PRIMARY PHOSPHINE HALFSANDWICH COMPLEXES OF IRON AND RUTHENIUM – SYNTHESIS AND HYDROPHOSPHINATION REACTIONS

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

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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.
- Number 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
t-Bu = tert-Butyl
i-Pr = iso-Propyl
Ph = Phenyl
Mes = Mesityl
C_5H_5 = Cyclopentadienyl
MeCN = Acetonitrile
BF_4 = Tetrafluoroborate
NEt_3 = Triethylamine
dppe = 1,2-Bis(diphenylphosphino)ethane
mppe = Dimethyldiphenylphosphinoethane
DIOP = (*4R,5R*)-(–)-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane
PROPHOS = (R)-(+)-1,2-Bis(diphenylphosphino)propane
o = *ortho*
p = *para*
m = *meta*
min = minute(s)
h = hour(s)
d = day(s)

LIST OF PUBLICATIONS

1. Synthesis and Reactivity of Polychlorinated Metallo-Siloxanes.

   D. Schumacher, K. Klüh, W. Malisch, N. Söger, M. Binnewies, 2nd European Organosilicon Days (München **2003**), Abstract P 102.

2. Synthesis and Reactivity of Silanol-Functionalized Cyclopentadienyl Iron Complexes.

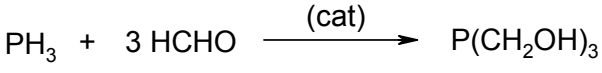
   A. Sohns, K. Klüh, W. Malisch, ISOS XIV 3rd European Silicon Days (Würzburg **2005**), Abstract P 041.

INTRODUCTION

Chiral phosphines attract increasing interest as ligands in transition metal complexes used in enantioselective synthesis and catalysis.[1,2] The Nobel Prize award for Knowles in 2001 for the enantioselective synthesis of L-Dopa catalysed by an optically pure DIPAMP-Rhodium complex indicates the importance of chiral phosphines as catalyst building blocks introducing stereochemical information.[3-5] The syntheses of chiral phosphines usually involve expensive procedures, including the use of chiral auxiliaries[6] or the separation of racemic mixtures by resolving methods.[7-9] The classical synthesis of P-chiral triorganophosphines involving a successive substitution of PX_3-compounds (X = halogen, OR) by grignard- or organolithium reagents.[10] Another approach to the formation of P-C-bonds is given by the hydrophosphination process, the addition of the P-H-function to multiple bonded organic compounds.[11]

In this context, Rauhut showed that for example the reaction of PH_3 with ethylacrylate in the presence of AIBN exhibits no chemoselectivity, resulting in a mixture of the primary, secondary and tertiary phosphines $P(H)_{2-n}[(CH_2)_2CO_2Et]_{n+1}$ (n = 0, 1, 2), as well as the side chain alkylated phosphine $P[(CH_2)_2CO_2Et]_2\{CH_2C(H)(CO_2Et)[(CH_2)_2CO_2Et]\}$.[12]

The metal-catalyzed addition of PH_3 to formaldehyde using platinum-, nickel- or cobalt halides is known since 1958.[13-15] Pringle has described the reaction of PH_3 with formaldehyde to tris(hydroxymethylene)phosphine in the presence of K_2PtCl_4 at room temperature and found that a Pt(0) complex is the catalytically active species (scheme 1).[16, 17]

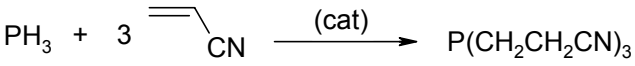


scheme 1: Addition of PH_3 on formaldehyde

Two mechanistic possibilities have been proposed. In one mechanism the phosphine undergoes an oxidative addition reaction followed by an insertion of the C=O bond into the

M-H bond finally resulting in the reductive elimination of the coordinated PH_2- and CH_2OH fragment. The other mechanism suggests, that the PH_2 ligand formed in the oxidative addition step attacks the formaldehyde as a nucleophile.[18-23]

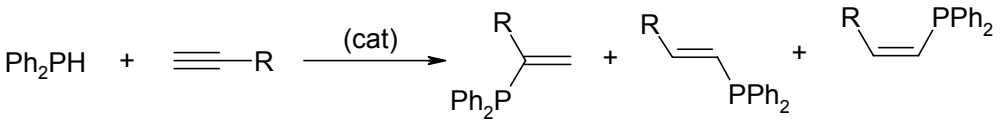
Michael reagents like acrylonitrile and ethyl acrylate are also used as insertion reagents in hydrophosphination reactions catalysed by various metal complexes.[24-28] The conversion of acrylonitrile with PH_3 in presence of $Pt[P(CH_2CH_2CN)_3]_3$ is illustrated in scheme 2.[29]



scheme 2 : Hydrophosphination reaction with acrylonitrile

Detailed mechanistic study carried out by Glueck has shown that the P-C bond formation follows the oxidative addition of the PH bond to the metal via insertion of the C=C bond into the P-M bond and reductive elimination of hydrogen and the formed phosphinoalkyl group.[30, 31] Pt(0)(MeDuphos) [MeDuphos = (R,R)-H_4C_6($\overline{PCH(Me)(CH_2)_2CH(Me)}$)$_2$] complexes catalyze asymmetric hydrophosphination excellently, but the enantioselectivity is low.[30]

The addition of the PH bond to alkynes in presence of various palladium and nickel catalysts was reported by Kazankova (scheme 3).[32-34] The selectivity of these reactions, which afford the E/Z-isomers of a anti-Markownikow addition together with α–addition product, is highly dependent on the catalyst.

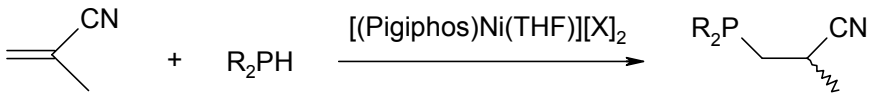


R = Ph, Pr, *t*-Bu, $MeOCH_2$, Me_2NCH_2

scheme 3: Addition of PH bond to alkynes

The synthesis affords the isolation of regioselective products, for example in the presence of the metal-catalyst $Pd(PPh_3)_4$ and $Pd_2(dba)_3$ in acetonitrile.

Enantioselective hydrophosphination could also be realized in context with the treatment of C=C double bonded system methacrylonitrile with the secondary phosphines R_2PH (R = Ph, Cy, Mes, *t*-Bu, *i*-Pr) catalysed by $[(Pigiphos)Ni(THF)][X]_2$ containing a C_1-symmetric triphosphine ligand (scheme 4).[35]



Pigiphos = $[H_5C_5FeC_5H_3(PPh_2)\overline{CH(CH_3)}]_2PC_6H_{11}$

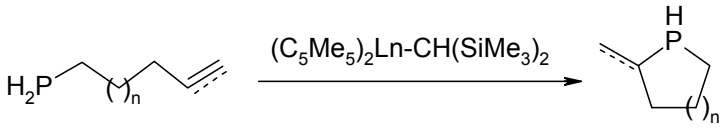
R = Ph, Mes, *t*-Bu

X = ClO_4, BF_4, BPh_4

scheme 4: Ni-catalyzed hydrophosphination reaction

The enantioselectivity in this reaction depends on the solvent, the counterion and the temperature. The best result of 89 % ee is obtained in acetone at – 25 °C using $ClO_4^{\ominus}$ as the counterion.

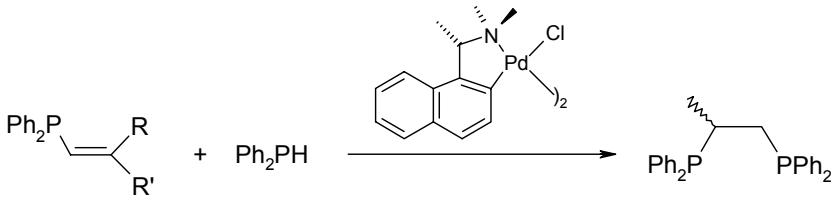
Organolanthanide-catalyzed intramolecular hydrophosphination leads to cyclic phosphines as reported by Marks (scheme 5).[36-38]



scheme 5: Lanthanide-mediated hydrophosphination

This type of hydrophosphination can also afford chiral phosphines in high enantiomeric ratio when C_1-symmetric derivates of the lanthanide catalyst of scheme 5 are used.[39]

The asymmetric hydrophosphination involving diphenylphosphine and vinylphosphines resulting in the formation of the important chiral chelatephosphine (R)- and (S)-PROPHOS has been reported by Leung (scheme 6). [40]



scheme 6: Synthesis of the chiral diphosphine PROPHOS

The catalyst used in this reaction is an organopalladium complex containing ortho-metalated (S)-(1-(dimethylamino)ethyl)naphthalene as the chiral auxiliary. The reaction of (Z)-diphenyl-1-propenylphosphine with diphenylphosphine provides (S)-PROPHOS as the major product.

In previous studies concerning the coupling reactions of metallo-phosphines with organic multiple bond systems, a preparative useful modification of this reaction with the phosphanido metal species $C_5R_5(OC)_2Fe$-P(H)R' (R = H, Me; R' = alkyl, aryl), generated as short-lived intermediates, has been used to build highly functionalized *secondary* and *tertiary* phosphines via interaction with activated alkenes, alkynes, aldehydes, ketones and quinones. In order to develop this method further, additional hydrophosphination reaction should be realized using besides the primary phosphine iron complexes the analogous ruthenium species. Moreover variation of the ligand sphere of the metal is taken into account exchanging the CO-ligands against the hemilabile ligand $Ph_2PCH_2CH_2OMe$ and achiral and chiral chelate phosphines.

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CHAPTER I:

Synthesis of Functionalized *Secondary* and *Tertiary* Phosphines via Hydrophosphination of Acrylonitrile, Ethylisocyanate or Methyl-1,3-butadiene-1-carboxylate with the *Primary* Phosphine Iron Complexes $\{R'_5C_5(OC)_2Fe\ [P(R)H_2]\}BF_4$ (R = *i*-Pr, *t*-Bu, Mes, Ph; R' = H, Me)

Abstract

Reaction of $[H_5C_5Fe(CO)_3]BF_4$ (**1**) with the *primary* phosphine *i*-$PrPH_2$ (**2**) yields the cationic *primary* phosphine iron complex $\{H_5C_5(OC)_2Fe[P(i\text{-}Pr)H_2]\}BF_4$ (**3**). Et_3N-assisted hydrophosphination of acrylonitrile (**5**) with **3** and $\{Me_5C_5(OC)_2Fe[P(R)H_2]\}BF_4$ (R = *t*-Bu, Mes) (**4a,b**) leads to the formation of the cyanethyl(alkyl/aryl)phosphine iron complexes $\{R'_5C_5(OC)_2Fe[PR(H)(CH_2)_2CN]\}BF_4$ [R = *i*-Pr, *t*-Bu, Mes; R' = H, Me] (**6a-c**). **6a** can be easily converted into the corresponding *tertiary* phosphine iron complex $\{H_5C_5(OC)_2Fe\{P(i\text{-}Pr)(CH_2CH_2CN)[C(O)NHEt]\}\}BF_4$ (**10**) by treatment with one equivalent of ethylisocyanate (**9**). The reaction of $\{H_5C_5(OC)_2Fe[P(Ph)H_2]\}BF_4$ (**4c**) with methyl-1,3-butadiene-1-carboxylate (**11**) generates the corresponding *secondary* phosphine iron complex $\{H_5C_5(OC)_2Fe[PPh(H)CH_2\ CH{=}CHCH_2CO_2Me)]\}BF_4$ (**12**). **12** can be transformed into the corresponding *tertiary* phosphine iron complexes $\{H_5C_5(OC)_2Fe[PPh(CH_2CH{=}CH\ CH_2CO_2Me)(CH_2CH_2CN)]\}BF_4$ (**13a**) and $\{H_5C_5(OC)_2Fe\{PPh(CH_2CH{=}CHCH_2CO_2Me)[C(O)NHEt]\}\}BF_4$ (**13b**) via insertion of acrylonitrile (**5**) or ethylisocyanate (**9**) into the PH-unit. The molecular structures of $\{H_5C_5(OC)_2Fe[P(i\text{-}Pr)H_2]\}BF_4$ (**3**) and $\{H_5C_5(OC)_2Fe[PPh(CH_2CH{=}CHCH_2CO_2Me)(CH_2CH_2CN)]\}BF_4$ (**13a**) are proved by x-ray analysis.

Introduction

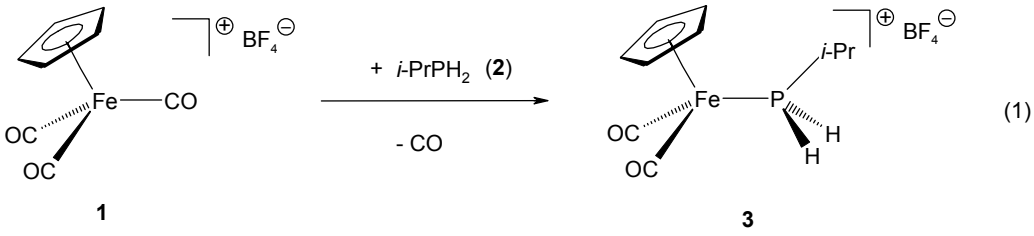
Chiral phosphines are essential ligands in catalytic reactions due to their high potential to control the stereochemical cause.[1-3] Although a considerable number of phosphine transition metal complexes have been used in enantioselective synthesis of organic substrates there is still a demand for novel type of phosphorus donors.[4, 5] One approach in synthesis involves hydrophosphination of organic double and triple bonded systems, which offers access to

highly functionalized phosphines. Advantage of this method is the activation of the PH-function by means of the metal coordination. However up to now, only few examples of controlled hydrophosphination reaction can be found in literature, since they usually result in mixtures of *secondary* and *tertiary* phosphines, when starting with *primary* phosphines.[6-9] The novel approach of hydrophosphination of transition metal coordinated *primary* phosphines allows the controlled transformation into *secondary* phosphines which show chirality at the phosphorus.[10, 11] In general the remaining second PH-function can be easily transformed by a further hydrophosphination step with the possibility of inserting a different organic multiple bond system leading to a chiral *tertiary* phosphine ligand. In total this method offers the possibility to carry out a successive build-up of highly functionalized phosphines of unknown type. In context with the studied *primary* phosphine iron complexes the alkylphosphines P(*i*-Pr)H_2 and P(*t*-Bu)H_2 as well as the arylphosphines P(Ph)H_2 and P(Mes)H_2 are preferred due to convenient preperation and handeling. In this chapter hydrophosphination reactions with iron complexes of these *primary* phosphines are studied with respect to acrylonitrile, ethylisocyanate or methyl-1,3-butadiene-1-carboxylate.

Results and Discussion

Synthesis of the Iron Complex $\{H_5C_5(OC)_2Fe[P(i\text{-}Pr)H_2]\}BF_4$ (3)

The cationic *primary* phosphine iron complex **3** used as staring material for the hydrophosphination reaction can be easily formed by thermal carbonmonoxide/phosphine exchange from the tricarbonyl cyclopentadienyl iron cation, used as the BF_4-salt **1** and isopropylphosphine **2**. The synthesis is carried out in acetonitrile at 70 °C and the isopropylphosphine iron complex **3** obtained as a yellow powder within 5 h in 89 % yield (eq. 1).



1 3 (1)

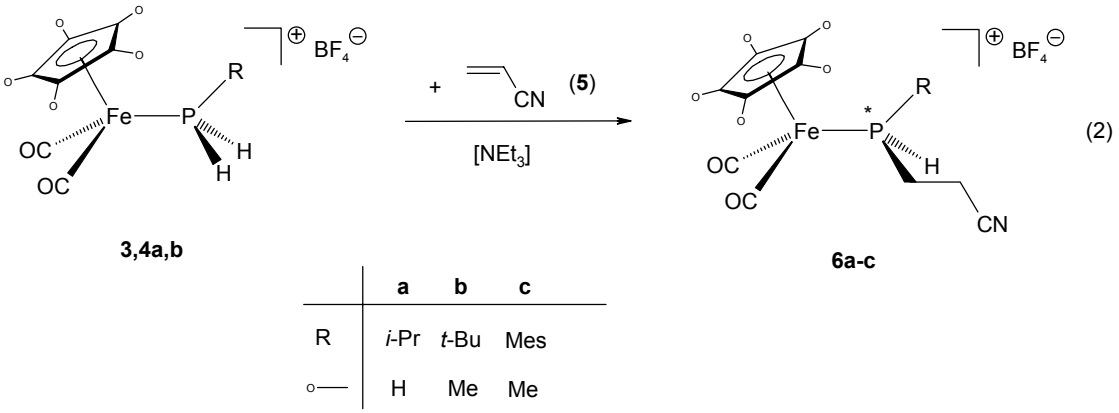
3 is soluble in polar solvents like dichloromethane and acetonitrile and can be stored for several months under an atmosphere of nitrogen at room temperature.

The ^{31}P-NMR spectrum of **3** shows a singlet signal for the phosphorus of the coordinated *primary* phosphine at – 10.45 ppm, indicating a coordination shift of 95 ppm [δ^{31}P(**3**) – δ^{31}P(**2**)].[12] The PH-resonance appears in the ^{1}H-NMR spectrum at 4.89 ppm with a ^{1}J-PH-coupling constant of 381.5 Hz characteristic for metal coordination of the *primary* phosphine **2**, which means an increase of 110 Hz with respect to the analogous coupling constant of free **2**.

Hydrophosphination of Acrylonitrile (5) with {R'$_5$C$_5$(OC)$_2$Fe[P(R)H$_2$]}BF$_4$ (R = i-Pr, t-Bu, Mes; R' = H, Me) (3,4a,b)

In addition to the isopropyl phosphine iron complex **3**, the halfsandwich *primary* phosphine iron complexes **4a,b** containing ligated *tert*-butyl- or mesitylphosphine are included in the hydrophosphination studies. **3;4a,b** react readily with acrylonitrile **5** in acetonitrile at room temperature to yield the corresponding cyanoethyl(alkyl/aryl)phosphine iron complexes **6a-c**, provided a catalytic amount of triethylamine is added. Insertion of the C=C-bond of **5** into one of the two PH-bonds of **3;4a,b** is complete after a reaction time of 1 d (**6b**, **6c**) or 2 d (**6a**) (eq. 2). Precipitation of **6a-c** as yellow fine-grained powders from solution is achieved by addition of diethylether to provide a nearly quantitative yield.

The hydrophosphination reaction of **5** leads to a chemoselective monoinsertion of the olefin leaving a PH-function for further insertion. Mentionable is in addition the stereoselectivity of the hydrophosphination which exclusively yields **6a-c** as the result of *anti*-Markownikow addition. This situation guarantees clean formation of a *secondary* phosphine ligand with a stereogenic phosphorus.



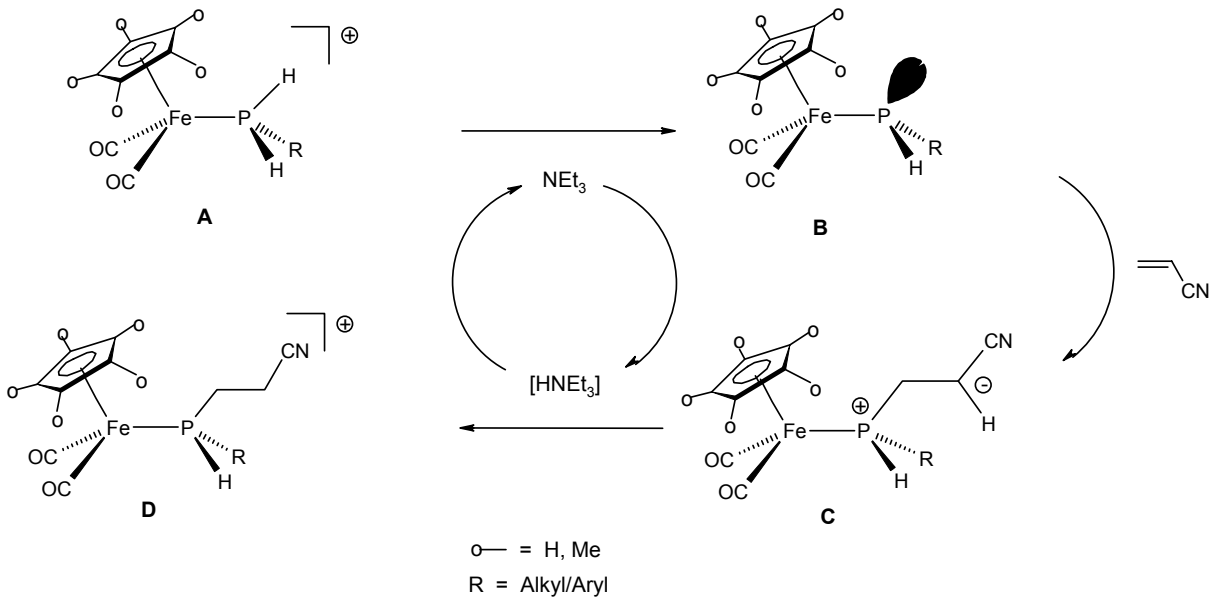
3,4a,b **6a-c**

	a	b	c
R	*i*-Pr	*t*-Bu	Mes
○—	H	Me	Me

The insertion of acrylonitrile according to eq.(2) is spectroscopically proved by the significant low-field shift of the ^{31}P-NMR- resonance from – 10.45 / – 41.40 / 25.71 for the *primary* phosphine ligand in **3;4a,b** to 35.79 / 4.18 / 59.36 for the phosphorus of the *secondary* phosphine in the complexes **6a-c**. Moreover the PH-resonances of **6a-c** appear in the ^{1}H-NMR spectra at 5.19 (**6a**), 4.41 (**6b**) and 6.09 (**6c**) with the characteristic large ^{1}J(PH)-coupling constants of 377.5 (**6a**), 347.1 (**6b**) and 371.6 Hz (**6c**).

The mechanism for the hydrophosphination of the olefin **5**, according to eq.(2), involves the formation of the *primary* ferrio-phosphine **B** as the crucial intermediate by deprotonation of the cationic complex **A** with NEt_3 in the initial step (scheme 1). **B** acts as a strong nucleophile – caused by the electron releasing property of transition metal fragment – attacking the electron defficient C-C-double bond of acrylonitrile via the trivalent phosphorus to produce the zwitterionic intermediate **C**. **C** is stabilised by protonation of carbanionic centre by the

ammoniumion $[HNEt_3]^+$ generated in the first step to form the *secondary* phosphine complex **D** with simultaneous regeneration of the amine.

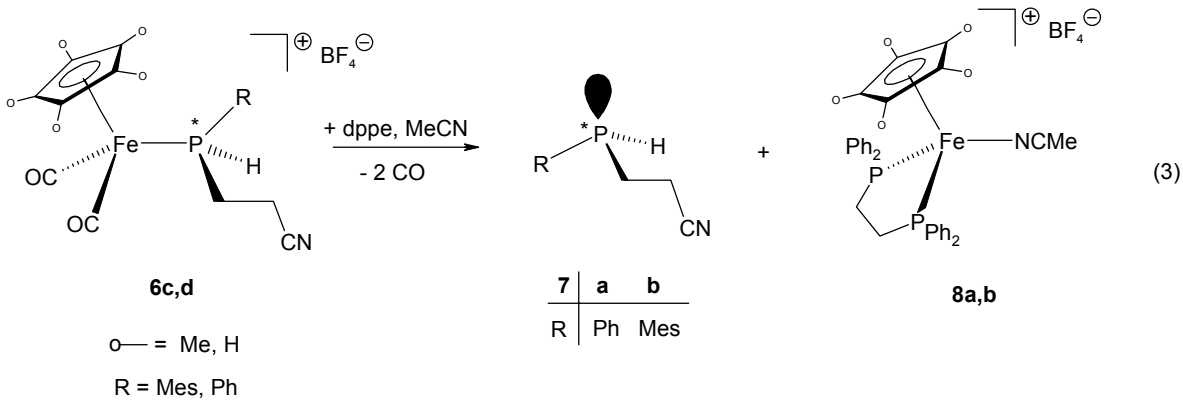


scheme 1: Mechanism of the acrylonitrile insertion

The release of the phosphine ligand from transition metal fragment can be achieved in the case of the *secondary* phosphine complexes **6c,d** by treatment with the chelating phosphine dppe in acetonitrile under ultraviolet irradiation. Under this conditions the functionalized *secondary* phosphines **7a,b** can be generated after 3 h in yields of 83-85 % together with the dppe-iron-complexes **8a,b** (eq. 3), identified by comparison with the data of authentic material.[10, 11]

The PH hydrogen of **7a,b** is found in the ^{1}H-NMR spectrum at 3.92 and 4.17 ppm with characteristic ^1J(PH)-coupling constant for *secondary* phosphines of 210 and 218 Hz. The ^{31}P-NMR spectra show a highfield singlet at – 53.86 (**7a**) and – 88.78 ppm (**7b**).

8a,b offer the possibility to substitute acetonitrile ligand with *primary* phosphines RPH_2 to generate a starting complex for an alternative hydrophosphination.



6c,d

o— = Me, H

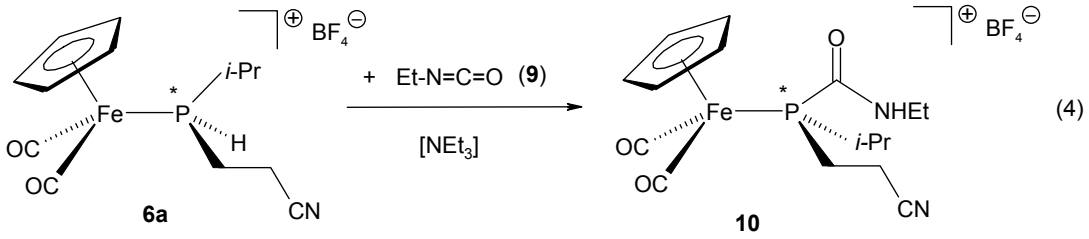
R = Mes, Ph

7	a	b
R	Ph	Mes

8a,b

Hydrophosphination of Ethylisocyanate (9) with the *Secondary* Phosphine Iron Complex {$H_5C_5(OC)_2Fe[P(i\text{-}Pr)(H)CH_2CH_2CN]$}$BF_4$ (6a)

In order to examine the possibility of a further hydrophosphination, the isopropylphosphine iron complex **6a** from eq. (2) is combined with ethylisocyanate (**9**) and Et_3N in acetonitrile and the reaction mixture stirred at room temperature for 5 d. PH-addition across the N=C double bond of the heteroallene according to the *anti*-Markownikow pattern yields the carbamoyl-phosphine complex **10**, containing phosphorus as a stereogenic centre (eq. 4). **10** is obtained as a brown powder in a yield of 74 %.



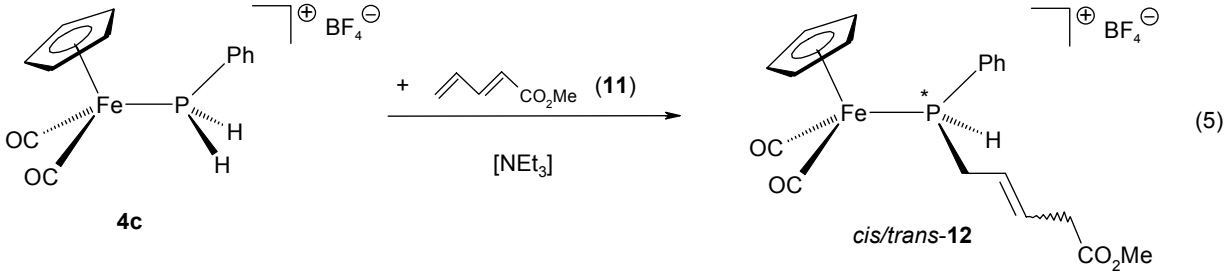
6a **10**

The ^{31}P-NMR resonance of **10** at 77.39 ppm reveals a significant shift of about 42 ppm to lower field in relation to the *secondary* phosphine complex **6a** (δ = 35.79). Chirality at phosphorus is indicated by distinct signals for the two methyl groups of the isopropylphosphine at 1.28 and 1.22 ppm with a coupling constant ^3J(PCCH) of about 1.2 Hz.

Synthesis of the *Tertiary* Phosphine Iron Complexes {$H_5C_5(OC)_2Fe$ [$PPh(CH_2CH{=}CHCH_2CO_2Me)(R)$]}$BF_4$ [R = CH_2CH_2CN, C(O)NHEt] (13a,b) via successive Hydrophosphination of Methyl-1,3-butadiene-1-carboxylate (11) and Acrylonitrile (5) or Ethylisocyanate (9) using $[H_5C_5(OC)_2FeP(Ph)H_2]BF_4$ (4c)

In a further two step hydrophosphination sequence starting with the phenylphosphine iron complex **4c** the activated olefines methyl-1,3-butadiene-1-carboxylate (**11**) and acrylonitrile (**5**) were used. In context with the reagent **11**, primarly the question must cleared up, wether 1,2- or 1,4-hydrophosphination is the preferred process.

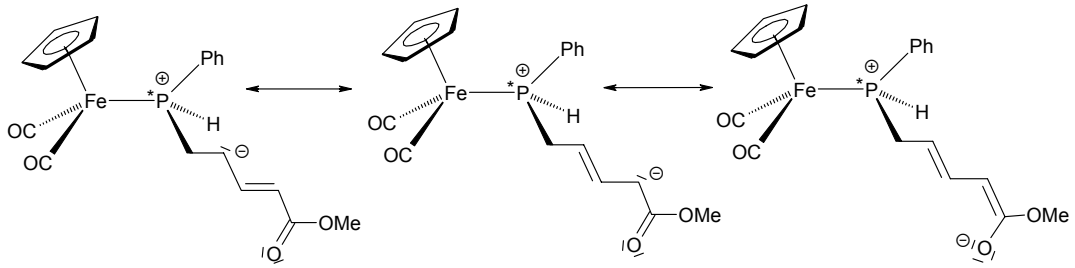
When **4c** is treated in acetonitrile at room temperature with methyl-1,3-butadiene-1-carboxylate (**11**) and catalytic amount of Et_3N after 4 d exclusively **12**, the product of a 1,4-addition is obtained in 86 % yield (eq. 5). **12** is obtained as a diastereomeric mixture with a ratio of 67 : 33 of *trans*- and *cis*- isomer.



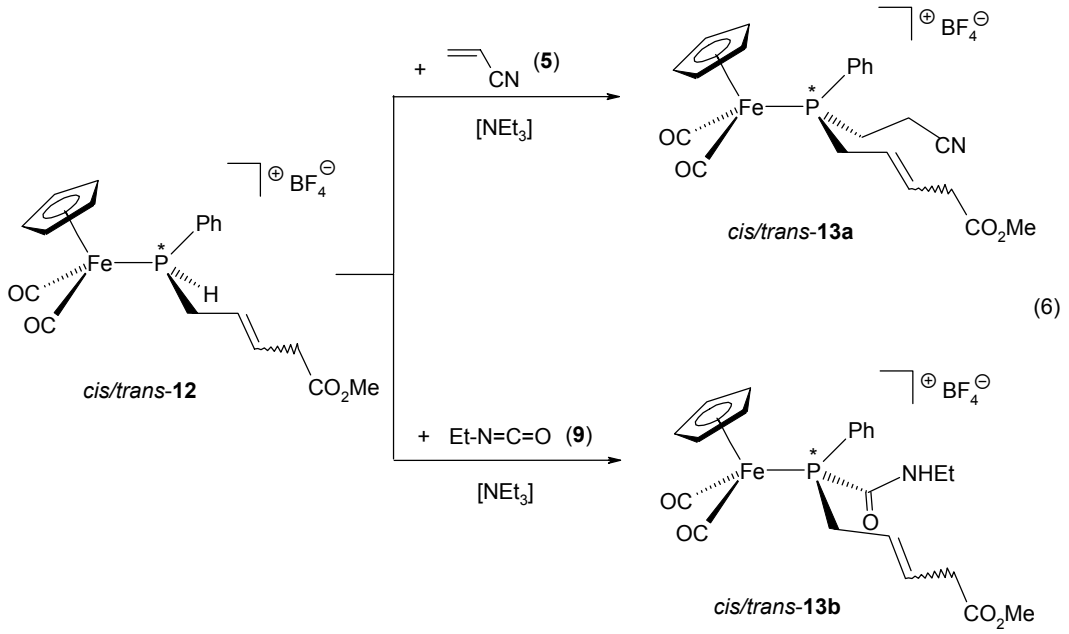
(5)

The evidence for the 1,4-addition product **12** is given by two dt-resonances at 5.68 and 5.66 for the olefinic hydrogens with the typical *cis*-, *trans*- or *geminal*-^3J(HH)-coupling constant of 12.5 (*cis*), 13.8 (*trans*) and 6.9 / 6.8 Hz (*geminal*). The ^{13}C-NMR resonance of the methylene carbon next to the carboxyl group at 37.88 / 33.08 with a ^4J(PCCCC)-coupling constants of 2.8 / 2.7 Hz is an additional prove of the proposed structure.

The observed type of P-C-coupling product is presumably strongly favoured due to the mesomeric stabilisation of the intermediate formed from the ferrio-phosphine $H_5C_5(OC)_2Fe$-P(Ph)H and the diene **11**, for which the carboxylate group is responsible. This stabilization is also possible in the case of 1,2-addition, however leading to a less favourable steric arrangement and less mesomeric structures.



Treatment of the *secondary* phosphine complex **12** with acrylonitrile **5** or ethylisocyanate **9** yields the *tertiary* phosphine complexes **13a,b** as yellow fine-grained powder in yield of 96 % after 2 h (**13a**) or 88 % after 5 h (**13b**) (eq. 6). The *trans*/*cis* ratio of 63 : 37 for **13a** and 72 : 28 for **13b** are identical to that of **12**, that means insertion into the PH bond doesn't change the original ratio.

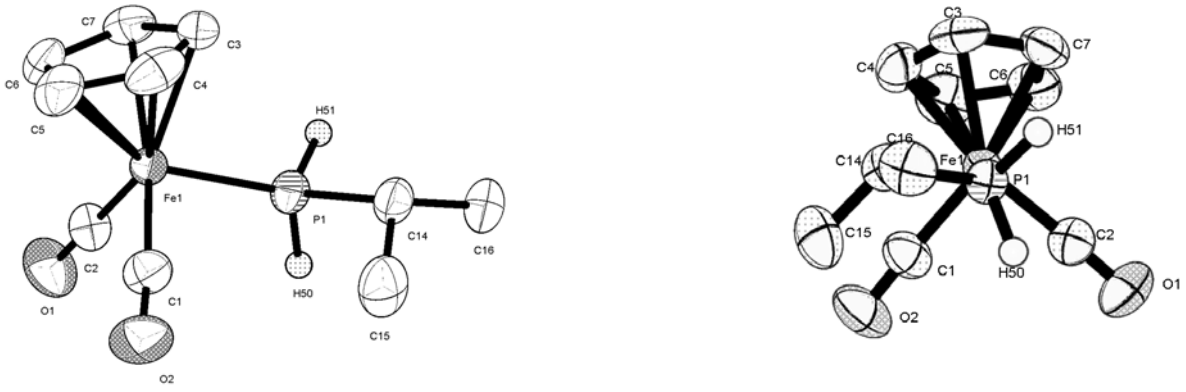


(6)

Formation of hydrophosphination products **13a,b** is supported by the significant low-field shift of the ^{31}P-NMR resonance from 29.09 (*trans*) / 28.23 (*cis*) in **12** to 55.79 / 55.00 for *trans*/*cis*-**13a** and 65.63 / 60.04 for *trans*/*cis*-**13b**.

Molecular structure of $\{H_5C_5(OC)_2Fe[P(i\text{-}Pr)H_2]\}BF_4$ (3) and $\{H_5C_5(OC)_2Fe[PhP(CH_2(CH)_2CH_2CO_2Me)(CH_2CH_2CN)]\}BF_4$ (trans-13a)

Suitable crystal for the structure determination of **3** could be obtained from a saturated acetonitrile solution at room temperature.



a.) b.)

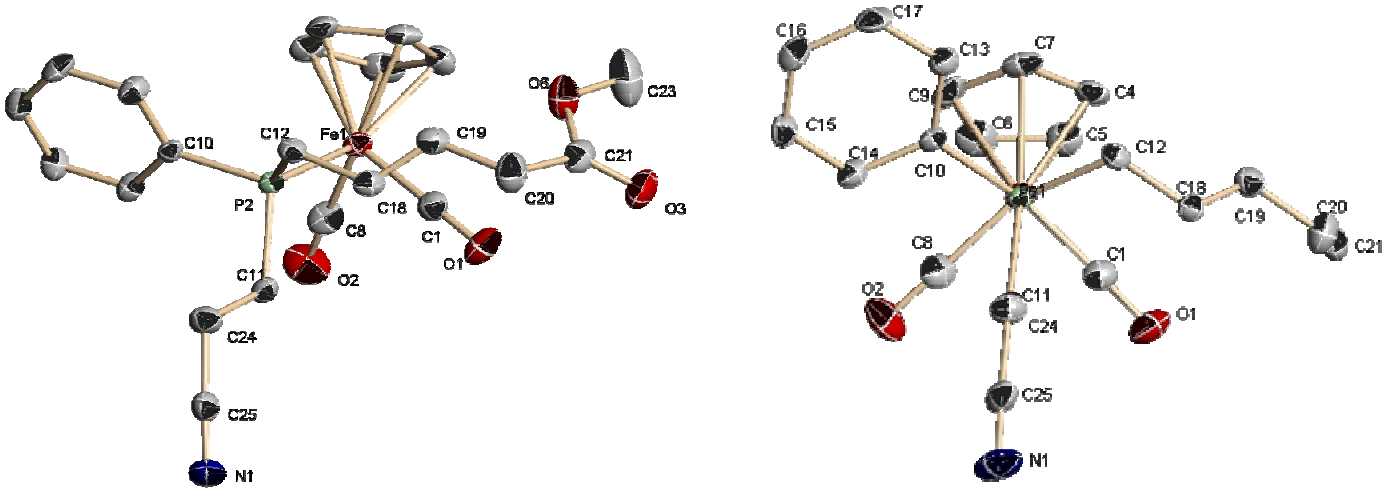
figure 2: *Molecular structure (a) and Newman projection (View along the Fe1-P1-axis) (b) of $\{H_5C_5(OC)_2Fe[P(i\text{-}Pr)H_2]\}BF_4$ (**3**). The BF_4-anion and hydrogen atoms except P-H have been omitted for clarity.*

Selected bond lengths [pm], bond and torsion angles[°]: Fe1-P1 219.42(11), P1-C14 183.2(4), Fe1-C2 177.6(4), Fe1-C1 177.8(4), C2-O1 112.9(5); C2-Fe1-C1 89.97(19), C2-Fe1-P1 92.97(13), C1-Fe1-P1 94.67(13), Fe1-P1-C14 119.69(13), C16-C14-C15 112.5(3), H51-P1-Fe1 116.2(18), H50-P1-Fe1 116.2(19) H51-P1-C14 101.5(18), H50-P1-C14 101.3(18); Cp_z-Fe1-P1-C14 75.9.

The asymmetric unit in complex **3** (fig. 2) contains two molecules, which differ only slightly in their bonding parameters. **3** shows a pseudooctahedral coordination of the iron ligands comprised by the cyclopentadienyl unit, the two carbonmonoxides and the *primary* phosphine ligand. In accordance the angles of the three-legged piano-stool molecule are close to 90° [C2-Fe1-C1 89.97(19)°, C2-Fe1-P1 92.97(13)°, C1-Fe1-P1 94.67(13)°]. The Fe1-P1 distance

of 219.42(11) pm in **3** lies in the range of literature known compounds [{Cp*$(OC)_2$Fe$(PMesH_2)$}BF_4: 221.75 pm, {Cp$(OC)_2$Fe[$P(Ph)_2C(CO_2Me)$=C(H)CO_2Me}BF_4: 223.34(10) pm]. [10, 13] The phosphorus atom in **3** exhibit a distorted tetrahedral coordination with the largest bond angles including the metal fragment [Fe1-P1-C14 119.69(13)°, H51-P1-Fe1 116.2(18)°, H50-P1-Fe1 116.2(19)°] and the smallest angles between the P-hydrogens and the *secondary* isopropyl carbon [H51-P1-C14 101.5(18)°, H50-P1-C14 101.3(18)°]. The isopropyl unit adopts the *gauche*-position with respect to the Cp-ligand [Cp_z-Fe1-P1-C14 75.9°], which is shown by the *newman* projection (fig. 2b).

Suitable crystal for the structure determination of *trans*-**13a** could be obtained from a saturated acetonitrile solution at room temperature.



a.) b.)

figure 3: *Molecular structure (a) and Newman projection (View along the Fe1-P2-axis) of {$H_5C_5(OC)_2$Fe[PhP(CH_2($CH)_2CH_2CO_2$Me)(CH_2CH_2CN)]}BF_4 (trans-**13a**). The BF_4-anion and hydrogen atoms have been omitted for clarity.*

Selected bonds [pm], bond and torsion angles [°]:Fe(1)-C(8) 176.9(6), Fe(1)-C(1) 178.5(5), Fe(1)-P(2) 222.18(14), O(1)-C(1) 114.1(6), P(2)-C(11) 183.0(5), P(2)-C(12) 183.7(5), C(18)-C(19) 130.9(7); C(8)-Fe(1)-C(1) 92.9(2), C(1)-Fe(1)-P(2) 92.55(17), C(8)-Fe(1)-P(2) 92.07(17), C(10)-P(2)-Fe(1) 113.35(15), C(11)-P(2)-Fe(1) 111.6(7), C(12)-P(2)-Fe(1)

115.69(16), C(11)-P(2)-C(12) 104.7(2), C(10)-P(2)-C(11) 104.4(2), C(10)-P(2)-C(12) 106.0(2); C(8)-Fe(1)-P(2)-C(10) -76.2(2), C(1)-Fe(1)-P(2)-C(10) -169.1(2), C(19)-C(18)-C(12) 123.5(5), C(18)-C(19)-C(20) 124.7(5), C(8)-Fe(1)-P(2)-C(11) 41.4(2), C(1)-Fe(1)-P(2)-C(11) -51.5(2), C(8)-Fe(1)-P(2)-C(12) 161.1(2), C(1)-Fe(1)-P(2)-C(12) 68.1(2), C(12)-C(18)-C(19)-C(20) -177.7(5), Cp_Z-Fe(1)-P(2)-C(12) – 65.8°, Cp_Z-Fe(1)-P(2)-C(10) 57.0°, Cp_Z-Fe(1)-P(2)-C(11) 174.5°.

13a shows a pseudooctahedral coordination of the iron ligands including the cyclopentadienyl unit, two carbonmonoxide ligands and the *tertiary* phosphine. In accordance the angles of the three-legged piano-stool molecule are close to 90° [C(8)-Fe(1)-C(1) 92.9(2)°, C(1)-Fe(1)-P(2) 92.55(17)°, C(8)-Fe(1)-P(2) 92.07(17)°]. The Fe(1)-P(2) distance of 222.18(14) pm is in accordance with literature known values $[H_5C_5\{1,2\text{-}C_6H_4(PMePh)_2\}FePHMePh]PF_6$: 217.6 pm, 218.3 pm , 217.5 pm].[14] The phosphorus atom in **13a** exhibit a distorted tetrahedral coordination with the largest bond angles including the metal fragment [C(10)-P(2)-Fe(1) 113.35(15)°, C(11)-P(2)-Fe(1) 111.6(7)°, C(12)-P(2)-Fe(1) 115.69(16)°, C(11)-P(2)-C(12) 104.7(2)°, C(10)-P(2)-C(11) 104.4(2)°, C(10)-P(2)-C(12) 106.0(2)°]. The torsion angle C12-C18-C19-C20 [-177.7(5)°] proves almost planarity of the sp^2-hybridized carbon atoms at the butenyl double bond. The bond length C18-C19 with 130.9 pm shows an almost identical value to that of double bonds in comparable complexes, for example $C_5Me_4CH_2CH\text{-}C(CH{=}CHCO_2Me){=}C(CO_2Me)O\text{-}P(=C(SiMe_3)_2]Fe(CO)_2$ (135.6(4) pm, 134.3(4) pm).[15] The *trans*-configuration of the double bond is proved by the angles C(19)-C(18)-C(12) 123.5(5)° and C(18)-C(19)-C(20) 124.7(5)°. The *Newman*-projection with respect to the P2-Fe1-bond reveals a *gauche*-arrangement of the phenyl and the butenyl ligand, indicated by the torsion angles [Cp_Z-Fe(1)-P(2)-C(12) – 65.8°, Cp_Z-Fe(1)-P(2)-C(10) 57.0°]. The cyanoethyl-ligand bisects the angle of the $(OC)_2Fe$ fragment indicated by Cp_Z-Fe(1)-P(2)-C(11) of 174.5°.

Experimental Section

General: All manipulations were performed under purified nitrogen using standard Schlenk techniques. Solvents were rigorously dried over an appropiate drying agent and distilled under nitrogen prior to use. ^{1}H-, ^{13}C-, ^{31}P- and ^{19}F-NMR spectra were obtained on a Bruker AMX 500, a Bruker AMX 400 and a Jeol JNM-LA300 spectrometer. Infrared spectra were recorded in solution on a Bruker IFS 25 grating spectrometer in NaCl cells with 0.1 mm path lengths. Melting points were determined by Differential Thermo Analysis (DTA) with the Du Pont Thermal Analysis System 9000. Elemental analyses were performed in the laboratories of the "Institut für Anorganische Chemie". – Starting materials: $[H_5C_5(OC)_3Fe]BF_4$,[10,16] $\{H_5C_5(OC)_2Fe[P(Ph)H_2]\}BF_4$,[10,11] $\{Me_5C_5(OC)_2Fe[P(t\text{-}Bu)H_2]\}BF_4$[10,11] and $\{Me_5C_5(OC)_2Fe[P(Mes)H_2]\}BF_4$[10,11] were synthesized according to the literature procedure. The insertion reagents $H_2C{=}CHCN$, EtNCO and $H_2C{=}CHCH{=}CHCO_2CH_3$ were obtained commercially.

*1. [Dicarbonyl(η^5-cyclopentadienyl)(isopropylphosphine)iron(II)]tetrafluoroborate(**3**)*

To a solution of 2.78 g (9.53 mmol) $[H_5C_5(OC)_3Fe]BF_4$ (**1**) in 30 ml acetonitrile 392 mg (11.5 mmol) of P(*i*-Pr)H_2 (**2**) are added. The reaction mixture is stirred for 48 h at 60°C and then reduced in vacuum to a volume of 3 ml. Addition of 15 ml of diethylether leads to the precipitation of **3**, which is separated by filtration, washed three times with 5 ml of diethylether and dried in vacuum. - Yield 2.87 g (89%). - Yellow microcrystalline powder. - M.p. 85°C (dec.). – $C_{10}H_{14}BF_4FeO_2P$ (339.84). calc.: C 35.34, H 4.15. found: C 34.99, H 4.11. - **^{1}H-NMR** (CD_3CN, 300.4 MHz): δ = 5.41 [d, ^{3}J(PFeCH) = 2.4 Hz, 5 H, H_5C_5], 4.89 [dd, ^{1}J(PH) = 381.5 Hz, ^{3}J(HCPH) = 6.0 Hz, 2 H, PH], 2.27 (dseptt, ^{2}J(PCH) = 21.3 Hz, ^{3}J(HCCH) = 6.9 Hz, ^{3}J(HCPH) = 1.2 Hz, 1 H, $\underline{H}C(CH_3)_2$], 1.31 ppm [dd, ^{3}J(PCCH) = 19.8 Hz, ^{3}J(HCCH) = 6.9 Hz, 6 H, $(\underline{H}_3C)_2CH$]. - **^{13}C-{^{1}H}-NMR** (CD_3CN, 75.45 MHz): δ = 209.52 [d, ^{2}J(PFeC) = 24.1 Hz, CO], 88.24 [d, ^{2}J(PFeC) = 1.1 Hz, C_5H_5], 24.58 [d, ^{1}J(PC) = 32.7 Hz, $\underline{C}H(CH_3)_2$], 21.79 ppm [d, ^{2}J(PCC) = 2.4 Hz, $(\underline{C}H_3)_2CH$]. - **^{31}P-{^{1}H}-NMR** (CD_3CN,

121.5 MHz): δ = -10.45 ppm (s). - **IR** (CH_3CN): ν (PH) = 2307 (w), ν (CO_{sym}) = 2064 (vs), ν (CO_{asym}) = 2017 (vs) cm^{-1}.

*2. {Dicarbonyl[(2-cyanoethyl)isopropylphosphine](η^5-cyclopentadienyl)iron(II)}tetrafluoro-borate (**6a**)*

To a solution of 400 mg (1.18 mmol) $\{H_5C_5(OC)_2Fe[P(i\text{-}Pr)H_2]\}BF_4$ (**3**) and 62 mg (1.18 mmol) acrylonitrile (**5**) in 30 ml acetonitrile 5 mg (0.05 mmol, 0.03 ml) NEt_3 are added. The reaction mixture is stirred for 2 d at ambient temperature and then reduced in vacuum to a volume of 3 ml. **6a** is precipitated by addition of 20 ml of diethylether, separated by filtration, washed three times with 5 ml of diethylether and dried in vacuum. - Yield 443 mg (96%). - Yellow microcrystalline powder. - M.p. 49°C (dec.). - $C_{13}H_{17}BF_4FeNO_2P$ (392.91). calc.: C 39.74; H 4.36; N 3.56. found: C 39.35; H 4.33; N 3.63. - **^{1}H-NMR** (CD_3CN, 300.4 MHz): δ = 5.44 [d, ^3J(PFeCH)= 1.8 Hz, 5 H, H_5C_5], 5.19 [ddt, ^1J(PH) = 377.5 Hz, ^3J(HCPH) = 6.3 Hz, ^3J(HCPH) = 4.2 Hz, 1 H, HP], 2.79 - 2.47 (m, 4 H, H_2C, H_2C), 2.28 - 2.19 [m, 1 H, $\underline{H}C(CH_3)_2$], 1.26 [dd, ^3J(PCCH) = 19.1 Hz, ^3J(HCCH) = 7.4 Hz, 3 H, H_3C], 1.23 ppm [dd, ^3J(PCCH) = 19.5 Hz, ^3J(HCCH) = 7.2 Hz, 3 H, H_3C]. - **^{13}C-{^{1}H}-NMR** (CD_3CN, 75.45 MHz): δ = 209.77 [d, ^2J(PFeC) = 23.1 Hz, CO], 209.71 [d, ^2J(PFeC) = 23.5 Hz, CO], 119.41 [d, ^3J(PCCC) = 13.1 Hz, CN], 88.31 (s, br, C_5H_5), 26.95 [d, ^1J(PC) = 30.3 Hz, PCH_2], 21.38 [d, ^1J(PC) = 27.9 Hz, $\underline{C}H(CH_3)_2$], 19.55 (s, $HC(\underline{C}H_3)_2$), 19.49 [d, ^2J(PCC) = 0.7 Hz, $HC(\underline{C}H_3)_2$], 15.69 ppm [d, ^2J(PCC) = 4.2 Hz, CH_2CN]. - **^{31}P-{^{1}H}-NMR** (CD_3CN, 121.5 MHz): δ = 35.79 ppm (s). - **IR** (CH_3CN): ν (PH) = 2316 (w), ν (CO_{sym}) = 2059 (vs), ν(CO_{asym}) = 2016 (vs) cm^{-1}.

*3. {Dicarbonyl[(2-cyanoethyl)tertbutylphosphine](η^5-pentamethylcyclopentadienyl)iron(II)} tetrafluoroborate (**6b**)*

Analogous to **6a** from 400 mg (0.94 mmol) of {$Me_5C_5(OC)_2Fe[P(t\text{-}Bu)H_2]$}$BF_4$ (**4a**), 50 mg (0.94 mmol) acrylonitrile (**5**) and 5 mg (0.05 mmol, 0.03 ml) NEt_3 in 25 ml of acetonitrile after 1 d. – Yield: 420 mg (93 %). - Orange microcrystalline powder. – M.p. 115 °C. - $C_{19}H_{29}BF_4FeNO_2P$ (477.07). calc.: C 47.84; H 6.13; N 2.94. found: C 47.16; H 6.05; N 3.02. - **^{1}H-NMR** (CD_3CN, 300.4 MHz): δ = 4.41 [ddd, ^1J(PH) = 347.1 Hz, $^3J(H_aCPH)$ = 7.3 Hz, $^3J(H_bCPH)$ = 3.9 Hz, 1 H, HP], 2.75 - 2.59 (m, 2 H, $\underline{H_2}CH_2CCN$), 2.14 - 2.04 (m, 2 H, $\underline{H_2}CCN$), 1.89 [d, ^4J(PFeCCH) = 1.5 Hz, 15 H, $(H_3C)_5\underline{C_5}$], 1.24 ppm [d, ^3J(PCCH) = 16.9 Hz, 9 H, $(H_3C)_3\underline{C}$]. - **^{13}C{^{1}H}-NMR** (CD_3CN, 75.45 MHz): δ = 214.10 [d, ^2J(PFeC) = 18.6 Hz, CO], 212.28 [d, ^2J(PFeC) = 20.0 Hz, CO], 119.55 [d, ^3J(PCCC) = 12.8 Hz, CN] 101.39 (s, br, $\underline{C_5}Me_5$), 33.82 [d, ^1J(PC) = 28.9 Hz, $\underline{C}(CH_3)_3$], 28.12 [d, ^2J(PCC) = 3.5 Hz, $C(\underline{C}H_3)_3$], 21.00 [d, ^1J(PC) = 25.9 Hz, $\underline{C}H_2CH_2CN$], 15.99 [d, ^2J(PCC) = 3.1 Hz, $CH_2\underline{C}H_2CN$], 9.96 ppm [d, ^3J(PFeCC) = 1.1 Hz, $C_5(\underline{C}H_3)_5$]. - **^{31}P{^{1}H}-NMR** (CD_3CN, 121.5 MHz): δ = 59.36 ppm (s). - **IR** (CH_3CN): ν(PH) = 2342(w), ν (CN) = 2279 (s), ν(CO_{sym}) = 2035 (vs), ν(CO_{asym}) = 1992 (vs) cm^{-1}.

*4. {Dicarbonyl[(2-cyanoethyl)mesitylphosphine](η^5-pentamethylcyclopentadienyl)iron(II)} tetrafluoroborate (**6c**)*

Analogous to **6a** from 400 mg (0.82 mmol) of {$Me_5C_5(OC)_2Fe[P(Mes)H_2]$}$BF_4$ (**4b**), 43 mg (0.82 mmol) acrylonitrile (**5**) and 5 mg (0.05 mmol) NEt_3 in 20 ml of acetonitrile after 2 d. - Yield 423 mg (95 %). - Orange microcrystalline powder. - M.p. 94 °C. – $C_{24}H_{31}BF_4FeNO_2P$ (539.14). calc.: C 53.47, H 5.80, N 2.60. found: C 53.66, H 5.91, N 2.73. - **^{1}H-NMR** (CD_3CN, 300.4 MHz): δ = 7.09 (s, 1 H, *m*-H), 7.04 (s, 1 H, *m*-H), 6.09 [ddd, ^1J(PH) = 371.6 Hz, $^3J(H_aCPH)$ = 12.1 Hz, $^3J(H_bCPH)$ = 11.7 Hz, 1 H, HP], 2.53 - 2.16 (m, 4 H, H_2C, H_2C), 2.46

(s, 3 H, *o*-H_3C), 2.37 (s, 3 H, *o*-H_3C), 2.29 (s, 3 H, *p*-H_3C), 1.88 ppm [s, 15 H, $(H_3C)_5C_5$]. - **$^{13}C\{^1H\}$-NMR** (CD_3CN, 75.45 MHz): δ = 213.42 [d, ^2J(PFeC) = 20.9 Hz, CO], 211.63 [d, ^2J(PFeC) = 20.7 Hz, CO], 143.78 [d, ^4J(PCCCC) = 2.8 Hz, *p*-C], 142.73 [d, ^2J(PCC) = 11.7 Hz, *o*-C], 142.21 [d, ^2J(PCC) = 5.6 Hz, *o*-C], 132.07 [d, ^3J(PCCC) = 9.3 Hz, *m*-C], 131.60 [d, ^3J(PCCC) = 7.9 Hz, *m*-C], 120.19 [d, ^1J(PC) = 49.6 Hz, i-C], 101.13 (s, br, $\underline{C}_5Me_5$), 23.87 [d, ^3J(PCCC) = 7.2 Hz, *o*-CH_3], 23.31 [d, ^1J(PC) = 26.9 Hz, PCH_2], 22.50 [d, ^3J(PCCC) = 7.2 Hz, *o*-CH_3], 21.05 [d, ^5J(PCCCCC) = 1.4 Hz, *p*-CH_3], 16.42 [d, ^2J(PCC) = 8.7 Hz, $\underline{C}H_2CN$], 9.75 ppm [d, ^3J(PFeCC) = 1.1 Hz, $C_5(\underline{C}H_3)_5$]. CN-signal is hidden under CN-signal of CD_3CN. - **$^{31}P\{^1H\}$-NMR** (CD_3CN, 121.5 MHz): δ = 4.18 ppm (s). - **IR** (CH_3CN): ν (PH) = 2325 (m), ν (CN) = 2272 (s), ν (CO_{sym}) = 2039 (vs), ν (CO_{asym}) = 1994 (vs) cm^{-1}.

*5. (2-Cyanoethyl)phenylphosphine (**7a**)*

To a solution of 400 mg (0.937 mmol) of **6c** in 20 ml acetonitrile 373 mg (0.937 mmol) of dppe are added and the reaction mixture is irradiated under stirring for 2 h at room temperature. After removal of all volatiles in vacuum, the remaining residue is extracted four times with each 20 ml diethylether. The diethylether is removed, whereby pure **7a** remains. - Yield 127 mg (83%). – Orange oil. – The phosphine **7a** is literature known,[17-19] but is characterised completely for the first time. – $C_9H_{10}NP$ (163.16). calc.: C 66.25, H 6.18, N 8.58. found: C 65.57, H 6.85, N 7.92. -**^{1}H-NMR** (C_6D_6, 300.4 MHz): δ = 7.16 - 6.99 (m, 5 H, H_5C_6), 3.92 [ddd, ^1J(PH) = 210.0 Hz, ^3J(HCPH) = 8.6 Hz, ^3J(HCPH) = 5.5 Hz, 1 H, HP], 1.62 - 1.39 (m, 2 H, H_2C),], 1.38 - 1.20 ppm (m, 2 H, H_2C).- **$^{13}C\{^1H\}$-NMR** (C_6D_6, 75.45 MHz): δ = 133.89 [d, ^2J(PCC) = 15.5 Hz, *o*-C], 133.32 [d, ^1J(PC) = 11.4 Hz, *i*-C], 128.88 [d, ^3J(PCCC) = 5.8 Hz, *m*-C], 128.78 (s, *p*-C), 118.81 [d, ^3J(PCCC) = 6.3 Hz, CN], 19.21 [d, ^1J(PC) = 18.3 Hz, PCH_2], 15.77 ppm [d, ^2J(PCC) = 6.9 Hz, $\underline{C}H_2CN$]. - **$^{31}P\{^1H\}$-NMR** (C_6D_6, 121.5 MHz): δ = -53.86 ppm (s).

*6. (2-Cyanoethyl)mesitylphosphine (**7b**)*

Analogous to **7a** from 515 mg (9.55 mmol) of **6d** and 380 mg (9.55 mmol) of dppe in 20 ml acetonitrile after 2 h irradiation. – Yield 152 mg (78%). – Orange oil. – $C_{12}H_{16}NP$ (205.24). calc.: C 70.23, H 7.86, N 6.82. found: C 69.94, H 7.71, N 6.86. - **^{1}H-NMR** (C_6D_6, 300.4 MHz): δ = 6.67 (s, br, 2 H, *m*-H), 4.17 [ddd, ^{1}J(PH) = 217.8 Hz, ^{3}J(H_aCPH) = 8.8 Hz, ^{3}J(H_bCPH) = 8.4 Hz, 1 H, HP], 2.21 (s, 6 H, *o*-CH_3), 2.06 (s, 3 H, *p*-CH_3), 1.63 - 1.21 ppm (m, 4 H, H_2C). - **^{13}C{^{1}H}-NMR** (C_6D_6, 75.45 MHz): δ = 141.81 [d, ^{2}J(PCC) = 12.1 Hz, *o*-C], 138.43 (s, *p*-C), 129.48 [d, ^{3}J(PCCC) = 3.1 Hz, *m*-C], 127.84 [d, ^{1}J(PC) = 14.8 Hz, *i*-C], 119.25 [d, ^{3}J(PCCC) = 5.9 Hz, CN], 22.92 [d, ^{3}J(PCCC) = 10.7 Hz, *o*-CH_3], 20.94 (s, *p*-CH_3), 17.49 [d, ^{1}J(PC) = 18.9 Hz, PCH_2], 15.89 ppm [d, ^{2}J(PCC) = 7.9 Hz, $\underline{C}H_2CN$]. - **^{31}P{^{1}H}-NMR** (C_6D_6, 121.5 MHz): δ = -88.78 ppm (s).

*7. {Dicarbonyl[(2-cyanoethyl)(N-ethylformamido)isopropylphosphine](η^5-cyclopenta-dienyl)iron(II)}tetrafluoroborate (**10**)*

A solution of 200 mg (0.51 mmol) of $\{H_5C_5(OC)_2Fe[P$*i*$-Pr(H)CH_2CH_2CN]\}BF_4$ (**6a**) and 36 mg (0.51 mmol) ethylisocyanate (**9**) in 20 ml acetonitrile were combined with 5 mg (0.05 mmol, 0.03 ml) of NEt_3. The reaction mixture is stirred for 4 d at ambient temperature and then reduced in vacuum to a volume of 3 ml. **10** is precipitated by addition of 10 ml of diethylether, separated by filtration, washed three times with 5 ml of diethylether and dried in vacuum. - Yield 175 mg (74 %). - Brown microcrystalline powder. – M.p. 39 °C (dec.). – $C_{16}H_{22}BF_4FeN_2O_3P$ (463.99) – calc.: C 41.42; H 4.78; N 6.04. found: C 40.66; H 4.96; N 5.64. – **^{1}H-NMR** (CD_3CN, 300.4 MHz): δ = 7.26 (s, 1 H, NH), 5.42 [d, ^{3}J(PFeCH)= 1.4 Hz, H_5C_5], 3.42 [dsept, ^{2}J(PCH) = 14.8 Hz, ^{3}J(HCCH) = 7.3 Hz, 1 H, $\underline{H}C(CH_3)_2$], 2.75 - 2.39 (m, 4 H, H_2C, H_2C), 2.53 [q, ^{3}J(HCCH) = 7.1 Hz, 2 H, NH($C\underline{H}_2CH_3$), 1.28 [dd, ^{3}J(HCCH) = 7.0 Hz, ^{3}J(PCCH) = 0.7 Hz, 3 H, $(\underline{H}_3C)_2CH$], 1.22 [dd, ^{3}J(HCCH) = 7.2 Hz, ^{3}J(PCCH) = 1.8 Hz, 3 H, $(\underline{H}_3C)_2CH$], 1.15 ppm [t, ^{3}J(HCCH) = 7.1 Hz, 3 H, NH($CH_2C\underline{H}_3$). - **^{13}C-{^{1}H}-NMR**

(CD_3CN, 75.45 MHz): δ = 209.66 [d, ^2J(PFeC) = 22.7 Hz, CO], 209.64 [d, ^2J(PFeC) = 22.0 Hz, CO], 168.26 [d, ^1J(PC) = 53.4 Hz, PC(=O)], 119.37 [d, ^3J(PCCC) = 16.2 Hz, CN], 88.29 (s, C_5H_5), 36.66 [d, ^3J(PCNC) = 2.4 Hz, N$\underline{C}H_2CH_3$], 30.83 [d, ^1J(PC) = 22.4 Hz, PCH_2], 23.08 [d, ^1J(PC) = 21.4 Hz, $\underline{C}H(CH_3)_2$], 18.84 [d, ^2J(PCC) = 1.4 Hz, $CH(\underline{C}H_3)_2$], 18.53 (s, $CH(\underline{C}H_3)_2$) 14.32 [d, ^2J(PCC) = 1.1 Hz, $\underline{C}H_2CN$], 9.18 ppm (s, $NCH_2\underline{C}H_3$). - **^{31}P-{^{1}H}-NMR** (CD_3CN,121.5 MHz): δ = 77.39 ppm (s). - **IR** (CH_3CN): ν(CO_{sym}) = 2061 (vs), ν(CO_{asym}) = 2019 (vs) cm^{-1}.

*8. {Dicarbonyl[(4-carbonicacidmethylester-2-butenyl)phenylphosphine](η^5-cyclopenta-dienyl)iron(II)}tetrafluoroborate (trans-**12**/cis-**12**)*

To a solution of 400 mg (1.08 mmol) of $[H_5C_5(OC)_2Fe(PhPH_2)]BF_4$ (**4c**) and 122 mg (1.08 mmol) of methyl-1,3-butadiene-1-carboxylate (**11**) in 20 ml acetonitrile 5 mg (0.05 mmol, 0.03 ml) NEt_3 are added. The reaction mixture is stirred for 4 d at room temperature and then reduced in vacuum to a volume of 5 ml. **12** is precipitated by addition of 25 ml of diethylether, separated by filtration, washed three times with 10 ml of diethylether and dried in vacuum. – Yield 449 mg (86 %). – Yellow microcrystalline powder. - M.p. 45°C (dec.). - $C_{19}H_{20}BF_4FeO_4P$ (485.99). calc.: C 46.96, H 4.15. found: C 46.52, H 4.08. – *trans*-**12 :** *cis*-**12** = 67 : 33. The isomeric ratio is determined by integration of the C_5H_5-signals in the ^{1}H-NMR-spectrum. - **^{1}H-NMR** (CD_3CN, 500.1 MHz): *trans*-**12**: δ = 7.66 - 7.62 (m, 3 H, H_5C_6), 7.61 - 7.57 (m, 2 H, H_5C_6), 6.23 [ddd, ^1J(PH) = 398.3 Hz, ^3J(H_aCPH) = 7.6 Hz, ^3J(H_bCPH) = 4.8 Hz, 1 H, HP], 5.72 [ddtt, ^3J(HCCH) = 15.4 Hz, ^3J(PCCH) = 8.4 Hz, ^3J(HCCH) = 5.6 Hz, ^4J(HCCCH) = 1.3 Hz, 1 H, $\underline{H}CCH_2P$], 5.49 [ddtt, ^3J(HCCH) = 15.4 Hz, ^3J(PCCH) = 7.5 Hz, ^3J(HCCH) = 5.9 Hz, ^4J(HCCCH) = 1.4 Hz, 1 H, $\underline{H}CCH_2CO_2CH_3$], 5.39 [d, ^3J(PFeCH) = 1.9 Hz, 5 H, H_5C_5], 3.62 (s, 3 H, H_3C), 3.21 - 3.04 (m, 2 H, H_2CP), 3.03 – 2.98 ppm (m, 2 H, $\underline{H}_2CCO_2CH_3$). – *cis*-**12**: δ = 7.66 - 7.62 (m, 3 H, H_5C_6), 7.61 - 7.57 (m, 2 H, H_5C_6), 6.22 [ddd, ^1J(PH) = 399.9 Hz, ^3J(H_aCPH) = 5.8 Hz, ^3J(H_bCPH) = 3.4 Hz, 1 H, HP], 5.72 [ddtt,

^{3}J(HCCH) = 13.8 Hz, ^{3}J(PCCH) = 8.8 Hz, ^{3}J(HCCH) = 5.6 Hz, ^{4}J(HCCCH) = 1.2 Hz, 1 H, HCCH$_2$P], 5.49 [ddtt, ^{3}J(HCCH) = 13.8 Hz, ^{3}J(PCCH) = 7.4 Hz, ^{3}J(HCCH) = 5.9 Hz, ^{4}J(HCCCH) = 1.4 Hz, 1 H, HCCH$_2$CO$_2$CH$_3$], 5.40 [d, ^{3}J(PFeCH) = 1.9 Hz, 5 H, H$_5$C$_5$], 3.64 (s, 3 H, H$_3$C), 3.21 - 3.04 (m, 2 H, H$_2$CP), 3.03 – 2.98 ppm (m, 2 H, H$_2$CCO$_2$CH$_3$). - **^{13}C-{^{1}H}-NMR** (CD$_3$CN, 75.45 MHz): *trans*-**12**: δ = 209.83 [d, ^{2}J(PFeC) = 15.5 Hz, CO], 209.51 [d, ^{2}J(PFeC) = 14.8 Hz, CO], 172.22 [d, ^{5}J(PCCC) = 4.5 Hz, CO$_2$Me], 133.05 [d,^{4}J(PCCCC) = 2.7 Hz, *p*-C], 132.68 [d, ^{2}J(PCC) = 9.3 Hz, *o*-C], 130.56 [d, ^{3}J(PCCC) = 11.0 Hz, *m*-C], 130.51 [d, ^{2}J(PCC) = 11.1 Hz, HC=CHCH$_2$CO$_2$Me], 129.02 [d, ^{1}J(PC) = 52.7 Hz, *i*-C], 125.89 [d, ^{3}J(PCCC) = 10.7 Hz, HC=CHCH$_2$CO$_2$Me], 88.56 [d, ^{2}J(PFeC) = 0.68 Hz, C$_5$H$_5$], 52.32 (s, CH$_3$O), 37.88 [d, ^{4}J(PCCCC) = 2.8 Hz, CH$_2$CO$_2$Me], 32.72 ppm [d, ^{1}J(PC) = 28.6 Hz, CH$_2$]. – *cis*-**12**: δ =209.79 [d, ^{2}J(PFeC) = 15.2 Hz, CO], 209.48 [d, ^{2}J(PFeC) = 14.8 Hz, CO], 172.07 [d, ^{5}J(PCCC) = 2.7 Hz, CO$_2$Me], 133.13 [d,^{4}J(PCCCC) = 2.8 Hz, *p*-C], 132.70 [d, ^{2}J(PCC) = 9.7 Hz, *o*-C], 130.41 [d, ^{3}J(PCCC) = 12.8 Hz, *m*-C], 128.89 [d, ^{1}J(PC) = 53.1 Hz, *i*-C], 127.98 [d, ^{2}J(PCC) = 12.7 Hz, HC=CHCH$_2$CO$_2$Me], 124.84 [d, ^{3}J(PCCC) = 11.0 Hz, HC=CHCH$_2$CO$_2$Me], 88.61 [d, ^{2}J(PFeC) = 0.68 Hz, C$_5$H$_5$], 52.43 (s, CH$_3$O), 33.08 [d, ^{4}J(PCCCC) = 2.7 Hz, CH$_2$CO$_2$Me], 28.65 ppm [d, ^{1}J(PC) = 29.0 Hz, CH$_2$]. - **^{31}P-{^{1}H}-NMR** (CDCl$_3$, 202.4 MHz): *trans*-**12**: δ = 29.22 (s), *cis*-**12**: 28.36 ppm (s). – **^{19}F-NMR** (CDCl$_3$, 282.4 MHz) : δ = - 151.79 ppm (s). - **IR** (CH$_3$CN): ν (PH) = 2281 (m), ν (CN) = 2237 (m),ν(CO$_{sym}$) = 2059 (vs), ν(CO$_{asym}$) = 2015 (vs)cm^{-1}, ν (C(O)) = 1735 (w).

*9. {Dicarbonyl[(4-carbonicacidmethylester-2-butenyl)(2-cyanoethyl)phenylphosphine](η^{5}-cyclopentadienyl)iron(II)}tetrafluoroborate (trans-**13a**/cis-**13a**)*

Analogous to **12** from 459 mg (0.95 mmol) of {H$_5$C$_5$(OC)$_2$Fe[PPh(H) CH$_2$CH=CHCH$_2$CO$_2$Me]}BF$_4$ (**12**), 50 mg (0.95 mmol) acrylonitrile (**5**) and 5 mg (0.05 mmol) NEt$_3$ in 20 ml of acetonitrile after 4 h and the color of the reaction mixture turned from yellow to brown.. - Yield 449 mg (88 %). - Brown microcrystalline powder. – M.p. 42 °C

(dec.). – $C_{22}H_{23}BF_4FeNO_4P$ (539.05) – calc.: C 49.02; H 4.30; N 2.60. found: C 48.63; H 4.40; N 2.72. *trans*-**13a** /*cis*-**13a** = 63 : 37. The isomeric ratio is determined by integration of the C_5H_5-signals in the ^{1}H-NMR-spectrum. - **^{1}H-NMR** (CD_3CN, 300.4 MHz): *trans*-**13a**: δ = 7.69 - 7.53 (m, 5 H, H_5C_6), 5.95 – 5.83 (m, 1 H, CH), 5.62 – 5.54 (m, 1 H, CH), 5.30 (s, br, 5 H, C_5H_5), 3.69 (s, 3 H, OCH_3), 3.24 - 3.10 (m, 2 H, CH_2), 2.79 - 2.46 (m, 2 H, CH_2). – *cis*-**13a**: δ = 7.69 - 7.53 (m, 5 H, H_5C_6), 5.95 – 5.83 (m, 1 H, CH), 5.62 – 5.54 (m, 1 H, CH), 5.27 (s, br, 5 H, C_5H_5), 3.72 (s, 3 H, OCH_3), 3.24 - 3.10 (m, 2 H, CH_2), 2.79 - 2.46 (m, 2 H, CH_2). – **^{1}H-{^{31}P}-NMR** (CD_3CN, 300.4 MHz): *trans*-**13a**: δ = 7.62 - 7.50 (m, 5 H, H_5C_6), 5.90 [dt, ^3J(HCCH) = 15.2 Hz, 7.0 Hz, 1 H, HC], 5.53 [dd, ^3J(HCCH) = 15.2 Hz, ^3J(HCCH) = 8.2 Hz, 1 H, HC], 5.26 (s, 5 H, H_5C_5), 3.63 (s, 3 H, H_3OC), 3.73 - 3.11 (m, 4 H, H_2C), 2.75 - 2.38 ppm (m, 4 H, H_2C). - *cis*-**13a**: δ = 7.62 - 7.50 (m, 5 H, H_5C_6), 5.90 [dt, ^3J(HCCH) = 15.2 Hz, 7.0 Hz, 1 H, HC], 5.53 [dd, ^3J(HCCH) = 15.2 Hz, ^3J(HCCH) = 8.2 Hz, 1 H, HC], 5.24 (s, 5 H, H_5C_5), 3.64 (s, 3 H, H_3OC), 3.73 - 3.11 (m, 4 H, H_2C), 2.75 - 2.38 ppm (m, 4 H, H_2C). - **^{13}C-{^{1}H}-NMR** (CD_3CN, 75.45 MHz): *trans*-**13a**: δ = 210.20 [d, ^2J(PFeC) = 15.2 Hz, CO], 172.44 (s, $\underline{C}O_2Me$), 133.15 [d,^4J(PCCCC) = 2.8 Hz, *p*-C], 131.97 [d, ^2J(PCC) = 12.8 Hz, CH], 131.50 [d, ^2J(PCC) = 8.6 Hz, *o*-C], 130.78 [d, ^3J(PCCC) = 10.3 Hz, *m*-C], 130.72 [d, ^1J(PC) = 46.9 Hz, *i*-C], 124.09 [d, ^3J(PCCC) = 6.9 Hz, CH], 119.28 [d, ^3J(PCCC) = 15.2 Hz, CN], 89.00 (s, C_5H_5), 52.45 (s, OCH_3), 37.91 (s, $\underline{C}H_2CO_2Me$), 33.06 [d, ^1J(PC) = 28.6 Hz, CH_2P], 25.87 [d, ^1J(PC) = 29.0 Hz, CH_2P], 23.24 ppm (s, $PCH_2\underline{C}H_2$). - *cis*-**13a**: δ = 209.89 [d, ^2J(PFeC) = 15.2 Hz, CO], 172.38 (s, $\underline{C}O_2Me$), 133.15 [d, ^4J(PCCCC) = 2.8 Hz, *p*-C], 131.97 [d, ^2J(PCC) = 12.8 Hz, CH], 131.50 [d, ^2J(PCC) = 8.6 Hz, *o*-C], 130.78 [d, ^3J(PCCC) = 10.3 Hz, *m*-C], 130.72 [d, ^1J(PC) = 46.9 Hz, *i*-C], 124.09 [d, ^3J(PCCC) = 6.9 Hz, CH], 118.75 [d, ^3J(PCCC) = 15.2 Hz, CN], 88.98 (s, C_5H_5), 52.37 (s, OCH_3), 37.95 (s, $\underline{C}H_2CO_2Me$), 32.68 [d, ^1J(PC) = 29.9 Hz, CH_2P], 25.49 [d, ^1J(PC) = 27.6 Hz, CH_2P], 23.20 ppm (s, $PCH_2\underline{C}H_2$). -

^{31}P-{^{1}H}-NMR (CD_3CN, 121.5 MHz): *trans*-**13a**: δ = 55.79 (s). – *cis*-**13a**: 55.00 ppm (s). - **IR** (CH_3CN): $\nu(CO_{sym})$ = 2056 (vs), $\nu(CO_{asym})$ = 2012 (vs) cm^{-1}.

*9. {Dicarbonyl[(4-carbonicacidmethylester-2-butenyl)(N-ethylformamido)phenylphosphine] (η^5-cyclopentadienyl)iron(II)}tetrafluoroborate (trans-**13b**/cis-**13b**)*

Analogous to **12** from 190 mg (0.39 mmol) of $\{H_5C_5(OC)_2Fe[PPh(H)CH_2CH{=}CHCH_2CO_2Me]\}BF_4$ (**12**), 37 mg (0.39 mmol) ethylisocyanate (**9**) and 5 mg (0.05 mmol) NEt_3 in 20 ml of acetonitrile after 5 h and the color of the reaction mixture turned from yellow to brown.. - Yield 449 mg (88 %). - Brown microcrystalline powder. – $C_{22}H_{25}BF_4FeNO_5P$ (539.05) – calc.: C 47.43; H 4.52; N 2.51. *trans*-**13** /*cis*-**13** = 72 : 28. The isomeric ratio is determined by integration of the C_5H_5-signals in the ^{1}H-NMR-spectrum. – **^{1}H-NMR** ($CDCl_3$, 500.1 MHz): *trans*-**13b**: δ = 7.60 - 7.39 (m, 5 H, H_5C_6), 7.24 (s, 1 H, NH), 5.84 – 5.80 (m, 1 H, CH), 5.37 – 5.22 (m, 1 H, CH), 5.27 (s, 5 H, H_5C_5), 3.57 (s, 3 H, H_3OC), 3.41 [q, ^3J(HCCH) = 7.0 Hz, 2 H, H_2CN], 3.21 – 2.91 (m, 4 H, H_2C), 1.13 ppm [t, ^3J(HCCH) = 7.0 Hz, 3 H, $\underline{H}_3CCH_2N$]. - *cis*-**13b**: δ = 7.60 - 7.39 (m, 5 H, H_5C_6), 7.24 (s, 1 H, NH), 5.77 – 5.74 (m, 1 H, CH), 5.37 – 5.22 (m, 1 H, CH), 5.30 (s, 5 H, H_5C_5), 3.58 (s, 3 H, H_3OC), 3.38 [q, ^3J(HCCH) = 7.1 Hz, 2 H, H_2CN], 3.21 – 2.91 (m, 4 H, H_2C), 1.11 ppm [t, ^3J(HCCH) = 7.1 Hz, 3 H, $\underline{H}_3CCH_2N$]. - **^{13}C-{^{1}H}-NMR** ($CDCl_3$, 125.8 MHz): *trans*-**13b**: δ = 208.67 [d, ^2J(PFeC) = 22.8 Hz, CO], 171.53 [d, ^4J(PCCCC) = 3.8 Hz, $\underline{C}O_2Me$], 167.97 [d,^1J(PC) = 59.3 Hz, C(O)N], 132.67 – 121.85 (m, CH, C_6H_5), 87.54 (s, C_5H_5), 51.92 (s, OCH_3), 37.37 [d, ^4J(PCCCC) = 2.4 Hz, $\underline{C}H_2CO_2Me$), 33.59 [d, ^1J(PC) = 24.0 Hz, CH_2P], 29.69 (s, CH_2N), 14.28 ppm (s, $\underline{C}H_3CH_2N$). - *cis*-**13b**: δ = 207.92 [d, ^2J(PFeC) = 23.0 Hz, CO], 171.64 (s, $\underline{C}O_2Me$), 168.24 [d,^1J(PC) = 57.4 Hz, C(O)N], 132.67 – 121.85 (m, CH, C_6H_5), 87.66 (s, C_5H_5), 52.08 (s, OCH_3), 36.40 [d, ^4J(PCCCC) = 2.4 Hz, $\underline{C}H_2CO_2Me$), 33.59 [d, ^1J(PC) = 24.0

Hz, CH_2P], 29.53 (s, CH_2N), 14.32 ppm (s, $\underline{C}H_3CH_2N$). - **^{31}P-{^{1}H}-NMR** ($CDCl_3$, 202.4 MHz): *trans*-**13b**: δ = 65.63 (s). – *cis*-**13b**: 60.04 ppm (s).

*11. X-ray analysis of **3** and **13a***

3: $C_{10}H_{14}BFeF_4O_2P$, M_r = 339.8, monoclinic, space group *P*2(1)/c (No. 14), a = 10.138(3) Å, b = 19.142(6) Å, c = 14.560(5) Å, β = 92.390(6)°, V = 2823.1(16) Å^3, Z = 8, ρ = 1.599 Mgm^{-3}, Nonius Kappa CCD diffractometer, radiation type: Mo-K_α, wavelength: λ = 0.71073 mm^{-1}, crystal size: 0.15 x 0.12 x 0.09 mm, temperature: 173 (2) K, scale range: 2.01° < Θ < 27.64°, F(000): 1376, total reflections: 63444, observed reflections: 6504 with [$I > 2\sigma$ (I)], absorption coefficient: μ = 1.219 mm^{-1}, empirical absorption correction, structure solution: SHELXS-97[20], structure refinement: SHELXL-97[21-24], R_1 = 0.0650, wR_2 = 0.1416.

13a: $C_{22}H_{23}BFeF_4NO_4P$, M_r = 539.1, orthorhombic, space group *P*bca (No. 61), a = 9.3750(16) Å, b = 16.563(3) Å, c = 30.564(5) Å, V = 4745.9(14) Å^3, Z = 8, ρ = 1.509 Mgm^{-3}, Nonius Kappa CCD diffractometer, radiation type: Mo-K_α, wavelength: λ = 0.71073 mm^{-1}, crystal size: 0.18 x 0.16 x 0.12 mm, temperature: 173 (2) K, scale range: 2.46° < Θ < 25.08°, F(000): 2208, total reflections: 85916, observed reflections: 4203 with [$I > 2\sigma$ (I)], absorption coefficient: μ = 0.764 mm^{-1}, empirical absorption correction, structure solution: SHELXS-97[20], structure refinement: SHELXL-97[21-24], R_1 = 0.0835, wR_2 = 0.1583.

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CHAPTER II:

Primary Phosphine Ruthenium Complexes $H_5C_5(Ph_3P)(H_2RP)RuCl$ (R = Ph, Mes, *i*-Pr, *t*-Bu, Cy) and $[H_5C_5(Ph_3P)_2Ru[P(Ph)H_2]BF_4$: Synthesis and Hydrophosphination of Methylacrylate

Abstract

Starting from the complex $H_5C_5(Ph_3P)_2RuCl$ (**1**) and the *primary* phosphines **2a-e** the neutral ruthenium complexes $H_5C_5(Ph_3P)(H_2RP)RuCl$ (R = Ph, Mes, *i*-Pr, *t*-Bu, Cy) (**3a-e**) are synthesized. Treatment of $H_5C_5(Ph_3P)_2RuCl$ (**1**) with silver tetrafluoroborate in acetonitrile leads to the cationic ruthenium complex $[H_5C_5(Ph_3P)_2Ru(NCMe)]BF_4$ (**4**). The conversion of compound **4** with the *primary* phosphine $P(Ph)H_2$ (**2a**) leads to the cationic *primary* phosphine complex $[H_5C_5(Ph_3P)_2Ru[P(Ph)H_2]BF_4$ (**5**). The [NEt_3]-catalysed hydro-phosphination reaction of **5** with methylacrylate (**6**) affords the chiral *secondary* phosphine ruthenium complex $[H_5C_5(Ph_3P)_2Ru[PPh(CH_2CH_2CO_2Me)H]BF_4$ (**7**). The complex **3b** can be transformed into the *secondary* phosphine ruthenium complex $H_5C_5(Ph_3P)$[PMes $(CH_2CH_2CO_2Me)H]RuCl$ (**8**) via hydrophosphination reaction with methylacrylate (**6**) in the presence of potassium-*tert*-butylate and ammoniumchloride. The molecular structures of **5** and **8** are proved by x-ray analysis.

Introduction

Transition metal complexes of ruthenium gain increasing interest due to high catalytic activity in diverse processes. Among those metathesis catalysts of the Grubbs-type are at the moment by far the most prominent.[1-8] Other examples involve ruthenium complexes of the type $[H_5C_5Ru(PR_3)(NCCH_3)_2]PF_6$ (R = Me, Ph, Cy), which were used in the catalytic redox isomerization of allyl alcohols.[9, 10] According to a recent report phosphanido complexes $H_5C_5(Et_3P)_2Ru(PR_2)$ (R = Ph, *t*-Bu, Cy) are effective ligands for palladium-catalyzed Suzuki coupling reactions, due to the electron-rich and bulky phosphorus donors.[11-13] The synthesis of chiral phosphine ligands usually includes long and expensive preparative methods and the reactions often lead to the formation of mixtures of *primary, secondary* and *tertiary* phosphines, when starting with PH_3.[14-16] The transition metal assisted hydrophosphination

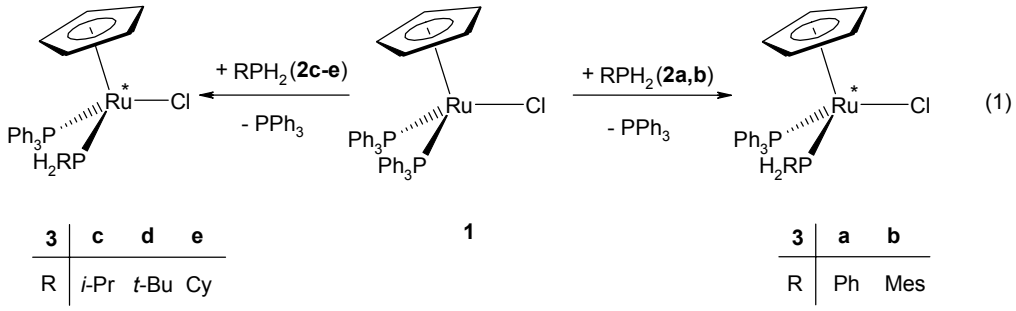
reaction offers the possibilty to synthesize chiral, highly functionalized phosphines by sucessive insertion into the PH-function of metal-coordinated *primary* phosphines.[17, 18] Due to the numerous examples in literature where ruthenium complexes were used as catalyst it seems reasonable to synthesize ruthenium complexes containing a *primary* phosphine ligand and study their reactivity and catalytical behaviour towards the hydrophosphination of activated olefins. The synthetic strategy focus in a first approach on the build up of neutral *primary* phosphine ruthenium complexes starting from the wellknown halfsandwich ruthenium-complex $H_5C_5(Ph_3P)_2RuCl$[19-21] and selected alkyl- and arylphosphines. Subsequent studies on the reactivity of the novel cationic *primary* phosphine ruthenium complex $[H_5C_5(Ph_3P)_2Ru[P(Ph)H_2]BF_4$ refer to hydrophosphination reactions.

Results and Discussion

Primary Phosphine Ruthenium Complexes $H_5C_5(Ph_3P)[H_2(R)P]RuCl$ [R = Ph, Mes, *i*-Pr, *t*-Bu, Cy] (3a-e) and $[H_5C_5(Ph_3P)_2Ru[P(Ph)H_2]BF_4$ (5)

The starting complex $H_5C_5(Ph_3P)_2RuCl$ (**1**) is treated with one equivalent of phenyl- or mesitylphosphine **2a,b** in toluene at ambient temperature to give the *primary* phosphine ruthenium complexes **3a,b** after a reaction time of 2 h (**3a**) or 7 h (**3b**) (eq. 1).

Yellow orange microcrystalline powders of **3a,b** are isolated in yields of 87 % (**3a**) to 92 % (**3b**) after evaporization of the solvent and washing the residue five time with 30 ml portion of pentane to separate **3a,b** from liberated triphenylphosphine. In an analogous manner the alkylphosphines **2c-e** are introduced at the ruthenium to give the *primary* alkylphosphine ruthenium complexes **3c-e** in a comparable yield [86 % (**3c**) – 96 % (**3d**)]. **3a-e** can be handled for a short time on air and can be stored under an atmosphere of nitrogen at room temperature for several months.



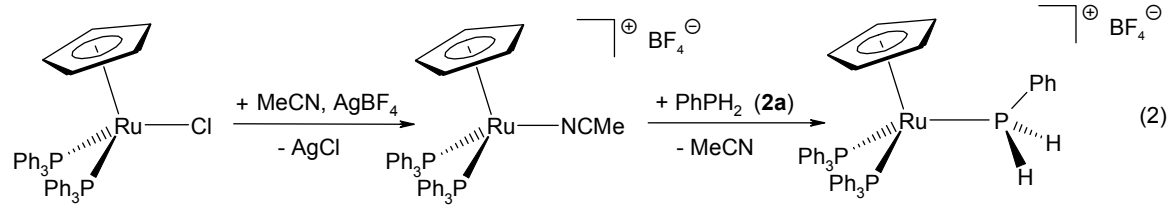
3	c	d	e
R	*i*-Pr	*t*-Bu	Cy

1

3	a	b
R	Ph	Mes

The ^{31}P-NMR spectrum of **3a-e** shows a doublet both for the coordinated *primary* phosphines ligand in the range from – 37.37 ppm (**3b**) to 8.27 ppm (**3d**) and for the triphenylphosphine at about 51 ppm with a coupling constant ^{2}J(PRuP) of about 53 Hz. The phosphorus bound hydrogens appear in the ^{1}H-NMR spectrum between 5.68 (**3a**) and 4.03 ppm (**3e**) as a dd-signal showing the characteristic ^{1}J-PH-coupling constant for coordinated *primary* phosphine ligands of 315.3 (**3c**) to 345.7 Hz (**3a**).

In order to provide the coordinated *primary* phosphine with a PH-acidity, high enough for deprotonation, a synthesis for cationic *primary* phosphine ruthenium complexes is worked out starting from **1**. In the first step chloride abstraction is accomplished with silver tetrafluoroborate in acetonitrile to give the cationic acetonitrile ruthenium complex **4** after a reaction time of 30 min (eq. 2). **4** is isolated as a yellow powder in a yield of 89 % after separation of precipitated silver chloride by filtration. The conversion of **4** into the *primary* phosphine complex **5** can be realized with the *primary* phosphine P(Ph)H$_2$ (**2a**) in acetonitrile at room temperature within 1 d (eq. 2). **5** is obtained as a yellow powder in a yield of 95 %.



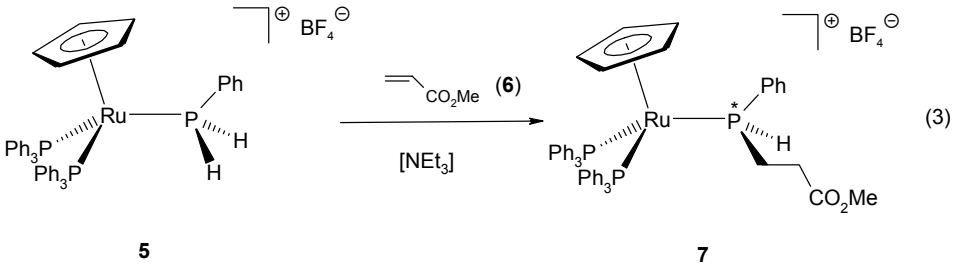
1 **4** **5**

The ^{31}P-NMR spectrum of **4** shows a singlet at 41.71 ppm for the triphenylphosphine ligands. In case of **5** a dublett, appears at 40.73 ppm for the coordinated triphenylphosphine, while a triplet at – 30.52 ppm is observed for the phenylphosphine showing a ^{2}J(PRuP)-coupling constant of 48.6 Hz. The PH-resonance appears in the ^{1}H-NMR spectrum of **5** at 5.77 ppm with a ^{1}J-PH-coupling constant of 360 Hz characteristic for metal coordination of phenylphosphine **2a**.

For the first hydrophosphination reactions exclusively ruthenium complexes containing the *primary* arylphosphines phenyl- and mesitylphosphine were used due to the higher acidity of the PH-function linked to an aryl group. Due to the same reason the first experiment was performed with the cationic phenylphosphine ruthenium complex **5**.

Hydrophosphination of Methylacrylate (6) with $H_5C_5(Ph_3P)[H_2(Mes)P]RuCl$ (3b) and $[H_5C_5(Ph_3P)_2Ru[P(Ph)H_2]BF_4$ (5)

The hydrophosphination reaction of methylacrylate (**6**) with the phenylphosphine ruthenium complex **5** leads in the presence of catalytic amounts of triethylamine to the phenyl(1-yl-methylpropionate)phosphine ruthenium complex **7** (eq. 3). The reaction is complete in dichloromethane at 40 °C after 2 d and **7** is isolated as orange-yellow solid in a yield of 83 %. **7** is soluble in polar solvents like acetonitrile and can be stored under an atmosphere of nitrogen at room temperature for several weeks.

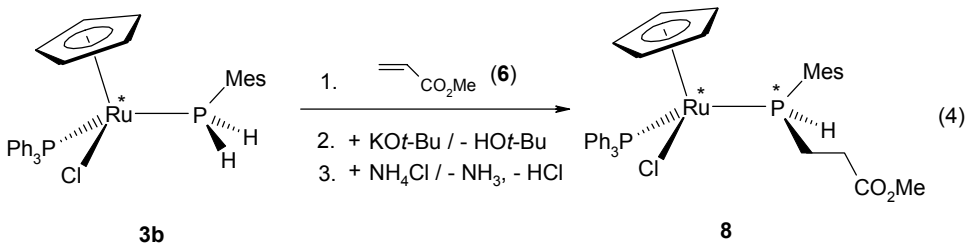


5 7 (3)

The ^{31}P-NMR resonance of the *secondary* phosphine ligand at 21.23 ppm exhibits a significant shift of about 51 ppm to lower field in relation to the *primary* phosphine ligand in

complex **5**. Chirality of the phosphorus is indicated by the different resonances of the two triphenylphosphine ligands appearing as dd-signals at 40.88 and 38.32 ppm showing ^{2}J(PRuP)-coupling constants of 43.7 and 45.0 Hz with the *primary* phosphine ligand.

The successful hydrophosphination using **5** according to eq. (3) suggests analogous experiments with the neutral arylphosphine complexes **3a,b**. However it is not possible to conduct the hydrophosphination reaction with **3b** with a catalytic amount of triethylamine, which apparently is no more a strong enough base to initiate the deprotonation step. Instead stochiometric amounts of a stronger base preferentially potassium-*tert*-butylate are required. Moreover separate protonation of the anionic coupling product is necessary, a process for which NH_4Cl proved to be suitable. Addition of a stochiometric amount of KO*t*Bu followed by that of NH_4Cl after 30 min guarantees transformation of the *primary* phosphine complex **3b** into the chiral *secondary* phosphine complex **8** by hydrophosphination of methylacrylate (**6**) at – 78 °C in toluene (eq. 4). **8** is isolated as a brown solid within 6 h in a yield of 69 %. It is exclusively obtained as the product of *anti*-Markownikow addition as is proved by x-ray analysis.

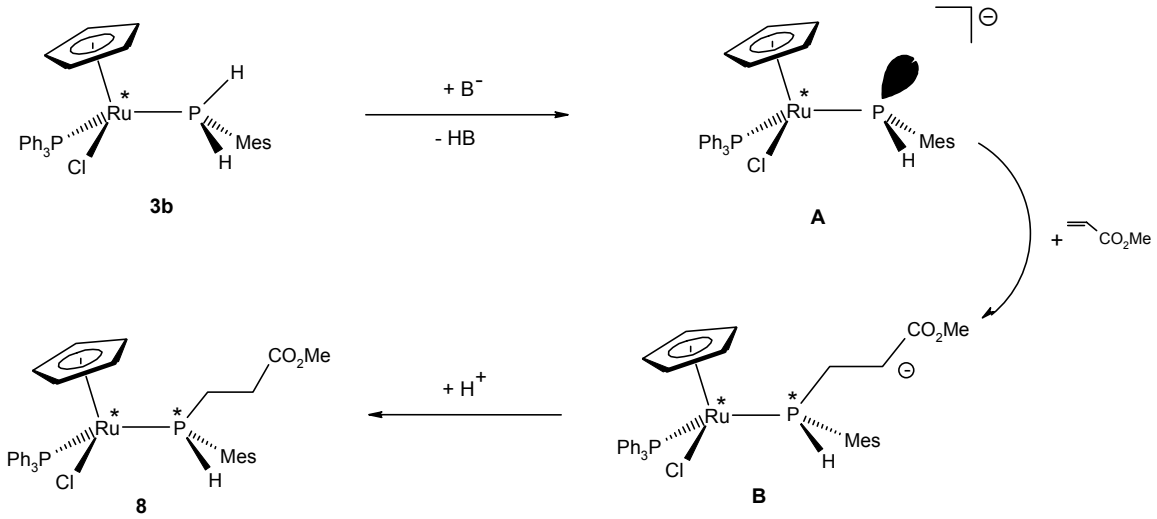


3b **8** (4)

The insertion of methylacrylate (**6**) causes a low-field shift of the ^{31}P-NMR resonance from – 37.37 for **3b** to – 2.70 ppm for the *secondary* phosphine ligand in the complex **8**.

The proposed mechanism for the hydrophosphination of the methylacrylate (**6**) involves the formation of the anionic phosphanido ruthenium complex **A** generated by deprotonation of the neutral *primary* phosphine complex **3b**, using the strong base KO*t*Bu. **A** represents a

powerful nucleophilie and attacks the electron defficient C-C-double bond of the acrylate to produce the anionic P-C-coupling product **B** as an intermediate, which is stabilised by protonation to the *secondary* phosphine complex **8** (Scheme 1).

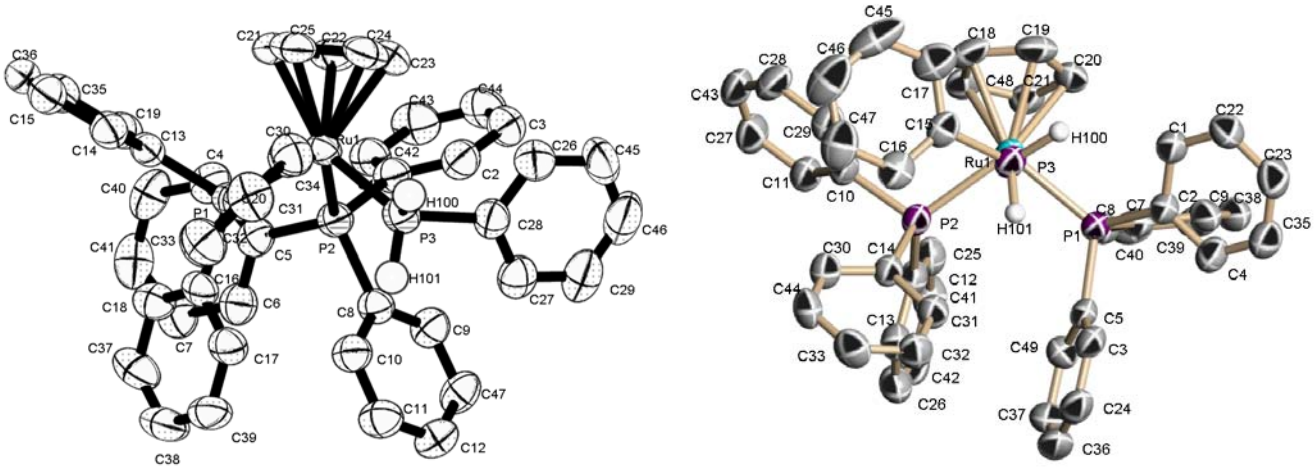


Scheme 1: Mechanism of the insertion reaction

Another important aspect in context with complexes of the type **3** is the dehydrochlorination to get neutral *primary* phosphenium complexes of ruthenium $H_5C_5(Ph_3P)Ru{=}P(R)H$ (R = Ph, Mes, *s*-Mes) containing a Ru-P double bond. These complexes should show a versatile cycloaddition behaviour towards organic double or triple bond system to build up novel P-H-functionalized phosphametallacycles. Attempts to dehydrochlorinate **3b** at – 78 °C in toluene by means of the base DBU or the phosphorusylide $Ph_3P{=}CH_2$ to get the functional phosphenium complex $H_5C_5(Ph_3P)Ru{=}PMesH$ were not successful. Even after reaction times up to 12 h **3b** is recovered unchanged under these conditions.

Molecular structure of $\{H_5C_5(Ph_3P)_2Ru[P(Ph)H_2]\}BF_4$ (5) and $\{H_5C_5(Ph_3P)[(Mes)(MeCO_2CH_2CH_2)HP]RuCl$ (8)

Suitable crystals for the structure determination of **5** and **8** are obtained form a saturated acetonitrile solution at room temperature.



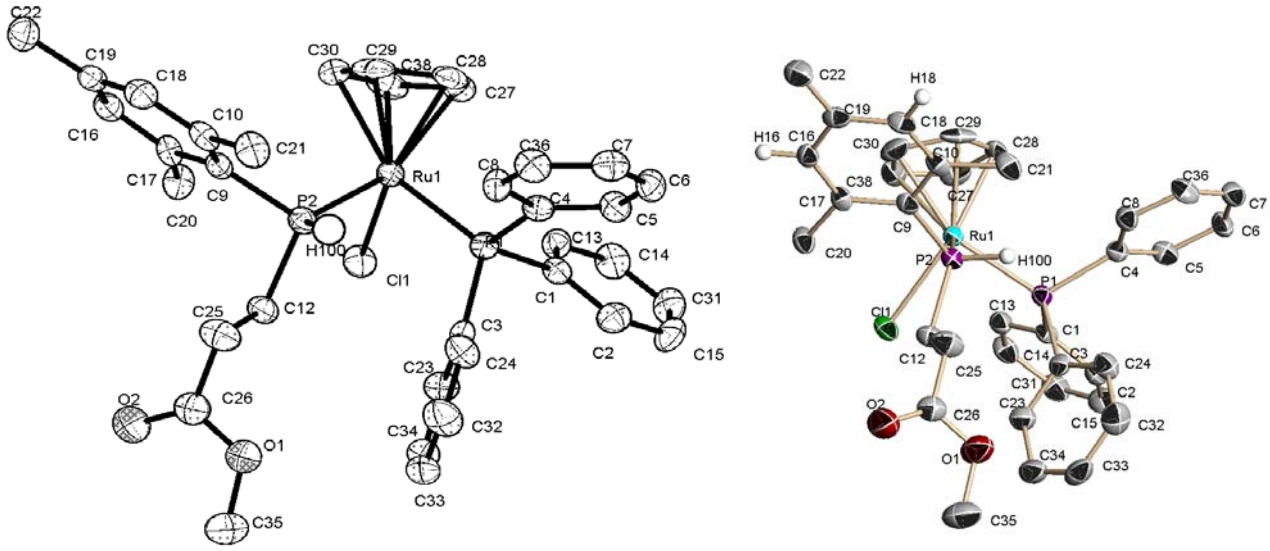
a.) b.)

figure 1: *Molecular structure a.) and Newman projection (View along the Ru1-P3-axis) b.) of $\{H_5C_5(Ph_3P)_2Ru[P(Ph)H_2]\}BF_4$ (**5**). The BF_4-anion and hydrogen atoms except PH have been omitted for clarity.*

Selected bond lengths [pm], bond and torsion angles[°]: Ru(1)-P(3) 228.79(12), Ru(1)-P(1) 233.87(11), Ru(1)-P(2) 235.93(12), P(3)-C(28) 181.3(5), P(3)-Ru(1)-P(1) 90.93(4), P(3)-Ru(1)-P(2) 92.76(4), P(1)-Ru(1)-P(2) 103.94(4), C(28)-P(3)-Ru(1) 119.00(14), P(1)-Ru(1)-P(3)-C(28) -167.74(18), P(2)-Ru(1)-P(3)-C(28) -63.74(18)].

The coordination of the ligands at the ruthenium atom of **5** shows the typical structure of a pseudo-octahedral three-legged piano stool of cyclopentadienyl halfsandwich ruthenium complexes. In accordance with this description the angles of the RuL_3-fragment are close to

90°, whereas the angle including the two triphenylphosphine ligand [P1-Ru1-P2 103.94(4)°; literature: $C_5H_5Ru[C{\equiv}CC{\equiv}CAu(PPh_3)]$ $(PPh_3)_2$ P-Ru-P 101.01(2)°][21] is significantly larger then the angles including the *primary* phosphine [P3-Ru1-P1 90.93(4)°, P3-Ru1-P2 92.76(4)°]. The Ru-P distances of 228.79(12) pm [Ru(1)-P(3)], 233.87(11) pm [Ru(1)-P(1)] and 235.93(12) pm [Ru(1)-P(2)] in **5** lie in the range of literature known compounds for example $C_5H_5Ru(PPh_3)_2(NCS)$ with 231.8(1) and 232.3(2) pm.[22] The newman projection along the Ru1-P3 axis shows that the phenyl group of the *primary* phosphine in **5** occupies the sterically unfavourable *gauche* position between the cyclopentadienyl ligand and one triphenylphosphane ligand [P1-Ru1-P3-C28 -167.74(18)°, P2-Ru1-P3-C28 -63.74(18)].



a.) b.)

figure 2: *Molecular structure a.) and Newman projection (View along the Ru1-P2-axis) b.) of* $\{H_5C_5(Ph_3P)[(Mes)(MeCO_2CH_2CH_2)HP]RuCl$ (***8***)*. Hydrogen atoms except PH have been omitted for clarity.*

Selected bond lengths [pm], bond and torsion angles[°]: Ru(1)-P(2) 227.86(11), Ru(1)-P(1) 229.48(10), Ru(1)-Cl(1) 245.26(9), C(26)-O(2) 119.8(5), C(26)-O(1) 132.1(5), P(2)-Ru(1)-P(1) 93.72(4), P(2)-Ru(1)-Cl(1) 91.06(4), C(9)-P(2)-Ru(1) 116.43(13), C(12)-P(2)-Ru(1) 122.67(13), Cp_z-Ru(1)-P(2)-C(9) 23.5°, Cp_z-Ru(1)-P(2)-C(12) 151.5°.

8 shows a pseudooctahedral coordination of the ruthenium ligands comprised by the cyclopentadienyl unit, the triphenylphosphine, the chloro and the *secondary* phosphine ligand. In accordance with this interpretation the angles of the three-legged piano-stool molecule are close to 90° [(P1-Ru1-P2) 93.72(4)° and (P2-Ru1-Cl1) 91.06(4)°]. The bond lengths Ru1-P1 [229.48(10) pm] and Ru1-P2 [227.86(11) pm] in **8** lie in the literature-known range for comparable compounds {$C_5H_5Ru[C{\equiv}CC{\equiv}CAu(PPh_3)](PPh_3)_2$ 229.80(5) pm, 229.75(4) pm}.[21-23] The phosphorus atom of the *secondary* phosphine ligand of **8** shows distorted tetrahedral coordination, indicated by the angles C9-P2-Ru1 [116.43(13)°] and C12-P2-Ru1 [122.67(13)°], whereas the angle between the organo substituents is slightly compressed [C9-P2-C12 [102.96(18)°]]. The mesityl unit adopts the *gauche*-position with respect to the Cp-ligand [Cp_z-Ru1-P2-C9 23.5°] (fig. 2b).

Experimental Section

General: All manipulations were performed under purified nitrogen using standard Schlenk techniques. Solvents were rigorously dried over an appropiate drying agent and distilled under nitrogen prior to use. ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were obtained on a Jeol JNM-LA300 spectrometer. Melting points were determined by Differential Thermo Analysis (DTA) with the Du Pont Thermal Analysis System 9000. Elemental analyses were performed in the laboratories of the "Institut für Anorganische Chemie". – Starting material: $H_5C_5(Ph_3P)_2RuCl$[19] is synthesized according to the literature procedure. The methyl acrylate is obtained commercially.

*1. [Chloro(η^5-cyclopentadienyl)(phenylphosphine)(triphenylphosphine)ruthenium(II)] (**3a**)*

To a solution of 363 mg (0.50 mmol) of $H_5C_5(Ph_3P)_2RuCl$ (**1**) in 50 ml toluene 55 mg (0.50 mmol) of $PhPH_2$ (**2a**) are added. The reaction mixture is refluxed for 2 h, then cooled to ambient temperature and evaporated to dryness. Remaining **3a** is washed with 30 ml of pentane, separated by filtration and dried in vacuum. - Yield 250 mg (87%). - Yellow microcrystalline powder. - M.p. 56 °C (dec.). – $C_{29}H_{27}ClP_2Ru$ (574.01). calc.: C 60.68, H 4.74. found: C 60.88, H 4.95. - **^{1}H-NMR(C_6D_6, 300.4 MHz)**: δ = 7.75 – 6.89 (m, 20 H, H_5C_6), 5.68 [dt, ^{1}J(PH) = 345.7 Hz, ^{2}J(HPH) = 4.4 Hz, ^{3}J(PRuPH) = 4.4 Hz, 1 H, HP], 5.56 [dt, ^{1}J(PH) = 331.6 Hz, ^{2}J(HPH) = 5.7 Hz, ^{3}J(PRuPH) = 4.2 Hz, 1 H, HP], 4.24 ppm (s, br, 5 H, H_5C_5). - **^{13}C-{^{1}H}-NMR(C_6D_6, 75.45 MHz)**: δ = 137.45 [dd, ^{1}J(PC) = 41.4 Hz, ^{3}J(PRuPC) = 3.5 Hz, *i*-C], 134.26 [d, ^{2}J(PCC) = 10.7 Hz, *o*-C], 134.10 [d, ^{2}J(PCC) = 13.1 Hz, *o*-C], 132.81 [d, ^{3}J(PCCC) = 8.9 Hz, *m*-C], 129.47 [d, ^{4}J(PCCCC) = 2.4 Hz, *p*-C], 128.80 [d, ^{1}J(PC) = 36.2 Hz, *i*-C], 128.41 [d, ^{2}J(PCC) = 12.1 Hz, *o*-C], 128.09 [d, ^{3}J(PCCC) = 7.9 Hz, *m*-C], 80.45 ppm [dd, ^{2}J(PRuC) = 2.8 Hz, 2.4 Hz, C_5H_5]. - **^{31}P-{^{1}H}-NMR(C_6D_6, 121.5 MHz)**: δ = 50.08 [d, ^{2}J(PRuP) = 56.6 Hz, PPh_3], - 20.31 ppm [d, ^{2}J(PRuP) = 56.6 Hz, $PPhH_2$].

*2. [Chloro(η^5-cyclopentadienyl)(mesitylphosphine)(triphenylphosphine)ruthenium(II)] (**3b**)*

Analogous to **3a** from 500 mg (0.69 mmol) of $H_5C_5(Ph_3P)_2RuCl$ (**1**) and 105 mg (0.69 mmol) of $MesPH_2$ (**2b**) in 30 ml toluene after 7 h. - Yield 392 mg (92%). – Yellow microcrystalline powder. - M.p. 158 °C (dec.). – $C_{32}H_{33}ClP_2Ru$ (616.09). calc.: C 62.39, H 5.40. found: C 62.43, H 5.56. – **^{1}H-NMR(C_6D_6, 300.4 MHz):** δ = 7.85 – 7.79 (m, 6 H, H_5C_6), 7.11 – 6.99 (m, 9 H, H_5C_6), 6.64 (s, 2 H, $\underline{H}_2C_6(CH_3)_3$), 5.57 [dd, ^1J(PH) = 301.6 Hz, ^2J(HPH) = 3.3 Hz, 1 H, HP], 5.56 [ddd, ^1J(PH) = 335.1 Hz, ^3J(PRuPH) = 13.8 Hz, ^2J(HPH) = 3.3 Hz, 1 H, HP], 4.10 (s, br, 5 H, H_5C_5), 2.38 (s, 6 H, *o*-H_3C), 2.05 ppm (s, 3 H, *m*-H_3C). - **^{13}C-{^{1}H}-NMR(C_6D_6, 75.45 MHz):** δ = 139.48 [d, ^3J(PCCC) = 7.9 Hz, *m*-C], 137.45 [dd, ^1J(PC) = 41.0 Hz, ^3J(PRuPC) = 2.8 Hz, *i*-C], 133.80 [d, ^2J(PCC) = 10.6 Hz, *o*-C], 129.20 [d, ^4J(PCCCC) = 2.1 Hz, *p*-C], 128.83 [d, ^3J(PCCC) = 7.2 Hz, *m*-C], 121.76 [d, ^2J(PCC) = 11.6 Hz, *o*-C], 80.49 [dd, ^2J(RuPC) = 2.8 Hz, 2.4 Hz, C_5H_5], 21.30 [d, ^3J(PCCC) = 8.7 Hz, *o*-CH_3], 20.68 ppm (s, br, *p*-CH_3). - **^{31}P-{^{1}H}-NMR(C_6D_6, 121.5 MHz):** δ = 51.27 [d, ^2J(PRuP) = 53.5 Hz, PPh_3], - 37.37 ppm [d, ^2J(PRuP) = 53.5 Hz, $PMesH_2$].

*3. [Chloro(η^5-cyclopentadienyl)(isopropylphosphine)(triphenylphosphine)ruthenium(II)] (**3c**)*

Analogous to **3a** from 350 mg (0.48 mmol) of $H_5C_5(Ph_3P)_2RuCl$ (**1**)and 37 mg (0.48 mmol) of *i*-$PrPH_2$ (**2c**) in 40 ml toluene after 6 h. - Yield 177 mg (86%). – Yellow microcrystalline powder. - M.p. 137 °C (dec.). – $C_{26}H_{29}ClP_2Ru$ (539.99). calc.: C 57.83, H 5.41. found: C 58.12, H 5.53. – **^{1}H-NMR(C_6D_6, 300.4 MHz)**: δ = 7.75 – 7.69 (m, 6 H, H_5C_6), 7.08 – 6.97 (m, 9 H, H_5C_6), 4.62 [dm, ^1J(PH) = 315.3 Hz, ^3J(PRuPH) = 11.3 Hz, ^2J(HPH) = 7.3 Hz, ^3J(HCPH) = 3.7 Hz, 1 H, HP], 4.29 (s, br, 5 H, H_5C_5) 4.06 [dddd, ^1J(PH) = 325.0 Hz, ^3J(PRuPH) = 10.4 Hz, ^2J(HPH) = 7.3 Hz, ^3J(HCPH) = 4.0 Hz, 1 H, HP], 2.17 [dsept, ^2J(PCH) = 9.9 Hz, ^3J(HCCH) = 3.8 Hz, 1 H, $\underline{H}C(CH_3)_2$], 1.14 [dd, ^3J(PCCH) = 17.6 Hz, ^3J(HCCH) = 7.0 Hz, 3 H, H_3C], 1.00 ppm [dd, ^3J(PCCH) = 14.7 Hz, ^3J(HCCH) = 7.0 Hz, 3 H, H_3C]. - **^{13}C-{^{1}H}-NMR(C_6D_6, 75.45 MHz)**: δ = 137.90 [dd, ^1J(PC) = 38.0 Hz, ^3J(PRuPC) =

3.1 Hz, *i*-C], 134.58 [d, ^{2}J(PCC) = 10.7 Hz, *o*-C], 129.72 [d, ^{4}J(PCCCC) = 2.0 Hz, *p*-C], 128.31 [d, ^{3}J(PCCC) = 9.4 Hz, *m*-C], 79.84 [dd, ^{2}J(PRuC) = 2.4 Hz, ^{2}J(PRuC) = 2.3 Hz, C_5H_5], 23.77 [d, ^{2}J(PCC) = 5.9 Hz, CH_3], 22.11 (s, CH_3), 21.72 ppm [dd, ^{1}J(PC) = 27.5 Hz, ^{3}J(PRuPC) = 2.0 Hz, $\underline{C}H(CH_3)_2$]. - **^{31}P-{^{1}H}-NMR(C_6D_6, 121.5 MHz)**: δ = 51.79 [d, ^{2}J(PRuP) = 52.3 Hz, PPh_3], - 1.73 ppm [d, ^{2}J(PRuP) = 52.3 Hz, P(*i*-Pr)H_2].

*4. [Chloro(η^{5}-cyclopentadienyl)(tertbutylphosphine)(triphenylphosphine)ruthenium(II)] (**3d**)*

Analogous to **3a** from 500 mg (0.69 mmol) of $H_5C_5(Ph_3P)_2RuCl$ (**1**) and 62 mg (0.69 mmol) of *t*-$BuPH_2$ (**2d**) in 30 ml toluene after 12 h. - Yield 367 mg (96%). – Yellow microcrystalline powder. - M.p. 75 °C (dec.). – $C_{27}H_{31}ClP_2Ru$ (554.02). calc.: C 58.54, H 5.64. found: C 58.77, H 5.64. – **^{1}H-NMR(C_6D_6, 300.4 MHz):** δ = 7.75 – 6.98 (m, 15 H, H_5C_6), 5.56 [ddd, ^{1}J(PH) = 335.1 Hz, ^{3}J(PRuPH) = 5.9 Hz, ^{2}J(HPH) = 5.2 Hz, 1 H, HP], 4.98 [ddd, ^{1}J(PH) = 316.6 Hz, ^{3}J(PRuPH) = 9.7 Hz, ^{2}J(HPH) = 5.2 Hz, 1 H, HP], 4.31 (s, br, 5 H, H_5C_5), 1.22 ppm [d, ^{3}J(PCCH) = 14.8 Hz, 9 H, H_3C]. - **^{13}C-{^{1}H}-NMR(C_6D_6, 75.45 MHz):** δ = 137.49 [dd, ^{1}J(PC) = 41.3 Hz, ^{3}J(PRuPC) = 2.4 Hz, *i*-C], 134.42 [d, ^{2}J(PCC) = 10.7 Hz, *o*-C], 129.40 [d, ^{4}J(PCCCC) = 2.0 Hz, *p*-C], 128.77 [d, ^{3}J(PCCC) = 6.9 Hz, *m*-C], 79.90 [dd, ^{2}J(PRuC) = 2.4 Hz, ^{2}J(PRuC) = 2.4 Hz, C_5H_5], 31.50 [dd, ^{1}J(PC) = 25.5 Hz, ^{3}J(PRuPC) = 3.5 Hz, $\underline{C}(CH_3)_3$], 30.86 ppm [d, ^{2}J(PCC) = 3.8 Hz, $C(\underline{C}H_3)_3$]. - **^{31}P-{^{1}H}-NMR(C_6D_6, 121.5 MHz):** δ = 51.81 [d, ^{2}J(PRuP) = 51.0 Hz, PPh_3], 8.27 ppm [d, ^{2}J(PRuP) = 51.0 Hz, *t*-$BuPH_2$].

*5. [Chloro(cyclohexylphosphine)(η^{5}-cyclopentadienyl)(triphenylphosphine)ruthenium(II)](**3e**)*

Analogous to **3a** from 350 mg (0.48 mmol) of $H_5C_5(Ph_3P)_2RuCl$ (**1**) and 56 mg (0.48 mmol) of $CyPH_2$ (**2e**) in 15 ml toluene after 5 h. - Yield 260 mg (93%). – Yellow microcrystalline powder. - M.p. 161 °C (dec.). – $C_{29}H_{32}ClP_2Ru$ (580.05). calc.: C 60.05, H 5.73. found: C 60.23, H 5.81. – **^{1}H-NMR(C_6D_6, 300.4 MHz)**: δ = 7.77 – 7.71 (m, 6 H, H_5C_6), 7.09 – 6.88 (m, 9 H, H_5C_6), 4.66 [dm, ^{1}J(PH) = 316.2 Hz, ^{3}J(PRuPH) = 10.8 Hz, ^{3}J(HCPH) = 6.8 Hz,

^{2}J(HPH) = 3.8 Hz, 1 H, HP], 4.31 (s, br, 5 H, H_5C_5) 4.03 [ddt, ^{1}J(PH) = 324.9 Hz, ^{3}J(PRuPH) = 10.1 Hz, ^{3}J(HCPH) = 6.6 Hz, ^{2}J(HPH) = 3.9 Hz, 1 H, HP], 1.70 – 1.53 (m, 2 H, $H_{11}C_6$), 1.35 – 0.84 (m, 9 H, $H_{11}C_6$). - **^{13}C-{^{1}H}-NMR(C_6D_6, 75.45 MHz)**: δ = 137.33 [dd, ^{1}J(PC) = 41.0 Hz, ^{3}J(PRuPC) = 2.8 Hz, *i*-C], 133.95 [d, ^{2}J(PCC) = 10.7 Hz, *o*-C], 129.07 [d, ^{4}J(PCCCC) = 2.4 Hz, *p*-C], 127.67 [d, ^{3}J(PCCC) = 9.3 Hz, *m*-C], 79.14 [dd, ^{2}J(PRuC) = 2.8 Hz, ^{2}J(PRuC) = 2.4 Hz, C_6H_5), 33.89 [d, ^{2}J(PCC) = 6.6 Hz, C-2,6], 30.22 [dd, ^{1}J(PC) = 27.2 Hz, ^{3}J(PRuPC) = 1.7 Hz, C-1], 26.80 [d, ^{3}J(PCCC) = 12.8 Hz, C-3,5], 25.97 [d, ^{4}J(PCCCC) = 1.4 Hz, C-4]. - **^{31}P-{^{1}H}-NMR(C_6D_6, 121.5 MHz)**: δ = 51.68 [d, ^{2}J(PRuP) = 52.3 Hz, PPh_3], - 9.74 ppm [d, ^{2}J(PRuP) = 52.3 Hz, P(Cy)H_2].

*6. {Acetonitrile[bis(triphenylphosphine)](η^5-cyclopentadienyl)ruthenium(II)}tetrafluoro-borate (**4**)*

100 mg (0.138 mmol) of $H_5C_5(Ph_3P)_2RuCl$ (**1**), dissolved in 30 ml acetonitrile, are combined with 27 mg (0.138 mmol) of $AgBF_4$. The reaction mixture is stirred for 30 min at ambient temperature and precipitated AgCl is separated by filtration. The solution is evaporated to dryness in vacuum and remaining **4** is washed three times with each 10 ml pentane and dried in vacuum. – Yield: 101 mg (89%). – Yellow microcrystalline powder. – M.p.: 116 °C. – $C_{43}H_{38}BF_4NP_2Ru$ (818.61). calc.: C 63.09, H 4.68, N 1.71. found: C 63.52, H 4.73, N 1.76. - **^{1}H-NMR(CD_3CN, 300.4 MHz)**: δ = 7.41 – 7.18 (m, 17 H, H_5C_6), 7.13 – 7.06 (m, 13 H, H_5C_6), 4.39 (s, br, 5 H, H_5C_5), 1.95 ppm (s, 3 H, H_3C). - **^{13}C-{^{31}P,^{1}H}-NMR(CD_3CN, 100.6 MHz)**: δ = 135.54 (s, *i*-C), 132.93 (s, *o*-C), 129.63 (s, *p*-C), 127.95 (s, *m*-C), 126.22 (s, CN) 82.93 (s, C_5H_5), 21.41 ppm (s, CH_3). - **^{31}P-{^{1}H}-NMR(CD_3CN, 162.1 MHz)**: δ = 41.71 ppm (s).

*7. {[Bis(triphenylphosphine)](η^5-cyclopentadienyl)(phenylphosphine)ruthenium(II)}tetra-fluoroborate (**5**)*

To a solution of 200 mg (0.244 mmol) $[H_5C_5(Ph_3P)_2Ru(NCMe)]BF_4$ (**4**) in 25 ml acetonitrile 27 mg (0.244 mmol) of $PhPH_2$ (**2a**) are added. The reaction mixture is stirred for 1 d at ambient temperature and then reduced in vacuum to a volume of 5 ml. **5** is precipitated by addition of 40 ml of diethylether, separated by filtration, washed three times with 10 ml of diethylether and dried in vacuum. – Yield: 206 mg (95 %). – Yellow solid. – M.p.: 68 °C (dec.). – $C_{47}H_{42}BF_4P_3Ru$ (887.65). calc.: C 63.60, H 4.77. found: C 63.89, H 4.83. – **^{1}H-NMR(CD_3CN, 300.4 MHz)**: δ = 7.50 – 7.11 (m, 35 H, H_5C_6), 5.77 [dt, ^1J(PH) = 360.0 Hz, ^3J(PRuPH) = 6.7 Hz, 2 H, HP], 4.58 ppm (s, br, 5 H, H_5C_5). - **^{13}C-{^{1}H}-NMR(CD_3CN, 75.45 MHz)**: δ = 136.48 [dd, ^1J(PC) = 39.4 Hz, ^3J(PRuPC) = 3.5 Hz, *i*-C], 134.60 – 134.06 (m, C_6H_5), 133.98 [d, ^2J(PCC) = 9.7 Hz, *o*-C], 133.56 [d, ^2J(PCC) = 10.9 Hz, *o*-C], 132.37 [d, ^3J(PCCC) = 9.3 Hz, *m*-C], 128.74 [d, ^4J(PCCCC) = 2.4 Hz, *p*-C], 128.69 – 127.95 (m, C_6H_5), 127.82 [d, ^3J(PCCC) = 7.9 Hz, *m*-C], 80.86 ppm [dt, ^2J(PRuC) = 2.8 Hz, ^2J(PRuC) = 2.4 Hz, C_5H_5]. - **^{31}P-{^{1}H}-NMR(CD_3CN, 121.5 MHz)**: δ = 40.73 [d, ^2J(PRuP) = 48.6 Hz, PPh_3], -30.52 ppm [t, ^2J(PRuP) = 48.6 Hz, $PPhH_2$].

*8. {[Bis(triphenylphosphine)](η^5-cyclopentadienyl)[phenyl(1-yl-methylpropionate)phosphine] ruthenium(II)}tetrafluoroborate (**7**)*

To a solution of 30 mg (0.034 mmol) $\{H_5C_5(Ph_3P)_2Ru[PhPH_2]\}BF_4$ (**5**) and 4 mg (0.034 mmol) methylacrylate (**6**) in 15 ml dichloromethane 5 mg (0.05 mmol) NEt_3 are added. The reaction mixture is stirred for 2 d at 40 °C and then reduced in vacuum to a volume of 3 ml. **7** is precipitated by addition of 10 ml of diethylether, separated by filtration, washed three times with 5 ml of diethylether and dried in vacuum. - Yield 27 mg (83 %). – Orange-yellow powder. – M.p.: 96 °C. – $C_{51}H_{48}BF_4O_2P_3Ru$ (973.74). calc.: C 62.91, H 4.97. found: C 63.37, H 5.12. – **^{1}H-NMR(CD_3CN, 300.4 MHz)**: δ = 7.63 – 6.93 (m, 35 H, H_5C_6), 6.31 [ddt, ^1J(PH)

= 355.0 Hz, ^{3}J(PRuPH) = 11.7 Hz, ^{3}J(HCPH) = 7.9 Hz, 1 H, HP], 4.68 (s, br, 5 H, H_5C_5), 3.49 (s, 3 H, H_3CO), 2.12 – 2.00 (m, 2 H, H_2C), 1.76 – 1.64 ppm (m, 2 H, H_2C). - **^{13}C-{^{1}H}-NMR(CD_3CN, 100.6 MHz)**: δ = 171.34 [d, ^{3}J(PCCC) = 9.2 Hz, C(O)OMe], 137.47 [d, ^{1}J(PC) = 32.5 Hz, *i*-C], 136.10 [d, ^{1}J(PC) = 33.3 Hz, *i*-C], 134.96 [d, ^{1}J(PC) = 35.2 Hz, *i*-C], 134.52 [d, ^{2}J(PCC) = 10.5 Hz, *o*-C], 134.31 [d, ^{2}J(PCC) = 10.5 Hz, *o*-C], 133.95 [d, ^{3}J(PCCC) = 9.1 Hz, *m*-C], 133.00 [d, ^{4}J(PCCCC) = 2.4 Hz, *p*-C], 132.66 [d, ^{3}J(PCCC) = 7.6 Hz, *m*-C], 131.56 [d, ^{4}J(PCCCC) = 2.4 Hz, *p*-C], 131.40 [d, ^{4}J(PCCCC) = 2.0 Hz, *p*-C], 129.61 [d, ^{3}J(PCCC) = 9.5 Hz, *m*-C], 129.48 [d, ^{2}J(PCC) = 10.0 Hz, *o*-C], 87.09 (s, br, C_5H_5), 52.23 (s, CH_3), 33.34 [d, ^{2}J(PCC) = 9.1 Hz, CH_2], 27.67 ppm [d, ^{1}J(PC) = 28.1 Hz, CH_2]. - **^{31}P-{^{1}H}-NMR(CD_3CN, 121.5 MHz)**: δ = 40.88 [dd, ^{2}J(PRuP) = 43.7 Hz, ^{2}J(PRuP) = 29.5 Hz PPh_3], 38.32 [dd, ^{2}J(PRuP) = 45.0 Hz, ^{2}J(PRuP) = 29.5 Hz, PPh_3], 21.23 ppm [dd, ^{2}J(PRuP) = 45.0 Hz, ^{2}J(PRuP) = 43.7 Hz, PPhH].

*9. [Chloro(η^5-cyclopentadienyl)[mesityl(1-yl-methyl-propionate)phosphine](triphenyl-phosphine)ruthenium(II)](**8**)*

To a solution of 50 mg (0.081 mmol) of $H_5C_5(Ph_3P)[MesPH_2]RuCl$ (**3b**) and 7.0 mg (0.81 mmol) of methylacrylate (**6**) in 10 ml toluene 9 mg (0.081 mmol) of KO*t*Bu are added at – 78 °C. After 30 min 4 mg (0.081 mmol) of NH_4Cl are added to the reaction mixture at – 78 °C, which is stirred for 2 h at this temperature and then allowed to warm up to ambient temperature. After removal of all volatiles in vacuum, remaining **8** is washed three times with each 5 ml pentane and dried in vacuum. - Yield 39 mg (69%). – Brown microcrystalline powder. - M.p.: 70 °C (dec.). – $C_{36}H_{39}ClO_2P_2Ru$ (702.18). calc.: C 61.58, H 5.60. found: C 62.16, H 5.82. - **^{1}H-NMR(C_6D_6, 300.4 MHz)**: δ = 7.93 – 7.79 (m, 6 H, H_5C_6), 7.13 – 6.98 (m, 9 H, H_5C_6), 6.68 [s, 1 H, *m*-H], 6.64 [s, 1 H, *m*-H], 6.01 [dm, ^{1}J(PH) = 335.5 Hz, 1 H, HP], 4.14 (s, br, 5 H, H_5C_5), 3.05 (s, 3 H, H_3CCO_2), 2.79 (s, 3 H, *o*-H_3C), 2.37 (s, 3 H, *o*-H_3C), 2.04 (s, 3 H, *p*-H_3C), 1.93 – 1.71 (m, 2 H, H_2C), 1.42 – 1.21 ppm (m, 2 H, H_2C). - **^{13}C-{^{1}H}-**

NMR(C_6D_6, 75.45 MHz): δ = 204.14 (s, CO_2Me), 138.27 [d, ^1J(PC) = 39.4 Hz, *i*-C], 134.97 [d, ^3J(PCCC) = 10.5 Hz, *m*-C], 134.54 [d, ^2J(PCC) = 11.0 Hz, *o*-C], 132.81 [d, ^3J(PCCC) = 9.5 Hz, *m*-C], 131.93 [d, ^4J(PCCCC) = 2.4 Hz, *p*-C], 129.92 [d, ^4J(PCCCC) = 2.1 Hz, *p*-C], 128.91 [d, ^2J(PCC) = 11.9 Hz, *o*-C], 128.46 [d, ^1J(PC) = 34.8 Hz, *i*-C], 81.57 (s, br, C_5H_5), 51.26 (s, CH_3CO_2), 30.46 (s, *o*-CH_3), 23.43 [d, ^2J(PCC) = 12.3 Hz, CH_2], 22.97 ppm [d, ^1J(PC) = 27.1 Hz, CH_2], 21.29 (s, *p*-CH_3). - **^{31}P-{^{1}H}-NMR**(C_6D_6, 121.5 MHz): δ = 48.65 [d, ^2J(PRuP) = 46.2 Hz, PPh_3], - 2.70 ppm [d, ^2J(PRuP) = 46.2 Hz, PH(Mes)].

*10. X-ray analysis of **5** and **8***

5: $C_{47}H_{42}BF_4P_3Ru$, M_r = 887.6, triclinic, space group *P*–1 (No. 2), *a* = 11.3672(15) Å, *b* = 14.1418(19) Å, *c* = 16.550(2) Å, α = 101.880(3)°, β = 105.934(3) °, γ = 103.326(3)°, *V* = 2384.1(6) Å^3, *Z* = 2, ρ = 1.236 Mgm^{-3}, Nonius Kappa CCD diffractometer, radiation type: Mo-K_α, wavelength: λ = 0.71073 mm^{-1}, crystal size: 0.25 x 0.13 x 0.10 mm, temperature: 293 (2) K, scale range: 1.34° < Θ < 25.05°, *F*(000): 1016, total reflections: 8397, observed reflections: 8397 with [$I > 2\sigma(I)$], absorption coefficient: μ = 0.482 mm^{-1}, empirical absorption correction, structure solution: SHELXS-97[24], structure refinement: SHELXL-97[25-28], R_1 = 0.0576, wR_2 = 0.1149.

8: $C_{36}H_{39}ClO_2P_2Ru$, M_r = 702.2, orthorhombic, space group *P*na2(1) (No. 33), *a* = 22.3522(18) Å, *b* = 11.6973(9) Å, *c* = 12.0706(9) Å, *V* = 3156.0(4) Å^3, *Z* = 4, ρ = 1.478 Mgm^{-3}, Nonius Kappa CCD diffractometer, radiation type: Mo-K_α, wavelength: λ = 0.71073 mm^{-1}, crystal size: 0.10 x 0.09 x 0.07 mm, temperature: 173 (2) K, scale range: 1.82° < Θ < 25.12°, *F*(000): 1448, total reflections: 5622, observed reflections: 5622 with [$I > 2\sigma(I)$], absorption

coefficient: μ = 0.715 mm^{-1}, empirical absorption correction, structure solution: SHELXS-97[24], structure refinement: SHELXL-97[25-28], R_1 = 0.0381, wR_2 = 0.0807.

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CHAPTER III:

Chelatephosphine Substituted *Primary* Phosphine Iron and Ruthenium Complexes $[H_5C_5(P_{[2]})Fe[P(R)H_2]BF_4$ [$P_{[2]}$ = dppe, mppe, (*R*)-(+)-PROPHOS, (*R*,*R*)-(–)-DIOP; R = Ph, *i*-Pr] and $[H_5C_5(DIOP)Ru[P(Ph)H_2]BF_4$: Synthesis and Hydrophosphination of Acrylonitrile and the Isocyanates RNCO (R = (S)-1-Phenylethyl, Et)

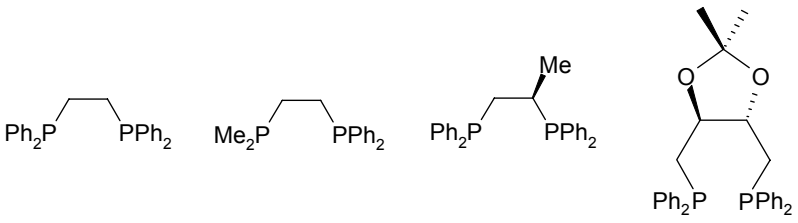
Abstract

Starting from $[H_5C_5(OC)_3Fe]BF_4$ (**1**) and dppe (**2a**), mppe (**2b**), (*R*)-(+)-PROPHOS (**2c**) or (*R,R*)-(–)-DIOP (**2d**) the cationic chelate phosphine iron complexes $[H_5C_5(P_{[2]})Fe(NCMe)]BF_4$ [$P_{[2]}$ = dppe, mppe, PROPHOS, DIOP] (**3a-d**) are obtained in acetonitrile. The neutral ruthenium complex H_5C_5(DIOP)RuCl (**7**) is analogously synthesized from $H_5C_5(Ph_3P)_2RuCl$ (**6**). Treatment of **3a-d** with the *primary* phosphines $P(R)H_2$ [R = Ph, *i*-Pr] (**4a,b**) gives the *primary* phosphine complexes $[H_5C_5(P_{[2]})Fe[P(R)H_2]BF_4$ [$P_{[2]}$ = dppe, mppe, PROPHOS, DIOP; R = Ph, *i*-Pr] (**5a-d**). The complex **7** is transformed into the cationic ruthenium complex $[H_5C_5$(DIOP)Ru(NCMe)$]BF_4$ (**8**) by treatment with silver tetrafluoroborate in acetonitrile. Treatment of **8** with the *primary* phosphine $P(Ph)H_2$ (**4a**) gives the *primary* phosphine ruthenium complex $[H_5C_5$(DIOP)Ru$[P(Ph)H_2]BF_4$ (**9**). Reaction of **5b,c** and **9** with acrylonitrile (**10**) affords the chiral *secondary* phosphine complexes $[H_5C_5(P_{[2]})Fe[PH(Ph)(CH_2)_2CN]BF_4$ [$P_{[2]}$ = mppe, PROPHOS] (**11a,b**) and $[H_5C_5$(DIOP)Ru$[PH(Ph)(CH_2)_2CN]BF_4$ (**11c**) by insertion of the C-C-bond into the PH-function. Analogous reaction of **5d** yields to the chelate phosphine iron complex $\{H_5C_5$(DIOP)Fe$[NC(HC{=}CH_2)]\}BF_4$ (**12**). Treatment of **5a,b** with the isocyanates **13a,b** leads to the secondary phosphine iron complexes $\{H_5C_5(P_{[2]})Fe[PH(Ph)[(C{=}O)N(R)H]\}BF_4$ [$P_{[2]}$ = dppe, mppe; R = (S)-1-Phenylethyl, Et] **14a,b**. The molecular structures of **8** and **14b** are proved by x-ray analysis.

Introduction

Chiral phosphines are significant as ligands in complexes applied for enantioselective synthesis and catalysis.[1, 2] For that reason the synthesis of transition metal complexes with chiral phosphine ligands has attracted widespread and general attention.[3,4] Especially BINAP-ruthenium complexes turned out to be very efficient in asymmetric catalysis.[5, 6] The

synthesis of enantiomerically pure chiral phosphines includes in general long and expensive preparative routes.[7-9] The opportunity to coordinate *primary* phosphines at transition metals, mainly of the iron and chromium group, creates a convenient situation concerning the successive synthesis of chiral *secondary* and *tertiary* phosphine ligands at the transition metal.[10] Previous investigations on transformation of *primary* phosphine iron complexes of the type $[H_5C_5(OC)_2FeP(R)H_2]BF_4$ into the corresponding chiral *secondary* or *tertiary* phosphine complexes by Et_3N-catalyzed insertion of electron deficient olefins into the PH-bond have shown, that this is an effective approach to build up chiral organosubstituted phosphines at the iron centre.[11] In context with a stereocontrolled generation it seems reasonable to introduce bidentate phosphine ligands, for which enantiomerically pure derivates are available. As chelate phosphine ligand dppe, mppe, (*R*)-(+)-PROPHOS and (*R,R*)-(–)-DIOP were used. While dppe is without influence on the stereochemistry of the iron, mppe generates a stereogenic metal centre, which should give rise to the formation of a diastereomeric hydrophosphination product, provided only one P-H-bond is used.



dppe **mppe** **PROPHOS** **DIOP**

In the case of optically pure chelatephosphines PROPHOS and DIOP the stereochemical measurement should produce epimers differing only in the stereochemistry of the phosphorus. Subsequent seperation of the epimers and detachment of the *secondary* phosphines from the iron should offer enantiomerically pure material. Of primary interest is however to establish efficient procedures for the synthesis of the *primary* phosphine complexes $[H_5C_5(P_{[2]})FeP(R)H_2]BF_4$ [$P_{[2]}$ = dppe, mppe, PROPHOS, DIOP; R = Ph, *i*-Pr] and to monitor the asymmetric induction on the hydrophosphination reaction by the chelating phosphine

ligand. Extension to analogous ruthenium complexes and the influence of a chiral organic group linked to the insertion reagent in the case of the achiral dppe derivatives should be examined. In general these experiments are expected to provide a basis for the development of asymmetric hydrophosphination. We report here about the influence of the chelate phosphine ligands mentioned above at the iron and ruthenium fragment on the hydrophosphination reactions and the possibility of realizing diastereoselective reactions.

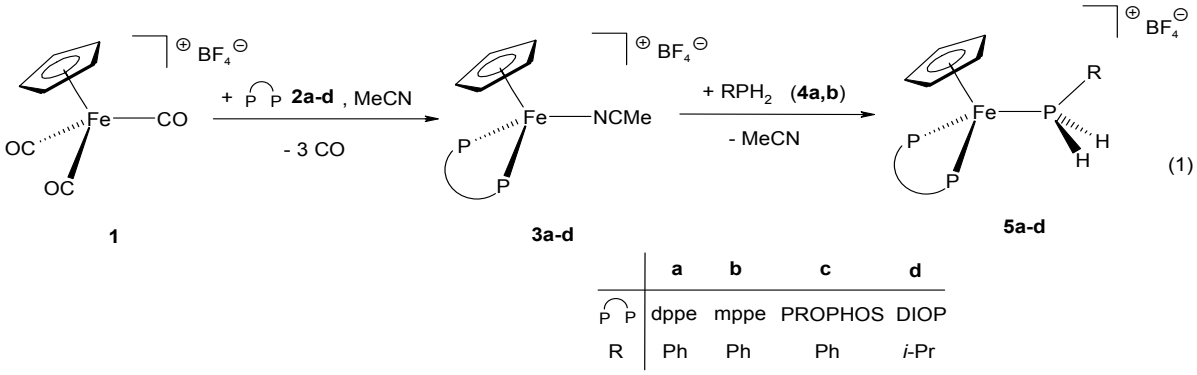
Results and Discussion

Primary Phosphine Iron and Ruthenium Complexes $[H_5C_5(P_{[2]})FeP(R)H_2]BF_4$ [$P_{[2]}$ = dppe, mppe, (*R*)-(+)-PROPHOS, (*R,R*)-(–)-DIOP; R = Ph, *i*-Pr] (5a-d) and $[H_5C_5(DIOP)RuP(Ph)H_2]BF_4$ (9)

Irradiation of the cationic iron complex $[(H_5C_5)Fe(CO)_3]BF_4$ (**1**) in the presence of one equivalent dppe (**2a**) or mppe (**2b**) in acetonitrile for 2-3 h results in the exchange of all carbonmonoxide ligands against the chelate phosphine and a solvent molecule to give the chelate phosphine acetonitrile iron complexes **3a,b** (eq. 1). Under the same conditions the chiral chelate phosphines PROPHOS (**2c**) and DIOP (**2d**) were introduced at the iron centre to yield the iron complexes **3c,d**. During the chelate phosphine/CO and CO/MeCN exchange the color of the solution turned from yellow to red. Precipitation of **3a-d** as violet or red fine-grained powders from solution in acetonitrile was achieved by addition of diethylether in yields of 83 % (**3b**) to 98 % (**3c**). **3b-d** are characterized by a stereogenic iron atom due to the inequivalence of the phosphorus donor atoms. **3c** is obtained as a mixture of diastereomers due to the chiral C-atom of the PROPHOS ligand. The diastereomeric ratio amounts to 95 : 5 with anti-**3c** strongly dominating having the methyl group orientated opposite to the Cp-ligand with respect to the chelate iron ring plane. This assignment is substantiated by the ^{1}H-

NOESY experiment which proves lack of interaction between the methyl group and the Cp-ligand.

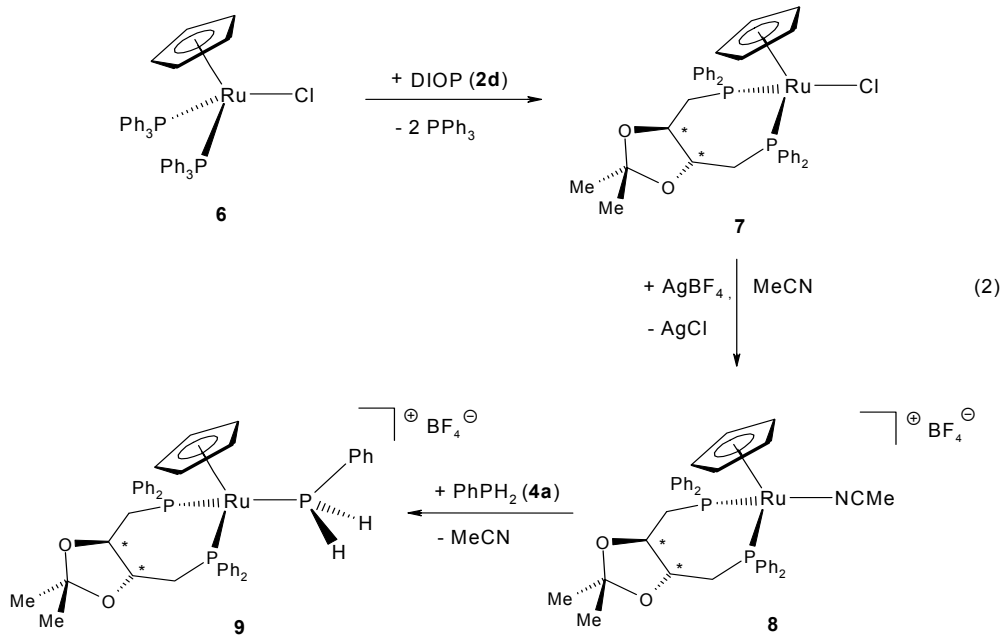
The reaction of the cationic chelate phosphine-acetonitrile iron complexes **3a-d** with the *primary* phosphines $P(R)H_2$ (R = Ph, *i*-Pr) (**4a,b**) at room temperature leads to the *primary* phosphine complexes **5a-d** with liberation of acetonitrile within 2 h (**5d**) to 2 d (**5c**) (eq. 1). **5a-d** are isolated as a yellow (**5b,c**) or orange (**5a,d**) powder, respectively, in yields of 76 % (**5d**) to 92 % (**5b**). **5a-d** can be stored for several months under an atmosphere of nitrogen at room temperature.



	a	b	c	d
P P	dppe	mppe	PROPHOS	DIOP
R	Ph	Ph	Ph	*i*-Pr

Metal chirality becomes evident in the case of **3b-d** from the diastereotopic character of the P-H-protons giving rise to separate ddd-signals in the ^{1}H-NMR-spectrum. The situation concerning the *syn*/*anti*-isomerism of **5c** (ratio: 89:11) is nearly identical to that discussed for the acetonitrile complex **3c**. The ^{31}P-NMR resonances of the chelate phosphine phosphorus of the acetonitrile complexes **3** appear as a singlet at 97.31 for **3a**, two doublets for **3b** (100.11 / 75.60) and **3d** (54.41 / 52.75) and four doublets for the two isomers of **3c** (anti-**3c**: 104.62 / 81.98; syn-**3c**: 106.31 / 92.47) with ^{2}J(PFeP)-coupling constants between 40 and 50 Hz. The ^{31}P-NMR spectrum of the cationic *primary* phosphine complexes **5b-d** shows dd-signals for the *primary* phosphines ligands and each phosphorus atom of the chelating phosphine. **5a** shows for the $PhPH_2$ ligand phosphorus the expected triplet, for dppe a doublet. The phosphorus bound-hydrogens are found in the ^{1}H-NMR spectrum between 5.23 (**5b**) and 4.09 ppm (**5a**) with the characteristic ^{1}J-PH-coupling constant of 315.9 (**5d**) to 358.4 Hz (**5c**).

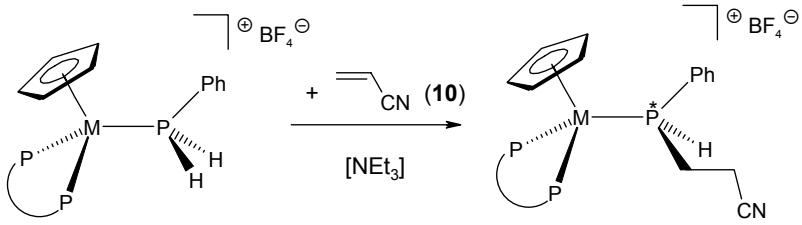
Analogous ruthenium complexes are, as demonstrated for the phenylphosphine-DIOP-complex **9**, accessible in an elegant way by a three step procedure starting from the neutral bis(triphenylphosphine)choro-ruthenium complex **6**. The first step involves a thermally induced exchange of both triphenylphosphine ligand against the chelate phosphine DIOP (**2d**)**,** which is complete in toluene at 60 °C within 4 d (eq. 2). In the subsequent step chloride abstraction from **7** is achieved with silver tetrafluoroborate in acetonitrile to give the cationic acetonitrile ruthenium complex **8** after a reaction time of 30 min (eq. 2). Final conversion of **8** with $P(Ph)H_2$ (**4a**) to the *primary* phosphine ruthenium complex **9** is performed in dichloromethane in the presence of an equimolar amount of phenylphosphine (**4a**) within 4 d at room temperature (eq.2).



7 - 9 are obtained as yellow microcrystalline powders in 73 % (**8**) to 78 % (**9**) yield. While **7** shows good solubility in benzene or toluene, **8** and **9** are only soluble in polar solvents like acetonitrile or dichloromethane. The ^{1}H-NMR spectrum of **9** exhibits the PH-resonances of the epimers with the characteristic ^{1}J-PH-coupling constants of 349.0 / 364.7 Hz. The ^{31}P-NMR-spectrum of **9** shows for the phosphorus donors three dd-signals at 34.40, 32.63 (DIOP) and – 24.29 ppm for the *primary* phosphorus atom.

Hydrophosphination Reactions of Acrylonitrile (10) with $[H_5C_5(P_{[2]})Fe[P(R)H_2]BF_4$ [$P_{[2]}$ = mppe, (*R*)-(+)-PROPHOS, (*R*,*R*)-(–)-DIOP; R = Ph, *i*-Pr] (5b-d) and $[H_5C_5$(DIOP)Ru $[P(Ph)H_2]BF_4$ (9)

Hydrophosphination of acrylonitrile (**10**) with the *primary* phosphine complexes **5b,c** and **9** in acetonitrile catalyzed by a trace of triethylamine leads within 2 d (**11b,c**) to 3 d (**11a**) to the formation of the corresponding cyanoethyl(phenyl)phosphine complexes **11a-c** (eq. 4).



(4)

5b,c; 9

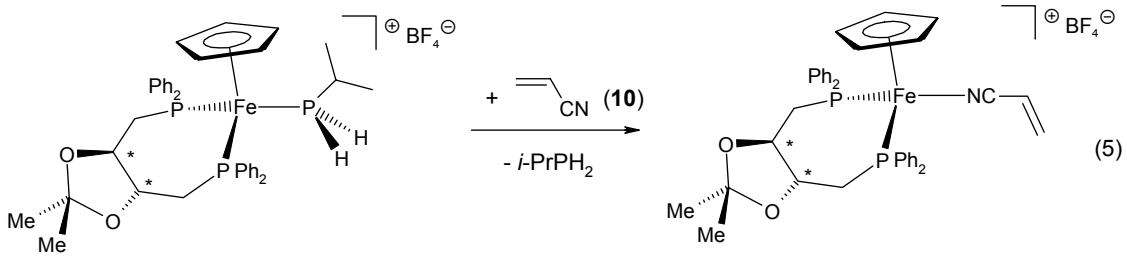
11	**a**	**b**	**c**
P P	mppe	PROPHOS	DIOP
M	Fe	Fe	Ru

Precipitation of the complexes **11a-c** as green (**11c**) or yellow (**11a,b**) powders from solution was achieved by addition of diethylether in yields of 74% (**11b**) to 95 % (**11a**). **11a,c** are isolated as diastereomeric mixtures [ratio: 68:32 (**11a**), 83:17 (**11c**)], **11b** due to *syn*/*anti*-isomerism with respect to the methyl substituent of the PROPHOS ligand and the chirality of the phosphorus and the metal as a mixture of four stereoisomers in the ratio of 62:26:8:4, indicating a *syn*/*anti*-ratio identical with that of **5c**.

The monoinsertion of acrylonitrile (**10**) is proved by the significant low-field shift of the ^{31}P-NMR-resonance of the *primary* phosphine ligand from –5.81 (**5b**) / 0.79 (anti-**5c**) / - 24.29 (**9**) to 50.86/45.88 (**11a**/**11a'**) / 50.10/49.68 (anti-**11b**/anti-**11b'**) / 27.80/24.92 (**11c**/**11c'**). Moreover chirality of the *secondary* phosphine ligand in the complexes **11a-c** is indicated by

a doubling of the resonance of the P-bound hydrogens at 4.92 / 4.64 (**11a/11a'**) / 4.63 (anti-**11b**) and 5.50 / 5.11 (**11c/11c'**) in relation to **5b,c,9** due to diastereomerism.

In contrast to the behaviour of the phenylphosphine complexes **5b,c,9** the treatment of the isopropylphosphine iron complex **5d** with acrylonitrile (**10**) generates only a cationic iron complex **12** with a N-coordinated acrylonitrile ligand due to phosphine substitution (eq. 5). There is no indication for an insertion of the acrylonitrile into the PH-function. **12** is isolated as brown fine-grained powder after a reaction time of 1 d in yield of 84 %.



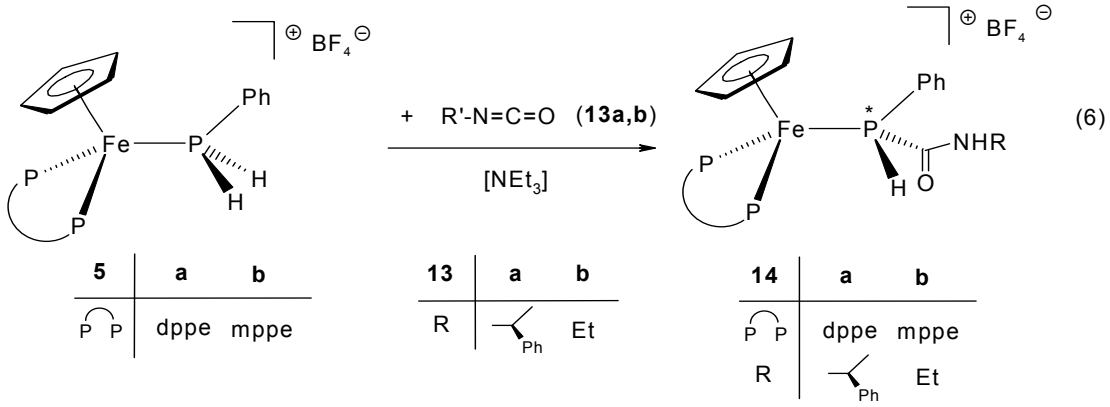
(5)

5d **12**

The structure of **12** is proved by the ^{31}P-NMR spectrum indicating the presence of only two phosphorus atoms by the two doublets at 54.16 and 52.52 ppm, characteristic for a DIOP ligand, with a ^{2}J(PFeP)-coupling constant of about 48.6 Hz. Moreover the ^{1}H-NMR resonance for the vinyl hydrogen is found between 6.23 and 5.72 ppm and the ^{13}C-NMR-resonances of the olefinic carbons appear at 136.54 and 129.70.

Hydrophosphination of the Isocyanates RNCO [R = (S)-1-phenylethyl, ethyl] (13a,b) with $[H_5C_5(P_{[2]})Fe[P(Ph)H_2]BF_4$ [$P_{[2]}$ = dppe, mppe] (5a,b)

In order to conceive the asymmetric induction of a chiral organic auxiliary group, bound to the insertion reagent, **5a** was reacted with (S)-1-phenylethyl-isocyanate (**13a**) to give the carbamoyl(phenyl)phosphine iron complex **14a** (eq. 6). After heating the reaction mixture in acetonitrile for 3 h to 70 °C **14a** is obtained in 98 % yield.



The diastereomeric ratio of 96:4 indicates a surprisingly high stereocontrol by the organic ligand.

Analogously ethylisocyanate (**13b**) reacts with **5b** (2h, 70°C), gives rise to the formation of a 58:42-mixture of diastereomers in 96 % yield indicating low effectiveness of the chiral iron atom with respect to an asymmetric induction.

The ^{31}P-NMR spectra of **14a,b** show dd-signals for the phosphorus of the *secondary* phosphine and the phosphorus atoms of the chelate phosphine [93.85 / 92.69 / 46.08 (**14a**)] [98.06 / 66.42 / 50.11 (**14b**), 98.03 / 70.96 / 47.35 (**14b'**)]. The chirality of the *secondary* phosphine ligands in the complexes **14b** is substantiated by a doubling of the resonance of the P-bound hydrogens at 6.18 / 5.64 (**14b**/**14b'**) in relation to **5b** due to diastereomerism.

Molecular structure of [H_5C_5(DIOP)RuNCMe]BF_4 (8) and {H_5C_5[$Ph_2P(CH_2)_2Me_2P$] Fe[PH(Ph)[(C=O)NHEt]]}BF_4 (14b)

Suitable crystal for the structure determination of **8** and **14b** are obtained from a saturated acetonitrile solution at room temperature.

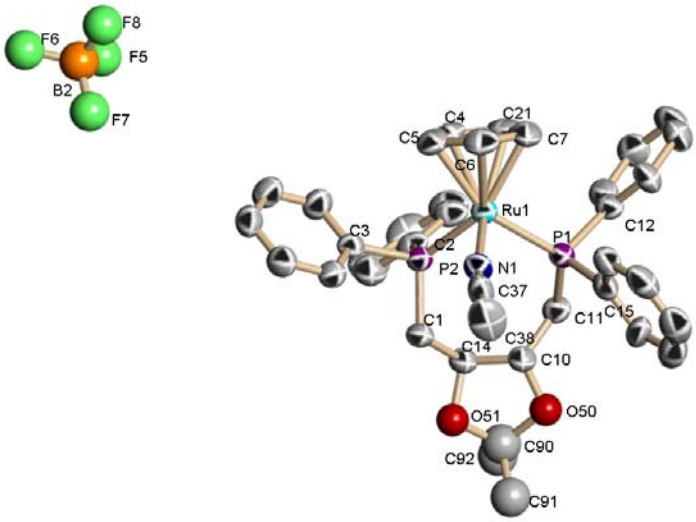


figure 1: *Molecular structure and Newman projection (View along the Ru1-N1-axis)of [H_5C_5 (–)-(DIOP)RuNCMe]BF_4 (**8**). The BF_4-anion and hydrogen atoms have been omitted for clarity.*

Selected bond lengths [pm], bond and torsion angles[°]: Ru(1)-P(2) 229.26(14), Ru(1)-P(1) 230.53(15), Ru(1)-N(1) 205.7(5), N(1)-C(37) 113.1(8), C(37)-C(38) 144.9(10), N(1)-Ru(1)-P(2) 90.65(13), N(1)-Ru(1)-P(1) 90.19(14), P(2)-Ru(1)-P(1) 98.61(5), C(37)-N(1)-Ru(1) 168.0(5), N(1)-C(37)-C(38) 175.7(7).

The pseudo-octahedral geometry of **8** is confirmed by the N1-Ru1-P1, N1-Ru1-P2 and P1-Ru1-P2 angles, which are all close 90° [N(1)-Ru(1)-P(2) 90.65(13)°, N(1)-Ru(1)-P(1) 90.19(14)°, P(2)-Ru(1)-P(1) 98.61(5)°]. This values agree well with the literature known values of the DIOP ruthenium complex [C_5H_5(+)-(DIOP)RuNCMe]PF_6 [N-Ru-P 88.7(4)°, N-Ru-P 90.4(3)°, P-Ru-P 98.92(15)°].[12] The Ru-P bond lengths [Ru(1)-P(2) 229.26(14) pm,

Ru(1)-P(1) 230.53(15) pm] and the Ru-N1 bond length [Ru(1)-N(1) 205.7(5) pm] are similar to that of the above mentioned Ru-DIOP-complex with distances of 229.6(3) pm, 230.3(4) pm for the Ru-P bonds and 204.7(14) pm for the Ru-N bond.[12] The DIOP ligand in **8** adopts a twisted chair conformation [fig. (1)]. The nitrile group shows an almost linear geometry with Ru1-N1-C37 and N1-C37-C38 angles of 168.0(5)° and 175.7(7)°, which indicate that the ruthenium atom and the acetonitrile ligand are almost in the same plane [fig. (1)].

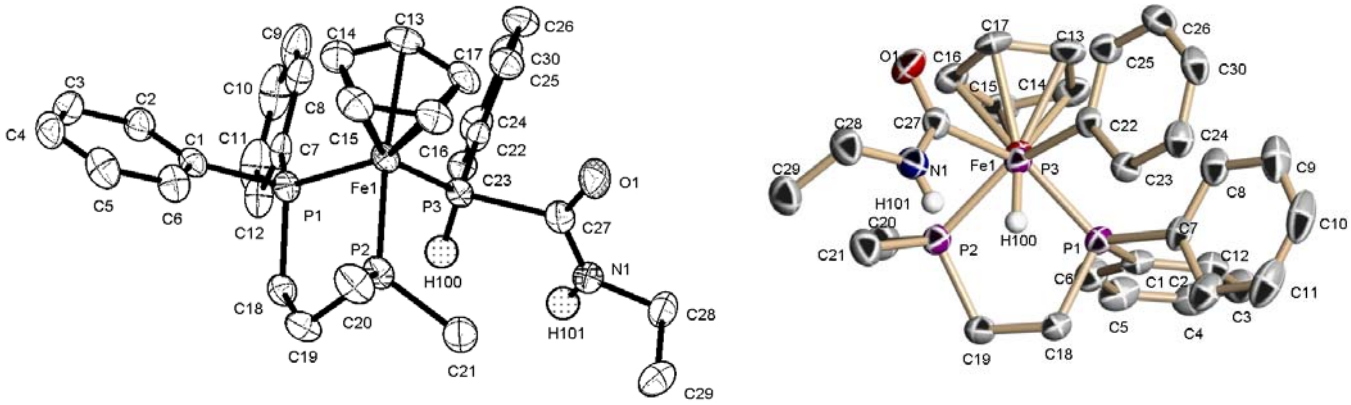


figure 2: *Molecular structure a.) and Newman projection (View along the Fe1-P3-axis) of* $\{H_5C_5[Ph_2P(CH_2)_2Me_2P]Fe[PH(Ph)[(C{=}O)NHEt]]\}BF_4$ ***(14b)****. The* BF_4*-anion and hydrogen atoms except PH have been omitted for clarity.*

Selected bond lengths [pm], bond and torsion angles[°]: Fe1-P1 216.81(10), Fe1-P2 218.31(9), Fe1-P3 216.26(10), P3-C27 187.4(3), C27-N1 132.9(4); P1-Fe1-P2 86.49(3), P1-Fe1-P3 90.52(3), P2-Fe1-P3 92.44(3), Fe1-P3-C27 116.95(11), Fe1-P3-H100 114.0(13), Fe1-P3-C22 123.88(10), P3-C27-N1 115.0(2), C22-P3-C27 98.88(13), P(1)-Fe(1)-P(3)-C(27) -159.01(11), P(2)-Fe(1)-P(3)-C(27) -72.50(11), P(1)-Fe(1)-P(3)-C(22) 77.62(12), P(2)-Fe(1)-P(3)-C(22) 164.13(12), Cp_z-Fe1-P3-C22 – 65.8, Cp_z-Fe1-P3-C27 57.0.

The molecular structure of the complex **14b** shows a pseudo-octahedral coordination of the iron atom with a P1-Fe1-P2 angle involving the two mppe phosphorus atoms smaller than the ideal value of 90° [86.49(3)°], while the angles including the phosphorus atom of the *secondary* phosphine ligand are slightly larger [(P1-Fe1-P3) 90.52(3)° and (P2-Fe1-P3) 92.44(3)°]. The bond lengths Fe1-P1 [216.81(10) pm] and Fe1-P2 [218.31(9) pm] lie in the literature-known range for comparable compounds {$[H_5C_5(dppe)Fe(H)_2]BF_4$ 217.0(2) pm, 216.6(2) pm}.[13, 14] The phosphorus atom of the *secondary* phosphine ligand of **14b** shows distorted tetrahedral coordination, indicated by the angles Fe1-P3-C27 [116.95(11)°], Fe1-P3-C22 [123.88(10)°] and C22-P3-C27 [98.88(13)°]. The angles including the metal fragment are enlarged which is in accordance with the literature-known values {$[H_5C_5(1,2\text{-}C_6H_4(PMePh)_2)Fe(PHMePh)_2]PF_6$ 121.2(2)°, 116.6(2)°}[15]. The Newman projection in fig. (2b.) shows that both organo groups of the *secondary* phosphine occupies the *gauche* position with respect to the cyclopentadienyl ligand [Cp_z-Fe(1)-P(3)-C(22) – 65.8°, Cp_z-Fe(1)-P(3)-C(27) 57.0°, P(2)-Fe(1)-P(3)-C(22) 164.13(12)°, P(1)-Fe(1)-P(3)-C(27) -159.01(11)°].

Experimental Section

General: All manipulations were performed under purified nitrogen using standard Schlenk techniques. Solvents were rigorously dried over an appropiate drying agent and distilled under nitrogen prior to use. ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were obtained on a Bruker AMX 400 and a Jeol JNM-LA300 spectrometer. Melting points were determined by Differential Thermo Analysis (DTA) with the Du Pont Thermal Analysis System 9000. Elemental analyses were performed in the laboratories of the "Institut für Anorganische Chemie". – Starting materials: $[H_5C_5(OC)_3Fe]BF_4$[16], $H_5C_5(Ph_3P)_2RuCl$[17], H_5C_5(DIOP)RuCl[18] and $[H_5C_5$(DIOP)Ru NCMe$]BF_4$[12] were synthesized according to the literature procedures. The insertion reagences acrylonitrile, ethylisocyanate and (S)-1-phenylethyl-isocyanate were obtained commercially.

*1. {Acetonitrile[1,2-bis(diphenylphosphino-κ^2P)ethane](η^5-cyclopentadienyl)iron(II)} tetrafluoroborate (**3a**)*

To a solution of 3.00 g (10.28 mmol) of $[H_5C_5(OC)_3Fe]BF_4$ (**1**) in 120 ml acetonitrile 4.10 g (10.28 mmol) of dppe (**2a**) are added. The reaction mixture is irradiated for 3 h at ambient temperature and then reduced in vacuum to a volume of 15 ml. **3a** is precipitated by addition of 60 ml of diethylether, separated by filtration, washed three times with 10 ml of diethylether and dried in vacuum. - Yield 6.32 g (95%). – Red microcrystalline powder. - M.p. 131°C. – $C_{33}H_{32}BF_4FeNP_2$ (647.22). calc.: C 61.24, H 4.98, N 2.16. found: C 61.20, H 4.84, N 2.17. - **^{1}H-NMR** (CD_3CN, 400.1 MHz): δ = 7.84 - 7.35 (m, 20 H, H_5C_6), 4.34 [t, ^{3}J(PFeCH) = 1.4 Hz, 5 H, H_5C_5], 2.57 - 2.32 (m, 4 H, H_2C), 1.88 ppm (s, 3 H, H_3C). - **^{13}C-{^{1}H}-NMR** (CD_3CN, 100.6 MHz): δ = 136.48 - 128.52 (m, C_6H_5, CN), 78.47 (s, C_5H_5), 27.15 [vt, $|{}^{1}J(PC) + {}^{2}J(PC)|$ = 21.1 Hz, CH_2CH_2], 2.41 ppm (s, CH_3). - **^{31}P-{^{1}H}-NMR** (CD_3CN, 162.0 MHz): δ = 97.31 ppm (s).

*2. {Acetonitrile(η^5-cyclopentadienyl)[(dimethydiphenylphosphino-κ^2P)ethane]iron(II)} tetrafluoroborate (**3b**)*

According to **3a** from 1.17 g (4.00 mmol) of $[H_5C_5(OC)_3Fe]BF_4$ (**1**) and 1.10 g (4.00 mmol) of mppe (**2b**) in 30 ml acetonitrile after 2.5 h UV-irradiation. - Yield 1.73 g (83%). – Red microcrystalline powder. - M.p. 89°C (dec.). – $C_{23}H_{28}BF_4FeNP_2$ (523.08). calc.: C 52.81, H 5.40, N 2.68. found: C 52.57, H 5.34, N 2.70. - **^{1}H-NMR** (CD_3CN, 300.4 MHz): δ = 7.89 - 7.14 (m, 10 H, H_5C_6), 4.27 [t, ^3J(PFeCH) = 1.7 Hz, 1.5 Hz, 5 H, H_5C_5], 2.39 - 2.23 (m, 2 H, H_2C), 1.95 (s, 3 H, H_3C), 1.86 [d, ^2J(PCH) = 9.3 Hz, 3 H, H_3CP], 1.79-1.63 (m, 2 H, H_2C), 1.58 ppm [d, ^2J(PCH) = 10.2 Hz, 3 H, H_3CP]. - **^{13}C-{^{1}H}-NMR** (CD_3CN, 75.45 MHz): δ = 138.34 [d, ^1J(PC) = 40.6 Hz, *i*-C], 133.38 [d, ^2J(PCC) = 9.7 Hz, *o*-C], 132.35 [d, ^1J(PC) = 36.2 Hz, *i*-C], 131.74 [d, ^3J(PCCC) = 10.0 Hz, *m*-C], 130.95 [d , ^4J(PCCCC) = 2.4 Hz, *p*-C], 130.42 [d, ^4J(PCCCC) = 2.4 Hz, *p*-C], 129.25 [dd, ^3J(PFeCN) = 8.6 Hz, ^3J(PFeCN) = 8.3 Hz, N<u>C</u>CH_3], 78.43 [t, ^2J(PFeC) = 1.1 Hz, C_5H_5], 29.21 [dd, ^1J(PC) = 29.5 Hz, ^2J(PCC) = 14.1 Hz, PCH_2], 28.02 [dd, ^1J(PC) = 29.1 Hz, ^2J(PCC) = 13.1 Hz, PCH_2], 17.17 [d, ^1J(PC) = 29.4 Hz, PCH_3], 14.83 [d, ^1J(PC) = 23.5 Hz, PCH_3], 4.18 ppm (s, NC<u>C</u>H_3). - **^{31}P-{^{1}H}-NMR** (CD_3CN, 121.5 MHz): δ = 100.11 [d, ^2J(PFeP) = 38.3 Hz, PPh_2], 75.60 ppm [d, ^2J(PFeP) = 38.3 Hz, $P(CH_3)_2$].

*3. {Acetonitrile[(R)-bis(1,2-diphenylphosphino-κ^2P)propane](η^5-cyclopentadienyl)iron(II)} tetrafluoroborate (**3c**)*

Analogous to **3a** from 354 mg (1.21 mmol) of $[H_5C_5(OC)_3Fe]BF_4$ (**1**) and 500 mg (1.21 mmol) of PROPHOS (**2c**) in 35 ml acetonitrile after 3 h UV-irradiation. - Yield 796 mg (99%). - Red powder. - M.p. 83°C (dec.). – $C_{34}H_{34}BF_4FeNP_2$ (661.25). calc.: C 61.76, H 5.18, N 2.12. found: C 61.74, H 5.28, N 2.05. – **3c / 3c'** = 95 : 5. The isomeric ratio is determined by integration of the C_5H_5-signals in the ^{1}H-NMR-spectrum. - **^{1}H-NMR** (CD_3CN, 300.4 MHz) : δ = 7.96 - 7.14 (m, 20 H, H_5C_6), 4.25 [dd, ^3J(PFeCH) = 1.5 Hz, ^3J(PFeCH) = 1.5 Hz, 5

H, H_5C_5], 3.01 [ddd, ^2J(PCH) = 47.3 Hz, ^3J(PCCH) = 11.8 Hz, ^3J(HCCH) = 9.7 Hz, 1 H, $\underline{H}CCH_3$], 2.12 - 2.02 (m, 2 H, H_2C), 1.95 (s, 3 H, H_3CCN), 1.09 ppm [dd, ^3J(PCCH) = 10.6 Hz, ^4J(PCCCH) = 5.3 Hz, 3 H, $\underline{H}_3CCH$]. - **^{13}C-{^{1}H}-NMR** (CD_3CN, 75.45 MHz) : δ = 137.93 [d, ^1J(PC) = 43.5 Hz, *i*-C], 135.75 [d, ^2J(PCC) = 10.3 Hz, *o*-C], 134.16 [d, ^3J(PCCC) = 10.0 Hz, *m*-C], 133.62 [d, ^1J(PC) = 41.3 Hz, *i*-C], 132.24 [d, ^2J(PCC) = 10.7 Hz, *o*-C], 132.01 [d, ^3J(PCCC) = 9.3 Hz, *m*-C], 131.49 [d, ^4J(PCCCC) = 2.4 Hz, *p*-C], 129.92 [d, ^3J(PFeCN) = 9.4 Hz, $N\underline{C}CH_3$], 129.70 [d, ^4J(PCCCC) = 1.5 Hz, *p*-C], 79.77 [d, ^2J(PFeC) = 1.1 Hz, C_5H_5], 34.65 [dd, ^1J(PC) = 29.4 Hz, ^2J(PCC) = 17.1 Hz, $\underline{C}HCH_3$], 32.21 [dd, ^1J(PC) = 26.2 Hz, ^2J(PCC) = 13.5 Hz, CH_2P], 16.27 [dd, ^2J(PCC) = 17.1 Hz, ^3J(PCCC) = 5.8 Hz, $\underline{C}H_3CH$], 15.59 ppm (s, $\underline{C}H_3CN$). - **^{31}P-{^{1}H}-NMR** (CD_3CN, 121.5 MHz) : **3c**: δ = 104.62 [d, ^2J(PFeP) = 46.2 Hz, PPh_2], 81.98 ppm [d, ^2J(PFeP) = 46.2 Hz, PPh_2]; **3c'**: δ = 106.31 [d, ^2J(PFeP) = 48.9 Hz, PPh_2], 92.47 ppm [d, ^2J(PFeP) = 48.9 Hz, PPh_2].

*4. {Acetonitrile[(4R,5R)-(–)bis(diphenylphosphino-κ^{2}P-methyl)-2,2-dimethyl-1,3-dioxolane] (η^5-cyclopentadienyl)iron(II)}tetrafluoroborate (**3d**)*

According to **3a** from 468 mg (1.60 mmol) $[H_5C_5(OC)_3Fe]BF_4$ (**1**) and 800 mg (11.5 mmol) of (–)-DIOP (**2d**) in 30 ml acetonitrile after 3 h UV-irradiation. - Yield 1.10 g (92%). - Violet microcrystalline powder. - M.p. 184°C (dec.). – $C_{38}H_{40}BF_4FeNO_2P_2$ (747.34). calc.: C 61.07, H 5.40, N 1.87. found: C 61.14, H 5.60, N 1.88. - **^{1}H-NMR** (CD_3CN, 300.4 MHz): δ = 8.05 - 7.24 (m, 20 H, H_5C_6), 3.90 [t, ^3J(PFeCH) = 1.7 Hz, 5 H, H_5C_5], 3.46 - 3.38 (m, 1 H, HC), 3.20 - 2.98 (m, 2 H, H_2C), 3.11 - 3.05 (m, 1 H, HC), 2.36 - 2.17 (m, 2 H, H_2C), 1.95 (s, 3 H, H_3CCN), 1.17 (s, 3 H, H_3C), 1.09 ppm (s, 3 H, H_3C). - **^{13}C-{^{1}H}-NMR** (CD_3CN, 75.45 MHz): δ = 142.23 [dd, ^1J(PC) = 42.4 Hz, ^3J(PFePC) = 5.0 Hz, *i*-C], 139.29 [d, ^1J(PC) = 43.8 Hz, *i*-C], 137.43 (s, $CH_3\underline{C}N$), 134.63 [d, ^2J(PCC) = 11.7 Hz, *o*-C], 134.39 [d, ^2J(PCC) = 10.0 Hz, *o*-C], 132.55 [d, ^4J(PCCCC) = 2.1 Hz, *p*-C], 131.46 [dd, ^1J(PC) = 33.8 Hz, ^3J(PFePC) =

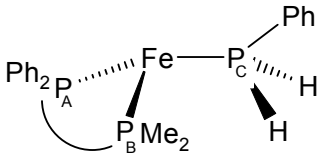
1.7 Hz, *i*-C], 131.37 [d, ^{4}J(PCCCC) = 2.4 Hz, *p*-C], 130.75 [d, ^{2}J(PCC) = 8.3 Hz, *o*-C], 130.48 [d, ^{1}J(PC) = 39.3 Hz, *i*-C], 130.03 [d, ^{4}J(PCCCC) = 2.4 Hz, *p*-C], 129.95 [d, ^{4}J(PCCCC) = 2.3 Hz, *p*-C], 129.79 [d, ^{2}J(PCC) = 8.7 Hz, *o*-C], 129.78 [d, ^{3}J(PCCC) = 9.9 Hz, *m*-C], 129.39 [d, ^{3}J(PCCC) = 9.3 Hz, *m*-C], 129.05 [d, ^{3}J(PCCC) = 9.0 Hz, *m*-C], 128.93 [d, ^{3}J(PCCC) = 9.3 Hz, *m*-C], 108.79 [s, $\underline{C}(CH_3)_2$], 80.26 [t, ^{2}J(PFeC) = 1.0 Hz, C_5H_5], 78.68 [dd, ^{2}J(PCC) = 8.6 Hz, ^{3}J(PCCC) = 2.0 Hz, CH], 75.39 [d, ^{2}J(PCC) = 12.4 Hz, CH], 31.65 [dd, ^{1}J(PC) = 24.1 Hz, ^{3}J(PFePC) = 4.5 Hz, CH_2], 28.45 [d, ^{1}J(PC) = 18.6 Hz, CH_2], 26.42 [s, ($\underline{C}H_3$)C], 26.22 [s, ($\underline{C}H_3$)C], 1.11 ppm (s, $H_3\underline{C}CN$). - **^{31}P-{^{1}H}-NMR** (CD_3CN, 121.5 MHz): δ = 54.41 [d, ^{2}J(PFeP) = 48.6 Hz], 52.75 ppm [d, ^{2}J(PFeP) = 48.6 Hz].

*5. {[1,2-Bis(diphenylphosphino-κ^{2}P)ethane](η^{5}-cyclopentadienyl)(phenylphosphine)iron(II)} tetrafluoroborate (**5a**)*

To a solution of 2.94 g (4.54 mmol) of $[H_5C_5(dppe)Fe(NCMe)]BF_4$ (**3a**) in 60 ml dichloromethane 500 mg (4.54 mmol) of $PhPH_2$ (**4a**) are added. The reaction mixture is stirred for 1 d at ambient temperature and then reduced in vacuum to a volume of 10 ml. **5a** is precipitated by addition of 50 ml of diethylether, separated by filtration, washed three times with 10 ml of diethylether and dried in vacuum. - Yield 2.97 g (91%). – Orange microcrystalline powder. - M.p. 123°C (dec.). – $C_{37}H_{36}BF_4FeP_3$ (716.27). calc.: C 62.04, H 5.07. found: C 61.78, H 5.05. - **^{1}H-NMR** (CD_3CN, 300.4 MHz): δ = 7.72 - 6.52 (m, 25 H, H_5C_6), 4.79 [dt, ^{1}J(PH) = 346.3 Hz, ^{3}J(PFePH) = 5.4 Hz, 2 H, HP], 4.49 [dt, ^{4}J(PFeCH) = 2.2 Hz, ^{4}J(PFeCH) = 1.3 Hz, 5 H, H_5C_5], 2.69 - 2.39 ppm [m, 4 H, $(CH_2)_2$]. - **^{13}C-{^{1}H}-NMR** (CD_3CN, 75.45 MHz): δ = 138.83 [dd, ^{1}J(PC) = 38.3 Hz, ^{3}J(PFePC) = 3.8 Hz, *i*-C_{dppe}], 138.65 [ddd, ^{1}J(PC) = 29.9 Hz, ^{3}J(PFePC) = 3.9 Hz, ^{3}J(PFePC) = 1.8 Hz, *i*-C_{dppe}], 133.18 [vt, $|^{2}J$(PCC) + ^{4}J(PFePCC)$|$ = 4.8 Hz, *o*-C_{dppe}], 132.78 [d, ^{2}J(PCC) = 8.9 Hz, *o*-C], 132.27 [vt, $|^{2}J$(PCC) + ^{4}J(PFePCC)$|$ = 4.8 Hz, *o*-C_{dppe}], 131.86 [vt, $|^{4}J$(PCCCC) + ^{6}J(PFePCCCC)$|$ = 1.0

Hz, *p*-C_{dppe}], 131.28 [vt, $|^4J(PCCCC) + {}^6J(PFePCCCC)|$ = 1.1 Hz, *p*-C_{dppe}], 131.04 [d, $^4J(PCCCC)$ = 2.4 Hz, *p*-C], 130.22 [vt, $|^3J(PCCC) + {}^5J(PFePCCC)|$ = 4.8 Hz, *m*-C_{dppe}], 132.83 [vt, $|^3J(PCCC) + {}^5J(PFePCCC)|$ = 4.8 Hz, *m*-C_{dppe}], 129.69 [d, $^3J(PCCC)$ = 10.3 Hz, *m*-C], 127.99 [dt, $^1J(PC)$ = 47.9 Hz, $^3J(PFePC)$ = 2.1 Hz, *i*-C], 81.24 [td, $^2J(PFeC)$ = 1.0 Hz, $^2J(PFeC)$ = 0.8 Hz, C_5H_5], 27.77 ppm [vtd, $|^1J(PC) + {}^3J(PFePC)|$ = 21.7 Hz, $^3J(PFePC)$ = 1.4 Hz, $(CH_2)_2$]. - **^{31}P-{^{1}H}-NMR** (CD_3CN, 121.5 MHz): δ = 95.74 [d, $^2J(PFeP)$ = 55.9 Hz, PPh_2], -3.59 ppm [t, $^2J(PFeP)$ = 55.9 Hz, $P(H)_2Ph$].

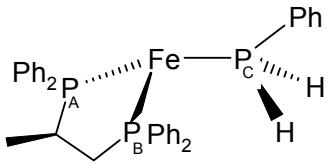
*6. {(η^5-Cyclopentadienyl)[(dimethydiphenylphosphino-κ^2P)ethane](phenylphosphine)iron(II)} tetrafluoroborate (**5b**)*



Analogous to **5a** from 1.73 g (3.31 mmol) of $[H_5C_5(mppe)Fe(NCMe)]BF_4$ (**3b**) and 364 mg (3.31 mmol) of $PhPH_2$ (**4a**) in 30 ml dichloromethane after 4 h. - Yield 1.79 g (92%). – Yellow microcrystalline powder. - M.p. 89°C (dec.). – $C_{27}H_{32}BF_4FeP_3$ (592.13). calc.: C 54.77, H 5.45. found: C 54.65, H 5.46. - **^{1}H-NMR** (CD_3CN, 300.4 MHz): δ = 7.65 7.05 (m, 15 H, H_5C_6), 5.23 [ddt, $^1J(PH)$ = 340.8 Hz, $^2J(HPH)$ = 5.4 Hz, $^3J(PFePH)$ = 5.9 Hz, $^3J(PFePH)$ = 5.9 Hz, 1 H, HP], 5.11 [dddd, $^1J(PH)$ = 342.6 Hz, $^2J(HPH)$ = 5.4 Hz, $^3J(PFePH)$ = 5.5 Hz, $^3J(PFePH)$ = 4.6 Hz, 1 H, HP], 4.47 [ddd, $^3J(PFeCH)$ = 1.5 Hz, 0.9 Hz, 0.8 Hz, 5 H, H_5C_5], 2.54 - 2.38 (m, 2 H, H_2CP), 2.19 - 1.96 (m, 2 H, H_2CP), 1.85 [d, $^2J(PCH)$ = 9.3 Hz, 3 H, H_3CP], 1.43 ppm [dd, $^2J(PCH)$ = 9.5 Hz, $^4J(PFePH)$ = 2.0 Hz, 3 H, H_3CP]. - **^{13}C-{^{1}H}-NMR** (CD_3CN, 75.45 MHz): δ = 136.35 [d, $^1J(PC)$ = 39.4 Hz, *i*-C], 136.21 [d, $^1J(PC)$ = 37.8 Hz, *i*-C], 133.70 [d, $^2J(PCC)$ = 9.4 Hz, *o*-C], 133.29 [d, $^1J(PC)$ = 42.3 Hz, *i*-C], 132.25 [d , $^2J(PCC)$ = 10.0 Hz, *o*-C], 131.82 [d, $^4J(PCCCC)$ = 2.4 Hz, *p*-C], 131.31 [d, $^4J(PCCCC)$ = 2.8 Hz, *p*-C], 131.19 [d, $^4J(PCCCC)$ = 2.4 Hz, *p*-C], 129.83 [d, $^3J(PCCC)$ = 9.9 Hz, *m*-C], 129.74 [d, $^3J(PCCC)$ = 9.7 Hz, *m*-C], 78.43 [dd, $^2J(PFeC)$ = 1.1 Hz, 0.7 Hz, H_5C_5], 29.35 [dd, $^1J(PC)$

= 30.7 Hz, ^{2}J(PCC) = 14.1 Hz, CH_2], 28.35 [dd, ^{1}J(PC) = 32.8 Hz, ^{2}J(PCC) = 11.8 Hz, CH_2], 20.66 [dd, ^{1}J(PC) = 30.0 Hz, ^{3}J(PFePC) = 3.4 Hz, CH_3], 18.42 ppm [ddd, ^{1}J(PC) = 27.2 Hz, ^{3}J(PFePC) = 6.9 Hz, 1.1 Hz, CH_3]. - **^{31}P-{^{1}H}-NMR** (CD_3CN, 121.5 MHz) : δ = 99.43 [dd, $^{2}J(P_CFeP_A)$ = 54.1 Hz, $^{2}J(P_BFeP_A)$ = 32.8 Hz, P_APh2], 70.73 [dd, $^{2}J(P_CFeP_B)$ = 63.2 Hz, $^{2}J(P_AFeP_B)$ = 32.8 Hz, $P_B(CH_3)_2$], - 5.81 ppm [dd, $^{2}J(P_BFeP_C)$ = 63.2 Hz, $^{2}J(P_AFeP_C)$ = 54.1 Hz, P_CPhH_2].

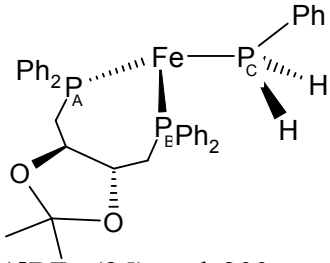
*7. {[(R)-Bis(1,2-diphenylphosphino-κ^{2}P)propane](η^{5}-cyclopentadienyl)(phenylphosphine) iron(II)}tetrafluoroborate(**5c**)*



According to **5a** from 860 mg (1.30 mmol) of $[H_5C_5(PROPHOS)Fe(NCMe)]BF_4$ (**3c**) and 143 mg (1.30 mmol) of $PhPH_2$ (**4a**) in 25 ml dichloromethane after 1 d. - Yield 721 mg (76%). - Yellow powder. - M.p. 93°C (dec.). – $C_{38}H_{38}BF_4FeP_3$ (730.29). calc.: C 62.50, H 5.25. found: C 61.99, H 5.23. – **5c / 5c'** = 89 : 11. The isomeric ratio is determined by integration of the C_5H_5-signals in the ^{1}H-NMR-spectrum.* - **^{1}H-NMR** ($CDCl_3$, 300.4 MHz) **5c**: δ = 7.62 - 7.35 (m, 25 H, H_5C_6), 4.72 [ddd, ^{1}J(PH) = 358.4 Hz, ^{2}J(HPH) = 5.3 Hz, ^{3}J(PFePH) = 12.3 Hz, 1 H, HP], 4.50 [ddd, ^{1}J(PH) = 336.8 Hz, ^{2}J(HPH) = 5.5 Hz, ^{3}J(PFePH) = 8.1 Hz, 1 H, HP], 4.33 (s, 5 H, H_5C_5), 4.26 (s, 5 H, H_5C_5) [**5c'**] 3.12 - 2.96 (m, 1 H, HCP), 2.61 - 2.54 (m, 1 H, H_2CP), 1.95 - 1.86 (m, 1 H, H_2CP), 1.16 ppm [dd, ^{3}J(PCCH) = 11.4 Hz, ^{3}J(HCCH) = 6.2 Hz, 3 H, H_3CCH]. - **^{13}C-{^{1}H}-NMR** (CD_3CN, 75.45 MHz) **5c**: δ = 138.13 [dd, ^{1}J(PC) = 38.3 Hz, *i*-C], 135.42 [d, ^{2}J(PCC) = 10.0 Hz, *o*-C], 134.43 [d, ^{1}J(PC) = 44.8 Hz, *i*-C], 133.04 [d, ^{3}J(PCCC) = 8.9 Hz, *m*-C], 132.86 (s, *p*-C), 132.52 [d, ^{3}J(PCCC) = 8.2 Hz, *m*-C], 132.19 [d, ^{4}J(PCCCC) = 2.8 Hz, *p*-C], 132.07 [d, ^{3}J(PCCC) = 9.0 Hz, *m*-C], 131.43 [d, ^{4}J(PCCCC) = 2.3 Hz, *p*-C], 131.21 [d, ^{4}J(PCCCC) = 2.4 Hz, *p*-C], 130.45 [d, ^{2}J(PCC) = 9.4 Hz, *o*-C], 130.11 [d, ^{2}J(PCC) = 9.7 Hz, *o*-C], 128.19 [d, ^{1}J(PC) = 49.3 Hz, *i*-C], 81.55 (s, C_5H_5) [**5c'**], 81.15 (s, C_5H_5), 34.36 [dd, ^{1}J(PC) = 28.3 Hz, ^{2}J(PCC) = 15.8 Hz, CHP], 33.16 [dd, ^{1}J(PC) = 29.7 Hz, ^{2}J(PCC) = 13.8

Hz, CH_2P], 16.67 ppm [dd, ^2J(PCC) = 17.3 Hz, ^3J(PCCC) = 5.9 Hz, $\underline{C}H_3CH$]. - **^{31}P-{^{1}H}-NMR** (CD_3CN, 121.5 MHz) : **5c**: δ = 101.31 [dd, $^2J(P_CFeP_A)$ = 53.5 Hz, $^2J(P_BFeP_A)$ = 38.9 Hz, P_APh_2], 75.96 [dd, $^2J(P_CFeP_B)$ = 52.3 Hz, $^2J(P_AFeP_B)$ = 38.9 Hz, P_BPh_2], 0.79 ppm [dd, $^2J(P_AFeP_C)$ = 53.5 Hz, $^2J(P_BFeP_C)$ = 52.3 Hz, P_CPhH_2]; **5c'**: δ = 98.86 [dd, $^2J(P_CFeP_A)$ = 54.7 Hz, $^2J(P_BFeP_A)$ = 35.2 Hz, P_APh_2], 87.10 [dd, $^2J(P_CFeP_B)$ = 52.2 Hz, $^2J(P_AFeP_B)$ = 35.2 Hz, P_BPh_2], - 1.99 ppm [dd, $^2J(P_AFeP_C)$ = 54.7 Hz, $^2J(P_BFeP_C)$ = 52.2 Hz, P_CPhH_2]. * Signals of **5c'** are in brackets. The missing signals of **5c'** are hidden by the signals of the major isomer **5c**.

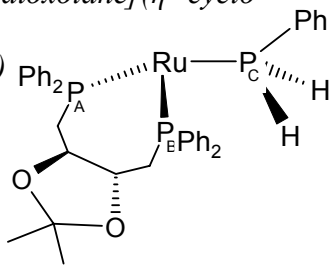
*8. {[(4R,5R)-(–)Bis(diphenylphosphino-κ^{2}P-methyl)-2,2-dimethyl-1,3-dioxolane](η^5-cyclopentadienyl)(iso-propylphosphine)iron(II)}tetrafluoroborate (**5d**)*



According to **5a** from 1.30 g (1.74 mmol) $[H_5C_5(DIOP)Fe(NCMe)]BF_4$ (**3d**) and 200 mg (2.60 mmol) of *i*-$PrPH_2$ (**4b**) in 25 ml dichloromethane after 2 h. – Yield: 1.03 g (76 %). – Orange solid. – M.p.: 93 °C. – $C_{39}H_{46}BF_4FeO_2P_3$ (782.37). calc.: C 59.87, H 5.93. found: C 59.56, H 5.86. – **^{1}H-NMR** ($CDCl_3$, 300.4 MHz): δ = 7.84 - 7.19 (m, 20 H, H_5C_6), 4.09 [dm,^1J(PH) = 315.9 Hz, 2 H, HP], 4.23 (s, 5 H, H_5C_5), 3.47 - 3.25 (m, 2 H, $\underline{H}CCH_2P$), 3.25 - 3.10 (m, 2 H, H_2CP), 2.29 - 2.25 [m, 3 H, H_2CP, $\underline{H}C(CH_3)_2$], 1.26 (s, 3 H, $(H_3C)_2C$), 1.25 (s, 3 H, $(H_3C)_2C$), 1.13 ppm [d, ^3J(HCCH) = 6.8 Hz, 6 H, $(\underline{H}_3C)_2CH$]. - **^{13}C-{^{1}H}-NMR** ($CDCl_3$, 75.45 MHz): δ = 133.87 [d, ^1J(PC) = 43.9 Hz, *i*-C], 132.43 [d, ^1J(PC) = 31.5 Hz, *i*-C],131.36 [d, ^2J(PCC) = 8.1 Hz, *o*-C], 130.28 [d, ^3J(PCCC) = 7.9 Hz, *m*-C], 130.14 [d, ^1J(PC) = 34.3 Hz, *i*-C], 129.86 [d, ^2J(PCC) = 9.6 Hz, *o*-C], 129.75 (s, *p*-C), 129.44 [d, ^1J(PC) = 44.2 Hz, *i*-C], 129.20 [d, ^2J(PCC) = 8.1 Hz, *o*-C],129.09 [d, ^4J(PCCCC) = 1.2 Hz, *p*-C], 128.89 [d, ^3J(PCCC) = 8.2 Hz, *m*-C], 128.79 [d, ^3J(PCCC) = 7.6 Hz, *m*-C], 109.29 (s, $\underline{C}(CH_3)_2$), 80.93 (s, C_5H_5), 78.35 [d, ^2J(PCC) = 9.3 Hz, $\underline{C}HCH_2P$], 74.92 [d, ^2J(PCC) = 11.6 Hz, $\underline{C}HCH_2P$], 30.95 [d, ^1J(PC) = 27.3 Hz, CH_2P], 30.59 [d, ^1J(PC) = 19.2 Hz, CH_2P], 26.81 [d, ^1J(PC) =

31.5 Hz, $\underline{C}H(CH_3)_2$], 25.89 [s,$(\underline{C}H_3)_2C$], 25.46 [s,$(\underline{C}H_3)_2C$], 22.98 [s, $(\underline{C}H_3)_2CH$], 22.94 ppm [s, $(\underline{C}H_3)_2CH$]. - **^{31}P-{^{1}H}-NMR** (CD_3CN, 121.5 MHz): δ = 52.49 [dd, $^2J(P_CFeP_B)$ = 56.5 Hz, $^2J(P_AFeP_B)$ = 43.1 Hz, P_BPh_2], 48.76 [dd, $^2J(P_CFeP_A)$ = 51.7 Hz, $^2J(P_BFeP_A)$ = 43.1 Hz, P_APh_2], 23.24 ppm [dd, $^2J(P_BFeP_C)$ = 56.5 Hz, $^2J(P_AFeP_C)$ = 51.7 Hz, P_CH_2iPr].

*9. {[(4R,5R)-(–)Bis(diphenylphosphino-κ^{2}P-methyl)-2,2-dimethyl-1,3-dioxolane](η^5-cyclopentadienyl)(phenylphosphine)ruthenium(II)}tetrafluoroborate (**9**)*



Analogous to **5a** from 350 mg (0.44 mmol) of $[H_5C_5(DIOP)Ru(NCMe)]BF_4$ (**8**) and 49 mg (0.44 mmol) of $PhPH_2$ (**4a**) in 20 ml dichloromethane after 4 d. - Yield 295 mg (78%). – Yellow-green microcrystalline powder. M.p. 93 °C (dec.). – $C_{42}H_{44}BF_4O_2P_3Ru$ (861.61). calc.: C 58.55, H 5.15. found: C 58.31, H 4.97. - **^{1}H-NMR** (CD_3CN, 400.1 MHz): δ = 7.69 – 7.11 (m, 25 H, H_5C_6), 5.60 [dddd, ^1J(PH) = 349.0 Hz, ^3J(PRuPH) = 9.6 Hz, ^3J(PRuPH) = 8.9 Hz, ^3J(HPH) = 4.6 Hz, 1 H, HP], 5.37 [dddd, ^1J(PH) = 364.7 Hz, ^3J(PRuPH) = 9.3 Hz, ^3J(PRuPH) = 8.7 Hz, ^3J(HPH) = 4.6 Hz, 1 H, HP], 4.44 (s, 5 H, H_5C_5), 3.72 – 3.57 (m, 1 H, $HCCH_2P$), 3.32 – 3.18 (m, 2 H, H_2CP), 2.74 – 2.67 (m, 1 H, $HCCH_2P$), 2.41 [dd, ^1J(PC) = 15.9 Hz, ^3J(PRuPC) = 8.9 Hz, 2 H, H_2CP], 1.31 (s, 3 H, $(H_3C)_2C$), 1.25 ppm (s, 3 H, $(H_3C)_2C$). - **^{13}C-{^{1}H}-NMR** (CD_3CN, 100.6 MHz): δ = 142.37 [dd, ^1J(PC) = 46.7 Hz, ^3J(PRuPC) = 3.8 Hz, *i*-C], 139.37 [d, ^1J(PC) = 48.2 Hz, *i*-C], 134.17 [d, ^2J(PCC) = 12.8 Hz, *o*-C], 133.89 [d, ^2J(PCC) = 11.1 Hz, *o*-C], 133.02 [d, ^1J(PC) = 34.8 Hz, *i*-C], 131.78 [d, ^4J(PCCCC) = 1.9 Hz, *p*-C], 131.64 [d, ^3J(PCCC) = 10.0 Hz, *m*-C], 131.59 – 129.94 (m, C_6H_5), 129.56 [d, ^3J(PCCC) = 9.1 Hz, *m*-C], 129.46 [d, ^4J(PCCCC) = 2.4 Hz, *p*-C], 129.29 – 128.06 (m, C_6H_5), 108.19 (s, $C(CH_3)_2$), 80.07 (s, C_5H_5), 78.38 [dd, ^2J(PCC) = 8.1 Hz, ^3J(PCCC) = 2.4 Hz, CH], 75.14 [d, ^2J(PCC) = 12.8 Hz, CH], 30.85 [dd, ^1J(PC) = 28.1 Hz, ^3J(PRuPC) = 5.2 Hz, CH_2], 28.41 [d, ^1J(PC) = 21.9 Hz, CH_2], 25.85 (s, CH_3), 25.68 ppm (s,

CH_3). - **^{31}P-{^{1}H}-NMR** (CD_3CN, 162.0 MHz): δ = 34.40 [dd, $^2J(P_CRuP_B)$ = 43.7 Hz, $^2J(P_ARuP_B)$ = 34.0 Hz, P_BPh_2], 32.63 [dd, $^2J(P_CRuP_A)$ = 42.1 Hz, $^2J(P_BRuP_A)$ = 34.0 Hz, P_APh_2], - 24.29 ppm [dd, $^2J(P_BRuP_C)$ = 43.7 Hz, $^2J(P_ARuP_C)$ = 42.1 Hz, P_CPhH_2].

*10. {[(2-Cyanoethyl)phenylphosphine](η^5-cyclopentadienyl)[(dimethydiphenylphosphino-κ^{2}P) ethane]iron(II)}tetrafluoroborate (**11a**)*

To a solution of 500 mg (0.84 mmol) of $[H_5C_5(mppe)Fe(PhPH_2)]BF_4$ (**5b**) and 44 mg (0.84 mmol) of acrylonitrile (**10**) in 25 ml dichloromethane 5 mg (0.05 mmol) NEt_3 are added. The mixture is stirred for 3 d at ambient temperature and then reduced in vacuum to a volume of 5 ml. **11a** is precipitated by addition of 30 ml of diethylether, separated by filtration, washed three times with 10 ml of diethylether and dried in vacuum. - Yield 541 mg (99%). – Yellow microcrystalline powder. - M.p. 61°C (dec.). – $C_{30}H_{35}BF_4FeNP_3$ (645.19). calc.: C 55.85, H 5.47, N 2.17. found: C 55.26, H 5.70, N 2.07. – **11a / 11a'** = 68 : 32. The isomeric ratio is determined by integration of the C_5H_5-signals in the ^{1}H-NMR-spectrum. - **^{1}H-NMR** (CD_3CN, 300.4 MHz): - **11a**: δ = 7.69 - 6.95 (m, 15 H, H_5C_6), 4.64 [ddd, ^1J(PH) = 334.2 Hz, ^3J(PFePH) =10.2 Hz, ^3J(PFePH) =10.1 Hz, 1 H, HP], 4.72 [d, ^3J(PFeCH) = 1.5 Hz, 5 H, H_5C_5], 2.46 – 1.82 [m, 8 H, $(H_2C)_2CN$, H_2CP], 1.75 [d, ^2J(PCH) = 10.2 Hz, 3 H, H_3CP], 1.70 ppm [d, ^2J(PCH) = 9.0 Hz, 3 H, H_3CP]. – **11a'**: δ = 7.69 - 6.95 (m, 15 H, H_5C_6), 4.92 [ddd, ^1J(PH) = 332.7 Hz, ^3J(PFePH) = 10.6 Hz, ^3J(PFePH) = 9.5 Hz, 1 H, HP], 4.57 [d, ^3J(PFeCH) = 1.4 Hz, 5 H, H_5C_5], 2.76 – 2.35 [m, 4 H, $(H_2C)_2CN$], 2.31 – 1.81 (m, 4 H, H_2CP), 1.75 [d, ^2J(PCH) = 10.2 Hz, 3 H, H_3CP], 1.70 ppm [d, ^2J(PCH) = 9.0 Hz, 3 H, H_3CP]. - **^{13}C-{^{1}H}-NMR** (CD_3CN, 75.45 MHz): **11a / 11a'**: δ = 138.98 [d, ^1J(PC) = 40.3 Hz, *i*-C], 138.41 [d, ^1J(PC) = 36.5 Hz, *i*-C], 134.16 [d, ^3J(PCCC) = 8.6 Hz, *m*-C], 132.90 [d, ^2J(PCC) = 10.0 Hz, *o*-C], 132.54 [d , ^2J(PCC) = 9.0 Hz, *o*-C], 132.18 [d, ^4J(PCCCC) = 1.4 Hz, *p*-C], 131.78 [d, ^4J(PCCCC) = 2.4 Hz, *p*-C], 130.98 [d, ^1J(PC) = 41.4 Hz, *i*-C], 130.36 [d, ^3J(PCCC) = 6.9 Hz, *m*-C], 130.23 [d, ^3J(PCCC) = 7.6 Hz, *m*-C], 129.80 [d , ^2J(PCC) = 9.5 Hz, *o*-C], 129.49 [d, ^4J(PCCCC) = 2.3

Hz, *p*-C], 119.21 [d, ^3J(PCCC) = 10.0 Hz, CN], 79.93 [s, C_5H_5], 29.11 [dd, ^1J(PC) = 32.7 Hz, ^2J(PCC) = 13.1 Hz, CH_2P], 26.93 [d, ^1J(PC) = 30.3 Hz, CH_2], 26.28 [dd, ^1J(PC) = 29.7 Hz, ^2J(PCC) = 11.0 Hz, CH_2P], 21.21 [d, ^1J(PC) = 32.4 Hz, CH_3], 19.29 ppm [d, ^1J(PC) = 30.6 Hz, CH_3], 16.78 [d, ^2J(PCC) = 7.5 Hz, CH_2CN]. - **^{31}P-{^{1}H}-NMR** (CD_3CN, 121.5 MHz): **11a**: δ = 98.96 [dd, $^2J(P_CFeP_A)$ = 49.8 Hz, $^2J(P_BFeP_A)$ = 34.0 Hz, P_APh_2], 67.57 [dd, $^2J(P_CFeP_B)$ = 58.3 Hz, $^2J(P_AFeP_B)$ = 34.0 Hz, $P_B(CH_3)_2$], 50.86 ppm [dd, $^2J(P_BFeP_C)$ = 58.3 Hz, $^2J(P_AFeP_C)$ = 49.8 Hz, P_CH]. – **11a'**: δ = 99.31 [dd, $^2J(P_CFeP_A)$ = 51.0 Hz, $^2J(P_BFeP_A)$ = 28.1 Hz, P_APh_2], 73.57 [dd, $^2J(P_CFeP_B)$ = 60.8 Hz, $^2J(P_AFeP_B)$ = 28.1 Hz, $P_B(CH_3)_2$], 45.88 ppm [dd, $^2J(P_BFeP_C)$ = 60.8 Hz, $^2J(P_AFeP_C)$ = 51.0 Hz, P_CH].

*11. {[(R)-Bis(1,2-diphenylphosphino-κ^{2}P)-propane][(2-cyanoethyl)phenylphosphine](η^5-cyclopentadienyl)iron(II)}tetrafluoroborate (**11b**)*

Analogous to **11a** from 700 mg (0.96 mmol) $[H_5C_5(PROPHOS)Fe(PhPH_2)]BF_4$ (**5c**) and 50 mg (0.96 mmol) acrylonitrile (**10**) in 30 ml dichloromethane after 2 d. - Yield 556 mg (74%). – Orange powder. – M.p. 112 °C. – $C_{41}H_{41}BF_4FeNOP_3$ (783.36). calc.: C 70.77, H 5.28, N 1.79. found: C 70.75, H 5.49, N 1.67. – **11b/11b'** = 88:12. The isomeric ratio is determined by integration of the C_5H_5-signals in the ^{1}H-NMR-spectrum. Only NMR-spectric data of diastereomer anti-**11b** (anti-**11b**/anti-**11b'** 71:29) are specified.* - **^{1}H-NMR** (CD_3CN, 300.4 MHz) : anti-**11b**: δ = 7.89 - 6.73 (m, 25 H, H_5C_6), 4.63 [ddd, ^1J(PH) = 332.7 Hz, ^3J(PFePH) = 12.9 Hz, 10.5 Hz, 1 H, HP], 4.69 (d, ^3J(PFeCH) = 1.5 Hz, 5 H, H_5C_5), 4.63 (d, ^3J(PFeCH) = 1.5 Hz, 5 H, H_5C_5) (anti-**11b'**), 3.25 - 2.78 (m, 5 H, HCP, H_2CP), 1.76 - 1.55 (m, 2 H, H_2CP), 1.13 ppm [dd, ^3J(PCCH) = 11.7 Hz, 3 H, $\underline{H}_3CCH$]. - **^{13}C-{^{1}H}-NMR** (CD_3CN, 75.45 MHz) : anti-**11b**: δ = 138.70 [dd, ^1J(PC) = 38.3 Hz,^4J(PCCPC) = 2.4 Hz, *i*-C], 135.63 [d, ^2J(PCC) = 10.0 Hz, *o*-C], 134.98 [d, ^2J(PCC) = 10.0 Hz, *o*-C], 133.52 [d, ^1J(PC) = 41.3 Hz, *i*-C], 133.08 [d, ^3J(PCCC) = 8.3 Hz, *m*-C], 132.62 [d, ^2J(PCC) = 10.3 Hz, *o*-C], 132.38 [d, ^3J(PCCC) = 8.2 Hz, *m*-C], 131.91 [d, ^4J(PCCCC) = 2.4 Hz, *p*-C], 131.70 [d, ^3J(PCCC) = 8.2 Hz, *m*-C], 131.51

[d, ^2J(PCC) = 9.3 Hz, *o*-C], 131.17 [d, ^4J(PCCCC) = 2.4 Hz, *p*-C], 130.98 [d, ^4J(PCCCC) = 2.4 Hz, *p*-C], 130.69 [d, ^3J(PCCC) = 9.0 Hz, *m*-C], 130.48 [d, ^1J(PC) = 39.7 Hz, *i*-C], 129.99 [d, ^2J(PCC) = 9.3 Hz, *o*-C], 129.37 [d, ^2J(PCC) = 9.3 Hz, *o*-C], 129.14 [d, ^3J(PCCC) = 7.6 Hz, *m*-C], 119.23 [d, ^3J(PCCC) = 12.0 Hz, CN], 80.66 (s, C_5H_5), 80.57 (s, C_5H_5) [anti-**11b'**], 35.13[dd, ^1J(PC) = 33.0 Hz, ^2J(PCC) = 14.8 Hz, CH] [anti-**11b'**], 34.28 [dd, ^1J(PC) = 28.2 Hz, ^2J(PCC) = 10.6 Hz, CH_2] [anti-**11b'**], 33.12 [dd, ^1J(PC) = 31.0 Hz, ^2J(PCC) = 15.9 Hz, CH], 32.50 [dd, ^1J(PC) = 28.9 Hz, ^2J(PCC) = 12.5 Hz, CH_2], 27.04 [dd, ^2J(PCC) = 3.1 Hz, $\underline{C}H_2CN$] [anti-**11b'**], 26.89 [dd, ^2J(PCC) = 3.1 Hz, $\underline{C}H_2CN$], 24.97 [dd, ^1J(PC) = 21.4 Hz, ^3J(PFePC) = 2.4 Hz, $P\underline{C}H_2CH_2CN$] [anti-**11b'**], [dd, ^1J(PC) = 21.7 Hz, ^3J(PFePC) = 1.4 Hz, $P\underline{C}H_2CH_2CN$], 17.29 [dd, ^2J(PCC) = 14.5 Hz, ^3J(PCCC) = 5.9 Hz, CH_3CH] [anti-**11b'**], 16.74 ppm [dd, ^2J(PCC) = 13.1 Hz, ^3J(PCCC) = 8.6 Hz, CH_3CH]. - **^{31}P-{^{1}H}-NMR** (CD_3CN, 121.5 MHz) : anti-**11b**: δ = 102.18 [dd, $^2J(P_CFeP_A)$ = 51.0 Hz, $^2J(P_BFeP_A)$ = 37.7 Hz, P_APh_2], 70.76 [dd, $^2J(P_CFeP_B)$ = 51.0 Hz, $^2J(P_AFeP_B)$ = 37.7 Hz, P_BPh_2], 50.10 ppm [dd, $^2J(P_AFeP_C)$ = 51.0 Hz, $^2J(P_BFeP_C)$ = 51.0 Hz, P_CH]. – anti-**11b'**: δ = 101.33 [dd, $^2J(P_CFeP_A)$ = 49.8 Hz, $^2J(P_BFeP_A)$ = 40.1 Hz, P_APh_2], 68.13 [dd, $^2J(P_CFeP_B)$ = 49.8 Hz, $^2J(P_AFeP_B)$ = 40.1 Hz, P_BPh_2], 49.68 ppm [dd, $^2J(P_AFeP_C)$ = 49.8 Hz, $^2J(P_BFeP_C)$ = 49.8 Hz, P_CH]. * Signals of anti-**11b'** are in brackets. The missing signals are hidden by the signals of the major isomer anti-**11b**.

From **syn-11b/11b'** only the following signals can be detected: **^{1}H-NMR** (CD_3CN, 300.4 MHz) : syn-**11b**: δ = 4.35 (d, ^3J(PFeCH) = 1.7 Hz, 5 H, H_5C_5). - syn-**11b'**: δ = 4.39 (d, ^3J(PFeCH) = 2.0 Hz, 5 H, H_5C_5).

*12. {[(4R,5R)-(–)Bis(diphenylphosphino-κ^{2}P-methyl)-2,2-dimethyl-1,3-dioxolane][(2-cyano-ethyl)phenylphosphine](η^5-cyclopentadienyl)ruthenium(II)}tetrafluoroborate (**11c**)*

Analogous to **11a** from 250 mg (0.29 mmol) of $[H_5C_5(DIOP)Ru(PhPH_2)]BF_4$ (**9**) and 16 mg (0.29 mmol) of acrylonitrile (**10**) in 20 ml dichloromethane after 2 d. - Yield 209 mg (79%). – Green microcrystalline powder. – $C_{45}H_{47}BF_4NO_2P_3Ru$ (914.67). calc.: C 59.09, H 5.18, N

1.53. found: C 58.56, H 5.11, N 1.60. – **11c / 11c'** = 78 : 22. The isomeric ratio is determined by integration of the C_5H_5-signals in the ^{1}H-NMR-spectrum. - **^{1}H-NMR** (CD_3CN, 300.4 MHz): **11c**: δ = 7.90 – 6.90 (m, 25 H, H_5C_6), 5.11 [dm, ^1J(PH) = 343.2 Hz, 1 H, HP], 4.82 (s, 5 H, H_5C_5), 3.71 – 3.47 (m, 3 H, HC, H_2C), 3.31 – 3.16 (m, 3 H, HC, H_2C), 2.76 – 2.17 (m, 4 H, H_2C), 1.45 (s, 3 H, H_3C), 1.33 ppm (s, 3 H, H_3C). **11c'**: δ = 7.90 – 6.90 (m, 25 H, H_5C_6), 5.50 [dm, ^1J(PH) = 343.2 Hz, 1 H, HP], 4.78 (s, 5 H, H_5C_5), 3.71 – 3.47 (m, 3 H, HC, H_2C), 3.31 – 3.16 (m, 3 H, HC, H_2C), 2.76 – 2.17 (m, 4 H, H_2C), 1.39 (s, 3 H, H_3C), 1.27 ppm (s, 3 H, H_3C). - **^{13}C-NMR** (CD_3CN, 75.45 MHz): **11c:** δ = 142.52 [dd, ^1J(PC) = 49.7 Hz, ^3J(PRuPC) = 3.8 Hz, *i*-C], 139.79 [dd, ^1J(PC) = 44.5 Hz, ^3J(PRuPC) = 2.4 Hz, *i*-C], 135.42 – 128.91 (m, C_6H_5), 118.91 [d, ^3J(PCCC) = 11.8 Hz, CN], 109.88 (s, $C(CH_3)_2$), 86.46 [d, ^2J(PRuC) = 1.4 Hz, C_5H_5], 79.35 [dd, ^2J(PCC) = 7.9 Hz, ^3J(PCCC) = 2.0 Hz, CH], 75.76 [d, ^2J(PCC) = 9.6 Hz, CH], 30.85 - 28.41 (m, CH_2), 27.12 (s, CH_3), 27.05 ppm (s, CH_3). **11c'**: δ = 143.34 [dd, ^1J(PC) = 49.9 Hz, ^3J(PRuPC) = 3.8 Hz, *i*-C], 140.54 [dd, ^1J(PC) = 46.5 Hz, ^3J(PRuPC) = 3.0 Hz, *i*-C], 135.42 – 128.91 (m, C_6H_5), 119.30 [d, ^3J(PCCC) = 11.1 Hz, CN], 110.01 (s, $C(CH_3)_2$), 86.61 [d, ^2J(PRuC) = 1.4 Hz, C_5H_5], 79.02 [dd, ^2J(PCC) = 8.9 Hz, ^3J(PCCC) = 3.2 Hz, CH], 76.73 [d, ^2J(PCC) = 10.3 Hz, CH], 30.85 - 28.41 (m, CH_2), 26.92 (s, CH_3), 26.87 ppm (s, CH_3). - **^{31}P-{^{1}H}-NMR** (CD_3CN, 121.5 MHz): **11c**: δ = 34.48 [dd, $^2J(P_CRuP_A)$ = 43.7 Hz, $^2J(P_BRuP_A)$ = 35.2 Hz, P_APh_2], 32.08 [dd, $^2J(P_CRuP_B)$ = 36.5 Hz, $^2J(P_ARuP_B)$ = 35.2 Hz, P_BPh_2], 27.80 ppm [dd, $^2J(P_ARuP_C)$ = 43.7 Hz, $^2J(P_BRuP_C)$ = 36.5 Hz, P_CH]. **11c'**: δ = 34.02 [dd, $^2J(P_CRuP_A)$ = 40.7 Hz, $^2J(P_BRuP_A)$ = 34.6 Hz, P_APh_2], 32.64 [dd, $^2J(P_CRuP_B)$ = 40.1 Hz, $^2J(P_ARuP_B)$ = 34.6 Hz, P_BPh_2], 24.92 ppm [dd, $^2J(P_ARuP_C)$ = 40.7 Hz, $^2J(P_BRuP_C)$ = 40.1 Hz, P_CH].

*13. {Acrylonitrile[(4R,5R)-(–)bis(diphenylphosphinomethyl-κ²P)-2,2-dimethyl-1,3-dioxolane] (η⁵-cyclopentadienyl)iron(II)}tetrafluoroborate (**12**)*

Analogous to **11a** from 1.00 g (1.28 mmol) of $[H_5C_5(DIOP)Fe(i\text{-}PrPH_2)]BF_4$ (**5d**) and 67 mg (1.28 mmol) of acrylonitrile (**10**) in 20 ml dichloromethane after 1 d. - Yield 661 mg (84%). – Brown microcrystalline powder. – M.p.: 92 °C (dec.). – $C_{39}H_{40}BF_4FeNO_2P_2$ (759.35). calc.: C 61.69, H 5.31, N 1.84. found: C 60.73, H 5.60, N 1.95. - **^{1}H-NMR** (CD_3CN, 300.4 MHz): δ = 8.06 - 7.29 (m, 20 H, H_5C_6), 6.23 - 5.72 (m, 3 H, H_2C=CH-CN), 3.92 (s, 5 H, H_5C_5), 3.44 - 3.28 (m, 1 H, $\underline{H}CCH_2P$), 3.22 - 2.99 (m, 2 H, H_2CP), 2.85 - 2.53 (m, 1 H, $\underline{H}CCH_2P$), 2.37 - 2.17 (m, 2 H, H_2CP), 1.19 [s, 3 H, $(H_3C)_2C$], 1.11 ppm [s, 3 H, $(H_3C)_2C$]. - **^{13}C-{^{1}H}-NMR** (CD_3CN, 75.45 MHz): δ = 142.92 [d, ^1J(PC) = 44.8 Hz, *i*-C], 139.99 [d, ^1J(PC) = 43.8 Hz, *i*-C], 136.54 (s, $H_2\underline{C}$=CH-CN), 135.34 [d, ^2J(PCC) = 11.7 Hz, *o*-C], 135.10 [d, ^2J(PCC) = 10.0 Hz, *o*-C], 134.42 [d, ^2J(PCC) = 10.4 Hz, *o*-C], 13.19 [d, ^2J(PCC) = 10.0 Hz, *o*-C], 133.50 [d, ^4J(PCCCC) = 2.0 Hz, *p*-C], 132.42 [d, ^4J(PCCCC) = 1.4 Hz, *p*-C], 132.07 [d, ^4J(PCCCC) = 2.4 Hz, *p*-C], 131.46 [d, ^3J(PCCC) = 8.3 Hz, *m*-C], 131.27 [d, ^3J(PCCC) = 7.2 Hz, *m*-C], 131.19 [d, ^1J(PC) = 39.3 Hz, *i*-C], 131.10 [d, ^3J(PCCC) = 6.9 Hz, *m*-C], 130.73 [d, ^3J(PCCC) = 5.9 Hz, *m*-C], 130.43 [d, ^4J(PCCCC) = 1.7 Hz, *p*-C], 129.70 [t, ^3J(PFeCC) = 8.9 Hz, H_2C=$\underline{C}$H-CN], 112.40 [d, ^4J(PFeCCC) = 4.3 Hz, H_2C=CH-$\underline{C}$N], 109.49 [s, $\underline{C}(CH_3)_{2D}$], 80.97 (s, C_5H_5), 79.37 [d, ^2J(PCC) = 8.6 Hz, $\underline{C}HCH_2P$], 76.10 [d, ^2J(PCC) = 12.1 Hz, $\underline{C}HCH_2P$], 32.37 [d, ^1J(PC) = 24.8 Hz, CH_2P], 29.17 [d, ^1J(PC) = 18.6 Hz, CH_2P], 27.11 [s, $(CH_3)_2C$], 26.92 ppm [s, $(CH_3)_2C$]. - **^{31}P-{^{1}H}-NMR** (CD_3CN, 121.5 MHz) : δ = 54.16 [d, ^2J(PFeP) = 48.6 Hz, PPh_2], 52.52 ppm [d, ^2J(PFeP) = 48.6 Hz, PPh_2].

*14. {[1,2-Bis(diphenylphosphino-κ²P)ethane](η⁵-cyclopentadienyl)[(N-1-phenylethyl-formamido)phenylphosphine]iron(II)}tetrafluoroborate (**14a**)*

To a solution of 530 mg (0.74 mmol) of $[H_5C_5(dppe)Fe(PhPH_2)]BF_4$ (**5a**) and 108 mg (4.54 mmol) of (S)-1-phenylethylisocyanate (**13a**) in 30 ml dichloromethane 5 mg (0.05 mmol)

NEt_3 are added. The reaction mixture is stirred for 4 h at 40 °C and then reduced in vacuum to a volume of 5 ml. **14a** is precipitated by addition of 30 ml of diethylether, separated by filtration, washed three times with 10 ml of diethylether and dried in vacuum. - Yield 168 mg (98%). – Yellow-brown microcrystalline powder. - M.p. 101°C (dec.). – $C_{46}H_{45}BF_4FeNOP_3$ (863.44). calc.: C 63.99, H 5.25, N 1.62. found: C 63.21, H 5.39, N 1.63. **14a/14a'** = 96 : 4. The isomeric ratio is determined by integration of the C_5H_5-signals in the ^{1}H-NMR-spectrum. - **^{1}H-NMR** (CD_3CN, 300.4 MHz): **14a**: δ = 7.79 - 6.76 (m, 31 H, NH, H_5C_6), 5.27 [ddd, ^1J(PH) = 330.9 Hz, ^3J(PFePH) = 4.6 Hz, ^3J(PFePH) = 4.2 Hz, 1 H, HP], 4.87 [d, ^3J(PFeCH) = 1.5 Hz, 5 H, H_5C_5], 4.26 [q, ^3J(HCCH) = 6.8 Hz, 1 H, HC], 2.92 - 2.63 (m, 4 H, H_2C), 0.89 ppm [d, ^3J(HCCH) = 6.9 Hz, 3 H, H_3C]. - **^{13}C-{^{1}H}-NMR** (CD_3CN, 75.45 MHz): **14a**: δ = 172.38 [d, ^1J(PC) = 47.4 Hz, CO], 133.88 -125.78 (m, C_6H_5), 80.57 (s, br, C_5H_5), 51.18 [d, ^3J(PCNC) = 12.5 Hz, NCH], 28.07 [dd, ^1J(PC) = 31.7 Hz, ^2J(PCC) = 12.1 Hz, CH_2], 27.16 [dd, ^1J(PC) = 31.4 Hz, ^2J(PCC) = 11.4 Hz, CH_2], 22.37 ppm [d, ^4J(PCNCC) = 1.5 Hz, CH_3]. - **^{31}P-{^{1}H}-NMR** (CD_3CN, 121.5 MHz): **14a**: δ = 93.85 [dd, $^2J(P_CFeP_A)$ = 48.6 Hz, $^2J(P_BFeP_A)$ = 48.6 Hz, 25.6 Hz, P_APh_2], 92.69 [dd, $^2J(P_CFeP_B)$ = 47.4 Hz, $^2J(P_AFeP_B)$ = 25.6 Hz, P_BPh_2], 46.08 ppm [dd, $^2J(P_AFeP_C)$ = 48.6 Hz, $^2J(P_BFeP_C)$ = 47.4 Hz, P_CH].

*15. {(η^5-Cyclopentadienyl)[(N-ethylformamido)phenylphosphine][(dimethydiphenyl-phosphino-κ^2P)ethane]iron(II)}tetrafluoroborate (**14b**)*

Analogous to **14a** from 500 mg (0.84 mmol) $[H_5C_5(mppe)Fe(PhPH_2)]BF_4$ (**5b**) and 59 mg (0.84 mmol) ethylisocyanate (**13b**) in 30 ml dichloromethane after 2 d at ambient temperature. - Yield 535 mg (96%). – Yellow powder. – M.p.: 88 °C. – $C_{30}H_{37}BF_4FeNOP_3$ (663.20). calc.: C 54.33, H 5.62, N 2.11. found: C 53.74, H 5.58, N 1.96. – **14b/14b'** = 58:42. The isomeric ratio is determined by integration of the C_5H_5-signals in the ^{1}H-NMR-spectrum. - **^{1}H-NMR** (CD_3CN, 300.4 MHz): **14b**: δ = 7.67 - 6.99 (m, 16 H, HN, H_5C_6), 6.18 [d, ^1J(PH) = 342.1 Hz, 1 H, HP], 4.82 [d, ^3J(CFePH) = 1.5 Hz, 5 H, H_5C_5], 2.97 [q, ^3J(HCCH) = 7.2 Hz, 2 H,

$\underline{H_2}CCH_3$], 2.61 - 2.02 (m, 4 H, H_2C), 1.81 [d, ^2J(PCH) = 9.3 Hz, 3 H, H_3C], 1.63 [d, ^2J(PCH) = 9.6 Hz, 3 H, H_3C], 0.82 ppm [t, ^3J(HCCH) = 7.4 Hz, $\underline{H_3}C\ CH_2$]. – **14b'**: δ = 7.67 - 6.99 (m, 16 H, HN, H_5C_6), 5.64 [ddd, ^1J(PH) = 330.5 Hz, ^3J(PFePH) = 3.9 Hz, ^3J(PFePH) = 3.7 Hz, 1 H, HP], 4.61 [d, ^3J(PFeCH) = 1.5 Hz, 5 H, H_5C_5], 2.97 [q, ^3J(HCCH) = 7.2 Hz, 2 H, $\underline{H_2}CCH_3$], 2.61 - 2.02 (m, 4 H, H_2C), 1.83 [d, ^2J(PCH) = 9.2 Hz, 3 H, H_3C], 1.58 [d, ^2J(PCH) = 10.2 Hz, 3 H, H_3C], 0.89 ppm [t, ^3J(HCCH) = 7.4 Hz, $\underline{H_3}CCH_2$]. - **^{13}C-{^{1}H}-NMR** (CD_3CN, 75.45 MHz) **14b**/**14b'**: δ = 169.32 [d, ^1J(PC) = 43.7 Hz, CO], 134.32 [d, ^3J(PCCC) = 8.6 Hz, *m*-C], 133.11 [d, ^2J(PCC) = 9.6 Hz, *o*-C], 132.81 [d, ^3J(PCCC) = 8.2 Hz, *m*-C], 132.53 [d, ^2J(PCC) = 10.0 Hz, *o*-C], 131.89 [d, ^2J(PCC) = 9.9 Hz, *o*-C], 131.63 [dd, ^1J(PC) = 49.0 Hz, ^4J(PCCPC) = 2.0 Hz, *i*-C], 131.39 [dd, ^1J(PC) = 48.9 Hz, ^4J(PCCPC) = 2.1 Hz, *i*-C], 130.99 [d, ^4J(PCCCC) = 2.4 Hz, *p*-C], 130.16 [d,^3J(PCCC) = 8.9 Hz, *m*-C], 129.75 [d,^3J(PCCC) = 9.2 Hz, *m*-C], 129.69 [d, ^2J(PCC) = 9.7 Hz, *o*-C], 80.48 (s, br, C_5H_5) [**14b**], 80.34 (s, br, C_5H_5) [**14b'**], 36.17 [dd, ^3J(PCNC) = 15.1 Hz, ^5J(PFePCNC) = 1.3 Hz, CH_2], 29.32 [dd, ^1J(PC) = 31.1 Hz, ^2J(PCC) = 12.8 Hz, PCH_2], 29.64 [dd, ^1J(PC) = 32.4 Hz, ^2J(PCC) = 10.0 Hz, PCH_2], 21.45 [dd, ^1J(PC) = 30.6 Hz, ^4J(PCCPC) = 4.2 Hz, PCH_3], 20.37 [dd, ^1J(PC) = 27.2 Hz, ^4J(PCCPC) = 4.8 Hz, PCH_3], 14.07 ppm [d, ^4J(PCNCC) = 2.4 Hz, CH_3]. - **^{31}P-{^{1}H}-NMR** (CD_3CN, 121.5 MHz): **14b**: δ = 98.05 [dd, $^2J(P_CFeP_A)$ = 42.5 Hz, $^2J(P_BFeP_A)$ = 34.0 Hz, P_APh_2], 66.42 [dd, $^2J(P_CFeP_B)$ = 55.9 Hz, $^2J(P_AFeP_B)$ = 34.0 Hz, $P_B(CH_3)_2$], 50.11 ppm [dd, $^2J(P_BFeP_C)$ = 55.9 Hz, $^2J(P_AFeP_C)$ = 42.5 Hz, P_CPh]. – **14b'**: δ = 98.04 [dd, $^2J(P_CFeP_A)$ = 46.0 Hz, $^2J(P_BFeP_A)$ = 31.0 Hz, P_APh_2], 70.96 [dd, $^2J(P_CFeP_B)$ = 58.3 Hz, $^2J(P_AFeP_B)$ = 31.0 Hz, $P_B(CH_3)_2$], 47.35 ppm [dd, $^2J(P_BFeP_C)$ = 58.3 Hz, $^2J(P_AFeP_C)$ = 46.0 Hz, P_CPh].

*16. X-ray analysis of **8** and **14b***

8: $C_{38}H_{40}BF_4NO_2P_2Ru$, M_r = 792.6, orthorhombic, space group *C*222(1) (No. 21), *a* = 15.549(3) Å, *b* = 19.939(4) Å, *c* = 23.928(4) Å, *V* = 7418(2) Å^3, *Z* = 8, *ρ* = 1.416 Mgm^{-3},

Nonius Kappa CCD diffractometer, radiation type: Mo-K_α, wavelength: λ = 0.71073 mm^{-1}, crystal size: 0.15 x 0.12 x 0.09 mm, temperature:293 (2) K, scale range: 1.70° < Θ < 25.09°, *F*(000): 3232, total reflections: 36194, observed reflections: 6573 with [$I > 2\sigma$ (*I*)], absorption coefficient: μ = 0.563 mm^{-1}, empirical absorption correction, structure solution: SHELXS-97[19], structure refinement: SHELXL-97[20-23], R_1 = 0.0455, wR_2 = 0.0934.

14b: $C_{72}H_{78}BFeF_4O_2P$, M_r = 339.8, monoclinic, space group *P*2(1)/c (No. 14), *a* = 10.138(3) Å, *b* = 19.142(6) Å, *c* = 14.560(5) Å, β = 92.390(6)°, *V* = 2823.1(16) $Å^3$, *Z* = 8, ρ = 1.599 Mgm^{-3}, Nonius Kappa CCD diffractometer, radiation type: Mo-K_α, wavelength: λ = 0.71073 mm^{-1}, crystal size: 0.15 x 0.12 x 0.09 mm, temperature: 173 (2) K, scale range: 2.01° < Θ < 27.64°, *F*(000): 1376, total reflections: 63444, observed reflections: 6504 with [$I > 2\sigma$ (*I*)], absorption coefficient: μ = 1.219 mm^{-1}, empirical absorption correction, structure solution: SHELXS-97[19], structure refinement: SHELXL-97[20-23], R_1 = 0.0650, wR_2 = 0.1416.

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CHAPTER IV:

Synthesis and Reactivity of *Primary* Phosphine Iron Complexes $\{H_5C_5(L)[H_3CO(CH_2)_2Ph_2P]Fe[P(R)H_2]\}BF_4$ (L = CO, PMe_3; R = *i*-Pr, Ph, Mes) containing a Hemilabile Ligand

Abstract

The complexes $H_5C_5(OC)[H_3CO(CH_2)_2Ph_2P]FeX$ (X = Cl, Br, I) (**3a-c**) were synthesized by irradiation of $H_5C_5(OC)_2FeX$ (X = Cl, Br, I) (**1a-c**) with the bidentate phosphine ligand $Ph_2P(CH_2)_2OCH_3$ (**2**) and were transformed to the cationic iron complex $\{H_5C_5(OC)Fe[PPh_2(CH_2)_2OCH_3]\}BF_4$ (**5**) by intramolecular cyclization induced by silver tetrafluoroborate. Irradiation of **1a** in the presence of the bidentate phosphine ligand **2** additionally leads to the elimination of chloride resulting in the formation of the cationic compound $\{H_5C_5(OC)_2Fe[PPh_2(CH_2)_2OCH_3]\}Cl$ (**4**). The reaction of the complex **5** with the *primary* phosphines $P(R)H_2$ (R = *i*-Pr, Ph, Mes) (**6a-c**) generates the *primary* phosphine iron complexes $\{H_5C_5(OC)[H_3CO(CH_2)_2Ph_2P]Fe[P(R)H_2]\}BF_4$ (R = i-Pr, Ph, Mes) (**7a-c**). $\{H_5C_5(Me_3P)[H_3CO(CH_2)_2Ph_2P]Fe(NCMe)\}BF_4$ (**9**), synthesized from the cationic complex $[H_5C_5(Me_3P)(OC)_2Fe]BF_4$ (**8**) and the hemilabile ligand $Ph_2P(CH_2)_2OCH_3$ (**2**) in acetonitrile, can analogously be transformed into the *primary* phosphine iron complexes $\{H_5C_5(Me_3P)[H_3CO(CH_2)_2Ph_2P]Fe(PRH_2)\}BF_4$ (**10a,b**) (R = Ph, Mes). The *primary* phosphine complexes **7a-c** and **10a,b** are transformed to the corresponding chiral *secondary* phosphine complexes $\{H_5C_5(L)[H_3CO(CH_2)_2Ph_2P]Fe[P(R)(H)(CH_2)_2CN]\}BF_4$ [L = CO, PMe_3; R = Ph, Mes] (**12a-c**) by hydrophosphination of the electron deficient alkene acrylonitrile (**11**) in the presence of triethylamine. The treatment of **7a-c** with ethylisocyanate (**14**) leads to the chiral *secondary* phosphine complexes $\{H_5C_5(OC)[H_3CO(CH_2)_2Ph_2P]Fe[P(R)(H)(C{=}O)NHCH_2CH_3]\}BF_4$ (R = Ph, Mes) (**15a,b**). The molecular structures of **3b** and **10b** are determined by x-ray crystallography.

Introduction

Coordinatively unsaturated transition metal complexes play an important role in catalytically operating processes, because they represent highly reactive intermediates.[1] For this reason

the synthesis and use of bifunctional "hemilabile ligands" has attracted increasing attention in the last few years. Especially ether-phosphines $R_2P(CH_2)_nOMe$ have been employed in the synthesis of catalytically active species. For example, in the hydrocarbonylation process of methanol to acetaldehyde the ether-phosphine $Cy_2P(CH_2)_2OMe$ is used as a ligand at a cobalt central atom.[2, 3] The hemilabile ether-phosphine ligands have a *tertiary* phosphorus atom, which allows close contact to the metal centre. On the other hand the oxygen atom can be considered as an intramolecular donor, which is only weakly bonded to the metal centre. Due to this fact the oxygen-metal bond can be easily cleaved, and guarantees high reactivity of these complexes. Moreover, when the substrate leaves a coordination site, it is closed by the oxygen atom of the hemilabile ligand. This reversible process of opening and closing was observed by Lindner in ruthenium complexes of the type $Cl_2(OC)[MeO(CH_2)_2R_2P]RuPR_2(CH_2)_2OMe$ (R = Cy, *i*-Pr, Ph), where the oxygen atom of two ether-phosphine ligands compete for a vacant coordination site.[4, 5]

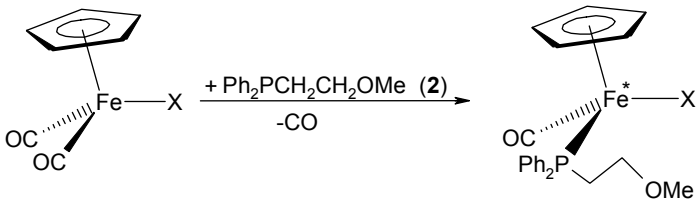
Due to the interest in chiral phosphines like CHIRAPHOS[6-9] or BINAP[10-14] in the last years, there have been several attempts to find new synthetic strategies for building up new chiral phosphines. The hydrophosphination reaction has been established in the last few years for the build up of *secondary* or *tertiary* phosphines.[15-27] However the synthesis of *tertiary* phosphines starting from *secondary* phosphines R_2PH, which is mainly demonstrated in literature, have not been exploited with respect to chiral phosphines, additionally the phosphines are obtained with diverse coproducts, mainly phosphorus polymers.[15-18, 28] The metal-assisted hydrophosphination is a method to avoid these problems, which has been extensively investigated in the last years by our group with respect to *primary* and *secondary* phosphines.[29-31] First step in this the synthesis is the coordination of the phosphine to a transition metal fragment to activate the PH-function, a measurement for which especially halfsandwich iron complexes have been used. In the following steps the PH-function is deprotonated and the lone pair of the phosphorus atom brought to reaction with electrophilic

multiple bonded system like electron-deficient alkenes, alkynes[18, 26, 32] and heteroallenes[33, 34]. A crucial point in the metal-assisted synthesis of chiral phosphines is the detachment of the phosphine ligands from iron centre. This process can cleanly be achieved to our experience by treatment of the corresponding phosphine complexes with stoichiometric amounts of dppe in acetonitrile under ultraviolet irradiation. To simplify these method the introduction of a hemilabile ligand seems reasonably, which should be prepared to close the coordination site created after release of the hydrophosphination product. In addition opening of the chelating hybride ligand at the ‘‘hard’’ donor site by the starting *primary* or *secondary* phosphine is expected, which means, that the hydrophosphination cycle can be repeated. In this context further investigations concerning a catalytic modification are very promising. As a hemilabile ligand we choose the 2-methoxyethyl-diphenylphosphine, which has been the subject of several reports.[1-4, 34-36] The primary goal was to synthezise *primary* phosphine complexes of the type $\{H_5C_5(L)[H_3CO(CH_2)_2Ph_2P]Fe[P(R)H_2]\}^+$ appropiate for hydrophosphination.

Results and Discussion

Primary Phosphine Iron Complexes $\{H_5C_5(L)[H_3CO(CH_2)_2Ph_2P]Fe[P(R)H_2]\}BF_4$ [L = CO, PMe_3; R = i-Pr, Ph, Mes] (7a-c, 9a,b)

The synthesis of the *primary* phosphine iron complexes starts with the photoreaction of the halogeno iron complexes **1a-c** in the presence of 2-methoxyethyl-diphenylphosphine (**2**) in toluene to give within 5 h at room temperature the iron complexes **3a-c** according to eq (1).[37] **3a-c** can be isolated as green fine grained powders in yields of 45 % (**3a**) to 97% (**3c**).



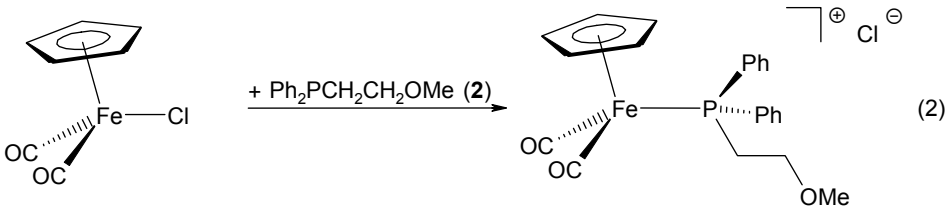
(1)

1a-c **3a-c**

	a	b	c
X	Cl	Br	I

The ^{31}P-NMR spectra of the iron complexes **3a-c** show singlets for the phosphorus atoms at 57.28 (**3a**), 57.96 (**3b**) and 59.10 ppm (**3c**). The IR spectra prove CO-substitution due to a single ν(CO) absorption at 1944 (**3a**), 1953 (**3b**) and 1949 cm^{-1} (**3c**). Both spectroscopic data reveal no significant influence of the hemilabile ligand.

The reason for the surprisingly low yield in the case of **3a** is a side-reaction occuring simultaneously to the carbonyl exchange in which the chloro ligand is substituted by the phosphorus of the hybride ligand **2** (eq.2). The cationic iron complex **4** precipitates as yellow-brown solid during irradiation.



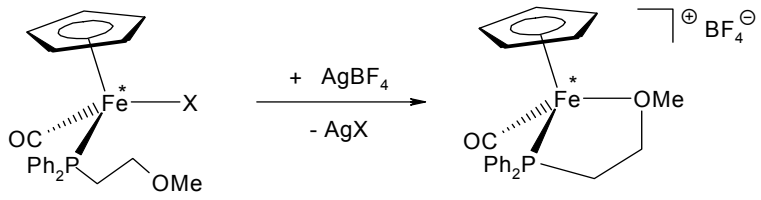
(2)

1a **4**

The structure of **4** is supported by the high frequency of the ν(CO_{sym}) and the ν(CO_{asym}) absorption at 2048 and 2003 cm^{-1} in the IR spectrum.

In order to get coordination of the methoxyethyldiphenylphosphine in a bidentate fashion to the iron, halogen abstraction was performed concerning **3b,c** (eq. 3). This process opens up a coordination site at iron, which can immediately be closed by the oxygen atom of the hemilabile ligand. The abstraction of bromide or iodide in the case of **3b,c** is realized in dichloromethane at room temperature with $AgBF_4$. The driving force for the reaction is the

precipitation of silver bromide or iodide, respectively. The resulting complex **5** is isolated after a reaction time of 1 h as a brown powder in yields from 83% to 98%.

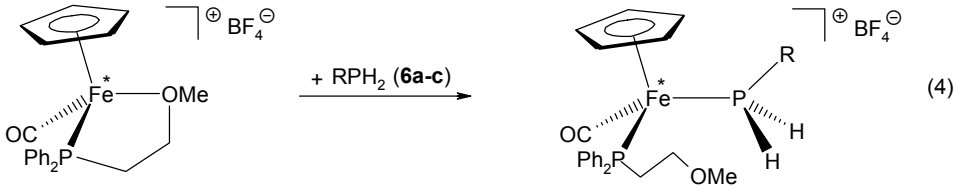


3	b	c
X	Br	I

5

The ^{31}P-NMR spectrum of **5** shows a singlet resonance at 55.96 ppm for the ligand phosphorus which means a highfield shift of about 2 to 3 ppm compared to **3b,c**. The ν(CO) absorption in the IR spectrum appears at 1983 cm^{-1}, ca. 40 cm^{-1} at higher frequency relative to that of **3b,c** as a consequence of the cationic character of **5** and the low donor capacity of the ‘‘hard’’ oxygen donor.

The starting materials for hydrophosphination are achieved by the reaction of the *primary* alkyl and arylphosphines **6a-c** with the complex **5** due to the opening of the chelating hybride ligand at the oxygen site (eq. 4). The synthesis is carried out in dichloromethane at 40 °C to give the phosphine complexes **7a-c** as yellow green (**7a**,**b**) or yellow-orange powders (**7c**) after reaction time of 2 h (**7b**) to 7 h (**7a**).



5 **7a-c**

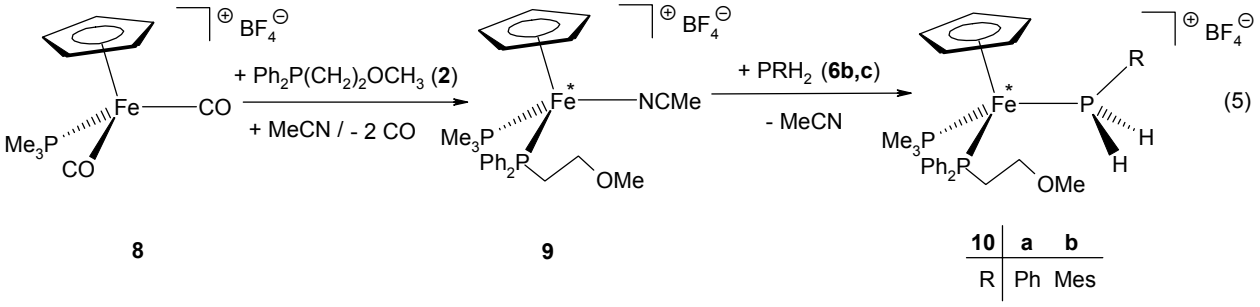
	a	b	c
R	*i*-Pr	Ph	Mes

The mild conditions of the ligand exchange are a consequence of the different donor qualities of the phosphorus and the oxygen atom towards the “soft’’ iron atom having the low oxidation state of II+. Therefore the hard oxygen-atom forms a weaker bond with iron than the soft phosphorus-atom. Consequently the ring opening occurs at the oxygen atom and the

coordination site is thus available to bind the respective *primary* phosphine.

The ^{31}P-NMR spectra of **7a-c** show a doublet for the ‘‘hemilabile’’ phosphine at 58.11 (**7a**), 57.52 (**7b**) and 56.23 (**7c**) and a doublet for the *primary* phosphine phosphorus at 6.83 ppm (**7a**), - 15.83 (**7b**) and - 47.14 (**7c**) with a ^{2}J(PFeP)-coupling constant of 57.1 (**7a**), 57.7 (**7b**) and 55.9 Hz (**7c**).

The substitution of the carbonyl ligand in **7b,c** by the phosphine ligand PMe_3 offers the possibility to increase the electron density at the metal center which should promote the detachment of the functionalized phosphines from the metal. Starting from the cationic Me_3P-complex **8** [38, 39] irradiation in the presence of the hybride ligand **2** in acetonitrile leads after a reaction time of 1 d at ambient temperature not only to the exchange of carbonmonoxide against the hybrid ligand **2**, but also to a substitution of CO by acetonitrile. This becomes evident by IR monitoring the reaction due to the disappearence of both carbonyl bands of the starting material **8**. **9** is isolated as red brown solid in 98 % yield.



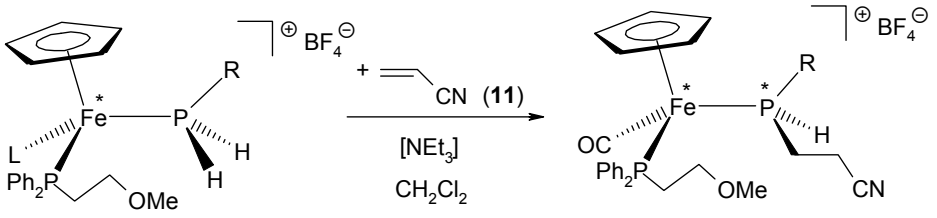
Transformation of **9** to the *primary* phosphine complexes **10a,b** occurs by treatment of **9** with the *primary* phosphines **6b,c** in dichloromethane at room temperature (eq. 5). **10a,b** are obtained as yellow-brown solids after a reaction time of 1 d (**10a,b**) in yields of 81 % (**10b**) and 85 % (**10a**) and can be stored for several weeks under a atmosphere of nitrogen at room temperature without decomposition.

The ^{31}P-NMR spectrum of **9** shows two signals at 56.48 ($Ph_2PCH_2CH_2OMe$) and 23.32 ppm (PMe_3) split by a ^{2}J(PFeP)-coupling of 54.5 Hz to a doublet. The ^{31}P-NMR spectra for **10a,b**

contain three dd-signals at 56.11 (**10a**) and 53.83 (**10b**) for $Ph_2PCH_2CH_2OMe$ 23.53 (**10a**) and 19.27 (**10b**) for PMe_3 and – 8.99 (**10a**) and – 43.44 ppm (**10b**) for the *primary* phosphine phosphorus due to the presence of three magnetically inequivalent phosphorus atoms [^2J(PFeP) of 49.2 Hz to 66.4 Hz]. The ^{1}H-NMR resonance of the diastereotopic PH hydrogens at 5.86/5.61 (**10a**) and 5.53/5.17 (**10b**) appears as a dd-signal with a PH-coupling constant of 340.2/338.0 (**10a**) and 334.8/332.3 Hz (**10b**).

Hydrophosphination of Acrylonitrile (11) and Ethylisocyanate (13) with $\{H_5C_5(L)[H_3CO(CH_2)_2Ph_2P]Fe[P(R)H_2]\}BF_4$ [L = CO, PMe_3; R = i-Pr, Ph, Mes] (7a-c, 10a,b)

The conversion of the complexes **7a-c** and **10a,b** with the electron deficient double bond system acrylonitrile (**11**) to the corresponding *secondary* phosphine complexes **12a-c** occurs in dichloromethane after stirring the reaction mixture for 1 d (**12a**) to 3 d (**12c**) at room temperature (eq. 6).



(6)

	7b	7c	10a
L	CO	CO	PMe_3
R	Ph	Mes	Ph

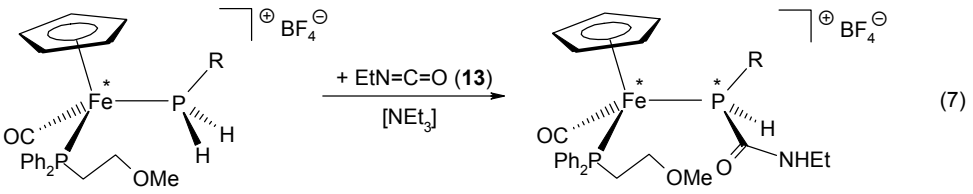
12	a	b	c
L	CO	CO	PMe_3
R	Ph	Mes	Ph

Due to the stereogenic centres iron and phosphorus the complexes **12a-c** are obtained as diastereomers showing a ratio of 60:40 (**12a**/**12a'**/**12c**/**12c'**) or 86:14 (**12b**/**12b'**) respectively. The identical ratio of **12a** and **12c** is surprising since CO and PMe_3 differ significantly both in the electronic behaviour and steric demand. The mechanism for the coupling reactions is comparable to that of analogous base assisted hydrophosphination reactions, discussed previously. [29-31] Therefore the phosphanido iron spezies $H_5C_5(L)[H_3CO(CH_2)_2Ph_2P]Fe$

[P(R)H] (L = CO, PMe_3; R = Ph, Mes) has to be postulated as the crucial intermediate.

12a-c are isolated as yellow (**12a,b**) or yellow brown (**12c**) solids after evaporization of the solvent and washing the residue three time with 15 ml portion of pentane in yields of 94 % (**12a**), 95 % (**12b**) and 81 % (**12c**). The insertion of acrylonitrile (**11**) into the PH-bond according to eq. 6 is supported by the significant low-field shift of the ^{31}P-NMR resonance of the *primary* phosphine phosphorus in **7b** (–15.83),**7c** (– 47.14) and **10a** (– 8.99) to 38.61/40.15 (**12a**/**12a'**) / 3.26/– 3.41 (**12b**/**12b'**) and 48.74/44.76 (**12c**/**12c'**) for the secondary phosphine ligands in **12**. Treatment of the isopropyl phosphine iron complex $\{H_5C_5(OC)[H_3CO(CH_2)_2Ph_2P]Fe[P(i\text{-}Pr)H_2]\}BF_4$ (**7a**) with acrylonitrile (**11**) under the conditions of eq. 6 does not result in the formation of the corresponding *secondary* phosphine complex $\{H_5C_5(OC)[H_3CO(CH_2)_2Ph_2P]Fe[P(i\text{-}Pr)(H)CH_2CH_2CN]\}BF_4$. After 12 d stirring at room temperature **7a** is recovered unchanged. Presumably due to the size of the isopropyl group coupling of the phosphanido-phosphorus with acrylonitrile is sterically hindered. The reaction of the mesitylphosphine iron complex **10b** affords free cyanoethyl-mesitylphosphine, mesitylphosphine and the hemilabile ligand **2**, the starting complex **10b** and a cationic complex of the type $\{H_5C_5(Me_3P)Fe[NCCH{=}CH_2]_2\}BF_4$.

The hydrophosphination reactions of the complexes **7a-c** with ethylisocyanate (**13**) in dichloromethane at 50 °C result succesfully in the formation of the corresponding *secondary* phosphine complexes **14a,b** within 5 h (**14a**) or 7 h (**14b**) (eq. 7). The complexes **14a,b** are isolated as an orange-brown (**14a**) or brown microcrystalline powder (**14b**) in a yield of 72 % (**14a**) or 69 % (**14b**), respectively.



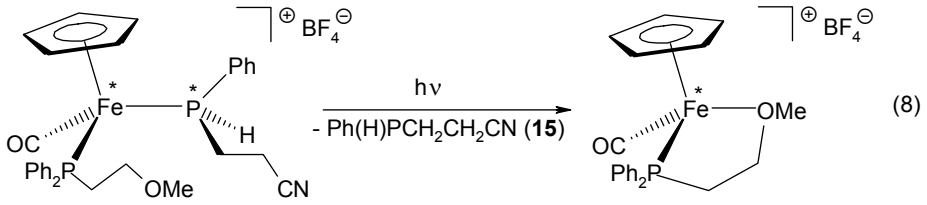
(7)

7	b	c
R	Ph	Mes

14	a	b
R	Ph	Mes

Again the synthesis of the *secondary* phosphine complex deriving from the isopropyl phosphine complex **7a** fails under these conditions. NMR-spectra reveal the existence of diastereomers showing a ratio of 63:37 (**14a**/**14a'**) or 88:12 (**14b**/**14b'**). The ^{31}P-NMR spectra of **14a,b** exhibit for both the *like* and *unlike* isomer a doublet at 55.66 / 54.75 (**14a**) and 54.35 / 56.59 (**14b**) for the O,P-ligand and at 32.11 / 29.28 (**14a**) and 17.76 (**14b**) for the phosphorus atom of the *secondary* phosphine with a ^{2}J(PFeP)-coupling constants of about 50 Hz.

A crucial aspect in the metal-assisted synthesis of chiral phosphines is the release of the phosphines from the metal centre under mild conditions. Taking into account the original concept, the expectation in context with the complexes **12a-c** and **14a,b** is an induction of ligand release by the free oxygen donor site due to chelatation with regeneration of **5**. To get a first idea concerning this possibility the behaviour of the *secondary* phosphine iron complex **12a** towards irradiation was studied. Actually this economically useful procedure can be realized, when complex **12a** is photolyzed with UV-light in dichloromethane to generate the *secondary* (cyanoethyl)phenylphosphine (**15**) after 5.5 h in about 92 % yield (eq.8).



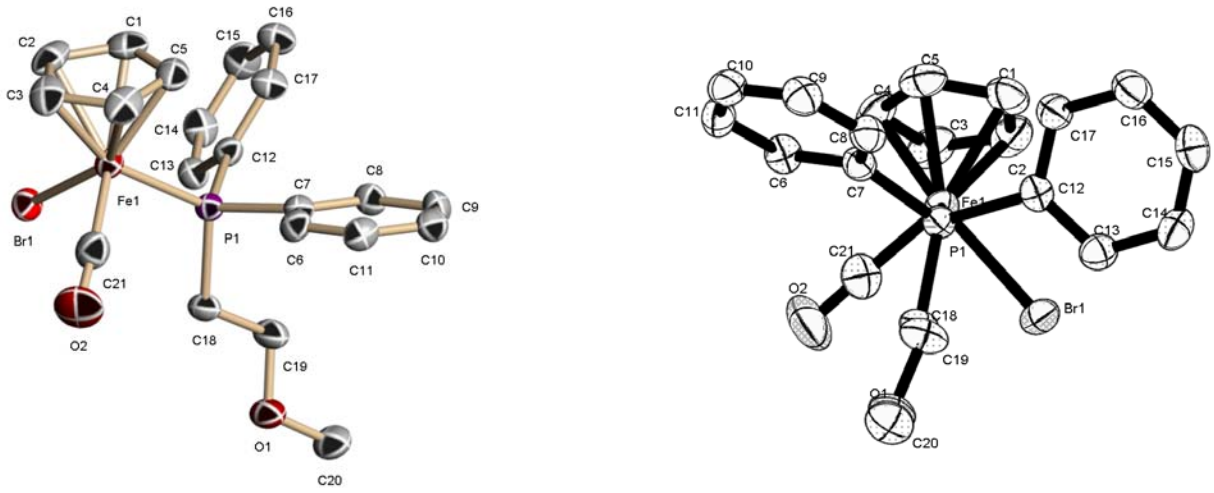
(8)

12a **5**

The ^{31}P-NMR spectra show a singlet at 56.76 ppm for the complex **5** and at – 53.86 ppm for the free *secondary* phosphine **15**. If coordinating solvents are used like acetonitrile or tetrahydrofuran, complexes of the type $\{H_5C_5(OC)[H_3CO(CH_2)_2Ph_2P]FeL\}BF_4$ (L = THF, NCMe) with the solvent ligated will be isolated instead of the complex **5**.

Molecular structure of $\{H_5C_5(OC)_2Fe[PPh_2(CH_2)_2OCH_3]\}BF_4$ (3b) and $\{H_5C_5(Me_3P)[H_3CO(CH_2)_2Ph_2P]Fe(PMesH_2)\}BF_4$ (10b)

Suitable crystal for the structure determination of **3b** is obtained from a saturated toluene at room temperature.



a.) b.)

figure 1: *Molecular structure a.) and Newman projection (View along the Fe1-P1-axis) b.) of $\{H_5C_5(OC)_2Fe[PPh_2(CH_2)_2OCH_3]\}BF_4$ (**3b**). The BF_4-anion and hydrogen atoms have been omitted for clarity.*

Selected bond lengths [pm], bond and torsion angles[°]: Fe(1)-C(21') 175.(2), Fe(1)-C(21) 175.3(8), Fe(1)-P(1) 221.13(8), Fe(1)-Br(1) 240.67(10), Fe(1)-Br(1') 240.8(3), P(1)-C(12) 182.7(3), P(1)-C(7) 183.1(3), P(1)-C(18) 184.0(3), C(21)-Fe(1)-P(1) 94.2(2), C(21')-Fe(1)-P(1) 91.2(5), C(21)-Fe(1)-Br(1) 90.1(2), C(21')-Fe(1)-Br(1') 90.4(5), C(12)-P(1)-C(7) 106.42(12), C(12)-P(1)-C(18) 104.31(12), C(7)-P(1)-C(18) 100.91(12), C(12)-P(1)-Fe(1) 112.09(9), C(7)-P(1)-Fe(1) 115.41(9), C(18)-P(1)-Fe(1) 116.40(9) O(2)-C(21)-Fe(1) 177.2(8), O(2')-C(21')-Fe(1) 177.6(16), C(21)-Fe(1)-P(1)-C(12) 157.6(2), Br(1)-Fe(1)-P(1)-C(7) 170.38(9), Cp_Z-Fe(1)-P(1)-C(19) 173.8°.

The molecular structure of the complex **3b** show a pseudo-octahedral coordination of the iron atom proved by the angle between the iron atom and the carbonyl or bromo ligand of 90.1° for C(21)-Fe(1)-Br(1) and 90.4° for C(21')-Fe(1)-Br(1'), respectively. Similarly, the angles between the iron atom and the phosphine and carbonyl ligand are near to 90° with values of 94.2° for C(21)-Fe(1)-P(1) and 91.2° for C(21')-Fe(1)-P(1), which is in agreement with the literature known complex $(C_5H_4CHPh_2)(OC)Fe(PPh_3)I$ [C-Fe-I 95.1(1)°, P-Fe-I 94.1(1)°].[40] The bond length Fe(1)-P(1) of **3b** with a value of 221.13(8) pm is similar to the Fe-P bond length of the above mentioned complex with 223.1(1) pm.[40] The phosphorus atom in **3b** exhibits a distorted tetrahedral coordination with the largest bond angles including the metal fragment [112.09(9)° C(12)-P(1)-Fe(1), 115.41(9)° C(7)-P(1)-Fe(1), 116.40(9)° C(18)-P(1)-Fe(1)]. The remaining not metal containing angles are smaller than the ideal value [106.42(12)° for C(12)-P(1)-C(7), 104.31(12)° for C(12)-P(1)-C(18) and 100.91(12)° for C(7)-P(1)-C(18)]. The methoxyethylligand bisects the angle of the (OC)(Br)Fe fragment indicated by Cp_Z-Fe(1)-P(2)-C(11) of 173.8° [fig. 1b.)].

Suitable crystal for the structure determination of **10b** is obtained from a saturated dichloromethane solution at room temperature.

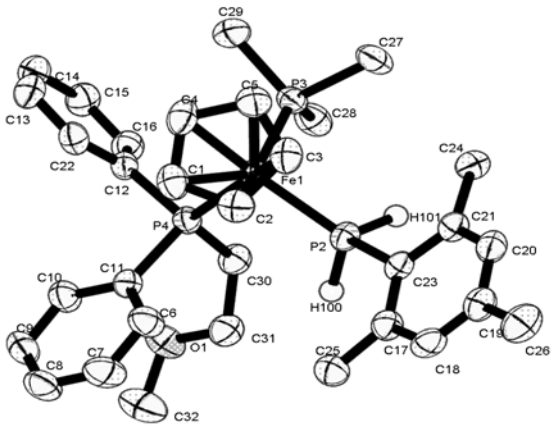


figure 2*: Molecular structure of {$H_5C_5(Me_3P)[H_3CO(CH_2)_2Ph_2P]Fe(PMesH_2)$}$BF_4$ (**10b**). Hydrogen atoms and the BF_4-anion have been omitted for clarity.*

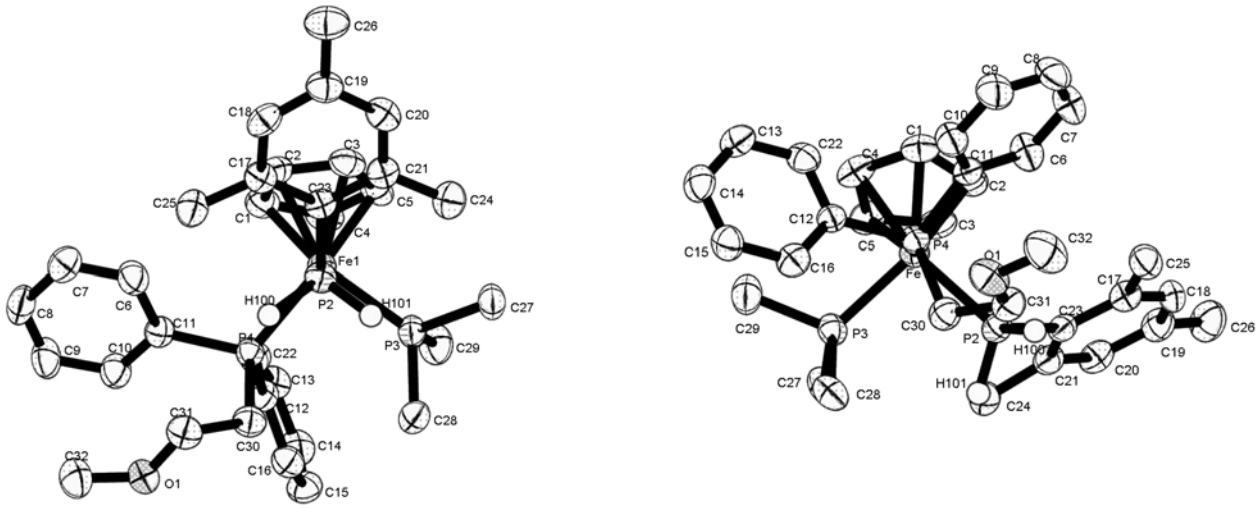


figure 3*: Newman projection (View along the Fe-P2-axis and the Fe-P4-axis) of {$H_5C_5(Me_3P)[H_3CO(CH_2)_2Ph_2P]Fe(PMesH_2)\}BF_4$ (**10b**). Hydrogen atoms and the BF_4-anion have been omitted for clarity.*

Selected bond lengths [pm], bond and torsion angles[°]: Fe(1)-P(2) 220.05(11), Fe(1)-P(3) 222.45(11), Fe(1)-P(4) 224.56(11), P(2)-C(23) 183.4(3), P(4)-C(30) 188.1(4), P(2)-Fe(1)-P(3) 94.95(4), P(2)-Fe(1)-P(4) 94.03(4), P(3)-Fe(1)-P(4) 92.84(4), C(23)-P(2)-Fe(1) 121.86(11), C(30)-P(4)-Fe(1) 116.73(12), P(4)-Fe(1)-P(2)-C(23) 140.80(14), P(3)-Fe(1)-P(2)-C(23) 125.99(14), P(3)-Fe(1)-P(4)-C(11) 172.16(12), P(2)-Fe(1)-P(4)-C(12) 149.56(12), Cp_Z-Fe(1)-P(4)-C(11) - 42.0°, Cp_Z-Fe(1)-P(4)-C(12) 75.8°, Cp_Z-Fe(1)-P(4)-C(30) - 162.6°, Cp_Z-Fe(1)-P(2)-C(23) - 4.3°.

10b shows a pseudooctahedral coordination of the iron ligands comprised by the cyclopentadienyl unit, the hemilabile ligand, trimethylphosphine and the *primary* phosphine. In accordance with this interpretation the angles of the three-legged piano-stool molecule are close to 90° [P(2)-Fe(1)-P(3) 94.95(4)°, P(2)-Fe(1)-P(4) 94.03(4)°, P(3)-Fe(1)-P(4) 92.84(4)°] and lie in the literature-known range for comparable compounds [$(C_5Me_5(dppe)FeC{\equiv}CC_6H_4CN)PF_6$: C-Fe-P1 90.06(11)°, C-Fe-P2 84.21(11)°].[41] The Fe1-P1

distances of 220.05(11) pm [Fe(1)-P(2)], 222.45(11) pm [Fe(1)-P(3)] and 224.56(11) pm [Fe(1)-P(4)] in **10b** lies in the range of literature known compounds {{$C_5H_5(OC)_2Fe[PPh_2(Me_2Pz)]$}$BF_4$ (Pz: 1-Pyrazolyl): Fe-P 221.1(1) pm}[42], whereas the shortest bond with 220 pm is observed between the iron atom and the phosphorus of the *primary* phosphine ligand. The phosphorus atom shows distorted tetrahedral coordination. However, the angles containing the iron fragment are larger than the ideal value of 109.5° [C(23)-P(2)-Fe(1) 121.86(11)°, C(30)-P(4)-Fe(1) 116.73(12)°]. The *newman*-projection of **10b** (fig. 3) with respect to the Fe1-P4-bond reveals a *gauche*-arrangement of both phenyl groups of the η^1-coordinated hemilabile ligand, indicated by the torsion angles Cp_Z-Fe(1)-P(4)-C(11) - 42.0° and Cp_Z-Fe(1)-P(4)-C(12) 75.8°. The *Newman*-projection along the Fe-P2-axis show that the mesityl group of the *primary* phosphine ligand "overlap" with the cyclopentadienyl ligand indicated by the angle Cp_Z-Fe(1)-P(2)-C(23) - 4.3° which is shown in figure 3.

Experimental Section

General: All manipulations were performed under purified nitrogen using standard Schlenk techniques. Solvents were rigorously dried over an appropiate drying agent and distilled under nitrogen prior to use. ^{1}H-, ^{13}C-, ^{31}P- and ^{19}F-NMR spectra were obtained on a Bruker AMX 500, Bruker AMX 400 and a Jeol JNM-LA300 spectrometer. Infrared spectra were recorded in solution on a Bruker IFS 25 grating spectrometer in NaCl cells with 0.1 mm path lengths. Melting points were determined by Differential Thermo Analysis (DTA) with the Du Pont Thermal Analysis System 9000. Irradiation reactions are carried out with a quartz lamp (500W, TQ 719, Hanau). Elemental analyses were performed in the laboratories of the "Institut für Anorganische Chemie". – The starting materials $H_5C_5(OC)_2FeCl$[43], $H_5C_5(OC)_2FeBr$[44], $H_5C_5(OC)_2FeI$[44, 45], $H_5C_5(CO)_3FeBF_4$[46-48], $[H_5C_5(OC)_2(PMe_3)Fe]BF_4$[38, 39] and $Ph_2PCH_2CH_2OCH_3$[49] were synthesized according to the literature procedures. The insertion reagences acrylonitrile and ethylisocyanate were obtained commercially.

1. *Carbonyl(chloro)(η^5-cyclopentadienyl)(2-methoxyethyldiphenylphosphine-κP)iron(II) (**3a**) and [Dicarbonyl(η^5-cyclopentadienyl)(2-methoxyethyldiphenylphosphine-κP)iron(II)] chloride (**4**)*

A solution of 100 mg (0.47 mmol) $H_5C_5(OC)_2FeCl$ (**1a**) and 114 mg (0.47 mmol) $PPh_2(CH_2)_2OCH_3$ (**2**) in 50 ml of toluene is irradiated for 5.5 h with UV-light. The color of the solution turns from brown to green and after 30 min yellow-brown **4** precipitates. **4** is separated by filtration, washed three times with each 10 ml pentane and dried in vacuum. The solvent of the green solution is removed in vacuum, remaining **3a** is washed three times with each 10 ml pentane at – 78 °C and dried in vacuum. – **3a:** Yield: 85 mg (45 %). – Green powder. – M.p. 74 °C. - $C_{21}H_{22}ClFeO_2P$ (428.67). calc.: C 58.84, H 5.17. found: C 57.96, H 5.13. - **^{1}H-NMR(C_6D_6, 500.1 MHz):** δ = 7.70 – 7.66 (m, 2 H, H_5C_6), 7.47 - 7.43 (m, 2 H,

H_5C_6), 7.05 – 6.95 (m, 6 H, H_5C_6), 4.03 [d, ^3J(PFeCH) = 1.1 Hz, 5 H, H_5C_5], 3.59 [ddt, ^3J(PCCH) = 9.5 Hz, ^2J(HCH) = 8.9 Hz, ^3J(HCCH) = 5.9 Hz, 1 H, $\underline{H}_2COCH_3$], 3.37 [ddt, ^3J(PCCH) = 9.4 Hz, ^2J(HCH) = 8.9 Hz, ^3J(HCCH) = 5.6 Hz, 1 H, $\underline{H}_2COCH_3$], 3.07 [ddt, ^3J(PCCH) = 14.1 Hz, ^2J(HCH) = 8.7 Hz, ^3J(HCCH) = 5.7 Hz, 1 H, H_2CP], 2.90 (s, 3 H, H_3CO), 2.64 [ddt, ^3J(PCCH) = 12.2 Hz, ^2J(HCH) = 8.7 Hz, ^3J(HCCH) = 5.3 Hz, 1 H, H_2CP]. - **^{13}C-{^{1}H}-NMR(C_6D_6, 125.77 MHz):** δ = 219.92 [d, ^2J(PFeC) = 32.6 Hz, CO], 134.21 [d, ^1J(PC) = 38.9 Hz, *i*-C], 133.75 [d, ^1J(PC) = 42.9 Hz, *i*-C], 132.08 [d, ^2J(PCC) = 9.6 Hz, *m*-C], 130.70 [d, ^3J(PCCC) = 8.6 Hz, *m*-C], 128.99 [d, ^4J(PCCCC) = 2.2 Hz, *p*-C], 128.48 [d, ^4J(PCCCC) = 2.4 Hz, *p*-C], 127.26 – 126.74 (m, C_6H_5), 81.89 [d, ^2J(PFeC) = 1.2 Hz, C_5H_5], 66.96 [d, ^2J(PCC) = 1.7 Hz, $\underline{C}H_2OCH_3$], 56.62 (s, CH_3), 28.73 ppm [d, ^1J(PC) = 26.9 Hz, PCH_2]. - **^{31}P-{^{1}H}-NMR(C_6D_6, 121.5 MHz):** δ = 57.28 ppm (s). - **IR (pentane):** ν(CO) = 1969(vs) cm^{-1}. – **4:** Yield: 112 mg (52 %). – Yellow-brown powder. – M.p. 84 °C. - $C_{22}H_{22}ClFeO_3P$ (456.69). calc.: C 57.86, H 4.86. found: C 58.34, H 5.01. **- ^{1}H-NMR(CD_3CN, 300.4 MHz):** δ = 7.53 – 7.17 (m, 10 H, H_5C_6), 5.08 (s, br, 5 H, H_5C_5), 3.41 – 3.29 (m, 2 H, H_2C), 3.07 (s, 3 H, H_3C), 2.86 – 2.79 ppm (m, 2 H, H_2C). – **^{13}C-{^{1}H}-NMR(CD_3CN, 75.45 MHz):** δ = 207.79 [d, ^2J(PFeC) = 24.5 Hz, CO], 131.48 – 126.18 (m, C_6H_5), 89.07 (s, C_5H_5), 65.86 [d, ^2J(PCC) = 2.4 Hz, CH_2], 56.92 (s, CH_3), 33.33 ppm [d, ^1J(PC) = 313.8 Hz, PCH_2]. - **^{31}P-{^{1}H}-NMR(CD_3CN, 121.5 MHz):** δ = 54.72 ppm (s). - **IR (dichloromethane):** ν(CO) = 2056(vs), 2011(vs) cm^{-1}.

*2. Bromo(carbonyl)(η^5-cyclopentadienyl)(2-methoxyethyldiphenylphosphine-κP)iron(II) (**3b**)*

Analogous to **3a** from 204 mg (0.794 mmol) $H_5C_5(OC)_2FeBr$ (**1b**) and 194 mg (0.794 mmol) $PPh_2(CH_2)_2OCH_3$ (**2**) in 50 ml of toluene after 30 min. – Yield: 327 mg (87 %). – Green powder. – M.p. 68 °C. - $C_{21}H_{22}BrFeO_2P$ (473.12). calc.: C 53.31, H 4.69. found: C 52.71, H 4.59. - **^{1}H-NMR(C_6D_6, 500.1 MHz):** δ = 7.83 – 7.79 (m, 2 H, H_5C_6), 7.59 – 7.55 (m, 2 H,

H_5C_6), 7.18 – 7.10 (m, 6 H, H_5C_6), 4.13 [d, ^3J(PFeCH) = 1.4 Hz, 5 H, H_5C_5], 3.69 [ddt, ^3J(PCCH) = 9.5 Hz, ^2J(HCH) = 8.9 Hz, ^3J(HCCH) = 5.9 Hz, 1 H, $\underline{H}_2COCH_3$], 3.45 [ddt, ^3J(PCCH) = 9.7 Hz, ^2J(HCH) = 8.9 Hz, ^3J(HCCH) = 5.5 Hz, 1 H, $\underline{H}_2COCH_3$], 3.24 [ddt, ^3J(PCCH) = 14.0 Hz, ^2J(HCH) = 8.7 Hz, ^3J(HCCH) = 5.9 Hz, 1 H, H_2CP], 3.01 (s, 3 H, H_3CO), 2.85 [ddt, ^3J(PCCH) = 11.9 Hz, ^2J(HCH) = 8.7 Hz, ^3J(HCCH) = 5.4 Hz, 1 H, H_2CP]. - **^{13}C-{^{1}H}-NMR(C_6D_6, 125.77 MHz):** δ = 219.83 [d, ^2J(PFeC) = 31.9 Hz, CO], 136.25 [d, ^1J(PC) = 38.9 Hz, *i*-C], 133.99 [d, ^1J(PC) = 43.2 Hz, *i*-C], 132.05 [d, ^2J(PCC) = 9.8 Hz, *m*-C], 130.77 [d, ^3J(PCCC) = 8.4 Hz, *m*-C], 128.93 [d, ^4J(PCCCC) = 2.4 Hz, *p*-C], 128.50 [d, ^4J(PCCCC) = 2.4 Hz, *p*-C], 127.14 – 126.83 (m, C_6H_5), 81.64 [d, ^2J(PFeC) = 1.2 Hz, C_5H_5], 66.97 [d, ^2J(PCC) = 1.7 Hz, $\underline{C}H_2OCH_3$], 56.61 (s, OCH_3), 30.28 ppm [d, ^1J(PC) = 27.8 Hz, PCH_2]. - **^{31}P-{^{1}H}-NMR(C_6D_6, 121.5 MHz):** δ = 57.96 ppm (s). - **IR (pentane):** ν(CO) = 1963(vs) cm^{-1}.

*3. Carbonyl(η^5-cyclopentadienyl)(iodo)(2-methoxyethyldiphenylphosphine-κP)iron(II) (**3c**)*

Analogous to **3a** from 300 mg (0.987 mmol) $H_5C_5(OC)_2FeI$ (**1c**) and 265 mg (1.086 mmol) $PPh_2(CH_2)_2OCH_3$ (**2**) in 50 ml of toluene after 3 h. – Yield: 497 mg (97%). – Green powder. – M.p. 78°C - $C_{21}H_{22}FeIO_2P$ (520.12). calc.: C 48.49, H 4.26. found: C 48.26, H 3.97. - **^{1}H-NMR(C_6D_6, 500.1 MHz):** δ = 7.83 – 7.79 (m, 2 H, H_5C_6), 7.60 - 7.56 (m, 2 H, H_5C_6), 7.17 – 7.11 (m, 6 H, H_5C_6), 4.12 [d, ^3J(PFeCH) = 1.5 Hz, 5 H, H_5C_5], 3.67 [ddt, ^3J(PCCH) = 9.6 Hz, ^2J(HCH) = 9.0 Hz, ^3J(HCCH) = 5.8 Hz, 1 H, $\underline{H}_2COCH_3$], 3.40 [ddt, ^3J(PCCH) = 9.3 Hz, ^2J(HCH) = 9.0 Hz, ^3J(HCCH) = 5.4 Hz, 1 H, $\underline{H}_2COCH_3$], 3.29 [ddt, ^3J(PCCH) = 12.2 Hz, ^2J(HCH) = 8.6 Hz, ^3J(HCCH) = 5.6 Hz, 1 H, H_2CP], 3.59 [ddt, ^3J(PCCH) = 11.6 Hz, ^2J(HCH) = 8.6 Hz, ^3J(HCCH) = 5.3 Hz, 1 H, H_2CP], 3.00 ppm (s, 3 H, H_3CP). - **^{13}C-{^{1}H}-NMR(C_6D_6, 125.77 MHz):** δ = 220.07 [d, ^2J(PFeC) = 30.7 Hz, CO], 136.21 [d, ^1J(PC) = 39.1 Hz, *i*-C], 134.24 [d, ^1J(PC) = 43.2 Hz, *i*-C], 132.01 [d, ^2J(PCC) = 9.6 Hz, *m*-C], 130.95 [d, ^3J(PCCC) = 8.6 Hz, *m*-C], 128.86 [d, ^4J(PCCCC) = 2.2 Hz, *p*-C], 128.55 [d, ^4J(PCCCC) = 2.6 Hz, *p*-C],

127.06 – 126.56 (m, C_6H_5), 81.28 [d, ^2J(PFeC) = 1.2 Hz, C_5H_5], 67.03 (s, $\underline{C}H_2OCH_3$), 56.63 (s, OCH_3), 33.15 ppm [d, ^1J(PC) = 28.6 Hz, PCH_2]. - **^{31}P-{^{1}H}-NMR(C_6D_6, 121.5 MHz):** δ = 59.10 ppm (s). - **IR (pentane):** ν(CO) = 1959(vs) cm^{-1}.

*4. {Carbonyl(η^5-cyclopentadienyl)(2-methoxyethyldiphenylphosphine-κO-κP)iron(II)}tetra-fluoroborate (**5**)*

466 mg (0.896 mmol) of $H_5C_5(OC)\{[H_3CO(CH_2)_2]Ph_2P\}FeI$ (**3c**), dissolved in 50 ml dichloromethane, are combined with 174 mg (0.896 mmol) of $AgBF_4$. The reaction mixture is stirred for one hour at ambient temperature and the precipitated AgI is separated by filtration. The brown filtrate is evaporated to dryness, remaining **5** washed three times with each 20 ml pentane and dried in vacuum. – Yield: 422 mg (98%). – Brown powder. – M.p. 46 °C (dec.). - $C_{21}H_{22}BF_4FeO_2P$.(480.02). calc.: C 52.54, H 4.62. found: C 51.86, H 4.58. - **^{1}H-NMR(CD_3CN, 300.4 MHz):** δ = 7.54 – 7.49 (m, 10 H, H_5C_6), 4.74 [d, ^3J(PFeCH) = 1.5 Hz, 5 H, H_5C_5], 3.40 – 3.34 (m, 2 H, H_2C), 3.11 (s, 3 H, H_3C), 2.83 – 2.75 ppm (m, 2 H, H_2C). - **^{13}C-{^{1}H}-NMR(CD_3CN, 75.45 MHz):** δ = 217.28 [d, ^2J(PFeC) = 27.9 Hz, CO], 133.76 [d, ^1J(PC) = 41.7 Hz, *i*-C], 132.94 [d, ^1J(PC) = 46.2 Hz, *i*-C], 132.84 [d, ^2J(PCC) = 9.2 Hz, *o*-C], 132.46 [d, ^2J(PCC) = 9.3 Hz, *o*-C], 131.71 [d, ^4J(PCCCC) = 2.7 Hz, *p*-C], 131.50 [d, ^4J(PCCCC) = 2.4 Hz, *p*-C], 129.42 [d, ^3J(PCCC) = 9.7 Hz, *m*-C], 84.69 (d, ^2J(PFeC) = 1.1 Hz, C_5H_5), 67.54 (s, CH_2), 58.05 (s, CH_3), 30.53 ppm [d, ^1J(PC) = 26.9 Hz, PCH_2]. - **^{31}P-{^{1}H}-NMR(CD_3CN, 121.5 MHz):** δ = 55.96 ppm (s). – **^{19}F-NMR(CD_3CN, 282.4 MHz):** δ = - 150.41 ppm (s). - **IR (CH_2Cl_2):** ν(CO) = 1983(vs) cm^{-1}.

*5. {Carbonyl(η^5-cyclopentadienyl)(isopropylphosphine)(2-methoxyethyldiphenylphosphine-κP) iron(II)}tetrafluoroborate (**7a**)*

To a solution of 153 mg (0.32 mmol) $H_5C_5(OC)\{[H_3CO(CH_2)_2]Ph_2P\}FeBF_4$ (**5**) in 20 ml of dichloromethane 243 mg (0.32 mmol) *i*-$PrPH_2$ (**6a**) are added. The reaction mixture is stirred

for 7 h at 45 °C and then reduced in vacuum to a volume of 5 ml. **7a** is precipitated by addition of 40 ml of diethylether, separated by filtration, washed three times with 20 ml of diethylether and dried in vacuum. – Yield: 167 mg (95%). – Yellow-green powder. – M.p. 105 °C. - $C_{24}H_{31}BF_4FeO_2P_2$ (556.11). calc.: C 51.84, H 5.62. found: C 51.58, H 5.47. - **^{1}H-NMR($CDCl_3$, 500.1 MHz):** δ = 7.61 – 7.03 (m, 10 H, H_5C_6), 4.73 (s, 5 H, H_5C_5), 4.71 [ddd, ^1J(PH) = 352.2 Hz, , ^2J(HPH) = 6.0 Hz, ^3J(PFePH) = 4.3 Hz, 1 H, PH], 4.38 [ddd, ^1J(PH) = 338.8 Hz, , ^2J(HPH) = 6.0 Hz, ^3J(PFePH) = 3.7 Hz, 1 H, PH], 2.89 (s, 3 H, H_3CO), 2.88 – 2.84 (m, 1 H, H_2CO), 2.69 – 2.62 (m, 1 H, $\underline{H}C(CH_3)_2$), 2.17 – 2.12 (m, 1 H, H_2CO), 2.08 – 1.99 (m, 1 H, H_2CP), 1.72 – 1.65 (m, 1 H, H_2CP), 1.35 (dd, ^3J(PCCH) = 18.3 Hz, ^3J(HCCH) = 6.9 Hz, 3H, H_3C}, 1.19 ppm [dd, ^3J(PCCH) = 17.8 Hz, ^3J(HCCH) = 6.9 Hz, 3H, H_3C]. - **^{13}C-{^{1}H}-NMR($CDCl_3$, 125.8 MHz):** δ = 219.90 [dd, ^2J(PFeC) = 29.0 Hz, CO], 135.20 – 127.43 (m, C_6H_5), 84.64 (s, C_5H_5), 66.72 [d, ^2J(PCC) = 5.0 Hz, CH_2O], 57.26 (s, OCH_3), 28.76 [d, ^1J(PC) = 19.0 Hz, PCH_2], 25.88 [d, ^1J(PC) = 31.7 Hz, $\underline{C}H(CH_3)_2$], 22.38 [d, ^2J(PCC) = 3.8 Hz, CH_3] 21.32 ppm (s, CH_3). - **^{31}P-{^{1}H}-NMR(CD_3CN, 121.5 MHz):** δ = 57.84 [d, ^2J(PFeP) = 55.9 Hz, PPh_2], 7.57 ppm [d, ^2J(PFeP) = 55.9 Hz, P(*i*-Pr)H_2].

*6. {Carbonyl(η^5-cyclopentadienyl)(2-methoxyethyldiphenylphosphine-κP)(phenylphosphine) iron(II)}tetrafluoroborate (7**b**)*

Analogous to **7a** from 190 mg (0.396 mmol) of **5** and 44.9 mg (0.396 mmol) $PhPH_2$ (**6b**) in 20 ml of dichloromethane after 2.5 h. – Yield: 184 mg (75 %). – Yellow-green powder. – M.p. 123 °C. - $C_{27}H_{29}BF_4FeO_2P_2$ (590.12). calc.: C 54.95, H 4.95. found: C 54.25, H 4.82. - **^{1}H-NMR(CD_3CN, 300.4 MHz):** δ = 7.60 – 7.40 (m, 15 H, H_5C_6), 5.96 [dd, ^1J(PH) = 372.3 Hz, ^3J(PFePH) = 3.8 Hz, 1 H, PH], 5.38 [dm, ^1J(PH) = 372.7 Hz, 1 H, PH], 4.87 (s, br, 5 H, H_5C_5), 3.37 (m, 2 H, H_2C), 3.07 (m, 3 H, H_3C), 2.80 ppm (m, 2 H, H_2C). - **^{13}C-{^{1}H}-NMR(CD_3CN, 75.45 MHz):** δ = 133.30 – 131.37 (m, C_6H_5), 129.56 – 129.21 (m, C_6H_5), 85.60 (s, br, C_5H_5), 67.23 [d, ^2J(PCC) = 2.1 Hz, CH_2], 57.83 (s, CH_3), 31.81 [dd, ^1J(PC) =

29.0 Hz, ^3J(PFePC) = 1.4 Hz, CH_2]. - **^{31}P-{^{1}H}-NMR(CD_3CN, 121.5 MHz):** δ = 57.52 [d, ^2J(PFeP) = 57.7 Hz, PPh_2], -15.83 ppm [d, ^2J(PFeP) = 57.7 Hz, $PPhH_2$]. **- IR (CH_2Cl_2):** ν(CO) = 1977(vs) cm^{-1}.

*7. {Carbonyl(η^5-cyclopentadienyl)(mesitylphosphine)(2-methoxyethyldiphenylphosphine-κP) iron(II)}tetrafluoroborate (**7c**)*

Prepared as described for **7a** from 190 mg (0.396 mmol) of **5** and 60 mg (0.396 mmol) $MesPH_2$ (**6c**) in 30 ml dichloromethane after 3 h. – Yield: 243 mg (97 %). – Yellow-orange powder. – M.p. 98 °C. - $C_{30}H_{35}BF_4FeO_2P_2$ (632.21). calc.: C 57.00, H 5.58. found: C 57.34, H 5.61. - **^{1}H-NMR(CD_3CN, 300.4 MHz):** δ = 7.60 – 7.53 (m, 10 H, H_5C_6), 7.02 [d, ^4J(PCCCH) = 3.5 Hz, 2 H, *m*-H), 5.53 [ddd, ^1J(PH) = 360.4 Hz, ^3J(PFePH) = 8.8 Hz, ^2J(HPH) = 5.5 Hz, 1 H, PH], 5.07 [dd, ^1J(PH) = 380.2 Hz, ^3J(PFePH) = 8.8 Hz, 1 H, PH], 4.60 [dd, ^3J(PFeCH) = 1.8 Hz, ^3J(PFeCH) = 1.7 Hz, 5 H, H_5C_5], 3.44 – 3.24 (m, 2 H, H_2C), 3.11 (s, 3 H, H_3C), 2.78 – 2.71 (m, 2 H, H_2C), 2.32 (s, 6 H, *o*-H_3C), 2.25 ppm (s, 3 H, *p*-H_3C). - **^{13}C-{^{1}H}-NMR(CD_3CN, 75.45 MHz):** δ = 216.66 [dd, ^2J(PFeC) = 25.9 Hz, ^2J(PFeC) = 25.2 Hz, CO], 134.02 – 129.80 (m, C_6H_5), 86.12 (s, br, C_5H_5), 67.68 [d, ^2J(PCC) = 2.4 Hz, CH_2], 58.40 (s, O-CH_3), 32.07 [dd, ^1J(PC) = 29.0 Hz, ^3J(PFePC) = 2.1 Hz, PCH_2], 21.79 [d, ^3J(PCCC) = 8.9 Hz, *o*-CH_3, *o*-CH_3], 20.88 ppm [d, ^5J(PCCCCC) = 1.0 Hz, *p*-CH_3]. - **^{31}P-{^{1}H}-NMR(CD_3CN, 121.5 MHz):** δ = 56.23 [d, ^2J(PFeP) = 55.9 Hz, PPh_2], - 47.14 ppm [d, ^2J(PFeP) = 55.9 Hz, $PMesH_2$].

*8. [Acetonitrile(η^5-cyclopentadienyl)(2-methoxyethyldiphenylphosphine(trimethylphosphine) iron]tetrafluoroborate (**9**)*

Analogous to **3a** from 256 mg (0.753 mmol) $[H_5C_5(PMe_3)(CO)_2Fe]BF_4$ (**8**) and 184 mg (0.753 mmol) $PPh_2(CH_2)_2OMe$ (**2**) in 15 ml acetonitrile after 1d. – Yield: 424 mg (98 %). – Yellow powder. - $C_{25}H_{34}BF_4FeNOP_2$ (569.15). calc.: C 52.76, H 6.02, N 2.46. found: C

51.27, H 5.60, N 2.08. - **^{1}H-NMR(CD_3CN, 400.1 MHz)**: δ = 7.54 – 7.49 (m, 2 H, H_5C_6), 7.44 - 7.38 (m, 8 H, H_5C_6), 4.13 [t, ^{3}J(PFeCH) = 1.8 Hz, 5 H, H_5C_5], 3.36 – 3.28 (m, 1 H, H_2CO), 3.21 - 3.11 (m, 1 H, H_2CO), 3.03 (s, 3 H, H_3CO), 2.55 – 2.37 (m, 2 H, H_2CP), 1.88 (s, 3 H, H_3CCN), 1.14 ppm [d, ^{2}J(PCH) = 9.1 Hz, 9 H, $(H_3C)_3P$]. - **^{13}C-{^{1}H}-NMR(CD_3CN, 100.6 MHz)**: δ = 135.98 [dd, ^{1}J(PC) = 36.8 Hz, ^{3}J(PFePC) = 2.4 Hz, *i*-C], 134.08 [d, ^{1}J(PC) = 37.1 Hz, *i*-C], 133.17 (s, CN) 131.90 [d, ^{3}J(PCCC) = 9.5 Hz, *m*-C], 129.77 [d, ^{4}J(PCCCC) = 2.4 Hz, *p*-C], 129.66 [d, ^{4}J(PCCCC) = 2.4 Hz, *p*-C], 128.37 [d, ^{2}J(PCC) = 8.8 Hz, *o*-C], 128.18 [d, ^{2}J(PCC) = 9.3 Hz, *o*-C], 78.05 [t, ^{2}J(PFeC) = 1.2 Hz, C_5H_5], 67.83 [d, ^{2}J(PCC) = 3.7 Hz, CH_2O], 57.21 (s, CH_3O), 28.82 [d, ^{1}J(PC) = 20.0 Hz, CH_2P], 17.40 ppm [dd, ^{1}J(PC) = 26.5 Hz, ^{3}J(PFePC) = 0.9 Hz, $(CH_3)_3P$], 0.15 ppm (s, CH_3CN). - **^{31}P-{^{1}H}-NMR(CD_3CN, 162.0 MHz)**: δ = 56.48 [d, ^{2}J(PFeP) = 54.5 Hz, PPh_2], 23.32 ppm [d ^{2}J(PFeP) = 54.5 Hz, $P(CH_3)_3$].

*9. [(η^5-Cyclopentadienyl)(2-methoxyethyldiphenylphosphine)(phenylphosphine)(trimethyl-phosphine)iron]tetrafluoroborate (**10a**)*

Prepared as described for complex **7a** from 121 mg (0.213 mmol) of {H_5C_5[$MeO(CH_2)_2Ph_2P$](Me_3P)Fe(MeCN)}BF_4 (**9**) and 23.5 mg (0.213 mmol) of $PhPH_2$ (**6b**) in 15 ml dichlormethane after 1 d. – Yield: 116 mg (85 %). – Orange-red powder.- $C_{29}H_{38}BF_4FeOP_3$ (638.19). calc.: C 54.58, H 6.00. found: C 53.21, H 5.63. - **^{1}H-NMR(CD_3CN, 500.1 MHz)**: δ = 7.56 – 7.22 (m, 15 H, H_5C_6), 5.86 [dtd, ^{1}J(PH) = 340.2 Hz, ^{2}J(HPH) = 6.0 Hz, ^{3}J(PFePH) = 3.8 Hz, 1 H, HP], 5.61 [dtd, ^{1}J(PH) = 338.0 Hz, ^{2}J(HPH) = 6.3 Hz, ^{3}J(PFePH) = 3.8 Hz, 1 H, HP], 4.30 (q, 5 H, ^{3}J(PFeCH) = 2.0 Hz, H_5C_5), 3.20 – 3.13 (m, 2 H, H_2CO), 2.96 (s, 3 H, H_3CO), 2.51 – 2.42 (m, 2 H, H_2CP), 1.02 ppm [d, ^{2}J(PCH) = 8.9 Hz, $(H_3C)_3P$]. - **^{13}C-{^{1}H}-NMR(CD_3CN, 125.8 MHz)**: δ = 134.16 – 127.80 (m, C_6H_5), 80.23 (s, br, C_5H_5), 67.56 [d, ^{2}J(PCC) = 5.5 Hz, CH_2O], 57.19 (s, CH_3O), 30.48 (s, CH_2P), 18.49 ppm [d, ^{1}J(PC) = 29.3 Hz, $(CH_3)_3P$]. - **^{31}P-{^{1}H}-NMR(CD_3CN, 202.4 MHz)**: δ = 56.11 [dd, ^{2}J(PFeP) = 59.0 Hz, ^{2}J(PFeP) = 49.2 Hz,

PPh_2], 23.53 [dd ^2J(PFeP) = 66.4 Hz, ^2J(PFeP) = 49.2 Hz, $P(CH_3)_3$], -8.99 ppm [dd, ^2J(PFeP) = 66.4 Hz, ^2J(PFeP) = 59.0 Hz, $PPhH_2$].

*10. [(η^5-Cyclopentadienyl)(mesitylphosphine)(2-methoxyethyldiphenylphosphine)(trimethyl-phosphine)iron]tetrafluoroborate (**10b**)*

Prepared as described for complex **7a** from 136 mg (0.239 mmol) of {H_5C_5[$MeO(CH_2)_2Ph_2P$] (Me_3P)Fe(MeCN)}BF_4 (**9**) and 36.4 mg (0.239 mmol) of $MesPH_2$ (**6c**) in 15 ml dichlormethane after 1 d. – Yield: 132 mg (81 %). – Orange powder.- $C_{32}H_{44}BF_4FeOP_3$ (680.28). calc.: C 56.50, H 6.52. found: C 56.11, H 6.00. -**^{1}H-NMR(CD_3CN, 400.1 MHz)**: δ = 7.46 – 7.40 (m, 10 H, H_5C_6), 6.95 [d, 2 H, ^2J(PCCCH) = 3.2 Hz, *m*-H], 5.53 [dm, 1 H, ^1J(PH) = 334.8 Hz, HP], 5.17 [dm, 1 H, ^1J(PH) = 332.3 Hz, HP], 4.11 [q, ^3J(PFeCH) = 2.1 Hz, 5 H, H_5C_5], 3.13 – 3.09 (m, 2 H, H_2CO), 2.97 (s, 3 H, H_3CO), 2.58 - 2.49 (m, 1 H, H_2CP), 2.42 - 2.35 (m, 1 H, H_2CP) , 2.27 (s, 6 H, *o*-H_3C), 2.24 (s, 3 H, *p*-H_3C), 1.15 ppm [d, ^2J(PCH) = 8.7 Hz, 9 H, $(H_3C)_3P$]. - **^{13}C-{^{1}H}-NMR(CD_3CN, 100.6 MHz)**: δ = 132.63 – 128.36 (m, C_6H_5), 79.41 (s, br, C_5H_5), 64.95 (s, CH_2O), 57.48 (s, CH_3O), 30.48 (s, CH_2P), 21.89 (s, *o*-CH_3), 21.80 (s, *p*-CH_3), 19.71 ppm [d, ^1J(PC) = 29.3 Hz, $(CH_3)_3P$]. - **^{31}P-{^{1}H}-NMR(CD_3CN, 162.0 MHz)**: δ = 53.83 [dd, ^2J(PFeP) = 53.5 Hz , ^2J(PFeP) = 51.5 Hz, PPh_2], 19.27 [dd ^2J(PFeP) = 58.5 Hz, ^2J(PFeP) = 51.5 Hz, $P(CH_3)_3$], - 43.44 ppm [dd, ^2J(PFeP) = 58.5 Hz, ^2J(PFeP) = 53.5 Hz, $PMesH_2$].

*11. {Carbonyl(2-cyanoethylphenylphosphine)(η^5-cyclopentadienyl)(2-methoxyethyldiphenyl-phosphine-κP)iron(II)}tetrafluoroborate (**12a/12a'**)*

To a solution of 184 mg (0.312 mmol) {H_5C_5(OC){[$H_3CO(CH_2)_2$]Ph_2P}FeP(Ph)H_2}BF_4 (**7b**) in 20 ml of dichloromethane 16.6 mg (0.312 mmol) of acrylonitrile (**11**) and 5 mg (0.005 mmol) NEt_3 are added. The reaction mixture is stirred for 1 d at ambient temperature. Volatile materials are removed in vacuum and remaining **12a** washed five times with each 20 ml

pentane and dried in vacuum. – Yield: 188 mg (94 %). – Yellow-brown powder. $C_{30}H_{32}BF_4FeNO_2P_2$ (643.18). calc.: C 56.02, H 5.02, N 2.18. found: C 56.45, H 5.13, N 2.15. – **12a / 12a'** = 60 : 40. The isomeric ratio is determined by integration of the C_5H_5-signals in the ^{1}H-NMR-spectrum. - **^{1}H-NMR(CD_3CN, 300.4 MHz): 12a**: δ = 7.73 – 7.19 (m, 15 H, H_5C_6), 6.54 (dm, ^1J(PH) = 360.0 Hz, 2 H, PH), 4.97 (s, br, 5 H, H_5C_5), 3.64 – 3.15 (m, 2 H, H_2C), 3.06 (s, 3 H, H_3C), 2.95 – 2.13 ppm (m, 6 H, H_2C). **12a'**: δ = 7.73 – 7.19 (m, 15 H, H_5C_6), 5.94 (dm, ^1J(PC) = 334.3 Hz, 2 H, PH), 4.93 (s, br, 5 H, H_5C_5), 3.64 – 3.15 (m, 2 H, H_2C), 3.11 (s, 3 H, H_3C), 2.95 – 2.13 ppm (m, 6 H, H_2C). - **^{13}C-{^{1}H}-NMR(CD_3CN, 75.45 MHz): 12a:** δ = 215.55 (t, ^2J(PFeC) = 26.3 Hz, CO), 133.78 – 131.93 (m, C_6H_5), 130.71 – 129.79 (m, C_6H_5), 118.52 (d, ^3J(PCCC) = 8.9 Hz, CN), 85.87 (s, br, C_5H_5), 67.94 (d, ^2J(PCC) = 14.3 Hz, CH_2O), 58.48 (s, CH_3), 31.91 (dd, ^1J(PC) = 29.7 Hz, ^3J(PFePC) = 1.4 Hz, P*C*$H_2CH_2OCH_3$), 24.62 (d, ^1J(PC) = 23.5 Hz, P*C*H_2CH_2CN), 16.10 ppm (d, ^2J(PCC) = 6.6 Hz, *C*H_2CN). **12a'**: δ = 215.90 (t, ^2J(PFeC) = 23.1 Hz, CO), 133.78 – 131.93 (m, C_6H_5), 130.71 – 129.79 (m, C_6H_5), 118.98 (d, ^3J(PCCC) = 10.6 Hz, CN), 86.06 (s, br, C_5H_5), 67.89 (d, ^2J(PCC) = 11.2 Hz, CH_2O), 58.52 (s, CH_3), 32.76 (dd, ^1J(PC) = 28.2 Hz, ^3J(PFePC) = 1.4 Hz, P*C*$H_2CH_2OCH_3$), 26.65 (dd, ^1J(PC) = 28.6 Hz, ^3J(PFePC) = 2.7 Hz, P*C*H_2CH_2CN), 16.34 ppm (d, ^2J(PCC) = 8.9 Hz, *C*H_2CN).- **^{31}P-{^{1}H}-NMR(CD_3CN, 121.5 MHz): 12a**: δ = 56.89 (d, ^2J(PFeP) = 54.7 Hz, PPh_2), 38.61 ppm (d, ^2J(PFeP) = 54.7 Hz, PPh(H)CH_2CH_2CN); **12a'**: δ = 55.35 (d, ^2J(PFeP) = 53.5 Hz, PPh_2), 40.15 ppm (d, ^2J(PFeP) = 53.5 Hz, PPh(H)CH_2CH_2CN).

*12. {Carbonyl(2-cyanoethylmesitylphosphine)(η^5-cyclopentadienyl)(2-methoxyethyldiphenyl-phosphine-κP)iron(II)}tetrafluoroborate (**12b/12b'**)*

Analogous to **12a** from 20.0 mg (0.032 mmol) {H_5C_5(OC){[$H_3CO(CH_2)_2$]Ph_2P} FeP(Mes)H_2}BF_4 (**7c**) and 1.67 mg (0.032 mmol) of acrylonitrile (**11**) in 10 ml of

dichloromethane after 1 d. – Yield: 20.8 mg (95 %). – Yellow-orange powder. - $C_{33}H_{38}BF_4FeNO_2P_2$ (685.26). calc.: C 57.84, H 5.59, N 2.04. found: C 56.99, H 5.63, N 2.05. - Isomer ratio 86:14 (**12b**/**12b**'). - **^{1}H-NMR(CD_3CN, 300.4 MHz):** δ = 7.63 – 7.30 (m, 10 H, H_5C_6), 7.05 (s, br, 2 H, *m*-H), 5.84 [dm, ^1J(PH) = 356.8 Hz, 1 H, PH], 4.92 [dd, ^3J(PFeCH) = 1.7 Hz, ^3J(PFeCH) = 1.8 Hz 5 H, H_5C_5] [**12b'**], 4,69 [dd, ^3J(PFeCH) = 1.8 Hz, ^3J(PFeCH) = 1.7 Hz, 5 H, H_5C_5], 3.54 – 3.38 (m, 4 H, H_2C), 3.15 (s, 3 H, H_3C), 2.93 – 2.82 (m, 2 H, H_2C), 2.53 – 2.41 (m, 2 H, H_2C), 2.41 (s, 3 H, *p*-H_3C), 2.31 (s, 3 H, *o*-H_3C), 2.28 ppm (s, 3 H, *o*-H_3C). - **^{13}C-{^{1}H}-NMR(CD_3CN, 75.45 MHz) 12b:** δ = 217.43 [d, ^2J(PFeC) = 25.1 Hz, CO], 133.39 – 130.93 (m, C_6H_5), 130.18 – 129.30 (m, C_6H_5), 86.36 (s, br, C_5H_5), 67.84 [d, ^2J(PCC) = 3.1 Hz, CH_2], 58.31 (s, CH_3), 32.69 [d, ^1J(PC) = 28.2 Hz, CH_2], 23.00 [d, ^3J(PCCC) = 6.9 Hz, *o*-CH_3], 20.71 [d, ^5J(PCCCCC) = 1.0 Hz, *p*-CH_3], 20.70 [dd, ^1J(PC) = 31.39 Hz, ^3J(PCCC) = 2.0 Hz, CH_2CH_2CN], 15.73 ppm [d, ^2J(PCC) = 9.0 Hz, CH_2CN]. **12b'**: δ = 215.89 [d, ^2J(PFeC) = 25.5 Hz, CO], 133.39 – 130.93 (m, C_6H_5), 130.18 – 129.30 (m, C_6H_5), 86.24 (s, br, C_5H_5), 67.79 [d, ^2J(PCC) = 4.2 Hz, CH_2], 58.13 (s, CH_3), 31.74 [d, ^1J(PC) = 29.0 Hz, CH_2], 22.95 [d, ^3J(PCCC) = 7.5 Hz, *o*-CH_3), 22.57 [d, ^5J(PCCCCC) = 1.5 Hz, *p*-CH_3], 20.70 [dd, ^1J(PC) = 31.39 Hz, ^3J(PCCC) = 2.0 Hz, CH_2CH_2CN], 16.20 ppm [d, ^2J(PCC) = 8.6 Hz, CH_2CN]. - **^{31}P-{^{1}H}-NMR(CD_3CN, 121.5 MHz): 12b**: δ = 54.71 [d, ^2J(PFeP) = 50.0 Hz, PPh_2], 3.26 ppm [d, ^2J(PFeP) = 50.0 Hz, PMes(H)CH_2CH_2CN]. **12b'**: δ = 54.19 [d, ^2J(PFeP) = 49.8 Hz, PPh_2], -3.41 ppm [d, ^2J(PFeP) = 49.8 Hz, PMes(H)CH_2CH_2CN].

*13. [(2-Cyanoethylphenylphosphine)(η^5-cyclopentadienyl)(2-methoxyethyldiphenylphosphine) (trimethylphosphine)iron]tetrafluoroborate (**12c/12c'**)*

Analogous to **12a** from 108 mg (0.169 mmol) {(H_5C_5)(Me_3P)[$MeO(CH_2)_2Ph_2P$] Fe[$PPhH_2$]}BF_4 (**10a**) and 8.97 mg (0.169 mmol) acrylonitrile (**11**) in 15 ml of dichloromethane after 1 d. – Yield: 132 mg (81 %). – Yellow powder. - $C_{32}H_{41}BF_4FeNOP_3$ (691.29). calc.: C 55.60, H 5.98, N 2.03. found: C 54.34, H 5.77, N 1.91. – Isomer ratio: 60 :

40 (**12c**/**12c'**). -**^{1}H-NMR(CD_3CN, 500.1 MHz)**: **12c**: δ = 7.65 – 6.92 (m, 15 H, H_5C_6), 5.32 [dm, 1 H ^{1}J(PH) = 332.7 Hz, HP], 4.48 [dd, 5 H, ^{3}J(Me_3PFeCH) = 1.9 Hz, ^{3}J(Ph_2PFeCH) = 1.9 Hz, H_5C_5], 3.39 – 3.33 (m, 2 H, H_2CO), 2.97 (s, 3 H, H_3CO), 2.34 – 2.22 (m, 2 H, H_2CP), 0.91 ppm [d, 9 H, ^{2}J(PCH) = 8.8 Hz, $(H_3C)_3P$]. – **12c'**: δ = 7.65 – 6.92 (m, 15 H, H_5C_6), 5.20 [dm, 1 H, ^{1}J(PH) = 338.6 Hz, HP], 4.46 [dd, 5 H, ^{3}J(Me_3PFeCH) = 1.9 Hz, ^{3}J(Ph_2PFeCH) = 2.0 Hz, H_5C_5], 3.54 – 3.49 (m, 2 H, H_2CP), 2.85 (s, 3 H, H_3CO), 2.63 – 2.48 (m, 2 H, H_2CO), 1.09 ppm [d, 9 H, ^{2}J(PCH) = 8.7 Hz, $(H_3C)_3P$]. - **^{13}C-NMR(CD_3CN, 125.8 MHz)**: **12c:** δ = 134.71 – 127.94 (m, C_6H_5), 79.32 (s, br, C_5H_5), 67.57 [d, ^{2}J(PCC) = 6.4 Hz, CH_2O], 57.24 (s, CH_3O), 29.38 (s, CH_2P), 27.24 [d, ^{1}J(PC) = 20.5 Hz, CH_2CH_2CN], 20.02 [d, ^{1}J(PC) = 28.4 Hz, $(CH_3)_3P$], 15.69 ppm [d, ^{2}J(PCC) = 10.1 Hz, CH_2CN]. – **12c':** δ = 132.57 – 127.94 (m, C_6H_5), 79.27 (s, br, C_5H_5), 67.40 [d, ^{2}J(PCC) = 6.4 Hz, CH_2O], 57.02 (s, CH_3O), 29.85 (s, CH_2P), 27.29 [d, ^{1}J(PC) = 20.8 Hz, CH_2CH_2CN] 19.24 [d, ^{1}J(PC) = 28.4 Hz, $(CH_3)_3P$], 15.65 ppm [d, ^{2}J(PCC) = 1.8 Hz, CH_2CN]. - **^{31}P-{^{1}H}-NMR(CD_3CN, 202.5 MHz)**: **12c:** δ = 54.53 [t, ^{2}J(PFeP) = 51.7 Hz, PPh_2], 48.74 [dd, ^{2}J(PFeP) = 61.5 Hz, ^{2}J(PFeP) = 51.7 Hz, PPhH], 19.00 ppm [dd ^{2}J(PFeP) = 61.5 Hz, ^{2}J(PFeP) = 51.7 Hz, $P(CH_3)_3$]. – **12c':** δ = 54.53 [dd, ^{2}J(PFeP) = 54.2 Hz, ^{2}J(PFeP) = 51.7 Hz, PPh_2], 44.76 [dd, ^{2}J(PFeP) = 61.5 Hz, ^{2}J(PFeP) = 54.2 Hz, PPhH], 20.30 ppm [dd ^{2}J(PFeP) = 61.5 Hz, ^{2}J(PFeP) = 51.7 Hz, $P(CH_3)_3$].

*14. Treatment of $\{(H_5C_5)(Me_3P)[MeO(CH_2)_2Ph_2P]Fe[MesPH_2]\}BF_4$ (**10b**) with acrylonitrile (**11**)*

Analogous to **12a** from 132 mg (0.194 mmol) of $\{(H_5C_5)(Me_3P)[MeO(CH_2)_2Ph_2P]Fe[MesPH_2]\}BF_4$ (**10b**) and 10.29 mg (0.194 mmol) of acrylonitrile (**11**) in 15 ml of dichloromethane after 4 d. The solvent is removed in vacuum and the yellow solid residue is washed three times each with 10 ml pentane and dried in vacuum. The ^{31}P-NMR spectrum shows a mixture of the starting complex **10b** (δ^{31}P = 53.91, 20.03, - 42.87 ppm) and a

cationic complex of the type $\{C_5H_5(Me_3P)Fe[NCCHCH_2]_2\}BF_4$ ($\delta^{31}P$ = 28.87 ppm). The pentane phases are combined and the solvent removed in vacuum. The ^{31}P-NMR spectrum of the colourless residue shows free mesitylphosphine ($\delta^{31}P$ = – 89.3 ppm) as well as the signals of $Ph_2P(CH_2)_2OMe$ ($\delta^{31}P$ = – 21.37 ppm) and $MesP(H)CH_2CH_2CN$ ($\delta^{31}P$ = 25.48 ppm).

*15. {Carbonyl(η^5-cyclopentadienyl)(N-ethylformamidophenylphosphine)(2-methoxyethyldi-phenylphosphine-κP)iron(II)}tetrafluoroborate (**14a/14a'**)*

To a solution of 154 mg (0.261 mmol) $\{H_5C_5(OC)\{[H_3CO(CH_2)_2]Ph_2P\}Fe[P(H)_2Ph]\}BF_4$ (**7b**) in 15 ml acetonitrile 18.6 mg (0.261 mmol) of ethylisocyanate (**13**) and 5 mg (0.005 mmol) NEt_3 are added. The reaction mixture is stirred for 5 h at 50 °C and then reduced in vacuum to a volume of 5 ml. **14a** is precipitated by addition of 40 ml of diethylether, separated by filtration, washed three times with 20 ml of pentane and dried in vacuum. – Yield: 115 mg (72%). – Orange-brown powder. $C_{30}H_{34}BF_4FeNO_3P_2$ (661.20). calc.: C 54.50, H 5.18, N 2.12. found: C 54.85, H 5.24, N 2.13. - Isomer ratio 63:37 (**14a**/**14a**').- **^{1}H-NMR(CD_3CN, 300.4 MHz)**: **14a**: δ = 7.63 – 7.20 (m, 15 H, H_5C_6), 7.03 (s, 1 H , NH), 5.84 [dd, ^1J(PH) = 353.1 Hz, ^3J(PFePH) = 9.7 Hz, 1 H, HP], 5.02 [t, ^3J(PFeCH) = 1.5 Hz, 5 H, H_5C_5], 3.56 – 2.51 (m, 6 H, H_2CO, H_2CP, H_2CN), 3.04 (s, 3 H, H_3CO), 1.23 ppm [t, ^3J(HCCH) = 7.3 Hz, 3 H, $\underline{H}_3CCH_2N$]. – **14a'**: δ = 7.63 – 7.20 (m, 15 H, H_5C_6), 7.03 (s, 1 H , NH), 5.69 [dd, ^1J(PH) = 324.9 Hz, ^3J(PFePH) = 3.1 Hz, 1 H, HP], 5.01 (s, H_5C_5), 3.56 – 2.51 (m, 6 H, H_2CO, H_2CP, H_2CN), 3.11 (s, 3 H, H_3CO), 1.07 ppm [t, ^3J(HCCH) = 6.6 Hz, 3 H, $\underline{H}_3CCH_2N$]. - **^{31}P-{^{1}H}-NMR(CD_3CN, 121.5 MHz): 14a**: δ = 55.66 [d, ^2J(PFeP) = 49.8 Hz, PPh_2], 32.11 ppm [d, ^2J(PFeP) = 49.8 Hz, $P(H)Ph(CONHCH_2CH_3)$]; **14a'**: δ = 54.75 [d, ^2J(PFeP) = 53.5 Hz, PPh_2], 29.28 ppm [d, ^2J(PFeP) = 53.5 Hz, $P(H)Ph(CONHCH_2CH_3)$]

*16. {Carbonyl(η^5-cyclopentadienyl)(N-ethylformamidomesitylphosphine)(2-methoxyethyldi-phenylphosphine-κP)iron(II)}tetrafluoroborate (**14b/14b'**)*

According to **14a** from 243 mg (0.384 mmol) of $\{H_5C_5(OC)\{[H_3CO(CH_2)_2]Ph_2P\}Fe[P(H)_2Mes]\}BF_4$ (**7c**), 27.3 mg (0.384 mmol) ethylisocyanate (**13**) and 5 mg (0.005 mmol) NEt_3 in 20 ml acetonitrile after 7 h. – Yield: 187 mg (69%). – Brown powder. - $C_{33}H_{40}BF_4FeNO_3P_2$ (703.28). calc.: C 56.36, H 5.73, N 1.99. found: C 55.78, H 5.64, N 2.03. - Isomer ratio 88:12 (**14b**/**14b**'). – **14b**: δ = 7.65 – 7.23 (m, 10 H, H_5C_6), 6.92 (s, 1 H , NH), 6-88 (s, 2 H, *m*-H), 5.35 [d, ^1J(PH) = 370.3 Hz, 1 H, HP], 4.33 (s, 5 H, H_5C_5), 3.42 – 2.45 (m, 6 H, H_2CO, H_2CP, H_2CN), 3.02 (s, 3 H, H_3CO), 1.23 (s, 3 H, *p*-H_3C) , 1.23 (s, 3 H, $\underline{H}_3CCH_2N$) 1.05 ppm [t, ^3J(PCCH) = 9.8 Hz, 3 H, *o*-H_3C]. - **^{31}P-{^{1}H}-NMR(CD_3CN, 121.5 MHz): 14b:** δ = 54.35 [d, ^2J(PFeP) = 53.5 Hz, PPh_2], 17.76 ppm [d, ^2J(PFeP) = 53.5 Hz, P(H)Mes($CONHCH_2CH_3$)].

*17. X-ray analysis of **3b** and **10b***

3b: $C_{21}H_{22}BrFeO_2P$, M_r = 473.1, monoclinic, space group *P*2(1)/c (No. 14), *a* = 7.4041(15) Å, *b* = 16.351(3) Å, *c* = 16.767(3) Å, *β* = 101.777(3)°, *V* = 1987.1(7) Å^3, *Z* = 8, *ρ* = 1.581 Mgm^{-3}, Nonius Kappa CCD diffractometer, radiation type: Mo-K_α, wavelength: λ = 0.71073 mm^{-1}, crystal size: 0.12 x 0.08 x 0.10 mm, temperature: 293(2) K, scale range: 1.76° < Θ < 25.06°, *F*(000): 960, total reflections: 35631, observed reflections: 3516 with [$I > 2\sigma(I)$], absorption coefficient: μ = 2.862 mm^{-1}, empirical absorption correction, structure solution: SHELXS-97[50], structure refinement: SHELXL-97[51-54], R_1 = 0.0340, wR_2 = 0.0880.

10b: $C_{32}H_{44}BFeF_4OP_3$, M_r = 680.3, triclinic, space group *P*-1 (No. 2), *a* = 10.087(2) Å, *b* = 11.673(2) Å, *c* = 13.892(3) Å, *α* = 99.334(5)°, *β* = 96.892(5)°, *γ* = 96.605(6)°, *V* = 1587.1(6)

Å^3, Z = 2, ρ = 1.423 Mgm^{-3}, Nonius Kappa CCD diffractometer, radiation type: Mo-K_α, wavelength: λ = 0.71073 mm^{-1}, crystal size: 0.25 x 0.16 x 0.10 mm, temperature: 173(2) K, scale range: 1.78° < Θ < 25.06°, F(000): 712, total reflections: 16855, observed reflections: 5579 with [$I > 2\sigma$ (I)], absorption coefficient: μ = 0.676 mm^{-1}, empirical absorption correction, structure solution: SHELXS-97[50], structure refinement: SHELXL-97[51-54], R_1 = 0.0695, wR_2 = 0.1433.

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CHAPTER V:

Synthesis and Reactivity of *Primary* Phosphine Ruthenium Complexes $\{H_5C_5(Ph_3P)[H_3CO(CH_2)_2Ph_2P]Ru[PRR'H]\}BF_4$ (R = Ph, Mes; R' = H, Ph) containing a Hemilabile Ligand

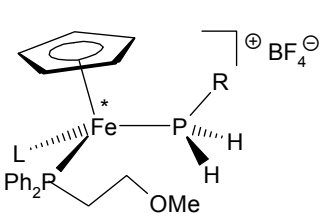
Abstract

The ruthenium complex $H_5C_5(Ph_3P)[H_3CO(CH_2)_2Ph_2P]RuCl$ (**3**) was generated by exchange of one triphenylphosphine ligand of the complex $H_5C_5(Ph_3P)_2RuCl$ (**1**) by the hemilabile ligand $PPh_2(CH_2)_2OCH_3$ (**2**). Starting from complex **3** the cationic ruthenium complex $\{H_5C_5(Ph_3P)Ru[PPh_2(CH_2)_2OCH_3]\}BF_4$ (**4**) can be synthesized by treatment with silver tetrafluoroborate in dichloromethane. The reaction of the complex **4** with the phosphines PPh_2H (**5**) and $P(R)H_2$ (R = Ph, Mes) (**6a,b**) generates the *secondary* phosphine complex $\{H_5C_5(Ph_3P)[H_3CO(CH_2)_2Ph_2P]Ru[PPh_2H]\}BF_4$ (**7**) and the *primary* phosphine complexes $\{H_5C_5(Ph_3P)[H_3CO(CH_2)_2Ph_2P]Ru[P(R)H_2]\}BF_4$ (R = Ph, Mes) (**8a,b**). The hydrophosphination reaction of **7** with the electron deficient alkene acrylonitrile (**9**) and potassium-*tert*-butylate yields the *tertiary* phosphine ruthenium complex $\{H_5C_5(Ph_3P)[H_3CO(CH_2)_2Ph_2P]Ru[PPh_2(CH_2)_2CN]\}BF_4$ (**11**). The *primary* phosphine complex **8a** can be transformed to the corresponding chiral *secondary* phosphine complex $\{H_5C_5(Ph_3P)[H_3CO(CH_2)_2Ph_2P]Ru[PPh(H)(CH_2)_2CN]\}BF_4$ (**12**) by hydrophosphination reaction with the acrylonitrile (**9**) in the presence of triethylamine.

Introduction

The previous chapter demonstrates, that iron complexes of the type **A** containing both the hemilabile ligand 2-methoxyethyl-diphenylphosphine and a *primary* alkyl or arylphosphine are available by treating the cationic iron complexes $\{H_5C_5(OC)[H_3CO(CH_2)_2Ph_2P]Fe\}BF_4$ and $\{H_5C_5(Me_3P)[H_3CO(CH_2)_2Ph_2P]Fe[NCMe]\}BF_4$ with one equivalent of the *primary* phosphines.

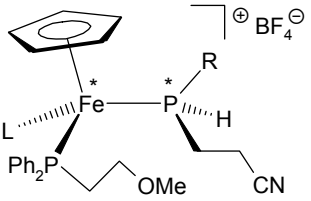
Preliminary studies have revealed that the complexes can be transformed by hydrophosphination of acrylonitrile or ethylisocyanate into the *secondary* iron complexes **B** and **C**.



A

L = CO, PMe_3

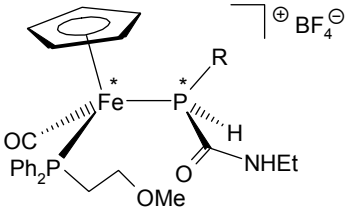
R = *i*-Pr, Ph, Mes



B

L = CO, PMe_3

R = Ph, Mes



C

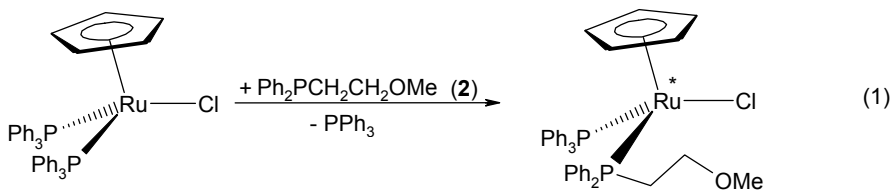
R = Ph, Mes

As a convenient access to structurally related ruthenium complexes a synthetic procedure is envisaged starting from the easily available bis(triphenylphosphine)ruthenium halfsandwich complex $H_5C_5(PPh_3)_2RuCl$.[1, 2]

Results and Discussion

Synthesis of the Ruthenium Complexes {$H_5C_5(Ph_3P)[H_3CO(CH_2)_2Ph_2P]Ru[PRR'H]$}$BF_4$ [R = *i*-Pr, Ph, Mes; R' = H, Ph] (7;8a,b)

A simple way to introduce the 2-methoxyethyl-diphenylphosphine at the ruthenium is given by the thermal reaction of **1** with the phosphine **2** in toluene at 50 °C (eq. 1).[3] Formation of **3** characterized by a stereogenic ruthenium centre is complete after 5 d. **3** is isolated as a yellow microcrystalline powder in a yield of 95 % and can be stored for several months under a atmosphere of nitrogen at room temperature.

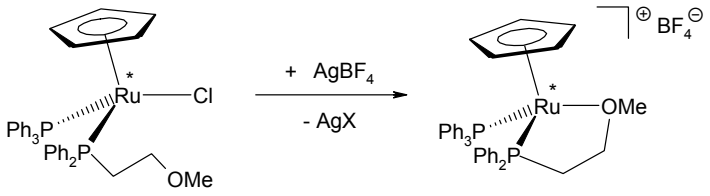


(1)

1 **3**

Although **3** was mentioned by Lindner in 1992 no spectroscopic data are available in literature.[3] The ^{31}P-NMR resonances of the two phosphorus atoms at 43.49 and 31.51 appear as doublets with a ^{2}J(PRuP)-coupling constant of 43.1 Hz.

Abstraction of the chloro ligand of **3** is achieved analogously to the iron case in dichloromethane at room temperature with silver tetrafluoroborate (eq. 2). After 2 h the complex **4** containing the hybride ligand coordinated in a bidentate fashion is isolated in a yield of 90 % as a yellow solid.

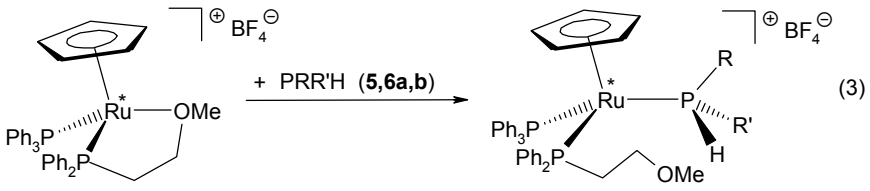


(2)

3 **4**

The ^{31}P-NMR spectrum of **4** shows two doublets at 56.07 (PPh_3) and 44.34 ppm (PPh_2) with a ^{2}J(PRuP)-coupling constant of 35.2 Hz. In comparison the iron complex $\{H_5C_5(OC)Fe[PPh_2(CH_2)_2OCH_3]\}BF_4$ shows the resonance of the hemilabile ligand at 55.96 ppm.

Opening of the chelate ring in complex **4** can be verified by the reaction of **4** with diphenylphosphine (**5**), phenyl- or mesitylphosphines (**6a,b**) in dichloromethane at 40 °C (eq. 3). The *secondary* and *primary* phosphine ruthenium complexes **7;8a,b** are isolated as a brown (**7**) and yellow-brown (**8a,b**) powders, respectively, after reaction times of 2 h (**8a**) to 10 h (**8a**) in yields of 95% (**8a**) to 99% (**7**). However **7;8a,b** can only be obtained in a mixture (65:35 **7**, 71:29 **8a**, 59:41 **8b**) with starting complex **4**.



(3)

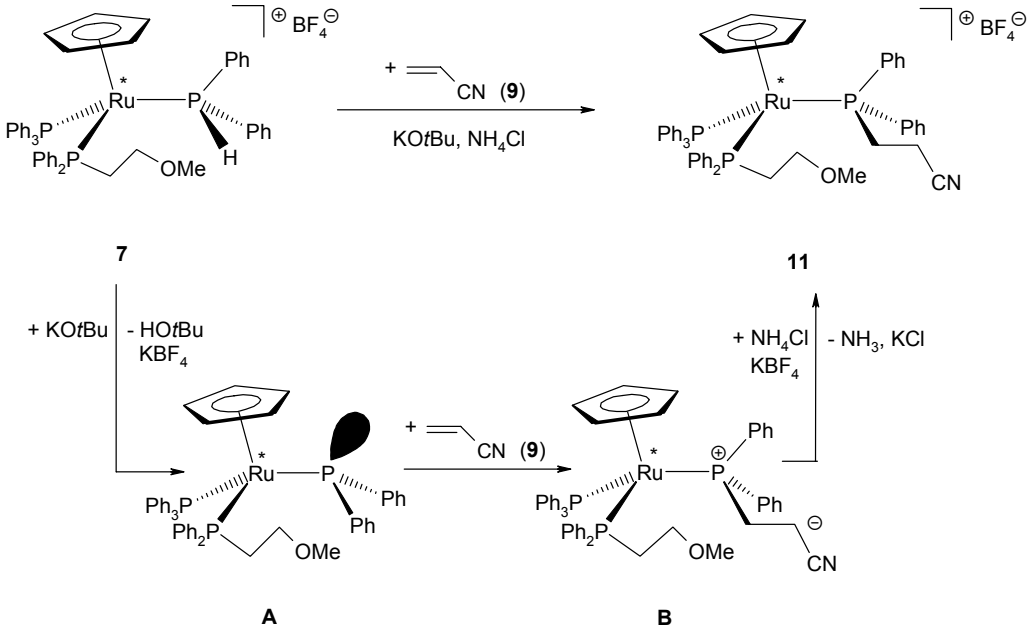
4 **7,8a,b**

	7	8a	8b
R	Ph	Ph	Mes
R'	Ph	H	H

The ^{31}P-NMR spectrum of **7** shows three dd-signals at 42.23, 39.50 and 29.94 ppm with ^{2}J-coupling constants of 40.1 and 31.6 Hz. The same finding is valid for **8a,b**. The P-bound hydrogen is found in the ^{1}H-NMR spectra between 5.99 and 4.41 ppm with the characteristic ^{1}J-PH-coupling for coordinated *primary* phosphine ligands from 330.0 to 380.2 Hz. The values of the ^{1}J-PH-coupling constants are in agreement with the ^{1}H-NMR spectra of the corresponding iron complexes $\{H_5C_5(OC)[H_3CO(CH_2)_2Ph_2P]Fe[P(Ph)H_2]\}BF_4$ with coupling constants of 372.7 to 373.2 Hz.

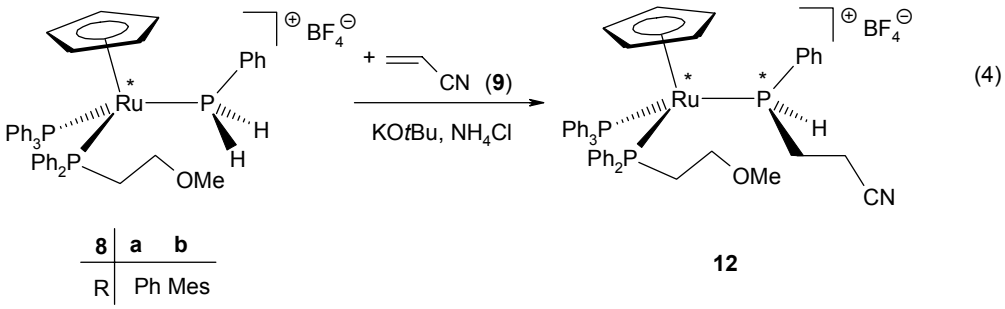
Hydrophosphination of Acrylonitrile (9) with $\{H_5C_5(Ph_3P)[H_3CO(CH_2)_2Ph_2P]Ru[PRR'H]\}BF_4$ [R = *i*-Pr, Ph, Mes; R' = H, Ph] (7;8a,b)

The hydrophosphination of acrylonitrile (**9**) with **7** (used in a 65:35 mixture with **4**) yields the *tertiary* phosphine ruthenium complex **11** in a mixture with **4** nearly identical to that of **7** (Scheme 1). Due to the decreased acidicity of the PH-function as a consequence of the electronrich ruthenium centre - triethylamine is not a strong enough base to induce the primary deprotonation step as in the case of the iron complexes.[4-6] Instead stoichiometric amounts of the stronger base potassium-*tert*-butylate are necessary. The hydrophosphination of the olefin involves deprotonation of **7** to form the corresponding neutral phosphanido complex **A**, which acts as a strong nucleophile attacking the electron deficient C-C-double bond of acrylonitrile via the trivalent phosphorus to give the zwitterionic P-C-coupling product **B.** The subsequent reprotonation of carbanionic centre with NH_4Cl produce the *tertiary* phosphine complex **11**. **11** is isolated as a brown solid after a reaction time of 7 d at room temperature in a yield of 78 % and can be stored for several months under a atmosphere of nitrogen at room temperature without decomposition.



Scheme 1: Mechanism of the acrylonitrile insertion

In the case of the *primary* phosphine complexes **8a,b** only **8a** undergoes reaction with acrylonitrile (**9**). In dichloromethane the corresponding *secondary* phosphine complex **12** (in a 73 : 27-mixture with **4**) is obtained after stirring 4 d at room temperature (eq. 4).



(4)

Yellow brown microcrystalline **12** is isolated after evaporization of the solvent and the formed *tert*-butanol in a yield of 76 %. Due to the stereogenic ruthenium and phosphorus **12** is obtained as a mixture of *like*/*unlike*-isomers in a ratio of 55 : 45 (**12**/**12'**). The formation of the *secondary* phosphine at the metal of **12** is supported by the low-field shift of the ^{31}P-resonance on going from **8a** (– 29.92 ppm) to **12**/**12'** (20.74/19.10 ppm).

In context with the detachment of the *secondary* phosphine ligand formed via hydrophosphination **12** was irradiated with UV-light in dichloromethane. After 12 h

irradiation complete decomposition of the complex **12** was observed, yielding triphenylphosphine as the only identified product.

Experimental Section

General: All manipulations were performed under purified nitrogen using standard Schlenk techniques. Solvents were rigorously dried over an appropiate drying agent and distilled under nitrogen prior to use. ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were obtained on a Bruker AMX 500 and a Jeol JNM-LA300 spectrometer. Melting points were determined by Differential Thermo Analysis (DTA) with the Du Pont Thermal Analysis System 9000. Irradiation reactions are carried out with a quartz lamp (500W, TQ 719, Hanau). Elemental analyses were performed in the laboratories of the "Institut für Anorganische Chemie". – The starting materials $H_5C_5(Ph_3P)_2RuCl$[2, 7] and $Ph_2PCH_2CH_2OCH_3$[8] were synthesized according to the literature procedures. The insertion reagence acrylonitrile is obtained commercially.

*1. {Chloro(η^5-cyclopentadienyl)(2-methoxyethyldiphenylphosphine-κP)(triphenylphosphine) ruthenium(II)} (**3**)*

A solution of 400 mg (0.551 mmol) $H_5C_5(Ph_3P)_2RuCl$ (**1**) and 135 mg (0.551 mmol) $PPh_2(CH_2)_2OCH_3$ (**2**) in 50 ml of toluene is stirred for 4 d at 50 °C. The solution color turns from orange to yellow. The solvent is removed in vacuum and remaining **3** washed three times with each 10 ml pentane and dried in vacuum. - Yield: 347 mg (98 %). – Yellow powder. - **^{1}H-NMR(C_6D_6, 500.1 MHz):** δ = 7.44 – 7.03 (m, 25 H, H_5C_6), 4.05 (s, br, 5 H, H_5C_5), 2.86 – 2.80 (m, 2 H, $\underline{H}_2COCH_3$), 2.82 (s, 3 H, H_3CO), 2.68 – 2.57 (m, 2 H, H_2CP). - **^{13}C-{^{1}H}-NMR(C_6D_6, 125.77 MHz):** δ = 219.92 [d, ^{2}J(PFeC) = 32.6 Hz, CO], 134.21 [d, ^{1}J(PC) = 38.9 Hz, *i*-C], 133.75 [d, ^{1}J(PC) = 42.9 Hz, *i*-C], 132.08 [d, ^{2}J(PCC) = 9.6 Hz, *m*-C], 130.70 [d, ^{3}J(PCCC) = 8.6 Hz, *m*-C], 128.99 [d, ^{4}J(PCCCC) = 2.2 Hz, *p*-C], 128.48 [d, ^{4}J(PCCCC) = 2.4 Hz, *p*-C], 127.26 – 126.74 (m, C_6H_5), 81.89 [d, ^{2}J(PFeC) = 1.2 Hz, C_5H_5], 66.96 [d, ^{2}J(PCC) = 1.7 Hz, $\underline{C}H_2OCH_3$], 56.62 (s, CH_3), 28.73 ppm [d, ^{1}J(PC) = 26.9 Hz,

PCH_2]. - **^{31}P-{^{1}H}-NMR($CDCl_3$, 121.5 MHz):** δ = 43.42 [d, ^2J(PRuP) = 43.7Hz, PPh_3], 31.53 ppm [d, ^2J(PRuP) = 43.7Hz, PPh_2].

*2. {η^5-Cyclopentadienyl(2-methoxyethyldiphenylphosphine-κO-κP)(triphenylphosphine) ruthenium(II)}tetrafluoroborate (**4**)*

200 mg (0.282 mmol) $H_5C_5(Ph_3P)[H_3CO(CH_2)_2Ph_2P]RuCl$ (**3**), dissolved in 50 ml dichloromethane, are combined with 55 mg (0.282 mmol.) of $AgBF_4$. The reaction mixture is stirred for one hour and precipitated AgCl separated by filtration. The filtrate is evaporated to dryness, remaining **4** washed three times with each 20 ml pentane and dried in vacuum. – Yield: 497 mg (0.254 mmol, 90 %). – Green powder. – M.p. 83 °C. – $C_{38}H_{37}BF_4OP_2Ru$.(759.53). **^{1}H-NMR($CDCl_3$, 500.1 MHz)**: δ = 7.75 – 7.03 (m, 25 H, H_5C_6), 4.51 (s, 5 H, H_5C_5), 3.76 (s, 3 H, H_3C), 3.74 – 3.65 (m, 2 H, H_2C), 2.08 – 2.02 (m, 1 H, H_2CP), 1.63 – 1.58 ppm (m, 1 H, H_2CP). - **^{13}C-{^{1}H}-NMR($CDCl_3$, 125.8 MHz)**: δ = 134.97 – 127.56 (m, C_6H_5), 78.09 [t, ^2J(PRuC) = 1.9 Hz, C_5H_5], 72.20 (s, $\underline{C}H_2OCH_3$), 57.60 (s, OCH_3), 27.93 ppm [d, ^1J(PC) = 22.5 Hz, PCH_2]. - **^{31}P-{^{1}H}-NMR($CDCl_3$, 202.4 MHz)**: δ = 56.10 [d, ^2J(PRuP) = 34.5 Hz, PPh_3], 44.78 ppm [d, ^2J(PRuP) = 34.5 Hz, $PPh_2(CH_2)_2OCH_3$].

*3. {η^5-Cyclopentadienyl(2-methoxyethyldiphenylphosphine-κP)(diphenylphosphine)(tri-phenylphosphine)ruthenium(II)}tetrafluoroborate (**7**)*

To a solution of 98 mg (0.13 mmol) of $\{H_5C_5(Ph_3P)Ru[PPh_2(CH_2)_2OCH_3]\}BF_4$ (**4**) in 20 ml of dichloromethane 24 mg (0.13 mmol) of Ph_2PH (**5**) are added. The reaction mixture is stirred for 2 h at 45 °C and then reduced in vacuum to a volume of 5 ml. **7** is precipitated by addition of 40 ml of diethylether, separated by filtration, washed three times with 20 ml of diethylether and dried in vacuum. – Yield: 123 mg (99 %). – Brown powder. – M.p. 79 °C. - $C_{50}H_{48}BF_4OP_3Ru$ (945.73). calc.: C 63.50, H 5.12. found: C 63.79, H 5.08. - **^{1}H-NMR($CDCl_3$, 500.1 MHz)**: δ = 7.63 – 6.83 (m, 35 H, H_5C_6), 6.40 [ddd, ^1J(PH) = 354.6 Hz,

^{3}J(PRuPH) = 5.1 Hz, ^{3}J(PRuPH) = 5.2 Hz, 1 H, HP], 4.86 (s, 5 H, H_5C_5), 2.91 (s, 3 H, H_3C), 2.67 – 2.58 (m, 2 H, H_2CO), 2.19 – 2.12 (m, 1 H, H_2CP), 2.07 – 1.99 ppm (m, 1 H, H_2CP). - **^{13}C-{^{1}H}-NMR($CDCl_3$, 125.8 MHz)**: δ = 133.97 [d, ^{2}J(PCC) = 12.7 Hz, *o*-C], 133.84 [d, ^{2}J(PCC) = 13.2 Hz, *o*-C], 131.64 [d, ^{3}J(PCCC) = 9.1 Hz, *m*-C], 131.19 [d, ^{3}J(PCCC) = 8.6 Hz, *m*-C], 130.22 [d, ^{3}J(PCCC) = 9.6 Hz, *m*-C], 129.58 – 126.54 (m, C_6H_5), 85.02 (s, C_5H_5), 66.91 [d, ^{2}J(PCC) = 4.6 Hz, $\underline{C}H_2OCH_3$], 57.12 (s, CH_3), 34.22 ppm [d, ^{1}J(PC) = 20.4 Hz, PCH_2]. - **^{31}P-{^{1}H}-NMR($CDCl_3$, 202.4 MHz)**: δ = 42.10 [dd, ^{2}J(PRuP) = 41.8 Hz, 32.0 Hz, PPh_3], 39.21 [dd, ^{2}J(PRuP) = 41.8 Hz, 32.0 Hz, $PPh_2(CH_2)_2OCH_3$], 29.27 ppm [dd, ^{2}J(PRuP) = 41.8 Hz, 32.0 Hz, PPh_2H].

*4. {η^5-Cyclopentadienyl(isopropylphosphine)(2-methoxyethyldiphenylphosphine-κP)(tri-phenylphosphine)ruthenium(II)}tetrafluoroborate (**8a**)*

Analogous to **7** from 100 mg (0.130 mmol) of $\{H_5C_5(Ph_3P)Ru[PPh_2(CH_2)_2OCH_3]\}BF_4$ **4** and 15 mg (0.130 mmol.) of $PhPH_2$ (**6a**) in 20 ml of dichloromethane after 10 h. – Yield: 107 mg (95 %). – Yellow-brown powder. – M.p. 74 °C. – $C_{44}H_{44}BF_4OP_3Ru$.(869.63). calc.: C 60.77, H 5.10. found: C 60.80, H 5.13. - **^{1}H-NMR($CDCl_3$, 500.1 MHz)**: δ = 7.61 – 7.02 (m, 30 H, H_5C_6), 5.99 [dm, ^{1}J(PH) = 348.7 Hz, 1 H, HP], 5.66 [dm, ^{1}J(PH) = 357.3 Hz, 1 H, HP], 4.56 (s, 5 H, H_5C_5), 2.89 (s, 3 H, H_3C), 2.72 – 2.56 (m, 2 H, H_2CO), 2.11 – 2.06 (m, 1 H, H_2CP), 1.76 – 1.69 ppm (m, 1 H, H_2CP). - **^{13}C-{^{1}H}-NMR($CDCl_3$, 125.8 MHz)**: δ = 136.93 – 126.47 (m, C_6H_5), 85.84 (s, C_5H_5), 66.62 [d ^{2}J(PCC) = 2.9 Hz, $\underline{C}H_2OCH_3$], 57.23 (s, OCH_3), 26.42 ppm [dd, ^{1}J(PC) = 22.8 Hz, ^{3}J(PRuPC) = 4.0 Hz, PCH_2]. - **^{31}P-{^{1}H}-NMR($CDCl_3$, 202.4 MHz)**: δ = 46.02 [dd, ^{2}J(PRuP) = 49.2 Hz, 32.0 Hz, PPh_3], 31.53 [dd, ^{2}J(PRuP) = 44.3 Hz, 32.0 Hz, $PPh_2(CH_2)_2OCH_3$], - 29.92 ppm [dd, ^{2}J(PRuP) = 49.2 Hz, 44.3 Hz, $PPhH_2$].

*5. {η^5-Cyclopentadienyl(mesitylphosphine)(2-methoxyethyldiphenylphosphine-κP)(tri-phenylphosphine)ruthenium(II)}tetrafluoroborate (**8b**)*

Analogous to **7a** from 92 mg (0.120 mmol) of {$H_5C_5(Ph_3P)Ru[PPh_2(CH_2)_2OCH_3]$}$BF_4$ (**4**) and 18 mg (0.120 mmol.) of $MesPH_2$ (**6b**) in 20 ml of dichloromethane after 5 h. – Yield: 105 mg (97 %). – Yellow-brown powder. – M.p. 83 °C. – $C_{47}H_{50}BF_4OP_3Ru$.(911.71). calc.: C 61.92, H 5.53. found: C 61.57, H 5.39. - **^{1}H-NMR($CDCl_3$, 500.1 MHz)**: δ = 7.53 – 6.98 (m, 27 H, H_5C_6), 6.89 (s, 2H, *m*-H), 5.74 [ddd, ^1J(PH) = 342.1 Hz, ^3J(PRuPH) = 9.4 Hz, ^2J(HPH) = 6.4 Hz, 1 H, HP], 5.56 [ddd, ^1J(PH) = 352.4 Hz, ^3J(PRuPH) = 11.9 Hz, ^2J(HPH) = 6.4 Hz, 1 H, HP], 4.53 (s, 5 H, H_5C_5), 2.90 (s, 3 H, H_3CO), 2.70 – 2.60 (m, 2 H, H_2CO), 2.27 (s, 3 H, *p*-H_3C), 2.18 (s, 6 H, *o*-H_3C) 1.64 – 1.58 ppm (m, 2 H, H_2CP). - **^{13}C-{^{1}H}-NMR($CDCl_3$, 125.8 MHz)**: δ = 140.74 – 126.47 (m, C_6H_5, $\underline{C}_6H_2(CH_3)_3$), 85.19 (s, C_5H_5), 66.71 [d, ^2J(PCC) = 6.7 Hz, $\underline{C}H_2OCH_3$], 57.19 (s, OCH_3), 24.35 [d, ^1J(PC) = 19.5 Hz, PCH_2], 22.09 [d, ^3J(PCCC) = 9.9 Hz, *o*-CH_3], 22.05 [d, ^3J(PCCC) = 8.4 Hz, *o*-CH_3], 21.32 ppm (s, *p*-CH_3). - **^{31}P-{^{1}H}-NMR(CD_3CN, 202.4 MHz)**: δ = 45.66 [dd, ^2J(PRuP) = 44.3 Hz, 32.0 Hz, PPh_3], 30.86 [dd, ^2J(PRuP) = 44.2 Hz, 32.0 Hz, $PPh_2(CH_2)_2OCH_3$], - 61.03 ppm [dd, ^2J(PRuP) = 44.3 Hz, 44.2 Hz, $PMesH_2$].

*6. {(2-Cyanoethyldiphenylphosphine)(η^5-cyclopentadienyl)(2-methoxyethyldiphenyl-phosphine-κP)(triphenylphosphine)ruthenium(II)}tetrafluoroborate (**11**)*

To a solution of 123 mg (0.13 mmol) {$H_5C_5(Ph_3P)[H_3CO(CH_2)_2Ph_2P]Ru[PPh_2H]$}$BF_4$ (**7**) in 10 ml of dichloromethane 6.9 mg (0.13 mmol) of acrylonitrile (**9**), 15 mg (0.13 mmol) KO*t*Bu and 6.7 mg (0.13 mmol) NH_4Cl are added. The reaction mixture is stirred for 7 d at ambient temperature. After removal of all volatiles in vacuum, remaining **11** is washed three times with each 10 ml pentane and dried in vacuum. – Yield: 101 mg (78%). – Brown powder. – M.p. 59 °C (dec.). - $C_{53}H_{51}BF_4NOP_3Ru$ (998.79). calc.: C 63.74, H 5.15, N 1.40. found: C

64.21, H 5.06, N 1.46. - **^{1}H-NMR(CD_3CN, 300.4 MHz)**: δ = 7.78 – 6.88 (m, 35 H, H_5C_6), 4.93 (s, br, 5 H, H_5C_5), 3.09 – 2.94 (m, 4 H, H_2C), 2.89 (s, 3 H, H_3C), 2.66 – 2.54 (m, 2 H, H_2C), 2.12 – 2.02 ppm (m, 2 H, H_2C). - **^{31}P-{^{1}H}-NMR(CD_3CN, 121.5 MHz)**: δ = 41.28 [dd, ^{2}J(PRuP) = 41.3 Hz, 31.6 Hz, PPh_3], 35.89 [t, ^{2}J(PRuP) = 41.3 Hz, PPh_2], 30.47 ppm [dd, ^{2}J(PRuP) = 41.3 Hz, 31.6 Hz, PPh_2].

*7. {(2-Cyanoethylphenylphosphine)(η^{5}-cyclopentadienyl)(2-methoxyethyldiphenyl-phosphine-κP)(triphenylphosphine)ruthenium(II)}tetrafluoroborate (**12/12'**)*

To a solution of 74 mg (0.085 mmol) $\{H_5C_5(Ph_3P)[H_3CO(CH_2)_2Ph_2P]RuPPhH_2\}BF_4$ (**8a**) in 20 ml of dichloromethane 4.6 mg (0.085 mmol) of acrylonitrile (**9**) and 5 mg (0.005 mmol) NEt_3 are added. The reaction mixture is stirred for 4 d at ambient temperature and then all volatiles are removed in vacuum. Remaining **12** is washed five times with each 20 ml pentane and dried in vacuum. – Yield: 60 mg (76 %). – Brown powder. – M.p. 95 °C.- $C_{47}H_{47}BF_4NO_3P_3Ru$ (922.69). calc.: C 61.18, H 5.13, N 1.52. found: C 61.58, H 5.43, N 1.87. - Isomer ratio 55:45 (**12**/**12**'). **^{1}H-NMR(CD_3CN, 300.4 MHz)**: δ = 7.53 – 6.49 (m, 60 H, H_5C_6), 5.59 [dm, ^{1}J(PH) = 367.0 Hz, 1 H, HP], 4.79 [dm, ^{1}J(PH) = 362.3 Hz, 1 H, HP], 4.91 (s, br, 5 H, H_5C_5), 4.82 (s, br, 5 H, H_5C_5), 3.42 – 3.27 (m, 4 H, H_2C), 2.95 (s, 3 H, H_3C), 2.86 (s, 3 H, H_3C), 2.57 – 2.28 (m, 8 H, H_2C), 1.83 – 1.64 ppm (m, 4 H, H_2C). - **^{13}C-{^{1}H}-NMR(CD_3CN, 75.45 MHz)**: δ = 135.48 – 128.23 (m, C_6H_5), 117.43 [d, ^{3}J(PCCC) = 7.3 Hz, CN], 116.93 [d, ^{3}J(PCCC) = 6.5 Hz, CN), 86.80 [d, ^{2}J(PRuC) = 0.7 Hz, C_5H_5), 86.67 [d, ^{2}J(PRuC) = 0.4 Hz, C_5H_5), 69.76 [d, ^{2}J(PCC) = 5.7 Hz, $\underline{C}H_2OCH_3$], 68.28 [d, ^{2}J(PCC) = 6.9 Hz, $\underline{C}H_2OCH_3$], 58.19 (s, CH_3), 58.04 (s, CH_3), 31.89 [d, ^{1}J(PC) = 22.3 Hz, CH_2], 31.85 [d, ^{1}J(PC) = 20.0 Hz, CH_2], 28.31 [d, ^{1}J(PC) = 19.3 Hz, CH_2], 28.25 [d, ^{1}J(PC) = 21.4 Hz, CH_2], 17.04 (s, CH_2), 28.31 ppm [d, ^{2}J(PCC) = 5.3 Hz, CH_2]. - **^{31}P-{^{1}H}-NMR(CD_3CN, 162.0 MHz)**: δ = 43.13 [dd, ^{2}J(PRuP) = 42.4 Hz, 32.2 Hz, PPh_3], 40.88 [dd, ^{2}J(PRuP) = 42.4 Hz, 32.3 Hz, PPh_3], 31.92 [dd, ^{2}J(PRuP) = 42.4 Hz, 32.2 Hz, $PPh_2(CH_2)_2OCH_3$], 30.50 [dd,

^{2}J(PRuP) = 42.4 Hz, 32.3 Hz, $PPh_2(CH_2)_2OCH_3$], 20.74 [t, ^{2}J(PRuP) = 42.4 Hz, PPhH], 19.10 ppm [t, ^{2}J(PRuP) = 42.4 Hz, PPhH].

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CHAPTER VI:

X-Ray Structure Analyses

- **{[HOiPr$_2$Si(C$_5$H$_4$)](OC)$_3$W}$_2$ (W-W)**
- **Cp(OC)$_2$W=P(*s*Mes)-W(CO)$_3$Cp**
- **Cp(OC)$_2$W-P(*s*Mes)-W(CO)$_2$Cp**
- **Cp(OC)$_2$W=P(OMe)*s*Mes**
- **Cp(OC)$_2$Fe-SiMePhH**

Introduction

The data collection was carried out on a BRUKER-SMART-APEX diffractometer, equipped with a D8-goniometer and a low temperature regulation at 173(2) K[1] with graphit-monochromatizated Mo-K_α-radiation with a wave length of $\lambda = 0.71073$ Å in ϖ-scan mode.

The determination and refinement of the cell parameters was accomplished with the SMART program, the integration of the data was carried out using the SAINT[2] program. The solution of the molecular structures was either made by using Direct Methods or the *Patterson*-method using the SHELXS-97[3] program. The refinement of the molecular structures was accomplished by the use of the SHELXL-97[4] program with the "full matrix least squares" method against F^2. These structure factor squares F^2 are directly proportional to the measured intensities. The non-hydrogen-atoms were calculated by Fourier-transformations and anisotropically refined by the method of the least mean-square errors (full-matrix least squares). The definitions of the denoted quality criteria R1 {for [$I > 2\sigma(I)$]} and *w*R2 (for all data) are as follows:

$$R1 = \frac{\Sigma \left| F_o - F_c \right|}{\Sigma F_o} \qquad wR2 = \sqrt{\frac{\Sigma w (F_o^2 - F_c^2)^2}{\Sigma w F_o^4}}$$

$$w^{-1} = \sigma^2(F_o)^2 + (g1P)^2 + g2P \quad \text{with} \quad P = \frac{(F_o^2 + 2 F_c^2)}{3}$$

The hydrogen atoms which were not found were positioned ideally and partially involved into the refinement with free U-values. If the U-values are not unblocked, the reference to the temperature factors of the bound atom with 120 % of the U_{ij}-values or 150 % for methyl groups, respectively. The torsion of the methyl groups was taken into account with one parameter each.

The isotropic temperature factor $U_{(eq)}$ and the anisotropic temperature factor U which are logged in the tables are defined as follows:

$$U_{(eq)} = \exp[-8\pi^2 * U(\sin\Theta/l)^2]$$

$$U = \exp\{-2\pi^2[h^2a^2U_{(1,1)} + k^2b^2U_{(2,2)} + l^2c^2U_{(3,3)} + 2klbcU_{(2,3)} + 2hlacU_{(1,3)} + 2hkabU_{(1,2)}]\}$$

The ORTEP-plots of the molecular structures which are shown on the following pages, were created with the program XSHELL and show deflection ellipsoids with a sojourn probability of 50 % of the corresponding atoms. The remaining graphics were created with the program XP-Interactive Molecular Graphics from *Bruker*, which was also used for the determination of the Cp(Z)-values.

The atom positions of disordered structure fragments were refined with geometrical and ADP-*restraints*. *Restraints* contain additional information about the molecular structure of the molecule which is provided with standard deviation. The *restraints* are reasonable with regard to chemical and/or structural considerations and are treated as additional data during the refinement step.

Restraints concerning the deflection parameters (ADP-*restraints*) are used in order to make an anisotropic refinement possible or to get a better resolution of disordered positions. *Rigid bond restraints* (DELU) are used to correlate the components of the anisotropic deflection parameters along the bonds within a certain standard deviation. This effects a reasonable oscillation of the atoms and prevents the compensation of electron densitiy, which is observed in the case of disorders, for example. *Similary restraints* (SIMU) are weak *restraints*, which make the deflection parameters of atoms similar in a certain radius.

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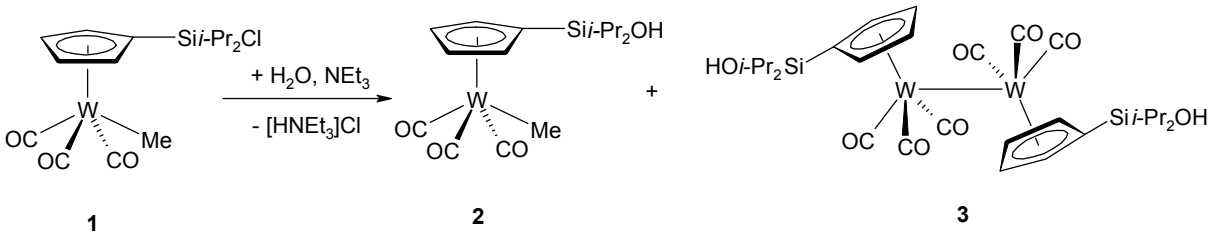
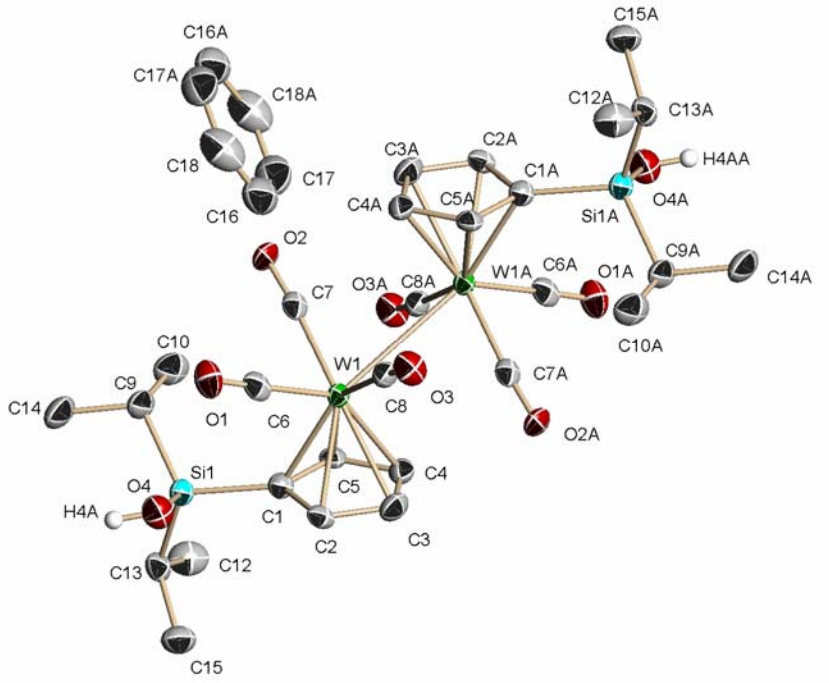
{[HO*i*Pr$_2$Si(C$_5$H$_4$)](OC)$_3$W}$_2$ (W-W) (3)

The NEt$_3$-assisted hydrolysis of the tungsten-chlorosilane **1** affords the corresponding silanol **2** together with the bis-silanol {[HO*i*Pr$_2$Si(C$_5$H$_4$)](OC)$_3$W}$_2$ (*W-W*) (**3**) containing a tungsten-tungsten bond.



1 **2** **3**

Red crystals of **3** are obtained from slow evaporation of a benzene-saturated solution at room temperature.



Molecular structure of {[HO*i*Pr$_2$Si(C$_5$H$_4$)](OC)$_3$W}$_2$ (*W-W*). The hydrogen atoms have been omitted for clarity except the silanol hydrogen atoms H4A and H4AA.

Selected bond lengths [pm], bond and torsion angles [°]:W1-C6 195.8(9), W1-C7 199.4(8), W1-C8 198.6(8), W1-C1 231.3(8), W1-C2 230.4(8), W1-C3 235.9(8), W1-C4 239.2(8), W1-C5 234.7(8), W1-W1A 320.6(13), C1-C5 141.5(11), C1-C2 145.1(10), C5-C4 141.0(11), C2-C3 140.9(11), C4-C3 138.7(12), C1-Si1 188.2(8), Si1-C9 188.3(8), Si1-C13 188.0(9), Si1-O4 164.4(6), C6-W1-C8 77.6(3), C6-W1-C7 78.8(3), C8-W1-C7 107.2(3), C6-W1-W1A 126.6(2), C1-Si1-O4 101.3(3), O4-Si1-C9 108.8(4), O4-Si1-C13 110.9(4), C1-Si1-C13 110.2(4), C5-C1-Si1-C13 75.5(8).

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

The tungsten complex reveals a pseudo tetragonal pyramidal arrangement of the three carbonyl ligands [mean W-C 198.6 pm] and the second tungsten atom, forming the basis while the cyclopentadienyl ring occupies the apical position. The tungsten-tungsten bond length of 320.6(13) pm is very close to that in the parent tungsten complex [(C$_5$H$_5$)(OC)$_3$W}$_2$.(*W-W*) [322.2(1) pm].[1] There is no significant difference of the W-C carbonyl [W1-C6 195.8(9) pm, W1-C7 199.4(8) pm, W1-C8 198.6(8) pm] and the C-O distances [mean 115.0 pm] to comparable tungsten complexes.[2] The C-C bond distances within the cyclopentadienyl ring are different. The shortest one C3-C4 is found in opposite to C1 [138.4(12) pm] and the largest bond is C1-C2 with a value of 145.1(10) pm.

The silyl group lies almost in the plane of the cyclopentadienyl ring [Si1-C1-C5-C4 – 173.8(6)]. The C1-Si1 distance amounts to 188.2(8) pm and is very similar to Si1-C9 [188.3(8) pm] and Si1-C13 [188.0(9) pm]. The Si1-O4 bond length of 164.4(6) pm lies in the expected range. The silyl group stands above the plane spanned by the cyclopentadienyl

ligand proved by the torsion angle C5-C1-Si1-C13 of 75.5(8)°. The orientation of the di*iso*propylsilyl moieties above the equatorial plane of the ring ligand is favoured due to their sterical requirements. The HO-groups adopts a position beneath the cyclopentadienyl ring.

The metal fragments show an *anti*-conformation, best illustrated by the lines described by the W1-C6-O1 and W1A-C6A-O1A atoms which stand exactly parallel to each other but pointing in apposite directions.

*Crystal Data for Compound **3***

Identification code	Katta1
mol formula	$C_{26}H_{32}O_8Si_2W_2$
mol wt	502.29
wavelength (Å)	0.71073
temp (K)	173(2)
cryst size (mm)	0.15 x 0.15 x 0.10
cryst syst	triclinic
space group	P-1
a (Å)	7.607(3)
b (Å)	10.919(4)
c (Å)	12.028(4)
α (°)	64.797(5)
β (°)	86.252(5)
γ (°)	82.457(6)
vol ($Å^3$)	896.1(6)
ρ (calcd) (Mgm^{-3})	1.862
F(000)	488
μ (mm^{-1})	6.528
θ range for data collecn (deg)	1.87 - 25.06
no. of rflns collected	6449
no. of indep reflns	3140
abs cor.	empirical
no. of data/restraints /params	3140 / 0 / 219

goodness of fit on F^2	0.981
R1[a]	0.0466
*w*R2[b]	0.0959
largest diff peak and hole (eÅ^{-3})	3.679 and -1.923

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

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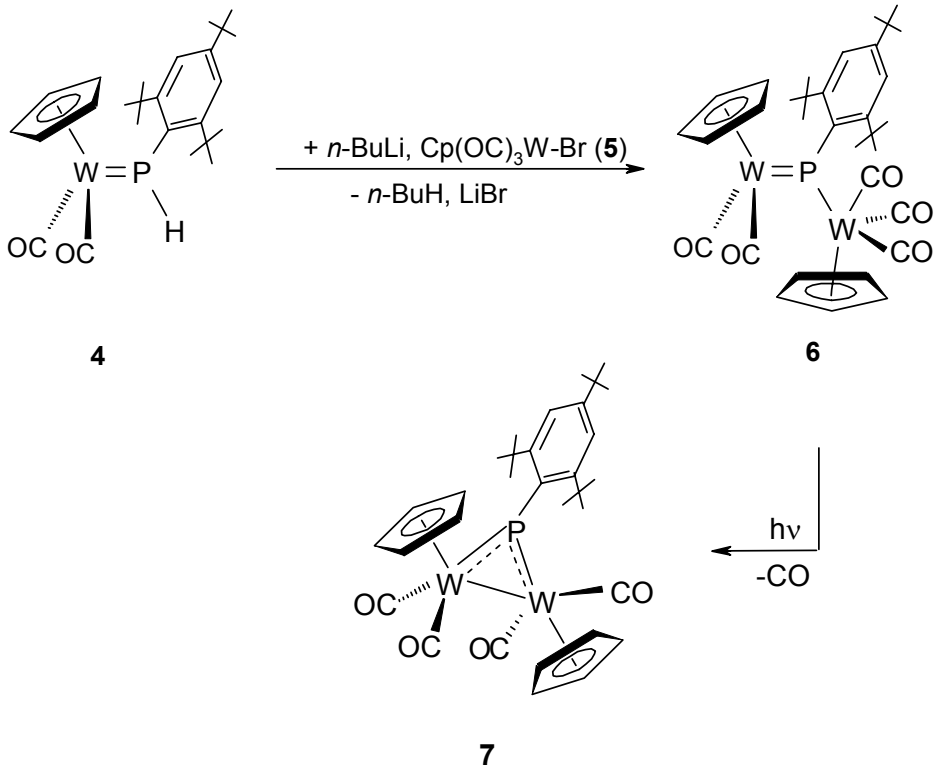
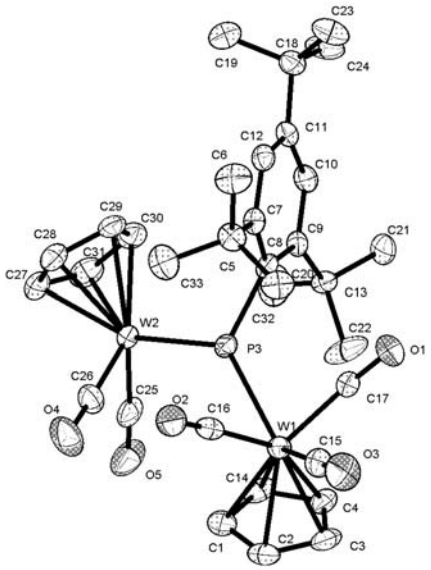
$Cp(OC)_2W=P(sMes)\text{-}W(CO)_3Cp$ (6) and $Cp(OC)_2\overline{W\text{-}P(sMes)\text{-}W}(CO)_2Cp$ (7)

When $[Cp(OC)_2W=P(sMes)]Li$, generated in situ from the super mesityl phosphenium complex **4** and *n*-BuLi, is treated with an equimolar amount of $Cp(OC)_3W\text{-}Br$ (**5**) after a reaction time of 18 h at room temperature the novel phosphinidene ditungsten complex **6** is obtained. Irradiation with UV-light converts **6** to the symmetric phosphinidene complex **7**.



4 **6** **7**

Crystals of $Cp(OC)_2W=P(sMes)\text{-}W(CO)_3Cp$ (**6**) and $Cp(OC)_2\overline{W\text{-}P(sMes)\text{-}W}(CO)_2Cp$ (**7**) suitable for structure determination could be obtained from a saturated toluene solution at room temperature.



Molecular structure of $Cp(OC)_2W=P(sMes)-W(CO)_3Cp$ (**6**). The hydrogen atoms have been omitted for clarity.

Selected bond lengths [pm] as well as bond- and torsion angles [°]: W(2)-C(25) 193.4(7), W(2)-C(26) 193.1(7), W(1)-C(15) 197.9(7), W(1)-C(16) 199.6(7), W(1)-C(17) 197.9(6), W(1)-P(3) 260.64(15), W(2)-P(3) 229.76(16), P(3)-C(8) 188.9(6), W(2)-C(25) 193.4(7), W(1)-C(22) 195.0(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, while 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 W(2)$(CO)_2$-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-phosphinidene 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 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 relativeley 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°.

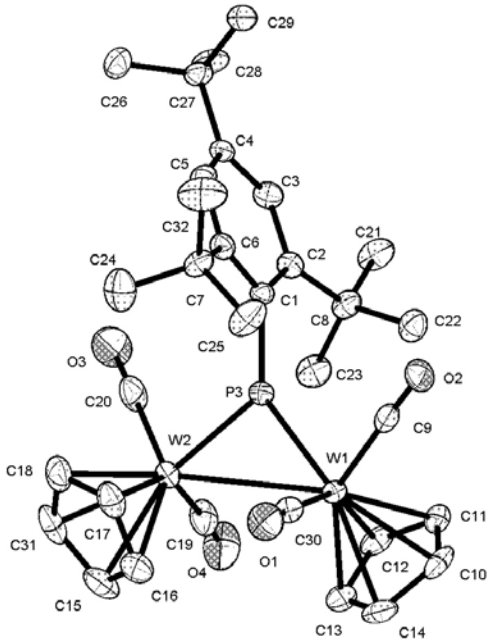
The P-C_{ipso} bond length (188.9 pm) is in the upper range for a P_{sp2}-C_{sp2} single bond[1] and excludes therefore a π–interaction between the phosphorus atom and the aromatic ring system.

The W2-P3 bond length of 230 pm is nearly identical to that of $Cp(OC)_2W{=}P(tBu)_2$ (228 pm)[2] and finds itself on the upper limit for a W-P-double-bond system for which a theoretical bond length of 226 pm is calculated.[3-5] The W1-P3 distance of 261 pm confirms single bond character for the σ-bond of the phosphorus to the W1 fragment.

The sterical 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°) 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°.[6]

The complex **6** 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**)[7] and $Cp(OC)_2W{=}P(R)$*s*Mes (R = Me, Et, *i*Pr, Bu, CH_2Ph)[6] and is in common with theoretical investigations.[7] Despite the aryl ligand distorsion the overall structure is comparable to that of the analogous mesityl-derivatives $Cp(OC)_2W{=}P(Mes)$-$W(CO)_3Cp$[8, 9] and $Cp(OC)_2W{=}P(Mes)$-$W(PH_2Mes)(CO)_2Cp$.[10]



Molecular structure of $Cp(OC)_2W$-P(*s*Mes)-$W(CO)_2Cp$ (**7**). The hydrogen atoms have been omitted for clarity.

Selected bond lengths [pm] as well as bond- and torsion angles [°]: W(1)-C(9) 195.4(4), W(1)-C(30) 195.7(4), W(1)-P(3) 231.78(10), W(1)-W(2) 320.50(9), W(2)-C(19) 195.8(4), W(2)-P(3) 229.99(11), P(3)-C(1) 185.1(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 $Cp(OC)_2W$-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 232 pm [W(1)-P(3)] and 230 pm [W(2)-P(3)] respectively are on the upper limit for a W-P-double-bonded system for which a theoretical bond length of 226 pm is calculated.[3-5] It is also nearly identical to the literature known tungsten phosphinidene complex with bulky phosphorus substituents like $Cp(OC)_2W$-P(tmp)-$W(CO)_2Cp$ (228 and 229 pm).[11]

With 321 pm the distance between the tungsten atoms is longer than the theoretical value for a W-W bond (260 pm).[12] This point is again in accordance with the result for $Cp(OC)_2W$-P(tmp)-$W(CO)_2Cp$ for which the W-W bond distance is 325 pm.[11]

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 sterical 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 **7** can be compared to the molybdenum complexes Cp(OC)(I) $\overline{\text{Mo-P(}s\text{Mes)-Mo}}$(CO)(I)Cp[13] and Cp(OC)$_2\overline{\text{Mo-P(}s\text{Mes)-Mo}}(CO)_2$Cp, respectively.[11, 13]

Crystal Data for Compound 6 and 7

	6	**7**
Identification code	Katta9	Katta7
mol formula	$C_{33}H_{39}O_5PW_2$	$C_{32}H_{39}O_4PW$
mol wt	914.3	886.3
wavelength (Å)	0.71073	0.71073
temp (K)	173(2)	173(2)
cryst size (mm)	0.20 x 0.20 x 0.20	0.20 x 0.20 x 0.20
cryst syst	monoclinic	monoclinic
space group	*P2(1)/c*	*P2(1)/c*
a (Å)	11.810(3)	13.248(4)
b (Å)	15.207(3)	13.633(4)
c (Å)	18.756(4)	16.931(5)
α (°)	90	90
β (°)	106.505(4)	97.725(5)
γ (°)	90	90
vol (Å^3), *Z*	3250.9(13), 4	3030.3(16), 4
ρ (calcd) (Mgm^{-3})	1.868	1.943
F(000)	1760	1704

μ (mm^{-1})	7.158	7.674
θ range for data collecn (deg)	1.75 - 25.06	1.55 - 25.11
no. of rflns collected	38673	21587
no. of indep reflns	5754	5361
abs cor.	empirical	empirical
no. of data/restraints /params	5754 / 33 / 410	5361 / 0 / 361
goodness of fit on F^2	1.010	1.089
R1[a]	0.0367	0.0219
*w*R2[b]	0.0786	0.0460
largest diff peak and hole (eÅ^{-3})	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.

References

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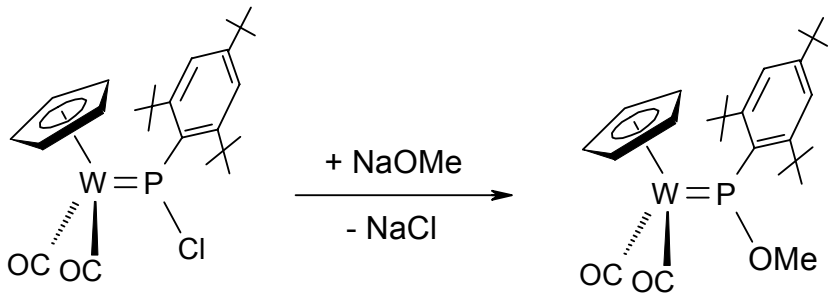
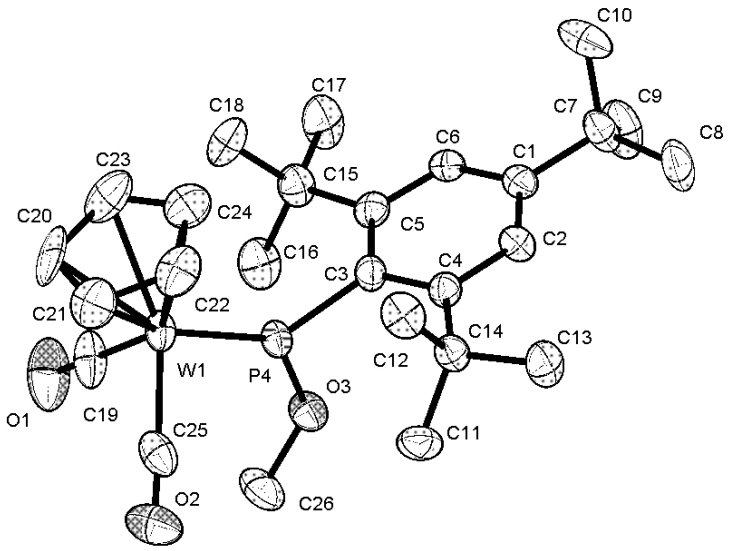
$Cp(OC)_2W{=}P(OMe)$*s*Mes (9)

Treatment of **8** with NaOMe in toluene yields the methoxyphosphenium complex **9**.



8 **9**

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



Molecular structure of $Cp(OC)_2W{=}P(OMe)$*s*Mes (**9**). The hydrogen atoms have been omitted for clarity.

Selected bond lengths [pm] as well as bond- and torsion angles [°]: W(1)-P(4) 221.43(12), P(4)-O(3) 162.4(3), P(4)-C(3) 183.7(4), W(1)-C(19) 195.8(6), W(1)-C(25) 195.4(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 expected 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 exactly 360°. As 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 $Cp(OC)_2W{=}P(t\text{Bu})_2$[2] (109.4°), the P-H-functionalized complex $Cp(OC)_2W{=}P(H)s\text{Mes}$[7] and the P-alkyl derivatives $Cp(OC)_2$ $W{=}P(R)s\text{Mes}$ (R = Me, Et, *i*Pr, *n*Bu, CH_2Ph).[6] As 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** of 162 pm is between the values for a single (172 pm) and a phosphorus-oxygen double bond (148 pm).[1] The P4-C3 bond length [183.7 pm] is in the range expected for a P_{sp2}-C_{sp2} single bond[1] and excludes therefore a π–interaction between the phosphorus atom and the aromatic ring system.

The value of 221 pm for the tungsten-phosphorus bond length, for which a theoretical bond length of 226 pm is calculated,[3-5] is on the lower end of the range typical for W-P-double-bonded systems compared to the compounds $Cp(OC)_2W=P(R)$*s*Mes [R = Me, Et, *i*Pr, *n*Bu, CH_2Ph (224 - 225 pm)][6] or the starting material $Cp(OC)_2W=P(H)$*s*Mes (225 pm).[7] 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 sterical 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)[6] and $Cp(OC)_2W=P(SnMe_3)$*s*Mes.[8] 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°.

Crystal Data for Compound 9

Identification code	Katta19
mol formula	$C_{26}H_{37}O_3PW$
mol wt	612.40
wavelength (Å)	0.71073
temp (K)	173(2)
cryst size (mm)	0.13 x 0.12 x 0.09
cryst syst	monoclinic
space group	*P2(1)/c*
a (Å)	8.8644(12)
b (Å)	16.645(2)
c (Å)	19.776(3)
α (°)	90
β (°)	98.662(3)
γ (°)	90
vol ($Å^3$), *Z*	2885.2(7),4

ρ (calcd) (Mgm^{-3})	1.410
$F(000)$	1327
μ (mm^{-1})	4.087
θ range for data collecn (deg)	1.617 - 25.10
no. of rflns collected	5129
no. of indep reflns	5129
abs cor.	empirical
no. of data/restraints /params	5129 / 0 / 303
goodness of fit on F^2	1.103
R1[a]	0.0391
*w*R2[b]	0.0916
largest diff peak and hole ($eÅ^{-3}$)	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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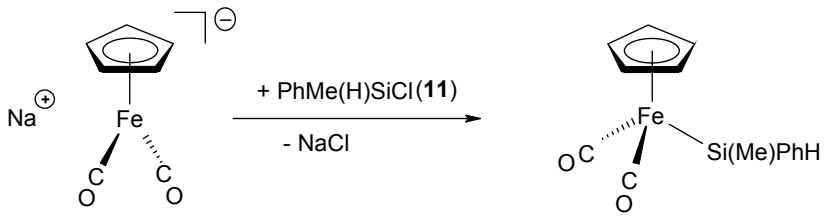
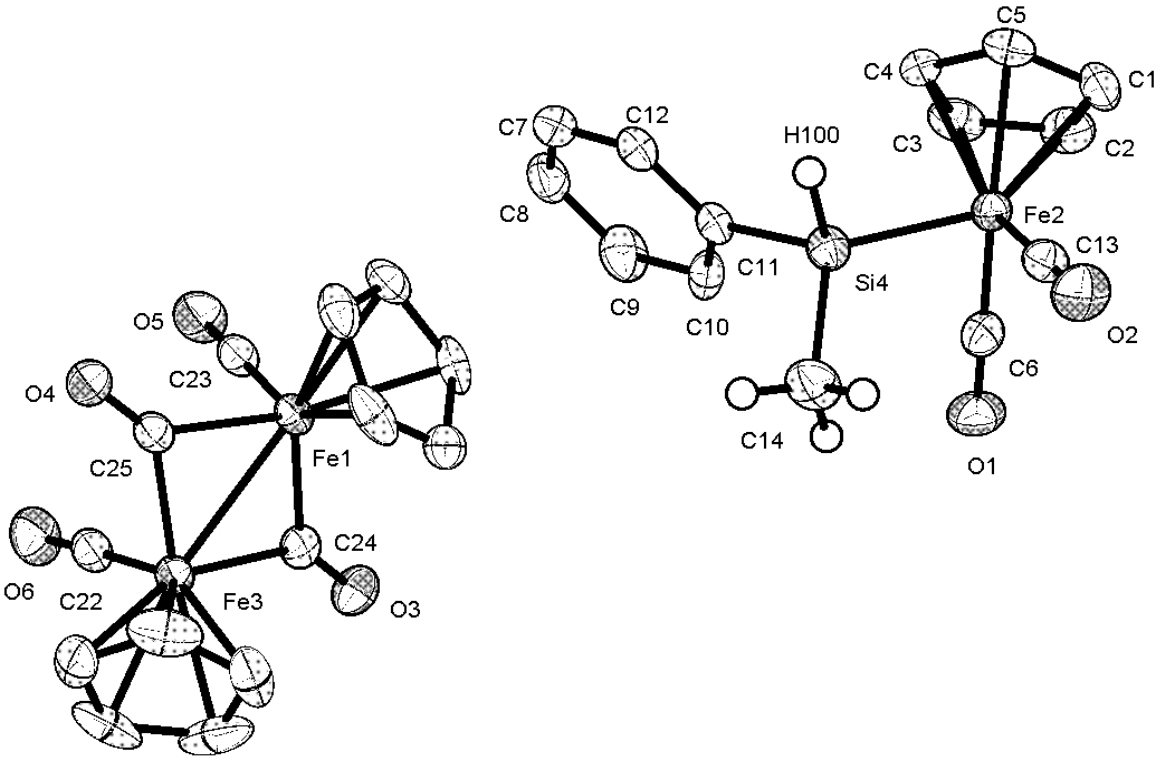
$Cp(OC)_2Fe$-SiMePhH (12)

Treatment of sodium dicarbonylcyclopentadienylferrate **10** with chloromethylphenylsilane **11** in cyclohexane at room temperature leads to the formation of the ferrio-silane **12** together with $[Cp(OC)_2Fe]_2$.



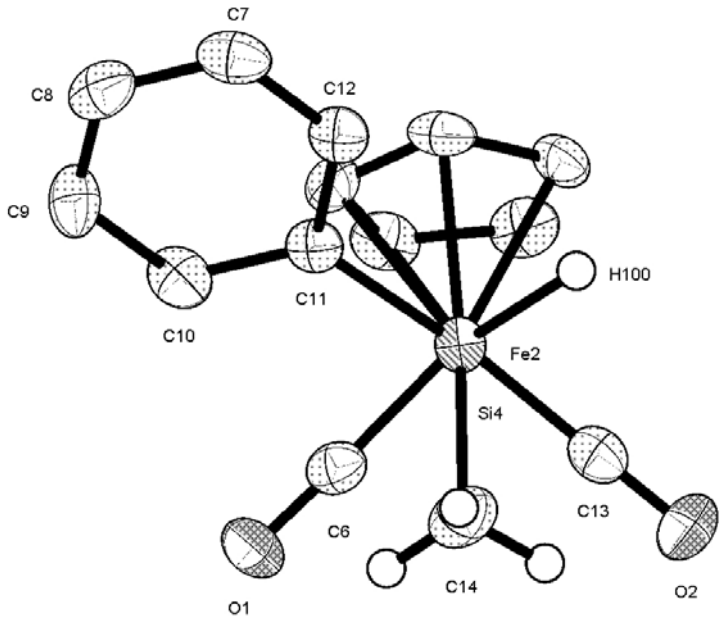
10 **12**

Crystals of **12** contaminated by $[Cp(OC)_2Fe]_2$ are obtained from a saturated solution of the ferrio-silane **12** in diethylether.



Molecular structure of $Cp(OC)_2Fe$-SiMePhH (**12**). Hydrogen atoms despite H100 have been omitted for clarity.

Selected bond lenghts [pm], bond and torsion angles [°]: Fe2-C13 176.1(5), Fe2-C6 175.0(4), Fe1-Si4 230.64(13), C14-Si4 190.3(4), C11-Si4 189.2(4), C6-Fe2-C13 94.92(18), Fe2-Si4-C11 112.43(13), Fe2-C13-O2 179.4(4), Fe2-C6-O1 177.5(4), C6-Fe2-Si4 86.87(14), C13-Fe2-Si4 85.75(14), Fe2-Si4-C11-C12 –119.1(3).



Newman projection of $Cp(OC)_2Fe$-SiMePhH (**3b**). View along the Fe2-Si4-axis.

The ferrio-silane $Cp(OC)_2Fe$-SiMePhH (**12**) co-crystallizes with *cis*-$[Cp(CO)(\mu\text{-}CO)Fe]_2$ (Fe-Fe), which presumably is formed in small traces during the preparation process of **12** and cannot be completely separated due to comparable solubility properties. Since the dimeric iron complex has been intensively studied in the past, this part of the molecular structure is not discussed here, because there are no noticeable discrepancies concerning bond lenghts and angles compared to the structure of the *cis*-isomer of $[Cp(CO)(\mu\text{-}CO)Fe]_2$ (Fe-Fe) reported in literature.[1] Considering the cyclopentadienyl ligand of **12** as a tridentate ligand, the central iron atom takes up an octahedral ligand sphere including the two carbonmonoxide ligands and the silyl moiety with the angles including the iron atom close to the ideal value of 90° {C6-

Fe2-C13 [94.92(18)°]; C6-Fe2-Si4 [86.87(14)°]; C13-Fe2-Si4 [85.75(14)°]} (Newman projection along the Fe-Si-axis).

The silicon atom is coordinated tetrahedrally with the angles containing the iron atom enlarged [C11-Si4-Fe2 112.43(13), C14-Si4-Fe2 115.64(15)] and the angle C11-Si4-C14 [108.43(18)°] reduced compared to the ideal value. The Fe-Si bond length of 230.64(13) pm lies in the literature known range.[2,3] The Si-H bond [Si4-H100 146.5(2)] is about 3 ppm shorter than reported for the complex $(C_5Me_5)(OC)_2Fe\text{-}SiH_3$.[4]

*Crystal Data for Compound **12***

Identification code	Katta10
mol formula	$C_{14}H_{14}FeO_2Si$
mol wt	298.2
wavelength (Å)	0.71073
temp (K)	173(2)
cryst size (mm)	0.20 x 0.13 x 0.08
cryst syst	monoclinic
space group	*P2(1)/n*
a (Å)	19.461(4)
b (Å)	6.4695(12)
c (Å)	21.706(4)
α (°)	90
β (°)	105.772(3)
γ (°)	90
vol (Å^3), *Z*	2629.9(8), 6
ρ (calcd) (Mgm^{-3})	1.693
F(000)	1316
μ (mm^{-1})	1.720
θ range for data collecn (deg)	1.65 and 25.10
no. of rflns collected	25306
no. of indep reflns	4678
abs cor.	empirical

no. of data/restraints /params	4678 / 0 / 347
goodness of fit on F^2	1.050
R1[a]	0.0631
*w*R2[b]	0.1108
largest diff peak and hole (eÅ^{-3})	0.685 and -0.307

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

[1] D. W. Macomber, W. P. Hart, M. Rausch, *Advances in Organometallic Chemistry* **1982**, *21*, 1.

[2] J. Okuda, *J. Organomet. Chem.* **2001**, *637-639*, 786.

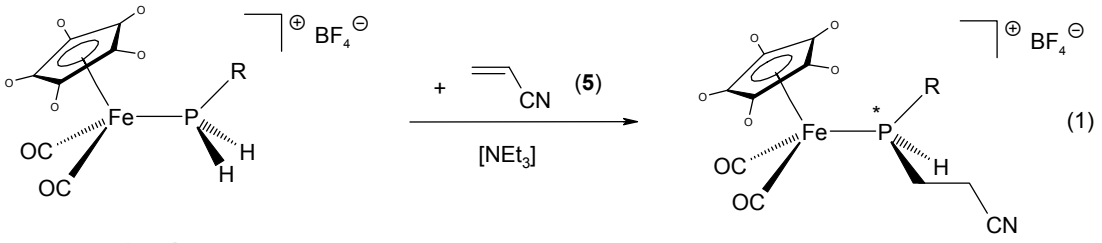
[3] K. Sünkel, C. Stramm, *Inorg. Chim. Acta* **2000**, *298*, 33.

[4] S. U. Son, K. H. Park, S. J. Lee, Y. K. Chung, D. A. Sweigart, *Chem. Comm.* **2001**, *14*, 1290.

SUMMARY

Chapter I: Synthesis of Functionalized *Secondary* and *Tertiary* Phosphines via Hydrophosphination of Acrylonitrile, Ethylisocyanate or Methyl-1,3-butadiene-1-carboxylate with the *Primary* Phosphine Iron Complexes $\{R'_5C_5(OC)_2Fe\,[P(R)H_2]\}BF_4$ (R = *i*-Pr, *t*-Bu, Mes, Ph; R' = H, Me)

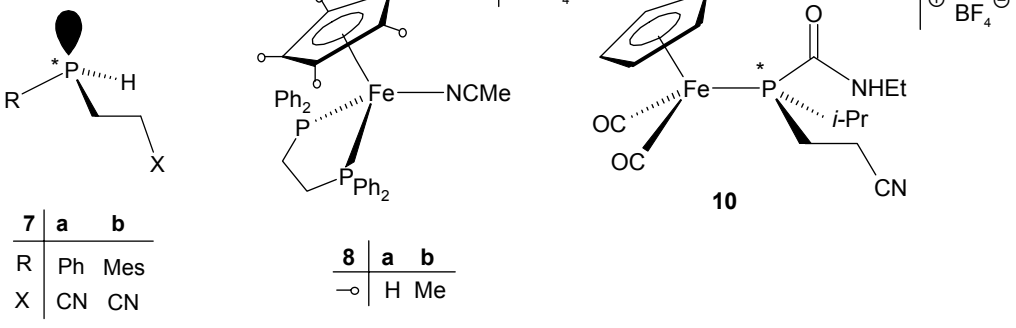
The cationic isopropylphosphine iron complex **3**, formed by thermal CO/phosphine exchange in acetonitrile from $[H_5C_5(OC)_3Fe]BF_4$ (**1**) and isopropylphosphine (**2**), as well as the known *tert*-butyl- and mesitylphosphine iron complexes **4a,b** are used for the hydrophosphination reaction of acrylonitrile (**5**) (eq. 1). Reaction in acetonitrile at room temperature yields the corresponding cyanoethyl(alkyl/aryl)phosphine iron complexes **6a-c** as a result of *anti*-Markownikow addition, provided a catalytic amount of triethylamine is added.



3,4a,b **6a-c**

	a	b	c
R	*i*-Pr	*t*-Bu	Mes
o—	H	Me	Me

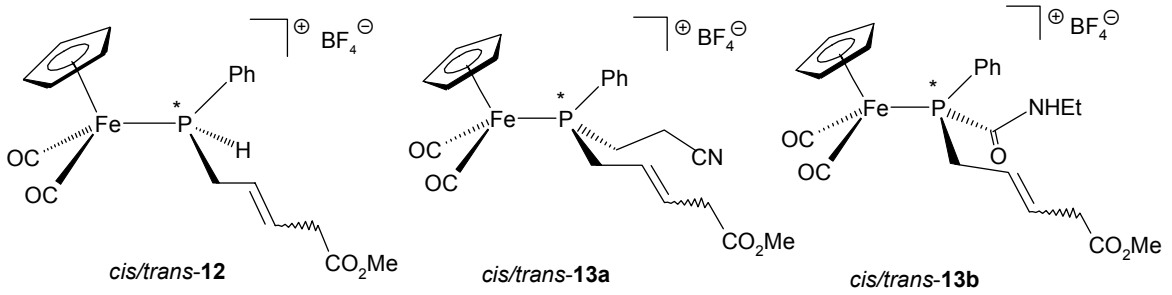
The release of the phosphine ligand from transition metal fragment can be achieved in the case of the *secondary* phosphine complexes **6c,d** by treatment with dppe in acetonitrile under ultraviolet irradiation. The functionalized *secondary* phosphines **7a,b** are obtained in high yields together with the dppe-iron-complexes **8a,b**.



7	a	b
R	Ph	Mes
X	CN	CN

8	a	b
⊸	H	Me

Further hydrophosphination is possible by combining the organocyanoethylphosphine iron complex $H_5C_5(OC)_2Fe[P(i\text{-}Pr)H(CH_2CH_2CN)]\}BF_4$ (**6a**) with ethyl isocyanate (**9**) and Et_3N in acetonitrile. At room temperature the carbamoyl(cyanoethyl)phosphine iron complex **10** is generated, characterized by a high functionality of its chiral phosphine ligand.

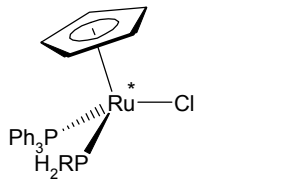


cis/trans-**12** *cis/trans*-**13a** *cis/trans*-**13b**

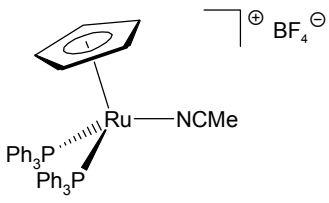
The hydrophosphination reaction of methyl-1,3-butadiene-1-carboxylate (**11**) with the phenylphosphine iron complex $H_5C_5(OC)_2Fe[P(Ph)H_2]\}BF_4$ (**4c**) exclusively generates the 1,4 addition product **12** in 86 % yield, obtained as a 67 : 33 mixture of the *trans*- and *cis*-isomer. The PH-bond of **12** proves to be reactive enough for further hydrophosphination of acrylonitrile (**5**) or ethylisocyanate (**9**) to yield the *tertiary* phosphine complex **13a,b** in a *trans*/*cis*-ratio identical to that of **12**.

Chapter II: *Primary* Phosphine Ruthenium Complexes $H_5C_5(Ph_3P)(H_2RP)RuCl$ (R = Ph, Mes, *i*-Pr, *t*-Bu, Cy) and $\{H_5C_5(Ph_3P)_2Ru[P(Ph)H_2]\}BF_4$: Synthesis and Hydrophosphination of Methylacrylate

Starting from the chloro ruthenium complex $H_5C_5(Ph_3P)_2RuCl$ (**1**) and the *primary* phosphines $P(R)H_2$ (R = Ph, Mes, *i*-Pr, *t*-Bu, Cy) (**2a-e**) the chiral aryl/alkylphosphine ruthenium complexes **3a-e** are synthesized via exchange of one Ph_3P-ligand.



3	a	b	c	d	e
R	Ph	Mes	*i*-Pr	*t*-Bu	Cy



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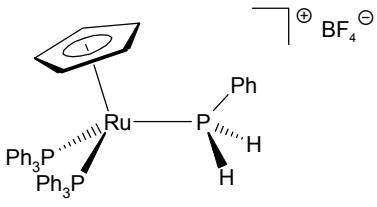
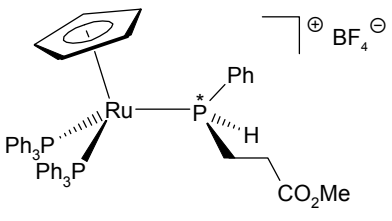


5

In order to provide the coordinated *primary* phosphine with a PH-acidity, high enough for deprotonation, the cationic *primary* phosphine ruthenium complex **5** is synthesized from **1** via chloride abstraction with silver tetrafluoroborate in acetonitrile to give the cationic acetonitrile ruthenium complex **4** followed by $MeCN/PhPH_2$-exchange.

Hydrophosphination of methylacrylate (**6**) with **5** in dichloromethane initiated by a catalytic amount of triethylamine yields to the phenyl(1-yl-methylpropionate)phosphine ruthenium complex **7**.



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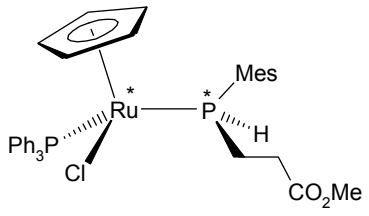
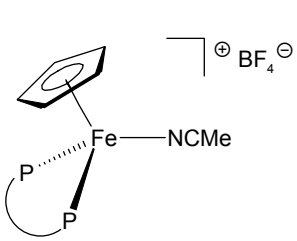


8

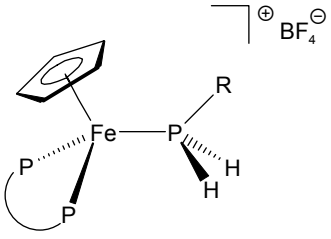
In the case of the neutral mesitylphosphine complex **3b** hydrophosphination of methylacrylate (**6**) demands stochiometric amounts of the strong base KO*t*Bu to yield the chiral methylcarboxylatephosphine complex **8**.

Chapter III: Chelatephosphine Substituted *Primary* Phosphine Iron and Ruthenium Complexes $[H_5C_5(P_{[2]})Fe[P(R)H_2]BF_4$ [$P_{[2]}$ = dppe, mppe, (*R*)-(+)-PROPHOS, (*R*,*R*)-(–)-DIOP; R = Ph, *i*-Pr] and $[H_5C_5$(DIOP)Ru $[P(Ph)H_2]BF_4$: Synthesis and Hydrophosphination of Acrylonitrile and the Isocyanates RNCO (R = (S)-1-Phenylethyl, Et)

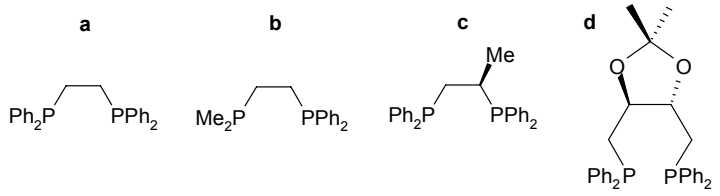
Irradiation of the cationic iron complex $[(H_5C_5)Fe(CO)_3]BF_4$ (**1**) in the presence of one equivalent dppe (**2a**), mppe (**2b**), PROPHOS (**2c**) or DIOP (**2d**) in acetonitrile results in the exchange of all carbonmonoxide ligands against the chelate phosphine and a solvent molecule to give the chelate phosphine acetonitrile iron complexes **3a-d**. **3c**, containing chiral PROPHOS, is obtained as a 95:5 mixture of diastereomers. The reaction of **3a-d** with $P(R)H_2$ (R = Ph, *i*-Pr) (**4a,b**) leads to formation of the *primary* phosphine complexes **5a-d**.



3a-d

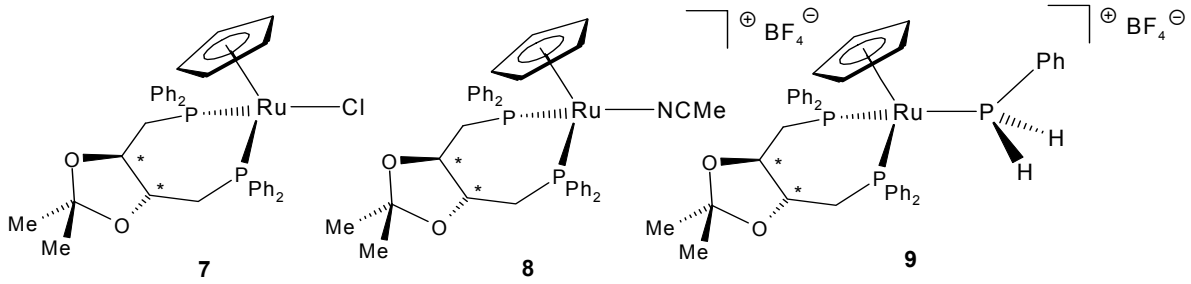


5a-d

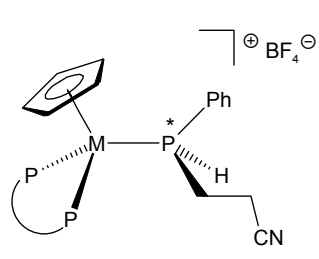


dppe **mppe** **PROPHOS** **DIOP**

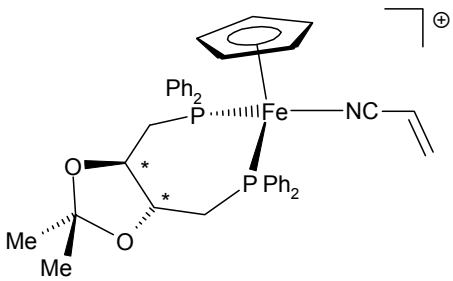
Starting from $H_5C_5(Ph_3P)_2RuCl$ (**6**) thermally induced exchange of both triphenylphosphine ligand against the chelate phosphine DIOP (**2d**) is achieved to give **7**, which is converted in acetonitrile via chloride abstraction with silver tetrafluoroborate to the cationic acetonitrile DIOP complex **8**. Treatment of **8** with an equimolar amount of $P(Ph)H_2$ (**4a**) yields the *primary* phosphine ruthenium complex **9**.



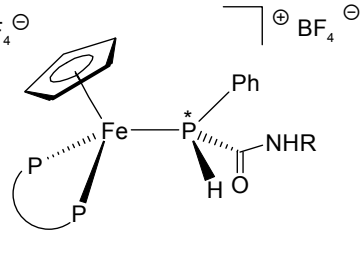
Hydrophosphination of acrylonitrile (**10**) with the phenylphosphine complexes **5b,c** and **9** in acetonitrile at room temperature catalyzed by a trace of triethylamine leads to the formation of the corresponding cyanoethyl(phenyl)phosphine complexes **11a-c**. **11a,c** are formed as diastereomeric mixture [ratio: 68:32 (**11a**), 83:17 (**11c**)]. In the case of **11b** due to *syn*/*anti*-isomerism concerning the PROPHOS ligand chirality of the phosphorus gives rise to the formation of four stereoisomers (Ratio: 62:26:8:4). In contrast, the reaction of the isopropylphosphine iron complex $[H_5C_5(DIOP)Fe[P(i\text{-}Pr)H_2]BF_4$ (**5d**) with acrylonitrile (**10**) generates only the cationic acrylonitrile iron complex **12** due to phosphine substitution.



11	a	b	c
P P	mppe	PROPHOS	DIOP
M	Fe	Fe	Ru



12

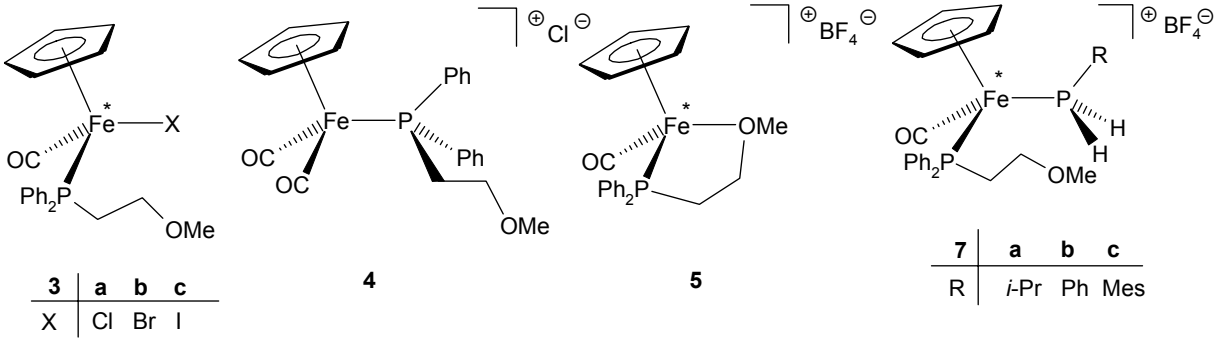


14	a	b
P P	dppe	mppe
R	Ph	Et

Reaction of $[H_5C_5(dppe)Fe[P(Ph)H_2]BF_4$ (**5a**) in acetonitrile with (S)-1-phenylethyl-isocyanate (**13a**) gives the diastereomeric carbamoyl(phenyl)phosphine iron complex **14a**. Analogously ethylisocyanate (**13b**) and the (mppe)phenylphosphine iron complex **5b** gives rise to the formation of diastereomeric **14b** (Ratio: 58:42).

Chapter IV: Synthesis and Reactivity of *Primary* Phosphine Iron Complexes $\{H_5C_5(L)[H_3CO(CH_2)_2Ph_2P]Fe[P(R)H_2]\}BF_4$ (L = CO, PMe_3; R = i-Pr, Ph, Mes) containing a Hemilabile Ligand

The halogeno iron complexes **3a-c** bearing the hybride ligand $PPh_2(CH_2)_2OCH_3$ (**2**) are obtained by irradiation of a 1:1-mixture of $H_5C_5(OC)_2FeX$ (X = Cl, Br, I) (**1a-c**) and $PPh_2(CH_2)_2OCH_3$ (**2**). In the case of **3a** the simultaneous formation of the cationic compound $\{H_5C_5(OC)_2Fe[PPh_2(CH_2)_2OCH_3]\}Cl$ (**4**) is observed due to substitution of the chloro ligand by **2**. **3a-c** can be transformed into the cationic iron complex **5** by intramolecular coordination of the donor oxygen induced by $AgBF_4$ assisted chloride abstraction.



3	a	b	c
X	Cl	Br	I

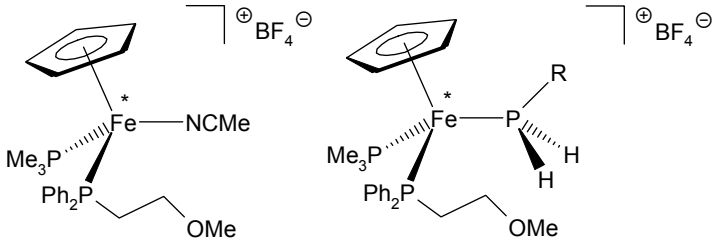
4 **5**

7	a	b	c
R	*i*-Pr	Ph	Mes

The reaction of **5** with the *primary* phosphines $P(R)H_2$ (R = *i*-Pr, Ph, Mes) (**6a-c**) in dichloromethane at 40 °C generates the *primary* phosphine iron complexes **7a-c** due to the opening of the chelate ligand coordination at the weakly bound oxygen.

Irradiation of the cationic Me_3P-substituted iron complex $[H_5C_5(Me_3P)(OC)_2Fe]BF_4$ (**8**) in acetonitrile in the presence of the hybride ligand $PPh_2(CH_2)_2OCH_3$ (**2**) at ambient temperature

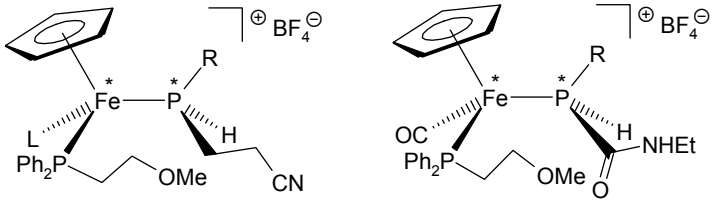
results in the exchange of both CO groups against the hemilabile ligand **2** and a solvent molecule to produce the η^1(2-methoxyethyldiphenylphosphine) acetonitrile iron complex **9**. Treatment of **9** with the arylphosphines $P(R)H_2$ (R = Ph, Mes) (**6b,c**) yields the *primary* phosphine iron complexes **10a,b**.



9

10	**a**	**b**
R	Ph	Mes

The conversion of **7b,c** and **10a** succeeds with acrylonitrile (**11**) to give the corresponding *secondary* cyanoethylphosphine complexes **12a-c**. Due to the stereogenic centres iron and phosphorus the complexes **12a-c** are obtained as a mixture of diastereomers showing a ratio of 60:40 (**12a**/**12a'**/**12c**/**12c'**) or 86:14 (**12b**/**12b'**). **10b** does not react with acrylonitrile (**11**) under the same conditions.



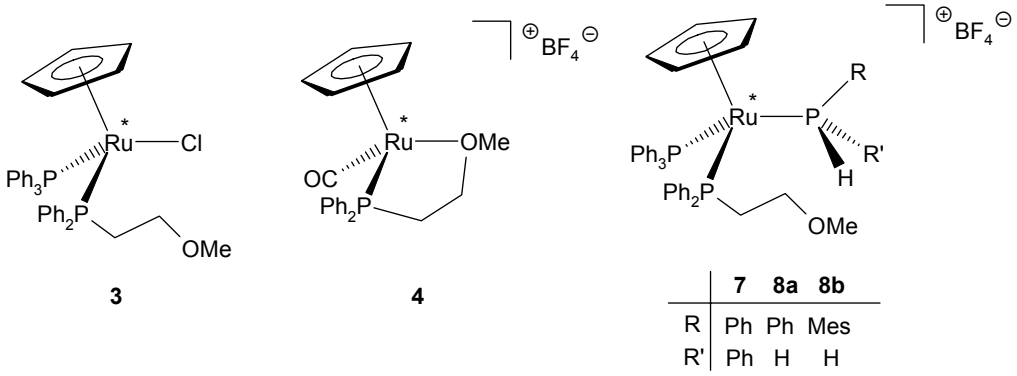
12	**a**	**b**	**c**
R	Ph	Mes	Ph
L	CO	CO	PMe_3

14	**a**	**b**
R	Ph	Mes

The hydrophosphination reactions of the complexes **7a-c** with ethylisocyanate (**13**) in result in the formation of the corresponding *secondary* phosphine complexes **14a,b**. The *iso*-propyl phosphine iron complex **7a** fails to react both with acrylonitrile (**11**) and ethylisocyanate (**13**). The release of the coordinated (cyanoethyl)phenylphosphine in **12a** can be achieved by photolysis with UV-light in dichloromethane with regeneration of complex **5** due to closure of the free coordination site by the oxygen donor.

Chapter V: Synthesis and Reactivity of *Primary* Phosphine Ruthenium Complexes $\{H_5C_5(Ph_3P)[H_3CO(CH_2)_2Ph_2P]Ru[PRR'H]\}BF_4$ (R = Ph, Mes; R' = H, Ph) containing a Hemilabile Ligand

The ruthenium chloro complex **3** is generated from $C_5H_5(Ph_3P)_2RuCl$ (**1**) by exchange of a triphenylphosphine ligand against the hybride ligand $Ph_2P(CH_2)_2OCH_3$ (**2**).

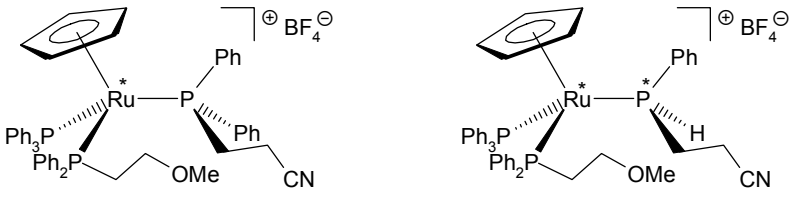


3 **4**

	7	8a	8b
R	Ph	Ph	Mes
R'	Ph	H	H

Abstraction of the chloro ligand of **3** is achieved with silver tetrafluoroborate to give **4** containing the hybride ligand coordinated in a bidentate fashion. Opening of the chelate ring of **4** can be verified by the reaction with diphenylphosphine (**5**), phenyl- or mesitylphosphines (**6a,b**) to generate the *secondary* and the *primary* phosphine ruthenium complexes **7;8a,b**, but only in an equilibrium with the starting complex **4**.

The hydrophosphination of acrylonitrile (**9**) with **7** in the presence of a stochiometric amounts of KO*t*Bu yields the *tertiary* phosphine ruthenium complex **11**. In the case of the *primary* phosphine complexes **8a,b** only **8b** undergoes reaction with acrylonitrile (**9**) to give **12**. **11** and **12** are isolated in a mixture with **4**.



11 **12**

Studies concerning the detachment of the secondary phosphine ligand of **12** via UV-irradiation lead to uncontrolled decomposition.

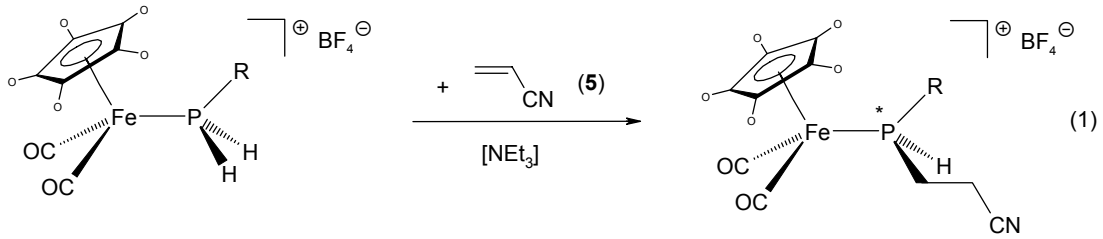
Chapter VI: X-Ray Structure Analyses

- $\{[HOiPr_2Si(C_5H_4)](OC)_3W\}_2$ (W-W)
- $Cp(OC)_2W{=}P(sMes)\text{-}W(CO)_3Cp$
- $Cp(OC)_2W\text{-}P(\overline{sMes)\text{-}W(CO)}_2Cp$
- $Cp(OC)_2W{=}P(OMe)sMes$
- $Cp(OC)_2Fe\text{-}SiMePhH$

ZUSAMMENFASSUNG

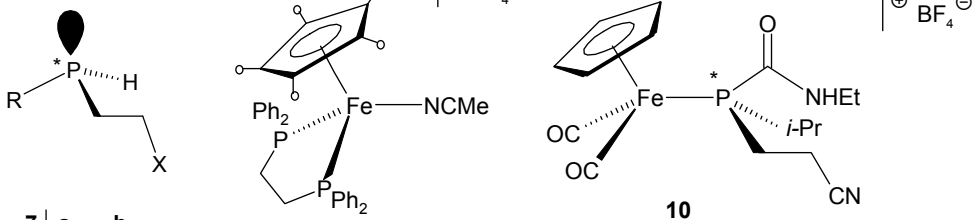
Kapitel I: Funktionalisierte *sekundäre* und *tertiäre* Phosphanliganden durch Hydrophosphorisierung von Acrylnitril, Ethylisocyanat oder 1,3-Butadien-1-carbonsäuremethylester mit den *primär*-Phosphan-Eisen-Komplexen $\{C_5R'_5(OC)_2Fe[P(R)H_2]\}BF_4$ (R = *i*-Pr, *t*-Bu, Ph, Mes; R' = H, Me)

Der kationische Isopropylphosphan-Eisen-Komplex **3**, der durch thermischen CO/Phosphan Austausch aus $[C_5H_5(OC)_3Fe]BF_4$ (**1**) und Isopropylphosphan (**2**) in Acetonitril zugänglich ist, sowie die bekannten *tert*-Butyl- und Mesitylphosphan-Eisen-Komplexe **4a,b** werden zur Hydrophosphinierung von Acrylnitril (**5**) eingesetzt (Gl. 1). Umsetzung in Acetonitril unter Zugabe katalytischer Mengen an Triethylamin liefert die korrespondierenden Cyanoethyl(Alkyl/Aryl)phosphan-Eisen-Komplexe **6a-c** als das Produkt einer *anti*-Markownikow-Addition.



	a	b	c
R	*i*-Pr	*t*-Bu	Mes
○—	H	Me	Me

Die Ablösung der Phosphane vom Übergangsmetallfragment kann im Fall der *sekundär*-Phosphan-Eisen-Komplexe **6c,d** durch Bestrahlung in Gegenwart einer äquimolaren Menge dppe in Acetonitril realisiert werden, wobei die funktionalisierten sekundären Phosphane **7a,b** in hoher Ausbeute zusammen mit den dppe-Eisen-Komplexen **8a,b** erhalten werden.

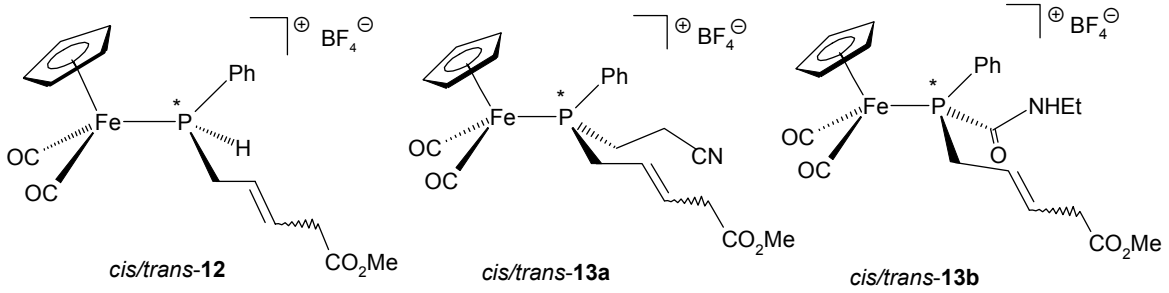


7	a	b
R	Ph	Mes
X	CN	CN

8	a	b
⊸	H	Me

10

Aus der Umsetzung des Cyanoethylphosphan-Eisen-Komplexes $H_5C_5(OC)_2Fe[P(i\text{-}Pr)H(CH_2CH_2CN)]\}BF_4$ (**6a**) mit Ethylisocyanat (**9**) und Et_3N resultiert der hoch funktionalisierte Carbamoyl(cyanoethyl)phosphan-Eisen-Komplex **10** mit chiralem *tertiär*-Phosphanliganden.

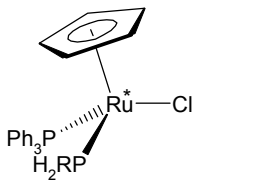


cis/trans-**12** *cis/trans*-**13a** *cis/trans*-**13b**

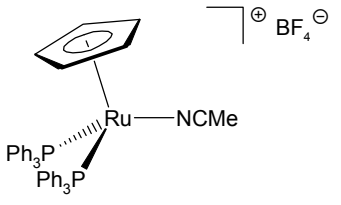
Die Hydrophosphinierung von 1,3-Butadien-1-carbonsäuremethylester (**11**) mit dem Phenylphosphan-Eisen-Komplex $H_5C_5(OC)_2Fe[P(Ph)H_2]\}BF_4$ (**4c**) liefert ausschließlich das 1,4-Additions-Produkt **12**, welches als *trans/cis*-Isomerengemisch im Verhältnis 67 : 33 erhalten wird. Die Umsetzung von **12** mit Acrylnitril (**5**) oder Ethylisocyanat (**9**) zu dem *tertiär*-Phosphan-Eisen-Komplexen **13a,b** belegt die Reaktivität der verbleibenden PH-Funktion bezüglich einer weiteren Hydrophosphinerung, wobei das Isomerenverhältnis mit dem von **12** übereinstimmt.

Kapitel II: *Primär*-Phosphan-Ruthenium-Komplexe $H_5C_5(Ph_3P)(H_2RP)RuCl$ (R = Ph, Mes, *i*-Pr, *t*-Bu, Cy) und $[H_5C_5(Ph_3P)_2Ru[P(Ph)H_2]BF_4$: Synthese und Hydrophosphinierung von Methylacrylat

Ausgehend von dem Chloro-Ruthenium-Komplex $H_5C_5(Ph_3P)_2RuCl$ (**1**) und den *primär*-Phosphanen **2a-e** werden die chiralen Aryl/Alkylphosphan-Ruthenium-Komplexe **3a-e** in Toluol bei Raumtemperatur durch Austausch eines Triphenylphosphanliganden erhalten.



3	a	b	c	d	e
R	Ph	Mes	*i*-Pr	*t*-Bu	Cy



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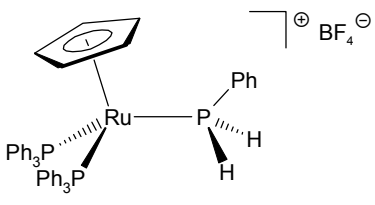
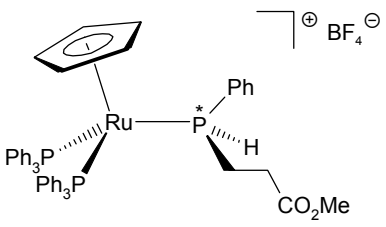


5

Der kationische Phenylphosphan-Ruthenium-Komplex **5,** den eine höhere PH-Acidität auszeichnet, wird ausgehend von **1** durch Chlorabstraktion mittels Silbertetrafluoroborat in Acetonitril und nachfolgenden MeCN/$PhPH_2$-Austausch des hierbei gebildeten kationischen Acetonitril-Ruthenium-Komplex **4** synthetisiert.

Die durch Triethylamin initiierte Hydrophosphinierungsreaktion von Methylacrylat **6** mit **5** in Dichloromethan führt zu dem Phenyl(1-yl-propionsäuremethylester)phosphan-Ruthenium-Komplex **7**.



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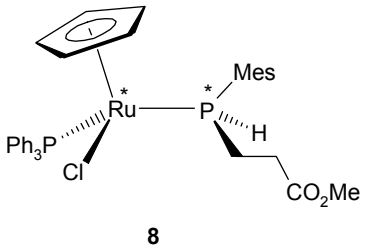
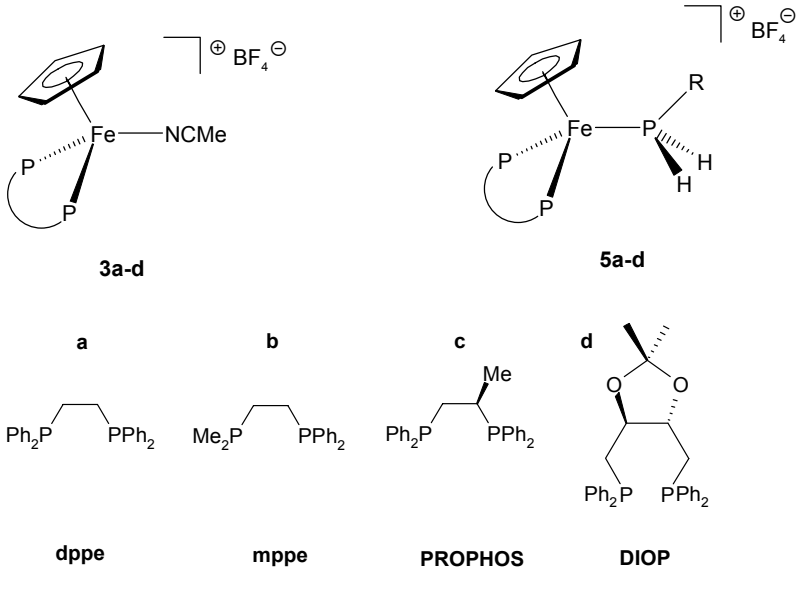


8

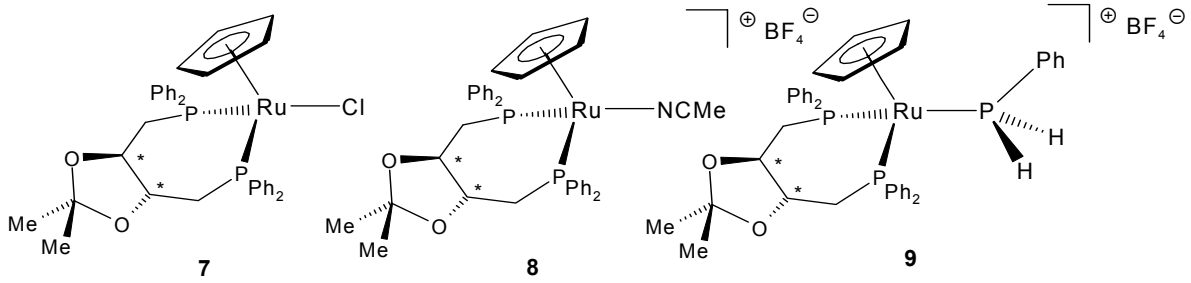
Im Falle der Hydrophosphinierungsreaktion von Methylacrylat **6** mit dem neutralen Mesityl-phosphan-Komplex **3b** zum chiralen Mesityl(1-yl-propionsäuremethylester)phosphan-Komplex **8** sind stöchiometrische Mengen der Base KOtBu erforderlich.

Kapitel III: Chelatphosphan-substituierte *Primär*-Phosphan-Komplexe des Eisens und Rutheniums $[H_5C_5(P_{[2]})Fe[P(R)H_2]BF_4$ [$P_{[2]}$ = dppe, mppe, (*R*)-(+)-PROPHOS, (*R*,*R*)-(–)-DIOP; R = Ph, *i*-Pr] und $[H_5C_5$(DIOP)Ru $[P(Ph)H_2]BF_4$: Synthese und Hydrophosphinierung von Acrylnitril sowie den Isocyanaten RNCO (R = Et, (S)-1-Phenylethyl)

Bestrahlung des kationischen Eisen-Komplexes $[(C_5H_5)Fe(CO)_3]BF_4$ (**1**) führt in Anwesenheit eines Äquivalents dppe (**2a**), mppe (**2b**), PROPHOS (**2c**) oder DIOP (**2d**) in Acetonitril zum Austausch aller Carbonylliganden gegen das Chelatphosphan und ein Solvensmolekül unter Bildung der Chelatphosphan-Acetonitril-Eisen-Komplexe **3a-d**. Komplex **3c**, der den chiralen Liganden PROPHOS enthält, wird als Diastereomerengemisch im Verhältnis von 95 : 5 isoliert. Die Reaktion der kationischen Chelatphosphan-Acetonitril-Eisen-Komplexe **3a-d** mit RPH_2 (R = Ph, *i*-Pr) (**4a,b**) führt zu den *primären* Phosphan-Eisen-Komplexen **5a-d**.

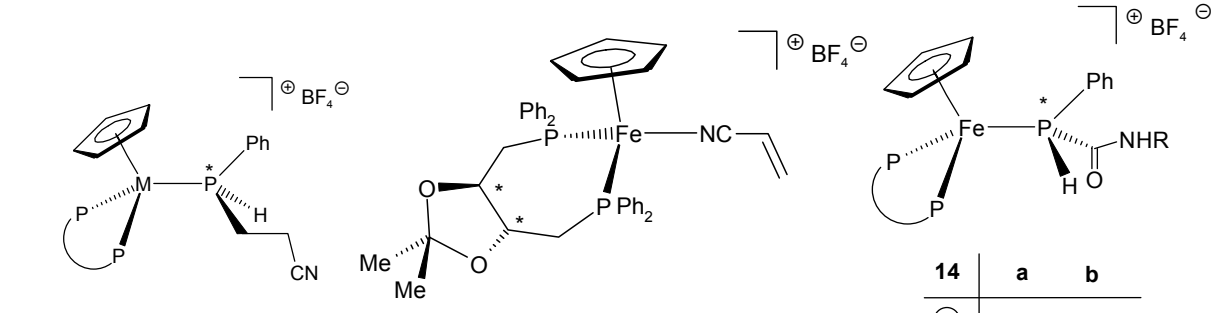


Ausgehend von $H_5C_5(Ph_3P)_2RuCl$ (**6**) wird durch thermisch induzierten Austausch beider Triphenylphosphanliganden gegen das Chelatphosphan DIOP (**2d**) der Komplex **7** dargestellt, welcher sich in Acetonitril nach Chlorabstraktion mittels Silbertetrafluoroborat in den kationischen Acetonitril-DIOP-Komplex **8** umwandelt. Umsetzung von **8** mit einem Äquivalent $P(Ph)H_2$ (**4a**) ergibt den *primär*-Phosphan-Ruthenium-Komplex **9**.



7 **8** **9**

Die Triethylamin-katalysierte Hydrophosphinierung von Acrylnitril (**10**) mit den *primär*-Phosphan-Komplexen **5b,c** und **9** liefert in Acetonitril bei Raumtemperatur die entsprechenden Cyanoethyl(phenyl)-Komplexe **11a-c**. **11a,c** fallen als Diastereomerengemisch im Verhältnis von 68:32 (**11a**) und 83:17 (**11c**) an. Aufgrund der *syn*/*anti*-Isomerie des PROPHOS-Liganden werden im Falle von **11b** vier Stereoisomere im Verhältnis 62:26:8:4 gebildet. Im Gegensatz dazu führt die Umsetzung des Isopropylphosphan-Eisen-Komplexes $[H_5C_5(DIOP)Fe[P(i\text{-}Pr)H_2]BF_4$ (**5d**) mit Acrylnitril (**10**) aufgrund bevorzugter Substitution des *primär*-Phosphans nur zum kationischen Acrylnitril-Eisen-Komplex **12**.



11	a	b	c
P P	mppe	PROPHOS	DIOP
M	Fe	Fe	Ru

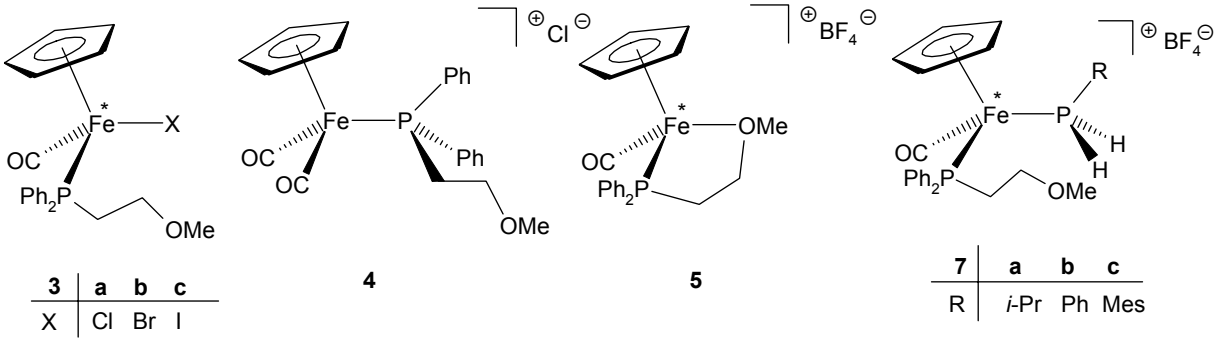
12

14	a	b
P P	dppe	mppe
R	Ph	Et

Die Umsetzung von **5a** mit (S)-1-Phenylethyl-isocyanat (**13a**) in Acetonitril ergibt den diastereomeren Carbamoyl(phenyl)phosphan-Eisen-Komplex **14a**. Analog reagiert Ethylisocyanat (**13b**) mit dem Phenylphosphan-(mppe)Eisen-Komplex **5b** zum diastereomeren *sekundär*-Phosphan-Eisen-Komplex **14b** (Verhältnis: 58:42).

Kapitel IV: *Primär*-Phosphan-Eisen-Komplexe $\{H_5C_5(L)[H_3CO(CH_2)_2Ph_2P]Fe[P(R)H_2]\}BF_4$ (L = CO, PMe_3; R = *i*-Pr, Ph, Mes) mit hemilabilem Liganden: Synthese und Reaktivität

Die Halogen-Eisen-Komplexe **3a-c** mit dem Hybridliganden $Ph_2P(CH_2)_2OCH_3$ (**2**) werden durch Bestrahlung des 1:1-Reaktionsgemisches von $H_5C_5(OC)_2FeX$ (X = Cl, Br, I) (**1a-c**) und $Ph_2P(CH_2)_2OCH_3$ (**2**) dargestellt. Im Falle von **3a** wird zusätzlich die Bildung der kationischen Verbindung $\{H_5C_5(OC)_2Fe[PPh_2(CH_2)_2OCH_3]\}Cl$ (**4**) aufgrund gleichzeitiger Substitution des Chlorliganden durch **2** beobachtet. **3a-c** können durch intramolekulare Koordination des Sauerstoffdonors nach Chlorabstraktion mittels Silbertetrafluoroborat in den kationischen Eisen-Komplex **5** umgewandelt werden.



3	a	b	c
X	Cl	Br	I

4

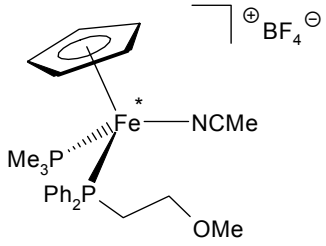
5

7	a	b	c
R	*i*-Pr	Ph	Mes

Die Umsetzung von **5** mit den *primären* Phosphanen $P(R)H_2$ (R = *i*-Pr, Ph, Mes) (**6a-c**) in Dichlormethan bei 40 °C generiert aufgrund der Öffnung der Koordination des

Chelatliganden am schwächer koordinierten Sauerstoff die *primär*-Phosphan-Eisen-Komplexe **7a-c**.

Bestrahlung des kationischen Me_3P-substitutierten Eisen-Komplexes $[H_5C_5(Me_3P)(OC)_2Fe]BF_4$ (**8**) in Acetonitril in Anwesenheit des Hybridliganden $Ph_2P(CH_2)_2OCH_3$ (**2**) bei Raumtemperatur resultiert in einem Austausch beider CO-Liganden gegen den hemilabilen Liganden **2** und ein Solvensmolekül unter Bildung des η^1(2-methoxyethyldiphenyl-phosphine)-Acetonitril-Eisen-Komplexes **9**. Die Reaktion von **9** mit den Arylphosphanen **6b,c** führt zu den *primär*-Phosphan-Eisen-Komplexen **10a,b**.



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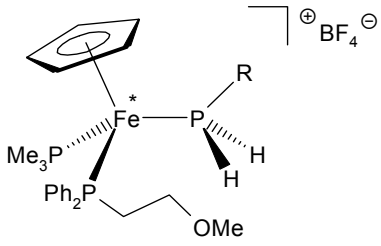
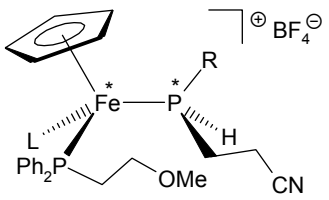
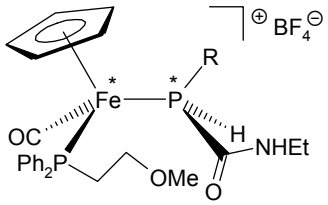


10	**a**	**b**
R	Ph	Mes

Die Umsetzung von **7b,c** und **10a** mit Acrylnitril (**11**) ergibt die korrespondierenden *sekundär*-Cyanoethylphosphan-Komplexe **12a-c**. Aufgrund der stereogenen Zentren Eisen und Phosphor werden die Komplexe **12a-c** als Diastereomerengemische erhalten, die ein Verhältnis von 60:40 (**12a**/**12a'**/**12c**/**12c'**) oder 86:14 (**12b**/**12b'**) aufweisen.



12	**a**	**b**	**c**
R	Ph	Mes	Ph
L	CO	CO	PMe_3



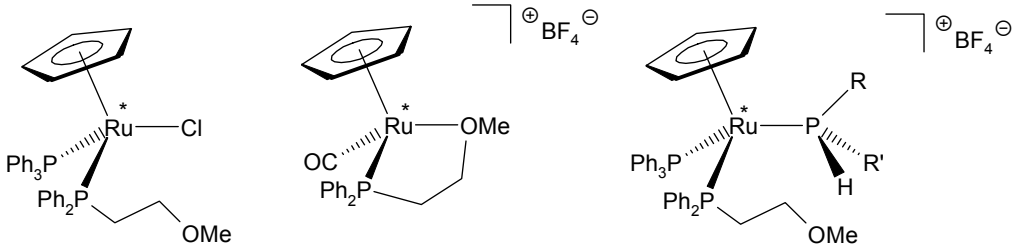
14	**a**	**b**
R	Ph	Mes

Die Bildung der korrespondierenden *sekundär*-Phosphan-Komplexe **14a,b** resultiert aus der Hydrophosphinierung der Komplexe **7a-c** mit Ethylisocyanat (**13**) in Dichlormethan. Der Isopropylphosphan-Eisen-Komplex **7a** reagiert weder mit Acrylnitril (**11**) noch mit

Ethylisocyanat (**13**). Die Freisetzung des koordinierten Cyanoethyl(phenyl)phosphans von **12a** unter Rückbildung von **5** kann durch Photolyse erzielt werden.

Kapitel V: *Primär*-Phosphan-Ruthenium-Komplexe $\{H_5C_5(Ph_3P)[H_3CO(CH_2)_2Ph_2P]Ru[PRR'H]\}BF_4$ (R = Ph, Mes; R' = H, Ph) mit hemilabilem Liganden: Synthese und Reaktivität

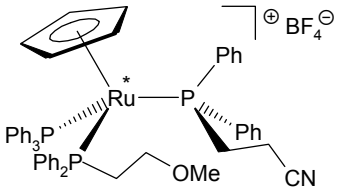
Der Ruthenium-Chloro-Komplex **3** wird ausgehend von $C_5H_5(Ph_3P)_2RuCl$ (**1**) durch Austausch eines Triphenylphosphanliganden gegen den hemilabilen Liganden $PPh_2(CH_2)_2OCH_3$ (**2**) synthetisiert.



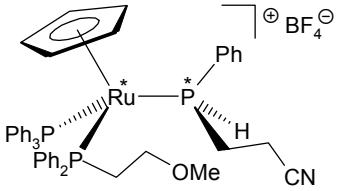
Die Abstraktion des Chlorliganden in **3** mittels Silbertetrafluoroborat führt zum Komplex **4** mit bidentatem Hybridliganden. Die Öffnung des Chelatrings in **4** wird durch die Reaktion mit Diphenylphosphan (**5**), Phenyl- oder Mesitylphosphan (**6a,b**) erzielt, wobei die *sekundär*- und *primär*-Phosphan-Ruthenium-Komplexe **7;8a,b** resultieren. Die Komplexe **7;8a,b** entstehen nur im Gleichgewicht mit dem Eduktkomplex **4**.

Die Hydrophosphinierung von Acrylnitril (**9**) mit **7** zum *tertiär*-Phosphan-Ruthenium-Komplex **11** macht die Anwesenheit stöchiometrischer Mengen der Base KO*t*Bu erforderlich. Von den *primär*-Phosphan-Komplexen **8a,b** reagiert nur **8b** mit Acrylnitril (**9**) zu dem

entsprechenden *sekundär*-Phosphan-Komplex **12.** Die Komplexe **11** und **12** werden ebenfalls als Gemische mit Komplex **4** isoliert.



11



12

Versuche den *sekundär*-Phosphanliganden von **12** photoassistiert abzulösen, führen zur unkontrollierten Zersetzung.

Kapitel VI: Röntgenstrukturanalysen

- $\{[HOiPr_2Si(C_5H_4)](OC)_3W\}_2$ (W-W)
- $Cp(OC)_2W{=}P(sMes)\text{-}W(CO)_3Cp$
- $Cp(OC)_2W\text{-}P(\overline{sMes)\text{-}W(CO)}_2Cp$
- $Cp(OC)_2W{=}P(OMe)sMes$
- $Cp(OC)_2Fe\text{-}SiMePhH$

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 ^{19}F-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 δ = 7.15 ppm (^{1}H) or δ = 128.0 ppm (^{13}C) and [D_3]-acetonitrile at δ = 1.93 ppm (^{1}H) or δ = 118.0 ppm (^{13}C). ^{31}P-NMR-spectrum chemical shifts are referenced to external H_3PO_4. 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 Bruker IFS 25 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 Analyses

The X-ray data of chapter VI were collected on a BRUKER SMART-APEX diffractometer with D8-goniometer [graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å)] equipped with a low temperature device in omega scan mode at 173(2) K. The data was integrated with SAINT and an empirical absorption correction was applied. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods against F^2 (SHELXL-97). All non-hydrogen atoms were refined with anisotropic displacement parameters.

I would like to thank the following persons for solving and refining some of my own molecular structures:

Dr. Martin Nieger (Universität Bonn):

$[H_5C_5(DIOP)RuNCMe]BF_4$

Dr. Dirk Schumacher (Universität Würzburg):

$\{H_5C_5(OC)_2Fe[P(i\text{-}Pr)H_2]\}BF_4$

Dr. Andreas Sohns (Universität Würzburg):

$\{H_5C_5(OC)_2Fe[PhP(CH_2(CH)_2CH_2CO_2Me)(CH_2CH_2CN)]\}BF_4$

$\{H_5C_5(Ph_3P)[(Mes)(MeCO_2CH_2CH_2)HP]RuCl$

$\{H_5C_5[Ph_2P(CH_2)_2Me_2P]Fe[PH(Ph)[(C{=}O)NHEt]]\}BF_4$

DANKSAGUNG

Als Erstes möchte ich mich bei Herrn Prof. Dr. Wolfgang Malisch für die Bereitstellung des interessanten Themas sowie die Betreuung während der Anfertigung der Doktorarbeit bedanken.

Folgenden Damen und Herren danke ich für die sorgfältigen Durchführungen der Analysen und Messungen: R. Schedl (CHN-Analysen und DTA), C. P. Kneis (CHN-Analyse), M.-L. Schäfer und Dr. R. Bertermann (NMR-Spektroskopie).

Ich danke allen ehemaligen Arbeitskreismitgliedern für die bereitwillige Unterstützung und das gute Arbeitsklima. Manche habe ich nur noch kurz manche länger miterlebt, und es war eine entspannte, angenehme Zeit mit so einigen schönen Feiern und Grillfesten. Zu Erwähnen wären da Marco Hofmann, den wirklich nichts so schnell aus der Ruhe brachte, Bernd Klüpfel, der mir das "Buch des Wissens" hinterlassen und hervorragende Vorarbeit geleistet hat, Dirk Schumacher, bei dem so mancher lustiger Abend mit Spielen verbracht wurde, und Holger Bera, den ich für seine entspannte Lebenseinstellung so einige Male beneidet habe.

Besonders bedanken möchte ich mich bei meinen beiden letzten Mitstreitern Andreas Sohns und Rainer Schmitt, die mich vor allem im vergangenen Jahr bei der Arbeit ab und zu aufgeheitert haben. Wir haben bis zum Schluss zusammengehalten und die Runden, in denen wir uns gegenseitig was vorjammert haben, werde ich vermissen. Bedanken möchte ich mich auch bei unseren administrativen Damen Sabine Timmroth sowie Conny Walter.

Besonders möchte ich mich bei meinen Eltern bedanken, die mir das Studium überhaupt erst durch finanzielle Mittel ermöglicht und mich immer wieder angetrieben haben, das ganze Projekt "Studium und Dissertation" durchzuziehen.

Zum Schluss möchte ich mich natürlich noch bei meinem Freund Leander bedanken, der mich in so manch schwerer Stunde der Verzweiflung immer wieder aufgebaut hat.

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LEBENSLAUF

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Okt. 2005	Vordiplom (schriftlich)

ERKLÄRUNG

Hiermit erkläre ich an Eides statt, dass ich die Dissertation „*Primary* Phosphine Halfsandwich Complexes of Iron and Ruthenium - Synthesis and Hydrophosphination Reactions“ selbständig angefertigt und keine anderen als die von mir angegebenen Quellen und Hilfsmittel benutzt habe.

Ich erkläre außerdem, dass diese Dissertation weder in gleicher noch in 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 25.05.2006

_____

Katharina Klüh