P-H-FUNCTIONALIZED PHOSPHENIUM TUNGSTEN COMPLEXES: EXCHANGE REACTIONS AT THE PHOSPHORUS AND CYCLOADDITIONS WITH HETEROALLENES

Dissertation zur Erlangung des naturwissenschaftlichen Doktorgrades der Bayerischen Julius-Maximilians-Universität Würzburg

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Rainer Schmitt

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Meinen Eltern

CONTENTS

ANNOTATIONS

- The following work is subdivided into six 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:

Me = methyl
Et = ethyl
Bu = butyl
*i*Pr = *iso*-propyl
Ph = phenyl
Bz = CH_2Ph
*t*Bu = *tert*-butyl
Mes = mesityl
*s*Mes = 2,4,6-tris-*tert*-butylphenyl
Cp = η^5-cyclopentadienyl
C_5Me_5 = η^5-pentamethylcyclopentadienyl
n-BuLi = *n*-butyllithium
min = minute(s)
h = hour(s)
d = day(s)
THF = tetrahydrofurane
DME = dimethoxyethane
triflato = OSO_2CF_3
o = *ortho*
m = *meta*
p = *para*

LIST OF PUBLICATIONS

1. Silyl-Functionalized Cyclopentadienyl Iron Complexes.
   A. Sohns, R. Schmitt, W. Malisch, 2nd European Silicon Days (München **2003**), Abstract P 101.

2. Funktionelle Derivate von $Cp(OC)_2W{=}P(H)\textit{s}Mes$ durch Austausch-, Cycloadditions- und Abstraktionsreaktionen.
   R. Schmitt, W. Malisch, 1st Ph. D. Seminar on Phosphorus Chemistry (Kaiserslautern **2004**), Abstract C2.

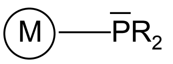
3. P-H-functional Phosphenium Complexes: Exchange and Cycloaddition Reaction.
   R. Schmitt, W. Malisch, 2nd Ph. D. Seminar on Phosphorus Chemistry (Bonn **2005**), Abstract A2.

4. Bis-Silanol-Cyclopentadienyl Iron Complexes.
   A. Sohns, P. Dopf, R. Schmitt, W. Malisch, 14th International Symposium on Organosilicon Chemistry / 3rd European Silicon Days (Würzburg **2005**), Abstract P 024.

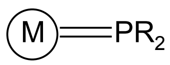
INTRODUCTION

In the last two decades the synthesis of organophosphorus compounds has attracted widespread attention in the area of metal-assisted chemistry.[1-8] A general concept in this context implies organophosphorus moieties which are activated via metal coordination, mainly realized by the use of cyclopentadienyl, carbonyl and triorganophosphine substituted fragments.

As a consequence of extensive investigations, the synthesis of metal-containing organophosphorus compounds, which either possess a lone pair at the phosphorus (**I**) or are connected to the metal via a double or triple bond (**II-V**) have been realized.

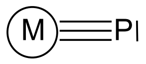


Phosphanido (**I**)



Phosphenium (**II**)

Phosphinidene (**III, IV**)

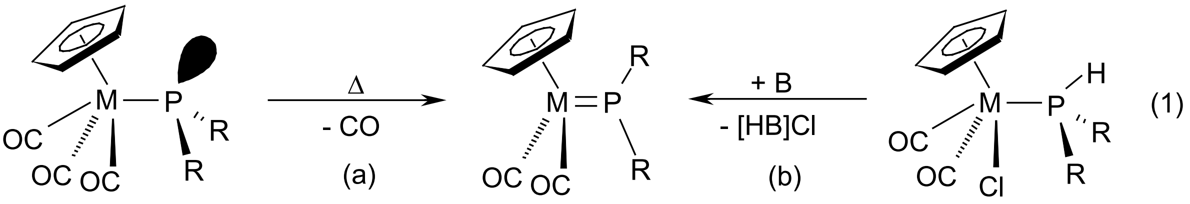


Phosphido (**V**)

Especially the phosphenium-metal-unit (**II**) features ideal requirements for the coupling with organic substrates, which mainly involves [2+n]-cycloadditon reactions (n = 1-4) with a wide series of unsatured organic compounds like heteroallenes, dienes or diazoalkanes.[9-17]

In the class of phosphenium-metal-complexes,[18, 19] systems of the type $C_5R_5(OC)_2M{=}PR'_2$ (M = Cr, Mo, W; R = H, Me; R' = alkyl, aryl, amino) take up an important role concerning this reactivity.[9, 20-22] An adequate stability of these complexes can only be reached via shielding of the double bond with organoligands of high steric demand or via electronic saturation of the sp^2-hybridized phosphorus atom by heteroatom-substituents like NR_2, OR or SR.[9, 20-30]

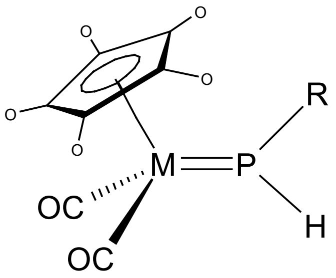
For the synthesis of these phosphenium metal complexes **A** either the thermically induced intramolecular decarbonylation of metallo-phosphines of the type **B** [Scheme (1a)][22, 31] or the base-assisted dehydrochlorination of bifunctional phosphine-metal-complexes of the type **C** [Scheme (1b)] can be used.[15, 21, 31, 32]



B **A** **C**

M = Cr, Mo, W; R = alkyl, aryl, amino

An attractive extension of this class of compounds with respect to metal-mediated coupling reactions is offered by P-H-functionalized derivatives, since in addition to the cycloaddition behaviour high tendency for the modification of the P-H-function due to insertion or exchange reaction is obvious. Despite the first synthesis of such a phosphenium complex by *Schrock* in 1982 with the generation of $(Me_3CC{\equiv}(Cl)_2(Et_3P)_2W{=}P(H)Ph$,[33] consolidated findings regarding stability and reactivity were made due to the systematic study of complexes of the type **D**.[32, 34-36]



o— = H, Me

M = Cr, Mo, W

R = *t*Bu, Ph, Mes, *s*Mes

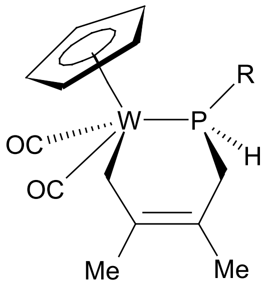
D

Among these the *super*-mesitylphosphenium complex $Cp(OC)_2W{=}P(H)$*s*Mes represents one of the few isolated P-H-functionalized derivatives[31] in addition to the complexes $(Me_3CC{\equiv}(Cl)_2(Et_3P)_2W{=}P(H)Ph$,[33] $[(Me_3SiNCH_2CH_2)_3N]MoP(H)Ph$,[37] $Cp°(Me_3P)_2Mo{=}P(H)$*s*Mes[38] (Cp° = C_5EtMe_4) and $Cp'_2(Cl)Zr\text{-}P(H)R$ (Cp' = C_5H_5, C_5Me_5, C_5H_4Me, C_5EtMe_4; R = Cy, Mes, *s*Mes, 2,6-Mes_2-C_6H_2).[39-43] It is the only member which can be generated via thermal decarbonylation reaction starting from the corresponding tricarbonyl-cyclopentadienyl-metallo-phosphine $Cp(OC)_3W\text{-}P(H)$*s*Mes.[31]

For the synthesis of the *tert*-butyl, phenyl- and mesityl derivatives the dehydrochlorination route affords the only access.[32] While the *super*-mesityl compound is stable at room temperature, the *tert*-butyl-derivatives $C_5R_5(OC)_2W{=}P(H)$*t*Bu (R = H, Me) could only be spectroscopically identified in solution at low temperatures,[34] the aryl-substituted species $Cp(OC)_2W{=}P(H)R$ (R = Ph, Mes) have never been directly observed before conversion to the double phenyl-phosphido-bridged complex $\{[(\mu^2\text{-}PH(Ph)][W(CO)_2Cp]\}_2$ or the phosphinidene-bridged dinuclear compound $Cp(OC)_2W{=}PMes[W(MesPH_2)(CO)_2Cp]$, respectively.[44] But the existence of both double bonded systems could be verified by trapping reactions with trimethylphosphine, yielding $Cp(OC)_2(Me_3P)W\text{-}P(H)R$ (R = *t*Bu, Ph, Mes).[35]

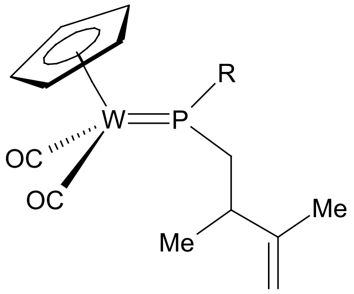
Analogous to the diorganophosphenium complexes the P-H-functionalized derivatives readily undergo cycloaddition reactions. Typical examples involve the reaction of $Cp(OC)_2W{=}P(H)R$

(R = *t*Bu, Mes) with 2,3-dimethyl-1,3-diene, yielding phosphametallacyles of the type **E** via regioselective [2+4] cycloaddition.

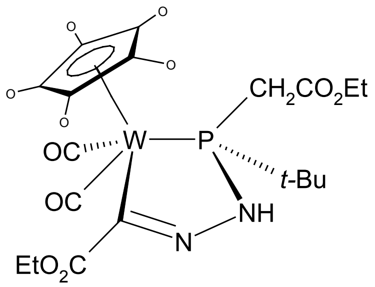


E

R = *t*Bu, Mes



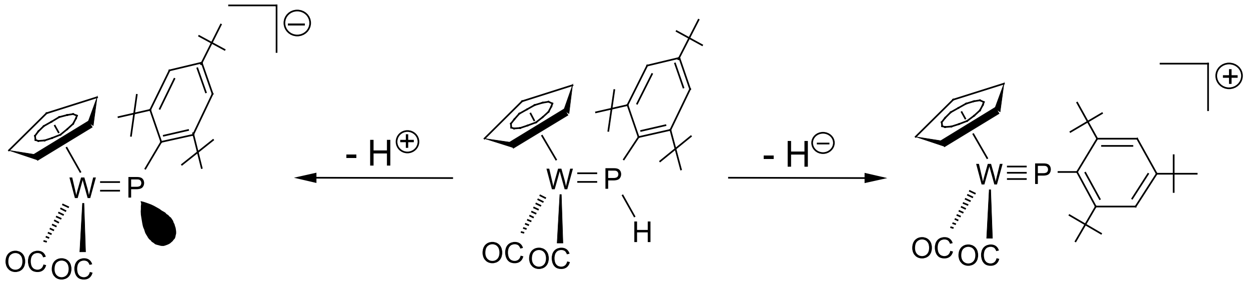
F



G

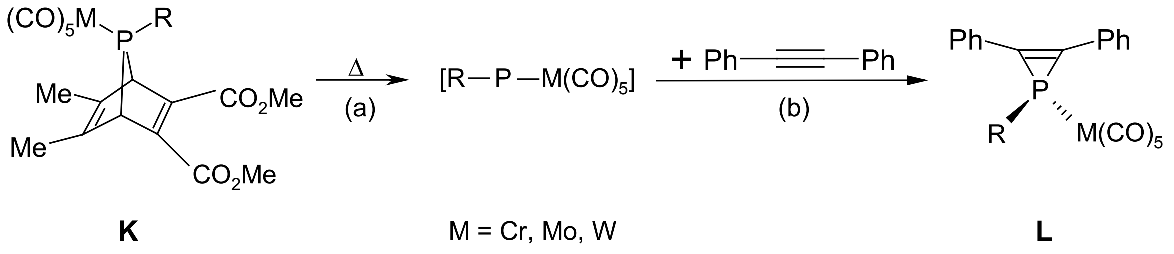
E is characterized by the high mobility of the P-bonded hydrogen, resulting via a formal P→C-hydrogen transfer in the formation of the alkenylphosphenium complexes **F**.[45] Another interesting example is the treatment of the C_5Me_5-substituted complex $C_5Me_5(OC)_2W{=}P(H)$*t*Bu with two equivalents of diazoacetic ethylester, yielding the five-membered ring system **G** via a complex cyloadditon-isomerization sequence.[46]

No attempts have been so far made to use P-H-phosphenium complexes $L_nM{=}P(H)R$ as precursors for the generation of cationic or anionic phosphinidene species via hydride or proton abstraction from the phosphorus. In this context the *super*-mesityl-substituted phosphenium complex $Cp(OC)_2W{=}P(H)$*s*Mes (**H**) appears to be an ideal starting material. Selective deprotonation reaction at the P-H-bond should lead to the anionic-“carbene-type“-phosphinidene complex of the type **I**, whereby the cationic-“carbyne-type“-system **J** implies hydride abstraction.



I **H** **J**

Since the fundamental studies by *Mathey* in 1982 concerning neutral phosphinidene complexes[47, 48] this type of compound has attracted widespread attention[49-52] and is still in the focus of the current research.[53-58] A pathway for the synthesis starts with thermal decomposition of the phosphanorbornadiene compounds of the chromium group **K** [Scheme (2a)], leading to the generation of terminal phosphinidene complexes, which can be used for the synthesis of novel organophosphorus compounds. For example trapping reactions with alkynes give access to metal-coordinated phosphirenes **L** [Scheme (2b)].[47]



(2)

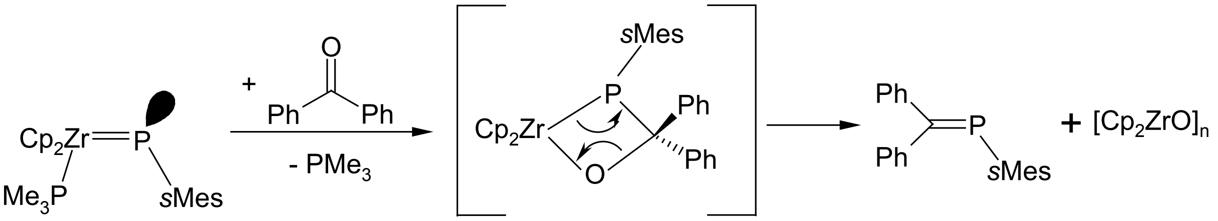
Despite the restriction of this method to the mentioned metals the substituents at the phosphorus atom can be extensively varied.[52, 59, 60] Recentely *Lammertsma et al.* reported on the use of benzophosphephine complexes as precursors for phosphinidene complexes due to a extrusion of a transition metal-stabilized phosphinidene [R-P=ML_n].[55]

An alternative approach to neutral phosphinidene complexes is given by dechlorination of $i\mathrm{Pr_2NPCl_2}$ with $\mathrm{Na_2Fe(CO_4)}$, leading to the formation of [$i\mathrm{Pr_2N\text{-}P{=}Fe(CO)_4}$].[61] This product can not be isolated in substance, but it could be identified by trapping reactions.[62]

In this context it has to be outlined that the phosphinidene ligand can act both as two electron and as four electron donor to the transition metal, making a differentiation into electrophilic Fischer-type- and nucleophilic Schrock-type phosphinidene complexes reasonable, analogous to the situation for the carbene compounds $L_nM{=}CR_2$.[52]

The electrophilic phosphinidene complexes react as outlined with different π-systems,[61, 63-66] but also add lewis bases,[67-69] e.g. phosphines to afford phosphinidene-phosphorane complexes like [$\mathrm{(Et_3P)(EtO_2C)P\text{-}W(CO)_5}$].[68] Moreover insertion reactions[70-73] e.g. in C-H-[70] or transition metal-carbon-bonds[73] were found.

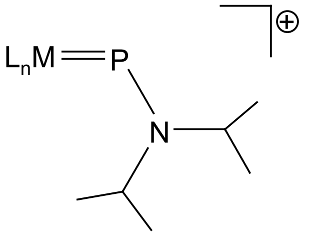
Concerning the nucleophilic phosphinidene compounds, first time described by *Lappert et al.*[74] and characterized by a bent M=PR-linkage, an adequate stability is reached only via severe sterical shielding. The up to now isolated derivatives contain metals in high oxidation states like $\mathrm{Mo^{IV}}$, $\mathrm{W^{IV}}$ [34, 74, 75], $\mathrm{Zr^{IV}}$ [76, 77], $\mathrm{Ta^{V}}$ [78, 79] and $\mathrm{U^{IV}}$ [80]. These systems mainly participate in [2+2]-cycloadditon reactions with alkines[81], 1,2-additions with protic reagents[77, 82] and in *phospha*-Wittig transformations with carbonyl containing compounds[78, 83, 84] as illustrated in Scheme (3) for the phosphinidene zirconium complex **M**.[83]



(3)

M

Recently the first heteroatom-substituted electrophilic phosphinidene complexes **N** were generated with $AlCl_3$ by chloride abstraction starting from the phosphanido metal complexes $C_5Me_5(OC)_3W\text{-}P(Cl)N\mathit{i}Pr_2$ (M = Mo, W) and $C_5Me_5(OC)_2Ru\text{-}P(Cl)N\mathit{i}Pr_2$.[85]



$L_nM = C_5Me_5(CO)_3Mo,W$
$C_5Me_5(CO)_2Ru$

N

The electrophilicity of the phosphorus was confirmed by the addition of trimethylphosphine leading to the phosphinidene-phosphorane $[C_5Me_5(CO)_3Mo\text{-}(\mathit{i}Pr_2NP)(PEt_3)][AlCl_4]$.[86]

The purpose of the work presented was to find ways for the generation of anionic "carbene-type" and cationic "carbyne-type" phosphinidene complexes, making for the first time use of P-H- and P-Cl-functionalized phosphenium-metal-complexes as adequate precursors. Moreover extensive studies of the charged phosphinidene complexes were targeted with selected electrophilic or nucleophilic reagents, involving appropriate organoelement and organometal complexes.

Finally the addition behaviour of the *super*-mesityl phosphenium complex $Cp(OC)_2W{=}P(H)\mathit{s}Mes$ towards unsatured organic compounds, especially isocyanates, isothiocyanates and diimides should be examined in order to get an idea concerning tautomerization, involving hydrogen migration from the phosphorus to other basic centers of the cycloadduct. Moreover the essential factors determining the stereochemistry of these addition reactions should be examined and the resulting cycloadducts structurally characterized.

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CHAPTER I

The *super*-Mesitylphosphenium Tungsten Complex $C_5H_5(OC)_2W{=}P(H)$*s*Mes: Structural and Theoretical Investigation. Addition Reactions with Trimethylphosphine, Elemental Sulphur and Selenium

Introduction

Despite the high interest in phosphenium transition metal chemistry[1-11] and the established synthesis of diorganophosphenium molybdenum and tungsten complexes of the type $C_5R'_5(OC)_2M{=}PR_2$ (R' = H, Me; R = alkyl, aryl),[12-30] the knowledge concerning analogous P-H-functionalized systems is still limited.[31-35] This fact is due to insufficient shielding of the M=P bond (M = Mo, W), which generally leads to serious problems concerning isolation. As a consequence the *tert*-butyl-substituted compounds $C_5R_5(OC)_2W{=}P(H)$*t*Bu [R = H (**7a**), Me] could only be spectroscopically identified in solution at low temperatures,[31] while the aryl-substituted species $Cp(OC)_2W{=}P(H)R$ [R = Ph (**7b**), Mes (**7c**)] have never been directly observed.[32]

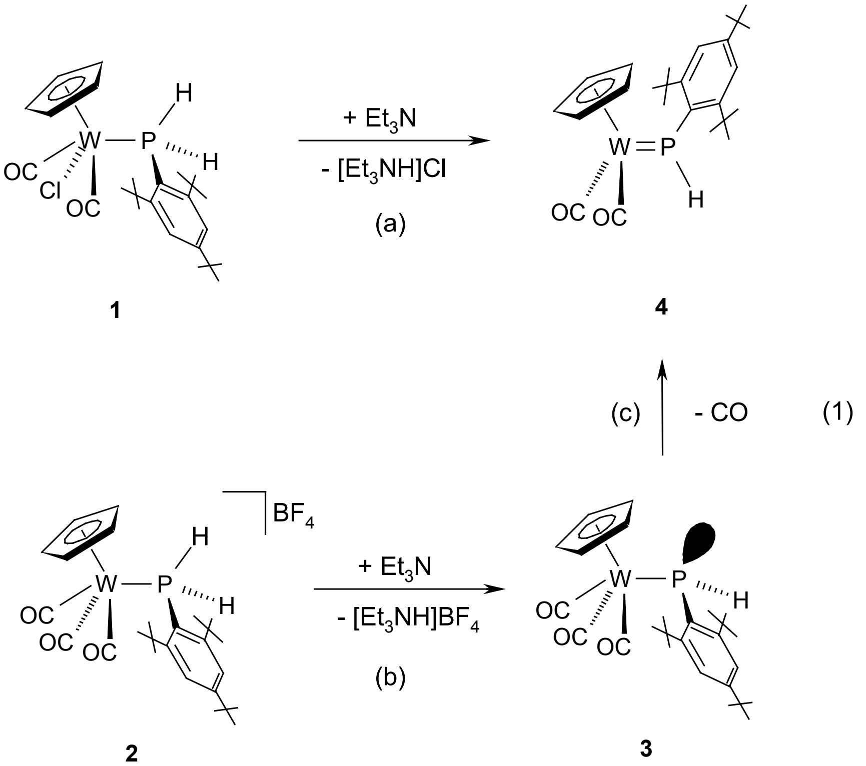
P-H-functionalized phosphenium molybdenum and tungsten complexes $Cp(OC)_2M{=}P(H)R$ (R = alkyl, aryl) are characterized by two highly reactive centers at the planar sp^2-hybridized phosphorus atom - the M=P-bond and the P-H-bond - promising extensive coupling reactions leading to novel organophosphorus ligands. However only limited information is available[31-35] with respect to the structure of the phosphenium complexes, especially the preferred conformation. This knowledge is a prerequisite to define the stereochemistry in reactions where the M=P- and the P-H-bond are involved. Previous investigations along these lines indicated the *super*-mesityl-substituted phosphenium complex $Cp(OC)_2W{=}P(H)$*s*Mes (**4**) to be an ideal candidate for the investigation of this topic, since it represents one of the few isolated P-H-functionalized derivatives[36] in addition to the complexes $(Et_3P)_2(Cl)_2(Me_3CC{\equiv})W{=}P(H)Ph$,[37] $[(Me_3SiNCH_2CH_2)_3N]MoP(H)Ph$,[38] $Cp°(Me_3P)_2Mo{=}P(H)$*s*Mes[39] (Cp° = C_5EtMe_4) and $Cp'_2(Cl)Zr{-}P(H)R$ (Cp' = Cp, Cp*, C_5H_4Me, C_5EtMe_4; R = Cy, Mes, *s*Mes, 2,6-Mes_2-C_6H_2).[40-45]

We now present structural information concerning the complex $Cp(OC)_2W{=}P(H)$*s*Mes (**4**) as well as theoretical calculations of **4** and diverse P-H-functionalized phosphenium tungsten complexes by varying the P-bonded organo ligands, which give detailed insight into the essential factors determining the stereochemistry.

Results and Discussion

Structural Investigation

As described previously[36] the *super*-mesitylphosphenium tungsten complex **4** can be generated via dehydrochlorination of the *super*-mesitylphosphine chloro-tungsten species **1** with triethylamine [Scheme (1a)]. An alternative route is offered by the decarbonylation of the *secondary* tungsten-phosphine **3** [Scheme (1c)], obtained from the cationic *super*-mesitylphosphine tungsten complex **2**, isolated as the BF$_4$-salt, via deprotonation with NEt$_3$ [Scheme (1b)]. In both routes, **4**, which shows high thermal stability as well as good solubility in *n*-pentane, is isolated as a microcrystalline violet powder in 69 (**1a**) or 80 % (**1b**) yield, respectively.



1, **2** and **4** have been structurally characterized by x-ray diffraction analysis. Crystals of Cp(OC)$_2$[*s*Mes(H)$_2$P]W-Cl (**1**) and [Cp(OC)$_3$W-P(H)$_2$(*s*Mes)]BF$_4$ (**2**), suitable for structure determination, could be obtained from a saturated toluene (**1**) or dichloromethane solution (**2**) at room temperature [Fig. (1) and (2)].

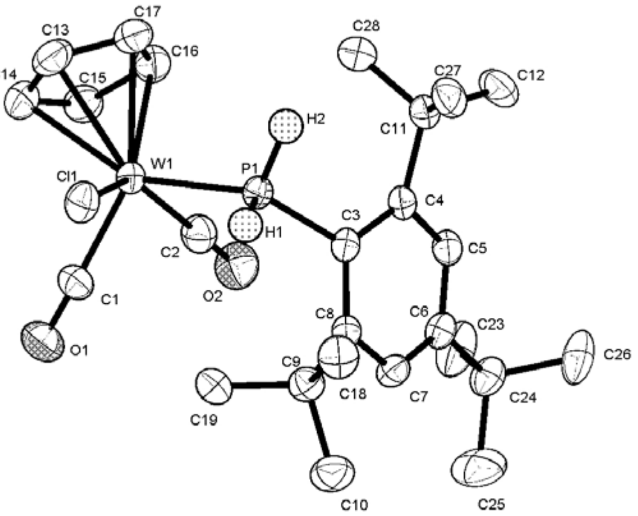


Fig. (1). Molecular structure of Cp(OC)$_2$[*s*Mes(H)$_2$P]W-Cl (**1**) - Due to the distortion of the *p*-*t*Bu-group, only one of the rotational isomers is shown. The hydrogen atoms except at P(1) have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: W(1)-P(1) 2.4801(10), W(1)-C(1) 1.975(4), W(1)-C(2) 1.973(4), W(1)-Cl(1) 2.5005(11), P(1)-C(3) 1.836(3), P(1)-H(1) 1.30(5), P(1)-H(2) 1.26(5), C(2)-W(1)-C(1) 75.49(16), C(2)-W(1)-P(1) 79.67(11), C(1)-W(1)-P(1) 112.80(11), C(2)-W(1)-Cl(1) 137.47(11), C(1)-W(1)-Cl(1) 81.77(12), P(1)-W(1)-Cl(1) 76.74(3), C(3)-P(1)-W(1) 120.93(11), C(3)-P(1)-H(1) 106(2), W(1)-P(1)-H(1) 112(2), C(3)-P(1)-H(2) 105(2), W(1)-P(1)-H(2) 114(2), H(1)-P(1)-H(2) 97(3), Cl(1)-W(1)-P(1)-H(1) 16.1°, C(2)-W(1)-P(1)-C(3) -2.39(17), P(1)-C(3)-C(4)-C(5) -155.0(13), P(1)-C(3)-C(8)-C(7) 154.9(3), C(8)-C(3)-C(4)-C(5) 12.1(5), C(6)-C(5)-C(4)-C(3) -2.7(5), C(4)-C(3)-C(8)-C(7) -12.5(5), C(6)-C(7)-C(8)-C(3) 3.4(5).

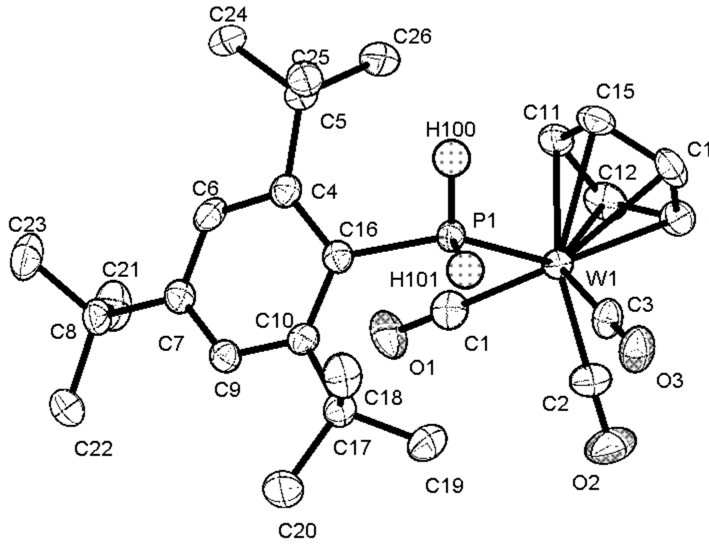


Fig. (2). Molecular structure of [Cp(OC)$_3$W-P(H)$_2$(*s*Mes)]BF$_4$ (**2**) - The BF$_4$-anion and the hydrogen atoms except at P(1) have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: W(1)-P(1) 2.5301(13), W(1)-C(1) 2.007(5), W(1)-C(2) 2.000(5), W(1)-C(3) 2.006(5), P(1)-C(16) 1.839(5), C(2)-W(1)-C(1) 76.8(2), C(3)-W(1)-C(1) 119.4(2), C(2)-W(1)-C(3) 76.2(2), C(1)-W(1)-P(1) 76.97(14), C(2)-W(1)-P(1) 124.13(16), C(3)-W(1)-P(1) 75.32(14), C(16)-P(1)-W(1) 120.80(15), H(100)-P(1)-H(101) 96(3), C(16)-P(1)-H(100) 104(2), W(1)-P(1)-

H(100) 113(2), C(16)-P(1)-H(101) 103.5(18), W(1)-P(1)-H(101) 116.5(18), C(1)-W(1)-P(1)-C(16) -6.0(2), P(1)-C(16)-C(4)-C(6) 158.7, P(1)-C(16)-C(10)-C(9) -160.3, C(7)-C(6)-C(4)-C(16) 4.6(7), C(9)-C(10)-C(16)-C(4) 10.3(6), C(7)-C(9)-C(10)-C(16) -0.6(7).

1 and **2** exhibit a square pyramidal arrangement of the ligands around the central tungsten atom with the cyclopentadienyl ring in the apical position and the basis formed by the *super*-mesitylphosphine ligand, the two carbonyl groups and the chloro ligand (**1**), or the three carbonyl groups (**2**), respectively. The most important finding with regard to the stereochemistry of **1** is the *cis*-arrangement of the chloro ligand and the phosphorus atom, as well as the two carbonyl groups at the square basis. The angles P1-W1-Cl1 (76.74°) and C2-W1-P1 (79.67°) provide additional evidence for this *cis*-position in **1**, which is also valid in solution [$I_{v(CO)sym} : I_{v(CO)asym} > 1$].[36, 46] In case of **2** the smallest angles are formed by C1 or C3 with W1 and P1 (C3-W1-P1 75.32°; C1-W1-P1 76.97°).

The torsion angle Cl1-W1-P1-H1 (16.1°) indicates a nearly ideal *cis*-configuration of the chloro atom and the phosphorus bonded hydrogen H1 in **1** as well as for the *ipso*-C-atom of the aryl ligand and the carbonyl C2 (C2-W1-P1-C3 -2.39°). This situation leads to an eclipsed conformation of the aromatic ring system and the carbonyl ligand, with respect to the W-C2- and the P1-C3-bond. A similar arrangement can be found for **2**, indicated by the small dihedral angle C1-W1-P1-C16 (-6.0°).

The W1-P1-distances for **1** (2.4801 Å) and **2** (2.5301 Å) are typical for tungsten complexes with a coordinated phosphine ligand.[47] The W1-Cl1 bond length of **1** (2.5005 Å) is similar to that found for $C_5H_5(OC)WCl_3$.[48] Both the P1-C3-distance (1.836 Å) of **1** and the P1-C16-distance (1.829 Å) of **2** coincide with that of a single bond between a tetravalent phosphorus and a sp^2-hybridized carbon atom (1.84 Å).[49] In both complexes the substituents at the phosphorus are arranged tetrahedrally with the smallest angles obtained for H1-P1-H2 in **1** (97°) and H100-P1-H101 in **2** (96°), respectively.

The steric demand of the *s*Mes-ligand causes on the one hand a severe distortion of the aryl-group planarity [**1**: C8-C3-C4-C5 12.1°, C4-C3-C8-C7 -12.5°; **2**: C7-C6-C4-C16 4.6°, C9-C10-C16-C4 10.3°]. On the other hand this effect determines the arrangement of the *super*-mesityl group. In order to avoid interaction of the *ortho*-*tert*-butyl-groups with the carbonyl-ligands, the aryl ligand is bent towards the metal-coordinated cyclopentadienyl unit leading to a deviation from the theoretical torsion angle of 180° (**1**: P1-C3-C4-C5 -155.0°, P1-C3-C8-C7 154.9°; **2**: P1-C16-C4-C6 158.7°, P1-C16-C10-C9 -160.3°).

Crystals of Cp(OC)$_2$W=P(H)*s*Mes (**4**), suitable for structure determination, could be obtained from a saturated *n*-pentane solution at room temperature.

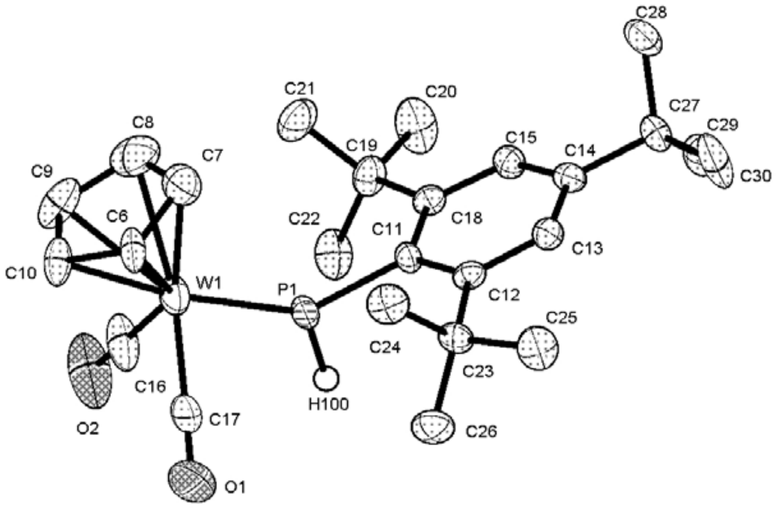


Fig. (3). Molecular structure of Cp(OC)$_2$W=P(H)*s*Mes (**4**) - The hydrogen atoms except P(1) have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: W(1)-P(1) 2.2471(12), P(1)-H(100) 1.31(4), P(1)-C(11) 1.841(4), W(1)-C(16) 1.936(5), W(1)-C(17) 1.96(3), M-W(1)-P(1) 133.6, C(11)-P(1)-W(1) 138.30(13), C(11)-P(1)-H(100) 98.9(18), W(1)-P(1)-H(100) 122.7(18), C(16)-W(1)-P(1) 90.85(15), C(17)-W(1)-P(1) 84.7(17), C(17)-W(1)-C(16) 84.3(16), P(1)-C(11)-C(18)-C(15) -178.3(3), P(1)-C(11)-C(12)-C(13) 178.0(3), C(12)-C(11)-C(18)-C(15) -1.4(6), C(12)-C(13)-C(14)-C(15) 0.3(6).

The coordination sphere of the tungsten atom can be described as a pseudo-octahedral three legged piano stool. The cyclopentadienyl ligand is occupying three facial coordination sites, whereby two legs are represented by the carbonyl ligands and the third leg by the double bonded phosphenium ligand. This is shown by the bond angles including the carbonyl ligands and the phosphine moiety, which are close to the expected value of 90° (C16-W1-P1 90.85°, C17-W1-P1 84.7°).

The geometry of the phosphorus atom is trigonal planar, shown by the sum of angles amount to 359.9°. In view of this trigonal planar structure, the phosphenium moiety can be regarded as three-electron donor, providing the tungsten atom with a 18-valence-electron count. The C11-P1-H100-angle of 98.9° is significantly reduced in comparison to the ideal value of 120°. A diminished angle was also found for Cp(OC)$_2$W=P(*t*Bu)$_2$[18] (109.4°). Due to this congestion, the C11-P1-W1- and W1-P1-H100-angles are expanded to 138.30° and 122.7°, respectively.

The P-H-bond distance in **4** (1.31 Å) is shorter than for Cp*(Me$_3$P)$_2$Mo=P(H)*s*Mes[39] (1.36 Å), consistent with the smaller electron releasing effect of the transition metal fragment. The P1-C11 bond length (1.841 Å) is in the range expected for a single bond between tricoordinate phosphorus and sp^2-hybridized carbon[50] and excludes π–interaction between the phosphorus and the aromatic ring system.

The tungsten-phosphorus double-bond length of 2.25 Å is nearly identical to $Cp(OC)_2W{=}P(tBu)_2$ (2.28 Å)[18] and close to the calculated value of 2.26 Å.[51-53]

The plane defined by C11, P1 and H100 is almost perpendicular to the $W(CO)_2$-moiety, which shows the smallest angle (C17-W1-C16 84.3°) in the piano-stool arrangement. Despite the steric demand of the *s*Mes-ligand the distortion of the aryl group planarity is negligible (C12-C11-C18-C15: -1.4°, C12-C13-C14-C15: 0.3°). Contrary to the structural finding in context with **1** and **2**, the aryl substituent on the phosphorus atom is not bent towards the cyclopentadienyl moiety at the metal fragment, indicated by the torsion angles P1-C11-C18-C15 (-178.3°) and P1-C11-C12-C13 (178.0), which are close to the ideal value of 180°. For **1** and **2** deviations in the range between 19.1° and 25.1° are observed.

In summary, the conformation of **4** and its short W-P-distance is in agreement with the description by frontier orbital interaction involving the fragments $Cp(OC)_2W^{\ominus}$ and $sMes(H)P^{\oplus}$. Thereby a σ-bond is formed through the overlapping of the d_{z^2}-orbital of the tungsten atom (LUMO, W) with an appropriate hybrid orbital at the phosphenium cation (HOMO, P). An additional π-bond results from overlap of the occupied d_π-orbital at the metal (HOMO, W) and the empty p-orbital at the phosphorus (LUMO, P). This interpretation corresponds to that of a metal-carbene-type-bonding.

The most important finding pertains to the mutual *cis*-configuration of the *super*-mesityl-ligand and the cyclopentadienyl moiety. This is in accordance with the situation in solution. ^{1}H-NOESY experiments indicate strong interactions between the hydrogens of the C_5H_5-ligand and the *ortho*-*tert*-butyl groups while the cyclopentadienyl moiety and the hydrogen atom at the P-H-bond are uneffected.

DFT Calculations of the Phosphenium Complexes $Cp(OC)_2W{=}P(H)R$ [R = *s*Mes (4), *tert*-Butyl, Ph, Mes (7a-c)] Performed by S. Riedel

The structure determination for **4** reveals a *cis*-orientation of the *s*Mes-substituent on phosphorus relative to the Cp-ligand [Fig. (3)]. In order to understand this stereochemistry, density functional calculations on a series of model systems $Cp(OC)_2W{=}P(H)R$ [R = *s*Mes (**4**), *tert*-Butyl, Ph, Mes (**7a**-**c**)], in both *cis*- and *trans*-configurations have been carried out.

As shown in Table (1), the computations confirm a higher stability for the *cis*-isomer in comparison to the *trans*-arrangement by 15.2 kJ/mol for R = *s*Mes (**4**). For all other investigated substituents R = *tert*-Butyl, Ph, Mes (**7a**-**c**) the *trans*-arrangement is slightly favoured. This suggests that the structural preference for **4** is steric in origin. The assumption is confirmed by the very large computed W1-P1-C11 angle of 150.2° in the *trans*-isomer, compared to 130.5° calculated for the more stable *cis*-structure. Differences between the angles of *cis*- and *trans*-isomers are much less pronounced for the smaller substituents [Table (1)]. Thus, it appears that the dominant steric interactions that regulate the structural preferences in **4** are not between the *s*Mes-substituent and the Cp-ligand but rather between the *s*Mes-substituent and the two carbonyl ligands. It is well known that Cp-ligands may adapt to steric repulsion with relative ease by a slight shift within the coordination sphere of the metal, and possibly by a moderate change in hapticity.[54] This is probably impossible for the more strongly and rigidly bound carbonyl ligands. Figure (4) shows that, indeed, the distances between the *tert*-butyl groups of the *s*Mes-substituent and the carbonyl carbon atoms are inacceptably short in the *trans*-arrangement (2.538 Å), they fall below the values for the distances between the *s*Mes-substituent and the Cp-ligand in the more stable *cis*-structure. The distances between the other substituents R and the carbonyl ligands in the *trans*-arrangement are 2.832, 3.059, 3.008 Å for R = Mes (**7c**), Ph (**7b**), *tert*-Butyl (**7a**), respectively. In these cases, steric repulsion with the carbonyl ligands will be much less pronounced than with R = *s*Mes (**4**), and the *trans*-structure is increasingly preferred [cf. Table (1)].

X-Ligand	**Isomer**	**E_{rel} [kJ/mol]**	**∠ (W-P-C) [°]**
*s*Mes	cis	-15.2	130.5 *(138.3[a])*
*s*Mes	trans	0	150.2
Mes	cis	0	131.7
Mes	trans	-1.8	135.8
Ph	cis	0	134.3
Ph	trans	-4.7	136.0
tert-Butyl	cis	0	135.8
tert-Butyl	trans	-5.8	137.8

[a]Experimental result for **4** [cf. Figure (3)].

Table (1). Computed *cis*/*trans* energy differences and W-P-C bond angles for $Cp(OC)_2W{=}P(H)R$ complexes [R = *s*Mes (**4**), *tert*-Butyl, Ph and Mes (**7a**-**c**)]

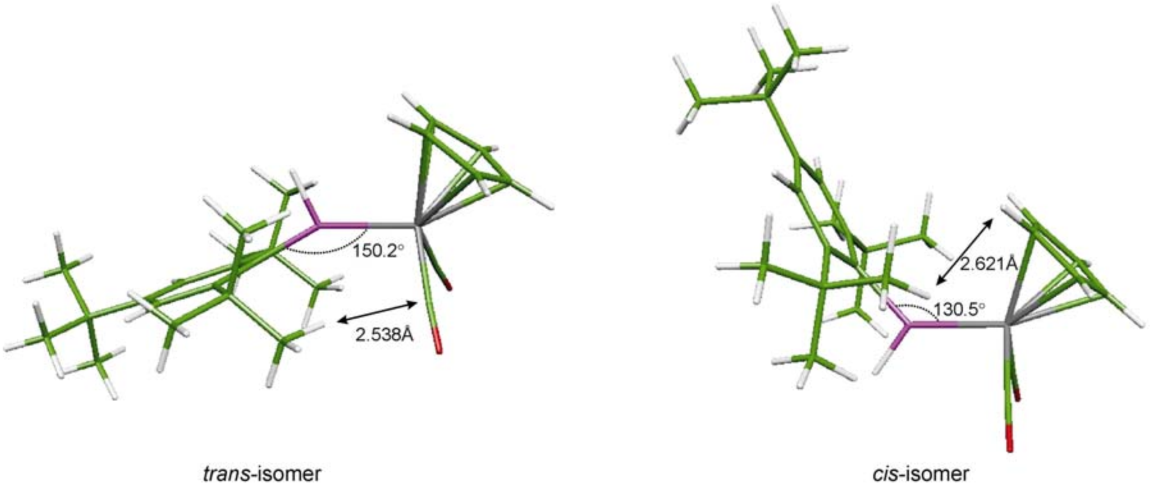
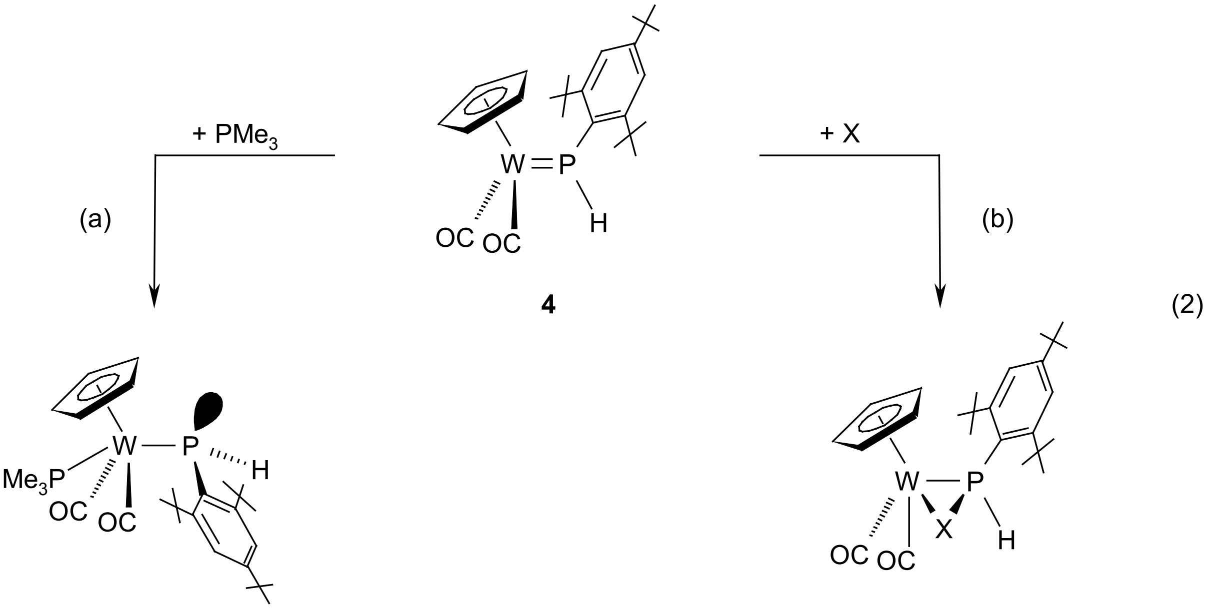


Fig. (4). Optimized structures for *cis*- and *trans*-isomers of $Cp(OC)_2W{=}P(H)$*s*Mes (**4**)

Addition Reactions of $Cp(OC)_2W{=}P(H)$*s*Mes (4) with Me_3P, S and Se

The reactivity of the double bond in phosphenium complexes of the type $C_5R'_5M{=}PR_2$ (R' = H, Me; R = alkyl, aryl) or in the P-H-complexes $C_5R'_5M{=}P(H)R$ can be divided mainly into two categories. The first category involves reaction of the M=P-bond with different dienophiles used for the preparation of highly functionalized phosphorus ligands.[22, 25, 30, 35] The second one is the addition of a donor ligand at the metal center with opening of the double bond, increase of the coordination number and generation of a phosphanido metal species with a lone pair of electrons at the phosphorus atom.[31, 32]

Treatment of a benzene solution of **4** with an excess of trimethylphosphine yields the phosphine-substituted *secondary* metallo-phosphine $Cp(OC)_2(Me_3P)W{-}P(H)$*s*Mes (**5**) as an orange powder with 66 % [Scheme (2a)]. Actually the addition of trimethylphosphine occurs immediately at room temperature with changing of colour of the solution from violet to orange.



6	a	b
X	S	Se

According to the spectroscopic data [^{2}J(PC) = 20.37 Hz and 19.32 Hz; ^{2}J(PWP) = 36.5 Hz; $I_{v(CO)sym} : I_{v(CO)asym} < 1$], **5** is formed as the *trans*-isomer with the phosphine and the organophosphorus-fragment mutually *trans*.[32] The stereochemistry of **5** is in line with the known phosphines Cp(OC)$_2$(Me$_3$P)W-P(H)R (R = *t*Bu, Mes)[31, 32] showing a pyramidal P-H-functionalized phosphorus atom, indicated by the typical ^{1}J(PW)-coupling of 58.3 Hz.

The phosphanido compound Cp(OC)$_2$(Me$_3$P)W-P(H)*s*Mes (**5**), the Me$_3$P-analogue of **3**, appears suitable for demonstrating the competitive behaviour of Me$_3$P and CO in context with an intramolecular ligand exchange leading to W=P-bond formation. Either the phosphenium complex **4** or its unknown derivative Cp(OC)(Me$_3$P)W=P(H)*s*Mes, characterized by a metal centered chirality, can be expected.

However the thermal stability of **5** is relatively high, so that it cannot be converted by refluxing in benzene to Cp(OC)(Me$_3$P)W=P(H)*s*Mes. Neither a Me$_3$P- nor a CO-elimination could be notified by spectroscopic investigations and after six hours of refluxing, **4** is recoverd almost quantitatively. The attempt to induce a W=P-bond formation via irradiation of **5** does only lead to decomposition.

In order to get a first insight into the cycloadditon behaviour of **4** reaction with sulphur or selenium is performed, which gives rise to the formation of three-membered phosphametallacycles. Stirring a solution of **4** in toluene at room temperature with an equimolar amount of either elemental sulphur or selenium (grey) for 3 or 4 h, respectively, yields **6a** and **6b** as orange-red solids in 66 % (**6a**) or 82 % (**6b**) yield, indicating a controlled cycloaddition of the chalcogen atom to the W=P-bond [Scheme (2b)].

6a shows high solubility in *n*-pentane or toluene and can be stored under nitrogen atmosphere almost unlimited. The ^1J(PW)-coupling of 240.6 Hz lies between the values for **4** [^1J(PW) = 911.3 Hz] and the metallo-phosphine Cp(OC)$_3$W-P(H)*s*Mes (**3**) [^1J(PW) = 55.0 Hz][36] and is typical for systems with a tetravalent phosphorus atom like $\mathrm{Cp(OC)_2\overline{W\text{-}P(H)\mathit{t}Bu\text{-}S}}$ [^1J(PW) = 223.3 Hz].[33]

For the heterocycle $\mathrm{Cp(OC)_2\overline{W\text{-}P(H)\mathit{s}Mes\text{-}Se}}$ (**6b**), a characteristic ^1J(PSe)-coupling of 424.0 Hz can be found. So far this type of complexes with a selenium bridge has also been realized in the case of $\mathrm{Cp(OC)_2\overline{W\text{-}P(H)(\mathit{t}Bu)\text{-}Se}}$ [^1J(PSe) = 446.3 Hz],[33] $\mathrm{Cp(OC)_2\overline{M\text{-}P(Mes)[M'(CO)_3Cp]\text{-}Se}}$ [^1J(PSe) = 412.6 Hz (M, M'= Mo), 410.2 Hz (M = Mo, M' = W), 380.8 Hz (M, M' = W)][55] and $\mathrm{Cp(OC)_2\overline{M\text{-}PPh[N(SiMe_3)_2]\text{-}Se}}$ [^1J(PSe) = 497.8 Hz (M = Mo), 469.2 Hz (M = W)].[28]

In view of the *cis*-configuration of **4** involving the *super*-mesityl-ligand and the cyclopentadienyl moiety in the solid state and solution, the addition of the chalcogen atom occurs under retention of this configuration. As proved by the ^{1}H-NOESY experiments concerning **6a**, no interactions between the cyclopentadienyl moiety and the hydrogen atom at the P-H-bond are indicated. Only a significant interaction of the hydrogens of the C$_5$H$_5$-ligand and the *ortho*-*tert*-butyl group can be recognized.

Experimental Section

General: All manipulations were performed under purified and dried nitrogen by standard Schlenk-type techniques. Solvents were rigorously dried with an appropriate drying agent, distilled and saturated with nitrogen prior to use. IR: Perkin-Elmer 283 grating spectrometer. NMR: JEOL LAMBDA 300 (300.4 MHz, 75.6 MHz and 121.5 MHz for ^{1}H, ^{13}C and ^{31}P, respectively). ^{1}H and ^{13}C spectra are referenced to the residual proton signal or natural abundance carbon signal of C$_6$D$_6$ at δ = 7.15 ppm (^{1}H) or δ = 128.0 ppm (^{13}C), respectively. ^{31}P chemical shifts are referenced to external H$_3$PO$_4$. ^{1}H-NOESY spectra were recorded on a AMX BRUKER 400 referenced to the residual proton signal of C$_6$D$_6$ at δ = 7.15 ppm. Elemental analyses were performed in the laboratories of our institute. Starting materials were prepared by literature methods: Cp(OC)$_2$W=P(H)*s*Mes (**4**)[36] and PMe$_3$.[56] Elemental sulphur and selenium were obtained commercially.

1. [Dicarbonyl(η^5-cyclopentadienyl)(trimethylphosphine)tungstic][2,4,6-tri(*tert*-butyl-phenyl]phosphine (5): A solution of Cp(OC)$_2$W=P(H)*s*Mes (**4**) (35 mg, 0.06 mmol) in benzene (5 mL) is treated with trimethylphosphine (37 mg, 0.49 mmol). After changing of colour from violet to orange, volatiles are removed in vacuo and remaining **5** is washed with *n*-pentane (3 mL) at -78 °C and then dried in vacuo. – Yield: 25 mg (66 %). – Orange powder. **Cp(OC)$_2$[Me$_3$P^2]W-P^1(H)*s*Mes (5): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.60 [d, ^4J(P^{1}CCCH) = 1.8 Hz, 2H, *m*-H], 5.32 [dd, ^1J(P^{1}H) = 216.3 Hz, ^3J(P^{2}WPH) = 4.2 Hz, 1H, P^{1}H], 4.74 [dd, ^3J(P^{2}WCH) = 1.8 Hz, ^3J(P^{1}WCH) = 1.5 Hz, 5H, C$_5$H$_5$], 1.91 [bs, 18H, *o*-C(CH$_3$)$_3$], 1.37 [s, 9H, *p*-C(CH$_3$)$_3$], 0.98 ppm [d, ^2JP^{2}CH = 9.0 Hz, 9H, P(CH$_3$)$_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 229.62 [d, ^2J(PWC) = 20.4 Hz, *cis*-CO], 222.18 [d, ^2J(PWC) = 19.3 Hz, *cis*-CO], 154.39 [d, ^2J(P^{1}CC) = 6.9 Hz, *o*-C], 146.83 (s, *p*-C), 140.26 [dd, ^1J(P^{1}C) = 61.4 Hz, ^3J(P^{2}WPC) = 2.2 Hz, *ipso*-C], 121.88 (s, *m*-C), 91.24 [d, ^2J(PWC) = 3.4 Hz, C$_5$H$_5$], 39.20 [s, *o*-$\underline{\text{C}}$(CH$_3$)$_3$], 34.83 [s, *p*-$\underline{\text{C}}$(CH$_3$)$_3$], 32.63 [d, ^4J(P^{1}CCCC) = 7.6 Hz, *o*-C($\underline{\text{C}}$H$_3$)$_3$], 31.52 [s, *p*-C($\underline{\text{C}}$H$_3$)$_3$], 20.35 ppm [d, ^1J(P^{2}C) = 35.2 Hz, P(CH$_3$)$_3$]. – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = -138.2 [d, ^1J(P^{1}W) = 58.3 Hz, ^2J(PWP) = 36.5 Hz,], -12.8 ppm [d, ^1J(P^{2}W) = 252.7 Hz, ^2J(PWP) = 36.5 Hz]. – **IR** (*n*-pentane): ν(CO) = 1923 (s), 1851 (vs) cm^{-1}. Calc. for C$_{28}$H$_{44}$O$_2$P$_2$W (658.4): C, 51.08; H, 6.73. Found: C, 51.03; H, 6.76.

2. Dicarbonyl(η^5-cyclopentadienyl)[(η^2-(2,4,6-tri(*tert*-butyl)phenyl)thiophosphinito-κS,κP]-tungsten(II) (6a): A solution of Cp(OC)$_2$W=P(H)*s*Mes (**4**) (38 mg, 0.07 mmol) in benzene (5 mL) is combined with elemental sulphur (3 mg, 0.07 mmol) at room temperature and stirred for 3 h. Insolubles are separated by filtration and the filtrate is evaporated in vacuo to yield **6a**, which is washed three times with cold (0 °C) *n*-pentane (2 mL each) and dried in vacuo. – Yield: 23 mg (66 %). – Orange-red powder. **Cp(OC)$_2$W-P(H)(*s*Mes)-S (6a): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.38 [d, ^4J(PCCCH) = 4.5 Hz, 2H, *m*-H], 5.65 [d, ^1J(PH) = 459.6 Hz, 1H, PH], 4.59 (s, 5H, C$_5$H$_5$), 1.58 [s, 18H, *o*-C(CH$_3$)$_3$], 1.12 ppm [s, 9H, *p*-C(CH$_3$)$_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 242.38 [d, ^2J(PWC) = 18.3 Hz, *cis*-CO], 228.33 (s, *trans*-CO), 158.77 [d, ^2J(PCC) = 7.5 Hz, *o*-C], 150.30 (s, *p*-C), 128.89 [d, ^1J(PC) = 57.9 Hz, *ipso*-C], 122.35 [d, ^3J(PCCC) = 12.1 Hz, *m*-C], 91.88 (s, C$_5$H$_5$), 40.16 [d, ^3J(PCCC) = 3.4 Hz, *o*-$\underline{\text{C}}$(CH$_3$)$_3$], 34.40 [s, *p*-$\underline{\text{C}}$(CH$_3$)$_3$], 33.69 [s, *o*-C($\underline{\text{C}}$H$_3$)$_3$], 30.87 ppm [s, *p*-C($\underline{\text{C}}$H$_3$)$_3$]. – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = -61.3 ppm [s, ^1J(PW) = 240.6 Hz]. – **IR** (*n*-pentane): ν(PH) = 2281 (w); ν(CO) = 1956 (vs), 1875 (s) cm^{-1}. Calc. for C$_{25}$H$_{35}$O$_2$PSW (614.4): C, 48.87; H, 5.74; S, 5.22. Found: C, 48.69; H, 5.71; S, 5.20.

3. Dicarbonyl(η^5-cyclopentadienyl)[(η^2-(2,4,6-tri(*tert*-butyl)phenyl)selenophosphinito-κSe,κP]-tungsten(II) (6b): Analogous to **6a** from 194 mg (0.33 mmol) Cp(OC)$_2$W=P(H)*s*Mes (**4**), 26 mg (0.33 mmol) elemental selenium in toluene (10 mL) after 4 h. – Yield: 176 mg (82 %). – Orange-red solid. **Cp(OC)$_2$W-P(H)(*s*Mes)-Se (6b): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.12 [d, ^4J(PCCCH) = 3.7 Hz, 2H, *m*-H], 6.16 [d, ^1J(PH) = 447.6 Hz, 1H, PH], 4.59 (s, 5H, C$_5$H$_5$), 1.57 [s, 18H, *o*-C(CH$_3$)$_3$], 1.11 ppm [s, 9H, *p*-C(CH$_3$)$_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 240.44 [d, ^2J(PWC) = 21.4 Hz, *cis*-CO], 227.27 (s, *trans*-CO), 159.00 [d, ^2J(PCC) = 7.6 Hz, *o*-C], 149.09 (s, *p*-C), 128.89 [d, ^1J(PC) = 57.6 Hz, *ipso*-C], 122.13 [d, ^3J(PCCC) = 12.4 Hz, *m*-C], 91.35 (s, C$_5$H$_5$), 40.29 [d, ^3J(PCCC) = 3.4 Hz, *o*-$\underline{C}$(CH$_3$)$_3$], 34.02 [s, *p*-$\underline{C}$(CH$_3$)$_3$], 33.88 [s, *o*-C($\underline{C}$H$_3$)$_3$], 30.87 ppm [s, *p*-C($\underline{C}$H$_3$)$_3$]. – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = -60.5 ppm [s, ^1J(PW) = 256.4 Hz, ^1J(PSe) = 424.0 Hz]. – **IR** (benzene): ν(CO) = 1955 (vs), 1875 (vs) cm^{-1}. Calc. for C$_{25}$H$_{35}$O$_2$PSeW (661.3): C, 45.41; H, 5.33. Found: C, 45.28; H, 5.35.

4. Quantum chemical calculations[1] : All calculations were done with the Turbomole 5.6[57, 58] program at the density functional level, using the hybrid B3LYP[59] functional (based on the work of Becke[60]), and a split-valence polarisation basis set (SVP)[61] for the light atoms H, C and P. For tungsten we used a quasirelativistic small-core 14-valence-electron pseudopotential with a (8s7p6d)/[6s5p3d] valence basis set.[62] All structures were fully optimized without symmetry constraints.

5. X-ray analyses of Cp(OC)$_2$[*s*Mes(H)$_2$P]W-Cl (1), [Cp(OC)$_3$W-P(H)$_2$(*s*Mes)]BF$_4$ (2) and Cp(OC)$_2$W=P(H)*s*Mes (4): Suitable crystals for the structure determination of **1**, **2** and **4** could be obtained from a saturated toluene (**1**), dichloromethane (**2**) or *n*-pentane (**4**) solution at room temperature. Data collection was performed on an Enraf-Nonius CAD4-diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) at 173(2) K.[63-65] The structures were solved using the Patterson-method and cell parameters were determined and refined using SHELXS-97[66] and SHELXL-97.[67]

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[1] DFT calculations performed by Dipl.-Chem. S. Riedel in the research group of Prof. Dr. M. Kaupp, Institut für Anorganische Chemie, Universität Würzburg.

*Crystal Data for Compounds **1**, **2** and **4**:*

	1	**2**	**4**
identification	andi10	andi19	andi14
mol formula	$C_{25}H_{36}WClO_2P$	$C_{18}H_{24}WBF_4O_2P$	$C_{25}H_{25}WO_2P$
mol wt	618.81	465.45	465.88
wavelength (Å)	0.71073	0.71073	0.71073
temp (K)	173(2)	173(2)	173(2)
cryst size (mm)	0.40 x 0.25 x 0.15	0.28 x 0.15 x 0.07	0.16 x 0.12 x 0.09
cryst syst	triclinic	monoclinic	monoclinic
space group	*P-1*	*P2(1)*/c	*P2(1)*/c
a (Å)	8.3635(19)	20.303(4)	20.911(5)
b (Å)	9.870(2)	8.1722(17)	10.577(2)
c (Å)	16.652(4)	16.829(4)	11.419(3)
α (°)	105.080(4)	90	90
β (°)	91.159(4)	95.796(4)	102.821(4)
γ (°)	107.843(4)	90	90
vol ($Å^3$), *Z*	1255.9(5), 2	2778.0(10), 6	2462.4(9), 4
ρ (calcd) (Mgm^{-3})	1.636	1.669	1.571
F(000)	616	1384	1160
μ (mm^{-1})	4.787	4.268	4.773
θ range for data collecn (deg)	2.26 – 25.07	2.54 – 25.09	2.66 – 25.04
no. of rflns collected	24485	4916	46352
no. of indep reflns	4487	4916	4346
abs cor.	empirical	empirical	empirical
no. of data/restraints/params	4487 / 0 / 319	4916 / 0 / 342	4346 / 243 / 340
goodness of fit on F^2	0.857	1.241	1.183
R1[a]	0.0241	0.0352	0.0385
wR2[b]	0.0589	0.0801	0.0710
largest diff peak and hole ($eÅ^{-3}$)	1.693 and -0.413	1.386 and -1.809	1.355 and -1.006

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

P-Alkylation and P-Acylation of the Phosphenium Complex $C_5H_5(OC)_2W{=}P(H)$*s*Mes via the Anionic Phosphinidene Complex $[Cp(OC)_2W{=}P($*s*Mes$)]Li$

Introduction

P-H-functionalized phosphenium metal complexes $Cp(OC)_2M=P(H)R$ (R = alkyl, aryl) of molybdenum and tungsten contain besides the M=P-bond a P-H-unit as a center of pronounced reactivity. However the knowledge concerning the reactivity of this function is still rather limited,[1-5] because of the often insufficient stability of the M=P(H)-complexes, preventing a targeted study.[1, 2] An important exception in this series is the *super*-mesitylphosphenium complex $Cp(OC)_2W=P(H)$*s*Mes (**1**) which is the first at room temperature isolable P-H-functionalized phosphenium tungsten complex.[6] In addition the structure was determined by x-ray analysis and the investigations towards stereoselective reactions at the W=P-bond started.[7]

Taking into account the reactivity of *primary* and *secondary* phosphines for which the lithiation is an established step in diverse reaction sequences,[8] the analogous process should be usable for the metallation of the P-H-function in phosphenium metal complexes like **1**.

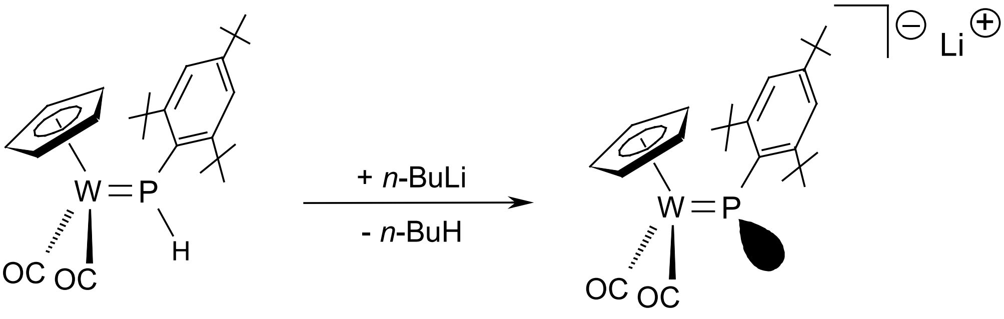
First evidence for a selective reaction at the P-H-bond is given by the introduction of a chloro substituent at the sp^2-phosphorus using tetrachloromethane to give the phosphenium complex $Cp(OC)_2W=P(Cl)$*s*Mes.[6] If a solution of **1** in THF is combined at room temperature with an equimolar amount of K(O*t*Bu) followed by the addition of an excess of methyliodide, the metyhlphosphenium complex $Cp(OC)_2W=P(Me)$*s*Mes (**4a**) is formed.[6] This reaction gives first indication for the formation of an anionic W=P(*s*Mes)$^{\ominus}$-species, at least as an intermediate, via deprotonation of the P-H-bond in the primary step. This observation encouraged us to perform controlled H/Li-exchange reactions at the phosphenium-phosphorus aiming to the formation of $[Cp(OC)_2W=P($*s*Mes$)]Li$ (**2**), which is a highly interesting reagent concerning diverse derivatizations.

In this chapter we present the first successful lithiation reaction to generate **2**, which is to our knowledge the first anionic phosphinidene[9-12] complex, and reactions with diverse carbon electrophiles.

Results and Discussion

Reactivity Studies

The treatment of the phosphenium complex $Cp(OC)_2W{=}P(H)$*s*Mes (**1**), dissolved in THF, with *n*-BuLi at -78 °C results in an immediately change of colour of the solution from violet to darkgreen. The generated anionic species $[Cp(OC)_2W{=}P($*s*Mes$)]Li$ (**2**), which shows a ^{31}P-NMR-resonance in $[D_8]$-THF at 861.4 ppm, is for several hours at room temperature storeable in the presence of donor solvents like THF or dimethoxyethane. On the basis of these data we formulate the anionic species **2** as shown in Scheme (1).

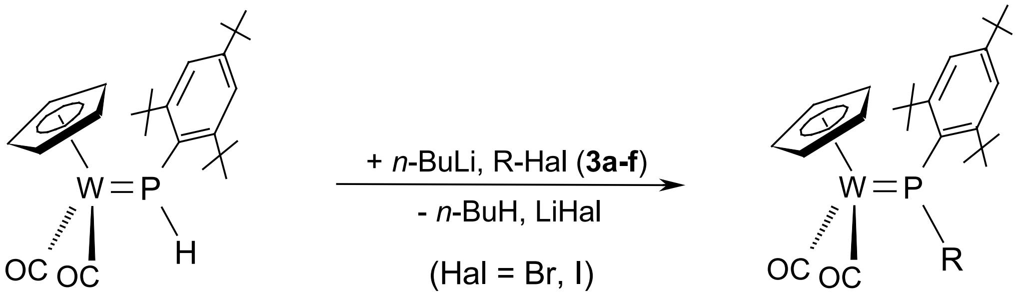


1 **2**

Removal of the stabilizing solvents leads to the decomposition of **2**. In addition degradation is also observed at room temperature within 1 h in aliphatic solvents as well as benzene or toluene. The high half intensity width of the phosphorus resonances prevents the detectation of the rather small ^1J(PW)-coupling constants. In comparison to the bent phosphinidene complexes found by *Lappert* 1987[13] {$Cp_2W{=}P(2,4,6\text{-}t\text{Bu-}C_6H_2)$ $\delta^{31}P$ = 661.1 ppm [^1J(PW) = 154 Hz]; $Cp_2W{=}PCH(SiMe_3)_2$ $\delta^{31}P$ = 679.6 ppm [^1J(PW) = 144 Hz]} we postulate **2** to be a bent anionic phoshinidene complex. The detected ^{7}Li-resonance ([D_8]-THF / 116.6 MHz) at 1.26 ppm can be compared to known lithium phosphanides, for example 3,5-(*t*-Bu)$_2$-C_6H_3(*t*-Bu)PLi (2.6 ppm),[14] $Li_2[RPCH_2CHMeO]$ (R = Ph, Mes, Tipp; 0.9 – 4.6 ppm)[15] or [{*t*-BuC(PMes)$_2$}Li(THF)$_3$] (-0.69 ppm).[16]

In order to examine the reactivity of **2** reactions with alkyl halides are performed. Combination of **1** in THF with an equimolar amount of *n*-BuLi followed by the addition of metyhl, ethyl, *iso*-propyl, butyl and allyl iodide (**3a-d,f**) as well as benzyl bromide (**3e**) leads to the P-alkylated phosphenium tungsten complexes $Cp(OC)_2W{=}P(R)$*s*Mes [R = Me (**4a**), Et (**4b**), *i*Pr (**4c**), *n*Bu

(**4d**), CH_2Ph (**4e**), $CH_2CH=CH_2$ (**4f**)] immediately after addition of the electrophile, whereby a colour change from violet to darkblue can be noticed [Scheme (2)].



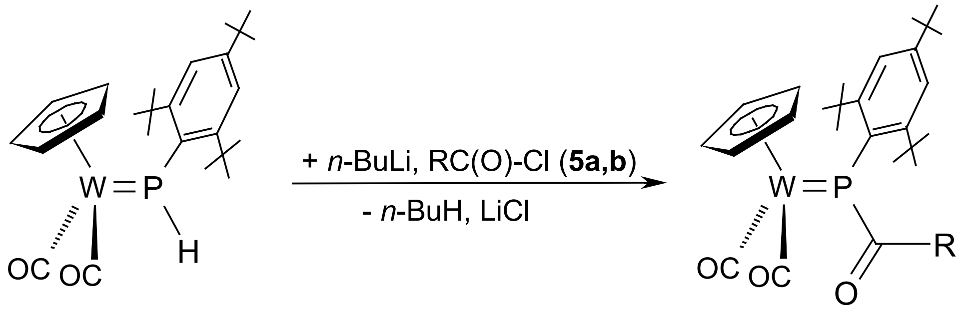
(2)

1 **4a-f**

	a	b	c	d	e	f
R	Me	Et	*i*Pr	*n*Bu	CH_2Ph	$CH_2CH=CH_2$

All complexes are obtained as violet solids in yields between 73 (**4c**) – 83 % (**4d**), respectively, with exception of **4f** which is isolated with 61 % yield as violet oil. The spectroscopical properties of **4a-f** are almost similar, obvious from the ^{31}P-NMR-data with the resonances of **4a-f** appearing in a narrow range from 264.0 (**4a**) – 311.2 ppm (**4c**) and the nearly identical ^{1}J(PW)-couplings [601.4 (**4c**) – 625.7 Hz (**4f**)]. All the diorganophosphenium tungsten complexes are soluble in aliphatic solvents and show a high tendency for crystallization especially in *n*-pentane. Therefore the structures of **4a-e** are confirmed by x-ray diffraction analyses [Fig. (1)-(5)].

In an analogous manner it is possible to generate the first tungsten acylphosphenium complexes after reaction of **1** with *n*-BuLi in THF and addition of acetyl or benzoyl chloride (**5a,b**) to give **6a**,**b** [Scheme (3)].



(3)

1 **6a,b**

	a	b
R	Me	Bz

6a,b are isolated as turquoise solids in a yield of 78 (**6a**) and 63 % (**6b**), respectively, after a reaction time of 12 h. The obtained ^{1}J(PW)-couplings of 573.5 (**6a**) and 575.9 Hz (**6b**), which are reduced around 50 Hz compared to the alkylphosphenium compounds **4a-f** reflect the different bonding situation P_{sp2}-C_{sp2} (**6a**,**b**) vs. P_{sp2}-C_{sp3} (**4a-f**). The ^{31}P-NMR-shifts of 291.4 ppm (**6a**) as well as 275.6 ppm (**6b**) are characteristic for phosphenium tungsten complexes. In both complexes no indication for an additional coordination of the carboxyl moiety to tungsten can be found, nevertheless the W=P-C=O-arrangement **6a**,**b** should be a valuable diene type system in cycloadditions.

Structural Investigation

Crystals of Cp(OC)$_2$W=P(R)*s*Mes [R = Me (**4a**), Et (**4b**), *i*Pr (**4c**), *n*Bu (**4d**), CH$_2$Ph (**4e**)] suitable for structure determination could be obtained from a saturated *n*-pentane solution at room temperature.

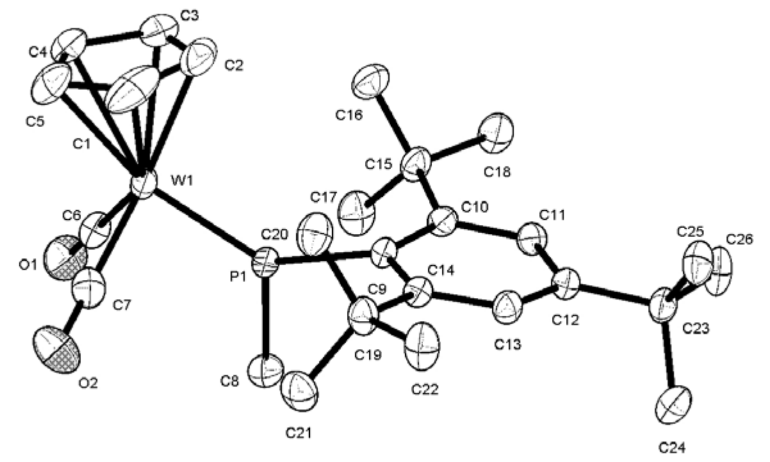


Fig. (1). Molecular structure of Cp(OC)$_2$W=P(Me)*s*Mes (**4a**) - The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: W(1)-P(1)2.2468(7), P(1)-C(9) 1.850(3), P(1)-C(8) 1.829(3), W(1)-C(6) 1.957(3), W(1)-C(7) 1.954(3), M-W(1)-P(1) 133.6, C(9)-P(1)-W(1) 137.29(8), C(8)-P(1)-W(1) 123.86(10), C(8)-P(1)-C(9) 98.79(12), C(6)-W(1)-P(1) 89.02(8), C(7)-W(1)-P(1) 88.43(9), C(7)-W(1)-C(6) 80.99(12), C(7)-W(1)-P(1)-C(9) -130.10(15), C(6)-W(1)-P(1)-C(9) 148.88(15), P(1)-C(9)-C(10)-C(11) -161.4(2), P(1)-C(9)-C(14)-C(13) 161.2(2), C(14)-C(9)-C(10)-C(11) 6.9(4), C(13)-C(14)-C(9)-C(10) -7.3(4).

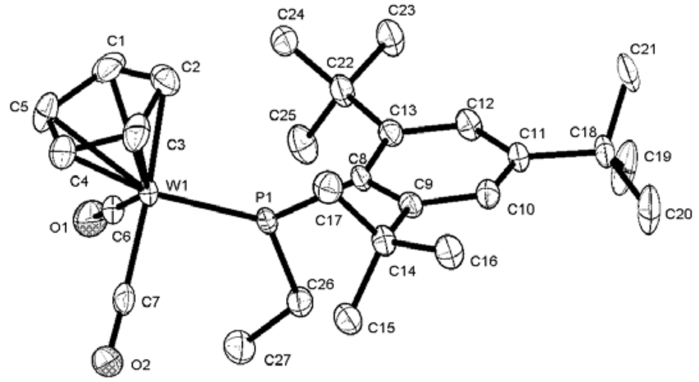


Fig. (2). Molecular structure of Cp(OC)$_2$W=P(Et)*s*Mes (**4b**) - The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: W(1)-P(1) 2.2540(11), P(1)-C(8) 1.853(3), P(1)-C(26) 1.847(3), W(1)-C(6) 1.946(4), W(1)-C(7) 1.959(4), M-W(1)-P(1) 128.73, C(8)-P(1)-W(1) 136.36(10), C(26)-P(1)-W(1) 128.36(11), C(26)-P(1)-C(8) 95.26(14), C(6)-W(1)-P(1) 90.70(11), C(7)-W(1)-P(1) 90.82(11), C(6)-W(1)-C(7) 82.47(15), C(6)-W(1)-P(1)-C(8) 131.00(19), C(7)-W(1)-P(1)-C(8) -146.52(19), P(1)-C(8)-C(13)-C(12) –156.6(2), P(1)-C(8)-C(9)-C(10) 155.7(2), C(9)-C(8)-C(13)-C(12) 7.80(4), C(10)-C(9)-C(8)-C(13) -8.60(4).

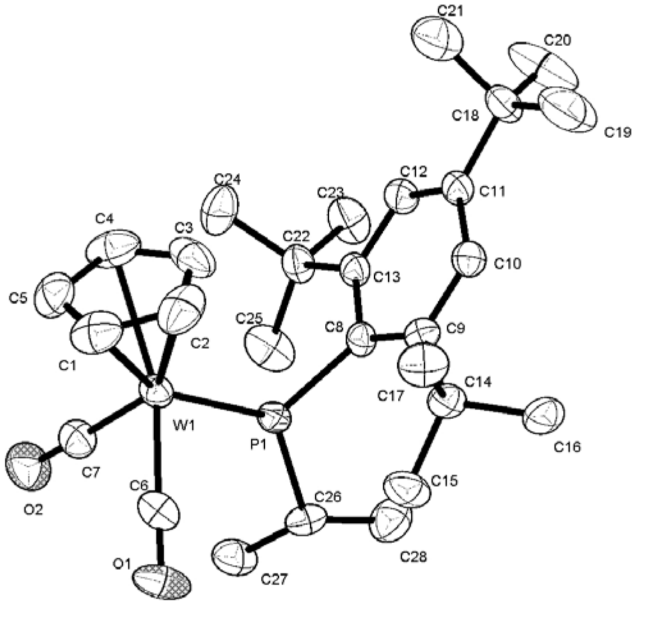


Fig. (3). Molecular structure of Cp(OC)$_2$W=P(*i*Pr)*s*Mes (**4c**) - The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: W(1)-P(1) 2.2436(11), P(1)-C(8) 1.839(4), P(1)-C(26) 1.873(4), W(1)-C(6) 1.954(4), W(1)-C(7) 1.947(4), M-W(1)-P(1) 129.10, C(8)-P(1)-W(1) 120.52(12), C(26)-P(1)-W(1) 127.60(14), C(8)-P(1)-C(26) 111.23(18), C(6)-W(1)-P(1) 87.05(13), C(7)-W(1)-P(1) 95.75(12), C(7)-W(1)-C(6) 79.43(18), C(7)-W(1)-P(1)-C(8) 140.62(19), C(6)-W(1)-P(1)-C(8) -140.32(19), P(1)-C(8)-C(13)-C(12) 157.5(3), P(1)-C(8)-C(9)-C(10) –159.9(3), C(12)-C(13)-C(8)-C(9) -7.0(5), C(10)-C(9)-C(8)-C(13) 4.1(5), C(9)-C(10)-C(11)-C(12) -5.9(6).

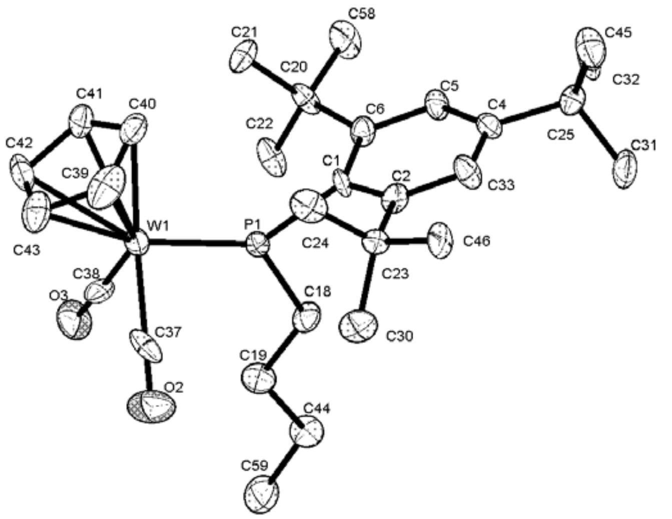


Fig. (4). Molecular structure of Cp(OC)$_2$W=P(*n*Bu)*s*Mes (**4d**) - The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: W(1)-P(1) 2.252(3), P(1)-C(18) 1.852(9), W(1)-C(37) 1.951(11), W(1)-C(38) 1.942(12), P(1)-C(1) 1.868(9), C(1)-P(1)-W(1) 135.2(3), C(18)-P(1)-C(1) 95.8(4), C(18)-P(1)-W(1) 128.9(3), C(37)-W(1)-P(1) 90.0(3), C(38)-W(1)-P(1) 93.2(3), C(38)-W(1)-C(37) 81.7(4), P(1)-C(1)-C(2)-C(33) 156.3(8), P(1)-C(1)-C(6)-C(5) -158.4(7), C(1)-C(6)-C(5)-C(4) -1.3(14), C(2)-C(1)-C(6)-C(5) 7.8(14).

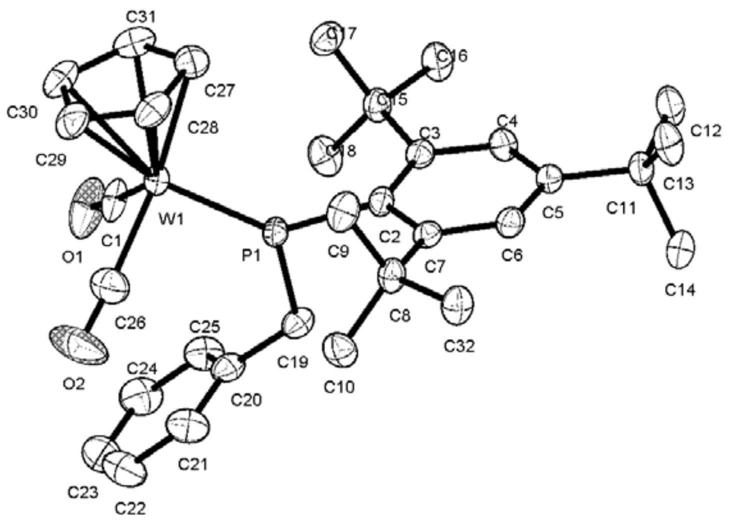


Fig. (5). Molecular structure of Cp(OC)$_2$W=P(CH$_2$Ph)*s*Mes (**4e**) - The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: W(1)-P(1) 2.2502(6), P(1)-C(2) 1.853(2) , P(1)-C(19) 1.864(2), W(1)-C(1) 1.942(2), W(1)-C(26) 1.953(3), C(2)-P(1)-W(1) 134.32(7), C(19)-P(1)-W(1) 129.96(7), C(2)-P(1)-C(19) 95.70(10), C(1)-W(1)-P(1) 89.84(7), C(26)-W(1)-P(1) 93.33(8), C(1)-W(1)-C(26) 82.30(12), C(1)-W(1)-P(1)-C(2) 135.65(139), C(26)-W(1)-P(1)-C(2) -142.07(13), C(4)-C(3)-C(2)-P(1) -168.19(16), P(1)-C(2)-C(7)-C(6) 167.53(16), C(4)-C(3)-C(2)-C(7) 3.2(3), C(3)-C(2)-C(7)-C(6) -3.8(3), C(4)-C(5)-C(6)-C(7) 0.9(3).

For all five complexes the coordination geometry around the central tungsten atom can be described as pseudo-octahedral three legged piano stool. The cyclopentadienyl ligand is occupying three facial coordination sites, whereby two legs are formed by the carbonyl ligands and the third leg by the double bonded phosphenium ligand. This is proved by the bond angles between the carbonyl ligands and the phosphine moiety, which are in the range from 89.0° (**4a**) to 95.8° (**4c**) or 87.1° (**4c**) to 93.3° (**4e**), respectively for the P1-W1-CO angles and from 79.4° (**4c**) to 82.5° (**4b**) for the OC-W1-CO angle. All these are close to the expected angle of 90°.

The geometry of the the phosphorus atom is exactly trigonal planar, with values for the sum of angles from 359.35° (**4c**) to 359.98° (**4b**,**e**). As a result of sp^2-hybridization, the phosphenium ligand can be regarded as a three-electron donor, giving the tungsten atom a number of 18 valence electrons.

The W1-P1-*ipso*-C angles (134.3°-137.3°) as well as the W1-P1-*alkyl*-C angles (123.7°-130.0°) are expanded. As a consequence the angles between the *ipso*-C-atom, P1 and the C-alkyl substituent are significantly reduced in comparison to the ideal value of 120° [98.79° (**4a**), 95.26° (**4b**), 95.80° (**4d**), 95.70° (**4e**)]. A similar diminished angle can also be found for $Cp(OC)_2W{=}P(tBu)_2$[17] (109.4°). Due to the greater steric demand of the *iso*-propyl ligand in **4c** in comparison to the other diorganophosphenium complexes the *ipso*-C-P1-C26-angle is closer to the ideal value (111.23°). Therefore the *super*-mesityl-ligand is bent closer to the cyclopentadienyl moiety than in the complexes **4a**,**b**,**d**,**e**, with a nearly ideal W1-P1-alkyl-C-angle (120.5°) and a slightly increased W1-P1-*ipso*-C-angle (127.6°).

The P1-*ipso*-C bond lengths (1.84 Å – 1.87 Å) are in the range expected for a P_{sp2}-C_{sp2} single bond[18] and exclude π–interaction between the phosphorus atom and the aromatic ring system.

The tungsten-phosphorus bond lengths are in the range from 2.24 Å - 2.25 Å and are typical for M-P-double-bond-systems, for which a theoretical bond length of 2.26 Å is calculated.[19-21] In addition they are nearly identical to the value of the symmetrically substituted phosphorus in $Cp(OC)_2W{=}P(tBu)_2$ (2.28 Å).[17] The bond lengths of the starting material [$Cp(OC)_2W{=}P(H)s$Mes (**1**); 2.25 Å][22] and the related P-H-phosphenium complex $Cp^*(Me_3P)_2Mo{=}P(H)s$Mes (2.25 Å)[23] are in the same range.

The high steric demand of the *s*Mes-ligand causes on the one hand a severe distortion of the aryl group planarity [C14-C9-C10-C11 6.9°, C13-C14-C9-C10 -7.3° (**4a**); C9-C8-C13-C12 7.80°, C10-C9-C8-C13 8.60° (**4b**); C12-C13-C8-C9 -7.0°, C9-C10-C11-C12 -5.9° (**4c**); C1-C6-C5-C4 -1.3°, C2-C1-C6-C5 7.8° (**4d**); C4-C3-C2-C7 3.2°, C3-C2-C7-C6 -3.8° (**4e**)], on the other hand this effect determines the arrangement of the *super*-mesityl group. In order to avoid interaction of the *ortho*-*tert*-butyl-groups with the cyclopentadienyl- and the carbonyl-ligands the aryl ligand is bent towards the metal fragment out of the expected linear position. The differences from the theoretical torsion angle of 180° are significant [P1-C9-C10-C11 -161.4°, P1-C9-C14-C13 161.2° (**4a**); P1-C8-C13-C12 –156.6°, P1-C8-C9-C10 155.7° (**4b**), P1-C8-C13-C12 157.5°, P1-C8-C9-C10 –159.9° (**4c**), P1-C1-C2-C33 156.3°, P1-C1-C6-C5 -158.4° (**4d**); C4-C3-C2-P1 -168.19°, P1-C2-C7-C6 167.53° (**4e**)].

In summary the conformation of **4a-e** and the short W-P-distance is in agreement with a frontier orbital interaction of the fragments $Cp(OC)_2W^{\ominus}$ and *s*Mes(R)$P^{\oplus}$ (R = Me, Et, *i*Pr, Bu, CH_2Ph) according to the description in chapter I.

The complexes **4a-e** are showing *cis*-configuration regarding the *super*-mesityl-ligand and the cyclopentadienyl moiety, which is in accordance with the situation for $Cp(OC)_2W=P(H)$*s*Mes (**1**).[22]

DFT Calculations of the Phosphenium Complexes $Cp(OC)_2W=P(R)$*s*Mes [R = Me, Et, *i*Pr, *n*Bu; CH_2Ph (4a-e)] Performed by S. Riedel

The structure determination for **4a-e** reveals a *cis*-orientation of the *s*Mes-substituent on the phosphorus atom relative to the Cp-ligand [Fig. (1)-(5)]. As theoretical calculations for the P-H-functionalized complexes $Cp(OC)_2W=P(H)R$ [R = *s*Mes (**1**), *tert*-Butyl, Ph and Mes (**4**, **7a**-**c**)] proved in chapter I,[22] a higher stability for the *cis*-isomer in comparison to the *trans*-arrangement is only found for the *s*Mes-system. For all the other investigated substituents (R = *tert*-Butyl, Ph, Mes) the *trans*-arrangement is slightly favoured.

Therefore we now focused on the *cis*-arranged compounds $Cp(OC)_2W=P(R)$*s*Mes [R = Me, Et, *i*Pr, *n*Bu, CH_2Ph (**4a**-**e**)] in order to investigate the influence of the introduced alkyl substituent on the stability of the isomers. As shown in Table (1), the computations confirm a higher stability for the *cis*-isomer in comparison to the *trans*-arrangement in all cases in the range from by 11.3 kJ/mol (**4e**) up to 34.8 kJ/mol (**4d**). Compared to the value for $Cp(OC)_2W=P(H)$*s*Mes (**1**) (15.2 kJ/mol) the bulkier alkyl substituents leads to an even more favoured *cis*-arrangement, despite for the benzyl system **4e**. This fact again confirms that the structural preference for *cis*-isomer is steric in origin with the determining interactions found between the *s*Mes-substituent and the two carbonyl ligands in the *trans*-arrangement. Because of the bulkier P-alkyl groups the *s*Mes-ligand is even more forced towards the strongly and rigidly bound carbonyl ligands in the *trans*-isomer thus favouring further the *cis*-arrangement.

R-Ligand	Isomer	E_{rel} [kJ/mol]
Me (**4a**)	cis	-17.4
Me	trans	0
Et (**4b**)	cis	-22.5
Et	trans	0
*i*Pr (**4c**)	cis	-18.4
*i*Pr	trans	0
*n*Bu (**4d**)	cis	-34.8
*n*Bu	trans	0
CH_2Ph (**4e**)	cis	-11.3
CH_2Ph	trans	00

Table (1). Computed *cis*/*trans* energy differences and for $Cp(OC)_2W{=}P(R)$*s*Mes
[R = Me, Et, *i*Pr, *n*Bu, CH_2Ph (**4a**-**e**)]

Experimental Section

General: All manipulations were performed under purified and dried nitrogen by standard Schlenk-type techniques. Solvents were rigorously dried with an appropriate drying agent, distilled and saturated with nitrogen prior to use. IR: Spectra were recorded using a Perkin-Elmer 283 grating spectrometer. Samples were prepared as solutions in a NaCl cell with 0.1 mm path length with a resolution of about 2 cm^{-1}. NMR: JEOL LAMBDA 300 (300.4 MHz, 75.6 MHz and 121.5 MHz for ^1H, ^{13}C and ^{31}P, respectively). ^1H and ^{13}C spectra are referenced to the residual proton signal or natural abundance carbon signal of C_6D_6 at $\delta = 7.15$ ppm (^1H) or $\delta = 128.0$ ppm (^{13}C), respectively. ^{31}P chemical shifts are referenced to external H_3PO_4. ^1H-NOESY spectra were recorded on a AMX BRUKER 400 referenced to the residual proton signal of C_6D_6 at $\delta = 7.15$ ppm. Melting points were obtained by differential thermoanalysis (Du Pont 9000 Thermal Analysis System). Elemental analyses were performed in the laboratories of the Institut für Anorganische Chemie der Universität Würzburg. $Cp(OC)_2W{=}P(H)$*s*Mes[6] (**1**) was prepared according to a literature procedure. $Cp(OC)_2W{=}P(Me)$*s*Mes[6] (**4a**) was obtained earlier via an alternative route too. *n*-BuLi was obtained commercially. Methyl, ethyl, *iso*-propyl, butyl and allyl iodide, benzyl bromide (**3a-f**) and acetyl or benzoyl chloride (**5a,b**) were obtained commercially and distilled before use.

1. Dicarbonyl(η^5-cyclopentadienyl){λ^4-[2,4,6-tri(*tert*-butyl)phenyl](methyl)phosphinediyl}-tungsten(II) (4a): To a solution of 89 mg (0.15 mmol) $Cp(OC)_2W{=}P(H)$*s*Mes (**1**) in 5 mL THF 10 mg (0.15 mmol) *n*-BuLi is added at -78 °C whereupon the colour of the solution turns from violet to dark green immediately. After stirring for 30 min addition of 28 mg (0.15 mmol) methyl iodide (**3a**) results in change of colour back to violet. The solution is allowed to warm up to room temperature, volatiles are removed in vacuo and the remaining solid is extracted five times with 5 mL *n*-pentane each. The combined *n*-pentane layers are evaporated to dryness and the resulting **4a** is dried in vacuo. – Yield: 72 mg (80 %). – Violet microcrystalline solid. M.p. 135 °C (dec.).[6] **$Cp(OC)_2W{=}P(Me)$*s*Mes (4a): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.47 [d, ^4J(PCCCH) = 2.1 Hz, 2H, *m*-H], 5.12 (s, 5H, C_5H_5), 1.72 [d, ^2J(PCH) = 14.7 Hz, 3H, PCH_3], 1.52 [s, 18H, *o*-$C(CH_3)_3$], 1.24 ppm [s, 9H, *p*-$C(CH_3)_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 230.98 [d, ^2J(PWC) = 13.7 Hz, *cis*-CO], 150.95 [d, ^2J(PCC) = 2.0 Hz, *o*-C], 150.19 (s, *p*-C), 127.95 [d, ^1J(PC) = 24.8 Hz, *ipso*-C], 122.69 [d, ^3J(PCCC) = 6.9 Hz, *m*-C], 94.10 [d, ^2J(PWC) = 1.1 Hz, C_5H_5], 41.17 [d, ^1J(PC) = 18.3, PCH_3], 38.34 [d, ^3J(PCCC) = 1.1 Hz, *o*-$\underline{C}(CH_3)_3$], 35.03 [s, *p*-$\underline{C}(CH_3)_3$], 33.89 [s, *o*-$C(\underline{C}H_3)_3$], 31.23 ppm [s, *p*-$C(\underline{C}H_3)_3$]. – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = 264.0 ppm [s, ^1J(PW) = 619.6 Hz]. – **IR** (*n*-pentane): ν(CO) = 1940 (vs), 1868 (vs) cm^{-1}.[6] Calc. for $C_{26}H_{37}O_2PW$ (596.4): C, 53.86; H, 6.62. Found: C, 53.68; H, 6.44.

2. Dicarbonyl(η^5-cyclopentadienyl){λ^4-[2,4,6-tri(*tert*-butyl)phenyl](ethyl)phosphinediyl}-tungsten(II) (4b): Analogous to **4a** from 183 mg (0.31 mmol) $Cp(OC)_2W{=}P(H)$*s*Mes (**1**), 20 mg (0.31 mmol) *n*-BuLi, 46 mg (0.31 mmol) ethyl iodide (**3b**) in 10 mL THF. – Yield: 156 mg (81 %). – Violet microcrystalline solid. M.p. 119 °C (dec.). **$Cp(OC)_2W{=}P(Et)$*s*Mes (4b): ^{1}H{^{31}P}-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.47 (s, 2H, *m*-H), 5.11 (s, 5H, C_5H_5), 1.63 [q, ^3J(HCCH) = 7.6 Hz, 2H, $C\underline{H_2}CH_3$], 1.51 [s, 18H, *o*-$C(CH_3)_3$], 1.41 [t, ^3J(HCCH) = 7.6 Hz, 3H, $CH_2C\underline{H_3}$], 1.25 ppm [s, 9H, *p*-$C(CH_3)_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 232.03 [d, ^2J(PWC) = 12.8 Hz, *cis*-CO], 150.68 [d, ^2J(PCC) = 1.7 Hz, *o*-C], 150.29 (s, *p*-C), 128.89 [d, ^1J(PC) = 57.7 Hz, *ipso*-C], 122.64 [d, ^3J(PCCC) = 6.2 Hz, *m*-C], 94.04 [d, ^2J(PWC) = 1.1 Hz, C_5H_5], 48.58 [d, ^3J(PCCC) = 13.4 Hz, *o*-$\underline{C}(CH_3)_3$], 38.45 [s, *p*-$\underline{C}(CH_3)_3$], 33.99 [s, *o*-$C(\underline{C}H_3)_3$], 31.23 [s, *p*-$C(\underline{C}H_3)_3$], 22.04 [d, ^1J(PC) = 97.9 Hz, PCH_2], 12.08 ppm [d, ^2J(PCC) = 0.4 Hz, $PCH_2\underline{C}H_3$]. –

^{31}P{^{1}H}-NMR ([D$_6$]-benzene, 121.5 MHz): δ = 293.0 ppm [s, ^{1}J(PW) = 616.0 Hz]. – **IR** (*n*-pentane): ν(CO) = 1940 (vs), 1866 (vs) cm^{-1}. Calc. for $C_{27}H_{39}O_2PW$ (610.4): C, 53.13; H, 6.44. Found: C, 52.24; H, 6.27.

3. Dicarbonyl(η^5-cyclopentadienyl){λ^4-[2,4,6-tri(*tert*-butyl)phenyl](*iso*-propyl)phosphinediyl}tungsten(II) (4c): Analogous to **4a** from 149 mg (0.26 mmol) Cp(OC)$_2$W=P(H)*s*Mes (**1**), 16 mg (0.26 mmol) *n*-BuLi, 44 mg (0.09 mmol) *iso*-propyl iodide (**3c**) in 5 mL THF. **4c** was crystallized by cooling the combined *n*-pentane layers to -78°C. **4c** is seperated from the solution and evaporated in vacuo. – Yield: 118 mg (73 %). – Violet solid. M.p. 96 °C (dec.). **Cp(OC)$_2$W=P(*i*Pr)*s*Mes (4c): ^{1}H{^{31}P}-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.46 (s, 2H, *m*-H), 5.13 (s, 5H, C_5H_5), 1.63 [sept, ^{3}J(HCCH) = 7.15 Hz, 1H, PCH], 1.49 [s, 18H, *o*-C(CH$_3$)$_3$], 1.31 [d, ^{3}J(HCCH) = 7.15 Hz, 6H, CH(C$\underline{H}_3$)$_2$], 1.24 ppm [s, 9H, *p*-C(CH$_3$)$_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 232.78 [d, ^{2}J(PWC) = 12.8 Hz, *cis*-CO], 150.61 [d, ^{2}J(PCC) = 1.7 Hz, *o*-C], 150.22 (s, *p*-C), 128.80 [d, ^{1}J(PC) = 43.1 Hz, *ipso*-C], 123.08 [d, ^{3}J(PCCC) = 6.2 Hz, *m*-C], 94.02 [d, ^{2}J(PWC) = 0.68 Hz, C_5H_5], 52.06 [d, ^{1}J(PC) = 10.7 Hz, PCH], 38.45 [d, ^{3}J(PCCC) = 0.68 Hz, *o*-$\underline{C}$(CH$_3$)$_3$], 34.93 [s, *p*-$\underline{C}$(CH$_3$)$_3$], 34.52 [s, *o*-C($\underline{C}$H$_3$)$_3$], 31.20 [s, *p*-C($\underline{C}$H$_3$)$_3$], 20.51 ppm [d, ^{2}J(PCC) = 0.68 Hz, PCH($\underline{C}$H$_3$)$_2$]. - **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = 311.2 ppm [s, ^{1}J(PW) = 601.4 Hz]. – **IR** (*n*-pentane): ν(CO) = 1938 (vs), 1867 (vs) cm^{-1}. Calc. for $C_{27}H_{39}O_2PW$ (624.5): C, 53.86; H, 6.62. Found: C, 53.24; H, 6.30.

4. Dicarbonyl(η^5-cyclopentadienyl){λ^4-[2,4,6-tri(*tert*-butyl)phenyl](*n*-butyl)phosphinediyl}tungsten(II) (4d): Analogous to **4a** from 163 mg (0.28 mmol) Cp(OC)$_2$W=P(H)*s*Mes (**1**), 18 mg (0.28 mmol) *n*-BuLi, 38 mg (0.28 mmol) *n*-butyl iodide (**3d**) in 10 mL THF. – Yield: 143 mg (80 %). – Violet solid. M.p. 94 °C (dec.). **Cp(OC)$_2$W=P(*n*Bu)*s*Mes (4d): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.48 ppm [d, ^{4}J(PCCCH) = 1.2 Hz, 2H, *m*-H], 5.12 (s, 5H, C_5H_5), 2.12 (m, 2H, PCH$_2$), 1.78 (m, 2H, PCH$_2$C$\underline{H}_2$), 1.56 [s, 18H, *o*-C(CH$_3$)$_3$], 1.25 [s, 9H, *p*-C(CH$_3$)$_3$], 1.24 (m, 2H, C$\underline{H}_2$CH$_3$), 0.86 ppm [t, ^{3}J(HCCH) = 7.2 Hz, 3H, CH$_2$C$\underline{H}_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 232.16 [d, ^{2}J(PWC) = 12.0 Hz, *cis*-CO], 150.70 [d, ^{2}J(PCC) = 1.4 Hz, *o*-C], 150.23 (s, *p*-C), 128.99 [d, ^{1}J(PC) = 43.1 Hz, *ipso*-C], 122.74 [d, ^{3}J(PCCC) = 6.2 Hz, *m*-C], 94.04 (s, C_5H_5), 54.88 [d, ^{1}J(PC) = 12.4 Hz, PCH$_2$], 38.57 [s, *o*-$\underline{C}$(CH$_3$)$_3$], 35.02 [s, *p*-$\underline{C}$(CH$_3$)$_3$], 34.10 (s, PCH$_2\underline{C}$H$_2$), 31.22 [s, *o*-C($\underline{C}$H$_3$)$_3$], 29.70 [s, *p*-C(CH$_3$)$_3$], 23.86 [d, ^{3}J(PCCC) = 15.8 Hz, $\underline{C}$H$_2$CH$_3$], 13.93 ppm (s, CH$_3$). – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ =

287.1 ppm [s, ^1J(PW) = 612.4 Hz]. – **IR** (*n*-pentane): ν(CO) = 1939 (vs), 1865 (vs) cm^{-1}. Calc. for $C_{29}H_{43}O_2PW$ (638.5): C, 54.55; H, 6.78. Found: C, 54.28; H, 6.41.

5. Dicarbonyl(η^5-cyclopentadienyl){λ^4-[2,4,6-tri(*tert*-butyl)phenyl](benzyl)phosphinediyl}-tungsten(II) (4e): Analogous to **4a** from 50 mg (0.09 mmol) $Cp(OC)_2W=P(H)$*s*Mes (**1**), 6 mg (0.09 mmol) *n*-BuLi, 11 mg (0.09 mmol) benzyl bromide (**3e**) in 5 mL THF. **4e** was crystallized by cooling the combined *n*-pentane layers to -78°C. **4e** is seperated from the solution and evaporated in vacuo. – Yield: 50 mg (83 %). – Violet solid. M.p. 88 °C (dec.). **$Cp(OC)_2W=P(CH_2Ph)$*s*Mes (4e): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.44 (s, 2H, *m*-H), 7.12-7.03 (m, 3H, Ph), 6.92-6.89 (m, 2H, Ph), 5.15 (s, 5H, C_5H_5), 3.37 [d, ^2J(HCP) = 14.7 Hz, 2H, PCH_2], 1.47 [s, 18H, *o*-$C(CH_3)_3$], 1.30 ppm [s, 9H, *p*-$C(CH_3)_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 231.42 [d, ^2J(PWC) = 13.5 Hz, *cis*-CO], 150.22 (s, *p*-C, Ph), 150.66 [d, ^4J(PCCCC) = 1.7 Hz, *p*-C], 149.59 [d, ^3J(PCCC) = 1.4 Hz, *o*-C, Ph], 135.53 [d, ^2J(PCC) = 9.3 Hz, *o*-C], 130.97 [d, ^2J(PCC) = 4.5 Hz, *ipso*-C, Ph], 128.86 [d, ^1J(PC) = 55.7 Hz, *ipso*-C], 126.65 [d, ^4J(PCCCC) = 1.7 Hz, *m*-C, Ph], 123.08 [d, ^3J(PCCC) = 6.2 Hz, *m*-C], 94.30 (s, C_5H_5), 66.63 [d, ^1J(PC) = 10.0 Hz, PCH_2], 38.47 [s, *o*-$\underline{C}(CH_3)_3$], 35.04 [s, *p*-$\underline{C}(CH_3)_3$], 34.14 [s, *o*-$C(\underline{C}H_3)_3$], 31.33 ppm [s, *p*-$C(\underline{C}H_3)_3$]. – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = 273.2 ppm [s, ^1J(PW) = 618.4 Hz]. – **IR** (cyclohexane): ν(CO) = 1938 (s), 1865 (vs) cm^{-1}. Calc. for $C_{32}H_{41}O_2PW$ (672.50): C, 57.15; H, 6.15. Found: C, 57.47; H, 6.06.

6. Dicarbonyl(η^5-cyclopentadienyl){λ^4-[2,4,6-tri(*tert*-butyl)phenyl](allyl)phosphinediyl}-tungsten(II) (4f): Analogous to **4a** from 98 mg (0.17 mmol) $Cp(OC)_2W=P(H)$*s*Mes (**1**), 11 mg (0.17 mmol) *n*-BuLi, 28 mg (0.09 mmol) allyl iodide (**3f**) in 5 mL THF. **4f** was crystallized by cooling the combined *n*-pentane layers to -78°C. **4f** is seperated from the solution and evaporated in vacuo. – Yield: 65 mg (61 %). – Violet oil. **$Cp(OC)_2W=P(CH_2CH=CH_2)$*s*Mes (4f): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.46 [d, ^4J(PCCCH) = 1.2 Hz, 2H, *m*-H], 6.33-6.18 (m, 1H, $C\underline{H}=CH_2$), 5.26-5.22 (m, 1H, $CH=C\underline{H_2}$), 5.17-5.15 (m, 1H, $CH=C\underline{H_2}$), 5.11 (s, 5H, C_5H_5), 2.57 [dd, ^2J(PCH) = 18.6 Hz, ^3J(HCCH) = 7.21 Hz, 2H, PCH_2], 1.52 [s, 18H, *o*-$C(CH_3)_3$], 1.25 ppm [s, 9H, *p*-$C(CH_3)_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 231.50 [d, ^2J(PWC) = 13.1 Hz, *cis*-CO], 229.42 (s, $\underline{C}H=CH_2$), 217.59 (s, $CH=\underline{C}H_2$), 150.70 [d, ^2J(PCC) = 1.4 Hz, *o*-C], 150.23 (s, *p*-C), 128.99 [d, ^1J(PC) = 43.1 Hz, *ipso*-C], 122.74 [d, ^3J(PCCC) = 6.2 Hz, *m*-C], 94.40 (s, C_5H_5), 59.62 [d, ^1J(PC) = 11.8 Hz, PCH_2], 38.56 [s, *o*-$\underline{C}(CH_3)_3$], 35.02 [s, *p*-$\underline{C}(CH_3)_3$], 34.08 [s, *o*-C(C̲H$_3$)$_3$], 31.23 ppm [s, *p*-C(C̲H$_3$)$_3$]. – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = 272.5 ppm [s, ^{1}*J*(PW) = 625.7 Hz]. – **IR** (*n*-pentane): ν(CO) = 1929 (vs), 1868 (vs) cm^{-1}. Calc. for $C_{28}H_{39}O_2PW$ (622.4): C, 54.03; H, 6.32. Found: C, 53.86; H, 6.24.

7. Dicarbonyl(η^5-cyclopentadienyl){λ^4-[2,4,6-tri(*tert*-butyl)phenyl](acetyl)phosphinediyl}-tungsten(II) (6a): To a solution of 174 mg (0.30 mmol) Cp(OC)$_2$W=P(H)*s*Mes (**1**) in 5 mL THF 20 mg (0.30 mmol) *n*-BuLi is added at -78 °C and, after stirring for 5 min, addition of 24 mg (0.30 mmol) acetyl chloride (**5a**) results in change of colour from darkgreen to violet. After stirring for 12 h and removal of volatiles in vacuo, the remaining solid is extracted five times with 2 mL *n*-pentane each. The combined organic layers are concentrated in vacuo, **5a** crystallized at –78°C, seperated from the solution and dried in vacuo. – Yield: 131 mg (70 %). – Turquoise solid. M.p. 43 C° (dec.). **Cp(OC)$_2$W=P[C(=O)Me]*s*Mes (6a): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.51 [d, ^{4}*J*(PCCCH) = 1.5 Hz, 2H, *m*-H], 5.07 (s, 5H, C$_5$H$_5$), 2.85 [d, ^{3}*J*(PCCH) = 4.8 Hz, 3H, CH$_3$], 1.38 [s, 18H, *o*-C(CH$_3$)$_3$], 1.25 ppm [s, 9H, *p*-C(CH$_3$)$_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 232.90 [d, ^{2}*J*(PWC) = 11.3 Hz, *cis*-CO], 215.32 [d, ^{1}*J*(PC) = 11.7 Hz, C=O], 151.57 [d, ^{2}*J*(PCC) = 2.0 Hz, *o*-C], 150.23 (s, *p*-C), 128.99 [d, ^{1}*J*(PC) = 41.1 Hz, *ipso*-C], 123.03 [d, ^{3}*J*(PCCC) = 7.5 Hz, *m*-C], 95.13 (s, C$_5$H$_5$), 38.82 [d, ^{3}*J*(PCCC) = 1.4 Hz, *o*-C̲(CH$_3$)$_3$], 38.56 [s, *p*-C̲(CH$_3$)$_3$], 33.70 [s, *o*-C(C̲H$_3$)$_3$], 33.07 [s, *p*-C(C̲H$_3$)$_3$], 31.21 ppm [d, ^{2}*J*(PCC) = 1.7 Hz, PC(O)C̲H$_3$]. – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = 291.4 ppm [s, ^{1}*J*(PW) = 566.2 Hz]. – **IR** (*n*-pentane): ν(CO) = 1947 (vs), 1874 (vs) cm^{-1}. Calc. for $C_{27}H_{37}O_3PW$ (624.4): C, 51.94; H, 5.97. Found: C; 51.72; H 5.41.

8. Dicarbonyl(η^5-cyclopentadienyl){λ^4-[2,4,6-tri(*tert*-butyl)phenyl](benzoyl)phosphinediyl}tungsten(II) (6b): Analogous to **5a** from 157 mg (0.27 mmol) Cp(OC)$_2$W=P(H)*s*Mes (**1**), 17 mg (0.27 mmol) *n*-BuLi, 38 mg (0.27 mmol) benzoyl chloride (**5b**) after 12 h. – Yield: 100 mg (64 %). – Turquoise solid. M.p. 50 °C (dec.). **Cp(OC)$_2$W=P[C(=O)Ph]*s*Mes (6b): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 8.20 (m, 2H, C$_6$H$_5$), 7.53 (s, 2H, *m*-H), 7.35 (m, 2H, C$_6$H$_5$), 7.23 (m, 1H, C$_6$H$_5$), 5.01 (s, 5H, C$_5$H$_5$), 1.46 [s, 18H, *o*-C(CH$_3$)$_3$], 1.28 ppm [s, 9H, *p*-C(CH$_3$)$_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 232.97 [d, ^{2}*J*(PWC) = 12.9 Hz, *cis*-CO], 209.81 [d, ^{1}*J*(PC) = 13.7 Hz, C=O], 151.30 [d, ^{2}*J*(PCC) = 2.7 Hz, *o*-C], 150.87 [d, ^{3}*J*(PCCC) = 1.4 Hz, *o*-C-Ph], 139.93 [d, ^{1}*J*(PC) = 51.4 Hz, *ipso*-C], 131.95 (s, *p*-C), 130.67 (s, *p*-C-Ph), 128.92 [d, ^{2}*J*(PCC) = 9.7 Hz, *ipso*-C-Ph], 127.13 [d, ^{4}*J*(PCCCC) = 8.6 Hz, *m*-C-Ph], 123.54 [d, ^{3}*J*(PCCC) =

7.6 Hz, *m*-C], 94.69 (s, C_5H_5), 39.98 [s, *o*-<u>C</u>$(CH_3)_3$], 39.46 [s, *p*-<u>C</u>$(CH_3)_3$], 34.45 [s, *o*-C(<u>C</u>$H_3)_3$], 31.29 ppm [s, *p*-C(<u>C</u>$H_3)_3$]. – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = 275.6 ppm [s, ^1J(PW) = 575.9 Hz]. – **IR** (*n*-pentane): ν(CO) = 1960 (s), 1866 (m) cm^{-1}. Calc. for $C_{32}H_{39}O_3PW$ (686.5): C, 55.99; H, 5.73. Found: C, 55.26; H, 5.39.

9. Quantum chemical calculations:[2] All calculations were done with Turbomole 5.6[24, 25] program at the density functional level, using the hybrid B3LYP[26] functional (based on the work of Becke[27]), and a split-valence polarisation basis set (SVP)[28] for the light atoms H, C and P. For tungsten we used a quasirelativistic small-core 14-valence-electron pseudopotential with a (8s7p6d)/[6s5p3d] valence basis set.[29] All structures were fully optimized without symmetry constraints.

10. X-Ray analyses for compounds 4a-e: Crystals of $Cp(OC)_2W{=}P(R)$*s*Mes [R = Me (**4a**), Et (**4b**), *i*Pr (**4c**), *n*Bu (**4d**), CH_2Ph (**4e**)] suitable for structure determination could be obtained from a saturated *n*-pentane solution at room temperature. Data collection was performed on an Enraf-Nonius CAD4-diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) at 173(2) K.[30-32] The structures were solved using the Patterson-method and cell parameters were determined and refined using SHELXS-97[33] and SHELXL-97.[34]

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[2] DFT calculations performed by Dipl. Chem. S. Riedel in the research group of Prof. Dr. M. Kaupp, Institut für Anorganische Chemie, Universität Würzburg.

Crystal Data for Compounds ***4a****,* ***4b*** *and* ***4c*****:**

	4a	**4b**	**4c**
identification	andi9	dirk24	dirk47
mol formula	$C_{26}H_{37}WO_2P$	$C_{28}H_{41}O_2PW$	$C_{27}H_{39}O_2P$
mol wt	596.38	610.4	624.5
wavelength (Å)	0.71073	0.71073	0.7107
temp (K)	173(2)	173(2)	173(2)
cryst size (mm)	0.20 x 0.15 x 0.08	0.2 x 0.15 x 0.2	0.14 x 0.12 x 0.08
cryst syst	triclinic	triclinic	monoclinic
space group	*P-1*	*P-1*	*P2(1)*/n
a (Å)	9.751(2)	9.868(5)	11.113(3)
b (Å)	9.859(2)	10.200(6)	14.404(4)
c (Å)	13.635(3)	13.706(8)	17.310(5)
α (°)	74.164(3)	93.020(10)	90
β (°)	82.855(3)	109.436(9)	99.333(4)
γ (°)	88.510(3)	91.045(9)	90
vol ($Å^3$), *Z*	1251.2(5), 2	1298.2(12), 2	2734.2(12), 4
ρ (calcd) (Mgm^{-3})	1.583	1.562	1.483
F(000)	596	612	1256
μ (mm^{-1})	4.699	4.531	4.304
θ range for data collecn (deg)	2.10 – 25.04	1.58 – 27.52	1.86 – 25.60
no. of rflns collected	4430	21981	27041
no. of indep reflns	4430	5817	5131
abs cor.	empirical	empirical	empirical
no. of data/restraints/params	4430 / 0 / 281	5817 / 27 / 321	5131 / 0 / 303
goodness of fit on F^2	0.713	1.025	1.061
R1[a]	0.0177	0.0267	0.0338
wR2[b]	0.0441	0.0544	0.0681
largest diff peak and hole ($eÅ^{-3}$)	0.829 and -0.286	1.117 and -0.475	1.269 and -0.587

*Crystal Data for Compounds **4d** and **4e**:*

	4d	**4e**
identification	andi51	andi37
mol formula	$C_{29}H_{43}WO_2P$	$C_{32}H_{41}WO_2P$
mol wt	638.46	672.47
wavelength (Å)	0.71073	0.71073
temp (K)	173(2)	173(2)
cryst size (mm)	0.25 x 0.20 x 0.08	0.16 x 0.12 x 0.10
cryst syst	triclinic	monoclinic
space group	*P-1*	*P2(1)*/n
a (Å)	10.063(2)	13.364(3)
b (Å)	14.276(3)	15.330(3)
c (Å)	19.631(4)	14.163(3)
α (°)	85.155(3)	90
β (°)	88.471(3)	96.947(3)
γ (°)	81.315(3)	90
vol (Å^3), *Z*	2777.7(10), 6	2880.3(11), 4
ρ (calcd) (Mgm^{-3})	1.527	1.551
F(000)	1288	1352
μ (mm^{-1})	4.239	4.092
θ range for data collecn (deg)	1.04 – 25.03	1.97 – 25.03
no. of rflns collected	20184	33963
no. of indep reflns	9692	5057
abs cor.	empirical	empirical
no. of data/restraints/params	9692 / 0 / 615	5057 / 0 / 334
goodness of fit on F^2	0.886	1.065
R1[a]	0.0462	0.0173
wR2[b]	0.0586	0.0429
largest diff peak and hole (eÅ^{-3})	1.017 and -0.333	0.649 and -0.241

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 III

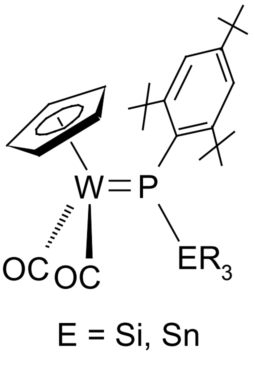
P-Silylated and P-Stannylated Phosphenium Complexes from the Anionic Phosphinidene Complex $[C_5H_5(OC)_2W{=}P(s\text{Mes})]Li$. Conversion of the Triflatophosphenium Complex $Cp(OC)_2W{=}P(OSO_2CF_3)s\text{Mes}$ to Cationic Phosphinidene-Phosphorane Tungsten Complexes

Introduction

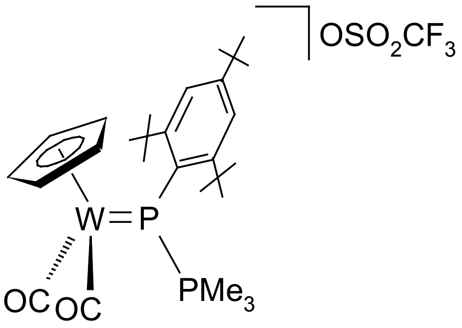
The high reactivity of P-H-functionalized molybdenum and tungsten phosphenium complexes $Cp(OC)_2M{=}P(H)R$ has its origin both in the M=P-double bond and the P-H unit,[1-5] leading to serious problems concerning characterization and isolation. Therefore in most cases the existence could only be spectroscopically proved in solution at low temperatures[1] or by distinct trapping experiments.[6] In the previous chapters we described the successful isolation[7] and crystallographic characterization[8] of the *super*-mesitylphosphenium complex $Cp(OC)_2W{=}P(H)$*s*Mes (**1**), which represents one of the few isolated P-H-functionalized derivatives.[7]

With the help of the extremly bulky *super*-mesityl substituent a selective deprotonation at the P-H-bond could be realized generating $[Cp(OC)_2W{=}P($*s*Mes$)]Li$ (**2**), a highly interesting anionic phosphinidene[9-12] reagent, which is not available in substance but can be used *in situ* for alkylation reactions.[13]

As a consequence we present further reactions of **2** with electrophilic group 14 element compounds, affording the first silyl- and stannyl-functionalized phosphenium complexes of the type **A**.



A



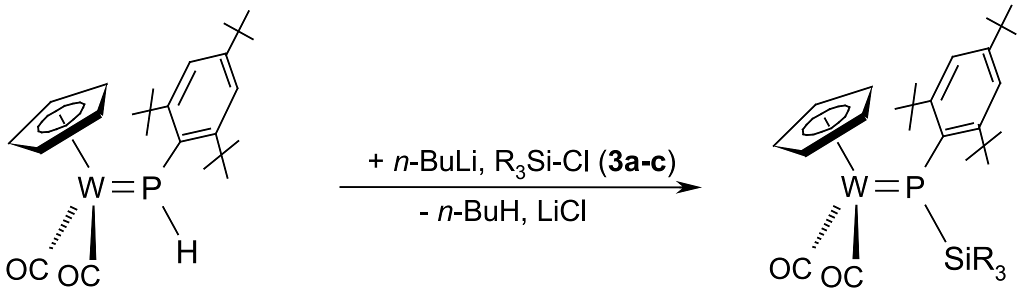
B

In addition an access to cationic phosphinidene-phosphorane complexes **B**, isoelectronic to the analogous silyl and stannyl derivatives **A**, have been worked out starting from the chloro- or triflatophosphenium tungsten complexes $Cp(OC)_2W{=}P(X)$*s*Mes ($X = Cl, OSO_2CF_3$).

Results and Discussion

Reactivity Studies

When a solution of **1** in THF is combined with an equimolar amount of *n*-BuLi the colour of the violet solution turns to darkgreen immediately, indicating the formation of the anionic phosphinidene complex [Cp(OC)$_2$W=P(*s*Mes)]Li (**2**).[13] The colour of the reaction mixture switches back to blue after the addition of the organochlorosilanes **3a-c**, yielding the silylphosphenium tungsten complexes **4a-c** [Eq. (1)].



(1)

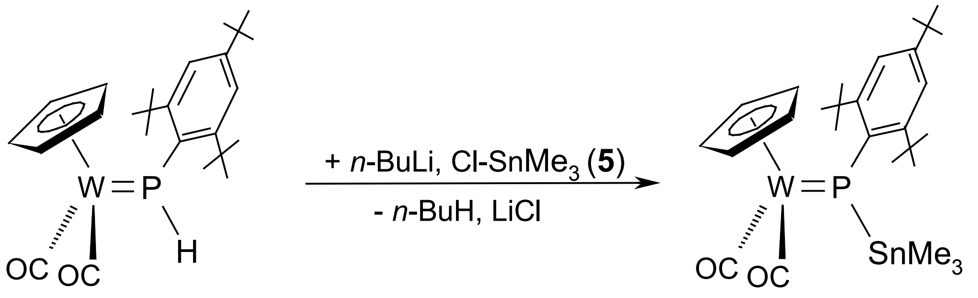
1

4a-c

	a	**b**	**c**
SiR$_3$	SiMe$_3$	SiMe$_2$H	SiPh$_2$H

4a-c can be isolated as blue powders in yields between 74 (**4a,b**) and 88 % (**4c**) after a reaction time between 1 (**4b**) and 4 h (**4a**). The ^{31}P-NMR chemical shifts and coupling constants [δ^{31}P / ^{1}J(PW)]: 314.5 / 512 (**4a**); 294.0 / 524 (**4b**); 269.5 / 536 (**4c**)] and especially the doublet resonances in the ^{29}Si-NMR spectra, originating from a J(PSi)-coupling [δ^{29}Si / ^{1}J(PSi)]: 24.96 / 26.8 (**4a**); 4.93 / 35.8 (**4b**); -8.09 / 23.9 (**4c**)] confirm the formation of the phosphenium complexes **4a-c** with a silyl function. **4a-c** are extremely moisture sensitive. Minimal traces of water lead to a cleavage of the P-Si-bond to give **1** and the corresponding siloxanes. Monitoring this process ^{31}P-NMR-spectroscopically, complete decomposition is noticed after 26 (**4a**), 47 (**4b**) or 42 d (**4c**) respectively.

A significantly improvement concerning stabilization of phosphenium complexes functionalized with a group 14 element is found using Cl-SnMe$_3$ (**5**). When a solution of **1** in THF is combined with an equimolar amount of *n*-BuLi and **5**, the first stannylphosphenium complex **6** is formed after a reaction time of 20 h as blue powder with 80 % yield [Eq. (2)].



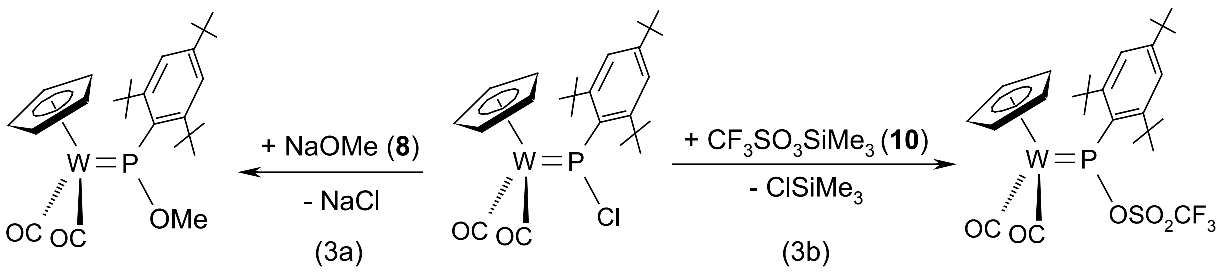
(2)

1 6

The ^{31}P-NMR-data of **6** [δ^{31}P = 314.7 ppm; ^{1}J(PW) = 498 Hz] prove the formation of a phosphenium complex comparable to the silylated compounds **4a-c**. The phosphorus-stannyl coupling constant [^{1}J(PSn) = 72.0 Hz] is on the lower limit of the range known for compounds containing a W-P-Sn-moiety like (OC)$_5$W-PC$_4$H$_2$Me$_2$-SnPh$_3$ [^{1}J(PSn) = 93.0 Hz][14] or Cp(OC)$_2$W-(SnMe$_2$)-PPh[N(SiMe$_3$)$_2$] [^{1}J(PSn) = 104.0 Hz].[15]

Taking into account the high polarity of the P-OTf moieties,[16-20] addition of lewis bases at the positively charged phosphorus atom is conceivable. Therefore we tried to synthesize the triflato phosphenium tungsten complex Cp(OC)$_2$W=P[OSO$_2$CF$_3$]*s*Mes (**11**) as precursor for the generation of cationic phosphinidene-phosphorane complexes starting from the P-Cl-functionalized complex **7**. A first impression concerning the exchange activity of the chlorine atom of **7** is obvious from the reaction with sodium methanolate (**8**).

When a toluene solution of **7** is treated with **8** and the reaction mixture is stirred for 24 h at room temperature, the methoxyphosphenium complex Cp(OC)$_2$W=P(OMe)*s*Mes (**9**) is generated in 75 % yield [Eq. (3a)].



9 7 11

9, which can be isolated as redbrown solid, is soluble in aromatic solvents like benzene or toluene and can be stored under an atmosphere of nitrogen for several weeks. The chemical shift and coupling constant of **9** [δ^{31}P = 330.3 ppm; ^{1}J(PW) = 707.1 Hz] are comparable to the complexes mentioned above. Additionally no indication for a possible valence isomerization to the cyclic species $\mathrm{Cp(OC)_2}\overline{\mathrm{W\text{-}P(}s\mathrm{Mes)\text{-}O}}\mathrm{Me}$ is detectable according to NMR-measurements.

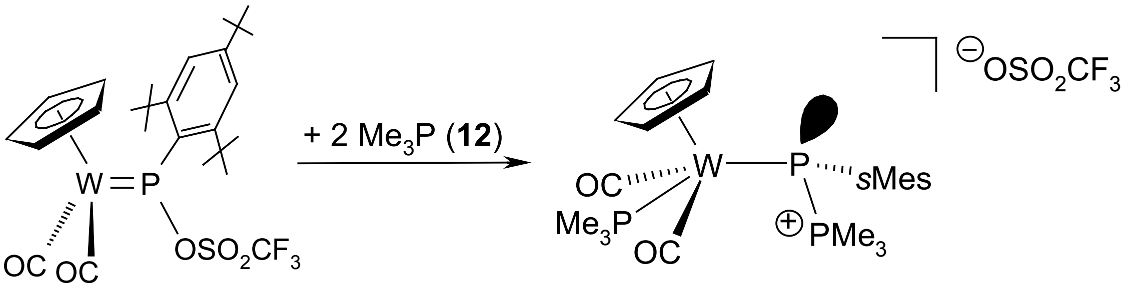
Motivated by the fact that the chlorine atom in **7** can be easily substituted, attempts concerning chloride-abstraction providing the cationic carbyne-type phosphinidene[9-12] complex $[\mathrm{Cp(OC)_2W{\equiv}P(}s\mathrm{Mes)}]^{\oplus}$ were undertaken.

7, dissolved in THF, is treated with trimethylsilyltriflate (**10**) at -78 °C, which results in an immediate change of the colour of the light-violet solution to orange-red, indicating the formation of a product, which showed to be **11** by NMR-spectroscopy. Workup of the reaction mixture by evaporating the solvent or addition of *n*-pentane to precipitate the product yields however only decomposition products, showing the high reactivity of **11**. Therefore this species has to be spectroscopically investigated exclusively in solution.

However the ^{31}P-NMR-chemical shift and ^{1}J(PW)-coupling-constant {297.1 ppm [s, ^{1}J(PW) = 703.5 Hz]; 295.9 ppm [s, ^{1}J(PW) = 702.3 Hz]}, typical for a phosphenium complex, prove the formation of the triflatophosphenium species **11** [Eq. (3b)]. Interesting enough the ^{31}P-NMR-spectrum of **11** shows two resonances, which suggest the formation of a *cis*- and a *trans*-isomer with respect to the arrangement of the cyclopentadienyl moiety and the P-aryl ligand. **11** is storable at room temperature for about 4 h in donor solvents like THF or dimethoxyethane. After that time a complete decompostion is observed.

The high polarity of the P-OTf moiety, characterizes **11** as a "masked" cationic phosphinidene complex $[\mathrm{Cp(OC)_2W{\equiv}P(}s\mathrm{Mes)}]^{\oplus}$. This suggestion is supported by the reaction of **11** with trimethylphosphine (**12**).

Addition of two equivalents of trimethylphosphine (**12**) to a freshly prepared solution of **11** in THF at -78 °C leads to the formation of the cationic phosphinidene-phosphorane tungsten complex **13** [Eq. (4)].

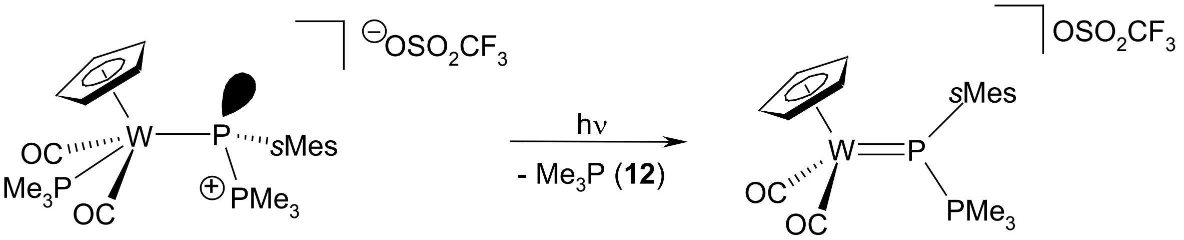


(4)

11 **13**

Because of the formation of several sideproducts the yield for the synthesis of **13** is in the range of only 20 %. Nevertheless the ^{1}H- and ^{31}P-NMR-data confirm the illustrated structure of $\{[Cp(OC)_2(Me_3P^2)W\text{-}P^3(s\text{Mes})P^1Me_3]OSO_2CF_3$ (**13**) especially by the chemical shifts of the P^2- ($\delta^{31}P$ = -15.2 ppm) and the P^3-atom ($\delta^{31}P$ = -132.7 ppm), as well as the typical $^1J(P^3P^1)$- (421.6 Hz) and $^3J(P^2WP^3P^1)$-coupling-constants (7.3 Hz) comparable to that of the analogous *tert*-butyl-derivative $[Cp(OC)_2(Me_3P)W\text{-}P(t\text{Bu})PMe_3]Cl$.[21] The relatively high $^1J(P^3P^1)$-coupling of 421.6 Hz indicates partial double-bond character for the the phosphanido-phosphorus. Overall the reaction meachanism can be described as nucleophlic substitution of the phosphorus coordinated triflato group by Me$_3$P, followed by the *trans*-selective coordination of a second Me$_3$P-molecule at the tungsten metal, generating the phosphanido type phosphinidene-phosphorane tungsten complex **13.**

When **13**, dissolved in [D$_3$]-chloroforme, is irradiated with UV-light for 5 h in a NMR-tube, due to loss of the tungsten-coordinated Me$_3$P-ligand formation of a different cationic phosphinidene-phosphorane compound **14** is observed [Eq. (5)].

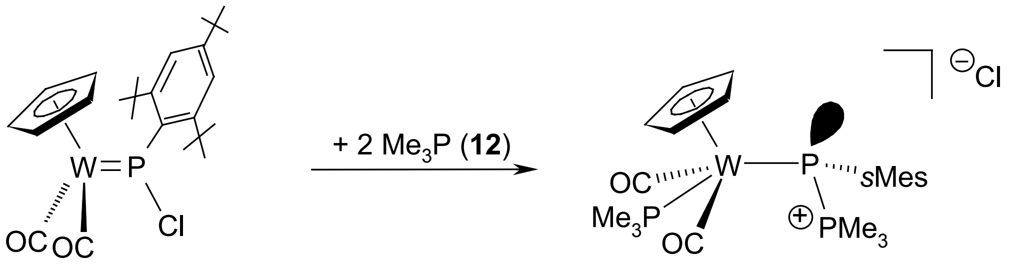


(5)

13 **14**

14 could be only identified by ^{31}P-NMR-spectroscopy because of the formation of a lot of sideproducts which are difficult to separate from the product **14**. However it is clear from the ^{31}P-NMR-spectrum, that the signal for the tungsten-bonded Me$_3$P-resonance has dissappeared leading to two dubletts at 24.0 and -87.4 ppm with a $^1J(PP)$-coupling of 281.9 Hz. While the synthesis[22] and reactivity[23-25] of the phosphoranylidenephosphine ArP=PMe$_3$ (Ar = 2,6-Mes$_2$C$_6$H$_3$ or *s*Mes) is well known, compound **14** is the first cationic phosphinidene-phosphorane complex with a (*s*Mes)P=PMe$_3$-ligand attached via a double bond to a transition metal fragment.

Surprisingly Cp(OC)$_2$W=P(Cl)*s*Mes (**7**) when treated in [D$_6$]-benzene with two equivalents of trimethylphosphine (**12**) directly affords a yellow solid which, after isolation, is identified by comparison with an authentic sample of $[Cp(OC)_2(Me_3P)W\text{-}P(t\text{Bu})PMe_3]Cl$ as the phosphinidene-phosphorane complex **15** [Eq. (6)].



(6)

7 **15**

The composition of **15** differs from **13** only with respect to the anion. Therefore it is not surprising that the ^{31}P-NMR-data of **13** and **15** are nearly identical.

In summary the synthesis, stabilization and isolation of novel cationic phoshinidene-phosphorane complexes is possible starting from P-Cl-functionalized phoshenium complexes via an selective chlorine-abstraction using trimethylsilyltriflate (**10**).

Structural Investigation

Crystals of Cp(OC)$_2$W=P(SnMe$_3$)*s*Mes (**6**) [Fig. (1)] suitable for structure determination could be obtained from a saturated *n*-pentane solution at room temperature.

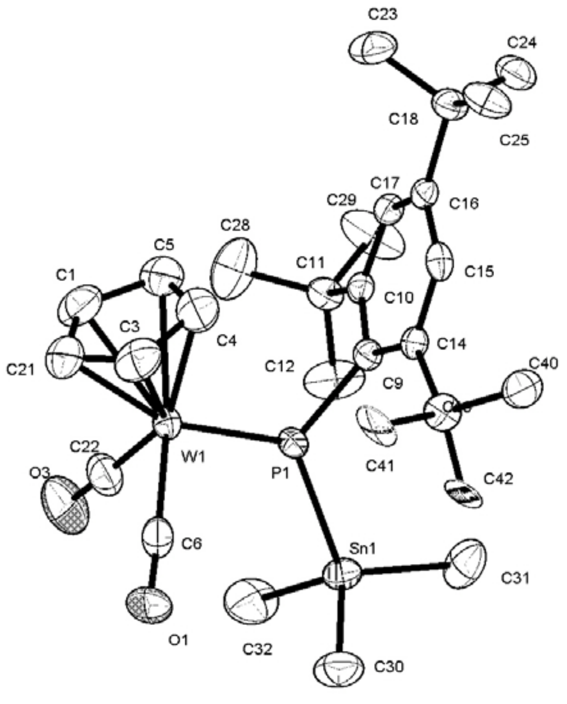


Fig. (1). Molecular structure of Cp(OC)$_2$W=P(SnMe$_3$)*s*Mes (**6**) - The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: W(1)-C(6) 1.942(5), W(1)-C(22) 1.950(5), W(1)-P(1) 2.2658(12), P(1)-C(9) 1.858(4), P(1)-Sn(1) 2.5287(12), C(6)-W(1)-P(1) 93.91(14), C(22)-W(1)-P(1) 94.27(15), C(6)-W(1)-C(22) 78.05(19), C(9)-P(1)-W(1) 116.15(14), C(9)-P(1)-Sn(1) 117.40(13), W(1)-P(1)-Sn(1) 126.43(4), C(9)-C(10)-C(17)-C(16) 1.5(6), C(17)-C(10)-C(9)-P(1) 152.5(3), P(1)-C(9)-C(14)-C(15) -151.8(3), C(10)-C(9)-C(14)-C(15) 10.8(5), C(17)-C(16)-C(15)-C(14) -5.5(6).

The coordination geometry of the tungsten atom can be described as pseudo-octahedral three legged piano stool. The cyclopentadienyl ligand is occupying three facial coordination sites, whereby two legs are formed by the carbonyl ligands and the third leg by the phosphenium ligand. This is proved by the bond angles between the carbonyl ligands and the phosphine moiety, which are close to the expected value of 90° (C6-W1-P1 93.9°, C22-W1-P1 94.3°, C6-W1-C22 78.1°).

The geometry of the phosphorus atom is exactly trigonal planar, with the sum of angles being 360°. However the C9-P1-Sn1-angle of 117.4° is very close to the ideal value of 120° and is therefore in contrast to Cp(OC)$_2$W=P(*t*Bu)$_2$[26] (109.4°) and other unsymmetrically substituted diorganophosphenium complexes Cp(OC)$_2$W=P(R)*s*Mes [R = Me, Et, *n*Bu, CH$_2$Ph] (95.3° - 98.8°).[13] The C9-P1-W1- (116.1°) and W1-P1-Sn1-angle (126.4°) are also relatively close to the ideal value with respect to the situation found in the above mentioned phosphenium complexes.

The value for the P1-Sn1-bond length (2.53 Å) is comparable to literature-known single bond systems like [Me$_2$In-P(SnMe$_3$)$_2$]$_3$ or [P(SnMe$_3$)$_4$]OTf.[27, 28] The P1-C9 bond length of 1.85 Å is in the range expected for a P$_{sp2}$-C$_{sp2}$ single bond[29] and excludes therefore π–interaction between the phosphorus atom and the aromatic ring system.

The tungsten-phosphorus bond length of 2.27 Å can be classified as double-bond-system for which a theoretical bond length of 2.26 Å is calculated.[30-32] In comparison it is nearly identical to the W-P-distance of Cp(OC)$_2$W=P(*t*Bu)$_2$ (2.28 Å)[26] and Cp(OC)$_2$W=P(R)*s*Mes (R = Me, Et, *i*Pr, Bu, CH$_2$Ph; 2.24 – 2.25 Å).[13]

The complex **6** is showing *cis*-configuration regarding the *super*-mesityl-ligand and the cyclopentadienyl moiety, which is in accordance with the situation for Cp(OC)$_2$W=P(R)*s*Mes (R = Me, Et, *i*Pr, Bu, CH$_2$Ph)[13] and Cp(OC)$_2$W=P(H)*s*Mes (**1**).[8]

The steric demand of the *s*Mes-ligand causes on the one hand a severe distorsion of the aryl group planarity [C(10)-C(9)-C(14)-C(15) 10.8°, C(17)-C(16)-C(15)-C(14) -5.5°], on the other hand this effect determines the arrangement of the *super*-mesityl group. In order to avoid interaction of the *ortho*-*tert*-butyl-groups with the cyclopentadienyl- and the carbonyl-ligands the aryl ligand is bent towards the cyclopentadienyl-metal fragment out of the expected linear position. The differences from the theoretical torsion angle of 180° are significant [C(17)-C(10)-C(9)-P(1) 152.5°, P(1)-C(9)-C(14)-C(15) -151.8(3)°].

Crystals of $Cp(OC)_2W{=}P(OMe)$*s*Mes (**9**) [Fig. (2)] suitable for structure determination could be obtained from a saturated toluene solution at room temperature.

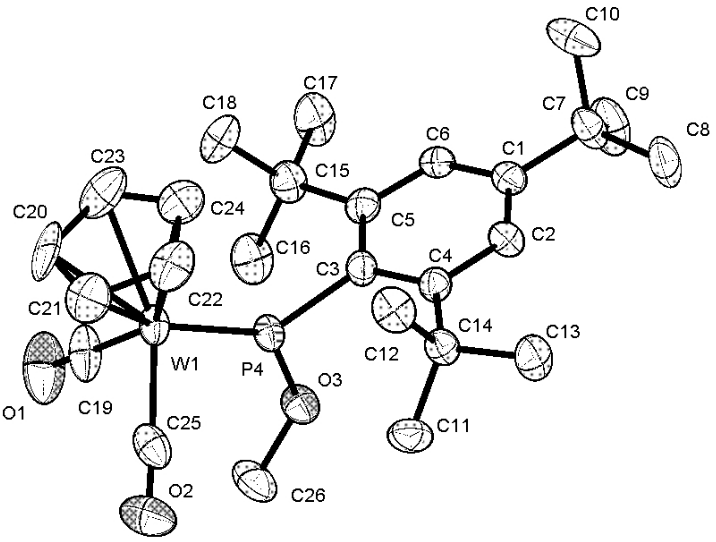


Fig. (2). Molecular structure of $Cp(OC)_2W{=}P(OMe)$*s*Mes (**9**) - The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: W(1)-P(4) 2.2143(12), P(4)-O(3) 1.624(3), P(4)-C(3) 1.837(4), W(1)-C(19) 1.958(6), W(1)-C(25) 1.954(6), M-W(1)-P(4) 131.2, C(3)-P(4)-W(1) 136.08(15), O(3)-P(4)-C(3) 93.36(19), O(3)-P(4)-W(1) 130.56(13), C(19)-W(1)-P(4) 91.13(15), C(25)-W(1)-P(1) 92.86(15), C(19)-W(1)-C(25) 83.7(3), C(2)-C(4)-C(3)-P(4) 175.0(3), P(4)-C(3)-C(5)-C(6) -175.7(3), C(3)-C(5)-C(6)-C(1) 0.5(7), C(3)-C(4)-C(2)-C(1) 1.1(7).

The coordination geometry of the tungsten atom can be described as a pseudo-octahedral three legged piano stool. The cyclopentadienyl ligand is occupying three facial coordination sites, whereby two legs are formed by the carbonyl ligands and the third leg by the double bonded phosphenium ligand. This is proved by the bond angles between the carbonyl ligands and the phosphorus moiety, which are close to the ideal value of 90° (C19-W1-P4 83.7°, C25-W1-P4 92.86°).

The geometry of the phosphorus atom is exactly trigonal planar, the sum of angles amounts to 360°. As a result of the sp^2-hybridization the phosphenium ligand can be regarded as three-electron donor, giving the tungsten atom a number of 18 valence electrons. The O3-P4-C3-angle of 93.36° is significantly reduced in contrast to the ideal value of 120°. A similar decreased angle can also be found for $Cp(OC)_2W{=}P(t\mathrm{Bu})_2$[26] (109.4°), the P-H-functionalized complex $Cp(OC)_2W{=}P(H)$*s*Mes (**1**)[8] and the P-alkyl derivatives $Cp(OC)_2W{=}P(R)$*s*Mes (R = Me, Et, *i*Pr, *n*Bu, CH_2Ph).[13] As a consequence of this compression the C3-P4-W1- and O3-P4-W1-angle are expanded to 136.08° and 130.56°, respectively.

The P4-O3-bond distance in **9** (1.62 Å) is between the values for a single (1.72 Å) and a phosphorus-oxygen double bond (1.48 Å).[29] Therefore a double bond quotient can be assumed. The P4-C3 bond length (1.837 Å) is in the range expected for a P_{sp2}-C_{sp2} single bond[29] and excludes therefore π–interaction between the phosphorus atom and the aromatic ring system.

The value of 2.21 Å for the tungsten-phosphorus bond length, for which a theoretical bond length of 2.26 Å is calculated, [30-32] is on the lower end of the range typical for W-P-double-bond systems compared to the compounds $Cp(OC)_2W{=}P(R)$*s*Mes [R = Me, Et, *i*Pr, *n*Bu, CH_2Ph (2.24 Å - 2.25 Å)][13] or the starting material $Cp(OC)_2W{=}P(H)$*s*Mes (**1**) (2.25 Å).[8] The plane defined by C3, P4 and O3 is almost vertical to the $W(CO)_2$-moiety, which also shows the smallest angle (C17-W1-C16 83.7°) in the piano stool fragment. Despite the steric demand of the *s*Mes-ligand the distorsion of the aryl group planarity is close to the ideal value of 0° (C3-C5-C6-C1 0.5°, C3-C4-C2-C1 1.1°). This fact is contrary to the above mentioned crystal structures of $Cp(OC)_2W{=}P(R)$*s*Mes (R = Me, Et, *i*Pr, *n*Bu, CH_2Ph)[13] and $Cp(OC)_2W{=}P(SnMe_3)$*s*Mes (**6**).[33] For the P-methoxy derivative the phosphorus-bonded aryl ligand is not bent towards the metal fragment, which can be recognized by the torsion angles C2-C4-C3-P4 (175.0°) and P4-C3-C5-C6 (175.7°) close to the ideal value of 180°.

In summary the overall structure of **9** is similar to $Cp(OC)_2W{=}P(H)$*s*Mes (**1**)[8] while the short W-P-distance is additionally in agreement with a frontier orbital interaction of the fragments $Cp(OC)_2W^{\ominus}$ and $sMes(H)P^{\oplus}$ as described in chapter I.

The most important structural finding refers to the *cis*-configuration regarding the *super*-mesityl-ligand and the cyclopentadienyl moiety. This is in accordance with the situation found for $Cp(OC)_2W{=}P(H)$*s*Mes (**1**)[8] and the complexes $Cp(OC)_2W{=}P(R)$*s*Mes (R = Me, Et, *i*Pr, *n*Bu, CH_2Ph)[13] as well as $Cp(OC)_2W{=}P(SnMe_3)$*s*Mes (**6**).[33]

Experimental Section

General: All manipulations were performed under purified and dried nitrogen by standard Schlenk-type techniques. Solvents were rigorously dried with an appropriate drying agent, distilled and saturated with nitrogen prior to use. IR: Spectra were recorded using a Perkin-Elmer 283 grating spectrometer. Samples were prepared as solutions in a NaCl cell with 0.1 mm path length with a resolution of about 2 cm^{-1}. NMR: JEOL LAMBDA 300 (300.4 MHz, 75.6 MHz and 121.5 MHz for ^{1}H, ^{13}C and ^{31}P, respectively). ^{1}H and ^{13}C spectra are referenced to the residual proton signal or natural abundance carbon signal of C_6D_6 at $\delta = 7.15$ ppm (^{1}H) or $\delta = 128.0$ ppm (^{13}C), respectively. ^{31}P chemical shifts are referenced to external H_3PO_4. ^{29}Si spectra are recorded on a AMX BRUKER 500 (99.36 MHz) and are referenced to external TMS. ^{1}H-NOESY spectra were recorded on a AMX BRUKER 400 referenced to the residual proton signal of C_6D_6 at $\delta = 7.15$ ppm. Melting points were obtained by differential thermoanalysis (Du Pont 9000 Thermal Analysis System). Elemental analyses were performed in the laboratories of the Institut für Anorganische Chemie der Universität Würzburg. Starting materials: Cp(OC)$_2$W=P(H)*s*Mes (**2**),[7] Cp(OC)$_2$W=P(Cl)*s*Mes (**7**)[7] and PMe_3 (**12**)[34] were prepared according to literature procedures. Trimethylsilyl triflate (**10**) and the chlorosilanes Me_3SiCl (**3a**), $Me_2Si(H)Cl$ (**3b**) and $Ph_2Si(H)Cl$ (**3b**) were obtained commercially and distilled before use. $ClSnMe_3$ (**5**) and sodium methoxide (**8**) were obtained commerically and used without further purification.

1. [Dicarbonyl(η^{5}-cyclopentadienyl){λ^{4}-[2,4,6-tri(*tert*-butyl)phenyl](trimethylsilyl)-phosphinediyl}tungsten(II) (4a): A solution of Cp(OC)$_2$W=P(H)*s*Mes (**1**) (112 mg, 0.19 mmol) in THF (10 mL) is treated with 12 mg *n*-BuLi (0.19 mmol, 0.12 mL, 1.6 mol/l) at -78 °C whereby the colour of the reaction mixture changed immediately from violet to green. Afterwards the chlorotrimethylsilane (**3a**) (22 mg, 0.19 mmol) is added and the solution stirred for 4 h at room temperature. Volatiles are removed in vacuo and the remaining residue is extracted three times with *n*-pentane (3 mL each). **4a** is isolated by evaporating of the combined organic layers to dryness. – Yield: 91 mg (74 %). – Darkblue powder. **Cp(OC)$_2$W=P(SiMe$_3$)*s*Mes (4a): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): $\delta = 7.40$ [d, ^{4}J(PCCCH) = 1.0 Hz, 2H, *m*-H], 5.05 (s, 5H, C_5H_5), 1.41 [s, 18H, *o*-$C(CH_3)_3$], 1.27 [s, 9H, *p*-$C(CH_3)_3$], 0.59 ppm [d, ^{3}J(PSiCH) = 5.6 Hz, 9H, $Si(CH_3)_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): $\delta = 235.87$ [d, ^{2}J(PWC) = 7.9 Hz, *cis*-CO], 151.49 [d, ^{2}J(PCC) = 1.7 Hz, *o*-C], 150.24 (s, *p*-C), 145.53 [d, ^{1}J(PC) = 14.2 Hz, *ipso*-C], 122.47 [d, ^{3}J(PCCC) = 6.6 Hz, *m*-C], 94.49 (s, $\mathrm{C_5H_5}$), 38.08 [d, ^{3}J(PCCC) = 0.7 Hz, *o*-$\underline{\mathrm{C}}(\mathrm{CH_3})_3$], 34.77 [s, *p*-$\underline{\mathrm{C}}(\mathrm{CH_3})_3$], 34.10 [s, *o*-$\mathrm{C}(\underline{\mathrm{C}}\mathrm{H_3})_3$], 31.22 [s, *p*-$\mathrm{C}(\underline{\mathrm{C}}\mathrm{H_3})_3$], 2.08 ppm [d, ^{2}J(PSiC) = 7.9 Hz, $\mathrm{PSi(CH_3)_3}$]. – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = 314.7 ppm [s, ^{1}J(PW) = 511.5 Hz]. – **^{29}Si{^{1}H}-NMR** ([D$_6$]-benzene, 99.36 MHz): δ = 24.96 ppm [d, ^{1}J(PSi) = 26.8 Hz]. – **IR** (*n*-pentane): ν(CO) = 1934 (s), 1857 (s) cm^{-1}.

2. [Dicarbonyl(η^5-cyclopentadienyl){λ^4-[2,4,6-tri(*tert*-butyl)phenyl](dimetyhlsilyl)-phosphinediyl}tungsten(II) (4b): Analogous to **4a** from 80 mg (0.14 mmol) **1**, 9 mg (0.14 mmol, 0.1 mL, 1.6 mol/l) *n*-BuLi and 9 mg (0.14 mmol) chlorodimethylsilane (**3b**) in 5 mL THF after 1 h at room temperature. – Yield: 91 mg (74 %). – Darkblue powder. **Cp(OC)$_2$W=P(SiMe$_2$H)*s*Mes (4b): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.43 [d, ^{4}J(PCCCH) = 1.2 Hz, 2H, *m*-H], 5.09 (s, 5H, $\mathrm{C_5H_5}$), 4.96 [sept, ^{3}J(HSiCH) = 3.0 Hz, 1H, SiH], 1.45 [s, 18H, *o*-$\mathrm{C(CH_3)_3}$], 1.26 [s, 9H, *p*-$\mathrm{C(CH_3)_3}$], 0.13 ppm [d, ^{3}J(HCSiH) = 3.0 Hz, 6H, $\mathrm{Si(CH_3)_2}$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 235.49 [d, ^{2}J(PWC) = 7.9 Hz, *cis*-CO], 150.95 [d, ^{2}J(PCC) = 1.1 Hz, *o*-C], 150.49 (s, *p*-C), 145.51 [d, ^{1}J(PC) = 13.8 Hz, *ipso*-C], 122.29 [d, ^{3}J(PCCC) = 6.9 Hz, *m*-C], 94.62 (s, $\mathrm{C_5H_5}$), 38.15 [s, *o*-$\underline{\mathrm{C}}(\mathrm{CH_3})_3$], 34.84 [s, *p*-$\underline{\mathrm{C}}(\mathrm{CH_3})_3$], 33.08 [s, *o*-$\mathrm{C}(\underline{\mathrm{C}}\mathrm{H_3})_3$], 31.26 [s, *p*-$\mathrm{C}(\underline{\mathrm{C}}\mathrm{H_3})_3$], -1.91 ppm [d, ^{2}J(PSiC) = 5.9 Hz, $\mathrm{PSi(CH_3)_2}$]. – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = 294.0 ppm [s, ^{1}J(PW) = 523.7 Hz]. – **^{29}Si{^{1}H}-NMR** ([D$_6$]-benzene, 99.36 MHz): δ = 4.93 ppm [d, ^{1}J(PSi) = 35.8 Hz].

3. [Dicarbonyl(η^5-cyclopentadienyl){λ^4-[2,4,6-tri(*tert*-butyl)phenyl](diphenylsilyl)-phosphinediyl}tungsten(II) (4c): Analogous to **4a** from 92 mg (0.16 mmol) **1**, 10 mg (0.14 mmol, 0.11 mL, 1.6 mol/l) *n*-BuLi and 34 mg (0.14 mmol) chlorodiphenylsilane (**3c**) in 5 mL THF after 2 h at room temperature. – Yield: 107 mg (88 %). – Darkblue powder. **Cp(OC)$_2$W=P(SiPh$_2$H)*s*Mes (4c): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.90 [m, 2H, $\mathrm{Si(C_6H_5)_2}$], 7.52 [m, 2H, $\mathrm{Si(C_6H_5)_2}$], 7.40 (s, 2H, *m*-H), 7.16 [m, 4H, $\mathrm{Si(C_6H_5)_2}$], 5.88 [d, ^{2}J(PSiH) = 24.6 Hz, 1H, SiH], 5.01 (s, 5H, $\mathrm{C_5H_5}$), 1.39 [s, 18H, *o*-$\mathrm{C(CH_3)_3}$], 1.24 ppm [s, 9H, *p*-$\mathrm{C(CH_3)_3}$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 234.50 [d, ^{2}J(PWC) = 7.9 Hz, *cis*-CO], 154.38 [d, ^{2}J(PCC) = 8.3 Hz, *o*-C], 150.56 (s, *p*-C), 150.36 (s, *o*-C, Ph), 148.95 [d, ^{1}J(PC) = 22.0 Hz, *ipso*-C], 145.52 [d, ^{2}J(PCC) = 14.1 Hz, *ipso*-C, Ph], 137.08 (s, *p*-C, Ph), 129.76 (s, *m*-C, Ph), 122.97 [d, ^{3}J(PCCC) = 6.5 Hz, *m*-C], 94.35 (s, $\mathrm{C_5H_5}$), 38.76 [s, *o*-$\underline{\mathrm{C}}(\mathrm{CH_3})_3$], 34.84 [s, *p*-

$\underline{C}(CH_3)_3$], 34.51 [s, *o*-C($\underline{C}H_3)_3$], 31.28 ppm [s, *p*-C($\underline{C}H_3)_3$]. – ^{31}**P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = 269.5 ppm [s, ^1J(PW) = 535.8 Hz]. – ^{29}**Si{^{1}H}-NMR** ([D$_6$]-benzene, 99.36 MHz): δ = -8.09 ppm [d, ^1J(PSi) = 23.8 Hz]. – **IR** (*n*-pentane): ν(CO) = 1943 (s), 1866 (s) cm^{-1}.

4. Dicarbonyl(η^5-cyclopentadienyl){λ^4-[2,4,6-tri(*tert*-butyl)phenyl](stannyltrimetyhl)-phosphinediyl}tungsten(II) (6): Analogous to **4a** from 192 mg (0.33 mmol) **1**, 21 mg (0.14 mmol, 0.20 mL, 1.6 mol/l) *n*-BuLi and 65 mg (0.14 mmol) stannyltrimethylchloride (**5**) in 5 mL THF after 20 h at room temperature. Volatiles are removed in vacuo and the remaining residue is extracted five times with *n*-pentane (3 mL each). The combined organic layers are evaporated to one third of their volume, **6** crystallized at -78 °C and, after seperation from the solution, dried in vacuo. – Yield: 196 mg (80 %). – Blue powder. M.p. 115 °C (dec.). **Cp(OC)$_2$W=P(SnMe$_3$)*s*Mes (6):** ^{1}**H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.39 (s, 2H, *m*-H), 5.06 (s, 5H, C_5H_5), 1.44 [s, 18H, *o*-C($CH_3)_3$], 1.27 [s, 9H, *p*-C($CH_3)_3$], 0.57 ppm [d, ^3J(PSnCH) = 3.4 Hz, 9H, Sn($CH_3)_3$]. – ^{13}**C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 236.23 [d, ^2J(PWC) = 16.9 Hz, *cis*-CO], 149.96 [d, ^2J(PCC) = 2.3 Hz, *o*-C], 149.67 (s, *p*-C), 128.88 [d, ^1J(PC) = 28.6 Hz, *ipso*-C], 122.74 [d, ^3J(PCCC) = 6.5 Hz, *m*-C], 94.41 (s, C_5H_5), 38.62 [d, ^3J(PCCC) = 1.1 Hz, *o*-$\underline{C}(CH_3)_3$], 34.80 [s, *p*-$\underline{C}(CH_3)_3$], 33.71 [s, *o*-C($\underline{C}H_3)_3$], 31.26 [s, *p*-C($\underline{C}H_3)_3$], -2.82 ppm [d, ^2J(PSnC) = 6.9 Hz, PSn($CH_3)_3$]. – ^{31}**P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = 314.7 ppm [s, ^1J(PW) = 498.0 Hz, ^1J(PSn) = 72.0 Hz]. – **IR** (*n*-pentane): ν(CO) = 1996 (s), 1897 (s) cm^{-1}. Calc. for $C_{28}H_{43}O_2PSnW$ (745.2): C, 45.13; H, 5.82. Found: C, 44.96; H, 5.30.

5. Dicarbonyl(η^5-cyclopentadienyl){λ^4-(2,4,6-tri(*tert*-butyl)phenyl)[methoxy]phosphine-diyl}tungsten(II) (9): To a solution of 153 mg (0.25 mmol) Cp(OC)$_2$W=P(Cl)*s*Mes (**7**) in 5 mL toluene 14 mg (0.25 mmol) NaOMe (**8**) are added and stirred for 24 h at room temperature. Insolubles are seperated by filtration and the filtrate is evaporated to dryness. The residue is dissolved in 2 mL toluene and purified by column chromatography (column 20 x 2 cm; Al_2O_3, activity III, neutral; toluene). **9** is isolated by evaporation of the first red-brown layer to dryness and washing the residue three times with 3 mL of *n*-pentane followed by drying in vacuo. – Yield: 114 mg (75 %). – Redbrown solid. M.p. 102 °C (dec.). **Cp(OC)$_2$W=P(OMe)*s*Mes (9):** ^{1}**H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.45 [d, ^4J(PCCCH) = 3.00 Hz, 2H, *m*-H], 4.83 (s, 5H, C_5H_5), 3.81 [d, ^1J(PC) = 14.1 Hz, 3H, OCH_3], 1.59 [s, 18H, *o*-C($CH_3)_3$], 1.21 ppm [s, 9H, *p*-C($CH_3)_3$]. – ^{13}**C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 226.69 [d, ^2J(PWC) = 12.4 Hz, *cis*-CO], 149.07 [d, ^{2}J(PCC) = 6.6 Hz, *o*-C], 137.53 (s, *p*-C), 128.57 [d, ^{1}J(PC) = 57.9 Hz, *ipso*-C], 122.55 [d, ^{3}J(PCCC) = 8.6 Hz, *m*-C], 90.96 [d, ^{2}J(PWC) = 1.7 Hz, C_5H_5], 55.68 [d, ^{2}J(PCC) = 1.4 Hz, OCH_3], 38.46 [d, ^{3}J(PCCC) = 2.0 Hz, *o*-$\underline{C}(CH_3)_3$], 34.66 [s, *p*-$\underline{C}(CH_3)_3$], 34.02 [s, *o*-$C(\underline{C}H_3)_3$], 30.75 ppm [s, *p*-$C(\underline{C}H_3)_3$)]. – **$^{31}P\{^{1}H\}$-NMR** ([D_6]-benzene, 121.5 MHz): δ = 300.3 ppm [s, ^{1}J(PW) = 707.1 Hz]. – **IR** (benzene): ν(CO) = 1943 (vs), 1856 (vs) cm^{-1}. Calc. for $C_{26}H_{37}O_3PW$ (612.40): C, 50.99; H, 6.17. Found: C, 50.20; H, 5.93.

6. Dicarbonyl(η^{5}-cyclopentadienyl){λ^{4}-(2,4,6-tri(*tert*-butyl)phenyl)[trifluoromethanesulfonate]phosphinediyl}tungsten(II) (11): A solution of 90 mg (0.15 mmol) $Cp(OC)_2W{=}P(Cl)$*s*Mes (**7**) in 5 mL THF is treated with 33 mg (0.15 mmol) trimethylsilyltriflate (**10**) at -78 °C. After changing the colour from light-violet to organge-red, **7** is identified spectroscopically in the obtained solution. **$Cp(OC)_2W{=}P[OSO_2CF_3]$*s*Mes (11):** d.r.: **a** / **a’** = 45 : 55 (from integration of the ^{31}P-resonances). **$^{31}P\{^{1}H\}$-NMR** (THF, 121.5 MHz): **a**: δ = 297.1 [s, ^{1}J(PW) = 703.5 Hz]. – **a’:** δ = 295.9 ppm [s, ^{1}J(PW) = 702.3 Hz].

7. [2,4,6-tri(*tert*-butyl)phenyl(phosphinidene)trimethylphosphorane]dicarbonyl(η^{5}-cyclopentadienyl)trimethylphosphine-tungsten(II)-trifluoromethanesulfonate (13): A solution of 80 mg (0.13 mmol) $Cp(OC)_2W{=}P(Cl)$*s*Mes (**7**) in 5 mL THF is treated with 29 mg (0.13 mmol) trimethylsilyltriflate (**10**) at -78 °C. The resulting orange-red solution is stirred for 30 min and afterwards 20 mg (0.26 mmol) Me_3P (**12**) are added. The colour of the solution changes immediately to red-yellow. After stirring at -78°C for further 30 min the mixture is warmed up to room temperature and then combined with 30 mL of *n*-pentane. The precipitating solid is seperated from the solution and after additon of 5 mL *n*-pentane ultrasonic treated. The now generated yellow solid is seperated as suspension from the residue, volatiles are removed and **13** dried in vacuo. – Yield: 22 mg (20 %). – Yellow solid. **[$Cp(OC)_2(Me_3P^2)W$-P^3(*s*Mes)$P^1Me_3]OSO_2CF_3$ (13):** **^{1}H-NMR** ([D_3]-chloroforme, 300.4 MHz): δ = 7.36 (s, 2H, *m*-H), 5.55 (s, 5H, C_5H_5), 1.91 [dd, $^{2}J(P^1CH)$ = 15.6 Hz, $^{3}J(P^3P^1CH)$ = 5.7 Hz, 9H, P^1CH_3], 1.51 [s, 18H, *o*-$C(CH_3)_3$], 1.36 [dd, $^{2}J(P^2CH)$ = 12.9 Hz, $^{4}J(P^3WP^2CH)$ = 3.6 Hz, 9H, P^3CH_3], 1.26 ppm [s, 9H, *p*-$C(CH_3)_3$]. – **$^{31}P\{^{1}H\}$-NMR** ([D_3]-chloroforme, 121.5 MHz): δ = 21.9 [dd, $^{1}J(P^3P^1)$ = 421.6 Hz, $^{3}J(P^2WP^3P^1)$ = 7.3 Hz, P^1], -15.2 [dd, $^{2}J(P^3WP^2)$ = 54.7 Hz, $^{3}J(P^1P^3WP^2)$ = 7.3 Hz, P^2], -132.7 ppm [dd, $^{1}J(P^1P^3)$ = 421.6 Hz, $^{2}J(P^2WP^3)$ = 54.7 Hz, P^3].

8. Dicarbonyl(η^5-cyclopentadienyl){λ^4-(2,4,6-tri(*tert*-butyl)phenyl)[trimethylphosphine-phosphorane]phosphinediyl}-tungsten(II)-trifluoromethanesulfonate (14): A solution of 15 mg (0.07 mmol) [Cp(OC)$_2$(Me$_3$P)W-P(*s*Mes)PMe$_3$]OSO$_2$CF$_3$ (**13**) in 0.5 mL [D$_3$]-chloroforme is irradiated with UV-light for 5 h. The compound **14** can then be identified spectroscopically besides unidentified sideproducts. **[Cp(OC)$_2$W=P^2(*s*Mes)P^{1}Me$_3$]OSO$_2$CF$_3$ (14): ^{31}P{^{1}H}-NMR** ([D$_3$]-hloroforme, 121.5 MHz): δ = 24.0 [d, ^1J(P^{1}P^2) = 281.9 Hz, P^2] -87.4 ppm [d, ^1J(P^{2}P^1) = 281.9 Hz, P^1].

9. [2,4,6-tri(*tert*-butyl)phenyl(phosphinidene)trimethylphosphorane]dicarbonyl(η^5-cyclopentadienyl)trimethylphosphine-tungsten(II)-chloride (15): To a solution of 20 mg (0.05 mmol) Cp(OC)$_2$W=P(Cl)*s*Mes (**7**) in 0.5 mL [D$_6$]-benzene, 3 mg (0.05 mmol) Me$_3$P (**12**) are added whereupon a yellow solid precipitates. The solid is seperated from the solution, washed three times with 2 mL of *n*-pentane each und dried in vacuo. The complex **15** can be identified spectroscopically by comparison with a NMR-sample of [Cp(OC)$_2$(Me$_3$P)W-P(*t*Bu)PMe$_3$]Cl. **Cp(OC)$_2$(Me$_3$P^2)W-P^3(*s*Mes)P^{1}Me$_3$]Cl (15): ^{31}P{^{1}H}-NMR** ([D$_3$]-chloroforme, 121.5 MHz): δ = 23.5 [dd, ^1J(P^{3}P^1) = 417.0 Hz, ^3J(P^{2}WP^{3}P^1) = 6.1 Hz, P^1], -15.1 [dd, ^2J(P^{3}WP^2) = 58.3 Hz, ^3J(P^{1}P^{3}WP^2) = 6.1 Hz, P^2], -133.3 ppm [dd, ^1J(P^{1}P^3) = 417.0 Hz, ^2J(P^{2}WP^3) = 58.3 Hz, P^3].

10. X-ray analyses of 6 and 9: Crystals of Cp(OC)$_2$W=P(SnMe$_3$)*s*Mes (**6**) and Cp(OC)$_2$W=P(OMe)*s*Mes (**9**) suitable for structure determination could be from a saturated *n*-pentane (**6**) or toluene solution (**9**), respectively, at room temperature. Data collection was performed on an Enraf-Nonius CAD4-diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) at 173(2) K.[35-37] The structures were solved using the Patterson-method and cell parameters were determined and refined using SHELXS-97[38] and SHELXL-97.[39]

*Crystal Data for Compounds **6** and **9**:*

	6	**9**
identification	andi54	katta19
mol formula	$C_{28}H_{43}WO_2PSn$	$C_{26}H_{37}O_3PW$
mol wt	745.14	612.40
wavelength (Å)	0.71073	0.71073
temp (K)	173(2)	173(2)
cryst size (mm)	0.15 x 0.11 x 0.08	0.13 x 0.12 x 0.09
cryst syst	monoclinic	monoclinic
space group	*P2(1)/c*	*P2(1)/c*
a (Å)	9.899(2)	8.8644(12)
b (Å)	35.552(8)	16.645(2)
c (Å)	9.1091(19)	19.776(3)
α (°)	90	90
β (°)	109.594(4)	98.662(3)
γ (°)	90	90
vol (Å^3), Z	3020.1(11), 6	2885.2(7), 5
ρ (calcd) (Mgm^{-3})	1.639	1.529
F(000)	1464	1327
μ (mm^{-1})	4.706	4.087
θ range for data collecn (deg)	2.26 – 25.05	1.61 – 25.10
no. of rflns collected	5329	5129
no. of indep reflns	5329	5129
abs cor.	empirical	empirical
no. of data/restraints/params	5329 / 76 / 373	5129 / 0 / 303
goodness of fit on F^2	0.987	1.103
R1^a	0.0375	0.0391
wR2^b	0.0652	0.0916
largest diff peak and hole (eÅ^{-3})	1.012 and -0.406	1.0377 and -0.595

$R1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ 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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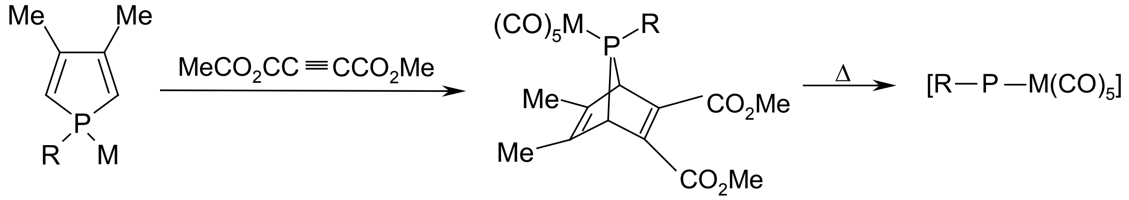
CHAPTER IV

Dinuclear Phosphinidene Complexes $Cp(OC)_2W{=}P(ML_n)$*s*Mes [$ML_n = Cp(OC)_3W$, $Cp(OC)_3Fe$]: Synthesis from $Cp(OC)_2W{=}P(H)$*s*Mes and Photochemical Transformation

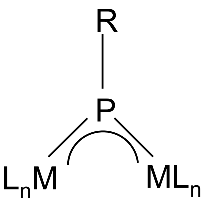
Introduction

Since the first isolation of a phosphinidene[1-4] complex by *Lappert* et al. in 1987[5] the coordination chemistry of the carbene analogous ligand (PR) has attracted widespread attention and is still in the focus of current research.[6-9] While *Mathey* performed fundamental studies concerning the generation of the terminal phosphinidene complexes **C** [(Scheme (1)] via thermal decomposition of 7-phosphabicyclo[2.2.1]hepta-2,5-diene-complexes **B**,[10, 11] obtained from a Diels-Alder-reaction of phosphol-metal complexes **A** with electron deficient alkynes, further access to a simple synthesis of phosphinidene complexes is still of interest.

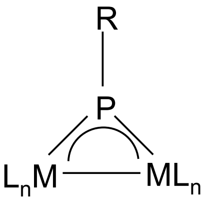


A M = Cr, Mo, W **B** **C**

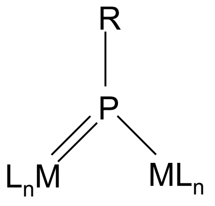
The high interest in the phosphinidene (PR) group as a ligand is based on the its coordination chemistry with organometal fragments, leading to diverse coordination modes. Several terminal (η^1, linear or bent)[5, 12, 13] and mainly bridging type (μ^2 - μ^4)[14-20] complexes support the rich bonding nature of the PR-group. Most of the known μ^2-phosphinidene complexes feature the open structure **D**, in which the sp^2-hybridized phosphorus atom is bridging two 16-electron-metal-fragments symmetrically [ML$_n$ = M(CO)$_5$ (M = Cr, Mo, W), Mn(CO)$_2$Cp].[15] More uncommon are compounds of the type **E**, containing a 15-electron-metal-fragment [ML$_n$ = (OC)$_3$Co, Cp(OC)$_2$M][14, 18-20] and an additional metal-metal-bond. The coordination mode **F** is a speciality in so far as it can be interpreted both as a metallo-phosphenium[21, 22] and as a phosphinidene complex, with the PR-group bridging two electronically inequivalent metalfragments – a 15- and a 17-electron-metal-fragment – establishing a M-P-double and single bond.[18]



D



E



F

By now we realized the synthesis of both homo- and heteronuclear complexes of the type **F**. In both cases the double bond is formed after connecting the second transition metal fragment to the phosphinidene-phosphorus atom. Thus reaction of the *secondary* metallo-phosphines $C_5R_5(OC)_3M\text{-}P(H)Mes$ with the organometallic lewis-acids $[C_5R_5(OC)_3M]BF_4$ (M = Mo, W; R = H, Me) leads to the bis(metallo)phosphonium salts $\{[C_5R_5(OC)_3M]_2P(H)Mes\}BF_4$, which can be converted to the phosphinidene complexes $C_5R_5(OC)_2M{=}P(Mes)\text{-}M(CO)_3Cp$ by deprotonation and subsequent decarbonylation.[23, 24]

We now present an alternative approach making use of the anionic phosphinidene complex [Cp(OC)$_2$W=P(*s*Mes)]Li (**2**) derived from the *super*-mesitylphosphenium complex Cp(OC)$_2$W=P(H)*s*Mes (**1**). Synthesis of **F** is achieved via controlled introduction of transition metal fragments at the anionic phosphorus.

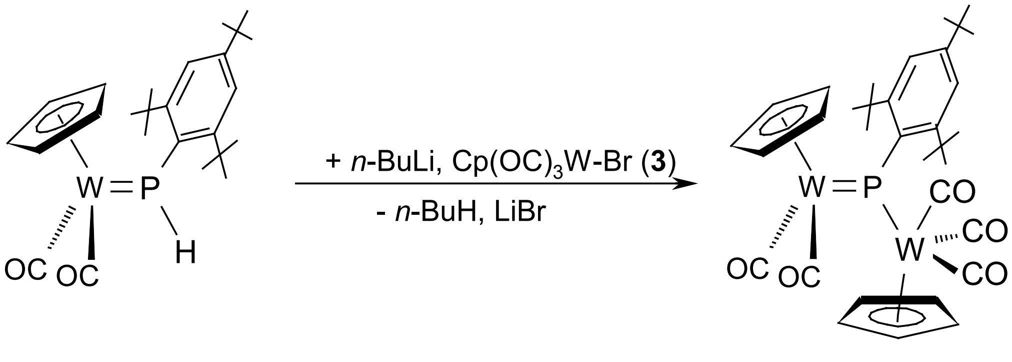
In the class of P-H-functionalized phosphenium complexes Cp(OC)$_2$M=P(H)R (M = Mo, W; R = alkyl, aryl), which are characterized by a sterically rather unshielded and therefore highly reactive M=P-bond,[18, 25] the *super*-mesitylphosphenium complex Cp(OC)$_2$W=P(H)*s*Mes (**1**) is the only example isolable at room temperature.[26] Due to the bulkiness of the *super*-mesityl substituent a selective H/Li-exchange reaction with *n*-BuLi can be realized to yield [Cp(OC)$_2$W=P(*s*Mes)]Li (**2**) as highly reactive compound, which can not be isolated in substance but is usable *in situ* for diverse alkylation reactions with carbon electrophiles[27] and other group 14 electrophiles.[28]

In this chapter we present the first successful reactions of **2** with diverse types of transition metal halides leading to novel homo- and heteronuclear phosphinidene complexes.

Results and Discussion

Reactivity Studies

The treatment of the phosphenium complex Cp(OC)$_2$W=P(H)*s*Mes (**1**), dissolved in THF, with *n*-BuLi at -78 °C results in an immediate change of colour of the solution from violet to darkgreen and formation of the anionic phosphinidene complex [Cp(OC)$_2$W=P(*s*Mes)]Li (**2**).[27, 28] When **2** is treated with an equimolar amount of Cp(OC)$_3$W-Br (**3**) after a reaction time of 18 h at room temperature the metallation of the phosphorus is complete, to give the novel phosphinidene complex **4** [Eq. (1)].

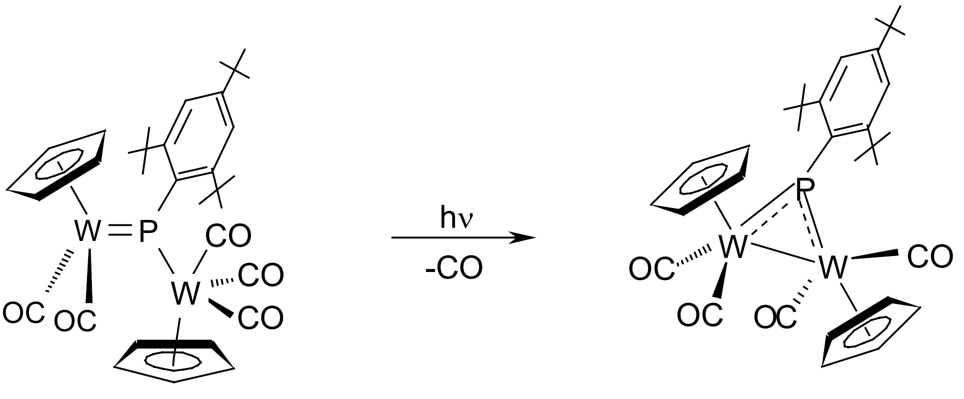


(1)

1 **4**

4 is obtained as green powder in 50 % yield. The ^{31}P-NMR-data correlates with the description of **4** as a phosphinidene complex with an unsymetrically coordinated phosphorus atom. The typical resonance of 255.2 ppm and the two different ^{1}J(PW)-couplings of 507.9 Hz and 94.8 Hz are in accordance with the formation of a single and double bonded tungsten fragment.

4 is stable in solid state and in solution but can be converted on irradiation with UV-light to the symmetric phosphinidene complex **5** [Eq. (2)] via carbonyl elimination reaction, connected with simultaneous tungsten-tungsten-bond generation.

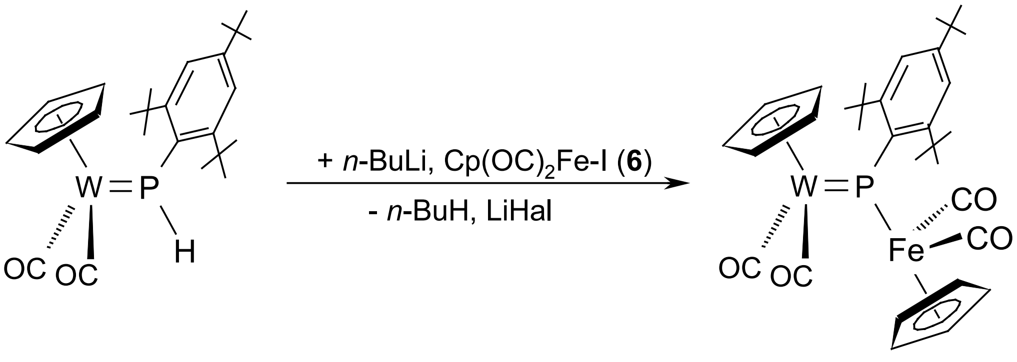


(2)

4 **5**

As a consequence the ^{31}P-NMR resonance is shifted dramatically downfield from 255.2 ppm (**4**) to 601.47 ppm (**5**) while the coupling constant amounts to 288.0 Hz (**5**). This value is nearly the half of the sum of the ^{1}J(PW)-couplings found for **4** (507.9 Hz and 94.8 Hz), indicating a delocalisation of the phosphorus lone pair within the W-P-W-linkage arrangement. This finding is supported by the x-ray structural data [Fig. (2)].

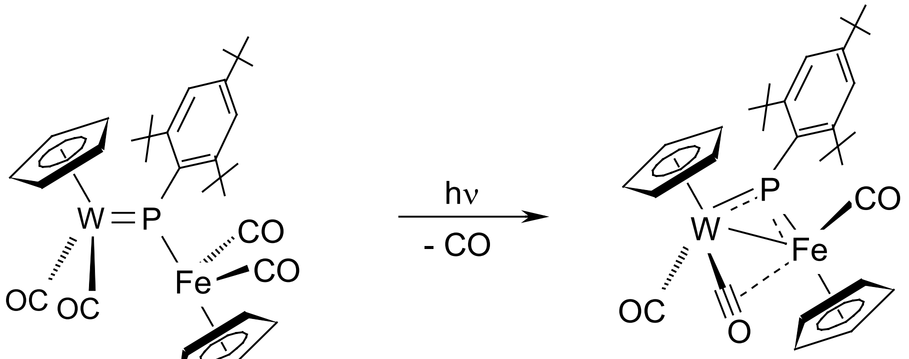
The novel synthetic pathway according to Eq. (1) is also effective for the synthesis of heteronuclear phosphinidene complexes of the type **C**. Treatment of **1** with *n*-BuLi and an equimolar amount of $Cp(OC)_2Fe$-I (**6**) yields, after a reaction time of 16 h at room temperature, the novel heteronuclear tungsten-iron-complex **7** [Eq. (3)].



(3)

1 **7**

The complex **7** is obtained as black powder in 68 % yield. The ^{31}P-NMR-resonance at 352.0 ppm and the ^1J(PW)-coupling of 496.8 Hz proves double bond character between the tungsten and the phosphorus atom. The NMR-data of the earlier obtained complex $Cp(OC)_2W$=P(Mes)-$Fe(CO)_2Cp$ (352.5 ppm; 487.6 Hz) are nearly indentical.[24] **7** is soluble in aromatic solvents like benzene or toluene but rather unstable in solution as well as in the solid state. The reason is a facile CO-elimination yielding the unsymmetric carbonyl bridged complex **8**. In contrast to the di-tungsten complex **5** one carbonyl ligand occupies a semibridging-type position. The decarbonylation process is strongly accelerated if a solution of **7** is is irradiated with UV-light [Eq. (4)].



(4)

7 **8**

8 can be isolated as darkbrown powder in 50 % yield. The bridging by the phosphinidene unit is obvious from the ^{31}P-NMR-resonance of **8** which is considerably shifted lowfield (616.1 ppm) in comparison to **7** (352.00 ppm). Surprisingly the ^1J(PW)-coupling remains in the same range like in the starting material [496.8 Hz (**7**); 432.5 Hz (**8**)], which proves the double bond character of the W-P-bond. A typical resonance for the bridging carbonyl ligand can be found both in the ^{13}C-NMR- [219.63 (s, *μ*-CO)] and in the IR-spectrum [ν(CO) = 1794 (m) cm^{-1}]. Additional evidence is given by the x-ray structure analysis of **8** [Fig. (3)].

Structural Investigation

Crystals of $Cp(OC)_2W{=}P$(*s*Mes)-$W(CO)_3Cp$ (**4**) suitable for structure determination could be obtained from a saturated toluene solution at room temperature.

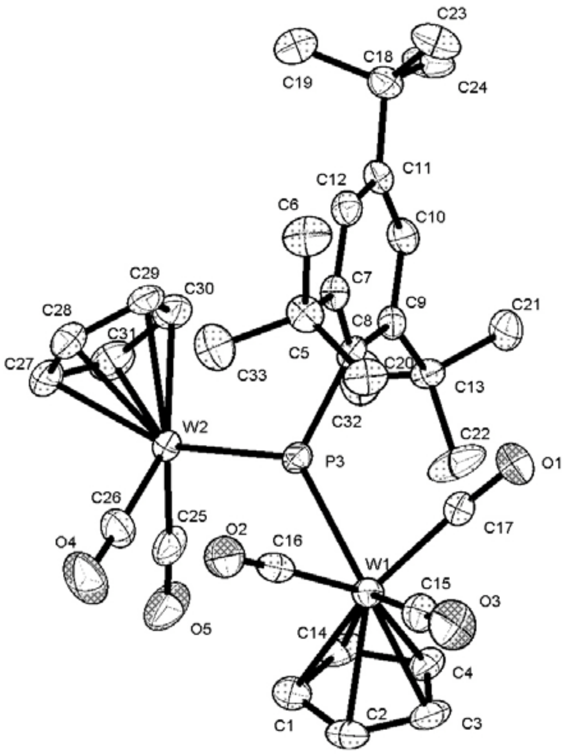


Fig. (1). Molecular structure of $Cp(OC)_2W{=}P$(*s*Mes)-$W(CO)_3Cp$ (**4**) - The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: Selected bond lengths [Å], bond- and torsion angles [°]:W(2)-C(25) 1.934(7), W(2)-C(26) 1.931(7), W(1)-C(15) 1.979(7), W(1)-C(16) 1.996(7), W(1)-C(17) 1.979(6), W(1)-P(3) 2.6064(15), W(2)-P(3) 2.2976(16), P(3)-C(8) 1.889(6), W(2)-C(25) 1.934(7), W(1)-C(22) 1.950(5), C(15)-W(1)-P(3) 129.50(19), C(25)-W(2)-P(3) 98.45(19), C(26)-W(2)-P(3) 93.1(2), C(26)-W(2)-C(25) 78.0(3), C(8)-P(3)-W(2) 110.70(18), C(8)-P(3)-W(1) 121.69(18), W(2)-P(3)-W(1) 127.60(6), P(3)-C(8)-C(7)-C(12) -153.6(5), P(3)-C(8)-C(9)-C(10) -155.5(4), C(9)-C(8)-C(7)-C(12) 9.2(8), C(11)-C(12)-C(7)-C(8) -3.7(9).

The coordination geometry of the tungsten atom W2 can be described as a pseudo-octahedral three legged piano stool. The cyclopentadienyl ligand is occupying three facial coordination sites, whereby two legs are formed by the carbonyl ligands at W2 and the third leg by the double bonded phosphenium ligand. This is proved by the bond angles between the carbonyl ligands and the phosphorus moiety, which are only slightly enlarged in comparison to the expected value of 90° (C25-W2-P3 98.45°, C17-W1-P1 93.1°). The plane defined by C8, P3 and W1 is almost vertical to the W2-$(CO)_2$-moiety, which shows the smallest angle (C26-W2-C25 78.0°) in the piano stool fragment. The tungsten atom W1 exhibits a square pyramidal arrangement of the ligands around the central metal atom with the cyclopentadienyl ring in the apical position and the basis formed by the *super*-mesityl-phosphine ligand and the three carbonyl groups.

The geometry of the phosphorus atom is exactly trigonal planar with the sum of angles amounting to 359.9°. As a result of the sp^2-hybridization the phosphenium ligand can be regarded as three-electron donor, giving the tungsten atom a total number of 18 valence electrons. The C8-P3-W1-angle (121.69°) is close to the ideal value (120.0°). Due to the sterical demand of the *tris*-carbonyl tungsten substituent and the repulsion between the C17-carbonyl moiety and the *super*-mesityl-ligand the *s*Mes-group is bent towards the cyclopentadienyl moiety at W2, leading to a relatively small C8-P3-W2-angle of 110.7°. As a consequence of this sterical situation the W2-P3-W1-angle is expanded to 127.6°.

The P-*ipso*-C bond length (1.89 Å) is in the upper range for a P_{sp2}-C_{sp2} single bond[29] and excludes therefore π–interaction between the phosphorus atom and the aromatic ring system.

The W2-P3 bond length of 2.30 Å is nearly identical to that of $Cp(OC)_2W{=}P(tBu)_2$ (2.28 Å)[22] and finds itself on the upper limit for a W-P-double-bond system, for which a theoretical bond length of 2.26 Å is calculated.[30-32] The W1-P3 distance of 2.61 Å confirms single bond character for the σ-bond of the phosphorus to the W1 fragment.

The steric demand of the *s*Mes-ligand causes on the one hand a severe distorsion of the aryl group planarity (C9-C8-C7-C12 9.2°, C11-C12-C7-C8 -3.7°) and on the other hand this effect determines the arrangement of the *super*-mesityl group. In order to avoid interaction of the *ortho*-*tert*-butyl-groups with the cyclopentadienyl- and carbonyl-ligands at W1 the aryl ligand is bent towards the W2 metal fragment, leading to a loss of planarity at C8. The differences from the torsion angle of 180° are significant (P3-C8-C7-C12 -153.6°, P3-C8-C9-C10 -155.5°). This fact can also be found for diorganophosphenium complexes like $Cp(OC)_2W{=}P(R)s$Mes (R = Me, Et, *i*Pr, Bu, CH_2Ph) where the values of the differences range from 11.8° to 24.3°.[27]

The complex **4** shows *cis*-configuration regarding the *super*-mesityl-ligand and the W2-bonded cyclopentadienyl moiety, which is in accordance with the situation for $Cp(OC)_2W{=}P(H)s$Mes

(**1**)[33] and $\text{Cp(OC)}_2\text{W=P(R)}s\text{Mes}$ (R = Me, Et, *i*Pr, Bu, CH_2Ph)[27] and is in common with theoretical investigations.[33] Despite the aryl ligand distorsion the overall structure is comparable to that of the analogous mesityl-derivatives $\text{Cp(OC)}_2\text{W=P(Mes)-W(CO)}_3\text{Cp}$[24, 34] and $\text{Cp(OC)}_2\text{W=P(Mes)-W(PH}_2\text{Mes)(CO)}_2\text{Cp}$.[18]

Crystals of $\text{Cp(OC)}_2\overline{\text{W-P(}s\text{Mes)-W}}\text{(CO)}_2\text{Cp}$ (**5**) suitable for structure determination could be obtained from a saturated toluene solution at room temperature.

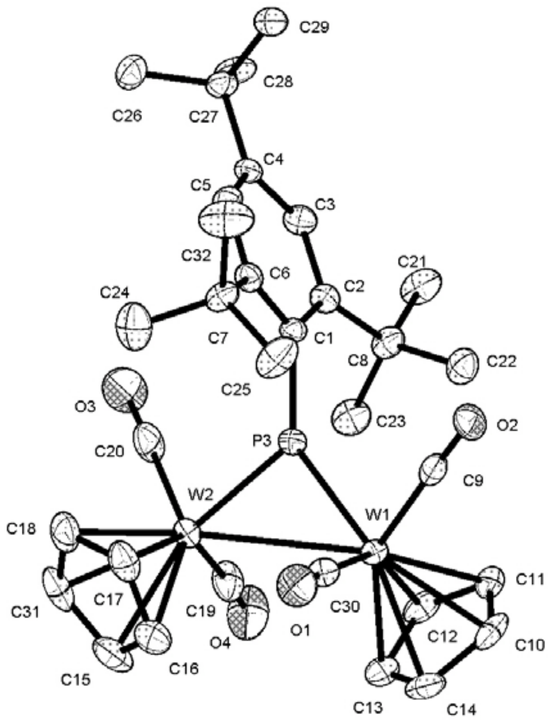


Fig. (2). Molecular structure of $\text{Cp(OC)}_2\overline{\text{W-P(}s\text{Mes)-W}}\text{(CO)}_2\text{Cp}$ (**5**) - The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: Selected bond lengths [Å], bond- and torsion angles [°]: W(1)-C(9) 1.954(4), W(1)-C(30) 1.957(4), W(1)-P(3) 2.3178(10), W(1)-W(2) 3.2050(9), W(2)-C(19) 1.958(4), W(2)-P(3) 2.2999(11), P(3)-C(1) 1.851(3), C(9)-W(1)-P(3) 83.24(11), P(3)-W(1)-W(2) 45.82(2), P(3)-W(2)-W(1) 46.28(3), W(2)-P(3)-W(1) 87.90(4), C(1)-P(3)-W(2) 128.35(12), C(1)-P(3)-W(1) 143.54(12), C(9)-W(1)-W(2) 123.53(10), C(19)-W(2)-P(3) 96.68(12), C(19)-W(2)-W(1) 82.44(12), C(1)-C(2)-C(3)-C(4) 2.1(6), M(1)-W(1)-W(2)-M(2) 96.0°, P(3)-W(1)-W(2)-M(2) 50.8°, P(3)-W(2)-W(1)-M(1) 45.1°, P(3)-C(1)-C(2)-C(3) 158.8(3), C(6)-C(1)-C(2)-C(3) -9.6(5).

Both tungsten atoms exhibit a square pyramidal arrangement of the ligands around the central metal atom with the cyclopentadienyl ring in the apical position and the basis formed by the two carbonyl groups as well as a tungsten-tungsten and a tungsten-phosphorus bond.

The Newman projection along the W1-W2-bond reveals that the two Cp(OC)$_2$W-moieties are in a *gauche* conformation, with a torsion angle of 96.0° including the centers (M1/2) of the cyclopentadienyl ligand and the W1-W2-bond. The bisector of the M1-W1-W2-M2-linkage is the W1-W2-P1 plane, which halves the angle of 96.0°. The discrepancies to the theoretical value for the halved angle (48°) are considerably infinitesimal (2.8° or 2.9°).

The bond lengths of 2.32 Å (W1-P3) and 2.30 Å (W2-P3), respectively, are on the upper limit for a W-P-double-bonded system for which a theoretical bond length of 2.26 Å is calculated.[30-32] It is also nearly identical to the literature-known tungsten phosphinidene complex with a bulky phosphorus substituent $\text{Cp(OC)}_2\overline{\text{W-P(tmp)-W}}\text{(CO)}_2\text{Cp}$ (2.28 and 2.29 Å).[14]

With 3.21 Å the distance between the tungsten atoms is longer than the theoretical value for a W-W bond (2.60 Å).[35] This point is again in accordance with the result for $\text{Cp(OC)}_2\overline{\text{W-P(tmp)-W}}\text{(CO)}_2\text{Cp}$ for which the W-W bond distance is 3.25 Å[14]

The geometry of the phosphorus atom is exactly trigonal planar, the sum of angles amounts to 359.8°. But due to the formation of the W1-P-W2-ring system and the steric demand of the *s*Mes-ligand, in all cases strong deviations from the ideal value of 120° can be found as demonstrated by the angles W2-P3-W1 (87.9°), C1-P3-W2 (128.5°) and C1-P3-W1 (143.5°).

The steric demand of the *ortho*-*tert*-butyl-groups in the *s*Mes-ligand determines the arrangement of the whole system. In order to reduce interactions of these groups with the cyclopentadienyl- or the carbonyl-ligands the aryl ligand does not take up a linear position at C1 as theoretically anticipated. Differences from the ideal torsion angle of 180° are significant as can be seen from the angle P3-C1-C2-C3 (158.8°). In addition a severe distorsion of the aryl group planarity (C6-C1-C2-C3 -9.6°) is caused due to this sterical approach.

Also, the overall structure of **5** can be compared to the molbydenum complexes $\text{Cp(OC)I}\overline{\text{Mo-P(}s\text{Mes)-Mo}}\text{(CO)ICp}$[20] and $\text{Cp(OC)}_2\overline{\text{Mo-P(}s\text{Mes)-Mo}}\text{(CO)}_2\text{Cp}$ respectively.[14, 20]

Crystals of Cp(OC)$\overline{\text{W(CO)P-(}s\text{Mes)-Fe}}$(CO)Cp (**8**) suitable for structure determination could be obtained from a saturated toluene solution at room temperature.

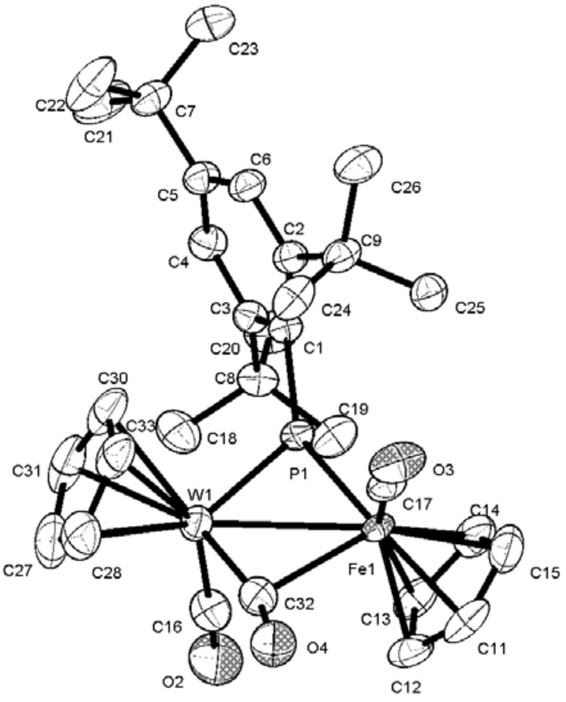


Fig. (3). Molecular structure of Cp(OC)$\overline{\text{W(CO)P-(}s\text{Mes)-Fe}}$(CO)Cp (**8**) - The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: W(1)-C(16) 1.979(4), W(1)-C(32) 1.985(3), W(1)-P(1) 2.2488(8), P(1)-Fe(1) 2.1616(9), P(1)-C(1) 1.844(3), Fe(1)-C(32) 2.433(3), Fe(1)-C(17) 1.749(3), C(32)-W(1)-P(1) 101.27(9), O(4)-C(32)-W(1) 162.0(3), Fe(1)-P(1)-W(1) 82.93(3), C(1)-P(1)-Fe(1) 147.97(9), C(1)-P(1)-W(1) 127.72(9), P(1)-Fe(1)-C(32) 90.82(8), W(1)-C(32)-Fe(1) 82.08(11), C(32)-W(1)-P(1)-Fe(1) 14.39(10), C(1)-C(2)-C(6)-C(5) -2.5(4), P(1)-C(1)-C(3)-C(4) 152.2(2).

The W1-P1 bond distance of 2.25 Å observed for **8**, almost agrees perfectly with the theoretical value of 2.26 Å for a W=P double bond[30-32] and lies in the range of literature-known double bond systems like Cp(OC)$_2$W=P(R)(*s*Mes) (R = Me, Et, *i*Pr, *n*Bu, CH$_2$Ph) (2.24 Å - 2.25 Å)[27] or Cp(OC)$_2$W=P(*t*Bu)$_2$ (2.28 Å).[22] The bond length of 2.16 Å for the Fe1-P1 bond is in accordance with the values observed for Fe-P-single bonds (2.19 Å[36]; 2.17 Å[37, 38]).

The bond distance to the bridging carbonyl ligand at C32 (W1-C32 1.99 Å) is very close to the value for a terminal metal-carbonyl bond (W1-C16 1.98 Å), which suggests to assign the bridging carbonyl moiety to the ligand sphere of the tungsten atom. The bond distance Fe1-C32 of 2.43 Å is strongly elongated and lies in the higher range of known distances for terminal bonded carbonyl ligands on iron atoms.[39-41] A further effect of the bridging carbonyl-unit is the reduction of the W1-C32-O4-bond angle to 162.0° compared to the ideal value of 180°.

The W1-C32-Fe1-P1-cycle shows a butterfly arrangement indicated by the C32-W1-P1-Fe1 torsion angle of 14.39°. The sum of angles of 358.62° at the phosphorus atom indicates a pronounced sp^2-hybridization, which causes a trigonal planar ligand arrangement. The single angles differ up to 27° (Fe1-P1-W1) from the ideal value of 120°.

The distorsion of the aryl group planarity [C(1)-C(2)-C(6)-C(5) –2.5°] of the *s*Mes-ligand is originated from its steric demand. Especially the *ortho*-*tert*-butyl-groups cause the arrangement of the whole *super*-mesityl group. In order to avoid interactions with the cyclopentadienyl- and the carbonyl ligands at W1 the aryl ligand is bent towards the tungsten metal fragment out of the expected linear position. The difference from the theoretical torsion angle of 180° is significant (P1-C1-C3-C4 152.2°).

Experimental Section

General: All manipulations were performed under purified and dried nitrogen by standard Schlenk-type techniques. Solvents were rigorously dried with an appropriate drying agent, distilled and saturated with nitrogen prior to use. IR: Spectra were recorded using a Perkin-Elmer 283 grating spectrometer. Samples were prepared as solutions in a NaCl cell with 0.1 mm path length with a resolution of about 2 cm^{-1}. NMR: JEOL LAMBDA 300 (300.4 MHz, 75.6 MHz and 121.5 MHz for ^1H, ^{13}C and ^{31}P, respectively). ^1H and ^{13}C spectra are referenced to the residual proton signal or natural abundance carbon signal of C_6D_6 at $\delta = 7.15$ ppm (^1H) or $\delta = 128.0$ ppm (^{13}C), respectively. ^{31}P chemical shifts are referenced to external H_3PO_4. ^1H-NOESY spectra were recorded on a AMX BRUKER 400 referenced to the residual proton signal of C_6D_6 at $\delta = 7.15$ ppm. Melting points were obtained by differential thermoanalysis (Du Pont 9000 Thermal Analysis System). Elemental analyses were performed in the laboratories of the Institut für Anorganische Chemie der Universität Würzburg. $Cp(OC)_2W{=}P(H)$*s*Mes (**1**),[26] $Cp(OC)_2W$-Br (**3**)[42] and $Cp(OC)_2Fe$-I (**6**)[42] were prepared according to literature procedures.

1. Dicarbonyl(η^5-cyclopentadienyl){λ^4-[tricarbonyl(η^5-cyclopentadienyl)tungstic]-(2,4,6-tri(*tert*-butyl)phenyl)phosphandiyl}tungsten(II) (4): A solution of 152 mg (0.26 mmol) $Cp(OC)_2W{=}P(H)$*s*Mes (**1**) in 10 mL THF is treated at -78 °C with 17 mg (0.26 mmol) *n*-BuLi. 108 mg (0.26 mmol) $Cp(OC)_3W$-Br (**3**) are added to the resulting darkgreen solution and the reaction mixture is allowed to warm up to room temperature. Volatiles are evaporated in vacuo after stirring for 18 h and the darkbrown residue is extracted five times with *n*-pentane (5 mL each). The volume of the combined organic layers is reduced to one third and **4** crystallized at -78 °C, seperated from the solution and dried in vacuo. – Yield: 119 mg (50 %). – Green powder. M.p. 54 °C (dec.). **Cp(OC)$_2$W^2=P(*s*Mes)-W^1(CO)$_3$Cp (4): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.42 (s, 2H, *m*-H), 5.39 (s, 5H, W^2-C$_5$H$_5$), 4.92 (s, 5H, W^1-C$_5$H$_5$), 1.59 [s, 18H, *o*-C(CH$_3$)$_3$], 1.26 ppm [s, 9H, *p*-C(CH$_3$)$_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 248.55 (s, br, W^2-CO), 225.40 (s, W^1-trans-CO), 213.54 [^2J(PW^{1}C) = 25.0 Hz, W^1-*cis*-CO], 148.54 (s, *o*-C), 137.82 (s, *p*-C), 128.86 [d, ^1J(PC) = 58.2 Hz, *ipso*-C], 123.86 (s, br, *m*-C), 93.89 (s, C$_5$H$_5$), 65.86 [s, *o*-$\underline{C}$(CH$_3$)$_3$], 36.05 [s, br, *p*-$\underline{C}$(CH$_3$)$_3$], 34.49 [s, br, *o*-C($\underline{C}$H$_3$)$_3$], 31.14 ppm [s, *p*-C($\underline{C}$H$_3$)$_3$]. – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = 255.2 ppm [s, ^1J(PW^2) = 507.9 Hz, ^1J(PW^1) = 94.8 Hz]. – **IR** (*n*-pentane): ν(CO) = 2027 (s, W^1), 1983 (s, W^1), 1934 (vs, W^2), 1862 (s, W^2) cm^{-1}. Calc. for $C_{33}H_{39}O_5PW_2$ (914.3): C, 43.35; H, 4.30. Found: C, 43.80; H, 4.62

2. Synthesis of Cp(OC)$_2$W-P(*s*Mes)-W(CO)$_2$Cp (5): A solution of 22 mg (0.20 mmol) Cp(OC)$_2$W=P(*s*-Mes)-W(CO)$_3$Cp (**4**) in 5 mL benzene is irradiated for 2 h with UV light. Unsolubles are filtrated and the solvent is evaporated in vacuo. The residue is washed three times with 5 mL *n*-pentane each and dried in vacuo. – Yield: 11 mg (55 %). – Black powder. M.p. 109 °C (dec.). **Cp(OC)$_2$W-P(*s*Mes)-W(CO)$_2$Cp (5): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.59 [d, ^4J(PCCCH) = 3.0 Hz, 2H, *m*-H], 5.16 (s, 10H, C$_5$H$_5$), 1.51 [s, 18H, *o*-C(CH$_3$)$_3$], 1.30 ppm [s, 9H, *p*-C(CH$_3$)$_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 224.74 [d, ^2J(PWC) = 8.0 Hz, *cis*-CO], 222.32 (s, *cis*-CO), 151.59 [d, ^2J(PCC) = 3.1 Hz, *o*-C], 150.91 (s, *p*-C), 132.86 [d, ^1J(PC) = 44.2 Hz, *ipso*-C], 123.83 [d, ^3J(PCCC) = 8.0 Hz, *m*-C], 89.20 [d, ^2J(PWC) = 0.8 Hz, C$_5$H$_5$], 38.88 [d, ^3J(PCCC) = 1.5 Hz, *o*-$\underline{C}$(CH$_3$)$_3$], 33.44 [s, *p*-$\underline{C}$(CH$_3$)$_3$], 33.07 [s, *o*-C($\underline{C}$H$_3$)$_3$], 31.14 ppm [s, *p*-C($\underline{C}$H$_3$)$_3$]. – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = 601.5 ppm [s, ^1J(PW) = 288.0 Hz]. – **IR** (toluene): ν(CO) = 1919 (vs), 1872 (s) cm^{-1}. Calc. for $C_{32}H_{39}O_4PW_2$ (886.3): C, 43.36; H, 4.44. Found: C, 43.11; H, 4.36.

3. Dicarbonyl(η^5-cyclopentadienyl){λ^4-[dicarbonyl(η^5-cyclopentadienyl)ferrio]-(2,4,6-tri-(*tert*-butyl)phenyl)phosphandiyl}tungsten(II) (7): Analogous to **4** from 130 mg (0.22 mmol) Cp(OC)$_2$W=P(H)*s*Mes (**1**), 14 mg (0.22 mmol) *n*-BuLi and 68 mg (0.22 mmol) Cp(OC)$_2$Fe-I (**6**) in 10 mL THF after 16 h. – Yield: 110 mg (68 %). – Black powder. M.p. 67 °C (dec.). **Cp(OC)$_2$W=P(*s*Mes)-Fe(CO)$_2$Cp (7): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.49 (s, 2H, *m*-H), 4.96 (s, 5H, W-C_5H_5), 4.71 (s, 5H, Fe-C_5H_5), 1.64 [s, 18H, *o*-$C(CH_3)_3$], 1.28 ppm [s, 9H, *p*-$C(CH_3)_3$]. – **^{13}C-NMR** ([D_6]-benzene, 75.45 MHz): δ = 241.56 [d, ^2J(PWC) = 6.9 Hz, W-CO], 214.0 [d, ^2J(PFeC) = 17.3 Hz, Fe-CO], 166.76 [d, ^1J(PC) = 46.5 Hz, *ipso*-C], 148.43 (s, *o*-C), 147.36 (s, *p*-C), 122.03 [d, ^3J(PCCC) = 4.8 Hz, *m*-C], 93.29 (s, W-C_5H_5), 87.75 (s, Fe-C_5H_5), 39.45 [s, *o*-$\underline{C}(CH_3)_3$], 35.62 [s, *p*-$\underline{C}(CH_3)_3$], 34.77 [s, *o*-$C(\underline{C}H_3)_3$], 31.07 ppm [s, *p*-$C(\underline{C}H_3)_3$]. – **^{31}P{^{1}H}-NMR** ([D_6]-benzene, 121.5 MHz): δ = 352.0 ppm [s, ^1J(PW) = 496.8 Hz]. – **IR** (*n*-pentane): ν(CO) = 2028 (vs, Fe), 1983 (vs, Fe), 1906 (vs, W), 1832 (vs, W) cm^{-1}. Calc. for $C_{32}H_{39}FeO_4PW$ (758.3): C, 50.68; H, 5.18. Found: C, 47.60; H, 4.85.

4. Synthesis of Cp(OC)W(CO)-P(*s*Mes)-Fe(CO)Cp (8): A solution of 356 mg (0.47 mmol) Cp$(OC)_2$W=P(*s*Mes)-Fe$(CO)_2$Cp (**8**) in 15 mL THF is irradiated for 2 h. Unsolubles are filtrated and the solvent is evaporated in vacuo. The residue is washed three times with 5 mL *n*-pentane each and dried in vacuo. – Yield: 172 mg (50 %). – Darkbrown powder. M.p. 134 °C (dec.). **Cp(OC)W(CO)-P(*s*Mes)-Fe(CO)Cp (8) :^{1}H-NMR** ([D]$_6$-benzene, 300.4 MHz): δ = 7.50 (s, 2H, *m*-H), 4.71 (s, 5H, W-C_5H_5), 4.69 (s, 5H, Fe-C_5H_5), 1.65 [s, 9H, *o*-$C(CH_3)_3$], 1.49 [s, 9H, *o*-$C(CH_3)_3$], 1.28 ppm [s, 9H, *p*-$C(CH_3)_3$]. – **^{13}C-NMR** ([D]$_6$-benzene, 75.45 MHz): δ = 239.76 (s, W-CO), 221.76 [d, ^2J(PFeC) = 17.9 Hz, Fe-CO], 219.63 (s, *μ*-CO), 152.67 [d, ^1J(PC) = 41.5 Hz, *ipso*-C], 152.49 (s, *o*-C), 149.63 (s, *p*-C), 123.42 [d, ^3J(PCCC) = 7.2 Hz, *m*-C], 91.67 (s, W-C_5H_5), 84.44 (s, Fe-C_5H_5), 38.77 [d, ^3J(PCCC) = 9.5 Hz, *o*-$\underline{C}(CH_3)_3$], 35.22 [s, *p*-$\underline{C}(CH_3)_3$], 32.47 [s, *o*-$C(\underline{C}H_3)_3$], 31.02 ppm [s, *p*-$C(\underline{C}H_3)_3$]. – **^{31}P{^{1}H}-NMR** ([D]$_6$-benzene, 121.5 MHz): δ = 616.1 ppm [s, ^1J(PW) = 432.5 Hz]. – **IR** (cyclohexane): ν(CO) = 1962 (s), 1944(s), 1912 (vs), 1794 (m) cm^{-1}. Calc. for $C_{31}H_{39}FeO_3PW$ (730.32): C 50.98; H 5.38; found: C 50.30; H 5.45.

5. X-ray analyses for compounds 4, 5 and 8: Crystals of **4**, **5** and **8** suitable for structure determination could be obtained via crystallization from a saturated toluene solution at room temperature. Data collection was performed on an Enraf-Nonius CAD4-diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) at 173(2) K.[43-45] The structures were solved using the Patterson-method and cell parameters were determined and refined using SHELXS-97[46] and SHELXL-97.[47]

*Crystal Data for Compounds **4**, **5** and **8**:*

	8	**4**	**5**
Identification code	andi49	katta9	katta7
mol formula	$C_{31}H_{26}FeWO_3P$	$C_{33}H_{39}O_5PW_2$	$C_{32}H_{39}O_4PW_2$
mol wt	730.29	914.3	886.3
wavelength (Å)	0.71073	0.71073	0.71073
temp (K)	173(2)	173(2)	173(2)
cryst size (mm)	0.20 x 0.13 x 0.10	0.20 x 0.20 x 0.20	0.20 x 0.20 x 0.20
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C2/c*	*P2(1)/c*	P2(1)/c
a (Å)	28.239(7)	11.810(3)	13.248(4)
b (Å)	13.493(3)	15.307(3)	13.633(4)
c (Å)	16.882(4)	18.756(4)	16.931(5)
α (°)	90	90	90
β (°)	111.953(4)	106.505(4)	97.725(5)
γ (°)	90	90	90
vol ($Å^3$), Z	5966(2), 12	3250.9(13), 4	3030.3(16), 7
ρ (calcd) (Mgm^{-3})	1.626	1.868	1.943
F(000)	2912	1760	1704
μ (mm^{-1})	4.422	7.158	7.674
θ range for data collecn (deg)	1.70 – 25.01	1.75 to 25.06	1.55 to 25.11
no. of rflns collected	49308	38673	21587
no. of indep reflns	5245	5754	5361
abs cor.	empirical	empirical	empirical
no. of data/restraints/params	5245 / 80 / 389	5754 / 33 / 410	5361 / 0 / 361
goodness of fit on F^2	1.092	1.010	1.089
$R1^a$	0.0208	0.0367	0.0219
$wR2^b$	0.0525	0.0786	0.0460
largest diff peak and hole ($eÅ^{-3}$)	1.141 and -0.392	4.456 and -0.860	1.050 and -0.543

$R1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ 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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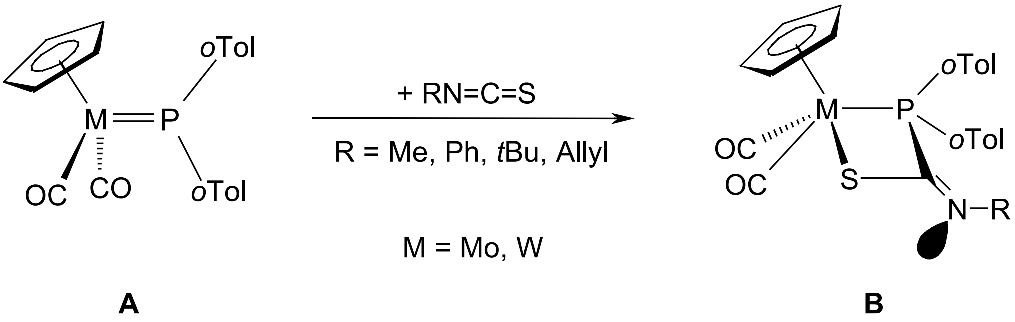
CHAPTER V

Cyclic Metallo-Phosphines $\mathrm{Cp(OC)_2}\overline{\mathrm{W\text{-}P(\mathit{s}Mes)\text{-}C(NHR)S}}$ (R = Alkyl) and $\mathrm{Cp(OC)_2}\overline{\mathrm{W\text{-}P(\mathit{s}Mes)\text{-}C[NH(\mathit{i}Pr)]{=}N}}\mathrm{(\mathit{i}Pr)}$ via [2+2] Cycloaddition of $\mathrm{Cp(OC)_2W{=}P(H)\mathit{s}Mes}$ with Alkylisothiocyanates and Diisopropylcarbodiimide Followed by P→N-Hydrogen Migration

Introduction

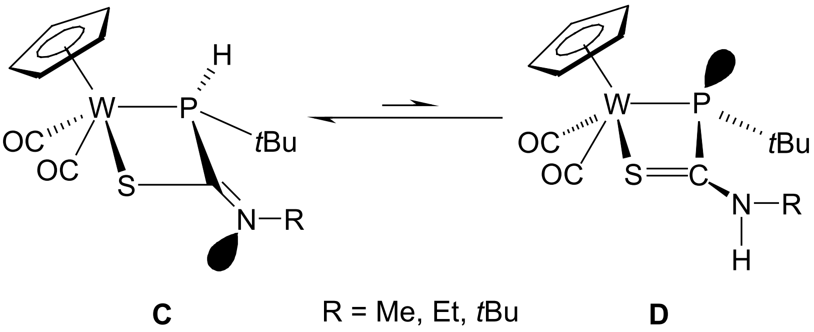
In contrast to the extensive development of transition metal-mediated organic synthesis, which is a central topic of organometallic chemistry,[1-5] much less attention has been paid to the possibility of using phosphorus metal complexes for the stoichiometric or even catalytic generation of organophosphorus species.[6-9] This situation is due to a limited number of suitable metal coordinated phosphorus moieties, showing diversities of controlled reactions with organic substrates.

Taking into account the reactivity of isothiocyanates and carbodiimides in transition-metal-containing synthesis, which is still in current focus,[10-12] studies concerning the reactivity of diorganophosphenium complexes **A** towards alkylisothiocyanates had been performed,[13-28] revealing a regiospecific cycloadditon of the sulphur and carbon atom of the isothiocyanate to the M=P-bond to yield phosphametallacycles of the type **B**.[29]



In context with our efforts to establish metal mediated synthesis of organophosphorus compounds we have approached P-H-functionalized molydenum and tungsten phosphenium complexes $Cp(OC)_2M=P(H)R$ (M = Mo, W; R = alkyl, aryl), which are characterized by a sterically rather unshielded and therefore highly reactive M=P- and P-H-bond.[30, 31]

Extension of the cycloadditions performed with alkylisothiocyanates and carbodiimides on P-H-functionalized phosphenium complexes, showed in context with the only *in situ* available *tert*-butylphosphenium complex $Cp(OC)_2W=P(H)tBu$, the formation of the expected P-H-functionalized phosphametallacycles **C**.[32, 33]



Interesting enough due to NMR- and IR-measurement these complexes undergo in solution a minor tautomerization involving hydrogen transfer from the phosphorus to the nitrogen atom to give the cyclic metallo-phosphines **D**.[32, 33] This finding suggests that a complete tautomerization should be verified by increasing the acidity of the P-H-bond in the primarily formed P-H-functionalized cycloadducts **C**. Especially substitution of the *tert*-butyl-ligand by an aryl substituent is regarded as an effective measurement to get access to novel cyclic metallo-phosphines of the type **D**.

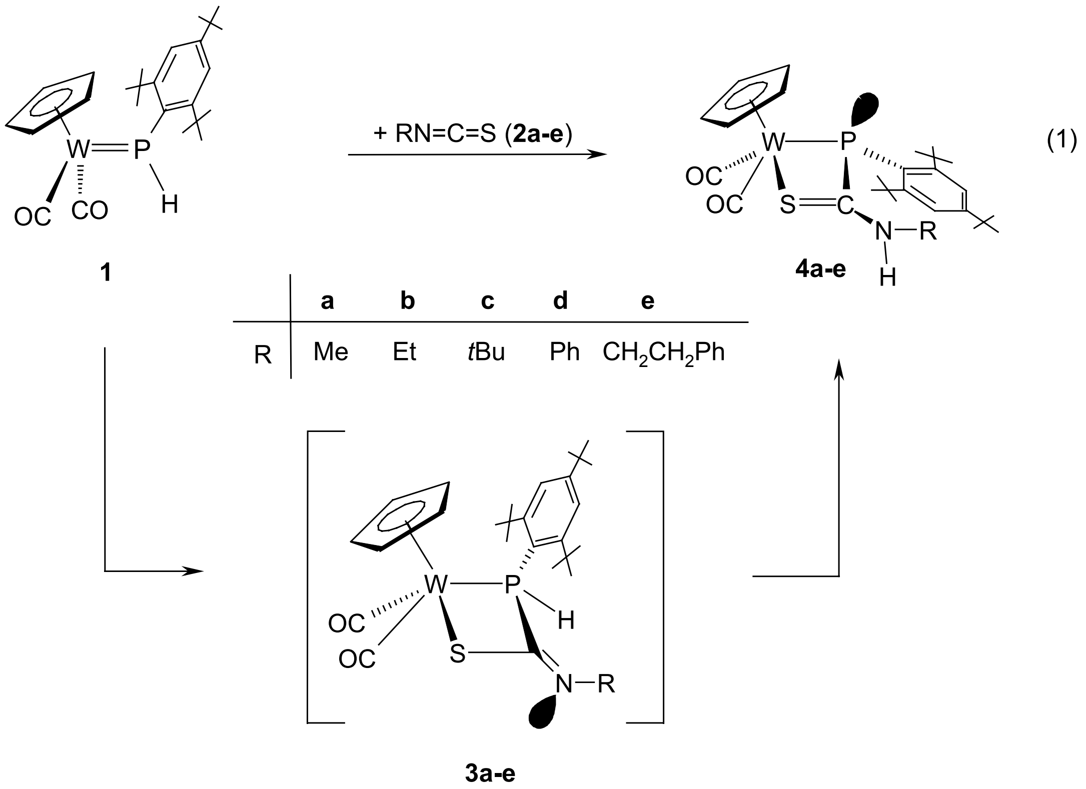
Therefore the reaction with the stable P-H-functionalized phosphenium complex Cp(OC)$_2$W=P(H)*s*Mes (**1**) with selected alkylisothiocyanates and diisopropylcarbodiimid was studied. Moreover the *super-m*esityl-group, due its high steric demand, should offer the possibility of a diastereoselective reaction with respect to the formed phosphametallacycles.

Results and Discussion

Reactivity Studies

In context with the already mentioned reactivity of diorganophosphenium complexes towards reagents like organoisocyanates[34, 35] or organoisothiocyanates[13-28] there is high interest on the extension of the knowledge regarding cycloadditions with a prostereogenic organophosphorus unit like it is present in Cp(OC)$_2$W=P(H)*s*Mes (**1**).[36]

Stirring of a 1:1-mixture of **1** and the alkylisothiocyanates **2a-e** in toluene at room temperature for 2 (**4a**) - 24 h (**4e**) yields the four-membered phosphametallacycles **4a-e**, which as the most striking feature show a trivalent phosphorus and a hydrogen substituted nitrogen atom, in yields from 40 (**4e**)- 84 % (**4a**) [Eq. (1)].



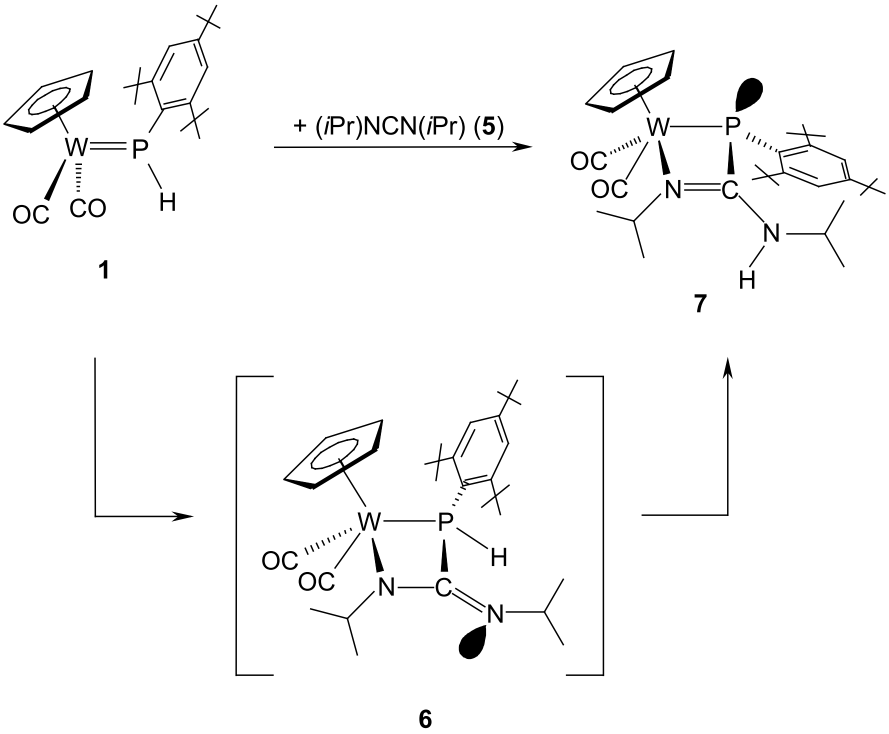
	a	b	c	d	e
R	Me	Et	*t*Bu	Ph	CH_2CH_2Ph

The product formation indicates a [2+2]-cycloaddition involving the C=S double bond of the isothiocyanate **2a-e** to give primarily the P-H-functionalized cycloadducts **3a-e**, followed by rapid P→N-hydrogen migration to the phosphametallacycles **4a-e**. **3a-e** can neither be isolated nor characterized spectroscopically in solution due to the accidity of the P-H-function in the [2+2]-intermediate. This finding is in contrast to the reaction of the *tert*-butylphosphenium complex Cp(OC)$_2$W=P(H)*t*Bu, for which the P-H-functionalized cycloadduct C$_5$Me$_5$(OC)$_2$W-P(H)(*t*Bu)-C(=NR)-S (R = Me, Et, *t*Bu) is more stable in solution. The corresponding N-H-tautomeric cycloadduct can be detected in solution by IR measurement only in about 20 % yield.[32, 33] Obviously the aryl ligand favours in the primarily cycloaddition products **3a-e** fast tautomerization to the complexes **4a-e**.

The phosphametallacycles **4a-e** are formed completely diastereoselective which means that only the *unlike*-isomers (S_WR_P/R_WS_P) are formed in the reaction with respect to the stereochemistry at the tungsten and phosphorus atom. This is due to the steric demand of the *s*Mes-ligand leading to a selective *trans*-configuration regarding the Cp- and the aryl moiety in the final cycloadducts **4a-e**. The obtained x-ray structure analyses of **4b** [Fig. (1)] and **4d** [Fig. (2)] prove this configuration.

Additional evidence for the structures of the compounds **4a-e** in solution is given by the ^{31}P-NMR resonances at high field [-72.2 (**4d**) to –85.1 (**4b**) ppm] and the small coupling-constant ^1J(PW) [176.2 (**4a**)– 196.8 (**4d**) Hz], characteristic for a trivalent pyramidal phosphorus σ-coordinated to tungsten,[37, 38] compared to the ^{31}P-values for the P-H-tautomers of $C_5Me_5(OC)_2W$-P(H)(*t*Bu)-C(=NR)-S (R = Me, Et, *t*Bu) [δ^{31}P / ^1J(PW) = 14.4 / 215.7 ; 13.4 / 211.6; 14.2 / 224.2][32] and the phosphanido compound Cp(OC)$_3$W-P(H)*s*Mes [δ^{31}P / ^1J(PW) = -141.0 / 50.6].[36] The N-bonded hydrogen is found in the ^{1}H-NMR spectra between 4.65 (**4c**) and 6.23 (**4d**) ppm as a slightly broadened signal.

An analogous product is formed from the reaction of **1** with diisopropylcarbodiimide (**5**) in toluene at room temperature. After a reaction time of 90 min the four-membered phosphametallacycle **7** is obtained as dark orange powder in 75 % yield [Eq. (2)].



(2)

The NMR data (^{1}H, ^{13}C, ^{31}P) definitely prove the diastereoselective formation of one isomer namely the *like*-derivative with a *trans*-configuration concerning the Cp- and *s*Mes-ligand [Fig. (3)]. **7** also shows as the most characteristic feature a trivalent phosphorus atom corporated in the ring system. This suggests for the first step [2+2]-cycloaddition affording the P-H-functionalized four-membered heterocycle Cp(OC)$_2$W-P(H)*s*Mes-C[=N(*i*Pr)]-N(*i*Pr) (**6**), followed by hydrogen migration from phosphorus to the exocyclic imine nitrogen. Again the primary cycloadduct **6** can not be detected spectroscopically due to fast tautomerization to **7** as a consequence of the high accidity of the P-H-function. Evidence for a trivalent pyramidal phosphorus is given by the ^{31}P-NMR highfield shift at 102.2 ppm and the characteristic coupling constant ^1J(PW) of 117.9 Hz compared to **4a-e** and the *tert*-butyl analogue $C_5Me_5(OC)_2W$-P(H)(*t*-Bu)-C(=NR)-S (R = Me, Et, *t*-Bu).[32]

The complex **1** is capable of sequential couplings involving isothiocyanates and carbodiimides, for which the spontaneous P→N hydrogen transfer is the product determining crucial reaction step. As an important aspect the high diastereoselectivity of the cycloadditions of prostereogenic phosphenium complexes has to be pointed out.

Structural Investigation

Crystals of Cp(OC)$_2$W-P(*s*Mes)-C[N(H)Et]=S (**4b**) and Cp(OC)$_2$W-P(*s*Mes)-C[N(H)Ph]=S (**4d**) suitable for structure determination could be obtained from a saturated cyclohexane (**4b**) or *n*-pentane (**4d**) solution, respectively.

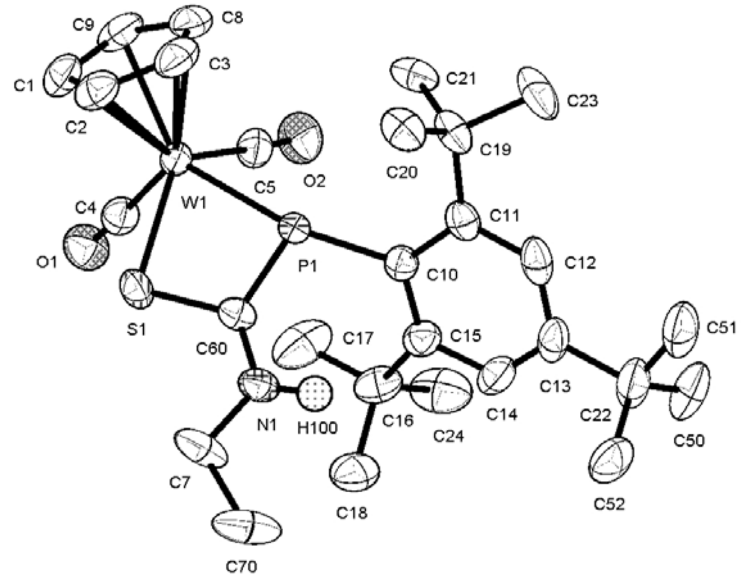


Fig. (1). Molecular structure of *unlike*-Cp(OC)$_2$W-P(*s*Mes)-C[N(H)Et]=S (**4b**). - The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: W(1)-S(1) 2.5168(11), W(1)-P(1) 2.4996(11), S(1)-C(60) 1.721(4), P(1)-C(60) 1.738(4), P(1)-C(10) 1.844(4), N(1)-C(60) 1.329(5), N(1)-C(7), 1.458(5), S(1)-W(1)-P(1) 66.20(3), C(4)-W(1)-C(5) 77.60(18), W(1)-S(1)-C(60) 93.92(13), W(1)-P(1)-C(60) 94.08(13), W(1)-P(1)-C(10) 142.74(13), C(60)-P(1)-C(10) 106.69(18), N(1)-C(60)-S(1) 123.5(3), N(1)-C(60)-P(1) 131.7(3), S(1)-C(60)-P(1) 104.8(2), C(60)-N(1)-C(7) 124.5(4), C(60)-N(1)-H(100) 117.4, C(7)-N(1)-H(100) 1118.0, W(1)-S(1)-C(60)-P(1) 9.01(18), W(1)-S(1)-C(60)-N(1) -171.9(3), C(7)-N(1)-C(60)-S(1) -5.0(6), C(7)-N(1)-C(60)-P(1) 173.8(3).

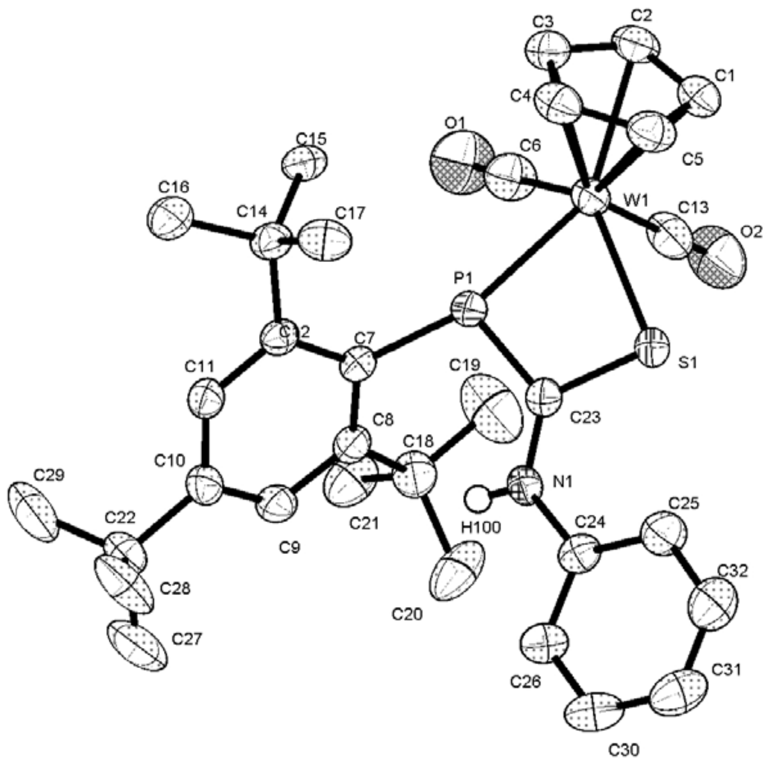


Fig. (2). Molecular structure of *unlike*-Cp(OC)$_2$W-P(*s*Mes)-C[N(H)Ph]=S (**4d**). - The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: W(1)-P(1) 2.4805(9), W(1)-C(6) 1.957(3), W(1)-C(13) 1.953(4), W(1)-S(1) 2.5147(9), S(1)-C(23) 1.734(3), P(1)-C(23) 1.724(3), P(1)-C(7) 1.843(3), N(1)-C(23) 1.344(4), N(1)-C(24) 1.411(3), N(1)-H(100) 0.714, C(13)-W(1)-C(6) 77.88(15), C(6)-W(1)-P(1) 83.55(11), C(13)-W(1)-P(1) 115.72(10), P(1)-W(1)-S(1) 65.86(2), C(23)-S(1)-W(1) 94.45(9), C(23)-P(1)-W(1) 95.91(10), C(7)-P(1)-W(1) 146.61(9), C(23)-P(1)-C(7) 106.83(12), N(1)-C(23)-P(1) 129.3(2) N(1)-C(23)-S(1) 127.2(2), P(1)-C(23)-S(1) 103.51(15), C(23)-N(1)-C(24) 131.3(3), C(6)-W(1)-S(1)-C(23) 55.81(17), C(13)-W(1)-S(1)-C(23) -121.11(14), P(1)-W(1)-S(1)-C(23) 3.35(9), C(6)-W(1)-P(1)-C(23) 134.01(14), C(13)-W(1)-P(1)-C(23) 60.80(15), C(6)-W(1)-P(1)-C(7) 0.71(19), C(13)-W(1)-P(1)-C(7) -72.5(2), S(1)-W(1)-P(1)-C(23) 3.38(9), W(1)-P(1)-C(23)-S(1) 4.60(13), W(1)-S(1)-C(23)-P(1) -4.53(12), W(1)-S(1)-C(23)-N(1) 173.8(2), C(7)-P(1)-C(23)-N(1) -18.4(3), W(1)-P(1)-C(23)-N(1) -173.6(3), S(1)-W(1)-P(1)-C(7) 136.68(16), C(24)-N(1)-C(23)-S(1) 18.3(5), C(9)-C(8)-C(7)-P(1) 151.6(2), C(11)-C(12)-C(7)-P(1) -154.4(2), C(11)-C(12)-C(7)-C(8) 10.7(4), C(9)-C(8)-C(7)-C(12) -12.5(4).

In both cases the obtained x-ray structure analyses of **4b** and **4d** shows a slightly folded four-membered phosphametallacycle with the phosphorus atom directed out of the plane [W1-S1-C60-P1 9.01° (**4b**); W1-S1-C23-P1 -4.53° (**4d**)]. The chelating C-S-ligand is characterized by the planarity of the ring-integrated carbon atom C60 (**4b**) or C23 (**4d**), respectively, and the exo-nitrogen atom (N1) proved by the sum of angles around 360°. This finding and the short C-N bond distance of 1.33 Å (C60; **4b**) and 1.34 Å (C23; **4d**), compared to the ideal C_{sp^2}=N_{sp^2} double bond value of 1.249 Å, indicates delocalization of the nitrogen lone electron pair towards the ring carbon atom.[39] As estimated from the short P-C distances of 1.74 Å (C60; **4b**) and 1.72 Å (C23; **4d**), which are between the value of a single and a double bond, the ring carbon atoms gain certain degree of electronic saturation from the lone pair of the trivalent phosphorus.[40] As a consequence the C-S bond lengths of 1.72 Å (C60; **4b**) and 1.73 Å (C23; **4d**) are significantly elongated in comparison to a the value for a C=S double bond [d(C=S) = 1.597 Å; d(C-S) = 1.820 Å].[41] The tungsten centers exhibit a square pyramidal arrangement of the ligands with the basis formed by the *cis*-positioned CO-groups and the P-C=S chelating ligand. With 343.51° (**4b**) and 349.35° (**4d**) the sum of angles around P1 differs in each structure enormously form the ideal tetrahedral arrangement by 16.51° (**4b**) or 22.35° (**4d**), respectively.

Crystals of Cp(OC)$_2$W-P(*s*Mes)-C[NH(*i*Pr)]=N(*i*Pr) (**7**) suitable for structure determination could be obtained from a saturated toluene solution.

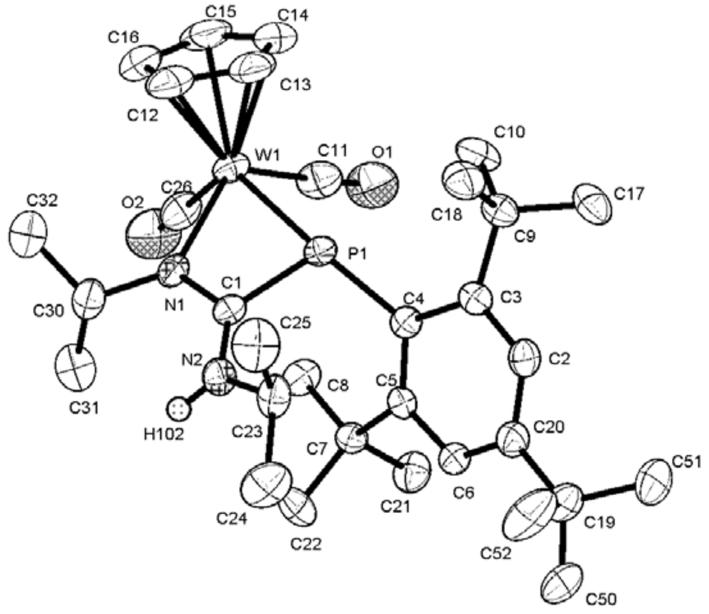


Fig. (3). Molecular structure of *like*-Cp(OC)$_2$W-P(*s*Mes)-C[NH(*i*Pr)]=N(*i*Pr) (**7**). - The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: W(1)-P(1) 2.5195(11), W(1)-N(1) 2.224(3), P(1)-C(1) 1.807(4), N(1)-C(1) 1.312(5), N(2)-C(1) 1.355(5), N(1)-C(30) 1.481(5), N(2)-C(23) 1.475(5), N(1)-W(1)-P(1) 63.36(9), C(1)-N(1)-W(1) 107.9(3), C(1)-P(1)-W(1) 82.72(13), N(1)-C(1)-P(1) 105.7(3), N(1)-C(1)-N(2) 126.3(4), N(1)-W(1)-P(1)-C(1) 3.06(15), W(1)-N(1)-C(1)-N2 -179.3(3), C(30)-N(1)-C(1)-P(1) -174.7(3).

The molecular structure of the cycloaddition product **7** [Fig. (3)] verifies the square pyramidal arrangement of the ligands at the tungsten center.[39, 42] The basis is formed by the *cis*-positioned carbonyl ligands and the P-C=N chelating moiety. Indicated by the C-N distances of 1.36 Å (C1-N2) and 1.31 Å (C1-N1), which lie between a single [d(C-N) = 1.47 Å][39] and a double bond [d(C=N) = 1.24 Å][39], the P-C=N-chelate shows strong delocalization within the N-C-N-bonding system. The sum of angles at C1 amounting to 359.8° proves sp^2-hybridization, while the sum of 326.7° at P1 inidcates nearly ideal sp^3-hybridization for the phosphorus atom with the lone pair occupying a tetrahedral position. The W1-P1 distance of 2.52 Å is on the upper limit for tungsten complexes qith a σ–coordinated phosphanido-phosphorus.

Experimental Section

General: All manipulations were performed under purified and dried nitrogen by standard Schlenk-type techniques. Solvents were rigorously dried with an appropriate drying agent, distilled and saturated with nitrogen prior to use. IR: Spectra were recorded using a Perkin-Elmer 283 grating spectrometer. Samples were prepared as solutions in a NaCl cell with 0.1 mm path length with a resolution of about 2 cm^{-1}. NMR: JEOL LAMBDA 300 (300.4 MHz, 75.6 MHz and 121.5 MHz for ^{1}H, ^{13}C and ^{31}P, respectively). ^{1}H and ^{13}C spectra are referenced to the residual proton signal or natural abundance carbon signal of C_6D_6 at $\delta = 7.15$ ppm (^{1}H) or $\delta = 128.0$ ppm (^{13}C), respectively. ^{31}P chemical shifts are referenced to external H_3PO_4. ^{1}H-NOESY spectra were recorded on a AMX BRUKER 400 referenced to the residual proton signal of C_6D_6 at $\delta = 7.15$ ppm. Melting points were obtained by differential thermoanalysis (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 by literature methods: Cp(OC)$_2$W=P(H)*s*Mes (**1**).[36] RNCS (R = Me, Et, *t*Bu, Ph, CH_2CH_2Ph) (**2a-e**) and the carbodiimide (*i*Pr)N=C=N(*i*Pr) (**5**) were obtained commercially and used without further purification.

1. Dicarbonyl(η^5-cyclopentadienyl){[2,4,6-tri(*tert*-butyl)phenyl][(N-methyl)thioformamido-κS]-phosphanido-κP}tungsten(II) (4a): To a solution of 214 mg (0.37 mmol) Cp(OC)$_2$W=P(H)*s*Mes (**1**) in 5 mL toluene 27 mg (0.37 mmol) methylisothiocyanate (**2a**) are added with a syringe and stirred for 24 h at room temperature. The solution is evaporated to dryness, the residue extracted four times with *n*-pentane (5 mL each) and **4a** crystallized out of the collected *n*-pentane layers by cooling to -78 °C and, after filtration, dried in vacuo. – Yield: 204 mg (84 %). – Orange powder. M.p. 57 °C (dec.). **Cp(OC)$_2$W-P(*s*Mes)-C[N(H)Me]=S (4a):**

^{1}H-NMR ([D$_6$]-benzene, 300.4 MHz): δ = 7.67 [d, ^4J(HCCCH) = 2.2 Hz, 1H, *m*-H], 7.57 [dd, ^4J(PCCCH) = 4.6 Hz, ^4J(HCCCH) = 2.2 Hz, 1H, *m*-H], 5.23 (s, 5H, H$_5$C$_5$), 4.70 (s, br, 1H, HN), 0.41 [vt, ^3J(HCCH) = ^3J(PCCH) = 5.0 Hz, 3H, H$_3$C], 1.69 [s, 9H, *o*-C(CH$_3$)$_3$], 1.55 [s, 9H, *o*-C(CH$_3$)$_3$], 1.30 ppm [s, 9H, *p*-C(CH$_3$)$_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 248.22 [d, ^2J(PWC) = 16.2 Hz, *cis*-CO], 244.00 [d, ^2J(PWC) = 15.2 Hz, *cis*-CO], 215.41 [d, ^1J(PC) = 13.1, C=S], 158.38 [d, ^2J(PCC) = 6.8 Hz, *o*-C], 158.06 [d, ^2J(PCC) = 21.4 Hz, *o*-C], 150.69 [d, ^4J(PCCCC) = 2.7 Hz, *p*-C], 128.89 [d, ^1J(PC) = 57.2 Hz, *i*-C], 126.57 [d, ^3J(PCCC) = 3.1 Hz, *m*-C], 121.97 [d, ^3J(PCCC) = 11.4 Hz, *m*-C], 92.70 [d, ^2J(PWC) = 1.1 Hz, C$_5$H$_5$], 42.02 (s, CH$_3$N), 38.92 [d, ^3J(PCCC) = 3.9 Hz, *o*-$\underline{\text{C}}$(CH$_3$)$_3$], 35.00 [d, ^3J(PCCC) = 0.6 Hz, *o*-$\underline{\text{C}}$(CH$_3$)$_3$], 35.35 [s, *p*-$\underline{\text{C}}$(CH$_3$)$_3$], 33.33 [d, ^4J(PCCCC) = 8.9 Hz, *o*-C($\underline{\text{C}}$H$_3$)$_3$], 31.26 [s, *p*-C($\underline{\text{C}}$H$_3$)$_3$], 27.97 ppm [d, ^4J(PCCCC) = 2.4 Hz, *o*-C($\underline{\text{C}}$H$_3$)$_3$]. – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = -85.0 ppm [s, ^1J(WP) = 176.2 Hz]. – **IR** (*n*-pentane): ν(CO) = 1943 (s), 1864 (s) cm^{-1}. Calc. for C$_{27}$H$_{38}$NO$_2$PSW (655.50): C, 49.47; H, 5.84; N, 2.14; S, 4.89. Found: C, 49.20; H, 5.76; N, 1.97; S, 4.33.

2. Dicarbonyl(η^5-cyclopentadienyl){[2,4,6-tri(*tert*-butyl)phenyl][(N-ethyl)thioformamido-κS]-phosphanido-κP}tungsten(II) (4b): A solution of 61 mg (0.10 mmol) Cp(OC)$_2$W=P(H)*s*Mes (**1**) in 5 mL toluene is combined with 91 mg (1.00 mmol) ethylisothiocyanate (**2b**) at 0 °C. The reaction mixture is brought to room temperature and stirred for 2 h. Volatiles are removed in vacuo and the red coloured residue is washed five times with *n*-pentane (2 mL each). The remaining **4b** is dried in vacuo. – Yield: 54 mg (80 %). – Orange powder. M.p. 56 °C (dec.). **Cp(OC)$_2$W-P(*s*Mes)-C[N(H)Et]=S (4b): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.67 [d, ^4J(HCCCH) = 2.1 Hz, 1H, *m*-H], 7.56 [dd, ^4J(PCCCH) = 4.5 Hz, ^4J(HCCCH) = 2.1 Hz, 1H, *m*-H], 5.26 (s, 5H, H$_5$C$_5$), 4.90 (s, br, 1H, HN), 2.87-2.73 (m, 2H, H$_2$C), 1.69 [s, 9H, *o*-C(CH$_3$)$_3$], 1.61 [s, 9H, *o*-C(CH$_3$)$_3$], 1.28 [s, 9H, *p*-C(CH$_3$)$_3$], 0.41 ppm [t, ^3J(HCCH) = 7.2 Hz, 3H, H$_3$C]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 247.99 [d, ^2J(PWC) = 15.2 Hz, *cis*-CO], 243.87 [d, ^2J(PWC) = 15.2 Hz, *cis*-CO], 214.06 [d, ^1J(PC) = 11.8 Hz, C=S], 158.59 [d, ^2J(PCC) = 6.6 Hz, *o*-C], 158.09 [d, ^2J(PCC) = 20.0 Hz, *o*-C], 150.94 [d, ^4J(PCCCC) = 2.7 Hz, *p*-C], 128.06 [d, ^1J(PC) = 49.6 Hz, *i*-C], 126.18 [d, ^3J(PCCC) = 3.5 Hz, *m*-C], 121.91 [d, ^3J(PCCC) = 11.0 Hz, *m*-C], 92.67 [d, ^2J(PWC) = 1.4 Hz, C$_5$H$_5$], 41.89 [d, ^3J(PCNC) = 0.4 Hz, CH$_2$], 38.94 [d, ^3J(PCCC) = 3.4 Hz, *o*-$\underline{\text{C}}$(CH$_3$)$_3$], 37.03 [d, ^3J(PCCC) = 2.1 Hz, *o*-$\underline{\text{C}}$(CH$_3$)$_3$], 35.01 [s, *p*-$\underline{\text{C}}$(CH$_3$)$_3$], 34.5 [s, *o*-C($\underline{\text{C}}$H$_3$)$_3$], 33.33 [d, ^4J(PCCCC) = 8.6 Hz, *o*-C($\underline{\text{C}}$H$_3$)$_3$], 31.25 [s, *p*-C($\underline{\text{C}}$H$_3$)$_3$], 13.73 ppm [d, ^4J(PCNCC) = 3.7 Hz, CH$_3$]. – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5

MHz): δ = -85.1 ppm [s, ^{1}J(WP) = 179.8 Hz]. – **IR** (cyclohexane): ν(CO) = 1941 (s), 1861 (s) cm^{-1}. Calc. for $C_{28}H_{46}NO_2PSW$ (675.57): C, 50.23; H, 6.02; N, 2.09; S, 5.79. Found: C, 49.64; H, 5.87; N, 1.83; S, 5.56.

3. Dicarbonyl(η^{5}-cyclopentadienyl){[2,4,6-tri(*tert*-butyl)phenyl][(N-*tert*-butyl)thioformamido-κS]-phosphanido-κP}tungsten(II) (4c): Analogous to **4a** from 26 mg (0.04 mmol) Cp(OC)$_2$W=P(H)*s*Mes (**1**) and 47 mg (0.40 mmol) *tert*-butylisothiocyanate (**2c**) in 5 mL toluene after 18 h. – Yield: 18 mg (75 %). – Darkorange powder. M.p. 72 °C (dec.). **Cp(OC)$_2$W-P(*s*Mes)-C[N(H)*t*Bu]=S (4c): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.60 [d, ^{4}J(HCCCH) = 2.1 Hz, 1H, *m*-H], 7.51 [dd, ^{4}J(PCCCH) = 4.2 Hz, ^{4}J(HCCCH) = 2.1 Hz, 1H, *m*-H], 5.26 (s, 5H, H_5C_5), 4.65 (d, ^{3}J(PCNH) = 2.4 Hz, 1H, HN), 1.66 [s, 9H, *o*-C(CH$_3$)$_3$], 1.65 [s, 9H, *o*-C(CH$_3$)$_3$], 1.27 [s, 9H, *p*-C(CH$_3$)$_3$], 1.08 ppm [s, 9H, (H$_3$C)$_3$CN]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 246.93 [d, ^{2}J(PWC) = 14.8 Hz, *cis*-CO], 242.77 [d, ^{2}J(PWC) = 15.0 Hz, *cis*-CO], 211.47 [d, ^{1}J(PC) = 11.6 Hz, C=S], 158.22 [d, ^{2}J(PCC) = 9.7 Hz, *o*-C], 158.15 [d, ^{2}J(PCC) = 12.4 Hz, *o*-C], 151.18 [d, ^{4}J(PCCCC) = 2.8 Hz, *p*-C], 132.86 [d, ^{1}J(PC) = 44.4 Hz, *i*-C], 124.90 [d, ^{3}J(PCCC) = 3.5 Hz, *m*-C], 121.58 [d, ^{3}J(PCCC) = 10.3 Hz, *m*-C], 92.51 [d, ^{2}J(PWC) = 1.4 Hz, C_5H_5], 54.78 [s, $\underline{C}(CH_3)_3$], 41.14 [s, *o*-$\underline{C}(CH_3)_3$], 38.84 [d, ^{3}J(PCCC) = 3.1 Hz, *o*-$\underline{C}(CH_3)_3$], 34.97 [s, *p*-$\underline{C}(CH_3)_3$], 34.20 [s, *o*-$C(\underline{C}H_3)_3$], 33.17 [d, ^{4}J(PCCCC) = 8.2 Hz, *o*-$C(\underline{C}H_3)_3$], 31.27 [s, *p*-$C(\underline{C}H_3)_3$], 14.24 ppm [s, $C(\underline{C}H_3)_3$]. – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = -82.4 ppm [s, ^{1}J(WP) = 185.9 Hz]. – **IR** (*n*-pentane): ν(CO) = 1953 (vs), 1872 (s) cm^{-1}. Calc. for $C_{30}H_{44}NO_2PSW$ (697.58): C, 51.65; H, 6.36; N, 2.01; S, 4.60. Found: C, 51.29; H, 6.27; N, 1.74; S, 4.43.

4. Dicarbonyl(η^{5}-cyclopentadienyl){[2,4,6-tri(*tert*-butyl)phenyl][(N-phenyl)thioformamido-κS]-phosphanido-κP}tungsten(II) (4d): Analogous to **4a** from 171 mg (0.29 mmol) Cp(OC)$_2$W=P(H)*s*Mes (**1**) and 40 mg (0.40 mmol) phenylisothiocyanate (**2d**) in 5 mL toluene after 16 h. – Yield: 114 mg (55 %). – Orange powder. M.p. 61 °C (dec.). **Cp(OC)$_2$W-P(*s*Mes)-C[N(H)Ph]=S (4d): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.51 [d, ^{4}J(HCCCH) = 2.2 Hz, 1H, *m*-H], 7.39 [dd, ^{4}J(PCCCH) = 4.4 Hz, ^{4}J(HCCCH) = 2.2 Hz, 1H, *m*-H], 7.22-7.13 (m, 4H, Ph), 6.95-6.90 (m, 1H, Ph), 6.23 [d, ^{3}J(PCNH) = 2.9 Hz, 1H, NH), 5.37 (s, 5H, C_5H_5), 1.64 [s, 9H, *o*-C(CH$_3$)$_3$], 1.40 [s, 9H, *o*-C(CH$_3$)$_3$], 1.29 ppm [s, 9H, *p*-C(CH$_3$)$_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 245.86 [d, ^{2}J(PWC) = 12.8 Hz, *cis*-CO], 242.53 [d,

^2J(PWC) = 21.4 Hz, *cis*-CO], 201.73 [d, ^1J(PC) = 9.7, C=S], 158.18 [d, ^2J(PCC) = 3.5 Hz, *o*-C], 157.42 [d, ^2J(PCC) = 13.4 Hz, *o*-C], 151.95 [d, ^4J(PCCCC) = 3.2 Hz, *p*-C], 138.03 (s, *o*-C, Ph), 128.92 (s, *p*-C, Ph), 124.70 [d, ^3J(PCNC) = 4.8 Hz, *ipso*-C, Ph], 123.27 [d, ^5J(PCNCCC) = 2.5 Hz, *m*-C, Ph], 121.60 [d, ^3J(PCCC) = 10.0 Hz, *m*-C], 120.20 [d, ^1J(PC) = 25.1 Hz, *ipso*-C], 117.68 [d, ^3J(PCCC) = 3.1 Hz, *m*-C], 92.34 [d, ^2J(PWC) = 0.7 Hz, C_5H_5], 40.58 [s, *o*-$\underline{C}(CH_3)_3$], 38.52 [d, ^3J(PCCC) = 2.8 Hz, *o*-$\underline{C}(CH_3)_3$], 35.08 [s, *p*-$\underline{C}(CH_3)_3$], 33.87 [s, *o*-$C(\underline{C}H_3)_3$], 33.03 [d, ^4J(PCCCC) = 6.2 Hz, *o*-$C(\underline{C}H_3)_3$], 31.19 ppm [s, *p*-$C(\underline{C}H_3)_3$]. – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = -72.2 ppm [s, ^1J(PW) = 196.8 Hz]. – **IR** (*n*-pentane): ν(CO) = 1942 (vs), 1860 (s) cm^{-1}. Calc. for $C_{32}H_{40}NO_2PSW$ (717.57): C, 53.56; H, 5.62; N, 1.95; S, 4.47. Found: C, 53.20; H, 5.48; N, 1.72; S, 4.03.

5. Dicarbonyl(η^5-cyclopentadienyl){[2,4,6-tri(*tert*-butyl)phenyl][(N-2-phenylethyl)thioformamido-κS]-phosphanido-κP}tungsten(II) (4e): Analogous to **4a** from 61 mg (0.10 mmol) Cp(OC)$_2$W=P(H)*s*Mes (**1**) and 11 mg (0.10 mmol) 2-phenylethylisothiocyanate (**2e**) in 5 mL toluene after 24 h and crystallization at 0 °C. – Yield: 32 mg (40 %). – Redorange powder. M.p. 64 °C (dec.). **Cp(OC)$_2$W-P(*s*Mes)-C[N(H)CH$_2$CH$_2$Ph]=S (4e): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.60 (s, br, 1H, *m*-H), 7.54 (s, br, 1H, *m*-H), 7.06-6.98 (m, 3H, Ph), 6.78-6.76 (m, 2H, Ph), 5.25 (s, 5H, H_5C_5), 4.99 (s, br, 1H, HN), 3.26-3.18 (m, 1H, $\underline{H_2}CNH$), 2.92-2.88 (m, 1H, $\underline{H_2}CNH$), 2.29-2.08 (m, 2H, H_2CPh), 1.67 [s, 9H, *o*-$C(CH_3)_3$], 1.57 [s, 9H, *o*-$C(CH_3)_3$], 1.28 ppm [s, 9H, *p*-$C(CH_3)_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 247.87 [d, ^2J(PWC) = 16.8 Hz, *cis*-CO], 243.73 [d, ^2J(PWC) = 13.8 Hz, *cis*-CO], 213.21 [d, ^1J(PC) = 9.0 Hz, C=S], 158.62 [d, ^2J(PCC) = 5.9 Hz, *o*-C], 157.95 [d, ^2J(PCC) = 18.9 Hz, *o*-C], 151.00 [d, ^4J(PCCCC) = 2.7 Hz, *p*-C], 150.33 (s, *o*-C, Ph), 133.15 (s, *p*-C, Ph), 128.75 [d, ^3J(PCCC) = 5.5 Hz, *m*-C], 126.69 (s, *i*-C, Ph), 123.34 [d, ^1J(PC) = 33.1 Hz, *i*-C], 121.81 [d, ^3J(PCCC) = 10.7 Hz, *m*-C], 119.66 (s, *m*-C, Ph), 92.62 [d, ^2J(PWC) = 1.1 Hz, C_5H_5], 43.52 [d, ^3J(PCCC) = 1.7 Hz, *o*-$\underline{C}(CH_3)_3$], 41.75 [s, *p*-$\underline{C}(CH_3)_3$], 38.90 [d, ^3J(PCCC) = 3.6 Hz, *o*-$\underline{C}(CH_3)_3$], 34.37 [s, *o*-$C(\underline{C}H_3)_3$], 33.29 [d, ^4J(PCCCC) = 8.3 Hz, *o*-$C(\underline{C}H_3)_3$], 31.26 ppm [s, *p*-$C(\underline{C}H_3)_3$]. – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = -84.4 ppm [s, ^1J(WP) = 182.3 Hz]. – **IR** (*n*-pentane): ν(CO) = 1947 (s), 1870 (s) cm^{-1}. Calc. for $C_{34}H_{44}NO_2PSW$ (745.62): C, 54.77; H, 5.95; N, 1.88; S, 4.30. Found: C, 54.47; H, 5.73; N, 1.69; S, 4.21.

6. Dicarbonyl(η^5-cyclopentadienyl){[2,4,6-tri(*tert*-butyl)phenyl][(N,N'-diisopropyl)imino-formamido-κN]-phosphanido-κP}tungsten(II) (7): A solution of 67 mg (0.12 mmol) Cp(OC)$_2$W=P(H)*s*Mes (**1**) in 10 mL toluene is combined with 15 mg (0.12 mmol) diisopropylcarbodiimide (**5**) at room temperature and stirred for 90 min. The solvent is removed in vacuo and the residue is washed five times with 5 mL of *n*-pentane each and dried in vacuo. – Yield: 60 mg (75 %). – Darkorange crystals. M.p. 69 °C (dec.). **Cp(OC)$_2$W-P(*s*Mes)-C[NH(*i*Pr)]=N(*i*Pr) (7): - ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.50 [d, ^4J(HCCCH) = 2.4 Hz, 1H, *m*-H], 7.43 [dd, ^4J(PCCCH) = 4.8 Hz, ^4J(HCCCH) = 2.4 Hz, 1H, *m*-H], 5.30 [d, ^3J(PWCH) = 1.2 Hz, 5H, H$_5$C$_5$], 3.92 [dd, ^3J(HCNH) = 9.6 Hz, ^3J(PCNH) = 3.3 Hz, 1H, NH], 2.96 [sept, ^3J(HCCH) = 6.3 Hz, 1H, CNCH], 2.29-2.20 (m, 1H, CNCH), 1.76 [s, 9H, *o*-C(CH$_3$)$_3$], 1.60 [s, 9H, *o*-C(CH$_3$)$_3$], 1.31 [s, 9H, *p*-C(CH$_3$)$_3$], 1.00 [d, ^3J(HCCH) = 6.9 Hz, 3H, CH$_3$], 0.85 [d, ^3J(HCCH) = 6.9 Hz, 3H, CH$_3$], 0.75 [d, ^3J(HCCH) = 6.3 Hz, 3H, CH$_3$], 0.58 ppm [d, ^3J(HCCH) = 6.3 Hz, 3H, CH$_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 257.14 [d, ^2J(PWC) = 9.3 Hz, *trans*-CO], 254.22 [d, ^2J(PWC) = 14.1 Hz, *cis*-CO], 187.87 [d, ^1J(PC) = 25.2 Hz, C=N], 161.55 [d, ^2J(PCC) = 31.7 Hz, *o*-C], 156.98 [d, ^2J(PCC) = 10.0 Hz, *o*-C], 148.95 [d, ^4J(PCCCC) = 3.1 Hz, *p*-C], 137.84 (s, *m*-C), 128.89 [d, ^1J(PC) = 57.9 Hz, *i*-C], 120.81 [d, ^3J(PCCC) = 13.8 Hz, *m*-C], 93.58 [d, ^2J(PWC) = 2.7 Hz, C$_5$H$_5$], 51.80 [d, ^3J(PCNC) = 4.1 Hz, CH], 44.28 [d, ^3J(PCCC) = 2.7 Hz, *o*-$\underline{C}$(CH$_3$)$_3$], 41.71 (s, CH), 39.22 [d, ^3J(PCCC) = 6.9 Hz, *o*-$\underline{C}$(CH$_3$)$_3$], 34.98 [s, *p*-$\underline{C}$(CH$_3$)$_3$], 34.37 [s, *o*-C($\underline{C}$H$_3$)$_3$], 33.33 [d, ^4J(PCCCC) = 13.8 Hz, *o*-C($\underline{C}$H$_3$)$_3$], 31.38 [s, *p*-C($\underline{C}$H$_3$)$_3$], 22.78 [d, ^4J(PCNCC) = 2.0 Hz, CH$_3$], 22.67 (s, CH$_3$), 21.98 [d, ^4J(PCNCC) = 4.8 Hz, CH$_3$], 21.91 ppm (s, CH$_3$). – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = -102.2 ppm [s, ^1J(PW) = 117.9 Hz]. – **IR** (*n*-pentane): ν(CO) = 1950 (s), 1873 (s) cm^{-1}. Calc. for C$_{32}$H$_{49}$N$_2$O$_2$PW (708.58): C, 52.24; H, 6.97; N, 3.95. Found: C, 52.78; H, 6.71; N, 3.25.

7. X-Ray analyses of compounds of 4b, 4d and 7: Crystals of **4b**, **4d** and **7** suitable for structure determination could be obtained from a saturated toluene solution at room temperature. Data collection was performed on an Enraf-Nonius CAD4-diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) at 173(2) K.[43-45] The structures were solved using the Patterson-method and cell parameters were determined and refined using SHELXS-97[46] and SHELXL-97.[47]

Crystal Data for Compounds ***4b, 4d*** *and* ***7:***

	4b	**4d**	**7**
identification	andi21	andi39	andi22
mol formula	$C_{32}H_{41}WNO_2PS$	$C_{32}H_{40}WNO_2PS$	$C_{32}H_{49}WN_2O_2P$
mol wt	718.58	717.53	708.55
wavelength (Å)	0.71073	0.71073	0.71073
temp (K)	173(2)	173(2)	173(2)
cryst size (mm)	0.23 x 0.12 x 0.08	0.17 x 0.14 x 0.06	0.18 x 0.12 x 0.08
cryst syst	triclinic	monoclinic	monoclinic
space group	*P-1*	*P2(1)/c*	*P2(1)/c*
a (Å)	10.126(2)	10.533(3)	9.861(2)
b (Å)	11.300(3)	13.908(4)	20.048(4)
c (Å)	13.429(3)	21.583(5)	17.199(4)
α (°)	111.260(3)	90	90
β (°)	90.563(4)	95.808(4)	104.209(4)
γ (°)	90.794(4)	90	90
vol (Å^3), *Z*	1431.7(6), 2	3145.3(14), 6	3295.9(13), 7
ρ (calcd) (Mgm^{-3})	1.557	1.515	1.428
F(000)	674	1440	1440
μ (mm^{-1})	4.187	3.818	3.582
θ range for data collecn (deg)	2.03 – 25.06	1.94 – 25.02	2.44 – 25.05
no. of rflns collected	27720	29595	31294
no. of indep reflns	5029	5532	5734
abs cor.	empirical	empirical	empirical
no. of data/restraints/params	5029 / 45 / 345	5532 / 36 / 387	5734 / 115 / 425
goodness of fit on F^2	1.169	1.056	1.153
R1^a	0.0257	0.0238	0.0343
wR2^b	0.0610	0.0570	0.0760
largest diff peak and hole (eÅ^{-3})	1.206 and -0.557	1.043 and -0.288	1.834 and -0.440

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.

References

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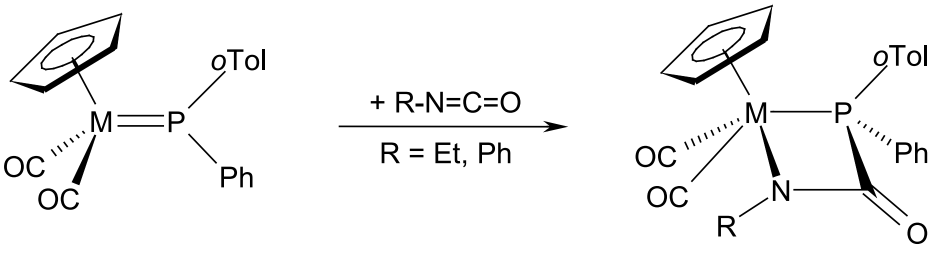
CHAPTER VI

[2+2] Cycloaddition of Phosphenium Tungsten Complexes with Alkylisocyanates: Synthesis of the Cyclic Tungsten-Phosphines $\mathrm{Cp(OC)_2}\overline{\mathrm{W\text{-}P(H)(R)\text{-}(C{=}O)N}}\mathrm{R'}$ (R = *t*Bu, Mes, *s*Mes; R’ = Et, Ph) and the Acylamidophosphenium Tungsten Complex $\mathrm{Cp(OC)_2W{=}P[C({=}O)N(H)Et]}$*s*Mes

Introduction

The chemical behaviour of phosphenium metal complexes of the chromium group Cp(OC)$_2$M=PR$_2$ (R = alkyl, aryl) is determined by the high reactivity of the M=P-bond, mainly involved in cycloadditions, the most prominent reaction pattern of these complexes.[1-17] Interesting representatives are reactions with alkylisothiocyanates or isocyanates, like the chemical transformation of the prostereogenic phosphenium complex Cp(OC)$_2$M=P(*o*Tol)(Ph) (**A**) with ethyl- or phenylisocyanate, yielding the phosphametallacycles **B**, in which the electrophilic carbon of the isocyanate is bonded to the phosphorus, while the nitrogen is coordinated to the metal atom, with high diastereoselectivity and regioselectivity.[18-20]



A M = Mo, W **B**

So far no knowledge exists about the analogous reaction of isocyanates with P-H-functionalized phosphenium complexes.

Having in mind the diastereoselective reactions of some diorganophosphenium complexes with isocyanates[18-20] and the use of isocyanates in transition metal-assissted chemistry[21-23] we got now focused on the reactivity of these heteroallenes towards P-H-phosphenium complexes.

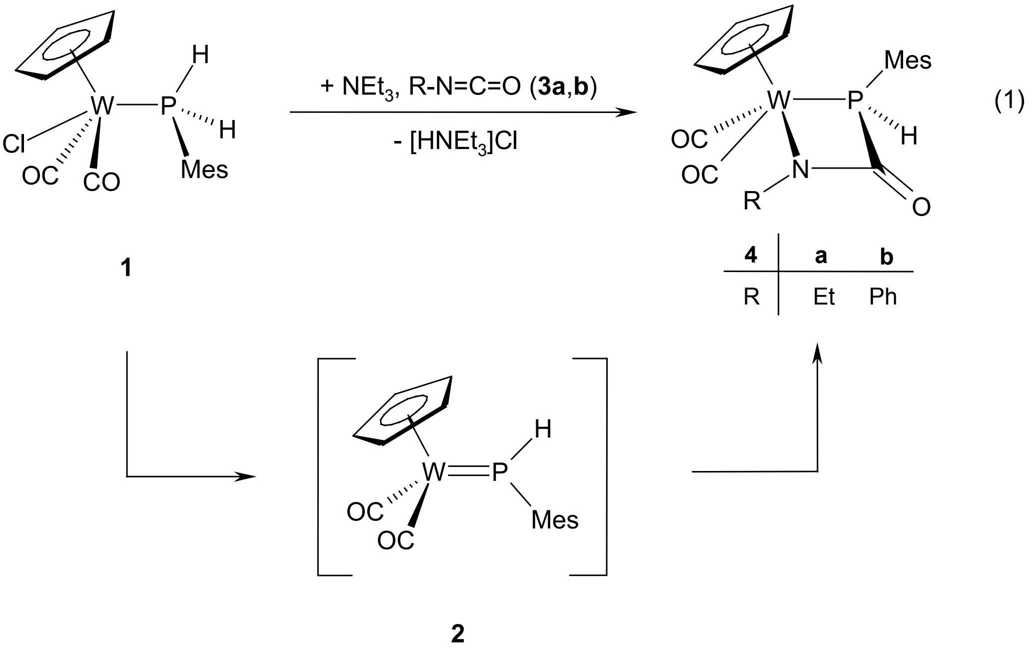
Taken into account the results of the prior chapter proving the fact, that the sterically demanding and at room temperature stable complex Cp(OC)$_2$W=P(H)*s*Mes (**1**)[24] reacts diastereoselctive and regiospecific with alkylisothiocyanates leading to the phosphametallacycles Cp(OC)$_2$W-P(*s*Mes)-C(NHR)=S (R = Me, Et, *t*Bu, Ph, CH$_2$CH$_2$Ph) via [2+2]-cycloaddition followed by P→N-hydrogen migration,[25] it seems attractive to study cycloaddition behaviour of the prostereogenic complexes Cp(OC)$_2$W=P(H)R [(R = *s*Mes (**1**), Mes (**5**), *t*Bu (**7**)] towards isocyanates.

As important aspects both the precise regio- and stereochemistry of the cycloadducts and the influence of the steric demand of the phosphorus ligands on the formed products has to be considered. In addition it is interesting to examine whether these adducts undergo subsequent transformations induced by the mobility of the P-H-hydrogen analogous to reactions with alkylisothiocyanates.[25-27]

Results and Discussion

Reactivity Studies

Treatment of a mixture of the mesitylphosphine tungsten complex Cp(OC)$_2$[(Mes)PH$_2$]W-Cl (**1**) and ethyl- or phenylisocyanate (**3a,b**) in toluene with Et$_3$N at 0° yield the stable four-membered phosphametallacycles Cp(OC)$_2$W-P(H)(Mes)-C(=O)NR [R = Et (**4a**), Ph (**4b**)] as a result of a controlled [2+2]-cycloadditon of the isocyanate to the W=P-bond of the complex Cp(OC)$_2$W=P(H)Mes (**2**) generated *in situ* via dehydrochlorination [Eq. (1)].



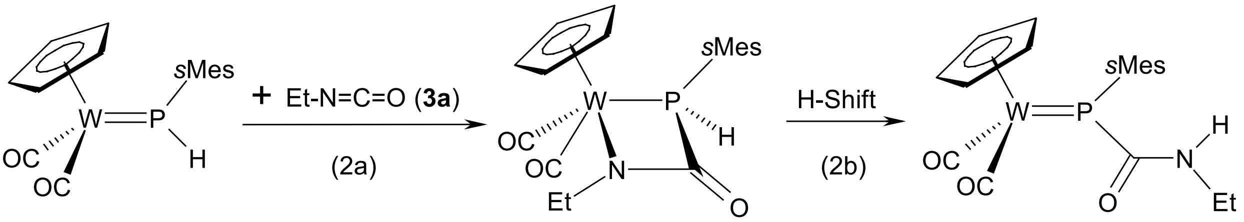
4	a	b
R	Et	Ph

The P-H-functionalized cycloadducts **4a**,**b** are obtained as yellow solids in 75 (**4a**) or 69 % (**4b**) yield, respectively, after reaction times of 1 (**4a**) or 2 h (**4b**). The isocyanate is coordinated through the nitrogen to the tungsten atom. N-coordination of the isocyanate could also be the first step in the reaction sequence leading to the phosphanido complex Cp(OC)$_2$[(O=C)NR]W-P(H)Mes, which exhibits free rotatability around the tungsten-phosphorus bond, followed by ring closure due to C-P-bond formation to give **4a,b**. In both cases a diastereomeric mixture is isolated with respect to the *like-trans-* or *unlike-cis-*arrangement of the mesityl group and the cylopentadienyl moiety (**4a**: 65 : 35; **4b**: 69 : 31). Theoretical calculations prove that for the P-H-functionalized complex $Cp(OC)_2W{=}P(H)Mes$ (**2**) a *trans*-conformation is slightly favoured,[28] wich is also valid for the dominating diastereomer of **4a**,**b** due to ^{1}H-NOESY-experiments.

Another mentionable point is that neither for **4a** nor for **4b** an insertion of the isocyanate fragment into the P-H-bond is observable. Both elongation of the reaction time (up to 3 d) and raise of the temperature (up to 60 °C) did not lead to the generation of phosphenium complexes of the type $Cp(OC)_2W{=}P[C({=}O)N(H)R]Mes$ (R = Et, Ph) but to decomposition of **4a,b**. Additionally no reaction occurs between the *tert*-butylisocyanate (**3c**) and the mesitylphoshenium complex **2**.

In order to get a first insight concerning the influence of the P-aryl ligand in P-H-functionalized phosphenium complexes regarding the diastereocontrol in cycloadditons with isocyanates reactions are performed with the sterically more demanding compound $Cp(OC)_2W{=}P(H)$*s*Mes (**5**).

Treatment of the *super*-mesitylphosphenium complex $Cp(OC)_2W{=}P(H)$sMes (**5**) with ethylisocyanate (**3a**) yields after stirring the reaction mixture for 30 min at room temperature the stable P-H-functionalized adduct $Cp(OC)_2\overline{W\text{-}P(H)(s\text{Mes})\text{-}C({=}O)N}Et$ (**6**) as yellow solid, deriving from a controlled [2+2]-cycloaddition of the isocyanate to the W=P-bond [Eq. (2a)].



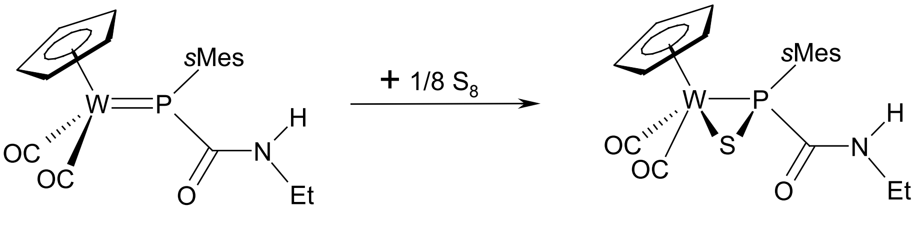
5 **6** **7**

In contrast to the cycloadducts **4a,b,** for which the *like-trans*-isomers are obtained around 70%, in case of **6** the reaction is even more diastereoselective. As can be seen from ^{1}H-NOESY-experiments, which prove no interactions between the cyclopentadienyl moiety and the *ortho-tert*-butyl-groups of the *s*Mes-substitutent, a *trans*-configuration regarding the Cp-unit and the aryl ligand is prefered in solution. Therefore only the *like-trans*-isomers of **6** are generated under inversion of the starting *cis*-configuration, due to the sterical demand of the *super*-mesityl group. This also indicates that **6** is only isolable if the reaction occurs stepwise and not concerted. This interpretation is additional proved by the obtained x-ray structure analysis showing the *like*-isomer of **6** [Fig. (1)].

When the reaction between **5** and ethylisocyanate (**3a**) is carried out under the same conditions but extending the reaction time to 24 h the phosphenium complex **7** is obtained as a blue, crystalline solid in 65 % yield, deriving from **6** via a P→N-hydrogen-shift [Eq. (2b)]. The result is the insertion of the isocyanate fragment into the P-H-bond generating the novel phosphenium complex **7** with an acylamide-functionalized phosphorus atom. **7** is insofar interesting as it represents a diene type system, which can be used as a special type of a bidentate chelating ligand.

Comparing the positions of the cyclopentadienyl moiety and the aryl ligand with the arrangements found for **5**, a rentention of the configuration is valid in solution as well as in solid state [Fig. (2)]. Similar to the starting material the *trans*-isomer of **7** is formed, which confirms again that phosphenium complexes with a phosphorus-bonded *super*-Mesityl ligand are only stable with respect to a *trans*-arrangement of the Cp- and the *s*Mes-group.[28-30] The W=P-double bond formulation for **7** is in accordance with the high ^{1}J(PW)-coupling-constant of 582.0 Hz typically for phosphenium complexes. The ^{31}P-NMR resonance of 286.32 ppm is also characteristic for such complexes.[24, 28-30] So the greater steric approach of the *super*-Mesityl-ligand is the prerequisite for the more diastereoselective cycloaddition step and the insertion reaction in comparison to the mesityl-substituted derivatives **4a**,**b**.

No reactions take place between **5** and the sterically more demanding phenylisocyanate (**3b**) and *tert*-butylisocyanate (**3c**). While no other dienophilic reagent like methylisothiocyanate, ethylisocyanate (**2a**) or phenylisocyanate (**3b**) can be attached to the W=P-bond of **7**, treatment of **7** with elemental sulphur yields under a controlled [2+1]-cycloadditon the sulphur-bridged three-membered phosphametallacycle Cp(OC)$_2$W-P[C(=O)NHEt]*s*Mes-S (**8**) as darkred solid in 69 % yield [Eq. (3)].



(3)

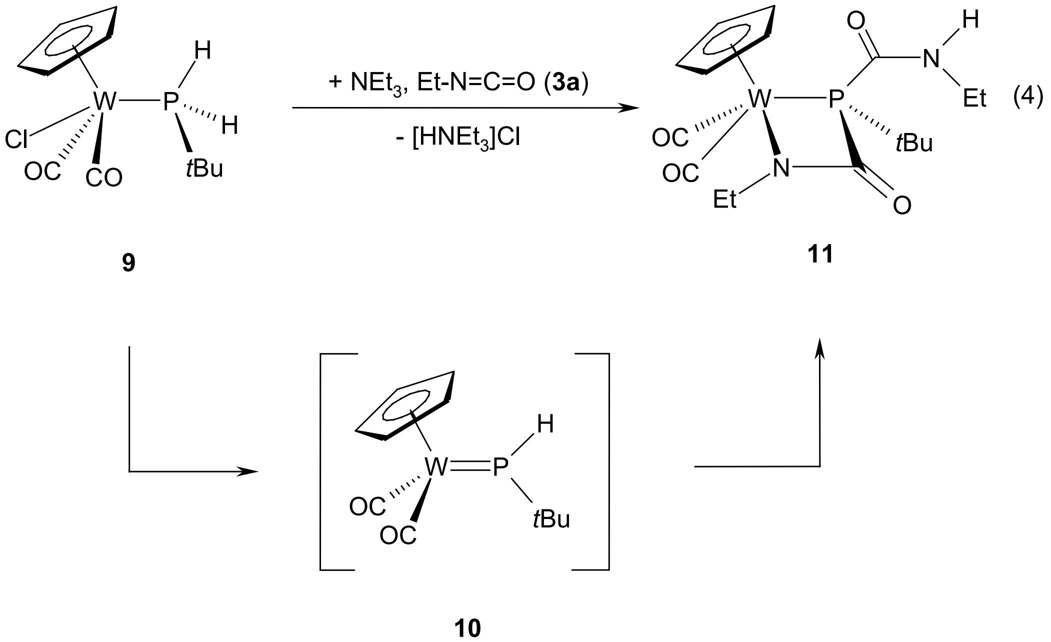
7

8

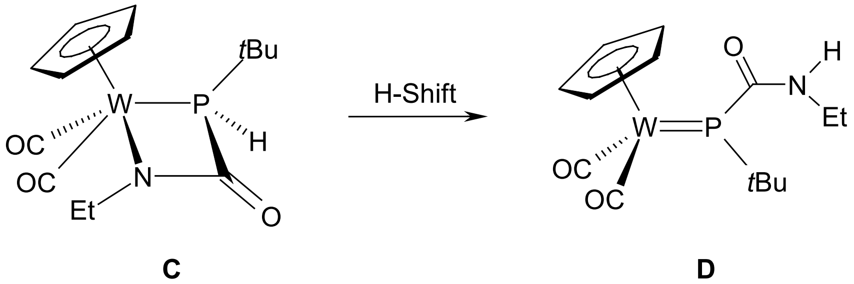
The formed heterocycle **8** shows high solubility in diverse aromatic solvents like benzene or toluene. Besides this it can be stored under nitrogen atmosphere almost unlimited. In comparison to the reaction of elemental sulphur with **5**, yielding the complex Cp(OC)$_2$W-P(H)*s*Mes-S[28] a significant increase of the reaction time from 3 h to 14 d for **7** is observed. This fact can be correlated to the sterical approach of the phosphorus substituents in **7** related to **5**. The ^{31}P-NMR-resonance and ^{1}J(PW)-coupling of **8** (-32.98 ppm; 211.4 Hz) is typical for such chalcogen bridged three-membered phoshametallacycles.[28]

For the *tert*-butyl derivative Cp(OC)$_2$W=P(H)*t*Bu (**10**) no reaction was found with phenylisocyanate (**2b**) or *tert*-butylisocyanate (**2c**). In the case of ethylisocyanate (**2a**) a remarkable discrepancy in the reaction pathway is observable.

When a mixture of **9** and ethylisocyanate (**2a**) in toluene is treated with Et$_3$N at 0° the phosphametallacycle **11** is formed via [2+2]-cycloadditon of one equivalent of the isocyanate with the *in situ* generated complex **10** and an additional insertion of a second mole of the reagent into the P-H-bond [Eq. (4)].



11 is obtained as yellow, crystalline solid in 84 % yield after a reaction time of 20 h. Using only one equivalent of **2a** the reaction also generates **11** in yields clearly under 50 %. In addition ^{31}P-NMR investigations did not allow to prove an intermediate cycloadduct nor a phosphenium complex with an inserted isocyanate fragment. Nevertheless the phosphametallacycle **C** can be formulated as primary product in the reaction sequence, followed by a P→N-hydrogen shift to yield the phosphenium intermediate **D**.



The phosphenium complex **D** undergoes an additional cyloaddition at the W=P-bond according to the pattern found for **7** leading to **11**.

In summary only the *super*-mesityl ligand and its diastereoselectivity allows to use the reaction sequence of cycloadditon and insertion for the synthesis of novel cycloadducts and highly functionalized phosphenium complexes.

Structural Investigation

Crystals of Cp(OC)$_2$W-P(H)(*s*Mes)-C(=O)NEt (**6**) suitable for structure determination could be obtained from a saturated toluene solution at room temperature.

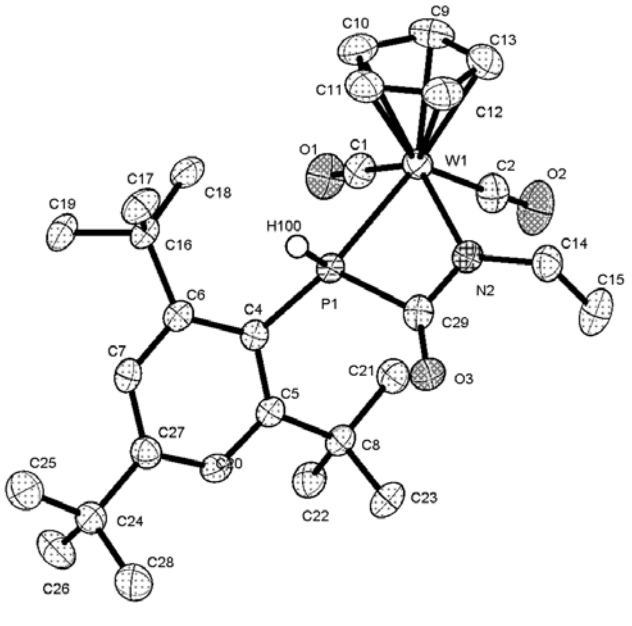


Fig. (1). Molecular structure of Cp(OC)$_2$W-P(H)(*s*Mes)-C(=O)NEt (**6**). - The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: W(1)-P(1) 2.4272(7), P(1)-C(4) 1.835(2), P(1)-C(29) 1.868(2), N(2)-C(29) 1.328(3), N(2)-C(14) 1.470(3), W(1)-C(1) 1.959(2), W(1)-C(2) 1.953(2), W(1)-N(2) 2.1729(18), C(29)-O(3) 1.235(3), M-W(1)-P(1) 117.9, C(4)-P(1)-W(1) 145.30(7), C(4)-P(1)-C(29) 116.07(9), C(29)-P(1)-W(1) 85.19(7), N(2)-W(1)-P(1) 62.99(5), C(1)-W(1)-C(2) 74.72(9), C(1)-W(1)-P(1) 84.01(7), C(2)-W(1)-N(2) 84.35(8), C(29)-N(2)-C(14) 118.75(18), C(29)-N(2)-W(1) 113.68(14), C(14)-N(2)-W(1) 127.55(14), O(3)-C(29)-N(2) 131.0(2), O(3)-C(29)-P(1) 131.08(16), N(2)-C(29)-P(1) 97.92(14), W(1)-P(1)-C(29)-N(2) 3.67(12), W(1)-N(2)-C(29)-P(1) -4.53(14), C(14)-N(2)-C(29)-O(3) -1.5(3), P(1)-C(4)-C(6)-C(7) -148.12(16), C(20)-C(5)-C(4)-P(1) 147.25(17), C(20)-C(5)-C(4)-C(6) –13.6(3), C(6)-C(7)-C(27)-C(20) –7.2(3), C(4)-C(6)-C(7)-C(27) –3.3(3), C(4)-C(5)-C(20)-C(27) 2.9(3).

The molecular structure of the cycloaddition product **6** exhibits the postulated square pyramidal arrangement of the ligands at the tungsten center[6, 31, 32] with the cyclopentadienyl ring in the apical position and the basis formed by the *cis*-positioned carbonyles and the P-(C=O)-N moiety, leading to a rather acute N2-W1-P1-angle of 62.99°.

The W1-N2 bond distance of 2.17 Å shows a typical value for ring systems formed by isocyanates like $\mathrm{Cp(OC)_2}\overline{\mathrm{W\text{-}P(Ph)(}o\mathrm{Tol)\text{-}C(=O)N}}\mathrm{Et}$ (2.18 Å)[33] and $\mathrm{Cp(OC)_2}\overline{\mathrm{W\text{-}P(}o\mathrm{Tol)_2\text{-}C(=O)N}}\mathrm{Et}$ (2.19 Å).[34] The tungsten phosphorus distance of 2.43 Å is significantely enlarged compared to W=P-double bond systems (2.26 Å)[35-37] but it corresponds to bond lenghts found for other four-membered metallacycles with an isocyanate-chelate ligand.[33, 34] The ring internal angles of the four-membered W1-P1-C29-N2-cycle vary from 62.99° (N2-W1-P1) to 113.68° (C29-N2-W1). The chelate ligand is characterized by a nearly ideal planarity. It is only slightly folded indicated by the small torsion angles W1-P1-C29-N2 (3.67°) and W1-N2-C29-P1 (-4.53°). This is due to the trigonal planar geometry both at the the N2- (sum of angles: 359.98°) and the C29-atom (sum of angles: 360°), a result of the sp^2-hybridization[38].

The endocyclic N2-C29-bond length (1.33 Å) is diminished compared to the exocyclic N2-C14-distance of 1.47 Å, which is in the range expected for a N-C single bond. This fact correlates with a significant double bond character for the N2-C29-bond due to the interaction of the nitrogen lone pair with the C_{sp2}-atom [d(C=N) = 1.232 Å].[39]

The P1-C4-bond length (1.84 Å) is in the range expected for P_{sp2}-C_{sp2} single bonds.[40] The steric demand of the *s*Mes-ligand causes on the one hand a severe distorsion of the aryl group planarity (C20-C5-C4-C6 –13.6°, C6-C7-C27-C20 –7.2°)] on the other hand this effect determines the arrangement of the *super*-mesityl group. In order to avoid interaction of the *ortho*-*tert*-butyl-groups with the cyclopentadienyl- and the carbonyl-ligands the aryl ligand is bent towards the cyclopentadienyl ligand leading to a loss of planarity at C4. The differences from the theoretical torsion angle of 180° are significant (P1-C4-C6-C7 -148.12°, C20-C5-C4-P1 147.25°).

Crystals of Cp(OC)$_2$W-P[C(=O)NEt]*s*Mes (**7**) suitable for structure determination could be obtained from a saturated toluene solution at room temperature.

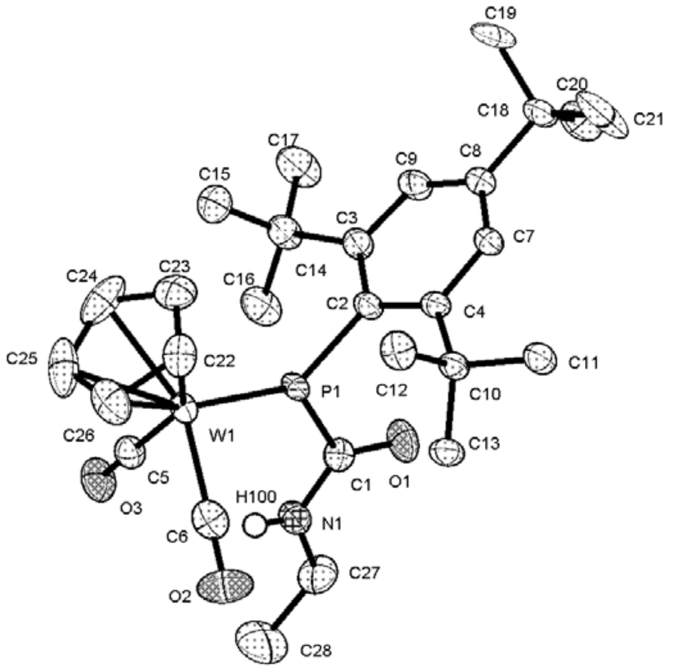


Fig. (2). Molecular structure of Cp(OC)$_2$W=P[C(=O)N(H)Et]*s*Mes (**7**). - The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: W(1)-P(1) 2.2591(7), P(1)-C(1) 1.894(3), P(1)-C(2) 1.841(2), W(1)-C(5) 1.946(3), W(1)-C(6) 1.956(3), O(1)-C(1) 1.215(3), N(1)-C(1) 1.332(3), M-W(1)-P(1) 132.9, C(2)-P(1)-W(1) 134.27(8), C(2)-P(1)-C(1) 99.41(11), C(1)-P(1)-W(1) 126.31(8), C(5)-W(1)-P(1) 91.43(7), C(6)-W(1)-P(1) 91.36(8), C(5)-W(1)-C(6) 79.88(11), C(9)-C(3)-C(2)-P(1) -178.49(19), P(1)-C(2)-C(4)-C(7) 179.74(18), C(2)-C(4)-C(7)-C(8) -2.2(4), C(2)-C(3)-C(9)-C(8) –1.6(4).

The coordination geometry of the tungsten atom can be described as a pseudo-octahedral three legged piano stool. The cyclopentadienyl ligand is occupying three facial coordination sites, whereby two legs are formed by the carbonyl ligands and the third leg by the double bonded phosphenium ligand. This is proved by the bond angles between the carbonyl ligands and the phosphine moiety, which are close to the ideal value of 90° (C5-W1-P1 91.43°, C6-W1-P1 91.36°).

The geometry of the phosphorus atom is exactly trigonal planar, the sum of angles amounts to 359.9°. As a result of the sp^2-hybridization the phosphenium ligand can be regarded as three-electron donor, giving the tungsten atom a number of 18 valence electrons. The C2-P1-C1-angle of 99.4° is significantly reduced in contrast to the ideal value of 120°. Similar decreased angles can be found for Cp(OC)$_2$W=P(H)*s*Mes (**4**) (98.9°)[28] and Cp(OC)$_2$W=P(*t*Bu)$_2$[6] (109.4°). As a consequence of this compression the C2-P1-W1- and C1-P1-W1-angle are expanded to 134.27° and 126.31°, respectively.

The P-C1-bond distance (1.89 Å) and the P1-C2 bond length (1.84 Å) are at the upper limit of P_{sp2}-C_{sp2} single bond distances.[40] Therefore π–interaction between the phosphorus atom and the aromatic ring system or the carboxyl moiety, respectively, can be excluded.

The tungsten-phosphorus bond length of 2.26 Å is typical for a W-P-double-bonded system for which a theoretical bond length of 2.26 Å is calculated.[35-37] It is also nearly identical to the diorganophosphenium complexes $Cp(OC)_2W{=}P(tBu)_2$ (2.28 Å),[6] $Cp(OC)_2W{=}P(R)$*s*Mes [R = Me, Et, *i*Pr, *n*Bu, CH_2Ph (2.24 Å - 2.25 Å)][30] or the complex $Cp(OC)_2W{=}P(H)$*s*Mes (**1**) (2.25 Å)[28] and the related species $Cp^*(Me_3P)_2Mo{=}P(H)$*s*Mes (2.25 Å).[41]

The plane defined by C2, P1 and C1 is almost vertical to the $W(CO)_2$-moiety, which also shows the smallest angle (C17-W1-C16 79.9°) in the piano stool fragment. Despite the steric demand of the *s*Mes-ligand the aryl group planarity is close to the ideal value of 0° (C2-C4-C7-C8 -2.2°, C2-C3-C9-C8 –1.6°). Contrary to the diorganophosphenium complexes $Cp(OC)_2W{=}P(R)$*s*Mes (R = Me, Et, *i*Pr, *n*Bu, CH_2Ph)[30] the phosphorus bonded aryl ligand is not bent towards the metal fragment, obvious from the torsion angles C9-C3-C2-P1 (-178.5°) and P1-C2-C4-C7 (179.7°) which are close to the ideal value of 180°. This contrasts significantly to systems of the type $Cp(OC)_2W{=}P(R)$*s*Mes (R = Me, Et, *i*Pr, *n*Bu, CH_2Ph)[30] where deviations in the range between 11.8° and 24.1° are found.

In summary the conformation of **7** and the short W-P-distance is in agreement with a frontier orbital interaction of the fragments $Cp(OC)_2W^{\ominus}$ and $sMes(H)P^{\oplus}$ as described in chapter I.

The most important structural feature refers to the *cis*-configuration regarding the *super*-mesityl-ligand and the cyclopentadienyl moiety. This is in accordance with the situation found for $Cp(OC)_2W{=}P(H)$*s*Mes (**5**)[28] and the complexes $Cp(OC)_2W{=}P(R)$*s*Mes (R = Me, Et, *i*Pr, *n*Bu, CH_2Ph)[30] as well as $Cp(OC)_2W{=}P(SnMe_3)$*s*Mes.[29]

Crystals of $\mathrm{Cp(OC)_2\overline{W\text{-}P[(C{=}O)NHEt(\mathit{t}Bu)\text{-}C({=}O)N}Et}$ (**11**) suitable for structure determination could be obtained from a saturated toluene solution at room temperature.

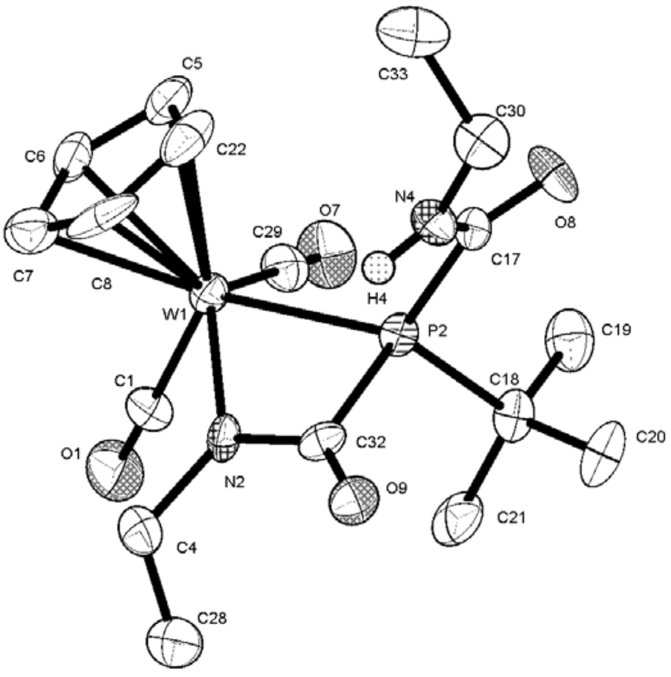


Fig. (3). Molecular structure of $\mathrm{Cp(OC)_2\overline{W\text{-}P[(C{=}O)NHEt(\mathit{t}Bu)\text{-}C({=}O)N}Et}$ (**11**). - The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], bond- and torsion angles [°]: W(1)-C(1) 1.963(6), W(1)-C(29) 1.958(8), W(1)-P(2) 2.4608(18), P(2)-C(17) 1.868(7), P(2)-C(18) 1.865(7), C(32)-P(2) 1.865(7), C(32)-N(2) 1.328(8), N(2)-C(4) 1.494(8), N(2)-W(1) 2.162(5), O(9)-C(32) 1.240(8), C(17)-O(8) 1.213(8), C(17)-N(4) 1.331(8), N(4)-C(30) 1.469(8), M-W(1)-P(2) 120.8, C(18)-P(2)-W(1) 124.9(2), C(18)-P(2)-C(17) 106.0(3), C(32)-P(2)-C(18) 106.0(3), C(17)-P(2)-W(1) 120.9(2), C(32)-P(2)-W(1) 84.9(2), N(2)-C(32)-P(2) 96.8(4), N(2)-W(1)-P(2) 62.56(13), W(1)-N(2)-C(32) 113.4(4), C(32)-N(2)-C(4) 116.8(5), C(4)-N(2)-W(1) 129.7(4), O(9)-C(32)-N(2) 131.3(6), P(2)-C(32)-O(9) 131.8(5), C(1)-W(1)-C(29) 73.3(3), N(2)-C(32)-P(2)-N(2) 11.9(3), W(1)-N(2)-C(32)-P(2) -14.7(4), O(9)-C(32)-N(2)-C(4) –9.8(10), C(30)-N(4)-C(17)-O(8) 3.9(10).

The molecular structure of **11** verifies the postulated square pyramidal arrangement of the ligands around the central tungsten atom[6, 31, 32] with the cyclopentadienyl ring in the apical position and the basis formed by the carbonmonoxide ligands and the P-(C=O)-N chelate with the phosphorus and the nitrogen atom in *cis*-positions at the tetragonal basis.

The N2-W1 bond length (2.16 Å) shows the typical value for four-membered ring systems derived from W=P-complexes by isocyanate cycloadditions, like **2** (2.17 Å), $\mathrm{Cp(OC)_2\overline{W\text{-}P(Ph)(\mathit{o}Tol)\text{-}C({=}O)N}Et}$ (2.18 Å)[33] and $\mathrm{Cp(OC)_2\overline{W\text{-}P(\mathit{o}Tol)_2\text{-}C({=}O)N}Et}$ (2.19 Å), respectively.[34] In comparison to tungsten phosphorus double bond systems, for which a theoretical bond length of 2.26 Å is calculated,[35-37] the obtained W-P-distance (2.46 Å) is significantly enlarged. But it corresponds to the values found for four-membered metallacycles having the C=N-unit incorporated.[33, 34] Related to **2** (2.43 Å) only a small difference of 0.03 Å is detectable. Within the W1-P1-C32-N2-chelate moitey the ring angles differ from 62.56° (N2-W1-P2) to 113.4° (C32-N2-W1) with the largest one found at the nitrogen atom. The smallest angle is located at the tungsten center. The same fact can be analogously found for **6**. Sums of angles of 359.9° around the N2- and C32-atom prove the trigonal planar geometry of both atoms as result of the sp^2-hybridization.[38] This fact should lead, in the same manner as found for **6**, to a planarity of the chelate ligand. However, the torsion angles N2-C32-P2-N2 (11.9°) and W1-N2-C32-P2 (-14.7°) indicate an essential folding with the C32-atom deflected out of the plane spanned by P1-W1-N2-C32.

The endocyclic N2-C32-bond length (1.33 Å) is decreased compared to the exocyclic N2-C4-distance of 1.47 Å, which lies as well as the N4-C30-distance (1.47 Å) for the acylamide unit, in the range expected for a N-C single bond. Therefore a significant double bond character for the N2-C32-bond due to the interaction of the nitrogen lone pair with the C_{sp2}-atom is established [d(C=N) = 1.232 Å].[39]

The P2-C17- (1.87 Å) as well as the P2-C18-bond (1.87 Å) are in the range expected for P-C single bonds.[40] The ligands around the phosphorus atom adopt a pseudo tetrahedral arrangement confirmed by the sum of angles of 321.6° (C32-P2-C18 106.0°, C32-P2-C17 109.6°, C18-P2-C17 106.0°). Due to significant mesomerism in the N4-C17-O8-moiety the P-bonded acylamide ligand is slightly deflected from a planar arrangment (C30-N4-C17-O8 3.9°). This point is additionally proved by the C17-N4-bond length of 1.33 Å, which is considerably shortened in comparison to C-N-single bond.[32]

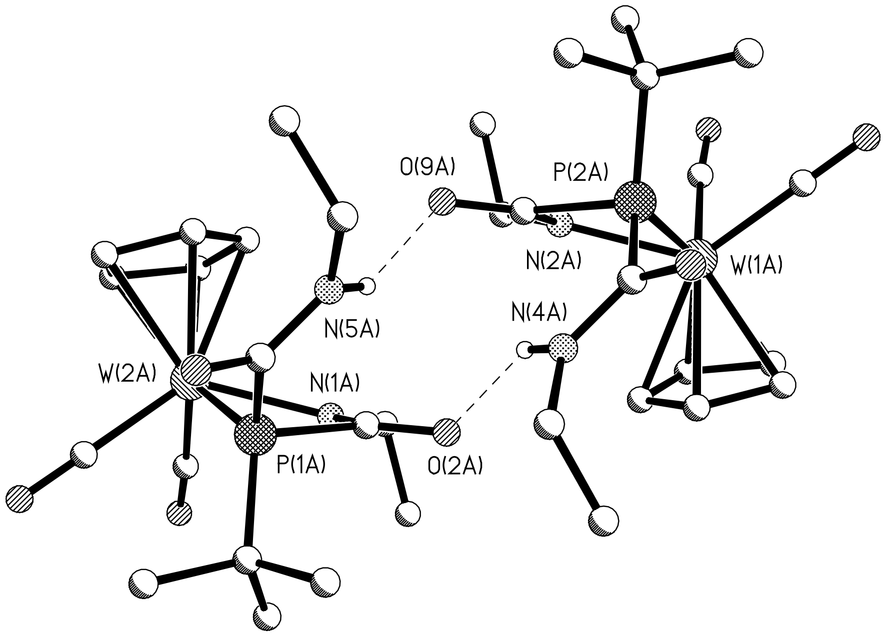


Fig. (4). Hydrogen bonds of Cp(OC)$_2$W-P[(C=O)NHEt(*t*Bu)-C(=O)NEt (**11**)

In addition intermolecular hydrogen bonds can be detected for the crystal structure of **11** (Fig. 4). Due to these bonds, which are formed by the N5A-H5A-O9A- and the N4A-H4A-O2A-linkage, respectively two molecules are connected to a dimer. The bond lenghts of 2.156 Å (H5A-O9A9) and 2.153 Å (H4A-O2A) are in the range exspected for N-H···O=C-bridges.[42] However, bond angles of 147.6° (N5A-H5A-O9A) and 147.3° (N4A-H4A-O2A) differ significantly from the ideal value of 180°.

Experimental Section

General: All manipulations were performed under purified and dried nitrogen by standard Schlenk-type techniques. Solvents were rigorously dried with an appropriate drying agent, distilled and saturated with nitrogen prior to use. IR: Spectra were recorded using a Perkin-Elmer 283 grating spectrometer. Samples were prepared as solutions in a NaCl cell with 0.1 mm path length with a resolution of about 2 cm^{-1}. NMR: JEOL LAMBDA 300 (300.4 MHz, 75.6 MHz and 121.5 MHz for ^{1}H, ^{13}C and ^{31}P, respectively). ^{1}H and ^{13}C spectra are referenced to the residual proton signal or natural abundance carbon signal of C_6D_6 at δ = 7.15 ppm (^{1}H) or δ = 128.0 ppm (^{13}C), respectively. ^{31}P chemical shifts are referenced to external H_3PO_4. ^{1}H-NOESY spectra were recorded on a AMX BRUKER 400 referenced to the residual proton signal of C_6D_6

at δ = 7.15 ppm. Melting points were obtained by differential thermoanalysis (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 by literature methods: Cp(OC)$_2$W=P(H)*s*Mes (**5**);[24] Cp(OC)$_2$[(R)PH$_2$]W-Cl [R = Mes (**1**), *t*Bu (**9**)].[43] RNCS [(R = Et, Ph, *t*Bu (**2a-c**)] and elemental sulphur were obtained commercially and used without further purification.

1. Dicarbonyl(η^5-cyclopentadienyl){[2,4,6-trimethylphenyl][(N-ethyl)formamido-κN]-phosphinito-κP}tungsten(II) (4a): To a solution of 131 mg (0.27 mmol) Cp(OC)$_2$(Cl)W-P(H)$_2$Mes (**1**) in 5 mL toluene 101 mg (1.00 mmol) triethylamine and 19 mg (0.27 mmol) ethylisocyanate (**2a**) were added at 0 °C and stirred for 1 h at room temperature. Insolubles are seperated by filtration and the filtrate is evaporated to dryness. The residue is dissolved in 2 mL toluene and purified by column chromatography (column 20 x 2 cm; Al$_2$O$_3$, activity III, neutral; toluene). **4a** is isolated by evaporation of the second yellow fraction to dryness and washing three times with 3 mL of *n*-pentane, followed by drying in vacuo. – Yield: 108 mg (75 %). – Yellow, crystalline solid. M.p. 69 °C (dec.). **Cp(OC)$_2$W-P(H)(Mes)-C(=O)NEt: (4a):** d.r.: **a** / **a'** = 65 : 35 (from integration of the H$_5$C$_5$-resonances). **^{1}H-NMR** ([D$_3$]-chloroforme, 300.4 MHz): δ = 6.89 [d, ^{4}*J*(PCCCH) = 3.66 Hz, 2H, *m*-H], 6.27 [d, ^{1}*J*(PH) = 382.8 Hz, 1H, HP], 5.59 (s, 5H, H$_5$C$_5$), 3.64-3.57 (m, 1H, H$_2$CN), 2.94-2.83 (m, 1H, H$_2$CN), 2.30 (s, 6H, *o*-CH$_3$), 2.27 (s, 3H, *p*-CH$_3$), 1.08 ppm [t, ^{3}*J*(HCCH) = 7.0 Hz, 3H, H$_3$C]. – **^{13}C-NMR** ([D$_3$]-chloroforme, 75.45 MHz): δ = 242.84 [d, ^{2}*J*(PWC) = 20.7, *cis*-CO], 237.44 [d, ^{2}*J*(PWC) = 4.5, *trans*-CO], 175.35 [d, ^{1}*J*(PC) = 45.9, C=O], 142.28 [d, ^{2}*J*(PCC) = 8.6 Hz, *o*-C], 141.37 (s, *p*-C), 130.06 [d, ^{3}*J*(PCCC) = 3.5 Hz, *m*-C], 114.83 [d, ^{1}*J*(PC) = 48.6 Hz, *ipso*-C], 91.98 [d, ^{2}*J*(PWC) = 1.1 Hz, C$_5$H$_5$], 46.94 [d, ^{3}*J*(PWNC) = 20.3 Hz, NCH$_2$], 21.60 (s, *o*-CH$_3$), 21.17 (s, *p*-CH$_3$), 13.90 ppm [d, ^{4}*J*(PWNCC) = 1.4 Hz, CH$_3$]. – **^{31}P{^{1}H}-NMR** ([D$_3$]-chloroforme, 121.5 MHz): δ = -72.32 ppm [s, ^{1}*J*(PW) = 222.3 Hz]. – **IR** (dichloromethane): ν(CO) = 1946 (vs), 1857 (s) cm^{-1}. – **a'**: **^{1}H-NMR** ([D$_3$]-chloroforme, 300.4 MHz): δ = 6.91 [d, ^{4}*J*(PCCCH) = 3.35 Hz, 2H, *m*-H], 6.39 [d, ^{1}*J*(PH) = 393.6 Hz, 1H, HP], 5.44 (s, 5H, H$_5$C$_5$), 3.52-3.45 (m, 1H, H$_2$CN), 3.21-3.10 (m, 1H, H$_2$CN), 2.42 (s, 6H, *o*-CH$_3$), 2.29 (s, 3H, *p*-CH$_3$), 1.06 ppm [t, ^{3}*J*(HCCH) = 6.8 Hz, 3H, H$_3$C]. – **^{13}C-NMR** ([D$_3$]-chloroforme, 75.45 MHz): δ = 245.48 [d, ^{2}*J*(PWC) = 20.0, *cis*-CO], 236.57 [d, ^{2}*J*(PWC) = 4.5, *trans*-CO], 176.07 [d, ^{1}*J*(PC) = 45.8, C=O], 141.33 [d, ^{2}*J*(PCC) = 11.7 Hz, *o*-C], 141.27 (s, *p*-C), 130.18 [d, ^{3}*J*(PCCC) = 3.1 Hz, *m*-C], 119.49 [d, ^{1}*J*(PC) = 38.9 Hz, *ipso*-C], 92.12 [d, ^{2}*J*(PWC) = 0.7 Hz, C$_5$H$_5$], 46.74 [d, ^{3}*J*(PWNC) = 20.0 Hz, NCH$_2$], 21.70 (s, *o*-CH$_3$), 21.15 (s, *p*-CH$_3$), 14.38

ppm [d, ^4J(PWNCC) = 1.0 Hz, CH$_3$]. – **^{31}P{^{1}H}-NMR** ([D$_3$]-chloroforme, 121.5 MHz): δ = -60.58 ppm [s, ^1J(PW) = 222.6 Hz]. – **IR** (dichloromethane): ν(CO) = 1946 (vs), 1857 (s) cm^{-1}. Calc. $C_{19}H_{22}NO_3PW$ (527.21): C, 43.29; H, 4.21; N, 2.66. Found: C, 43.17; H, 4.37; N, 2.66.

2. Dicarbonyl(η^5-cyclopentadienyl){(2,4,6-trimethylphenyl)[(N-phenyl)formamido-κN]-phosphinito-κP}tungsten(II) (4b): Analogous to **4a** from 116 mg (0.24 mmol) Cp(OC)$_2$(Cl)W-P(H)$_2$Mes (**1**), 101 mg (1.00 mmol) triethylamine and 28 mg (0.24 mmol) phenylisocyanate (**2b**) in 5 mL toluene after 2 h at room temperature. **4b** is isolated by evaporation of the second yellow fraction to dryness and washing three times with 3 mL of *n*-pentane followed by drying in vacuo. – Yield: 95 mg (69 %). – Yellow solid. M.p. 148 °C (dec.). **Cp(OC)$_2\overline{\text{W-P(H)(Mes)-C(=O)N}}$Ph: (4b):** d.r.: **a** / **a'** = 69 : 31 (from integration of the H$_5$C$_5$-resonances). **^{1}H-NMR** ([D$_3$]-chloroforme, 300.4 MHz): δ = 7.35-7.32 (m, 2H, Ph), 7.26-7.24 (m, 3H, Ph), 6.90 (s, 2H, *m*-H), 6.27 [d, ^1J(PH) = 382.8 Hz, 1H, HP], 5.59 (s, 5H, H$_5$C$_5$), 2.30 (s, 6H, *o*-CH$_3$), 2.27 ppm (s, 3H, *p*-CH$_3$). – **^{13}C-NMR** ([D$_3$]-chloroforme, 75.45 MHz): δ = 241.62 [d, ^2J(PWC) = 21.7, *cis*-CO], 236.57 [d, ^2J(PWC) = 4.5, *trans*-CO], 174.88 [d, ^1J(PC) = 57.2 Hz, C=O], 148.16 [d, ^2J(PCC) = 25.1 Hz, *o*-C], 142.45 [d, ^4J(PCCCC) = 3.6 Hz, *p*-C], 141.38 (s, *o*-C, Ph), 130.26 (s, *p*-C, Ph), 128.68 [d, ^3J(PWNC) = 3.1 Hz, *ipso*-C, Ph], 125.20 [d, ^1J(PC) = 52.1 Hz, *ipso*-C], 120.70 [d, ^3J(PCCC) = 5.6 Hz, *m*-C], 115.04 (s, *m*-C, Ph), 92.50 (s, C$_5$H$_5$), 21.84 (s, *o*-CH$_3$), 21.20 ppm (s, *p*-CH$_3$). – **^{31}P{^{1}H}-NMR** ([D$_3$]-chloroforme, 121.5 MHz): δ = -68.86 ppm [s, ^1J(PW) = 235.5 Hz]. – **IR** (dichloromethane): ν(CO) = 1951 (vs), 1864 (s) cm^{-1}. – **a'**: **^{1}H-NMR** ([D$_3$]-chloroforme, 300.4 MHz): δ = 7.07-7.03 (m, 2H, Ph), 6.97-6.92 (m, 3H, Ph), 6.89 (s, 2H, *m*-H), 6.39 [d, ^1J(PH) = 393.6 Hz, 1H, HP], 5.44 (s, 5H, H$_5$C$_5$), 2.42 (s, 6H, *o*-CH$_3$), 2.29 ppm (s, 3H, *p*-CH$_3$). – **^{13}C-NMR** ([D$_3$]-chloroforme, 75.45 MHz): δ = 249.98 [d, ^2J(PWC) = 21.3, *cis*-CO], 235.15 [d, ^2J(PWC) = 5.4, *trans*-CO], 173.50 [d, ^1J(PC) = 53.2 Hz, C=O], 147.45 [d, ^2J(PCC) = 20.1 Hz, *o*-C], 141.66 (s, *p*-C), 141.27 (s, *o*-C, Ph), 130.13 (s, *p*-C, Ph), 128.65 [d, ^3J(PWNC) = 2.8 Hz, *ipso*-C, Ph], 125.03 [d, ^1J(PC) = 42.7 Hz, *ipso*-C], 119.57 [d, ^3J(PCCC) = 4.5 Hz, *m*-C], 114.35 (s, *m*-C, Ph), 92.63 (s, C$_5$H$_5$), 21.74 (s, *o*-CH$_3$), 21.11 ppm (s, *p*-CH$_3$). – **^{31}P{^{1}H}-NMR** ([D$_3$]-chloroforme, 121.5 MHz): δ = -55.91 ppm [s, ^1J(PW) = 228.4 Hz]. – **IR** (dichloromethane): ν(CO) = 1951 (vs), 1864 (s) cm^{-1}. Calc. for $C_{23}H_{22}NO_3PW$ (575.26): C, 48.02; H, 3.85; N, 2.43. Found: C, 47.93; H, 3.98; N, 2.41.

3. Dicarbonyl(η^5-cyclopentadienyl){(2,4,6-tri(*tert*-butyl)phenyl)[(N-ethyl)formamido-κN]-phosphinito-κP}tungsten(II) (5): To a solution of 184 mg (0.32 mmol) $Cp(OC)_2W{=}P(H)$*s*Mes (**5**) in 5 mL toluene, 227 mg (0.32 mmol) ethylisocyanate (**2a**) were added and the mixture stirred for 30 min at room temperature. Insolubles are seperated by filtration and the filtrate is evaporated to dryness. The residue is dissolved in 2 mL of toluene and purified by column chromatography (column 20 x 2 cm; Al_2O_3, activity III, neutral; toluene). **5** is isolated by evaporation of the first yellow fraction to dryness and washing three times with 3 mL of *n*-pentane followed by drying in vacuo. – Yield: 150 mg (72 %). – Yellow, crystalline solid. M.p. 94 °C (dec.). **$Cp(OC)_2W$-P(H)(*s*Mes)-C(=O)NEt (6): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.54 (s, br, 2H, *m*-H), 6.45 [d, ^1J(PH) = 345.2 Hz, 1H, HP], 4.84 (s, 5H, H_5C_5), 3.99-3.87 (m, 1H, H_2CN), 2.60-2.49 (m, 1H, H_2CN), 1.65 [s, br, 9H, *o*-$C(CH_3)_3$], 1.45 [s, br, 9H, *o*-$C(CH_3)_3$], 1.38 [t, ^3J(HCCH) = 7.15 Hz, 3H, H_3C], 1.20 ppm [s, 9H, *p*-$C(CH_3)_3$]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 241.64 [d, ^2J(PWC) = 19.3, *cis*-CO], 238.98 [d, ^2J(PWC) = 3.5, *trans*-CO], 178.16 [d, ^1J(PC) = 50.3, C=O], 152.07 [d, ^2J(PCC) = 3.5 Hz, *o*-C], 150.33 (s, *p*-C), 128.89 [d, ^1J(PC) = 57.9 Hz, *ipso*-C], 119.66 (s, *m*-C), 92.98 [d, ^2J(PWC) = 1.0 Hz, C_5H_5], 47.89 [d, ^3J(PWNC) = 22.0 Hz, NCH_2], 34.77 [d, ^3J(PCCC) = 1.4 Hz, *o*-$\underline{C}(CH_3)_3$], 33.83 [s, *p*-$\underline{C}(CH_3)_3$], 31.75 [s, *o*-$C(\underline{C}H_3)_3$], 30.97 [s, *p*-$C(\underline{C}H_3)_3$], 14.26 ppm [d, ^4J(PWNCC) = 1.4 Hz, CH_3]. – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = -62.2 ppm [s, ^1J(PW) = 229.6 Hz]. – **IR** (toluene): ν(CO) = 1943 (vs), 1857 (s) cm^{-1}. Calc. for $C_{28}H_{40}NO_3PW$ (653.46): C, 51.47; H, 6.17; N, 2.14. Found: C, 51.15; H, 6.51; N, 1.67.

4. Dicarbonyl(η^5-cyclopentadienyl){λ^4-(2,4,6-tri(*tert*-butyl)phenyl)[(N-ethyl)formamido]-phosphinediyl}tungsten(II) (7): To a solution of 154 mg (0.26 mmol) $Cp(OC)_2W{=}P(H)$*s*Mes (**5**) in 10 mL toluene, 282 mg (0.26 mmol) ethylisocyanate (**2a**) were added and stirred for 1 d at room temperature. Insolubles are seperated by filtration and the filtrate is evaporated to dryness. The residue is dissolved in 2 mL of toluene and purified by column chromatography (column 20 x 2 cm; Al_2O_3, activity III, neutral; toluene). **7** is isolated by evaporation of the blue fraction to dryness and washing three times with 3 mL of *n*-pentane, followed by drying in vacuo. – Yield: 111 mg (65 %). – Blue, crystalline solid. M.p. 70 °C (dec.). **$Cp(OC)_2W$-P[C(=O)N(H)Et]*s*Mes (7): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.51 [d, ^4J(HCCCH) = 1.8 Hz, 2H, *m*-H], 5.02 (s, 5H, H_5C_5), 3.27-3.20 (m, 2H, H_2C), 1.51 [s, 18H, *o*-$C(CH_3)_3$], 1.25 [s, 9H, *p*-$C(CH_3)_3$], 1.06 ppm [t, ^3J(HCCH) = 7.15 Hz, 3H, H_3C].1) – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 232.12 [d, ^2J(PWC) = 11.4 Hz, *cis*-CO], 175.37 [d, ^1J(PC) = 32.7, C=O], 151.76 [d, ^2J(PCC) = 1.4 Hz, *o*-

C], 151.59 [d, ^4J(PCCCC) = 2.4 Hz, *p*-C], 128.90 [d, ^1J(PC) = 57.6 Hz, *ipso*-C], 123.19 [d, ^3J(PCCC) = 7.9 Hz, *m*-C], 94.46 (s, C_5H_5), 39.08 [d, ^3J(PCCC) = 1.1 Hz, *o*-$\underline{C}(CH_3)_3$], 36.32 [d, ^3J(PCCC) = 4.4 Hz, *o*-$\underline{C}(CH_3)_3$], 35.02 [s, *p*-$\underline{C}(CH_3)_3$], 33.81 [s, *p*-$C(\underline{C}H_3)_3$], 31.12 (s, CH_2N), 14.76 ppm (s, CH_3). – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = 286.32 ppm [s, ^1J(PW) = 582.0 Hz]. – **IR** (toluene): ν(CO) = 1941 (vs), 1857 (s) cm^{-1}. Calc. for $C_{28}H_{40}NO_3PW$ (653.46): C, 51.47; H, 6.17; N, 2.14. Found: C, 51.15; H, 6.51; N, 1.67.

1) NH-resonance not detecable.

5. Dicarbonyl(η^5-cyclopentadienyl)[(η^2-(2,4,6-tri(*tert*-butyl)phenyl)[(N-ethyl)formamido]-thio-phosphinito-κS,κP]tungsten(II) (8): To a solution of 78 mg (0.12 mmol) Cp(OC)$_2$W=P[C(O)N(H)Et]*s*Mes (**7**) in 5 mL toluene, 4 mg (0.12 mmol) of sulphur were added and stirred for 14 d at room temperature. Insolubles are seperated by filtration and the filtrate is evaporated to dryness. The residue is dissolved in 1 mL toluene and purified by column chromatography (column 20 x 1 cm; Al_2O_3, activity III, neutral; toluene). **8** is isolated by evaporation of the first red fraction to dryness and extraction with *n*-pentane (3 x 5 mL), followed by evaporation of the combined organic layers in vacuo. – Yield: 57 mg (69 %). – Darkred solid. M.p. 96 °C (dec.). **$\mathrm{Cp(OC)_2\overline{W\text{-}P[C(=O)NHEt]\mathit{s}Mes\text{-}S}}$ (8): ^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): δ = 7.32 [dd, ^4J(PCCCH) = 4.8 Hz, ^4J(HCCCH) = 2.2 Hz, 1H, *m*-H], 7.29 [d, ^4J(HCCCH) = 2.2 Hz, 1H, *m*-H], 6.34 [t, ^3J(HCNH) = 5.5 Hz, 1H, HN], 4.60 (s, 5H, H_5C_5), 3.28-3.21 (m, 1H, H_2C), 2.97-2.88 (m, 1H, H_2C), 1.79 [s, 9H, *o*-$C(CH_3)_3$], 1.71 [s, 9H, *o*-$C(CH_3)_3$], 1.14 [s, 9H, *p*-$C(CH_3)_3$], 0.89 ppm [dt, ^3J(HCCH) = 7.2 Hz, ^5J(PCNCCH) = 1.1 Hz, 3H, H_3C]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): δ = 240.48 [d, ^2J(PWC) = 16.8 Hz, *cis*-CO], 229.84 (s, *cis*-CO), 169.97 [d, ^1J(PC) = 54.5, C=O], 160.62 [d, ^2J(PCC) = 18.9 Hz, *o*-C], 159.18 (s, *o*-C), 151.86 [d, ^4J(PCCCC) = 4.5 Hz, *p*-C], 128.89 [d, ^1J(PC) = 56.9 Hz, *ipso*-C], 124.37 [d, ^3J(PCCC) = 10.0 Hz, *m*-C], 122.59 [d, ^3J(PCCC) = 15.2 Hz, *m*-C], 92.17 [d, ^3J(HCWP) = 0.7 Hz, C_5H_5], 41.34 [d, ^3J(PCCC) = 3.1 Hz, *o*-$\underline{C}(CH_3)_3$], 40.59 [d, ^3J(PCCC) = 3.5 Hz, *o*-$\underline{C}(CH_3)_3$], 35.87 [d, ^5J(PCCCCC) = 4.1 Hz, *p*-$\underline{C}(CH_3)_3$], 34.66 [d, ^4J(PCCCC) = 1.7 Hz, *o*-$C(\underline{C}H_3)_3$], 33.99 [s, *p*-$C(\underline{C}H_3)_3$], 33.94 [d, ^4J(PCCCC) = 1.4 Hz, *o*-$C(\underline{C}H_3)_3$], 30.80 [d, ^3J(PCNC) = 0.8 Hz, CH_2N], 14.73 ppm (s, CH_3). – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): δ = -32.98 ppm [s, ^1J(PW) = 211.4 Hz]. – **IR** (*n*-pentane): ν(CO) = 1949 (vs), 1868 (s) cm^{-1}. Calc. for $C_{28}H_{40}NO_3PSW$ (685.46): C, 49.06; H, 5.88; N, 2.03; S, 4.68. Found: C, 49.12; H, 6.12; N, 1.74; S, 4.77.

6. Dicarbonyl(η^5-cyclopentadienyl){[(*tert*-butyl)[(N-ethyl)formamido][(N-ethyl)formamido-κN]-phosphanido-κP}tungsten(II) (11): To a solution of 187 mg (0.43 mmol) $Cp(OC)_2[P(H)_2tBu]W\text{-}Cl$ (**9**) in 5 mL toluene, 101 mg (1.00 mmol) triethylamine and 124 mg (0.86 mmol) ethylisocyanate (**2a**) were added at 0 °C and stirred for 20 h at room temperature. Insolubles are seperated by filtration and the filtrate is evaporated to dryness. The residue is dissolved in 2 mL of toluene and purified by column chromatography (column 20 x 2 cm; Al_2O_3, activity III, neutral; toluene). **11** is isolated by evaporation of the second yellow fraction to dryness and washing three times with 3 mL of *n*-pentane followed by drying in vacuo. – Yield: 188 mg (84 %). – Yellow solid. M.p. 70 °C (dec). **$Cp(OC)_2\overline{W\text{-}P[(C{=}O)NHEt(tBu)\text{-}C({=}O)N}Et$: (11):** **^{1}H-NMR** ([D$_6$]-benzene, 300.4 MHz): $\delta = 7.41$ (s, br, 1H, NH), 4.91 (s, 5H, H_5C_5), 3.80-3.68 (m, 1H, $\underline{H_2}CNH$), 3.14-3.00 (m, 1H, H_2CN), 2.94-2.80 (m, 1H, $\underline{H_2}CNH$), 2.68-2.57 (m, 1H, H_2CN), 1.43 [d, ^3J(PCCH) = 16.1 Hz, 9H, $C(CH_3)_3$], 1.13 [t, ^3J(HCCH) = 7.0 Hz, 3H, H_3C], 0.74 ppm [t, ^3J(HCCH) = 7.2 Hz, 3H, H_3C]. – **^{13}C-NMR** ([D$_6$]-benzene, 75.45 MHz): $\delta = 247.10$ [d, ^2J(PWC) = 18.9, *cis*-CO], 238.65 [d, ^2J(PWC) = 4.1, *trans*-CO], 180.01 [d, ^1J(PC) = 44.8 Hz, C=O], 168.71 [d, ^1J(PC) = 38.9, C=O], 92.27 [d, ^2J(PWC) = 1.1 Hz, C_5H_5], 46.60 [d, ^3J(PWNC) = 17.3 Hz, $\underline{C}(CH_3)_3$], 34.64 [d, ^3J(PCCC) = 1.4 Hz, CH_2], 33.81 [d, ^3J(PWNC) = 15.5 Hz, CH_2], 26.82 [d, ^4J(PCCCC) = 2.7 Hz, $C(\underline{C}H_3)_3$], 15.06 [d, ^4J(PCNCC) = 1.1 Hz, CH_3], 14.74 ppm (s, CH_3). – **^{31}P{^{1}H}-NMR** ([D$_6$]-benzene, 121.5 MHz): $\delta = -1.33$ ppm [s, ^1J(PW) = 240.6 Hz]. – **IR** (toluene): ν(CO) = 1945 (s), 1858 (s) cm^{-1}. Calc. for $C_{17}H_{25}N_2O_4PW$ (536.20): C, 38.08; H, 4.70; N, 5.22. Found: C, 37.86; H, 4.75; N, 5.10.

7. X-ray analyses for compounds 6, 7 and 11: Crystals of **6**, **7** and **11** suitable for structure determination could be obtained from a saturated toluene solution at room temperature. Data collection was performed on an Enraf-Nonius CAD4-diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) at 173(2) K.[44-46] The structures were solved using the Patterson-method and cell parameters were determined and refined using SHELXS-97[47] and SHELXL-97.[48]

*Crystal Data for Compounds **6**, 7 and **11**:*

	6	**7**	**11**
identification	andi34	andi38	andi40
mol formula	$C_{28}H_{40}NO_3PW$	$C_{28}H_{40}NO_3PW$	$C_{17}H_{25}N_2O_4PW$
mol wt	653.46	653.46	536.20
wavelength (Å)	0.71073	0.71073	0.71073
temp (K)	173(2)	173(2)	173(2)
cryst size (mm)	0.21 x 0.11 x 0.09	0.19 x 0.13 x 0.08	0.15 x 0.11 x 0.10
cryst syst	triclinic	monoclinic	monoclinic
space group	*P-1*	*P2(1)/n*	*Cc*
a (Å)	10.250(2)	13.565(4)	9.059(3)
b (Å)	12.005(3)	15.214(4)	23.357(9)
c (Å)	13.273(3)	13.889(4)	18.724(7)
α (°)	107.015(3)	90	90
β (°)	107.276(3)	98.546(4)	102.206(6)
γ (°)	103.273(3)	90	90
vol ($Å^3$), *Z*	1395.1(5), 2	2834.4(12), 4	3872.0(2), 8
ρ (calcd) (Mgm^{-3})	1.555	1.531	1.840
F(000)	656	1312	2096
μ (mm^{-1})	4.225	4.159	6.072
θ range for data collecn (deg)	1.75 – 25.04	2.02 – 25.01	1.74 – 25.12
no. of rflns collected	23600	26563	13737
no. of indep reflns	4919	4976	6315
abs cor.	empirical	empirical	empirical
no. of data/restraints/params	4919 / 0 / 321	4976 / 0 / 352	6315 / 2 / 461
goodness of fit on F^2	1.065	1.058	1.087
R1[a]	0.0154	0.0478	0.0250
wR2[b]	0.0379	0.0483	0.0568
largest diff peak and hole ($eÅ^{-3}$)	0.792 and -0.273	0.838 and -0.544	0.950 and -0.446

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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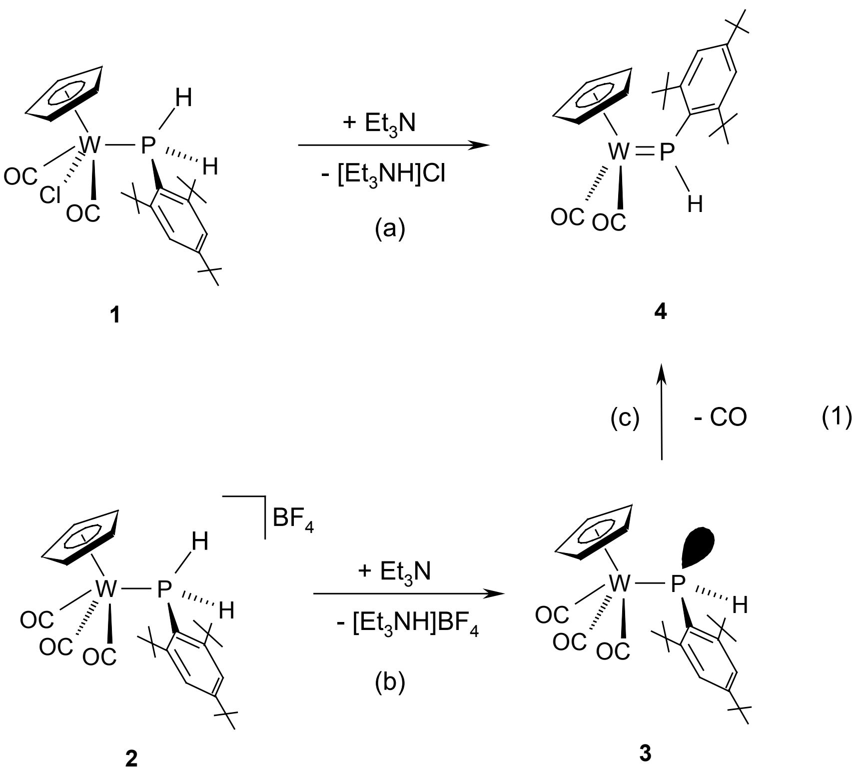
SUMMARY

Chapter I: The *super*-Mesitylphosphenium Tungsten Complex $C_5H_5(OC)_2W=P(H)$*s*Mes: Structural and Theoretical investigation. Addition Reactions with Trimethylphosphine, Elemental sulphur and Selenium

The *super*-mesitylphosphenium tungsten complex **4** can be generated via dehydrochlorination of the *super*-mesitylphosphine chloro-tungsten species **1** with triethylamine [Scheme (1a)] or by decarbonylation of the *secondary* tungsten-phosphine **3** [Scheme (1c)] obtained from the cationic *super*-mesitylphosphine tungsten complex **2**, isolated as the BF_4-salt, via deprotonation with triethylamine [Scheme (1b)].



1, **2** and **4** [Fig. (1)] have been structurally characterized by x-ray diffraction analyses. For the *super*-mesitylphosphenium tungsten complex **4** a *cis*-configuration of the *super*-mesityl-ligand at the phosphorus and the cyclopentadienyl moiety at the tungsten atom is found, both in solid state and in solution.

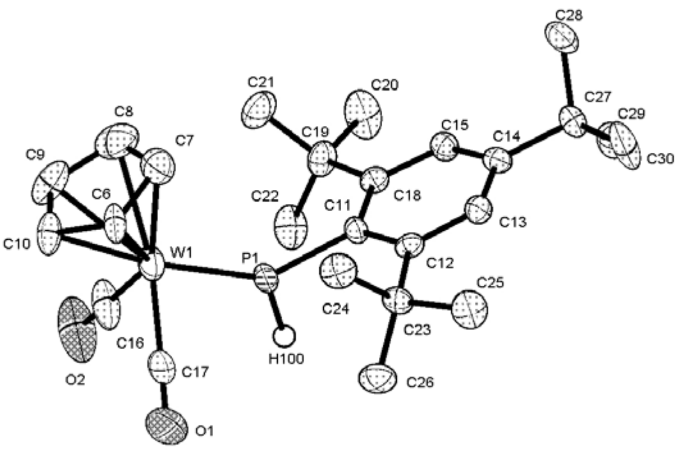
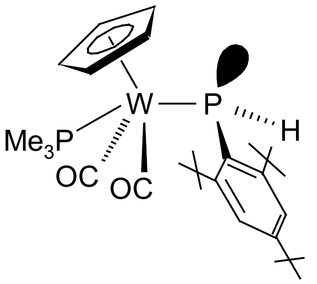


Fig. (1): Molecular Structure of $Cp(OC)_2W{=}P(H)$*s*Mes (**4**)

Density functional calculations on a series of model systems $Cp(OC)_2W{=}P(H)R$ [R = *s*Mes (**4**), *tert*-Butyl, Ph, Mes], in both *cis*- and *trans*-configurations have been carried out. The computations confirm a higher stability for the *cis*-isomer in comparison to the *trans*-arrangement for **4**. For all the other investigated substituents the *trans*-arrangement is slightly favoured.

Treatment of a benzene solution of **4** with an excess of trimethylphosphine yields the phosphine-substituted *secondary* metallo-phosphine **5**.



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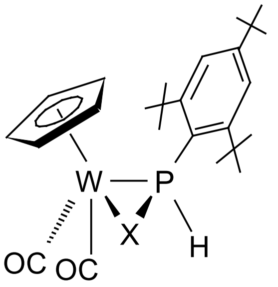
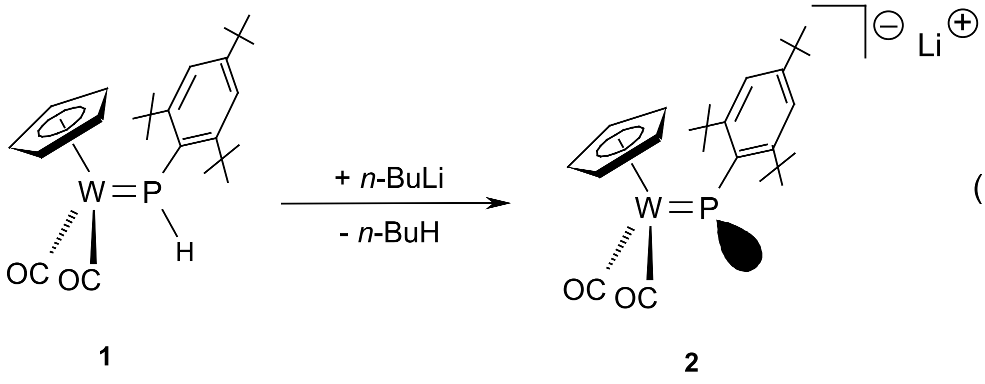


6	**a**	**b**
X	S	Se

Reaction of **4** with sulphur or selenium generates the three-membered phosphametallacycles **6a**,**b**, indicating a controlled cycloaddition of the chalcogen atom to the W=P-bond.

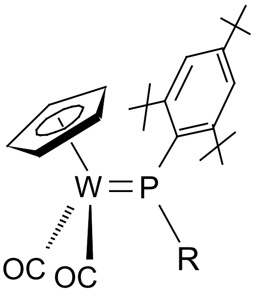
Chapter II: P-Alkylation and P-Acylation of the Phosphenium Complex $C_5H_5(OC)_2W=P(H)$*s*Mes via the Anionic Phosphinidene Complex $[Cp(OC)_2W=P($*s*Mes$)]Li$.

Treatment of the *super*-mesitylphosphenium tungsten complex **1**, dissolved in THF, with *n*-BuLi at -78 °C results in the generation of the lithium tungsten salt **2**, containing an anionic phosphinidene complex [Eq. (1)], which exists for several hours at room temperature but only in the presence of donor solvents like THF or dimethoxyethane.

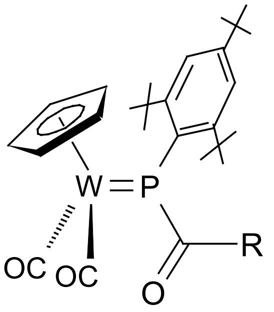


(1)

Reaction of **2**, *in situ* generated, with an equimolar amount of *n*-BuLi and the alkyl halides R-Hal (**3a-f**) leads to alkylated phosphenium tungsten complexes **4a-f**.



4a-f



	a	b	c	d	e	f
R	Me	Et	*i*-Pr	*n*-Bu	CH_2Ph	$CH_2CH=CH_2$

	5a	5b
R	Me	Bz

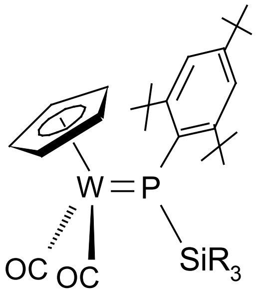
Due to x-ray diffraction analyses **4a-e** show *cis*-configuration regarding the *super*-mesityl-ligand and the cyclopentadienyl moiety, which is in accordance with the situation for Cp(OC)$_2$W=P(H)*s*Mes (**1**).

The first acylphosphenium tungsten complexes **5a**,**b** are generated analogously from the reaction of **2** with acetyl or benzoyl chloride. **5a**,**b** show no indication for an additional coordination of the carboxyl moiety to tungsten.

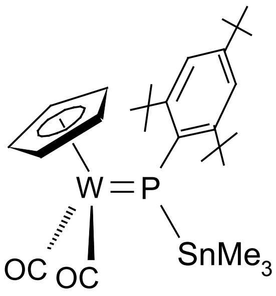
Quantum chemical calculations for the *cis*-arranged compounds Cp(OC)$_2$W=P(R)*s*Mes [R = Me (**4a**), Et (**4b**), *i*Pr (**4c**), *n*Bu (**4d**)] confirm a higher stability for the *cis*-isomer in comparison to the *trans*-arrangement in all cases.

Chapter III: P-Silylated and P-Stannylated Phosphenium Complexes from the Anionic Phosphinidene Complex [C$_5$H$_5$(OC)$_2$W=P(*s*Mes)]Li. Conversion of the Triflatophosphenium Complex Cp(OC)$_2$W=P(OSO$_2$CF$_3$)*s*Mes to Cationic Phosphinidene-Phosphorane Tungsten Complexes.

Treatment of [Cp(OC)$_2$W=P(*s*Mes)]Li (**2**) with the chlorosilanes R$_3$Si-Cl [R$_3$Si = SiMe$_3$ (**3a**), SiMe$_2$H (**3b**), SiPh$_2$H (**3c**)] yields so far unknown silylphosphenium tungsten complexes **4a-c**.



4a-c



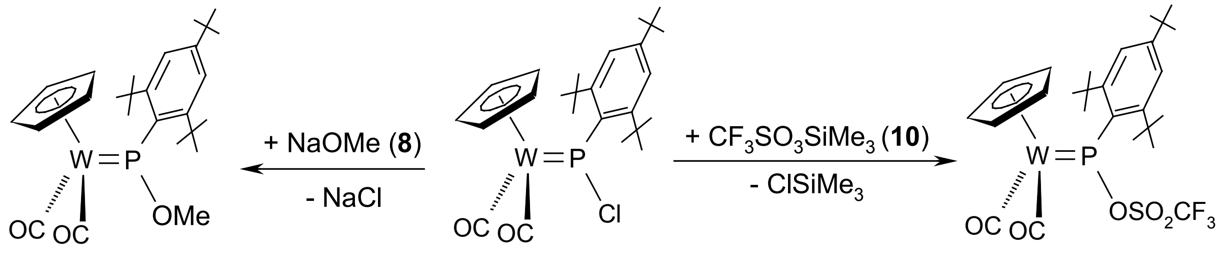
6

	a	b	c
SiR$_3$	SiMe$_3$	SiMe$_2$H	SiPh$_2$H

The existence of **4a-c**, isolated as extremely sensitive blue powders, is especially proved by the ^1J(PSi) coupling constants of 26.8 (**4a**), 35.8 (**4b**) and 23.9 Hz (**4c**).

2 combined with Me$_3$Sn-Cl yields the first stannylphosphenium complex **6**. The stability of **6** allows even a structure analysis.

Another attractive system for derivatization is offered by the chloro-*super*-mesitylphosphenium complex Cp(OC)$_2$W=P(Cl)*s*Mes (**7**), as the reaction with sodium methanolate (**8**) showed, yielding the methoxyphosphenium complex **9**, even structurally characterized [Scheme (1)].

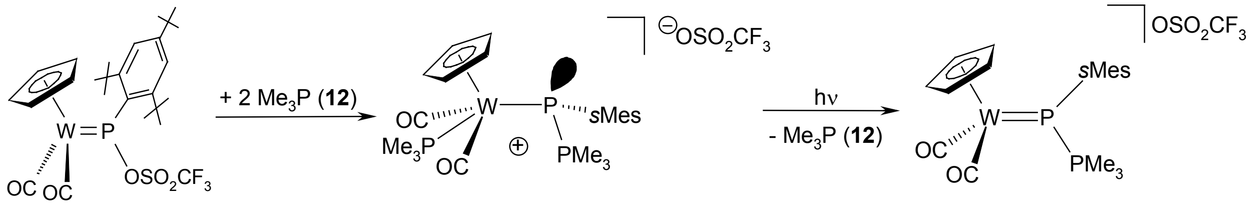


(1)

9 **7** **11**

The phosphenium complex **11** containing the extremely reactive leaving group triflate is obtained, when **7**, dissolved in THF, is treated with trimethylsilyltriflate (**10**) at -78 °C. The ^{31}P-NMR-spectrum suggests formation of a *cis*- and *trans*-isomer regarding the cyclopentadienyl/*super*-mesityl arrangement [Scheme (1)].

Due to the high polarity of the P-OTf moiety **11** can be interpreted as a "masked" cationic phosphinidene complex [Cp(OC)$_2$W≡P(*s*Mes)]$^{\oplus}$, as is demonstrated in the reaction with trimethylphosphine (**12**) in THF at -78 °C, resulting in the formation of the cationic phosphinidene-phosphorane complex **13** of the phosphanido type [Eq. (2)].



(2)

11 **13** **14**

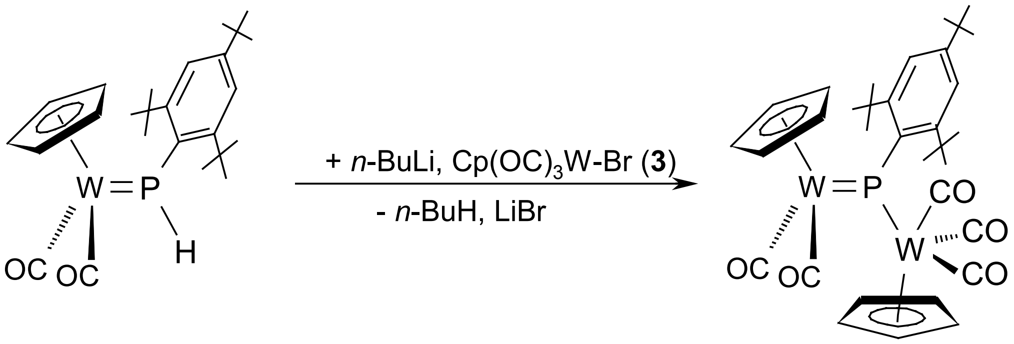
The overall reaction involves a nucleophilic substitution of the phosphorus coordinated triflato group by Me$_3$P (**12**), followed by the *trans*-selective coordination of a second Me$_3$P-molecule at the tungsten.

Irradiation of **13**, dissolved in [D$_3$]-chloroforme, with UV-light for 5 h leads to the cationic "phosphenium type" phosphinidene-phosphorane complex **14** after loss of the tungsten-coordinated Me$_3$P-ligand.

An access to [Cp(OC)$_2$(Me$_3$P)W-P(*s*Mes)PMe$_3$]Cl (**15**), the chloride analogue of **13**, is given by the reaction of **7** in [D$_6$]-benzene with trimethylphosphine (**12**).

Chapter IV: Dinuclear Phosphinidene Complexes Cp(OC)$_2$W=P(ML$_n$)*s*Mes [ML$_n$ = Cp(OC)$_3$W, Cp(OC)$_3$Fe]: Synthesis from Cp(OC)$_2$W=P(H)*s*Mes and Photochemical Transformation

The treatment of the phosphenium complex Cp(OC)$_2$W=P(H)*s*Mes (**1**) dissolved in THF with *n*-BuLi and an equimolar amount of Cp(OC)$_3$W-Br (**3**) yields the dinuclear phosphinidene complex **4** [Eq. (1)].

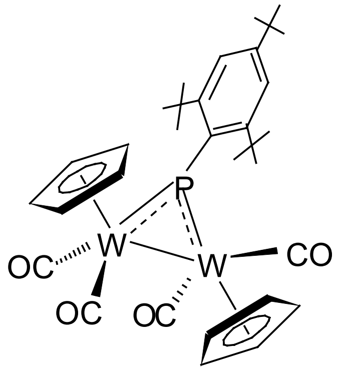


(1)

1 **4**

The ^{31}P-NMR-data {[δ/^1J(PW)]: 255.2 ppm / 507.9; 94.8 Hz} correlates with the description of **4** as an unsymmetric phosphinidene complex.

4 can be converted on irradiation with UV-light to the symmetrically substituted phosphinidene complex **5** via a carbonyl elimination, connected to a simultaneous tungsten-tungsten-bond generation.



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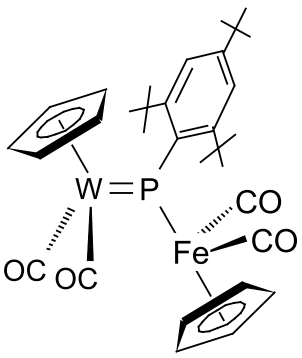

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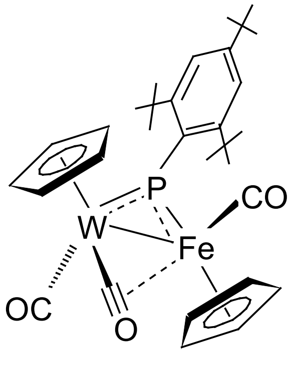
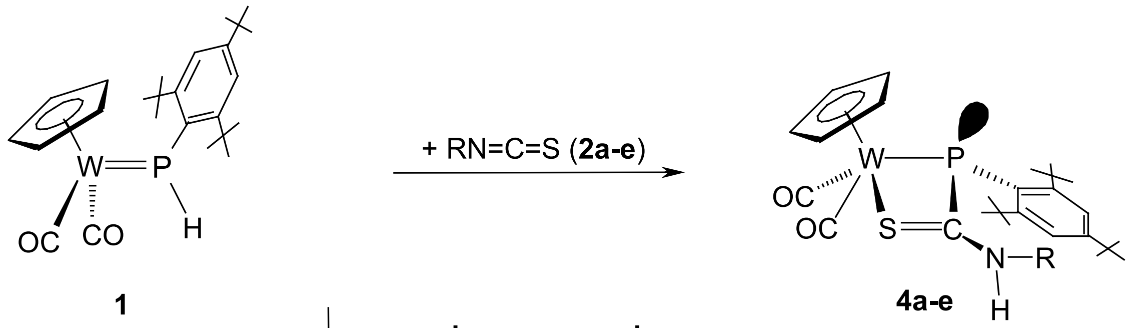


8

The novel synthetic pathway to phosphinidene complexes according to Eq. (1) is also effective for the synthesis of heteronuclear phosphinidene complexes. Treatment of **1** with *n*-BuLi and Cp(OC)$_2$Fe-I afterwards yields the heteronuclear tungsten-iron-complex **7**, which is rather unstable in solution as well as in the solid state due to a facile CO-elimination. The result is the CO-bridged heteronuclear phosphinidene complex **8**, with one carbonyl ligand occupying a semi-bridging position. **4**, **5** and **8** are characterized via x-ray diffraction analysis.

Chapter V: Cyclic Metallo-Phosphines $\mathbf{Cp(OC)_2\overline{W\text{-}P(\mathit{s}Mes)\text{-}C(NHR)S}}$ (R = Alkyl) and $\mathbf{Cp(OC)_2\overline{W\text{-}P(\mathit{s}Mes)C[NH(\mathit{i}Pr)]\text{=}N}(\mathit{i}Pr)}$ via [2+2] Cycloaddition of Cp(OC)₂W=P(H)*s*Mes with Alkylisothiocyanates and Diisopropylcarbodiimide Followed by P→N-Hydrogen Migration

Stirring of a 1:1-mixture of **1** and the alkylisothiocyanate **2a-e** in toluene at room temperature yields the four-membered phosphametallacycles **4a-e**, which as the most striking feature show a trivalent phosphorus and a hydrogen substituted nitrogen atom [Eq. (1)].



1

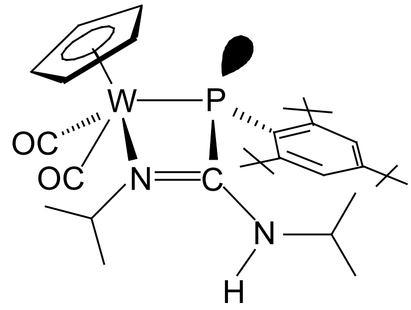
4a-e

(1)

	a	b	c	d	e
R	Me	Et	*t*Bu	Ph	CH_2CH_2Ph

The product formation indicates a [2+2]-cycloaddition involving the C=S double bond of the isothiocyanate **2a-e** to be followed by a P→N-hydrogen migration to give **4a-e**. The phosphametallacycles **4a-e** are formed completely diastereoselective, exclusively the *unlike*-isomers (S_WR_P/R_WS_P) are obtained with respect to the stereochemistry at the tungsten and phosphorus atom.

Analogous reaction of **1** with diisopropylcarbodiimide in toluene at room temperature yields the four-membered phosphametallacycle **7**.

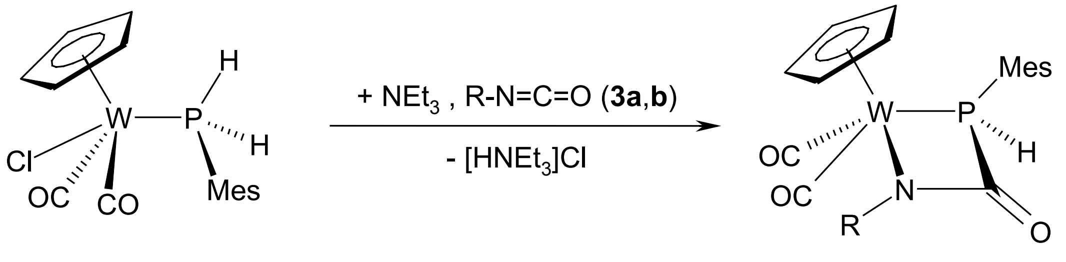


7

The diastereoselective formation of **7**, namely the formation of the *like*-derivative with a *trans*-configuration concerning the Cp- and *s*Mes-ligand, is confirmed both by the NMR-data and the crystal structure.

Chapter VI: [2+2] Cycloaddition of Phosphenium Tungsten Complexes with Alkylisocyanates: Synthesis of the Cyclic Tungsten-Phosphines Cp(OC)₂W-P(H)(R)-(C=O)NR' (R = *t*Bu, Mes, *s*Mes; R' = Et, Ph) and the Acylamidphosphenium Tungsten Complex Cp(OC)₂W=P[C(=O)N(H)Et]*s*Mes

Treatment of a mixture of the mesitylphosphine tungsten complex $Cp(OC)_2(MesH_2P)W\text{-}Cl$ (**1**) and ethyl- or phenylisocyanate (**3a,b**) in toluene with Et_3N at 0° yield the stable four-membered phosphametallacycles **4a**,**b** under a controlled [2+2]-cycloadditon involving the *in situ* via dehydrochlorination generated complex $Cp(OC)_2W{=}P(H)Mes$ (**2**) [Eq. (1)].



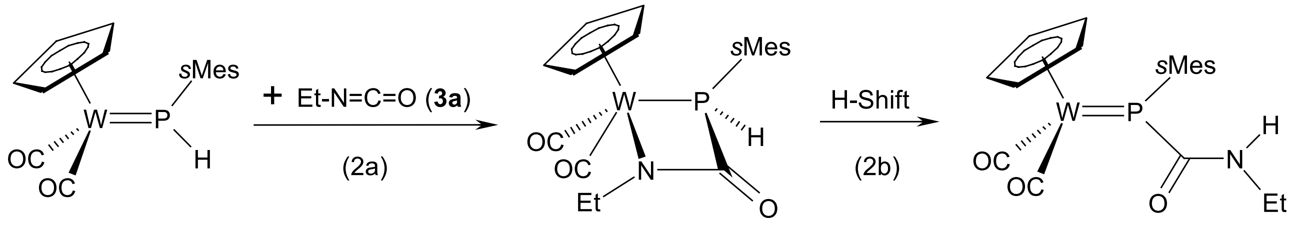
(1)

1

4	**a**	**b**
R	Et	Ph

4a,**b** are isolated as a diastereomeric mixture (**4a**= 65 : 35; **4b** = 69 : 31) regarding the *like*-*trans*- or *unlike*-*cis*-arrangement of the mesityl group and the cylopentadienyl moiety. Predominance of the *like*-*trans*-product as major isomer is proved by ^{1}H-NOESY-experiments. Treatment of

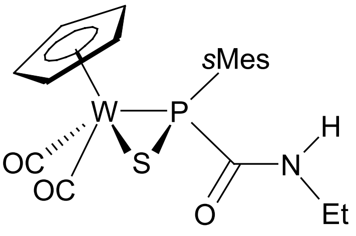
Cp(OC)$_2$W=P(H)*s*Mes (**5**) with ethylisocyanate (**3a**) yields diastereoselective the stable P-H-functionalized [2+2]-cycloadduct **6** [Eq. (2a)] in form of the *like*-*trans*-isomer. The stereochemistry is confirmed due to ^{1}H-NOESY-experiments and the crystal structure of **6**.



5 **6** **7**

Stirring a solution of **6** in toluene at room temparature induces rearrangement to the acylamidophosphenium tungsten complex **7** due to a P→N-hydrogen-shift, resulting in the insertion of the isocyanate fragment into the P-H-bond [Eq. (2b)]. The *trans*-structure in the solid state is confirmed via x-ray diffraction analysis.

The reactivity of the W=P bond is proved by treatment of **7** with elemental sulphur generating the sulphur-bridged three-membered phosphametallacycle **8**.



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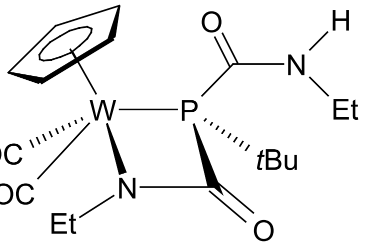


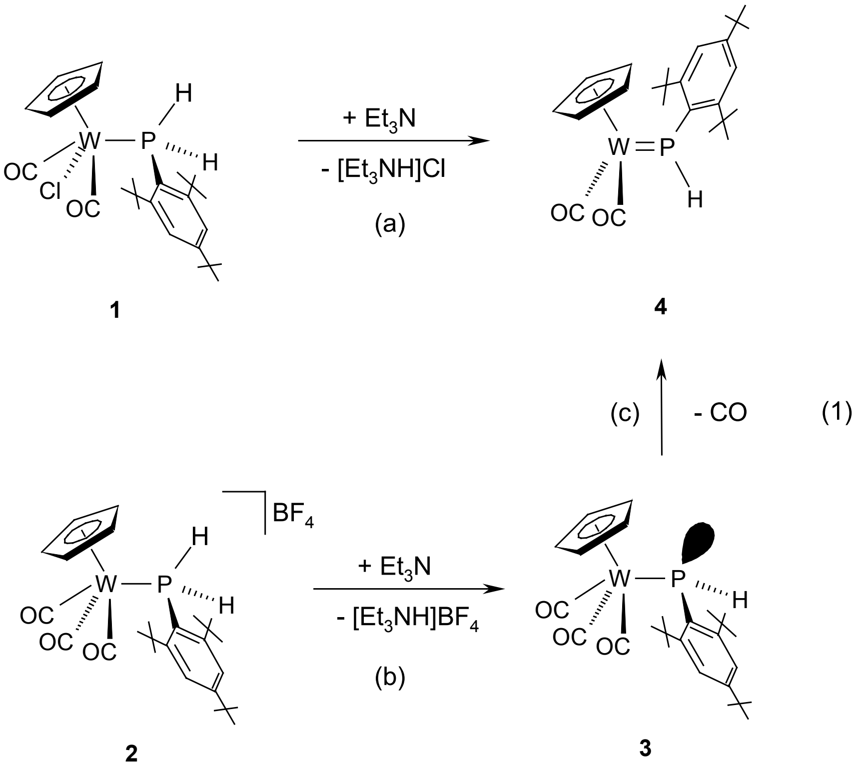
11

If a mixture of Cp(OC)$_2$(*t*BuH$_2$P)W-Cl (**9**) and ethylisocyanate (**2a**) in toluene is treated with Et$_3$N at 0°, the phosphametallacycle **11** is formed via a [2+2]-cycloadditon of one equivalent of the isocyanate with the *in situ* generated complex Cp(OC)$_2$W=P(H)*t*Bu (**10**) and an additional insertion of a second mole of the heteroallene into the P-H-bond. The structure of **11** is confirmed via x-ray diffraction analysis.

ZUSAMMENFASSUNG

Kapitel I: Der *super*-Mesitylphosphenium-Wolfram-Komplex $C_5H_5(OC)_2W{=}P(H)s\mathrm{Mes}$: Strukturelle und theoretische Untersuchungen. Additionsreaktionen mit Trimethylphosphan, elementarem Schwefel und Selen

Der *super*-Mesitylphosphenium-Wolfram-Komplex **4** kann durch Dehydrochlorierung mittels Triethylamin aus der *super*-Mesitylphosphan-Chlor-Wolfram-Verbindung **1** dargestellt werden [Schema (1a)]. Alternativ lässt sich **4** durch thermische Decarbonylierung des sekundären Wolframio-Phosphans **3** erhalten [Schema (1c)], welches aus dem als BF_4-Salz vorliegenden, kationischen *super*-Mesityl-Wolfram-Komplex **2** durch Deprotonierung mit Triethylamin darstellbar ist [Schema (1b)].



1, **2** und **4** [Abb. (1)] wurden durch Röntgenbeugung strukturell charakterisiert. Für den *super*-Mesitylphosphenium-Wolfram-Komplex **4** wurde sowohl im Feststoff als auch in Lösung eine *cis*-Konfiguration bezüglich der Stellung des *super*-Mesityl-Liganden am Phsophor und der Cyclopentadienyl-Einheit am Metall gefunden.

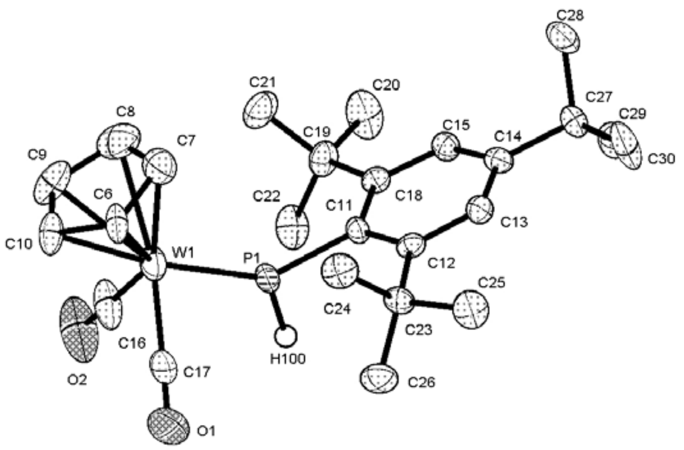
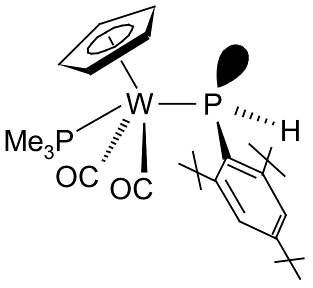


Abb. (1). Molekülstruktur von Cp(OC)$_2$W=P(H)*s*Mes (**4**)

Zur Klärung der Strukturverhältnisse wurden DFT-Berechnungen an Modellsystemen des Typs Cp(OC)$_2$W=P(H)R [R = *s*Mes (**4**), *tert*-Butyl, Ph, Mes] durchgeführt. Für alle diese Systeme wurde sowohl das *cis*- als auch das mögliche *trans*-Isomer untersucht, wobei für **4** eine erhöhte Stabilität der *cis*-Anordnung nachgewiesen wurde. Für die Komplexe mit einem *tert*-Butyl-, Phenyl- oder Mesitylliganden ist die entsprechende *trans*-Konfiguration leicht bevorzugt.

Die Umsetzung einer Lösung von **4** in Benzol mit einem Überschuss an Trimethylphosphan führt zum Phosphan-substituierten *sekundären* Metallo-phosphan **5**.



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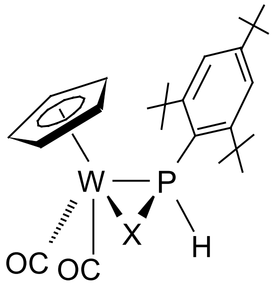
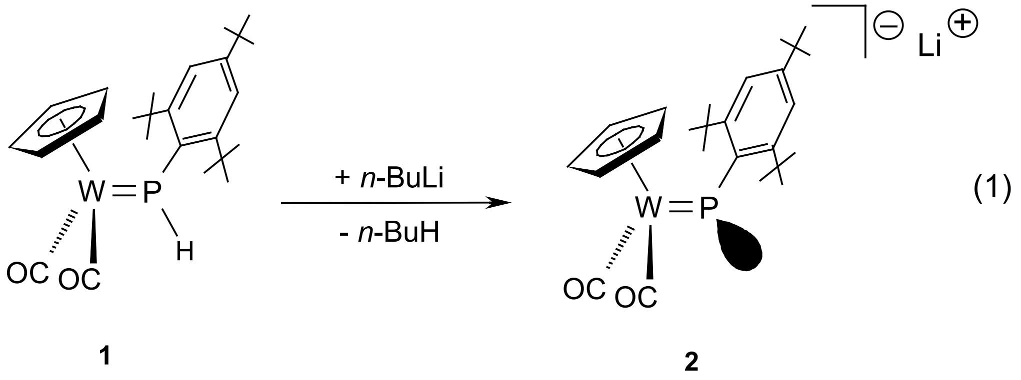


6	**a**	**b**
X	S	Se

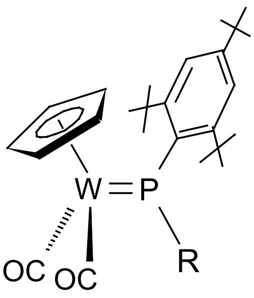
Durch die Reaktion von **4** mit elementarem Schwefel oder Selen lassen sich die dreigliedrigen Phosphametallacyclen **6a,b** generieren, was eine kontrollierte Addition des Chalkogenatoms an die W=P-Bindung belegt.

Kapitel II: P-Alkylierung und P-Acylierung des Phosphenium-Komplexes $C_5H_5(OC)_2W{=}P(H)$*s*Mes über den anionischen Phosphiniden-Komplex [Cp(OC)$_2$W=P(*s*Mes)]Li.

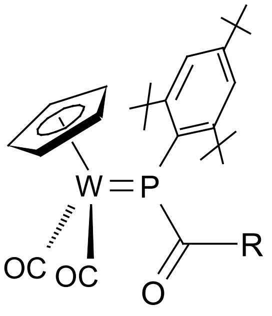
Die Umsetzung des *super*-Mesitylphosphenium-Wolfram-Komplexes **1**, gelöst in THF, bei -78 °C mit *n*-BuLi, führt zur Synthese des Lithium-Wolfram-Salzes **2**, das einen anionischen Phosphiniden-Komplex enthält [Gl. (1)]. **2** ist für einige Stunden bei Raumtemperatur unter N_2-Atmosphäre handhabbar, allerdings nur in der Gegenwart von donierenden Solventien wie THF oder Dimethoxyethan.



Die Umsetzung von *in situ* dargestelltem **2** mit den Alkylhalogeniden R-Hal (**3a-f**) ermöglicht die Synthese der alkylierten Phosphenium-Wolfram-Komplexe **4a-f**.



4a-f



	a	b	c	d	e	f
R	Me	Et	*i*-Pr	*n*-Bu	CH_2Ph	$CH_2CH{=}CH_2$

	5a	5b
R	Me	Bz

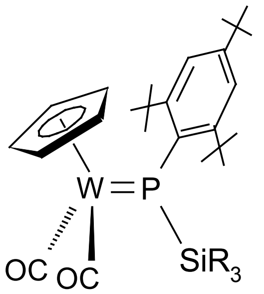
Mittels Röntgenbeugung konnte für die Verbindungen **4a-e** im festen Zustand eine *cis*-Konfiguration bezüglich des *super*-Mesityl-Liganden und der Cyclopentadienyl-Einheit nachgewiesen werden, was mit der Bindungssituation bei $Cp(OC)_2W{=}P(H)$*s*Mes (**1**) übereinstimmt.

Die ersten Acylphosphenium-Wolfram-Komplexe **5a**,**b** können in Analogie zu **4a-f** durch die Reaktion von **2** mit Acetyl- oder Benzoylchlorid dargestellt werden. **5a,b** zeigen keinerlei Anzeichen für eine zusätzliche Koordination der Carboxylgruppe ans Übergangsmetall.

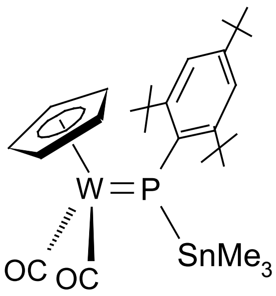
Quantenchemische Berechungen für die Systeme $Cp(OC)_2W{=}P(R)$*s*Mes [R = Me (**4a**), Et (**4b**), *i*Pr (**4c**), Bu (**4d**)] bestätigen in allen Fällen eine höhere Stabilität des *cis*-Isomers im Vergleich zur *trans*-Anordnung.

Kapitel III: P-Silylierte und P-Stannylierte Phosphenium-Komplexe aus dem anionischen Phosphiniden-Komplex [$C_5H_5(OC)_2W{=}P$(*s*Mes)]Li. Überführung des Triflat-Phosphenium-Komplexes $Cp(OC)_2W{=}P(OSO_2CF_3)$*s*Mes in kationische Phosphiniden-Phosphoran-Wolfram-Verbindungen

Die Reaktion von [$Cp(OC)_2W{=}P$(*s*Mes)]Li (**2**) mit den Chlorsilanen R_3Si-Cl [R_3Si = $SiMe_3$ (**3a**), $SiMe_2H$ (**3b**), $SiPh_2H$ (**3c**)] ergibt die Silylphosphenium-Wolfram-Komplexe **4a-c**, die eine bisher unbekannte Klasse von Phosphenium-Verbindungen darstellen.



4a-c

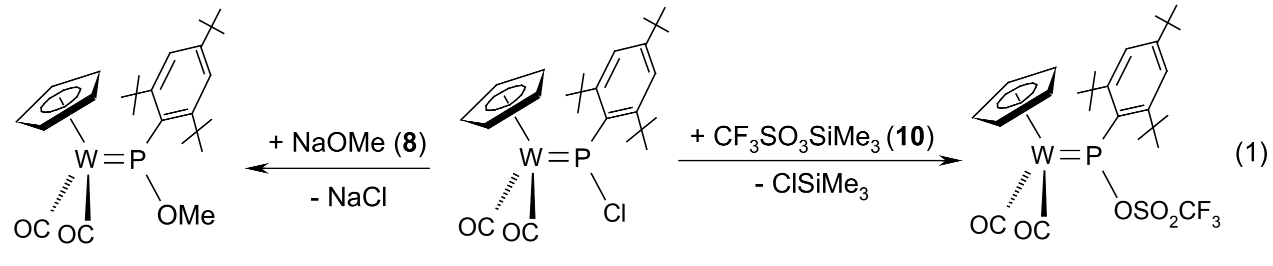


6

	a	**b**	**c**
SiR_3	$SiMe_3$	$SiMe_2H$	$SiPh_2H$

Die Existenz von **4a-c**, isolierbar als blaue Pulver von extremer Empfindlichkeit, ist besonders durch die ^1J(PSi)-Kopplungskonstanten von 26.8 (**4a**), 35.8 (**4b**) und 23.9 Hz (**4c**) nachgewiesen. Setzt man **2** mit Me_3Sn-Cl um, so erhält man den ersten Stannylphosphenium-Komplex **6**, der zudem strukturell charakterisert ist.

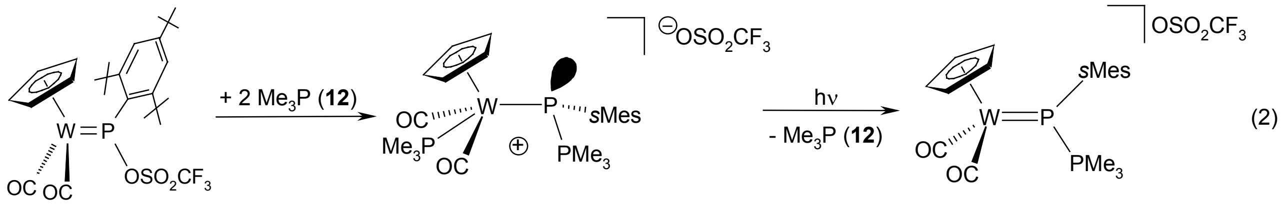
Eine attraktive Verbindung für weitere Derivatisierungen ist mit dem Chlor-*super*-Mesitylphosphenium-Komplex Cp(OC)$_2$W=P(Cl)*s*Mes (**7**) verfügbar. Die Umsetzung mit Natriummethanolat (**8**) führt zu dem auch strukturell charakterisierten Methoxyphosphenium-Komplex **9** [Schema (1)].



9 **7** **11**

Der Phosphenium-Komplex **11**, der eine extrem reaktive Triflat-Abgangsgruppe besitzt, ist erhältlich wenn **7**, gelöst in THF, mit Trimethylsilyltriflat (**10**) bei -78 °C umgesetzt wird. Das ^{31}P-NMR-Spektrum legt die Generierung eines *cis*- und *trans*-Isomeren bezüglich der Cyclopentadienyl/*super*-Mesityl-Anordnung nahe [Scheme (1)].

Die hohe Polarität der P-OTf-Einheit, die eine Interpretation von **11** als "maskierten" kationischen Phosphiniden-Komplex des Typs [Cp(OC)$_2$W≡P(*s*Mes)]$^{\oplus}$ zulässt, ist durch die Umsetzung von **11** mit Trimethylphosphan (**12**) in THF bei -78 °C nachweisbar. Dabei resultiert der kationische Phosphiniden-Phosphoran-Komplex **13** in der Phosphanido-Form [Gl. (2)].



11 **13** **14**

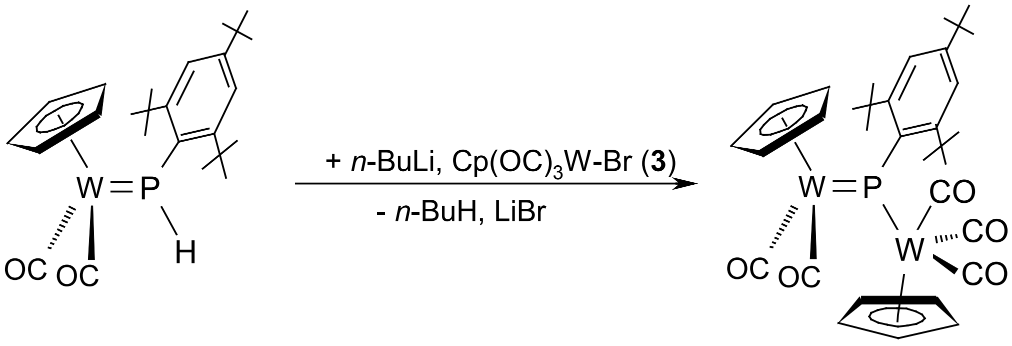
Der Reaktionsmechanismus schließt eine nukleophile Substitution der am Phosphoratom koordinierten Triflatgruppe durch Me$_3$P (**12**) und eine anschliessende *trans*-selektive Koordination eines zweiten Me$_3$P-Moleküls am Wolfram ein.

Bestrahlt man **13** gelöst in [D$_3$]-Chloroform mit UV-Licht für 5 Stunden, führt dies infolge Abspaltung des wolframkoordinierten Me$_3$P-Liganden zu dem kationischen „phospheniumartigen" Phosphiniden-Phosphoran-Komplex **14.**

Eine Synthesemöglichkeit für [Cp(OC)$_2$(Me$_3$P)W-P(*s*Mes)PMe$_3$]Cl (**15**), dem Chlorid-Analogon zu **13**, ist durch die Reaktion von **7** in [D$_6$]-Benzol mit Trimethylphosphan (**12**) gegeben.

Kapitel IV: Zweikernige Phosphiniden-Komplexe Cp(OC)$_2$W=P(ML$_n$)*s*Mes [ML$_n$ = Cp(OC)$_3$W, Cp(OC)$_3$Fe]: Synthese über den Komplex Cp(OC)$_2$W=P(H)*s*Mes und deren photochemische Umwandlung

Die Umsetzung des in THF gelösten Phosphenium-Komplexes Cp(OC)$_2$W=P(H)*s*Mes (**1**) mit *n*-BuLi und einer äquimolaren Menge an Cp(OC)$_3$W-Br (**3**) führt zur Synthese der zweikernigen Phosphiniden-Verbindung **4** [Gl. (1)].

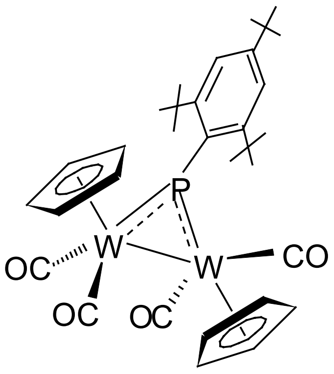


(1)

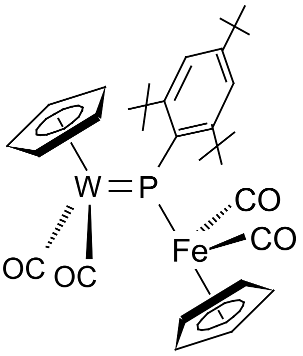
1 **4**

Die ^{31}P-NMR-Daten {[δ/^1J(PW)]: 255.2 ppm / 507.9; 94.8 Hz} stimmen mit einer Beschreibung von **4** als unsymmetrischer Phosphiniden-Komplex überein.

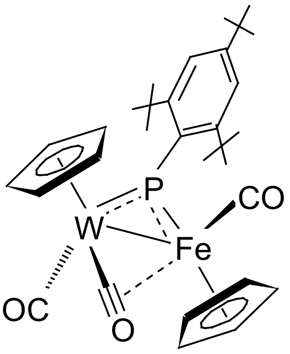
4 lässt sich durch Bestrahlung mit UV-Licht in den symmetrisch-substituierten Phosphiniden-Komplex **5** überführen, wobei neben einer Carbonyl-Eliminierung eine gleichzeitige Wolfram-Wolfram-Bindungsknüpfung stattfindet.



5



7

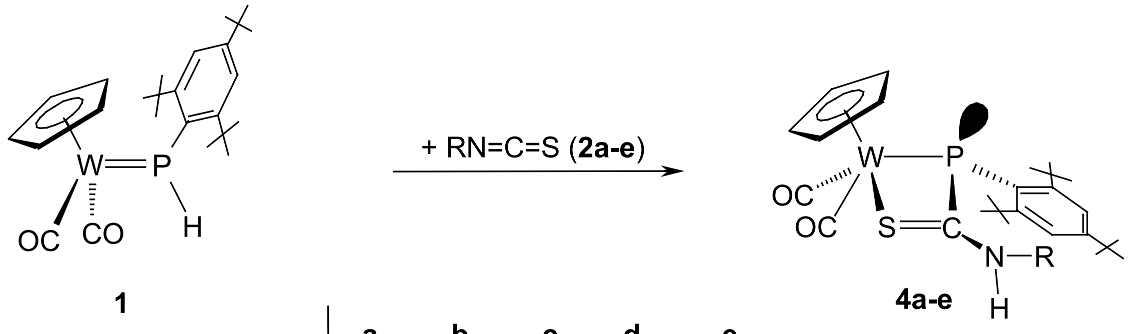


8

Die neuartige Syntheseroute entprechend Gl. (1) kann auch für die Darstellung von heteronuklearen Phosphiniden-Komplexen genutzt werden. So führt die Reaktion von **1** mit *n*-BuLi bei anschliessender Zugabe von Cp(OC)$_2$Fe-I zu dem heteronuklearen Wolfram-Eisen-Komplex **7**, der sich infolge CO-Eliminierung sowohl in Lösung als auch in Substanz in den Phosphiniden-Komplex **8** mit einem halbverbrückenden Carbonylliganden umwandelt. **4**, **5** und **8** wurden durch Röntgenbeugung charakterisiert.

Kapitel V: Cyclische Metallophosphane Cp(OC)$_2$W-P(*s*Mes)-C(NHR)S (R = Alkyl) und Cp(OC)$_2$W-P(*s*Mes)C[NH(*i*Pr)]=N(*i*Pr) durch [2+2]-Cycloaddition von Cp(OC)$_2$W=P(H)*s*Mes mit Alkylisothiocyanaten und Diisopropylcarbodiimid gefolgt von einer P→N-Wasserstoff-Wanderung

Rührt man eine 1:1-Mischung von **1** und dem enstprechenden Alkylisothiocyanat **2a-e** in Toluol bei Raumtemperatur, so erhält man die viergliedrigen Phosphametallacyclen **4a-e**, die als besonderes Merkmal ein trivalentes Phosphoratom und ein Wasserstoff-substiuiertes Stickstoffatom besitzen [Gl. (1)].



1

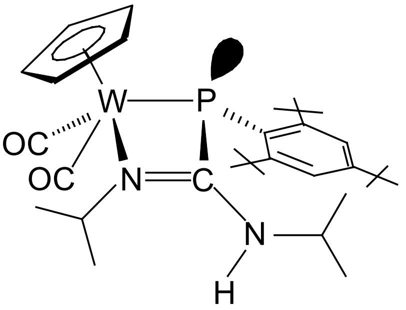
4a-e

(1)

	a	b	c	d	e
R	Me	Et	*t*Bu	Ph	CH_2CH_2Ph

Die Produktbildung erklärt sich über eine [2+2]-Cycloaddition unter Beteiligung der C=S-Doppelbindung der Isothiocyanate **2a-e** und anschliessender P→N-Wasserstoff-Wanderung. Dabei werden die Komplexe **4a-e** vollständig diastereoselektiv gebildet, wobei sich lediglich die *unlike*-Isomere (S_WR_P/R_WS_P) bezüglich der Stereochemie am Wolfram- und Phosphorzentrum bilden.

Die Reaktion von **1** mit Diisopropylcarbodiimid in Toluol bei Raumtemperatur liefert entsprechend den viergliedrigen Phosphametallacyclus **7**.

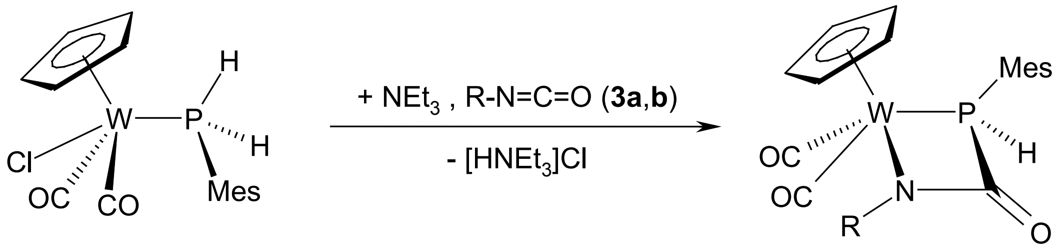


7

Die diastereoselektive Synthese von **7**, und zwar die Darstellung des *like*-Isomers bezüglich einer *trans*-Anordnung des Cp- und *s*Mes-Liganden, wird sowohl durch die NMR-Daten als auch durch die Kristallstruktur bestätigt.

Kapitel VI: [2+2]-Cycloadditionen von Phosphenium-Wolfram-Komplexen mit Alkylisocyanaten: Synthese der Cyclischen Metallophosphane $Cp(OC)_2\overline{W\text{-}P(H)(R)\text{-}(C{=}O)N}R'$ (R = *t*Bu, Mes, *s*Mes; R' = Et, Ph) und des Acylamidphosphenium-Wolfram-Komplex $Cp(OC)_2W{=}P[C({=}O)N(H)Et]$*s*Mes

Die Umsetzung einer Mischung des Mesitylphosphan-Wolfram-Komplexes $Cp(OC)_2(MesH_2P)W\text{-}Cl$ (**1**) und Ethyl- oder Phenylisocyanat (**3a,b**) mit Et_3N in Toluol bei 0° liefert die stabilen viergliedrigen Phosphametallacyclen **4a**,**b** infolge kontrolliert verlaufender [2+2]-Cycloadditon von **3a**,**b** an die W=P-Bindung des *in situ* durch Dehydrochlorierung gebildeten Komplexes $Cp(OC)_2W{=}P(H)Mes$ (**2**) [Gl. (1)].



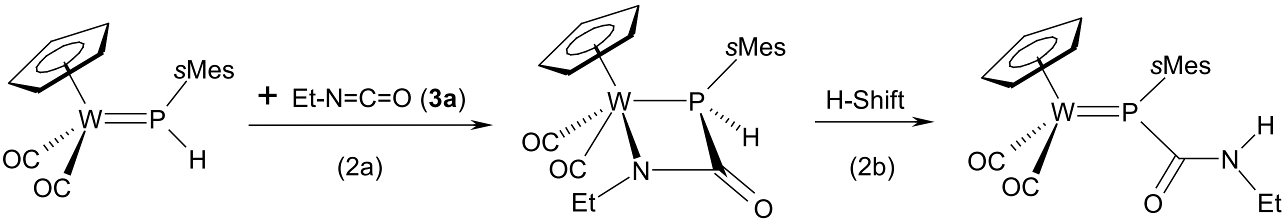
(1)

1

4	**a**	**b**
R	Et	Ph

4a,**b** werden als Diastereomerengemisch (**4a**= 65 : 35; **4b** = 69 : 31) bezüglich der *like-trans-* oder *unlike-cis*-Anordnung der Mesityl- und Cylopentadienyl-Einheit erhalten. Das Vorliegen des *like-trans*-Produktes als Hauptisomer ist durch ^{1}H-NOESY-Experimente nachgewiesen.

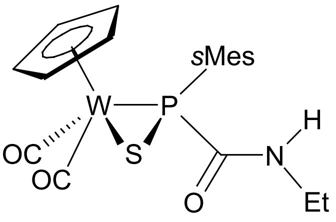
Die Reaktion von $Cp(OC)_2W{=}P(H)$*s*Mes (**5**) mit Ethylisocyanat (**3a**) führt zur diastereoselektiven Bildung des P-H-funktionalisierten [2+2]-Cycloaddukts **6** [Gl. (2a)] in Form des *like-trans*-Isomers. Die Stereochemie ist durch ^{1}H-NOESY-Spektren und eine Kristallstruktur von **6** belegt.



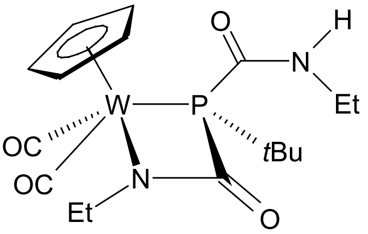
5 **6** **7**

Rührt man eine Lösung von **6** in Toluol bei Raumtemperatur, so erfolgt Umlagerung zum dem Acylamidphosphenium-Wolfram-Komplex **7** infolge einer P→N-Wasserstoff-Wanderung, die einer Insertion des Isocyanatfragmentes in die P-H-Bindung entspricht [Gl. (2b)]. Die ausschliessliche Bildung des *cis*-Isomers von **7** im festen Zustand ist durch Röntgenbeugung nachgewiesen.

Die Reaktivität der W=P-Bindung ist durch die Umwandlung von **7** mit elementarem Schwefel in den dreigliedrigen Phosphametallacyclus **8** belegt.



8



11

Versetzt man eine Mischung von $Cp(OC)_2(tBuH_2P)W\text{-}Cl$ (**9**) und Ethylisocyanat (**2a**) in Toluol bei 0 °C mit NEt_3, so bildet sich **11** infolge der [2+2]-Cycloadditon eines Äquivalentes Isocyanates an den *in situ* generierten Komplex $Cp(OC)_2W{=}P(H)tBu$ (**10**) und zusätzliche Insertion eines weiteren Mols des Heteroallens in die P-H-Bindung. Die Struktur von **11** wurde durch Röntgenbeugung bestimmt.

APPENDIX

1. Elemental Analyses

Elemental analyses were performed by the microchemical method in the laboratories of the Institut für Anorganische Chemie der Universität Würzburg.

2. NMR-spectra

The ^{1}H-, ^{13}C-, ^{31}P- and ^{29}Si-NMR-spectra were recorded on a Jeol Lambda 300, Bruker AMX 400 and Bruker AMX 500. ^{1}H-NOESY-spectra were recorded on a AMX Bruker 400.
The substances were measured as solutions (1-10 %) and chemical shifts are given in ppm. ^{1}H- and ^{13}C-NMR-spectra are referenced to the residual proton signal or natural abundance carbon signal of [D_6]-benzene at $\delta = 7.15$ ppm (^{1}H) or $\delta = 128.0$ ppm (^{13}C), respectively. ^{31}P- and ^{29}Si-NMR-spectra chemical shifts are referenced to external H_3PO_4 (^{31}P) or TMS (^{29}Si). The coupling constants are specified in Hertz. For the multiplicities, the following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quadruplet, sept = septet, m = multiplet.

3. IR-spectra

The spectra were recorded using a Perkin-Elmer 283 grating spectrometer. Samples were prepared as solutions in a NaCl cell with a length of pass of 0.1 mm and a resolution of about 2 cm^{-1}. The intensities of the bands are specified with the following abbreviations: vs = very strong, s = strong, m = medium, w = weak, br = broad.

4. Melting points

Melting points were obtained by differential thermoanalysis (Du Pont 9000 Thermal Analysis System) in the laboratories of the Institut für Anorganische Chemie der Universität Würzburg.

5. X-ray structure analyses

I would like to thank the following persons for solving and refining the molecular structures:

Dr. Dirk Schumacher:	$\mathrm{Cp(OC)_2W{=}P(Et)}s\mathrm{Mes}$
	$\mathrm{Cp(OC)_2W{=}P(}i\mathrm{Pr)}s\mathrm{Mes}$
Dipl. Chem. Andreas Sohns:	$\mathrm{Cp(OC)_2(Cl)W\text{-}P(H)_2(}s\mathrm{Mes)}$
	$\mathrm{[Cp(OC)_3W\text{-}P(H)_2(}s\mathrm{Mes)]BF_4}$
	$\mathrm{Cp(OC)_2W{=}P(H)}s\mathrm{Mes}$
	$\mathrm{Cp(OC)_2W{=}P(Me)}s\mathrm{Mes}$
	$\mathrm{Cp(OC)_2W{=}P(Bu)}s\mathrm{Mes}$
	$\mathrm{Cp(OC)_2W{=}P(CH_2Ph)}s\mathrm{Mes}$
	$\mathrm{Cp(OC)_2W{=}P(SnMe_3)}s\mathrm{Mes}$
	$\mathrm{Cp(OC)}\overline{\mathrm{W(CO)P(}s\mathrm{Mes)\text{-}F}}\mathrm{e(CO)Cp}$
	$\mathrm{Cp(OC)_2}\overline{\mathrm{W\text{-}P(}s\mathrm{Mes)\text{-}C[N(H)Et]{=}S}}$
	$\mathrm{Cp(OC)_2}\overline{\mathrm{W\text{-}P(}s\mathrm{Mes)\text{-}C[N(H)Ph]{=}S}}$
	$\mathrm{Cp(OC)_2}\overline{\mathrm{W\text{-}P(}s\mathrm{Mes)\text{-}C[NH(}i\mathrm{Pr)]{=}N}}\mathrm{(}i\mathrm{Pr)}$
	$\mathrm{Cp(OC)_2}\overline{\mathrm{W\text{-}P(H)(}s\mathrm{Mes)\text{-}C({=}O)N}}\mathrm{Et}$
	$\mathrm{Cp(OC)_2W\text{-}P[C({=}O)N(H)Et]}s\mathrm{Mes}$
	$\mathrm{Cp(OC)_2}\overline{\mathrm{W\text{-}P[(C{=}O)NHEt(}t\mathrm{Bu)\text{-}C({=}O)N}}\mathrm{Et}$
Dipl. Chem. Katharina Klüh:	$\mathrm{Cp(OC)_2W{=}P(OMe)}s\mathrm{Mes}$
	$\mathrm{Cp(OC)_2W{=}P(}s\mathrm{Mes)\text{-}W(CO)_3Cp}$
	$\mathrm{Cp(OC)_2}\overline{\mathrm{W\text{-}P(}s\mathrm{Mes)\text{-}W}}\mathrm{(CO)_2Cp}$

6. Quantum chemical calculations : All calculations were performed by Dipl. Chem. Sebastian Riedel in the research group of Prof. Dr. Martin Kaupp at the Institut für Anorganische Chemie, Universität Würzburg. Calculations were done with the Turbomole 5.6 program at the density functional level, using the hybrid B3LYP functional (based on the work of Becke), and a split-valence polarisation basis set (SVP) for the light atoms H, C and P. For tungsten we used a quasirelativistic small-core 14-valence-electron pseudopotential with a (8s7p6d)/[6s5p3d] valence basis set. All structures were fully optimized without symmetry constraints.

Danksagung

An erster Stelle danke ich meinem Chef, Herrn Prof. Dr. Wolfgang Malisch, für die Betreuung, Unterstützung und die eingeräumten Freiheiten während der Anfertigung der vorliegenden Arbeit.

Folgenden Damen und Herren danke ich für die sorgfältige Anfertigung der Analysen und Messungen: R. Schedl (CHN-Analyse und DTA), C. P. Kneis (CHN-Analyse), Dr. W. Buchner, M.-L. Schäfer und Dr. R. Bertermann (^{13}C- und ^{29}Si-NMR).

Ausserdem möchte ich mich bei allen Mitgliedern des Arbeitskreises bedanken, die durch das hervorragende Arbeitsklima und ihre immer vorhandene Hilfsbereitschaft zum Gelingen der Arbeit beigetragen haben.

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Ausserdem möchte ich mich bei den Ehemaligen Bernd „BK“ Klüpfel für seinen stets vorhandenen Einsatz („Ich mach die Tintenpatrone mal schnell sauber“), Matthias „MV“ Vögler für die gelassen ausgesprochenen Weisheiten und das Betreuen meines F-Praktikums, sowie Marco „Kreuzrunde“ Hofmann für die Adresse der Kart-Schule bedanken.

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Für seine engagierte Mitarbeit bedanke ich mich bei meinem F-Praktikanten Paul Dopf, der sich nicht abschrecken ließ und inzwischen den Weg in unseren AK gefunden hat.

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Last but not least danke ich meiner Familie, speziell meinen Eltern, ohne deren Unterstützung ich überhaupt nicht zum Abschluss dieser Arbeit gekommen wäre und natürlich meiner Freundin Constanze, die meine Stimmungen ertrug und verbesserte, meine Knie(Leidens)zeit erträglich machte und bei der ich immer wieder gerne vorbeigeschlendert bin. Danke!

Lebenslauf

Name	Rainer Schmitt
Geburtsdatum	20.09.1976
Geburtsort	Würzburg
Familienstand	ledig
Eltern	Ewald Schmitt Luzia Schmitt, geb. Reuss
1983-1986	Besuch der Grundschule in Euerdorf bzw. Nüdlingen
1986-1995	Besuch des Jack-Steinberger-Gymnasiums in Bad Kissingen
Juni 1995	Abitur
Juli 1995 - Juni 1996	Grundwehrdienst in Feldkirchen und Mellrichstadt Tätigkeit: Sanitäter
Oktober 1996	Immatrikulation an der Bayerischen Julius-Maximilians-Universität Würzburg für das Fach Chemie (Diplom)
Oktober 1998	Diplom-Vorprüfung
April/Mai 2001	Diplom-Hauptprüfung (mündlich)
Juni 2001 - März 2002	Anfertigung der Diplomarbeit bei Herrn Prof. Dr. W. Malisch am Institut für Anorganische Chemie der Universität Würzburg mit dem Thema: "Ionische Phosphiniden-Wolfram-Verbindungen über P-funktionalisierte Phosphenium-Komplexe"
März 2002 - September 2005	Anfertigung der Dissertation bei Herrn Prof. Dr. W. Malisch
Oktober 2000 -Juli 2002	Studentische Hilfskraft
August 2002 - September 2005	Wissenschaftlicher Mitarbeiter am Institut für Anorganische Chemie der Universität Würzburg

ERKLÄRUNG

Hiermit erkläre ich an Eides statt, dass ich die Dissertation "P-H-FUNCTIONALIZED PHOSPHENIUM TUNGSTEN COMPLEXES: EXCHANGE REACTIONS AT THE PHOSPHORUS AND CYCLOADDITIONS WITH HETEROALLENES" selbständig angefertigt und keine anderen 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 14.09.2005

RAINER SCHMITT