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Hydrophosphination with cationic primary phosphine iron complexes: synthesis of P-chiral functionalized phosphines

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This work is dedicated to Professor Helmut Werner, on the occasion of his retirement, in recognition of his outstanding scientific contributions to organometallic chemistry, and also for his continual support of our work in the SFB 347.

Abstract

The synthesis of P-chiral secondary phosphines, characterized by phosphorus and side chain chirality, has been realized via insertion of various organic multiple bond systems into the P–H-bond of the primary phosphine complexes $\{C_5R_5(OC)_2Fe[P(R')H_2]\}BF_4$ (R = H, Me; R′ = alkyl, aryl). In the case of acetylenedicarboxylic acid dimethylester a double hydrophosphination is observed, leading diastereospecifically to the dinuclear complexes $\{C_5R_5(OC)_2Fe\{P(H)(R')[C(H)(CO_2Me)]\}\}_2(BF_4)_2$ (R = H, Me; R′ = *t*-Bu, 2-py), bearing four stereogenic centers. The use of *p*-benzoquinone gives access to secondary 2,5-bis(hydroxy)aryl phosphine ligands, suitable for further derivatizations. α-Hydroxyalkyl phosphine iron complexes can be obtained by hydrophosphination of aldehydes and ketones. Transformation into highly functionalized tertiary phosphine complexes is performed by a further hydrophosphination step using the alkenes $H_2C{=}CHX$ (X = CN, 2-py), diazoacetic ethylester, *p*-benzoquinone or ethylisocyanate, respectively, in special cases formation of functionalized azaphospholane ligands is observed. Release of the phosphines from the metal is achieved by photoinduced ligand exchange. In addition, primary phosphine iron complexes $\{C_5H_5(diphos)Fe[P(R)H_2]\}BF_4$ (diphos = DIOP, CHIRAPHOS) bearing chiral bis(phosphine) ligands have been used to provide the stereocontrol of the hydrophosphination process.

Keywords: Metal-assisted hydrophosphination; Chiral secondary and tertiary phosphines; Stereoselectivity Catalysis

1. 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 catalyzed by an optically pure DIPAMP-Rhodium complex [3–5] indicates the importance of chiral phosphines as catalyst building blocks introducing stereochemical information.

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 alkenes [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]. One possibility to increase the chemoselectivity of the hydrophosphination process is the activation of the P–H-bond by transition metal

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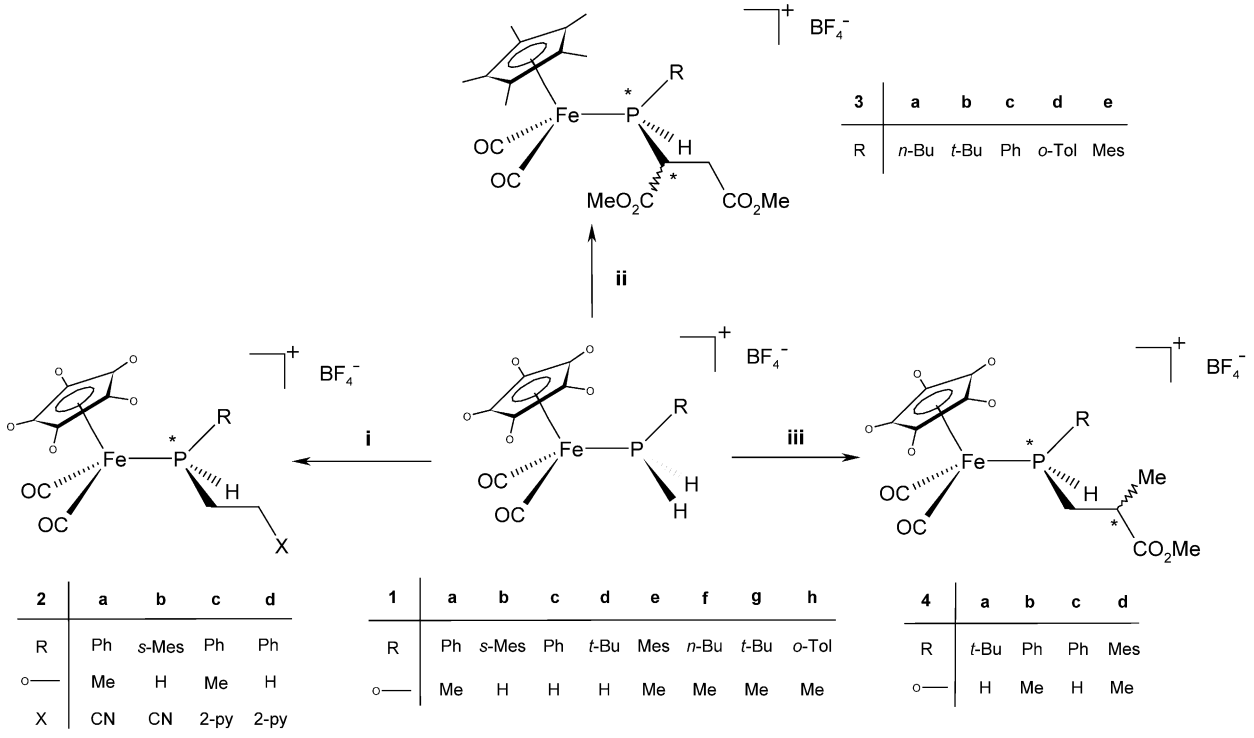
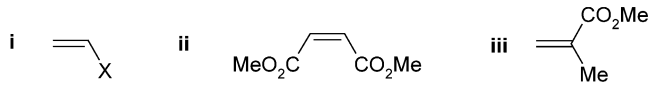


Reagents and conditions: [NEt_3], MeCN, room temperature



Scheme 1.

fragments [13], but only limited information is available concerning this topic [14–18].

Huttner obtained a vinylphosphine ligand by reacting $Cp(OC)_2Mn(PPhH_2)$ with alkynes [19]. In addition, formation of a chelate phosphine ligand is described, when the bis(phosphine) complexes $(CO)_4Cr(PPh_2H)_2$ and $[C_5H_5(OC)_2Fe(PPh_2H)_2]BF_4$ are reacted with acetylenedicarboxylic acid dimethylester [20,21]. One of the first metal catalyzed hydrophosphination involved the formation of $P(CH_2OH)_3$ by reaction of PH_3 with formaldehyde in the presence of $K_2[Pt(Cl)_4]$ [22], a procedure subsequently extended to acrylic acid methylester and acrylonitrile [23]. Recent studies by Glueck proved the catalytic activity of (dppe)Pt[η^2-H_2C=C(H)CN] for the hydrophosphination of acrylonitrile by several primary and secondary phosphines [24,25]. In this context, the efficiency of chiral bidentate bis(phosphine) ligands like *CHIRAPHOS, R-Tol-BINAP* [26] and *DUPHOS* [27] for the insertion step of the C–C-double bond into the Pt–P-bond have been examined, leading to chiral tertiary phosphines in moderate optical purity.

Regarding our previous studies concerning the coupling reactions of metallo-phosphines with organic multiple bond systems [28–33], 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, is presented here. We have carried out extensive studies concerning the conversion of primary phosphine iron complexes $\{C_5R_5(OC)_2Fe[P(R')H_2]\}BF_4$ (R = H, Me; R′ = alkyl, aryl) into derivatives with tertiary phosphine ligands containing diverse functionalities.

2. Functionalized secondary phosphine iron complexes by metal assisted hydrophosphination of organic multiple bond systems

2.1. Electron-deficient alkenes

Insertion of one equivalent of acrylonitrile or 2-vinylpyridine into the P–H-bond of the primary phosphine complexes **1a**,**b** leads to the corresponding cyano- or pyridino-ethylphosphine complexes **2a**–**d**, characterized by a stereogenic phosphorus atom [34]. The reaction usually demands the presence of catalytic amounts of NEt_3 with the exception of 2-vinylpyridine due to the basic properties of the heterocycle.

Scheme 2.

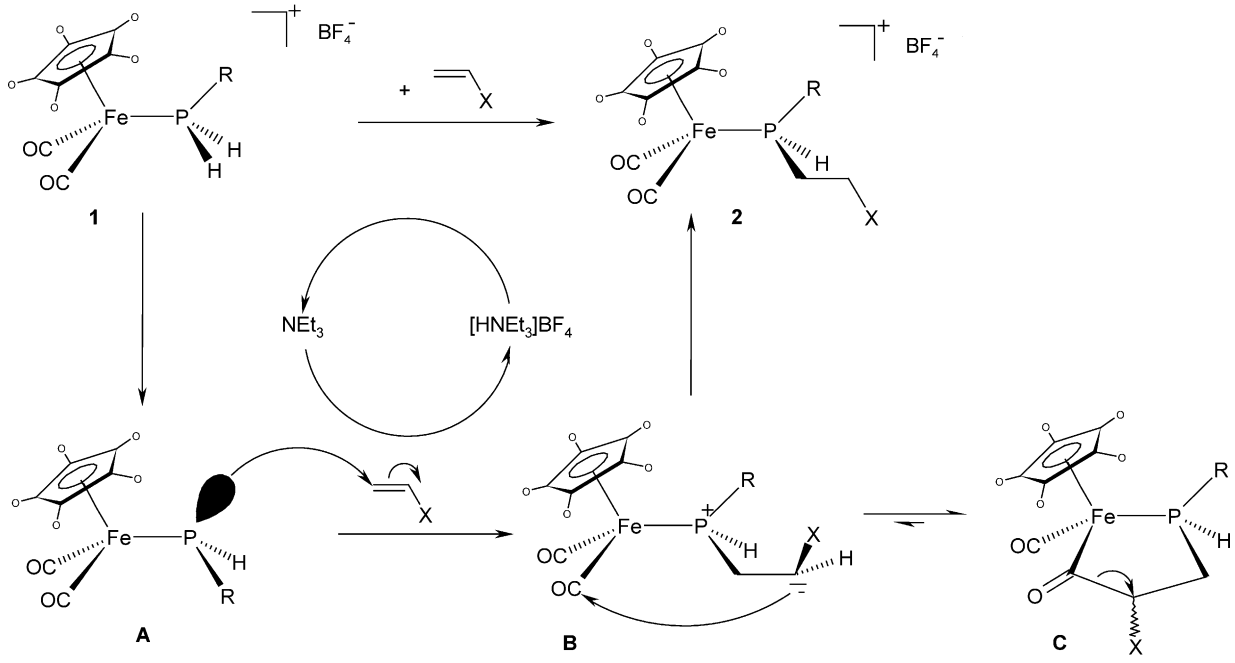
The formation of diastereomeric secondary phosphine complexes **3a**–**e** and **4a**–**d** can be achieved by base catalyzed insertion of prostereogenic alkenes like dimethyl maleate [35] or methyl methacrylate [34] creating an additional stereocentre in the carbon chain in α- or β-position to the phosphorus. **3a**–**e** and **4a**–**d** are obtained in high yields and show a diastereomeric ratio of up to 98:2 (**3c**) (Scheme 1). The hydrophosphination reactions can be easily extended to special alkenes like *trans*-ω-nitrostyrene or 2(5*H*)-furanone, which give almost quantitatively the complexes **5** and **6** bearing nitro- or lactonyl functionalized phosphine ligands in a diastereomeric ratio of 81:19 (**5**) and 61:39 (**6**), respectively [34] (Scheme 2).

As the crucial step for the insertion reaction we propose the generation of the ferrio-phosphine **A** by deprotonation of **1** with NEt_3, which acts as a pronounced nucleophile towards the electron deficient β-carbon of the C–C-double bond. The resulting zwitterionic intermediate **B** can be stabilized by intramolecular interaction of the carbanionic centre with the electrophilic carbonyl carbon to give the cyclic species **C**, a [3 + 2]-cycloaddition product of **A** and the alkene. Protonation of **B** or **C** by $[HNEt_3]BF_4$, generated in the primary deprotonation step, yields the secondary phosphine complex **2**, with reformation of the basic catalyst.

The activation of the hydrophosphination reaction by the metal fragment is predominately based on the extraordinary phosphorus nucleophilicity of ferrio-phosphine **A** in comparison to the uncoordinated primary phosphine RPH_2 [28,29] (Scheme 3).

2.2. Electron-deficient alkynes

Basically, alkynes should give rise to vinylphosphine complexes, provided an insertion of the type discussed in Section 2.1 is valid. However, in this case, repetition of the insertion process is possible, transforming the vinylphosphine complex into bis(arylphosphino)-bridged dinuclear species. It is found, that the chemoselectivity for the hydrophosphination of the ester substituted alkynes **7a**,**b** is strongly determined by the substitution pattern of the phosphorus and the cyclopentadienyl ligand. For the base catalyzed reaction of



Scheme 3.

the C_5Me_5-derivatives **1e**,**g** with propiolic acid methylester **7a** or acetylenedicarboxylic acid dimethylester **7b**, the P–H-functional vinylphosphine complexes **8a**–**c** can be isolated as a mixture of *E*-/*Z*-isomers in a ratio of up to 90:10 [36] (Scheme 4).

In the case of the C_5H_5-derivative **1d** [36] and the 2-pyridyl species **1i** [37] the formation of the dicationic binuclear complexes **9** and **10** is observed, respectively, bearing a novel type of bridging P–H-functional bisphosphinoethane ligand. A vinylphosphine complex similar to **8** containing an electron deficient double bond acts as an intermediate, which readily reacts with a second equivalent of the primary phosphine complex **1** to give **9** and **10** (Scheme 4). The formation of these symmetrical binuclear species bearing four stereogenic centers occurs highly diastereoselective. Compound **9** is obtained as the ***SSRR***/***RRSS***- diastereomer showing an inversion center (Fig. 1), **10** as the ***RSSR***/***SRRS***-diastereomer, characterized by a C_2 axis (Fig. 2), as is proven by X-ray analyses.

2.3. *p*-Benzoquinone

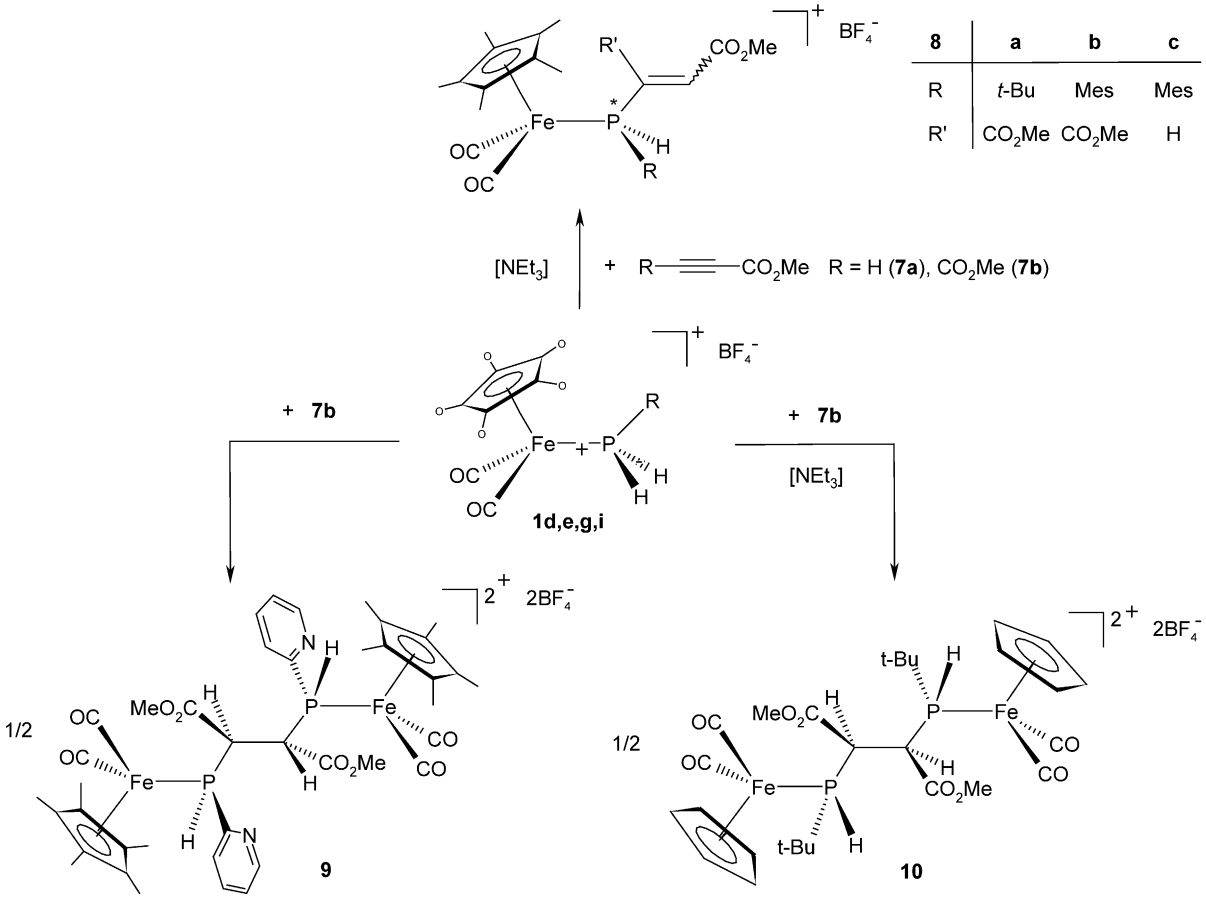
Hydrophosphination of *p*-benzoquinone offers the opportunity to generate hydroxy-functionalized aryl substituents at the phosphorus atom, for which a great variety of further derivatizations can be predicted. Actually, secondary phosphines with a 2,5-hydroxyphenyl substituent are, to the best of our knowledge, still unknown. It has been reported, that primary phosphines react with *p*-benzoquinone exclusively under formation of hydroquinone and diphosphines [38].

In contrast, metal assisted hydrophosphination of *p*-benzoquinone by **1a**,**c**–**e**,**g**,**i** smoothly leads to the formation of the 2,5-bis(hydroxy)phenyl phosphine complexes **11a**–**f** in good yields [39]. Aromatization of the quinoide system is the driving force for this reaction involving tautomerization of the secondary ferrio-phosphine-/quinone adduct **E** to the zwitterionic species **F**, which is protonated by $[HNEt_3]BF_4$ to the secondary phosphine complexes **11a**–**f** (Scheme 5).

X-ray analysis of **11d** proves the formation of a dimer in the solid state via interaction of the hydroxyl-oxygen O3/O3′ and the aryl hydrogen atom H9/H9′, evident from a C9–O3′ distance of 3.475(3) Å (Fig. 3).

2.4. Aldehydes, ketones and cyclohexene oxide

In contrast to the hydrophosphination process described in Sections 2.1, 2.2 and 2.3 the reaction of the



Scheme 4.

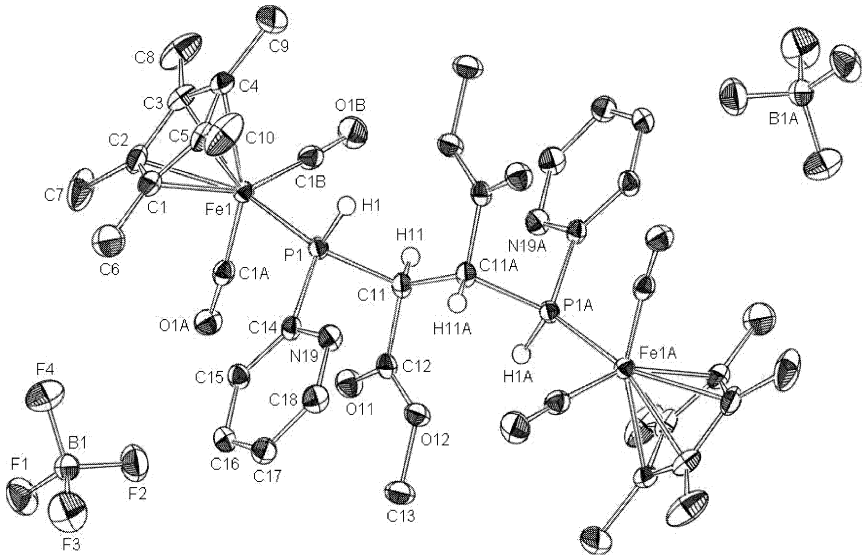


Fig. 1. Molecular structure of **9**.

phenylphosphine iron complexes **1a**,**c** with the aldehydes and ketones **12a**–**h** proceeds only in the absence of an auxiliary base [40]. In this case the organic carbonyl compound acts as the base, transforming the primary phosphine complex to the ferrio-phosphine, which subsequently attacks the protonated carbonyl compound of enhanced reactivity. The resulting α-hydroxyalkyl phosphine complexes **13a**–**h** are obtained in good yields with moderate diastereoselectivity (Scheme 6). However, a fast reverse reaction in solution is observed in the case of **13e**–**g**. X-ray analysis of the α-hydroxyethyl-phosphine complex **13a** exhibits a distorted tetrahedral coordination sphere at the phosphorus atom. Newman projection along the P–Fe-bond reveals the *anti*-position of the 1-hydroxyethyl group to the pentamethylcyclopentadienyl ligand (Fig. 4).

This 'uncatalyzed' metal assisted hydrophosphination reaction in addition allows the ring opening of cyclohexene oxide **14** [41], for which the mechanism is supposed to be very similar to the hydrophosphination of the carbonyl group of **12a**–**h**. The resulting 2-hydroxycyclohexyl phosphine complexes **15a**–**f** bearing three stereogenic centers are isolated as a mixture of two diastereomers (Scheme 6). The relative configuration of the carbon atoms of the cyclohexyl substituent is determined by the *trans*-selective ring opening of the epoxide ring.

The molecular structure of **15d** reveals the presence of a *trans*-substituted cyclohexyl ligand with the phosphorus atom and the hydroxyl group in equatorial positions (Fig. 5).

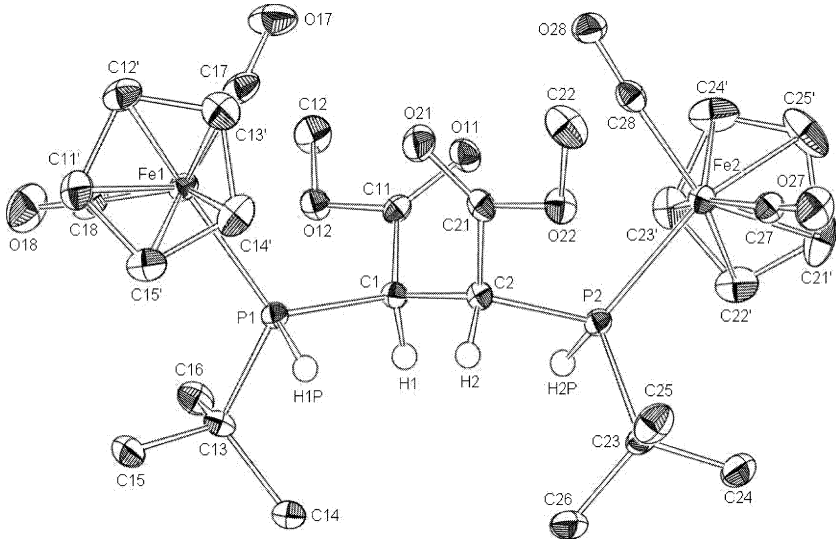
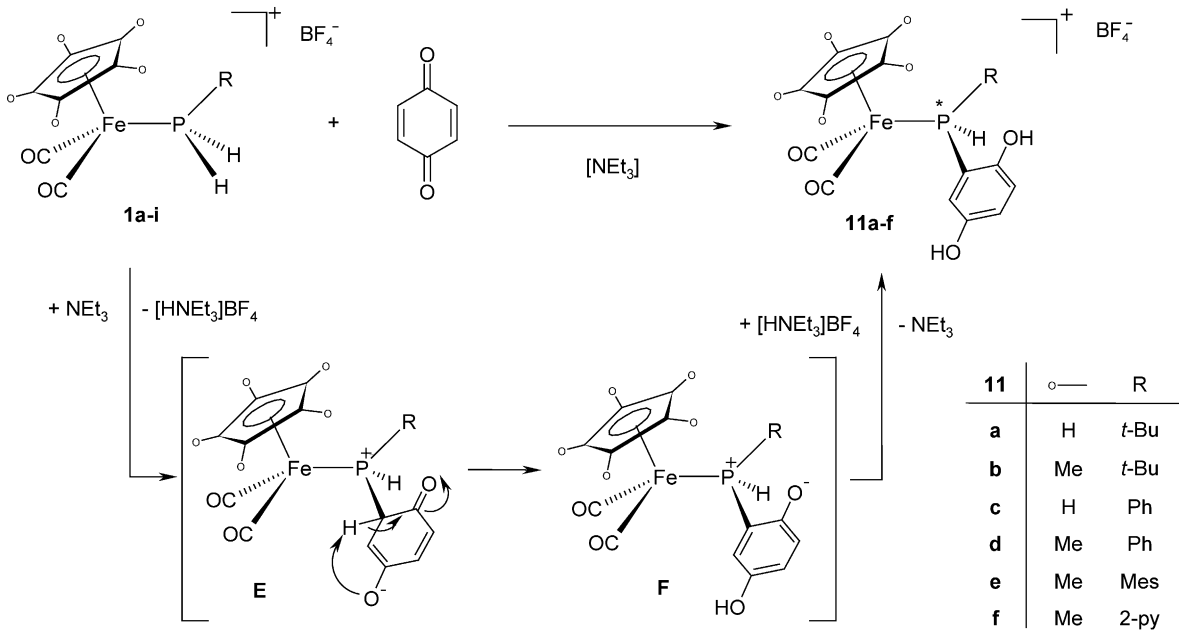


Fig. 2. Molecular structure of **10**.



Scheme 5.

3. Highly functionalized tertiary phosphine iron complexes via hydrophosphination with the secondary phosphine complexes 5c, 11c,d, 22a–c

The secondary phosphine complexes described in Sections 2.1, 2.2, 2.3 and 2.4 are characterized by a P–H-function, which promises further transformations by hydrophosphination or deprotonation/methylation. In general, the P–H-function of these complexes is less reactive than in primary phosphine complexes, which demands more severe reaction conditions for the additional hydrophosphination step. The deprotonation of cationic primary and secondary phosphine metal complexes is a well established method for the generation of phosphanido-species [28,29], which can be transformed into tertiary phosphine complexes via alkylation. This method has been applied for the first time to functionalized secondary phosphine complexes, yielding **16a**,**b**, the first known ferrio-phosphines bearing functional groups (Scheme 7) [35,39].

Methylation of **16a**,**b** with MeI or $[Me_3O]BF_4$, respectively, leads to the tertiary methylphosphine complexes **17a**,**b** [35,39] (Scheme 7).

Amine catalyzed hydrophosphination using acryl derivatives is also suitable for the transformation of the mono insertion products **18a**–**c** into tertiary phosphine complexes with a stereogenic phosphorus atom [34]. The reaction of the secondary cyano- or pyridinoethylphosphine complexes **18a**,**b**, as well as the 2-hydroxycylohexyl phosphine complex **18c** with acrylonitrile or 2-vinyl pyridine, give rise to the tertiary phosphine complexes **19a**–**d** (Scheme 8). In the case of

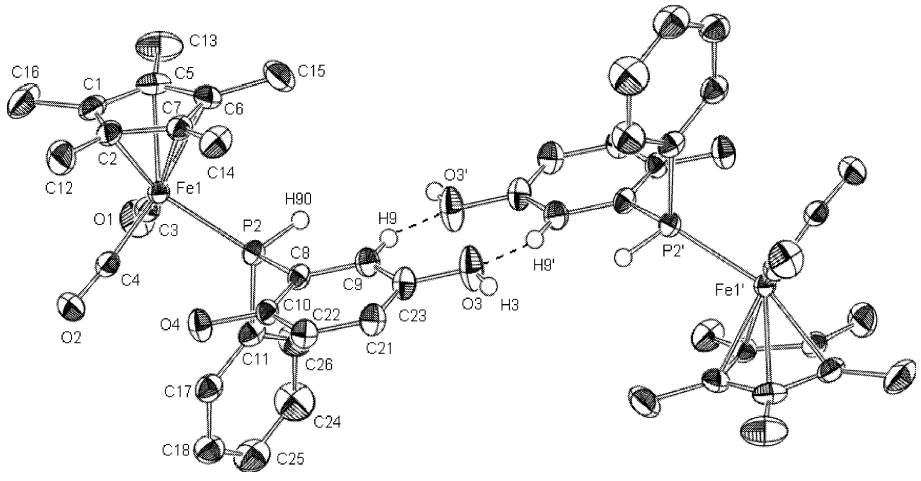
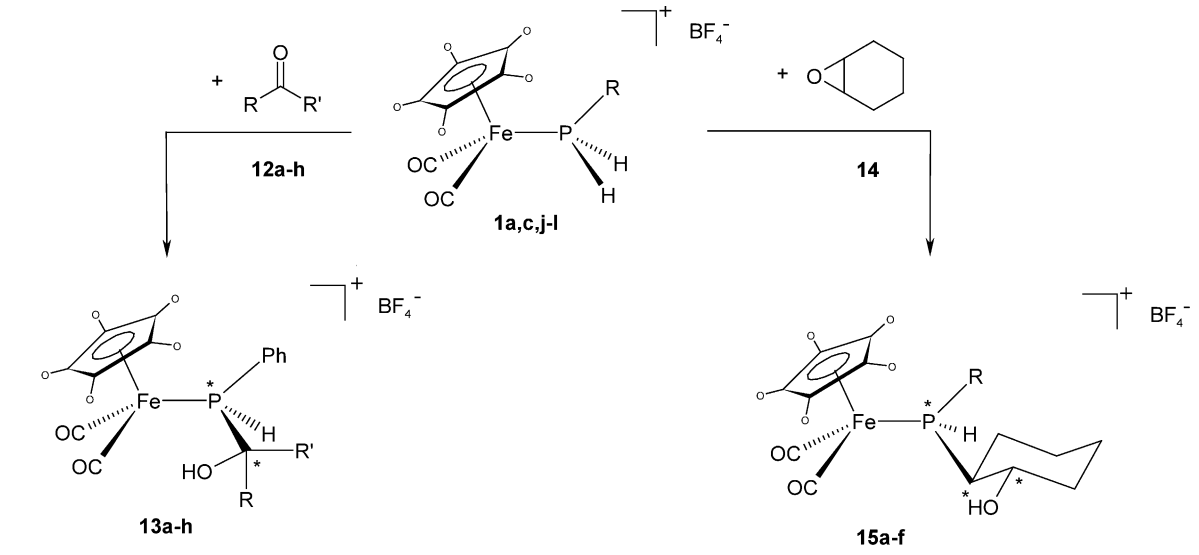


Fig. 3. Molecular structure of **11d**.



	a	b	c	d	e	f	g	h
o—	Me	Me	H	H	H	H	H	H
R	H	Me	H	H	Me	Ph	Me	H
R'	Me	Me	CH_2Ph	Ph		C(O)Ph	Ph	

	a	b	c	d	e	f
o—	H	Me	H	Me	H	Me
R	Ph	Ph	*p*-F-C_6H_4	*p*-F-C_6H_4	Mes	Mes

Scheme 6.

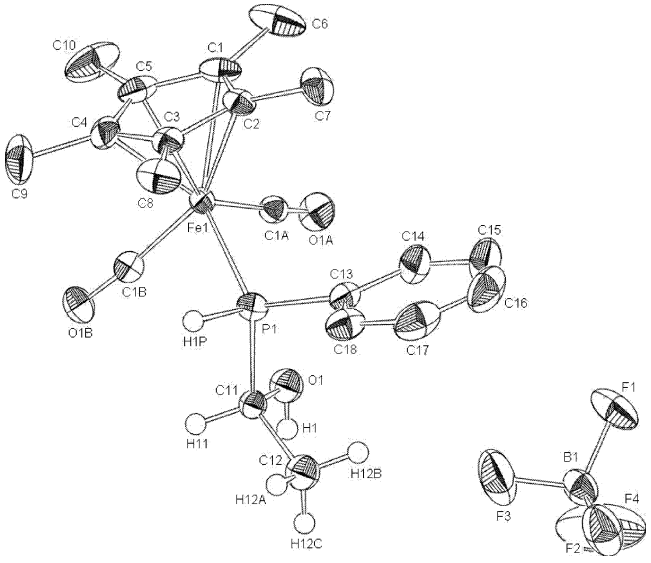


Fig. 4. Molecular structure of **13a**.

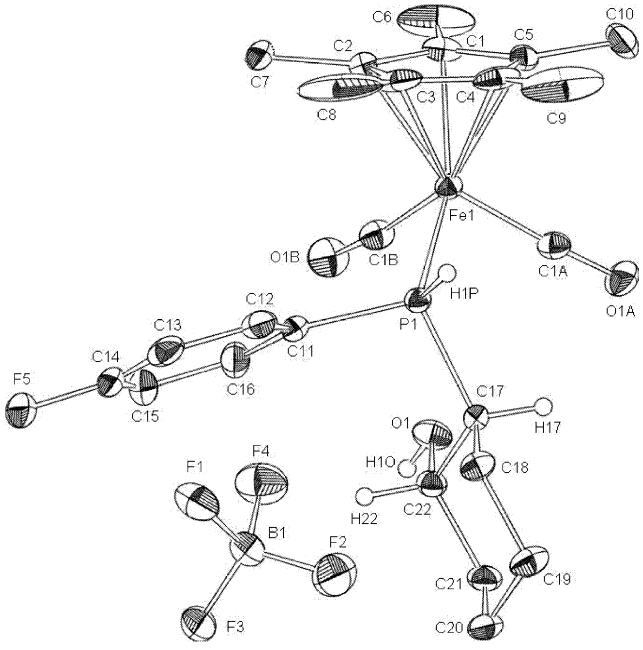
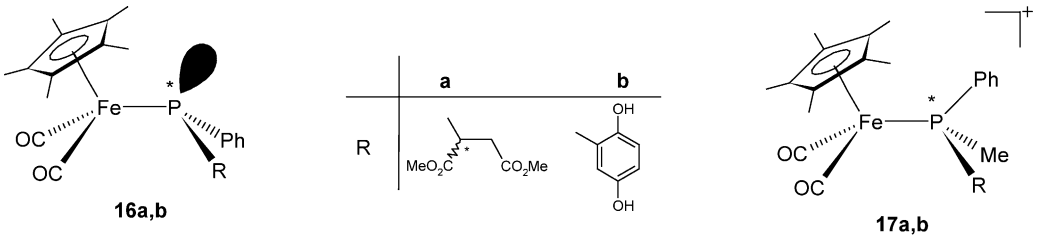


Fig. 5. Molecular structure of **15d**.

18b the auxiliary base functionality is taken over by the pyridyl substituent, but this activation seems to be not very efficient, indicated by the extended reaction time of 8 days in comparison to the base catalyzed formation of **18a** (2 h). The diastereomeric tertiary 2-hydroxycyclohexyl phosphine complexes **19c**,**d** are isolated almost quantitatively, in a diastereomeric ratio of 72:28 (**19c**) and 97:3 (**19d**). Formation of **19c** requires the presence of KO*t*-Bu, while the uncatalyzed reaction of **18c** with 2-vinyl pyridine to **19d** occurs at a temperature of 70 °C (Scheme 8).

Furthermore, the P–H-function of the 2,5-bis(hydroxy)phenylphosphine complexes **11c**,**d** can be converted by an additional hydrophosphination step with various organic multibonded systems. As a remarkable



Scheme 7.

fact, the substitution of the cyclopentadienyl ligand has a significant influence on the insertion mode of the second equivalent of *p*-benzoquinone [39].

In the case of the cyclopentadienyl derivative **11c** the bis-(2,5-bis-hydroxyphenyl)phosphine complex **20** can be isolated [$\delta(^{31}P) = 46.28$ ppm], whereas in the case of the pentamethylcyclopentadienyl derivative **11d** the ^{31}P-NMR shift of $\delta = 160.59$ ppm and X-ray analysis prove the product to be the 4-hydroxy-phenoxyphosphine complex **21** (Scheme 9).

We assume that selective formation of the sterically less hindered product occurs by a radical mechanism of the addition of the P–H-function to the quinoide system via the oxygen atom. The molecular structures of **20** (Fig. 6) and **21** (Fig. 7) show the distorted tetrahedral environment of the phosphorus atoms with bond angles in a range between 119.96° [C20–P1–Fe1 (**20**)] and 96.47° [C20–P1–O41 (**21**)].

The introduction of further functional groups into **11d** [39] (Scheme 9) can be achieved by insertion of acrylonitrile or vinyl pyridine, which leads to the formation of the tertiary phosphine complexes **22a**,**b** in good yield. Compounds **22a**,**b** bear additional nitrogen donor groups, thus giving the phosphine hybrid ligand character. Moreover, the hydrazonylphosphine complex **22c** can be obtained by reaction of **11d** with ethyl diazoacetate. The molecular structure of **22b** (Fig. 8) exhibits the pseudo octahedral coordination sphere of the iron atom, with the bond angles involving the CO and the phosphine ligands varying between 99.70(9)° (C1A–Fe1–C1B) and 89.64(6)° (C1B–Fe1–P1).

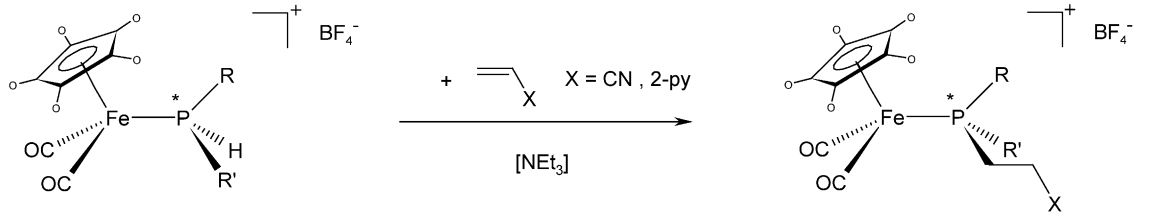
Base catalyzed reaction of **11d** with an excess of ethylisocyanate represents an impressive example for the generation of highly functionalized phosphine ligands in the coordination sphere of a metal. In this case, a further derivatization of the P–H and O–H functions of **11d** is leading to the tertiary phosphine complex **23**, bearing two aryl-bonded urethane groups (Scheme 9).

4. Synthesis of iron-coordinated phospholanes

Hydrophosphination of electron-deficient conjugated C–C-double bond systems allows repetition of the insertion process, which should lead to cyclic phosphine ligands, assuming an intramolecular mechanism. Indeed, the reaction of the primary phosphine complexes **1a**,**e**,**g**,**l** with butadiene-2,3-dicarboxylic acid dimethylester in the presence of NEt_3 results in the formation of the phospholane complexes **24a**–**d** via **D** as intermediate (Scheme 10) [41].

For the main diastereomer of **24** the ester groups of the phospholane ligand adopt a *trans*-configuration, while *cis*-arrangements are valid for the minor diastereomers, which is proven by ^{13}C-NMR spectroscopy. For **24d** the *trans*-diastereomer is obtained exclusively.

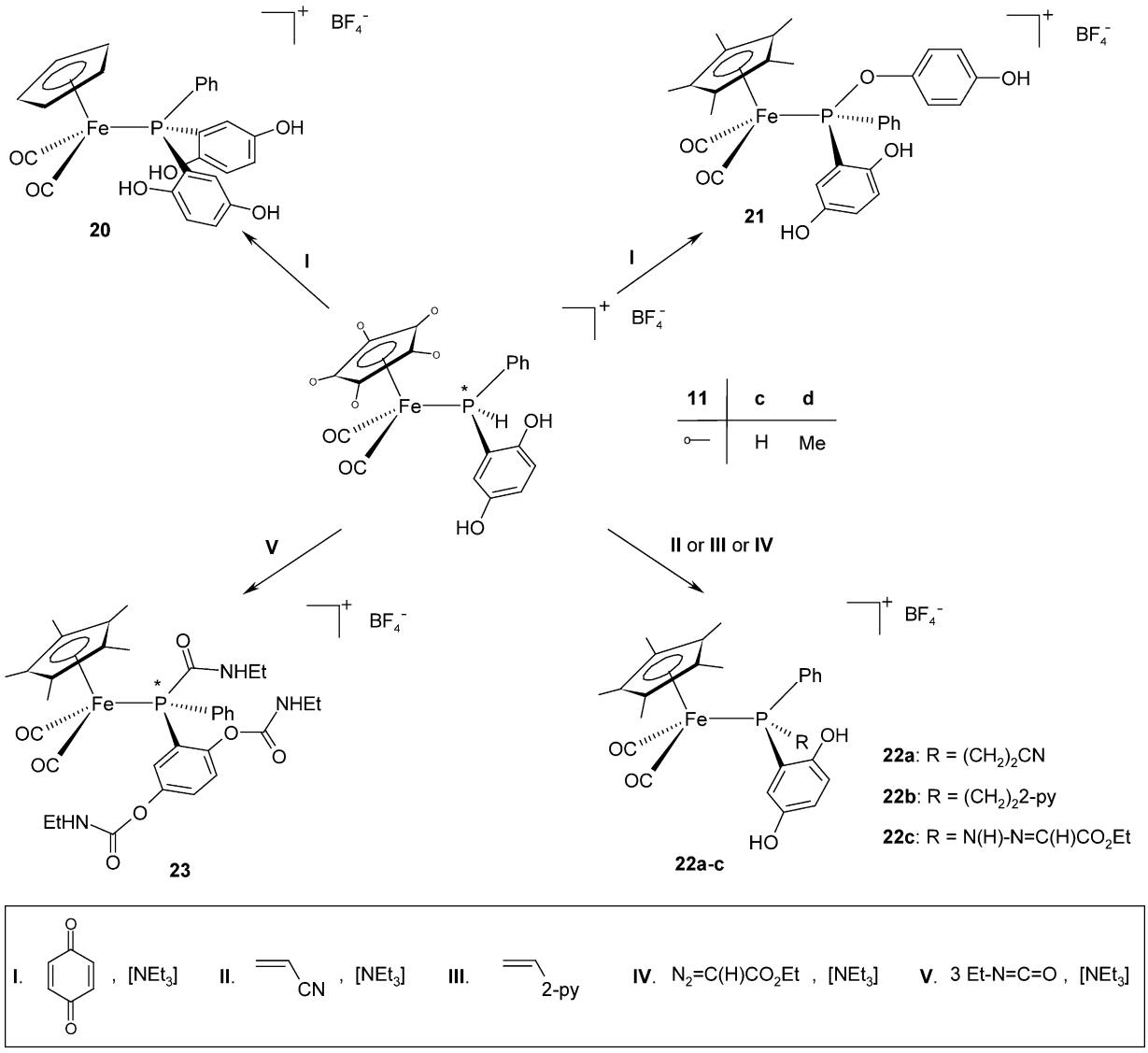
Formation of **23** (Scheme 9) proves the possibilities of the functional groups introduced in the first hydropho-



18	a	b	c
—	Me	H	Me
R	$(CH_2)_2CN$	$(CH_2)_2$2-py	2-OH-cyc
R'	Ph	Ph	*p*-F-C_6H_4

19	a	b	c	d
o—	Me	H	Me	Me
R	$(CH_2)_2CN$	$(CH_2)_2$2-py	2-OH-cyc	2-OH-cyc
R'	Ph	Ph	*p*-F-C_6H_4	*p*-F-C_6H_4
X	CN	CN	CN	2-py

Scheme 8.



Scheme 9.

sphination step to undergo a further reaction. In this context, an impressive example is given by the reaction of the succinyl group of the secondary phosphine complex **3c**, inducing the formation of a cyclic phosphine ligand after treatment with ethylisocyanate in the presence of NEt_3 [42]. The resulting azaphospholane complex **25** can be obtained in a diastereomeric ratio of 83:17 (Scheme 11). Formation of **25** involves nucleophilic attack of the electrophilic carbon atom of EtNCO by the ferrio-phosphine **E** leading to the zwitterionic species **F** bearing an anionic nitrogen atom, which intramolecularly substitutes methoxide of the β-ester group to give the imide group.

X-ray analysis of **25** (Fig. 9) reveals the presence of an almost planar heterocyclic five membered ring, with the atoms C19–N1–C20–C21 located approximately in a plane, as the torsion angle of 4.5(2)° indicates. The phosphorus atom is found slightly above the ring plane [P1–C19–N1–C20–10.08(18)° and N1–C20–C21–P1 16.53(17)°]. A further proof for the twist envelope conformation of the heterocyclic ring is given by the torsion angle C19–P1–C21–C20 of −18.12(12)°.

5. Release of the functionalized phosphines

An essential step in the metal assisted synthesis of functionalized phosphines is the release of the formed organophosphorus compounds from the metal fragment. This procedure should be distinguished by high efficiency, a minimum of side reactions, easy separation from the iron complex without complicated purification processes and recovery of the metal fragment.

In the case of the secondary phosphine iron complex **3c** the cleavage of the succinylphosphine **26a** from the metal fragment is achieved in acetonitrile in the presence

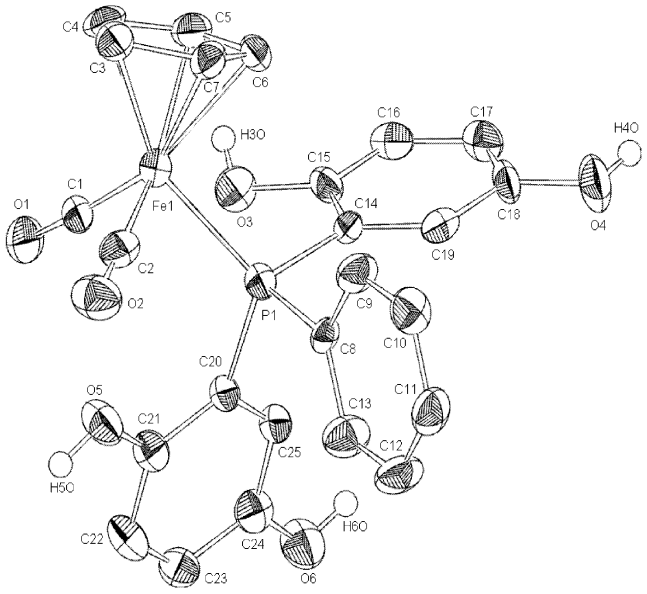


Fig. 6. Molecular structure of **20**.

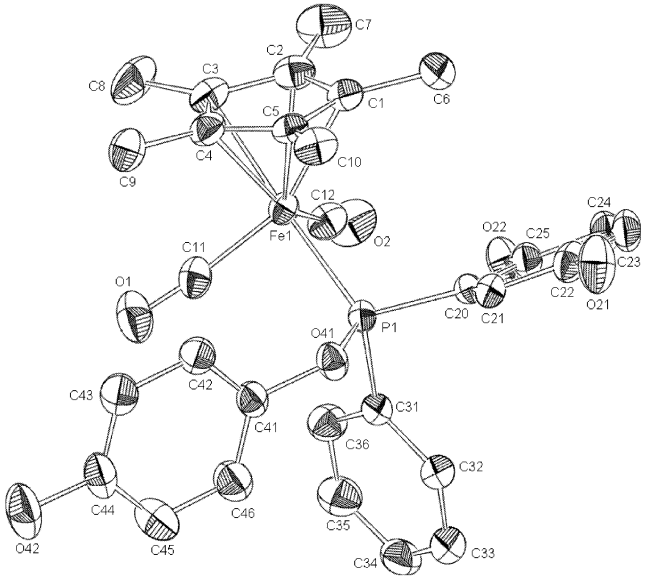


Fig. 7. Molecular structure of **21**.

of dppe with UV light [35] (Scheme 12). Separation of **26a** from the simultaneously formed cationic dppe-acetonitrile iron complex **27** is realized by almost quantitative precipitation of **27** in diethyl ether.

Using the method of Scheme 12, liberation of selected phosphine ligands of the hydrophosphination products described in Sections 2–4 has been accomplished, leading to the isolation of **28**–**32** in yields between 56 and 90% [34–37,39–42] (Scheme 13).

The molecular structure (Fig. 10) of the azaphospholane **30** shows, in contrast to the coordinated state, an almost planar heterocyclic ring, indicated by torsion angles with a maximum of -3.38(16)° (N3–C4–C5–P1).

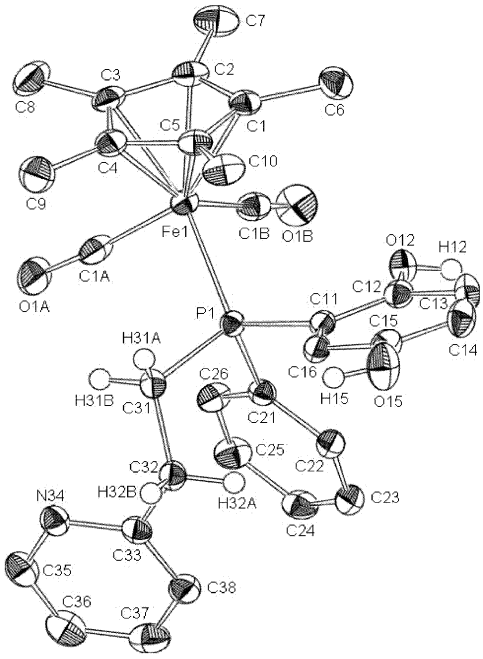


Fig. 8. Molecular structure of **22b**.

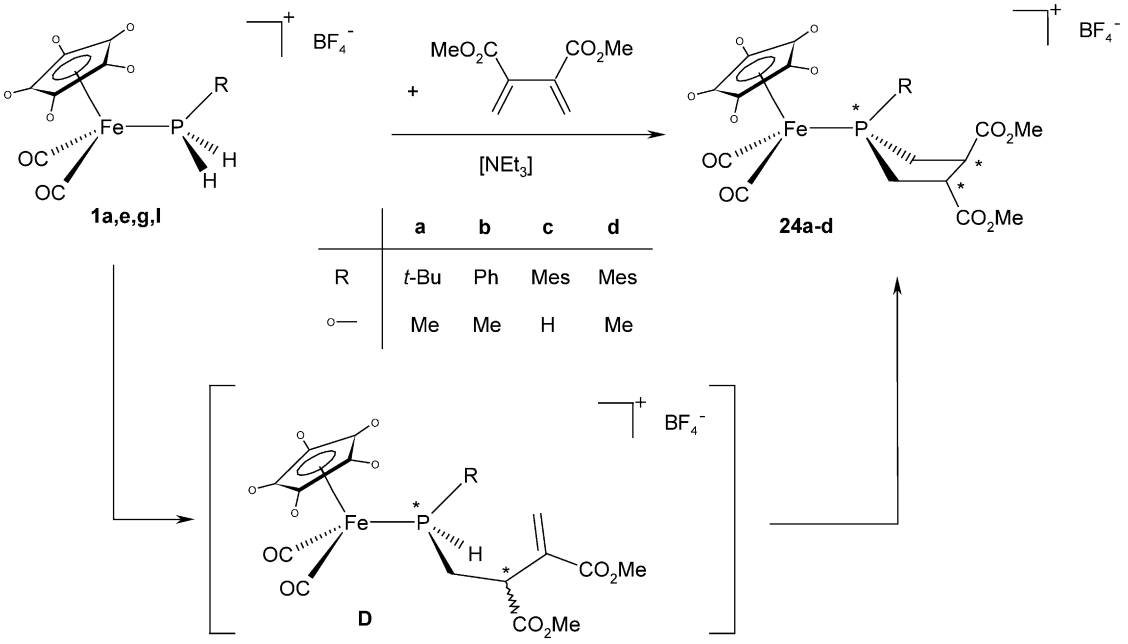
6. Hydrophosphination reactions of chelate phosphine substituted primary phosphine iron complexes

Chelate phosphine substituted primary phosphine complexes offer an elegant possibility for introduction of stereochemical information into hydrophosphination reactions by using enantiomerically pure diphosphines. As pointed out by the studies described so far, diphosphine substituted insertion products release the functionalized phosphine ligands more easily. Experiments, using the achiral dppe-substituted phenylphosphine complex **34a** prove that diphosphine substituted primary phosphine complexes follow the reactivity pattern described in Sections 2–4 [35].

The primary phosphine complexes **34a**–**f** are obtained by UV irradiation of $[C_5H_5(OC)_3Fe]BF_4$ in the presence of the corresponding diphosphines in acetonitrile, leading to the acetonitrile complexes $[C_5H_5(diphos)Fe(NC\text{-}Me)]BF_4$ (diphos = dppe, DIOP, CHIRAPHOS) (**33a**–**c**) in almost quantitative yield. Subsequent treatment of **33a**–**c** with primary phosphines in dichloromethane results in the formation of **34a**–**f** by ligand exchange in yields of more than 90% (Scheme 14) [35,43].

The diastereotopic property of the P–H-protons of **34b**–**f** is evident from the ^{1}H-NMR data with remarkable differences in the chemical shift ($\Delta\delta$ up to 0.50 ppm) and ^1J(PH) coupling constants (ΔJ up to 40.9 Hz). This aspect is additionally emphasized by X-ray analysis of **34c** (Fig. 11), exhibiting two obviously different P–H-bond distances of 1.3227(11) Å (P3–H1P) and 1.4114(11) Å (P3–H4P).

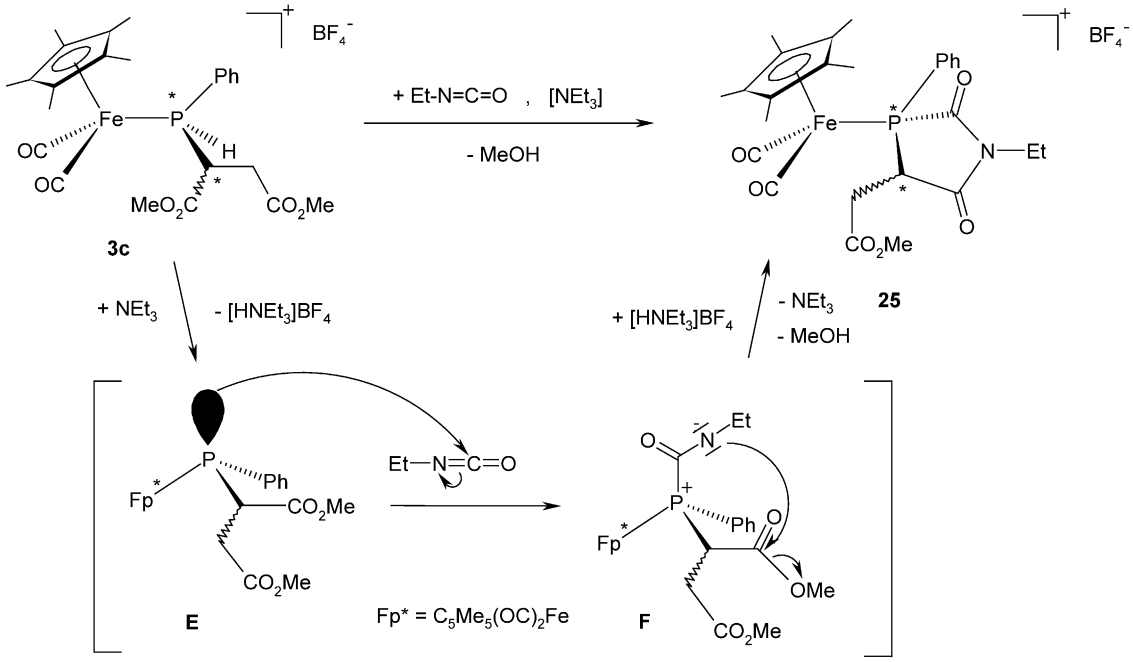
Hydrophosphination of *p*-benzoquinone by the primary phosphine iron complexes **34c**,**f** results in the



Scheme 10.

formation of the secondary 4-hydroxy-phenoxy phosphine complexes **35a**,**b**, which are isolated in more than 90% yield in a diastereomeric ratio of 70:30 (**35a**) and 84:16 (**35b**), respectively [44] (Scheme 15). Compounds **35a**,**b** exhibit a typical ^{31}P-NMR resonance at low field at 180.90 (**35a**)/166.34 ppm (**35a**′) and 137.80 (**35b**)/140.13 ppm (**35b**′), respectively. In contrast to the use of the bis-carbonyl iron derivatives **1**, for which exclusively the 2,5-bis(hydroxy)phenylphosphine complexes **11a**–**f** are obtained (Scheme 5), this addition mode could so far only be observed for the reaction of the sterically demanding secondary phosphine complex **11d** (Scheme 9).

Base catalyzed insertion of the simple acryl derivatives like acrylonitrile, 2-vinylpyridine or acrylic acid methylester into the P–H-bond of **34a**–**f** according to Scheme 1 leads to the corresponding diastereomeric secondary phosphine complexes **36a**–**d**, which can be isolated in good yields after a reaction time of up to 7 days [44]



Scheme 11.

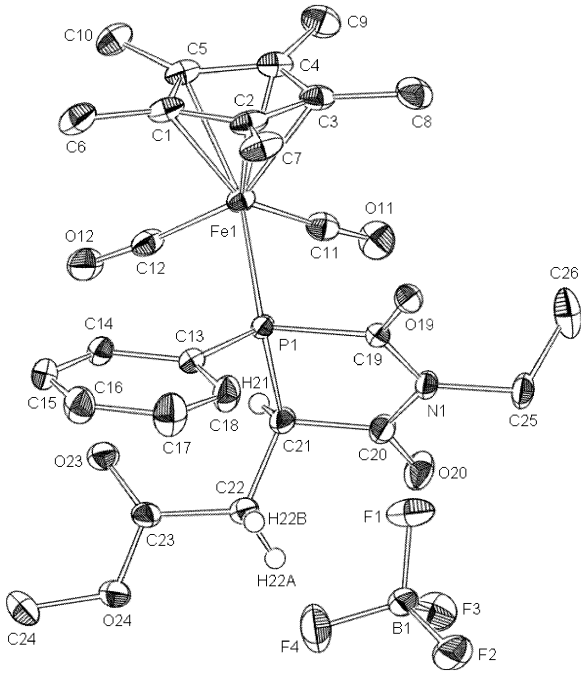


Fig. 9. Molecular structure of **25**.

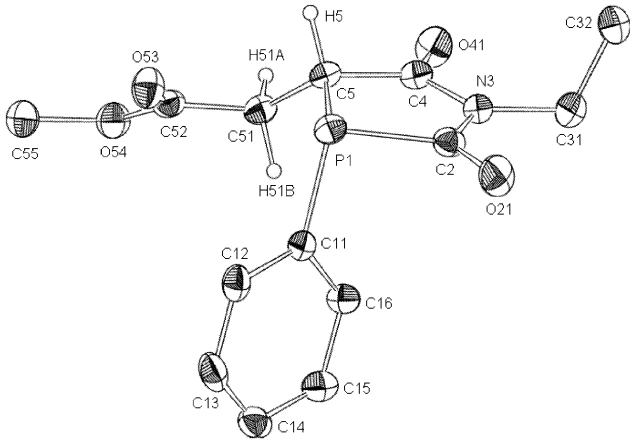


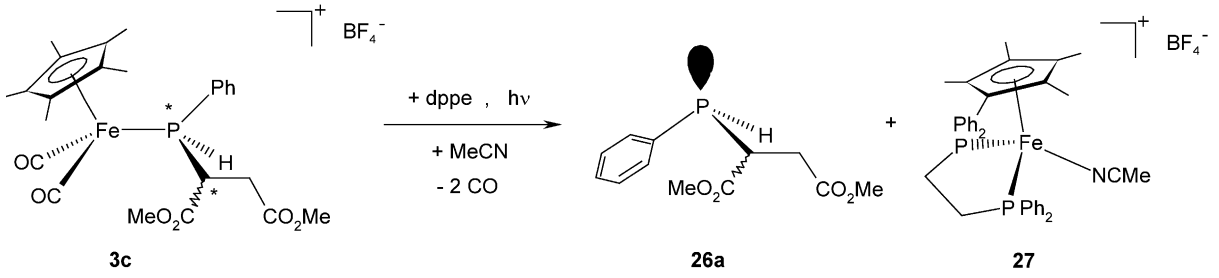
Fig. 10. Molecular structure of **30**.

(Scheme 16). The maximum of diastereoselectivity is observed for the CHIRAPHOS-derivative **36d** (85:15).

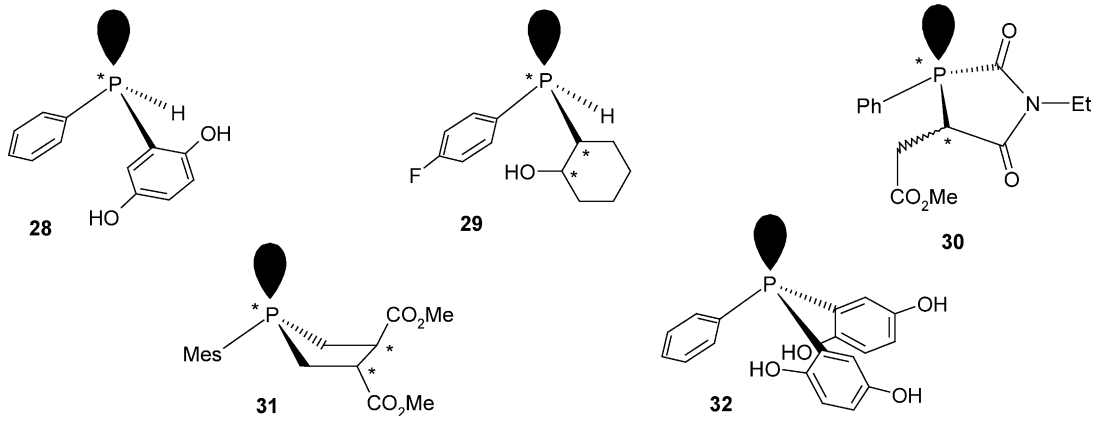
By dissolving the insertion products **36a**–**d** in acetonitrile a slow ligand exchange of the secondary phosphine against acetonitrile occurs, which can be accelerated significantly by UV irradiation to provide the secondary phosphines **37a**–**d** in 64–79% yield. The chiral metal fragment is recovered almost quantitatively in form of the acetonitrile complexes **33a**–**c** (Scheme 16).

A remarkable result is found for the reaction of the CHIRAPHOS-substituted mesitylphosphine complex **34f** with an excess of acrylonitrile in the presence of NEt_3, in which the 2-cyanoethylphosphine complex **G** is detected as an intermediate by means of ^{31}P-NMR spectroscopy [44] (Scheme 17).

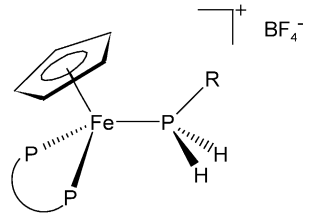
The formation of **G** is followed by a spontaneous exchange of the coordinated secondary phosphine



Scheme 12.



Scheme 13.



34	a	b	c	d	e	f
P P	dppe	DIOP	DIOP	DIOP	CHIRAPHOS	CHIRAPHOS
R	Ph	*n*-Bu	Ph	2-py	Ph	Mes

Scheme 14.

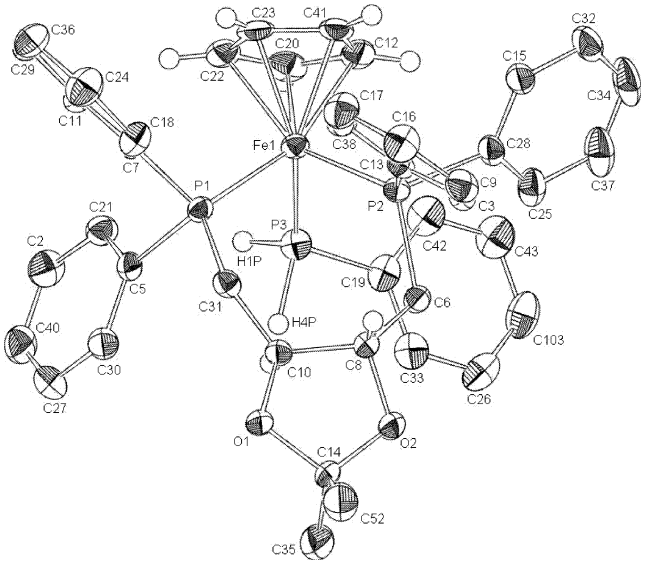


Fig. 11. Molecular structure of **34c**.

against acrylonitrile, leading to the CHIRAPHOS-acrylonitrile complex **38** and the phosphine **37e**.

This observation indicates a pronounced tendency of **G** for substitution of the coordinated secondary phosphine against sterically less demanding donors like alkylnitriles. Taking advantage of this fact, the synthesis of free secondary phosphines should be achieved by using sterically demanding double bond systems as insertion reagent in combination with donating solvents like acetonitrile.

Indeed, when the DIOP-substituted secondary phosphine complexes **34c**,**d** are treated with dimethyl maleate in the presence of NEt_3 in acetonitrile the formation of the succinyl dimethylester phosphines **26a**,**b** and the acetonitrile complex **33b** is observed [44] (Scheme 18).

The almost quantitative recovery of the acetonitrile complex **33b**, which on treatment with primary phosphines gives the starting material **34d**,**f**, allows to establish a cyclic process.

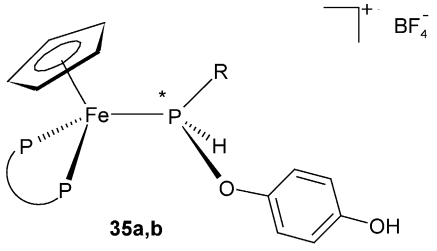
Regarding all the experimental facts discussed so far, a catalytic hydrophosphination process has been worked out, using $[C_5H_5(DIOP)Fe(NCMe)]BF_4$ (**33b**) for the base catalyzed hydrophosphination of dimethyl maleate with phenylphosphine in acetonitrile to give **26a** (yield: 97%, *dr*: 69:31) with full recovery of the catalyst **33b** [44].

The mechanism of this hydrophosphination reaction can be explained by the catalytic cycle presented in Scheme 19. In the first step the acetonitrile ligand of **33b** is replaced by phenylphosphine to form the DIOP-substituted primary phosphine complex **34c**, detected in the reaction mixture by ^{31}P-NMR-spectroscopy. Subsequent base catalyzed insertion of dimethyl maleate into the P–H-bond of **34c** is leading to the hydrophosphination product **H**, followed by spontaneous substitution of the secondary phosphine ligand by acetonitrile with simultaneous regeneration of the catalyst **33b**.

In contrast to the catalytic hydrophosphination carried out by Glueck [24–27], for which oxidative P–H-addition and alkene insertion into the P-metal bond are determined as the key steps, for our stoichiometric and catalytic hydrophosphination experiments the activating influence of the metal fragment for the nucleophilic phosphorus attack at the C–C-double bond is crucial. Scheme 19 represents the basis for further investigations concerning the influence of the bidentate ligand, the organic double bond system, the organophosphorus substituent and the reaction conditions for the hydrophosphination process.

7. Conclusion

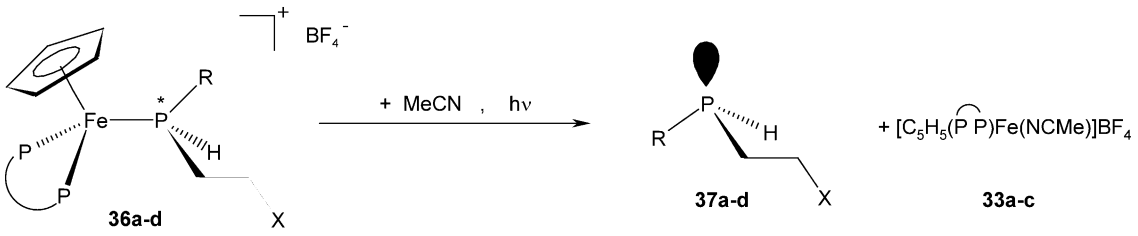
An attractive synthesis of highly functionalized phosphine ligands has been presented, characterized by high



35a,b

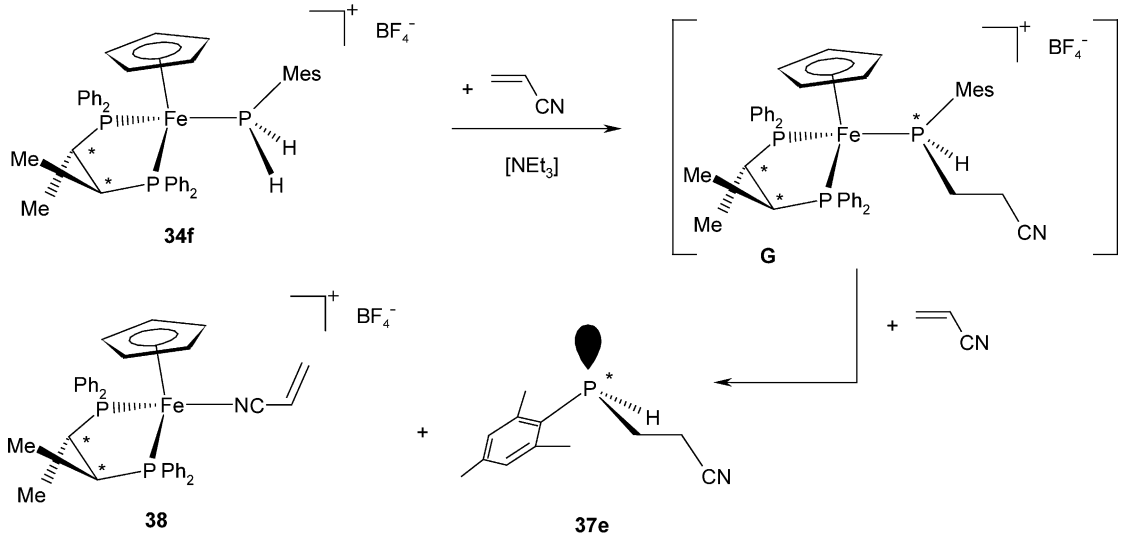
35	a	b
$P_{[2]}$	DIOP	CHIRAPHOS
R	Ph	Mes

Scheme 15.

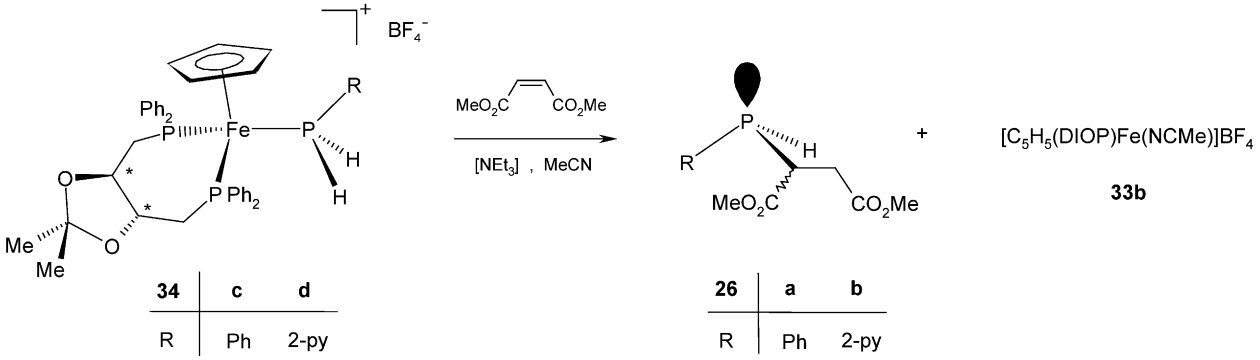


36/37	a	b	c	d
P P	dppe	DIOP	DIOP	CHIRAPHOS
R	Ph	*n*-Bu	Ph	Ph
X	2-py	CN	CO_2Me	CN

Scheme 16.



Scheme 17.

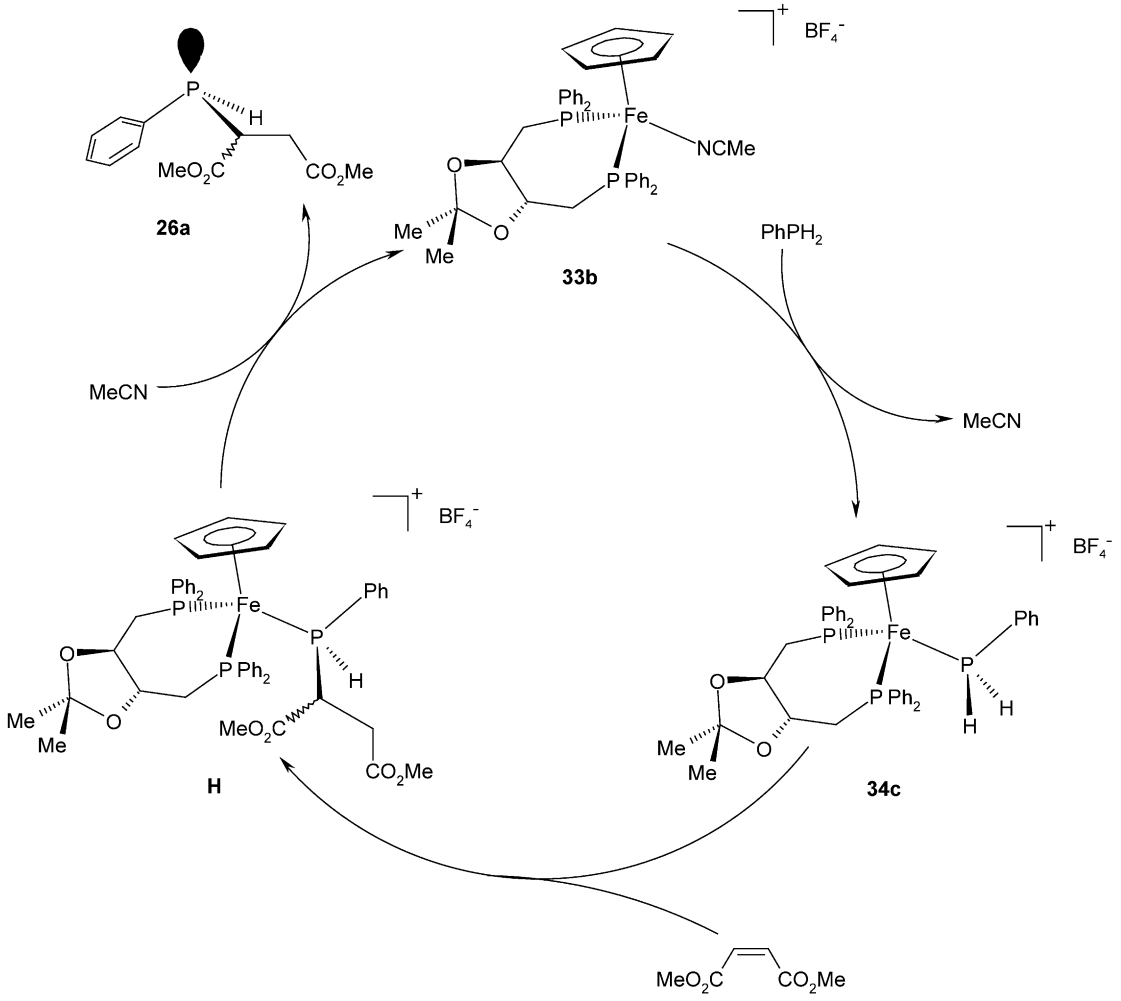


34	c	d
R	Ph	2-py

26	a	b
R	Ph	2-py

Scheme 18.

diastereoselectivity involving two consecutive metal assisted hydrophosphination reactions valid for various organic multibonded systems and primary phosphine iron complexes. A simple preparative route has been worked out concerning the release of the organophosphorus compounds with almost quantitative recovery of the metal fragment. In this context, hydrophosphination of difunctional organic multibonded systems allows the formation of new types of phosphine ligands useful as hybrid ligands. Analogous studies involving primary



Scheme 19.

phosphine complexes of the type $[C_5H_5(OC)(R_3'P)Fe[P(R)H_2]BF_4$ (R = alkyl, aryl), with iron centered chirality promise further increase of diastereoselectivity. The catalytic version of the hydrophosphination reaction can be regarded as a powerful method for the generation of enantiomerically enriched secondary phosphines. In this context, the influence of the chiral diphosphine ligand, the organic phosphorus substituent and the multibonded reagent with respect to the efficiency of this catalytic procedure will be investigated in more detail.

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