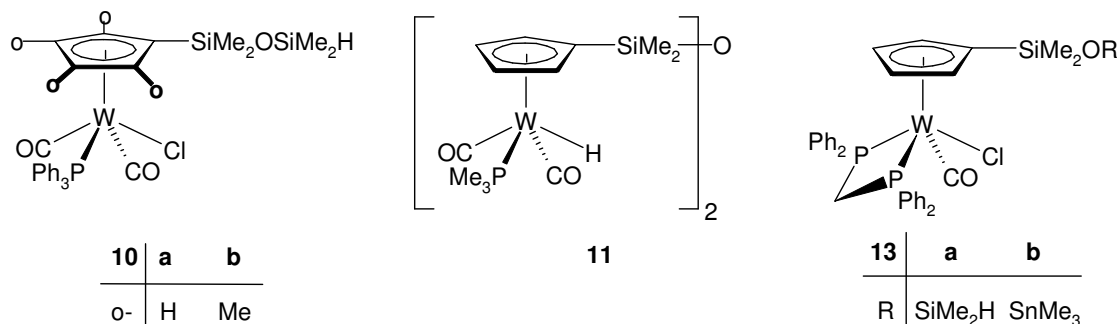
10	a	b
o-	H	Me

11

13	a	b
R	SiMe$_2$H	SnMe$_3$

CHAPTER IV: HALFSANDWICH TUNGSTEN COMPLEXES WITH METAL- AND η^5-CYCLOPENTADIENYL-BOUND FUNCTIONAL SILYL GROUPS

Li[W(C$_5$H$_4$Li)(CO)$_3$] (**1**) allows the conversion with two equivalents of R$_2$Si(H)Cl (R = Me, Ph) under heterogeneous conditions in cyclohexane, leading to the bis(silyl)tungsten complexes **3a,b**, whereas the stepwise treatment of **1** with Me$_2$Si(H)Cl and Me$_3$SiBr affords the complex **6** with different silyl groups.

3	a	b	6
R	Me	Ph	Me
R'	H	H	Me

9
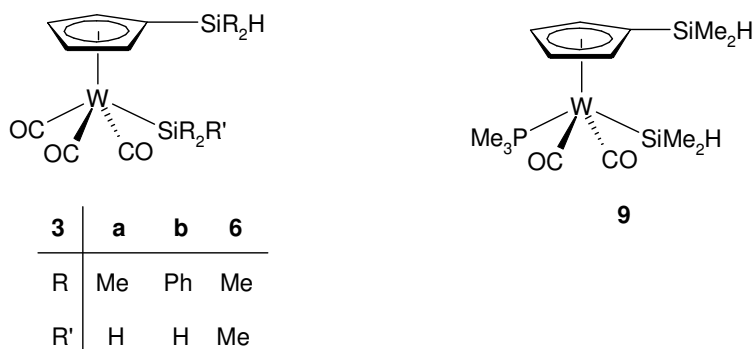
Deprotonation of [HMe$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WH (**7**) with *n*BuLi generates the lithium tungstate Li{W[(C$_5$H$_4$)SiMe$_2$H](PMe$_3$)(CO)$_2$} (**8**) whose treatment with Me$_2$Si(H)Cl results in the formation of the Me$_3$P-subsituted tungsten-silane **9**.

The reaction of **3a** with an excess of CCl$_4$ results in the formation of the tungsten-chlorosilane **11a**. The mixture of CCl$_4$ and catalytical amounts of Pd/C chlorinates only the metal-bound Si-H function of **3b**, giving **11b**. PdCl$_2$ in benzene converts **9** regioselectively into the corresponding tungsten-chlorosilane **11c**. The double ClPh$_2$Si-substituted **12** is obtained by reaction of **11b** with PdCl$_2$.

11	a	b	c
R	Me	Ph	Me
L	CO	CO	PMe$_3$
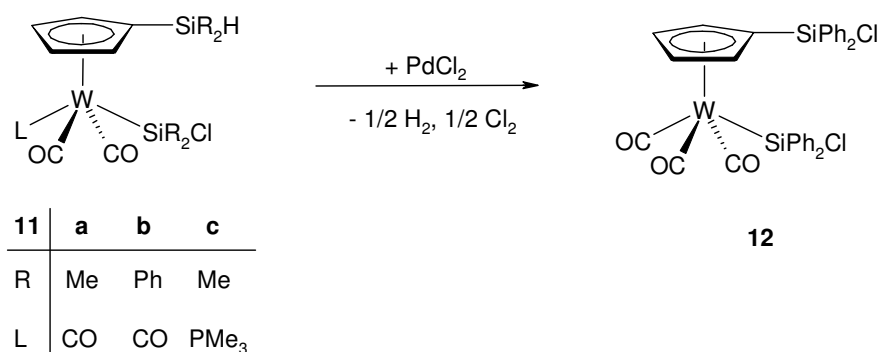
The hydrolysis of **11a** at -40 °C in the presence of NEt$_3$ enables the isolation of the metallo-silanol **13**. The reaction of **12** with water occurs regioselectively at the cyclopentadienyl-bound Si-Cl function and affords the silanol **16** which undergo in solution intramolecular co-condensation to [η^1-SiPh$_2$OPh$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$W.

	13	14
L	CO	PMe$_3$
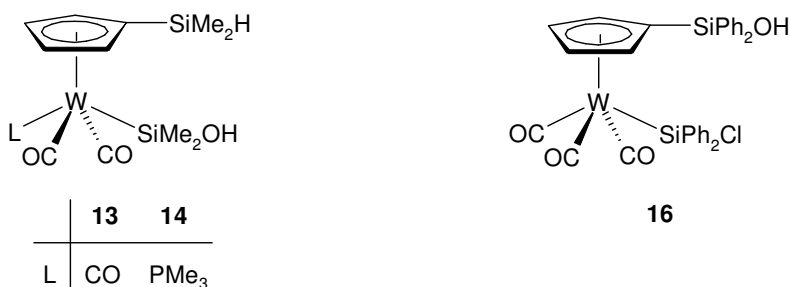
The successive treatment of **9** with DMD in acetone at –78 °C allows formation of the silanol **14** in a first step and the short-lived bis-silanol **A** in a second one. However, **14** undergoes intramolecular condensation to give **15**, bearing a disiloxane bridge connecting the cyclopentadienyl ligand and the metal center.
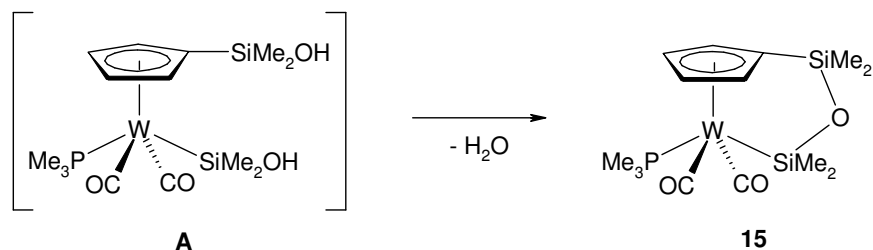
CHAPTER V: Tungsten Complexes Containing A

η⁵-Cyclopentadienyl-Bound Alkoxysilyl-Group And Novel *Ansa*-Complexes From Dianionic Tungsten Precursors

Li[W(C$_5$H$_4$Li)(CO)$_3$] reacts with Me$_{4-n}$Si(OMe)$_n$ (n = 2 - 4) to afford the alkoxysilyl-cyclopentadienyl lithium tungstates Li{W[(C$_5$H$_4$)SiMe$_{3-n}$(OMe)$_n$](CO)$_3$} [n = 1-3 (**5a-c**)], which are converted to the alkoxysilyl-functionalized methyl and hydrido complexes [(MeO)$_n$Me$_{3-n}$Si(C$_5$H$_4$)](OC)$_3$WR [n = 1-3, R = Me (**6a-c**); n = 3, R = H (**2**)] upon treatment with MeI or HOAc. The conversion of Li[W(C$_5$H$_4$Li)(CO)$_3$] and Si(OMe)$_4$ in a 2:1-stoichiometric ratio allows the double substitution of OMe, affording Li$_2${W[(C$_5$H$_4$)Si(OMe)$_2$](CO)$_3$}$_2$ (**7**) which is converted with an excess of MeI into the dinuclear methyl tungsten complex **8**.

6	a	b	2	6c
n	1	2	3	3
R	Me	Me	Me	H

	8	21	22
R	Me	H	SiMe$_2$H
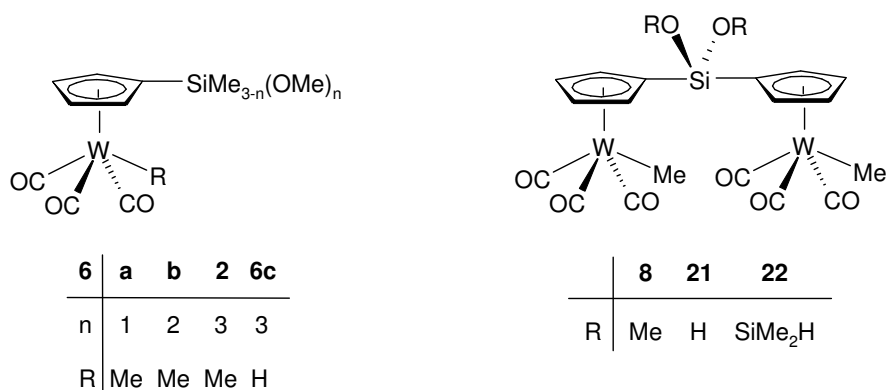
Interaction of the dianionic complex Li[W(C$_5$H$_4$Li)(CO)$_3$] with (3-iodopropyl)-trimethoxysilane, (2-chloroethyl)-dimethoxymethylsilane or (chloromethyl)-

*iso*propoxy-dimethylsilane, respectively affords the novel *ansa*-tungsten compounds $[\eta^1\text{-}(CH)_{n+1}(MeO)_nMe_{2-n}Si(\eta^5\text{-}C_5H_4)](OC)_3W$ [n = 0 - 2 (**14a-16**)].

	14a			**15**	**19**			**16**	**20**
			R	Me	H		R	Me	H
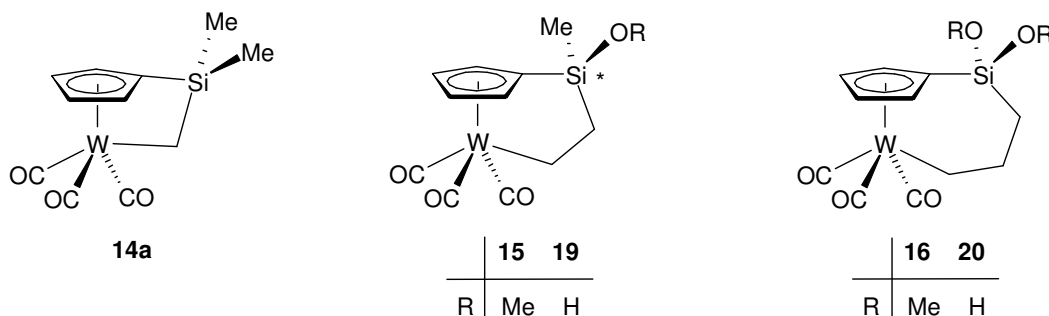
Transformation of methoxysilyl-functionalized **15** into the corresponding *ansa*-silanol **19** is achieved by use of NaOH in diehtylether. When starting with the (OMe)$_2$-functionalized **16** and **8** the same procedure yields the tungsten-silanediols **20** and **21**. Proof of the existence of **20** is given by mass-spectroscopy and in the case of **21** by the transformation into the trisiloxane **22** with Me$_2$Si(H)Cl.

CHAPTER VI: HALFSANDWICH TUNGSTEN COMPLEXES WITH A SILANEDIOL-FUNCTIONALIZED η^5-CYCLOPENTADIENYL LIGAND

The reaction of Cl$_2$MeSiC$_5$H$_5$ with (MeCN)$_3$W(CO)$_3$ is performed in refluxing THF and results in the formation of the **2** whose W-H function is chlorinated by treatment with an excess of CCl$_4$ giving the tungsten chloride **3**.

	2	**3**		*cis*-**4**	**a**	**b**		*trans*-**4a**
R	H	Cl		R	H	Cl		
				R'	Me	Ph		
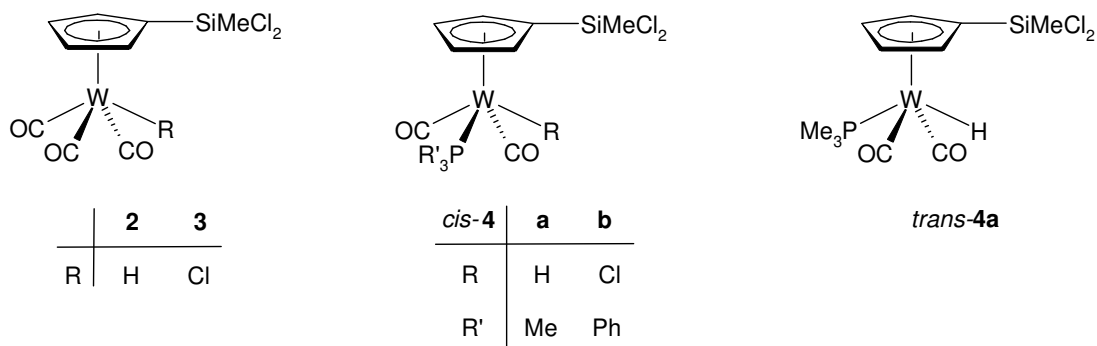
Modification of the ligand sphere is achieved by addition of PMe$_3$ to a solution of **2** in PE and results in the displacement of one CO ligand to give **4a**. *Cis*-**4b** is stereospecifically formed by the photochemical reaction of **3** with PPh$_3$.

Subsequent treatment of Cp(OC)$_3$WMe with *n*BuLi at –78 °C in THF and MeSiCl$_3$ affords **6**. In THF suspended Li[W(C$_5$H$_4$Li)(CO)$_3$] reacts with *t*BuSiCl$_3$ to the lithium tungstate Li[W(C$_5$H$_4$)Si*t*BuCl$_2$(CO)$_3$] which is transformed with MeI into the neutral methyl complex **9**.

	6	**9**
R	Me	*t*Bu

	10b	**11**
R	H	SiMe$_2$H
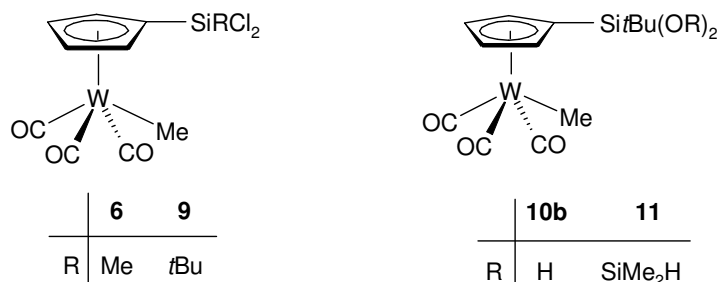
The hydrolysis of **9** in the presence of NEt$_3$ leads to the corresponding silanediol **10b** which is stable with respect to self-condensation due the bulkyness of the *tert*-butyl group. **10b** allows the NEt$_3$-assisted co-condensation to the tungsten-trisiloxane **11** with an excess of Me$_2$Si(H)Cl.

In contrast to **9** no conditions has been found for the clean hydrolysis of the MeSiCl$_2$-substituted tungsten complexes **2, 4a,b** and **6**.

CHAPTER VII: NOVEL MOLYBDENUM AND TUNGSTEN HALFSANDWICH COMPLEXES WITH ALKOXYSILYLALKYL-FUNCTIONALIZED η^5-CYCLOPENTADIENYL LIGAND

Coordination of the methoxysilylalkyl cyclopentadienes Cp(CH$_2$)$_n$SiMe$_{3-m}$(OMe)$_m$ (n = 1, 3; m = 1-3) (**2, 4a-c**) is achieved either by the reaction of Cp(CH$_2$)$_3$Si(OMe)Me$_2$ with (MeCN)$_3$W(CO)$_3$ in refluxing THF (**5c**) or by successive treatment of **2, 4a-c** with NaH and molybdenum- or tungstenhexacarbonyl in DME resulting in the formation of

the sodium metallates Na{M[(C$_5$H$_4$)(CH$_2$)$_n$SiMe$_{3-m}$(OMe)$_m$ [M = Mo, W; n = 1, 3; m = 1-3 (**6a-f**)].

Variation of σ-bonded ligand is realized by treatment with HOAc, MeI or 3-iodopropyldimethoxymethylsilane, giving the molybdenum- and tungsten hydrides **5a-f** or the alkylated complexes **8a-c**.

The deprotonation of the tungsten hydride **5c** with *n*BuLi generates the lithium tungstate Li{W[(C$_5$H$_4$)(CH$_2$)$_3$SiMe$_2$OMe](CO)$_3$} whose reaction with Me$_2$Si(H)Cl gives the double silyl-functionalized tungsten-silane **10**.

5	a	b	c	d	e	f	8a	b	c		10
n	1	1	3	3	3	3	3	3	3		
m	1	1	1	2	2	3	1	3	2		
R	Et	Et	Me	Me	Me	Me	Me	Me	Me		
M	Mo	W	W	Mo	W	Mo	W	W	W		
R'	H	H	H	H	H	H	Me	Me	(CH$_2$)$_3$Si(OMe)$_2$Me	SiMe$_2$H

The hydrolysis of **5a-c**,**g** leads directly to the formation of the metal fragment-substituted disiloxanes **12a-d** via the corresponding silanol stage.
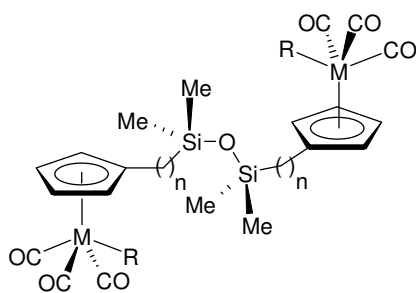
12	a	b	c	d
n	1	1	3	3
R	H	H	H	Me
M	Mo	W	W	W
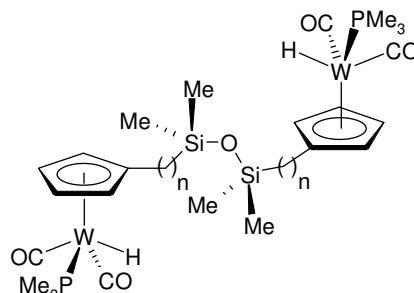
14	a	b
n	1	3

The ligand sphere around the metal centers of **12a,b** is modified by CO/PMe₃-exchange, leading to **14a,b** which are isolated as mixtures of *cis-* and *trans*-isomers in the ratio of about 45:55.

14a,b are transformed to the disiloxane-brigded dinuclear tungsten-silanes **16a**,**b** via the corresponding dilithium dianions, obtained by treatment with two equivalents of *n*BuLi, followed by heterogeneous alkali salt elimination with two equivalents of Me₂Si(H)Cl.

	16a	16b	18	19
n	1	3	3	3
R	H	H	OH	OSiMe₂H
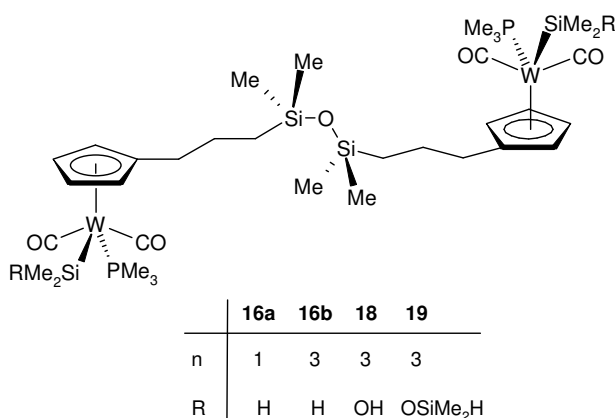
16b is converted with dimethyldioxirane in acetone into the corresponding bis-tungsten-silanol **18** which is co-condensated with two equivalents of Me₂Si(H)Cl to give the disiloxane-bridged bis-tungsten-disiloxane **19**.

KAPITEL I: Synthese und Reaktivität von Halbsandwich-Wolframhydrido- und Chlorokomplexen mit einer η⁵-Cyclopentadienyl-gebundenen Silanolfunktion

Die Behandlung der Wolframio-silane **1a,b** mit LiN(iPr)$_2$, nBuLi oder tBuLi induziert nach der Bildung der Cyclopentadienyl-lithiierten Species (LiC$_5$H$_4$)L(OC)$_2$WSiMe$_2$H (L = CO, PMe$_3$) einen Shift der metallgebundenen Silylgruppe zum Cyclopentadienyl-Liganden, so daß die Lithium-Wolframate Li{W[(C$_5$H$_4$)SiMe$_2$H]L(CO)$_2$} [L = CO (**2a**), PMe$_3$ (**2b**)] resultieren.

Einen weiteren Zugang zu **2a** eröffnet die regioselektive Reaktion der dilithiierten Verbindung **4**, gebildet aus dem Wolframhydridokomplex **3** mit zwei Äquivalenten nBuLi, bei der ausschließlich die am Cyclopentadienyl-Liganden lithiierte Position mit Me$_2$Si(H)Cl bei –78 °C in THF eine Silylierung erfährt.

1	**a**	**b**
L	CO	PMe$_3$

R = nBu, tBu, (iPr)$_2$N

2	**a**	**b**
L	CO	PMe$_3$

X = Cl, OAc

+ Me$_2$Si(H)Cl   - LiCl

	5	**6a**	**b**	**c**
L	CO	PMe$_3$	PMe$_3$	PMe$_3$
R	H	Me	SiMe$_2$H	SiMe$_3$

3 + 2 nBuLi → **4**
- 2 nBuH
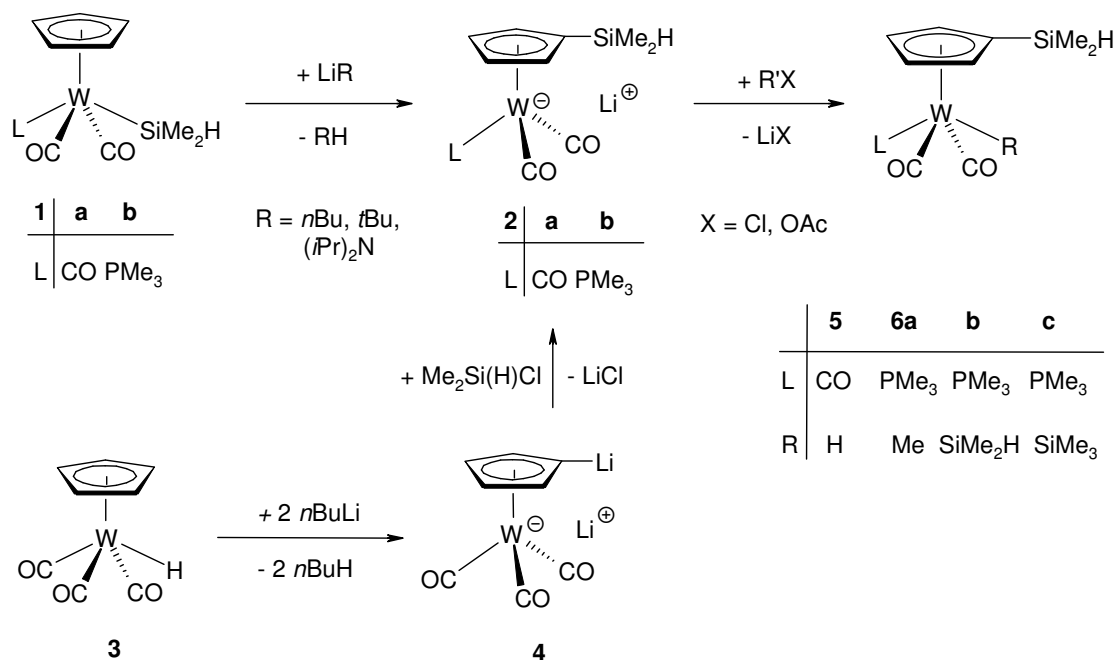
2a,b können mit HOAc, MeI, Me$_2$Si(H)Cl oder Me$_3$SiCl unter heterogenen Bedingungen in Cyclohexan in die entsprechenden neutralen Hydrido-, Methyl- oder Silyl-Wolframkomplexe **5** und **6a-c** überführt werden.

Durch die Umsetzung der Cyclopentadiene HC$_5$R$_4$(SiMe$_2$X) [R = H, Me; X = H, Cl (**7, 8a,b**)] mit (MeCN)$_3$W(CO)$_3$ in siedenem THF werden die SiH- und SiCl-funktionalisierten Wolframkomplexe **5** und **9a,b** dargestellt.

PdCl$_2$ chloriert in Benzol sowohl die SiH- als auch die WH-Funktionen von **5** unter Bildung des Wolframchlorokomplex **10a**, der alternativ durch die Reaktion von **9a** mit einem Überschuß an CCl$_4$ zugänglich ist. Analog entsteht aus **9b** das Chlorierungsprodukt **10b**.
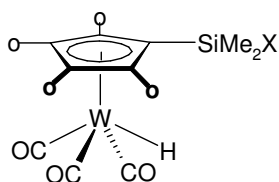
	5	**9a**	**9b**
o-	H	H	Me
X	H	Cl	Cl
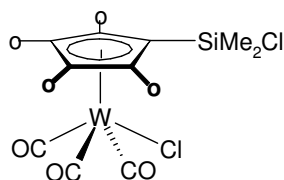
10	**a**	**b**
o-	H	Me

Die Wolframio-silanole **11** und **13a**-**c** können durch Hydrolyse der entsprechenden SiCl-Vorläufer **9a,b** und **10a,b** in Gegenwart der Hilfsbase NEt$_3$ dargestellt werden und sind stabil bezüglich von Eigenkondensation. Hiervon ausgenommen ist **13a**, das zusammen mit dem Kondensationsprodukt O{[Me$_2$Si(C$_5$H$_4$)](OC)$_3$WCl}$_2$ (**14**) anfällt.
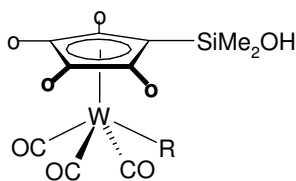
	11	**13a**	**b**	**c**
o-	H	H	Me	Me
R	H	Cl	H	Cl
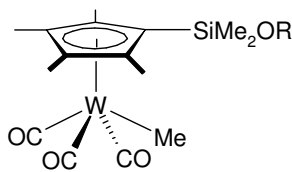
	16	**18**
R	H	Me

Die regioselektive WH-Deprotonierung von **13b** mit einem Äquivalent *n*BuLi führt zum Lithium-Wolframat Li{W[(C$_5$H$_4$)SiMe$_2$OH](CO)$_3$}, das anschließend mit MeI in den neutralen Wolframmethylkomplex **16** überführt wird.

Mit zwei Äquivalenten *n*BuLi ist die Bildung der zweifach-lithiierten Species Li{W[(C$_5$H$_4$)SiMe$_2$OLi](CO)$_3$} möglich, die mit MeI zur Methoxylsilylverbindung **18** abreagiert.

Das Silanol **11** läßt sich mit Me$_2$Si(H)Cl in Gegenwart der Hilfsbase NEt$_3$ gezielt zum SiH-funktionellen Wolframio-disiloxan **19** co-kondensieren. Die Reaktion von **13b** mit *i*Bu$_3$Al liefert unter *iso*-Butanabspaltung das Wolframfragment-substituierte Alumosiloxan-Dimer **20**.

19 **20**
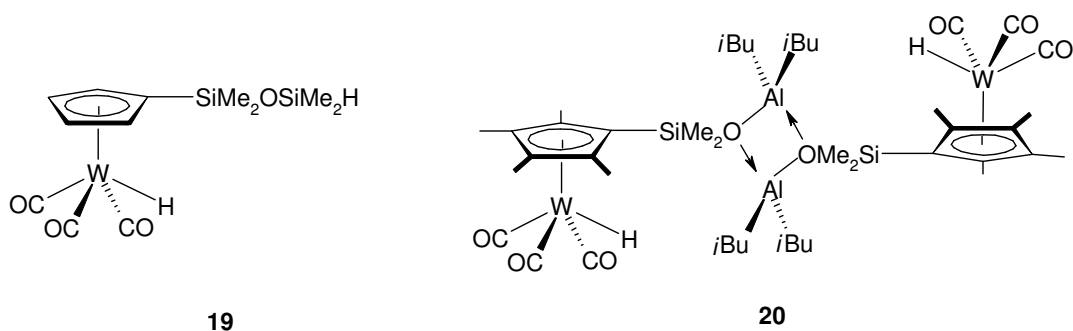
KAPITEL II: HALBSANDWICH-WOLFRAMMETHYLKOMPLEXE MIT EINER η^5-CYCLOPENTADIENYL-GEBUNDENEN SILANOLFUNKTION

Die Einwirkung von *n*BuLi auf Cp(OC)$_3$WMe (**1**) bei –78 °C in THF generiert die Cyclopentadienyl-lithiierte Species (LiC$_5$H$_4$)(OC)$_3$WMe, die *in situ* mit RR'Si(H)Cl [R, R' = Me, Ph, *i*Pr (**5a-d**)] zu den Wolframio-silanen **6a-d** abreagiert.

5	a	b	c	d
R	Me	Ph	*i*Pr	Me
R'	Me	Ph	*i*Pr	Ph
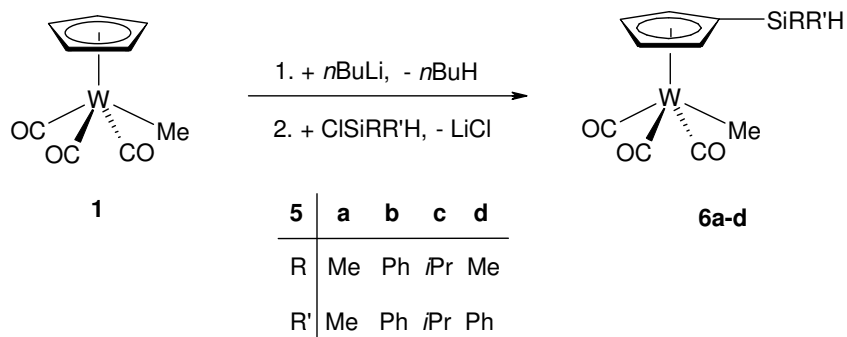
Die Chlorierung der SiH-Funktionen von **6a-c** kann durch PdCl$_2$ in Benzol unter Bildung von **3a,b** und **7** erreicht werden, wobei im Fall von **6c** zusätzlich der Wolframchlorokomplex **8** entsteht. **6c** und **7** lassen sich durch weitere Zugabe von PdCl$_2$ vollständig in **8** überführen.

Die Darstellung von reinem **7** wird durch die regioselektive Reaktion des dilithiierten Li[W(LiC$_5$H$_4$)(CO)$_3$] mit einem Überschuß *i*Pr$_2$SiCl$_2$ erreicht. Es resultiert zunächst das Lithium-Wolframat Li{W[(C$_5$H$_4$)Si*i*Pr$_2$H](CO)$_3$}, das abschließend mit MeI den Wolframmethylkomplex **7** ergibt.

Die NEt$_3$-assistierte Hydrolyse von **3a,b** und **7** führt zur Bildung der korrespondierenden Wolfamio-silanole **13a**-**c**, die frei von Kondensationsprodukten erhalten werden.

3	a	b	7	8
R	Me	Ph	*i*Pr	*i*Pr
R'	Me	Me	Me	Cl

13	a	b	c
R	Me	Ph	*i*Pr
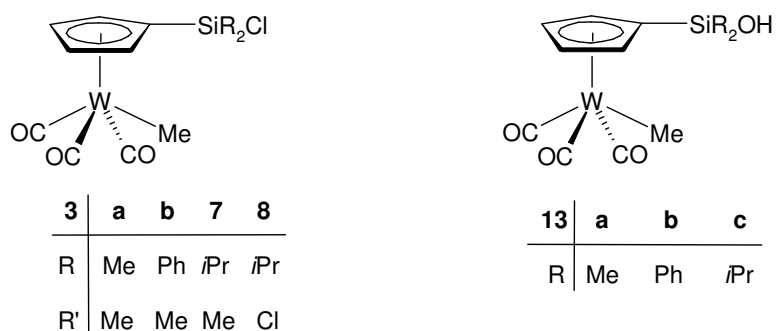
Außerdem ist es möglich den SiH-funktionalisierten Komplex **6a** in das Silanol **13a** durch eine sukzessive Umsetzung mit Co$_2$(CO)$_8$ und Wasser zu überführen, wobei der hetero-dinukleare Komplex [(OC)$_4$CoMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe (**B**) durchlaufen wird.

13a läßt sich kontrolliert unter NEt$_3$-Assistenz mit Me$_2$Si(H)Cl, Me$_3$SnCl und Cp$_2$TiCl$_2$ zum Wolframfragment-substituierten Disiloxan **17a**, beziehungsweise den entsprechenden Heterosiloxanen **17b**,**c** co-kondensieren.

17	a	b	c	20
R	Me$_2$(H)Si	Me$_3$Sn	Cp$_2$Ti(Cl)	Me

18

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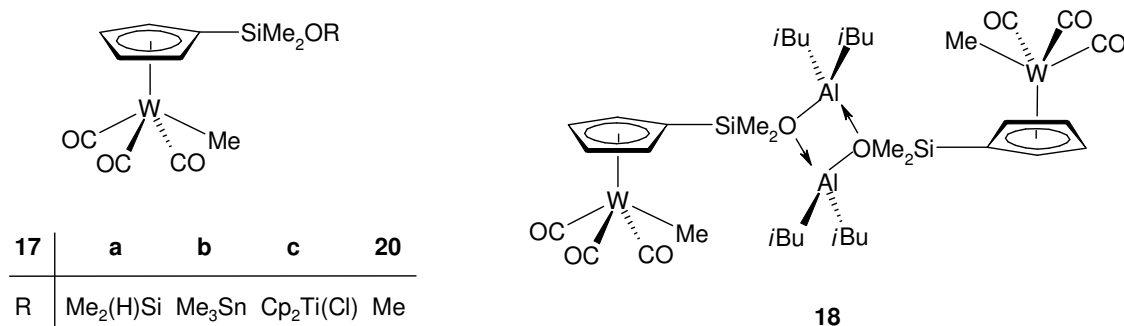
13a läßt sich mit *i*Bu$_3$Al unter *iso*-Butaneliminierung zum Wolframfragment-substituierten Alumosiloxan-Dimer **18** umsetzen.

13a kann mit *n*BuLi zum entsprechenden Lithium-Silanolat [LiOMe$_2$Si(C$_5$H$_4$)](OC)$_3$WMe **19** deprotoniert werden, das dann mit MeI zur Methoxysilyl-funktionalisierten Verbindung **20** abreagiert. Durch die Umsetzung von **20** mit wäßriger NaOH in Et$_2$O eröffnet sich ein weiterer Zugang zum Silanol **13a**.

KAPITEL III: PHOSPHAN-SUBSTITUIERTE WOLFRAMKOMPLEXE MIT EINER η^5-CYCLOPENTADIENYL-GEBUNDENEN SILANOLFUNKTION

Die Ligandensphäre des Wolframatoms ist durch Substitution von Carbonyl-Liganden durch Phosphane modifizierbar. Die Reaktion der Wolframhydridokomplexe **1a,b** mit PMe$_3$ resultiert in der Bildung der CO/PMe$_3$-Austauschprodukte **2a,b**, die als 1:1-Gemisch der *cis*- und *trans*-Isomeren erhalten werden.

Dagegen verläuft die Photo-induzierte Reaktion der Chlorowolframkomplexe **3a-c** mit PPh$_3$ stereoselektiv zu chiralem *cis*-**4a-c**.

Die Reaktion von **3a** mit Bis-diphenylphosphino-methan (dppm) unter UV-Bestrahlung verläuft über die η^1-Phosphan-gebundene Species *cis*-[ClMe$_2$Si(C$_5$H$_4$)](OC)$_2$(η^1-dppm)WCl zum η^2-Chelatkomplex **6**.
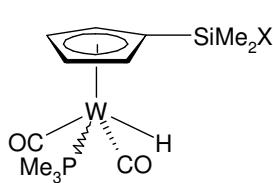
cis/trans-**2a,b**

	a	b
X	H	Cl
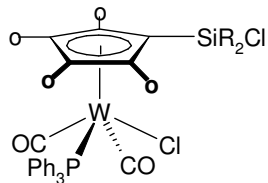
cis-**4**

	a	b	c
o-	H	Me	H
R	Me	Me	*i*Pr
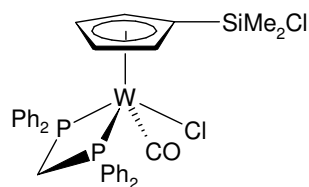
6

Die Hydrolyse von **2b, 4a-c** and **6** unter NEt$_3$-Assistenz ergibt erwartungsgemäß die kondensationsstabilen Wolframio-silanole **7a-c**, **8** und **9**.

7	a	b	c
o-	H	H	Me
R	H	Cl	Cl
R'	Me	Ph	Ph
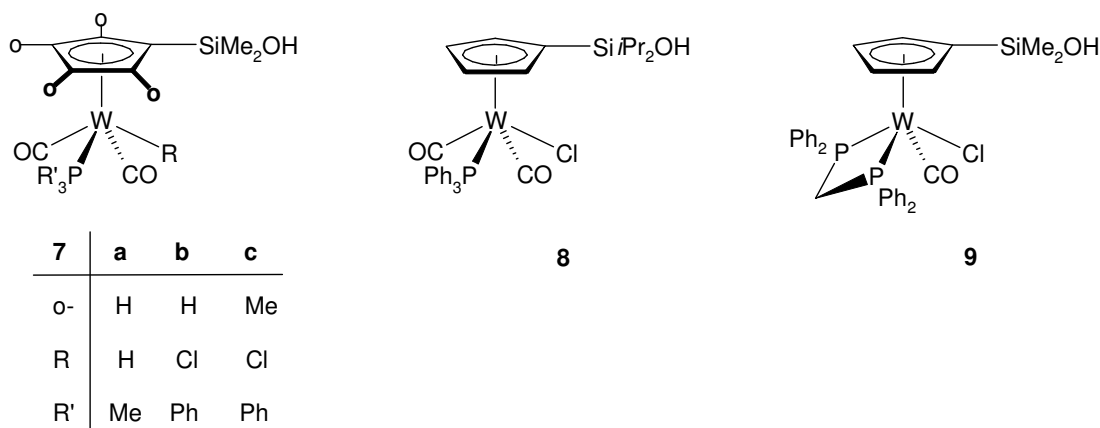
7b,c und **9** können NEt$_3$-assistiert mit Me$_2$Si(H)Cl zu den Wolframio-disiloxanen **10a,b** und **13a** co-kondensiert werden. Zusätzlich eröffnet sich die Möglichkeit **7a** mit dem Chlorosilylkomplex [ClMe$_2$Si(C$_5$H$_4$)](OC)$_2$(Me$_3$P)WH (**2b**) zum Disiloxan-verbrückten Zweikernkomplex **11** umzusetzen. Die Reaktion von **9** mit Me$_3$SnCl ergibt das Stanna-heterosiloxan **13b**.

10	a	b
o-	H	Me

13	a	b
R	SiMe$_2$H	SnMe$_3$
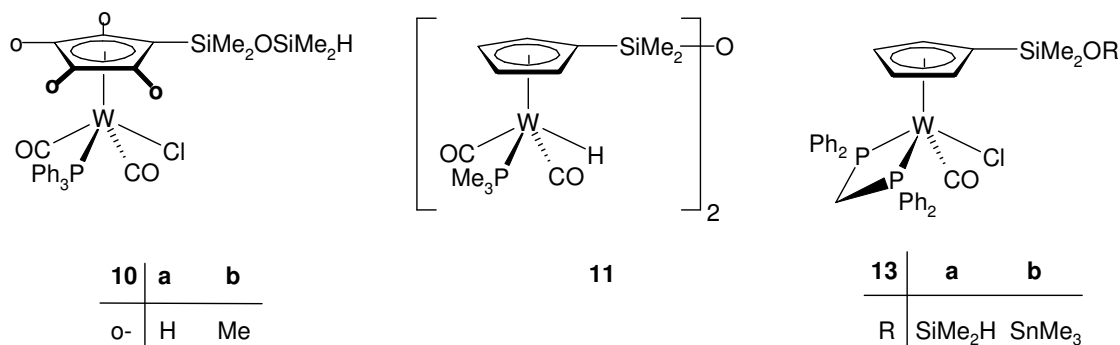
KAPITEL IV: HALBSANDWICH-WOLFRAMKOMPLEXE MIT METALL- UND η^5-CYCLOPENTADIENYL-GEBUNDENEN FUNKTIONELLEN SILYLGRUPPEN

Die Reaktion von Li[W(C$_5$H$_4$Li)(CO)$_3$] mit zwei Äquivalenten R$_2$Si(H)Cl (R = Me, Ph) führt unter heterogenen Bedingungen in Cyclohexan zu den zweifach Silyl-funktionalisierten Komplexen **3a,b**.

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Eine stufenweise Einführung unterschiedlicher Silylgruppen (**6**) wird durch die sukzessive Umsetzung von **1** mit $Me_2Si(H)Cl$ und Me_3SiBr erreicht, die über das Lithium-Wolframat $Li\{W[(C_5H_4)SiMe_2H](CO)_3\}$ als Zwischenstufe verläuft.

9 läßt sich durch die Deprotonierung von $[HMe_2Si(C_5H_4)](OC)_2(Me_3P)WH$ (**7**) zum Lithium-Wolframat $Li\{W[(C_5H_4)SiMe_2H](PMe_3)(CO)_2\}$ (**8**) mittels *n*BuLi und anschließender Silylierung mit $Me_2Si(H)Cl$ synthetisieren.

3	**a**	**b**	**6**
R	Me	Ph	Me
R'	H	H	Me
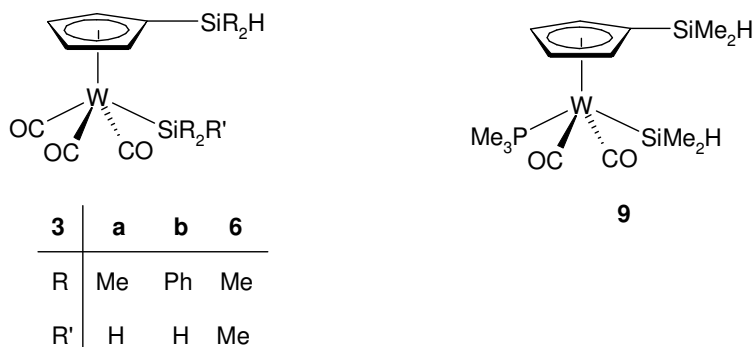
Eine regioselektive Reaktion von **3a** zum Wolframio-chlorsilan **11a** wird durch einen Überschuß an CCl_4 erzielt. Im Fall von **3b** führt ein Gemisch von CCl_4 und Pd/C zur Chlorierung der Metall-gebundenen SiH-Einheit, so daß man **11b** isoliert. Schließlich überführt $PdCl_2$ **9** in das Wolframio-chlorsilan **11c**. Die verbleibende SiH-Funktion von **11b** wird mit $PdCl_2$ in Benzol zur Reaktion gebracht, so daß der doppelt Ph_2SiCl-substituierte Wolframkomplex **12** resultiert.

11	**a**	**b**	**c**
R	Me	Ph	Me
L	CO	CO	PMe₃
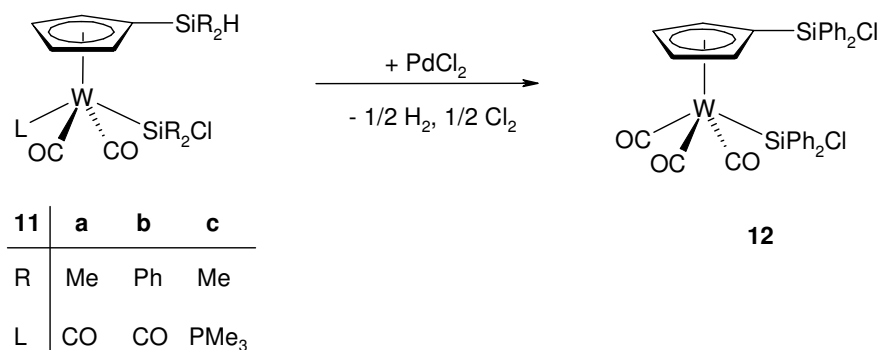
Die Hydrolyse von **11a** bei –40 °C ermöglicht die Darstellung des Wolframio-silanols **13**.

Hydrolysiert man **12** so reagiert nur die Cyclopentadienyl-gebundene SiCl-Funktion und man erhält das Silanol **16**, das in Lösung intramolekulare Co-Kondensation zu [η^1-SiPh$_2$OPh$_2$Si(η^5-C$_5$H$_4$)](OC)$_3$W erfährt.
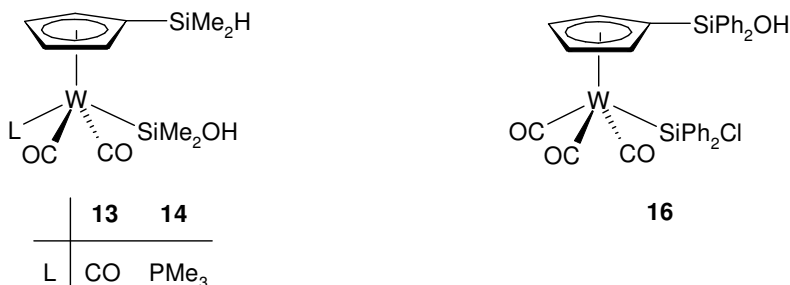
Die sukzessive Umsetzung von **9** mit Dimethyldioxiran in Aceton bei −78 °C führt im ersten Schritt zur regioselektiven Reaktion der Metall-gebundenen SiH-Funktion und es resultiert das Wolframio-silanol **14**. Im zweiten Schritt erhält man dann das Bis-silanol **A**, das umgehend durch intramolekulare Kondensation zum Komplex **15** abreagiert.
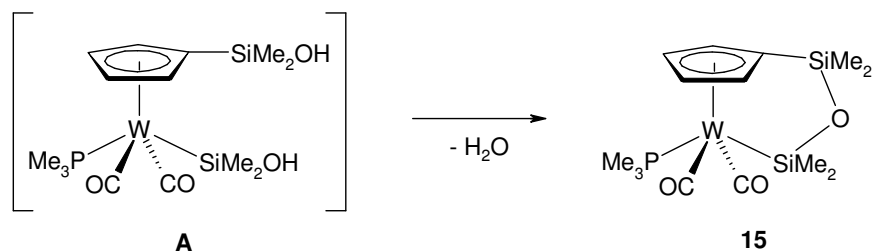
KAPITEL V: WOLFRAMKOMPLEXE MIT EINER η^5-CYCLOPENTADIENYL-GEBUNDENEN ALKOXYSILYL-FUNKTION SOWIE NEUE *ANSA*-KOMPLEXE AUSGEHEND VON DIANIONISCHEN WOLFRAM-VORLÄUFERN

Wolframkomplexe mit einer Cyclopentadienyl-gebundenen Alkoxysilylgruppe können durch die Reaktion von Li[W(C$_5$H$_4$Li)(CO)$_3$] mit den Silanen Me$_{4-n}$Si(OMe)$_n$ (n = 2 - 4) dargestellt werden. Als Zwischenstufe erhält man die Lithium-Wolframate Li{W[(C$_5$H$_4$)SiMe$_{3-n}$(OMe)$_n$](CO)$_3$} [n = 1 - 3 (**5a-c**)], deren Umsetzung mit MeI oder HOAc die neutralen Verbindungen **2** und **6a-c** hervorbringt.

Die gleiche Reaktion von Li[W(C$_5$H$_4$Li)(CO)$_3$] und Si(OMe)$_4$ in einem 2:1-stöchiometrischen Verhältnis führt zur Bildung der dianionischen Zwischenstufe Li$_2${W[(C$_5$H$_4$)Si(OMe)$_2$](CO)$_3$}$_2$ (**7**), die mit MeI zu **8** abreagiert.

6	**a**	**b**	**2**	**6c**
n	1	2	3	3
R	Me	Me	Me	H

	8	**21**	**22**
R	Me	H	SiMe$_2$H
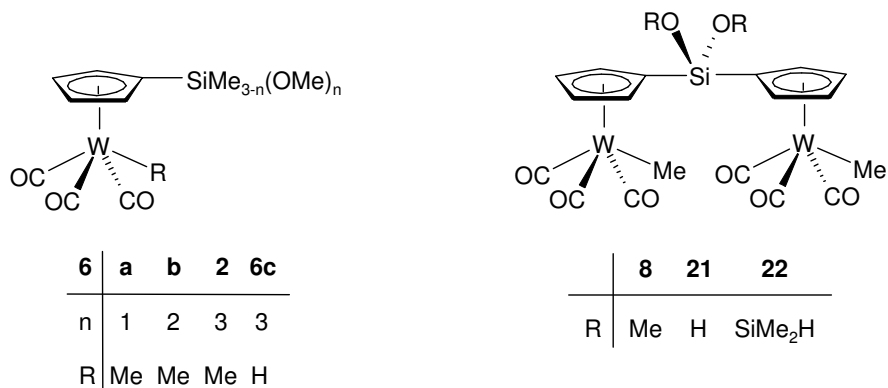
Werden die bifunktionellen Silane (3-Iodopropyl)-trimethoxysilan, (2-Chloroethyl)-dimethoxymethylsilan oder (Chloromethyl)-*iso*propoxy-dimethylsilan eingesetzt, führt dies zur Bildung der neuen *Ansa*-Wolframverbindungen [η^1-(CH)$_{n+1}$(MeO)$_n$Me$_{2-n}$Si(η^5-C$_5$H$_4$)](OC)$_3$W [n = 0 - 2 (**14a-16**)], die eine verbrückende Silylalkylgruppe zwischen dem Metall und dem Cyclopentadienyl-Liganden aufweisen.

14a

	15	**19**
R	Me	H

	16	**20**
R	Me	H
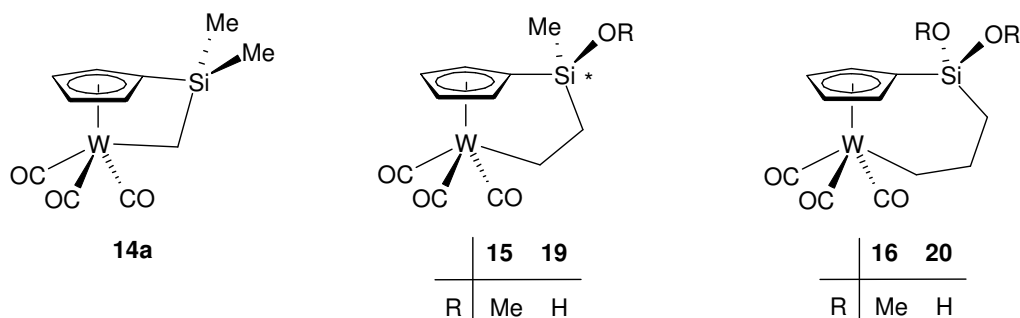
Der *Ansa*-Methoxysilyl-Vertreter **15** reagiert mit wäßriger NaOH in Et$_2$O zum korrespondierenden Silanol **19**.

Ausgehend von **16** und **8** entstehen unter gleichen Bedingungen auch die Wolframio-silandiole **20** und **21**, die mittels Massenspektroskopie (**20**) oder weiterer Umsetzung mit Me$_2$Si(H)Cl in Gegenwart von NEt$_3$ zum Wolframio-trisiloxan **22** nachgewiesen wurden (**21**).

KAPITEL VI: HALBSANDWICH-KOMPLEXE DES WOLFRAMS MIT EINEM SILANDIOL-FUNKTIONALISIERTEN η^5-CYCLOPENTADIENYL-LIGANDEN

Das Cyclopentadien $Cl_2MeSiC_5H_5$ reagiert mit $(MeCN)_3W(CO)_3$ in siedendem THF zum Hydridokomplex **2**. Die WH-Funktion von **2** wird mittels einem Überschuß CCl_4 chloriert, so daß das Wolframchlorid $[Cl_2MeSi(C_5H_4)](OC)_3WCl$ (**3**) gebildet wird.

Der Hydridokomplex **2** und PMe_3 reagieren zu **4a**, welches als *cis-/trans*-Isomerengemisch anfällt, während die Umsetzung des Wolframchlorids **3** mit PPh_3 unter UV-Bestrahlung stereospezifisch zur Darstellung von *cis*-**4b** führt.

	2	**3**
R	H	Cl

cis-**4**	**a**	**b**
R	H	Cl
R'	Me	Ph

trans-**4a**
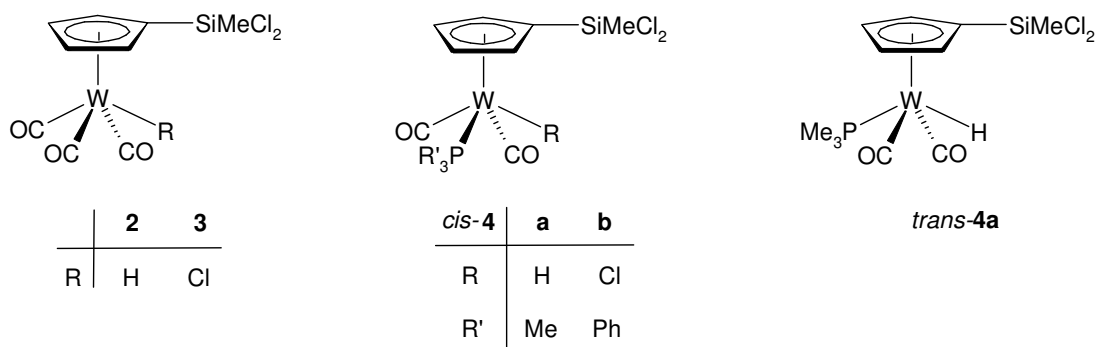
Cp(OC)$_3$WMe wird mit *n*BuLi zu $(LiC_5H_4)(OC)_3WMe$ deprotoniert, dessen *in situ* Reaktion mit $MeSiCl_3$ den Dichlorosilylkomplex **6** hervorbringt.

In THF suspendiertes $Li[W(C_5H_4Li)(CO)_3]$ läßt sich mit *t*BuSiCl$_3$ zum Lithium-Wolframat $Li\{W[(C_5H_4)Si\textit{t}BuCl_2](CO)_3\}$ (**8**) umsetzen, das mit MeI den neutralen Methylkomplex **9** liefert.

	6	**9**
R	Me	*t*Bu

	10b	**11**
R	H	SiMe$_2$H
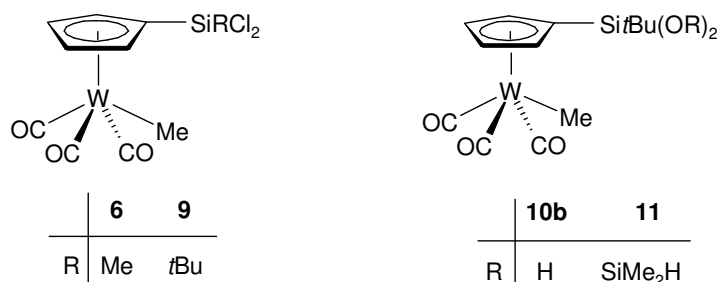
Nur im Falle von **9** ist durch NEt$_3$-assistierte Hydrolyse ausschließlich das korrespondierende Wolframio-silandiol (**10b**) erhältlich. **10b** ist stabil bezüglich einer Eigenkondensation, was jedoch vermutlich mehr auf sterischen Aspekten beruht und

kann daher kontrolliert mit $Me_2Si(H)Cl$ in Gegenwart von NEt_3 zum entsprechenden Wolframio-trisiloxan **11** co-kondensiert werden.

KAPITEL VII: HALBSANDWICH-KOMPLEXE DES MOLYBDÄNS UND WOLFRAMS MIT EINEM ALKOXYSILYLALKYL-FUNKTIONALISIERTEN η^5-CYCLOPENTADIENYL-LIGANDEN

Die Silylalkylcyclopentadienyldiene $Cp(CH_2)_nSiMe_{3-m}(OMe)_m$ (n = 1, 3; m = 1-3) (**2**, **4a-c**) ergeben mit $(MeCN)_3W(CO)_3$ oder nach Deprotonierung mit NaH und anschließender Umsetzung mit Molybdän- oder Wolframhexacarbonyl sowie HOAc, MeI oder 3-Iodopropyldimethoxymethylsilan die entsprechenden Wasserstoff- bzw. Alkylkomplexe des Molybdäns und Wolframs (**5a-f** bzw. **8a-c**).

5	a	b	c	d	e	f	8a	b	c	10
n	1	1	3	3	3	3	3	3	3	
m	1	1	1	2	2	3	1	3	2	
R	Et	Et	Me	Me	Me	Me	Me	Me	Me	
M	Mo	W	W	Mo	W	Mo	W	W	W	
R'	H	H	H	H	H	H	Me	Me	$(CH_2)_3Si(OMe)_2Me$	$SiMe_2H$

Der Hydridokomplex **5c** wird durch Deprotonierung mittels *n*BuLi zum korrespondierenden Lithium-Wolframat $Li\{W[(C_5H_4)(CH_2)_3SiMe_2OMe](CO)_3\}$ (**6c**) umgesetzt, dessen anschließende heterogene Alkalisalzeliminierung mit $Me_2Si(H)Cl$ den zweifach Silyl-funktionalisierten Komplex **10** liefert.

Im Gegensatz zu Komplexen mit direkt Cyclopentadienyl-gebundener Methoxysilyleinheit führt die Hydrolyse von **5a-c**,**g** nicht zu stabilen Silanolen,

sondern es findet eine rasche Eigenkondensation zu den entsprechenden Disiloxan-verbrückten Zweikernkomplexen **12a-d** statt.
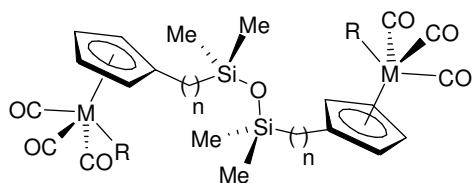
12	a	b	c	d
n	1	1	3	3
R	H	H	H	Me
M	Mo	W	W	W
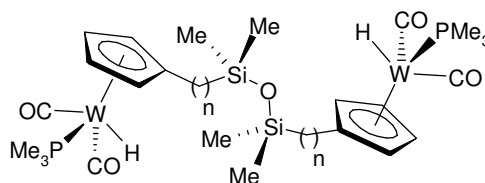
14	a	b
n	1	3

Der Ligandenaustausch an **12a,b** mit PMe₃ führt zu **14a,b**, die nach Deprotonierung mit *n*BuLi und anschließender Reaktion mit Me₂Si(H)Cl die Einführung einer Silylgruppe am Metall ermöglichen, so daß die Disiloxan-verbrückten zweikernigen Wolframio-silane **16a**,**b** erhalten werden.

Das zweifach SiH-funktionalisierte **16b** wird mit Dimethlydioxiran in das korrespondierende zweikernige Bis-silanol **18** überführt, das mit Me₂Si(H)Cl zum Disiloxan-verbrückten Wolframio-Disiloxan **19** co-kondensiert.
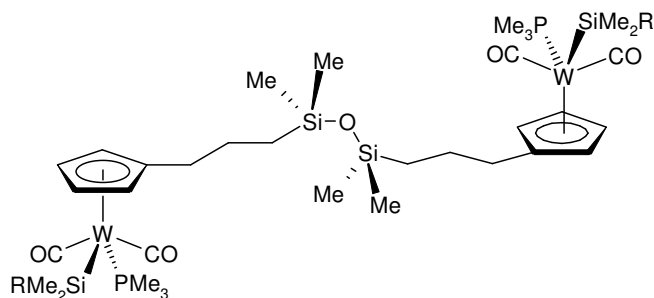
	16a	16b	18	19
n	1	3	3	3
R	H	H	OH	OSiMe₂H

APPENDIX

1. Elementaranalysen

Die C-H-N-Analysen wurden nach dem mikrochemischen Verfahren im Laboratorium des Instituts für Anorganische Chemie der Universität Würzburg angefertigt.

2. NMR-Spektren

Die [1]H-. ^{13}C- sowie ^{29}Si-NMR-Spektren wurden an Geräten des Typs Jeol Lambda 300 und Bruker AMX 400 aufgezeichnet.

Die Substanzen wurden als 1-10 %-ige Lösungen vermessen, die chemische Verschiebung ist als δ-Wert in ppm angegeben. Negative Werte geben die Lage bei höheren Feldstärken relativ zum jeweiligen Standard an (^{1}H-NMR: Restprotonensignale des Lösungsmittels rel. TMS, ^{13}C-NMR: Lösungsmittelsignale als interner Standard rel. TMS, ^{29}Si-NMR: [2]H-Lock intern, rel. TMS extern).

Die Kopplungskonstanten sind in Hertz angegeben. Für die Multiplizitäten der Signale wurden folgende Abkürzungen verwendet: s = Singulett, d = Dublett, t = Triplett, q = Quartett, sext = Sextett, sept = Septett, n = Nonett, dec = Dezett, m = Multiplett.

3. IR-Spektren

Die Infrarot-Spektren wurden mit einem Spektralphotometer der Firma Perkin Elmer, Modell 283 aufgenommen. Die Substanzen wurden als Lösungen in NaCl-Flüssigkeitsküvetten der Schichtdicke 0.1 mm nach der Kompensationsmethode vermessen. Als Standard diente die Polystyrolbande bei der Wellenzahl 1601.4 cm^{-1}. Zur Angabe der Intensität der Banden wurden folgende Abkürzungen verwendet: vs = very strong, s = strong, m = medium, w = weak, b = broad.

4. Schmelzpunkte

Die Bestimmung der Schmelzpunkte erfolgte durch Differentialthermoanalyse (DTA) am Anorganischen Institut der Universität Würzburg mit einem Gerät der Firma Du Pont, Thermal Analyzer und einer DSC-Zelle.

5. Röntgenstrukturanalysen

Für die Anfertigung der Röntgenstrukturanalysen danke ich folgenden Damen und Herren:

Dipl.-Chem. Dirk Schumacher: $[HPh_2Si(\eta^5\text{-}C_5H_4)](OC)_3WMe$

$[\eta^1\text{-}CH_2Me_2Si(\eta^5\text{-}C_5H_4)](OC)_3W$

$[\eta^1\text{-}SiMe_2OMe_2Si(\eta^5\text{-}C_5H_4)](OC)_2(Me_3P)W$

Dipl.-Chem. Andreas Sohns: $Ph_2Si[(\eta^5\text{-}C_5H_4)(OC)_3WMe]_2$

$[HOiPr_2Si(\eta^5\text{-}C_5H_4)](OC)_2(Ph_3P)WCl$

$[HOMe_2Si(\eta^5\text{-}C_5Me_4)](OC)_3WCl$

$[HOMe_2Si(\eta^5\text{-}C_5Me_4)](OC)_2(Ph_3P)WCl$

$O\{[Me_2Si(\eta^5\text{-}C_5H_4)](OC)_2(Me_3P)WH\}_2$

$[\eta^1\text{-}(CH_2)_3(MeO)_2Si(\eta^5\text{-}C_5H_4)](OC)_3W$

Dipl.-Chem. Katharina Klüh: $\{[HOiPr_2Si(\eta^5\text{-}C_5H_4)](OC)_3W\}_2$

Danksagung

Meinem Chef, Herrn Prof. Dr. Wolfgang Malisch, danke ich für die Betreuung und Unterstützung der vorliegenden Arbeit sowie für die großen Freiräume, die mir ein kreatives Arbeiten ermöglicht haben.

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Den beiden anderen Übriggebliebenen, meinem Labornachbarn Rainer – ich kau nur dreimal beim Essen – (Schmitt) und Katta Klüh (Katharina), danke ich für so manch lustigen und geistigen Erguß, der sich dann in Form von englischsprachigen und poetisch tiefsinnigen Versen an Wänden und Böden der Räume des AK`s wiederfanden, für das Versorgen mit trockenen Lösungsmitteln sowie für die vielen erfrischenden Momente auf den gemeinsamen Feiern und während der Arbeit.

Viel zu kurz war die Zeit mit den verflossenen Mitgliedern des AK`s. Insbesondere natürlich mit meinem Labornachbarn Mike (Boras), der mir immer tatkräftig unter die Arme griff und mich schon zu Beginn vor unüberschaubaren Spektren gewarnt hat; der mir aber letztendlich

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ERKLÄRUNG

Hiermit erkläre ich ehrenwörtlich, daß ich die Dissertation "*Halfsandwich Tungsten Complexes with a Silanol-functionalized Cyclopentadienyl Ligand - Synthesis and Reactivity -*" selbständig angefertigt und keine anderen Hilfsmittel als die von mir angegebenen Quellen und Hilfsmittel benutzt habe.

Ich erkläre außerdem, daß diese Dissertation weder in gleicher oder anderer Form bereits in einem anderen Prüfungsverfahren vorgelegen hat.

Ich habe früher außer den mit dem Zulassungsgesuch urkundlich vorgelegten Graden keine weiteren akademischen Grade erworben oder zu erwerben versucht.

Würzburg, den 29.01.2005

<div style="text-align: right">

HOLGER BERA

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