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Iron complexes with terminal and nonbridging phosphanido ligands

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Contents

Abstract: This review discusses known iron complexes with terminal-bonded phosphanido ligands R_2P^- and their analogs, such as phosphanylphosphanido and oligophosphanido groups, that have been reported since 1960s. Particular attention is focused on the synthesis and structural features of these complexes, which have a direct impact on their philicity and further reactivity. Moreover, their application in catalysis and materials science will be described.

Keywords: phosphanido ligands, phosphides, iron complexes, phosphenium ligands, phosphanylphosphanido ligands, oligophosphanido ligands

Abbreviations

Cp	cyclopentadienyl
Cp*	pentamethylocyclopentadienyl
Cy	cyclohexyl
DFT	density functional theory
Dipp	2,6-di*iso*propylphenyl
dme	1,2-dimethoxyethane as a ligand
Et	ethyl
HOMO	highest occupied molecular orbital
I*i*PrMe	1-di*iso*propyl-4,5-dimethylimidazol-2-ylidene
*i*Pr	*iso*propyl
Is	2,4,6-tri*iso*propylphenyl
L	ligand
LUMO	lowest unoccupied molecular orbital
MesIm	3-(2,4,6-trimesitylphenyl)imidazole-1-yl
nacnac	*β*-diketiminate ligand
NHCs	*N*-heterocyclic carbenes
NHPs	*N*-heterocyclic phosphenium ligands
nor-AZADO	9-azanoradamantane *N*-oxyl
Mes	2,4,6-trimethylphenyl
Mes*	2,4,6-tri(tert-butyl)phenyl
o-	ortho
R, R'	substituents
Ph	phenyl
ppbz*	1-(diphenylphosphino)-2-(phenylphosphanido)benzene
thf	1,4-epoxybutane/tetrahydrofuran as a ligand
Tol	methylbenzene/toluene
*t*Bu	*tert*-butyl
TM	transition metal

1. Introduction

Low-valent phosphorus compounds are of particular interest because of their unique coordination patterns. This interest is mainly due to the diagonal relationship between phosphorus and carbon [1], and in the case of transition metal (TM) complexes, phosphorus is mainly found in the form of phosphane ligands. Another very significant pillar of coordination chemistry is the phosphanides (phosphanido ligands, phosphido ligands, R_2P^-), whose popularity can be mostly explained by their ability to bridge two, often electronically different, metal centers. In addition to complexes with bridging R_2P^- ligands, due to the presence of two lone electron pairs on the phosphorus atom, phosphanides can also adopt a terminal pyramidal or terminal planar geometry. Moreover, this research area has grown significantly, not only in terms of the tremendous diversity of new complexes but also as a result of recent studies that demonstrate the utility of compounds with this class of ligands in catalysis and materials science.

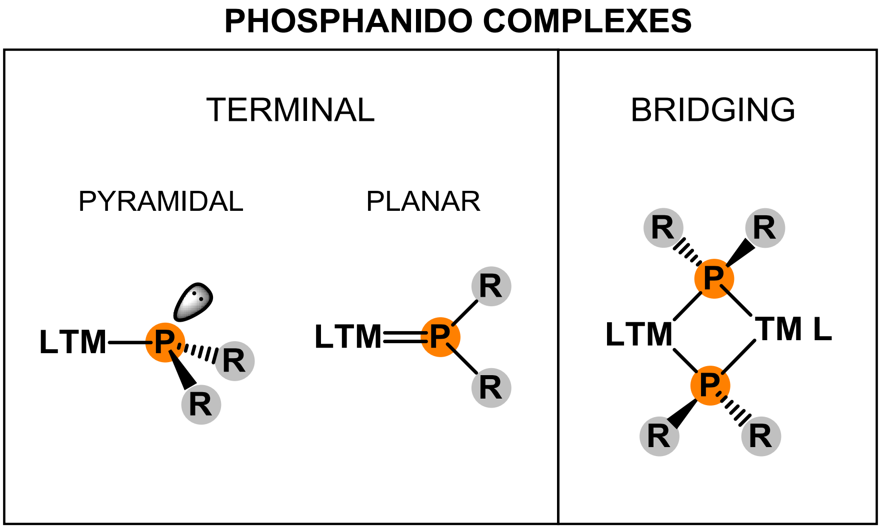


Figure 1. Common coordination modes of phosphanido ligands in transition metal complexes.

1.1. Scope of review: nomenclature, structure and synthesis

In this review, the formula R_2P^- corresponds to 'phosphanido ligands' according to the IUPAC nomenclature. Commonly found in the literature is the term 'phosphido', frequently used as a synonym of this group, which should rather be exploited in the case of P^{3-} complexes [2]. Moreover, phosphanido complexes and their derivatives discussed herein were chosen based on their occurrence in the Cambridge Structural Database (CSD, v5.41, updated May 2020) (Tables 1–4) and are classified by the coordination of the central metal ion.

Phosphanido complexes of TMs can be classified into two distinct structural classes based on the phosphorus coordination number. First, the well-known binding mode of R_2P^- involves the coordination of two phosphorus-based electron pairs to form an extremely flexible bridge between two metal centers characterized by a tetrahedral geometry (Figure 1). These 3-electron donors have attracted considerable attention in the synthesis of homo- and heteronuclear compounds, resulting in over a hundred di- and multinuclear iron complexes and their clusters according to the CSD [3–6]. However, this topic will not be discussed in this paper.

Complexes with terminally bonded R_2P moieties [7–10] may be primarily divided into two groups on the basis of (a) the ligand geometry and (b) the electron donor-acceptor properties of the ligand together with the nature of the binding TM (Figure 2). In the case of electron-rich TM complexes, the R_2P fragment most often adopts a pyramidal geometry characterized by having a nonbonding but sterically active lone electron pair on the phosphorus atom. This corresponds to the one-electron donor R_2P^- phosphanido ligands, which are mostly present in coordinatively saturated complexes with metal centers in high oxidation states. As reported by Rosenberg, 'the transition metal gauche effect', resulting from the repulsion of the metal HOMO and the lone electron pair on the phosphorus, causes elongation of the M-P bond (av. 2.3-2.4 Å) compared to the bond lengths in analogous TM phosphane complexes $M\text{-}PR_3$ [11]. Electronic repulsion of this sterically accessible lone pair at the P atom and the presence of metal electrons intensify the nucleophilicity and basicity of the terminal R_2P^- group. Interestingly, assuming that the TM is one of the substituents, terminal complexes with the phosphanido ligands in a pyramidal geometry are considered substituted phosphanes and are called metallophosphanes.

The presence of a lone electron pair offers opportunities for a variety of bonding types. In the case of metal centers, the presence of a low-lying empty orbital with appropriate symmetry, allows formation of terminal planar TM-PR$_2$. Considering their structural features and reactivity, which are similar to those of the well-known phosphinidenes [12–14], TM complexes possessing planar R$_2$P moieties can be considered analogs of Fischer and Schrock carbene complexes [11]. According to a review by Rosenberg [11], the phosphorus counterparts of carbenes can be divided into phosphenium R$_2$P$^+$ [11,15–18] and planar phosphanido R$_2$P$^-$ [11,19–21] ligands, which can be classified as Fischer [22–25] and Schrock [26–28] metal carbene analogs, respectively. According to the acknowledged criteria for carbenes (substituents, present coligands, character of the metal center) and considering that phosphorus has an extra valence electron (compared to carbon), it can be assumed that the phosphenium moiety acts as a σ-donor and π-acceptor, while the phosphanido ligand donates the lone pair in π-fashion to the LUMO of the TM. Thus, phosphenium complexes are P-electrophiles, and phosphanido complexes are P-nucleophiles. Binding between the metal center and the R$_2$P moiety results in a double bond, but in the case of R$_2$P$^-$, this bond has greater covalent character than the in R$_2$P$^+$. Nevertheless, in the case of both considered ligands, the geometry of phosphorus is planar, and the Fe-P bond length is in the range of 2.0-2.1 Å.

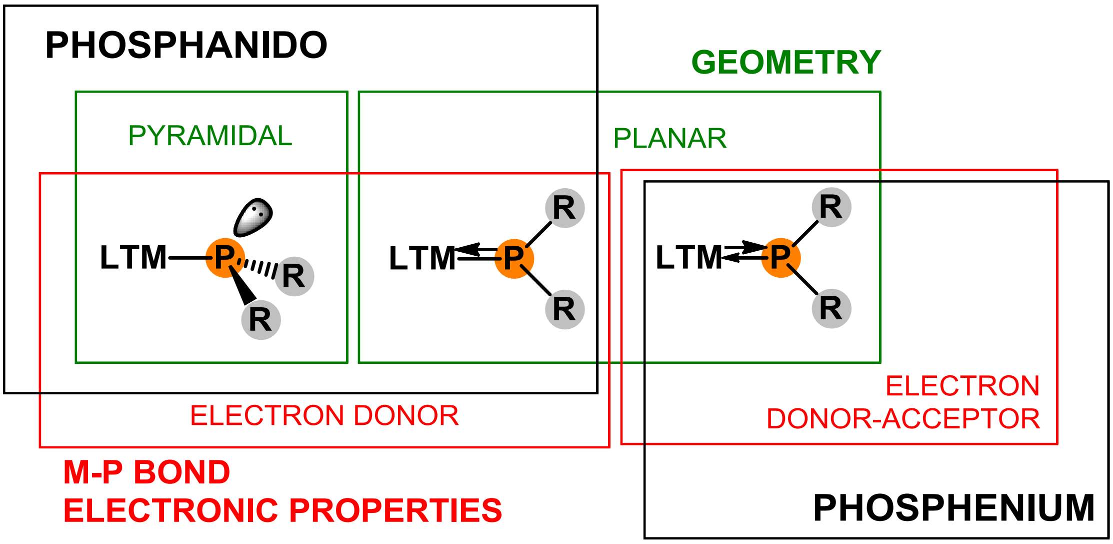


Figure 2. Diversity of planar PR$_2$ ligands in transition metal complexes depending on the ligand geometry and its electronic properties.

Planar R$_2$P ligands exhibit rich coordination chemistry. Among the large number of phosphenium complexes characterized by the presence of π-acidic ancillary ligands, heteroatoms bonded to the P atom and low oxidation states of the metal center, particular attention should be given to *N*-heterocyclic phosphenium ligands (NHPs), which are the closest carbon analogs of *N*-heterocyclic carbenes (NHCs) (Figure 3). Due to their σ-donor and π-acceptor character, NHPs are commonly known as Lewis ambiphiles, but because of their ability to adopt linear (2-electron-acceptor ligand NHP$^+$) and bent (phosphanido ligand NHP$^-$) geometries, they can also be considered analogs of nitrosyls, which highlights their potential as 'noninnocent' ligands. On the other hand, considering planar phosphanido complexes, we should search for compounds with alkyl or acyl substituents on the phosphorus, non-electron-withdrawing coligands and metal centers with high oxidation states. Unfortunately, there are many deviations from the typical planar phosphanido and phosphenium complexes for any TM, and to categorize such complexes, a few factors should be taken into account: the synthesis method, the oxidation state of the metal center, and, most importantly, the reactivity.

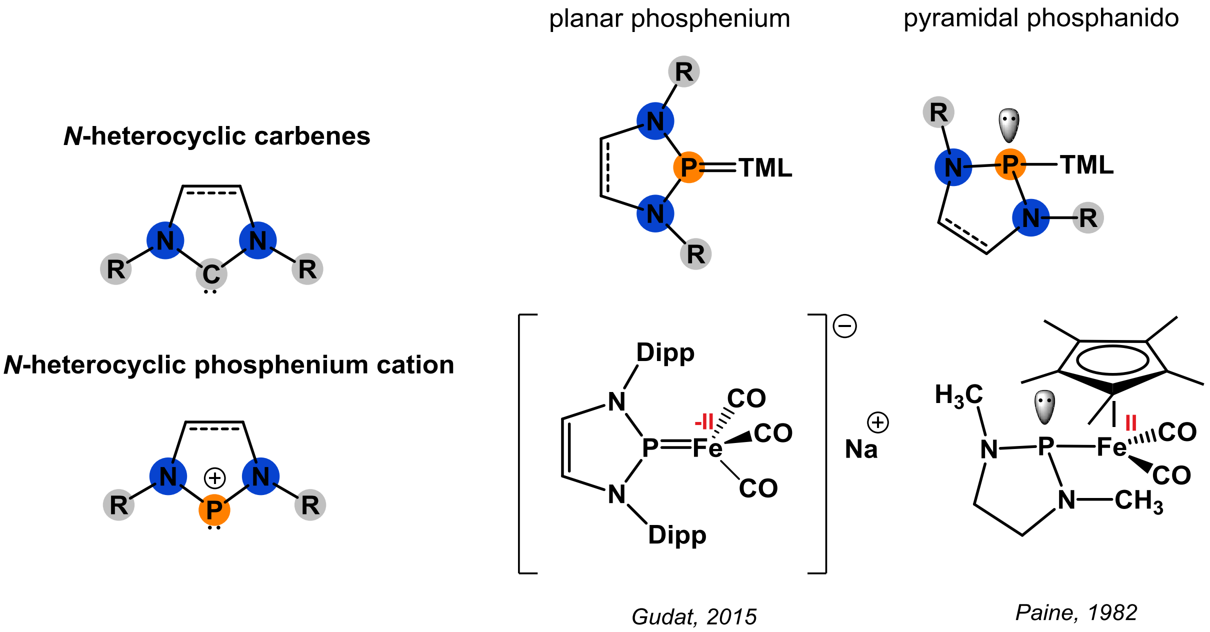


Figure 3. General structures of *N*-heterocyclic carbenes and *N*-heterocyclic phosphenium cations (left). Structural representation of planar phosphenium and pyramidal phosphanido ligands and examples of corresponding iron complexes (right) [29,30]**.**

The main synthetic approach for obtaining phosphanido ligand precursors that has been known since the 1950s is to detach a proton from primary or secondary phosphanes, which leads to the formation of phosphides, usually phosphides of alkali metals [31,32]. Reactions between this kind of precursor and metal starting materials (most often halides) are the most frequently exploited procedures to obtain terminal phosphanido complexes via the salt metathesis route (based on the Schäfer method described in 1980 [33], Figure 4) and are also applied in the case of the iron compounds described in this paper [34–39]. Another method that has been utilized in the case of pyramidal phosphanido complexes of iron stabilized by π-acceptor carbonyl and σ-donor cyclopentadienyl ligands consists of a nucleophilic metalation process accompanied by an intramolecular redox reaction and oxidation of the iron center, which involves the reaction of strong nucleophilic anions such as $[R(CO)_2Fe]^-$ (R = Cp, Cp*) and chlorophosphanes [40–42] (Figure 4). A reaction between similar reagents is also very often used in the synthesis of phosphenium iron complexes, especially in terms of NHPs. In 2015, Gudat *et al* synthetized a planar phosphenium anionic complex $[(NHP^{Dipp})Fe(CO)_3]^-Na^+$ (Figure 3, NHP^{Dipp} = 1,3-di-(2,6-di*iso*propylphenyl-1,3,2-diazaphospholenium) via the reaction of 2-chloro-1,3,2-diazaphospholene with Collman's reagent $Na_2[Fe(CO)_4]$ [29].

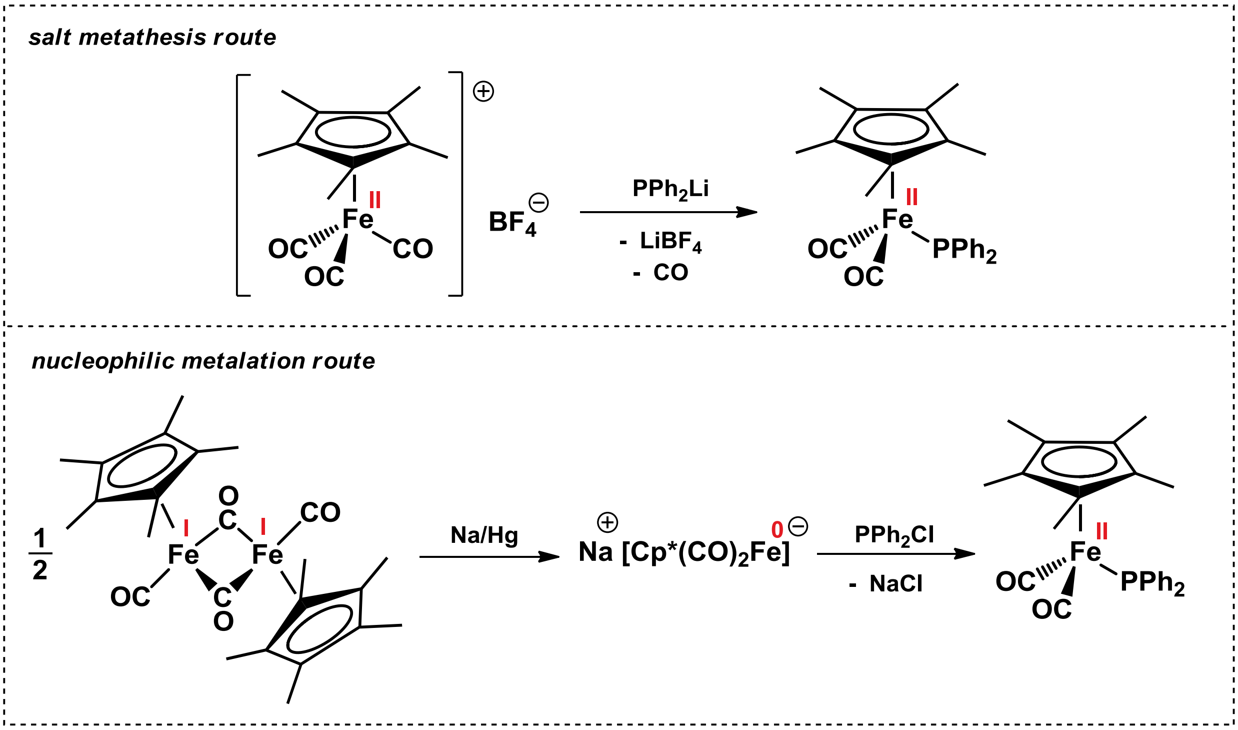


Figure 4. Two main approaches for the synthesis of phosphanido iron complexes.

All iron complexes presented in this review possess the R_2P^- ligand in pyramidal geometry, as confirmed by X-ray structural analysis, and are considered phosphanido complexes. Given that there are only four examples of planar terminal R_2P^- complexes of iron, each of them is discussed in detail separately.

1.2. Development of phosphanido chemistry

The synthesis of unique highly reactive phosphorus bonding motifs and the stabilization within the coordination of metals are still intriguing and continuously expanding fields. Of particular interest is oligophosphorus chemistry, which opens new opportunities for preparing new compounds with at least two directly bonded phosphorus atoms with novel electronic properties, allowing stereochemical tuning of the obtained features and thus their reactivity [43].

The most important development of well-known R_2P^- ligands is the phosphanylphosphanido ligand $R'_2P\text{-}P(R)^-$, in which one of the substituents in typical phosphanides has been substituted with the R'_2P phosphanyl group. To date, all phosphanylphosphanido TM complexes described in the literature adopt terminal [44–49] or *side-on* coordination [48–52] (Figure 5). The binding mode of ligands to the metal center strongly depends on the steric and electronic properties of the ancillary ligands present in the complex [53].

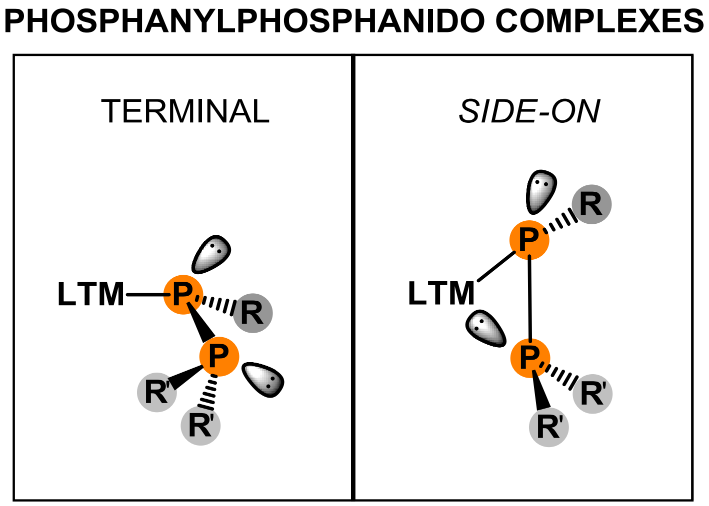


Figure 5. Coordination modes of phosphanylphosphanido ligands in transition metal complexes.

The most commonly used phosphanylphosphanido ligand precursors are lithium salts of diphosphanes $R'_2P\text{-}P(SiMe_3)Li$ (R' = *i*Pr, *t*Bu, *i*Pr_2N, Et_2N) obtained in the reaction between $P(SiMe_3)_2Li$ and an appropriate chlorophosphane R_2PCl, which leads in the first step to diphosphane [54] (Figure 6). These lithium derivatives of diphosphanes play a significant role in the chemistry of phosphorus TM complexes, especially nucleophilic metal complexes in high oxidation states. The most commonly used salts are characterized by the presence of trimethylsilyl groups linked to a phosphanido phosphorus atom (R, Figure 5) and *i*Pr or *t*Bu groups as substituents of the phosphanyl phosphorus atom (R', Figure 5). Lithiated diphosphanes containing these groups are very stable, crystallize easily and do not undergo undesirable rearrangement reactions compared with salts in which R' = Et_2N, *i*Pr_2N, Me_3Si or Ph.

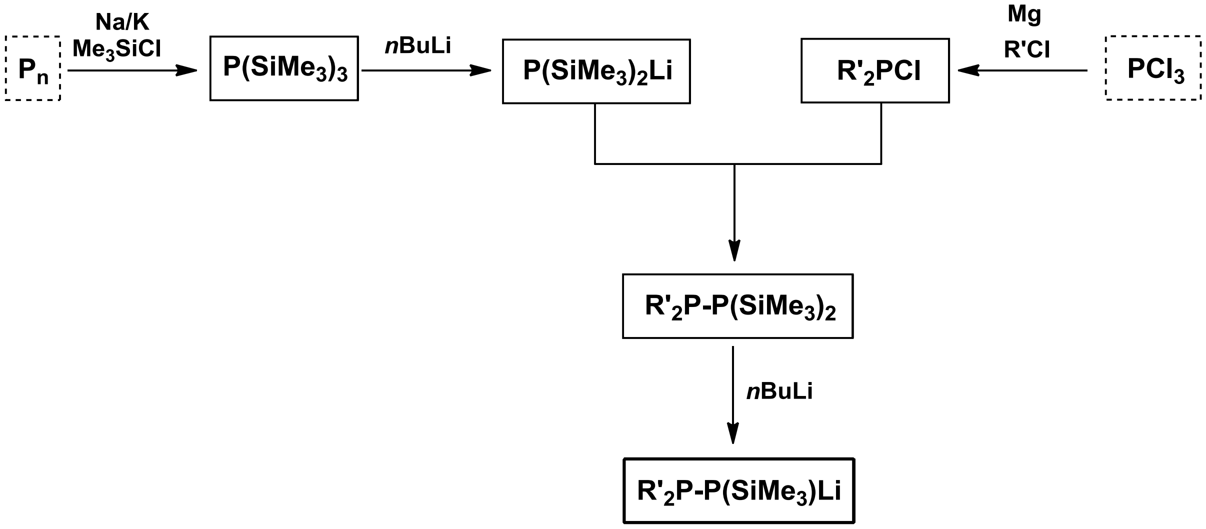


Figure 6. Schematic view of the synthesis the phosphanylphosphanido ligand precursor $R'_2P\text{-}P(SiMe_3)Li$.

Another interesting representative of phosphanides is cyclooligophosphanido anions such as *cyclo*-$(P_nR_{n-1})^-$ or $(P_nR_n)^{2-}$, which date back to 1877 [55]. Extremely advanced studies include experiments conducted by Hey-Hawkins and coworkers who developed a selective method for the one-pot synthesis of alkali metal (Na, K) cyclooligophosphanides [56–58]. The reaction between PCl_3, chlorophosphanes and alkali metals in experimentally selected and controlled stoichiometric ratio led to a variety of ligands that have proven to be useful cyclic precursors in many TM complexes [56,58–62] (Figure 7). Moreover, these P-rich analogs of cycloalkanes, especially in the context of metal complexes, seem to be perfect precursors of metal phosphides M_xP_y, which are generally considered to be excellent (electro)catalysts [63–69], magnetic materials [69,70] and anode materials in lithium-ion batteries [71–74].

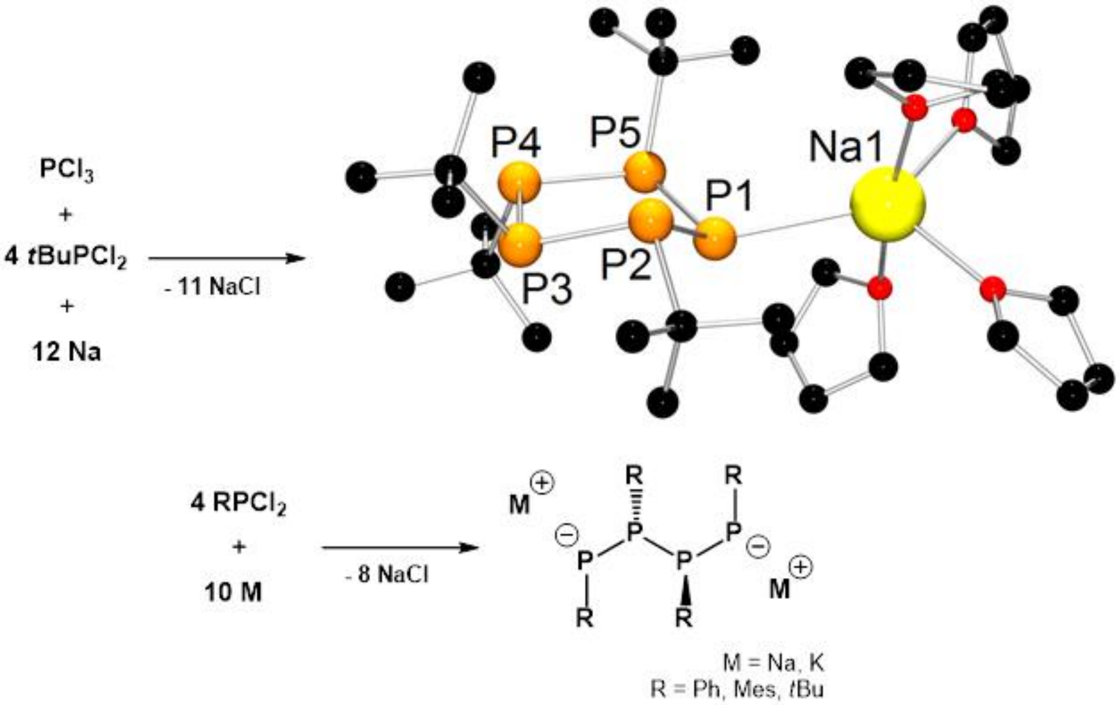


Figure 7. Alkali metal oligophosphanide synthesis methods. The drawing of the crystal structure was generated from a cif file obtained from the CSD. ORTEP software was used for illustration.

2. Low-coordinate iron phosphanido complexes

β-Diketiminate ligands (*β*-diketiminato ligands, *β*-diketiminates, BDI, BDK, nacnac) play a significant role in coordination chemistry primarily due to their very high ability to stabilize metal ions at various, often low, oxidation states. The first literature reports about these monoanionic systems appeared in the 1960s and concerned mainly the synthesis and properties of homoleptic *β*-diketiminate complexes of Co, Ni and Cu [75,76]. The greatest development, however, dates back to the 1990s, when Lappert and coworkers [77,78] proved that *β*-diketiminate ligands, in addition to the well-known cyclopentadienyl ligands, due to their strong ability to bind to metal centers and the ease with which their steric properties can be changed, can also be excellent coligands in iron complexes. These studies attracted the attention of many scientists worldwide, which resulted in the application of these ligands in many metal complexes of the s, p, d and f blocks, resulting in a total of almost 2000 articles (according to the Chemical Abstracts Service online database, SciFinder). Although they are still considered excellent stable coligands, they can also actively participate in many reactions, significantly affecting the reactivity of the complexes in which they occur [79].

As shown in Table 1, among only five low-coordinate iron phosphanido complexes, four are stabilized by *β*-diketiminate ligands [39,48]. All of these compounds (**1**–**5**, Figure 8, Table 1), which were reported recently by our group and which were obtained in reactions between the starting metal complex [(Dippnacnac)FeCl$_2$Li(dme)$_2$] and appropriate precursors of phosphanido and phosphanylphosphanido ligands, have many common features. Two of these iron(II) compounds are phosphanylphosphanido complexes: [(Dippnacnac)Fe(η^1-Me$_3$SiP-P*t*Bu$_2$)] (**1**) and [Fe(η^1-Me$_3$SiP-P*t*Bu$_2$)$_3$][Li(dme)$_3$] (**5**) [48,80]. Our research showed that the reaction outcome can be controlled by properly adjusting the reagent molar ratio, reaction medium and bulkiness of the phosphorus substituents in the ligand precursors.

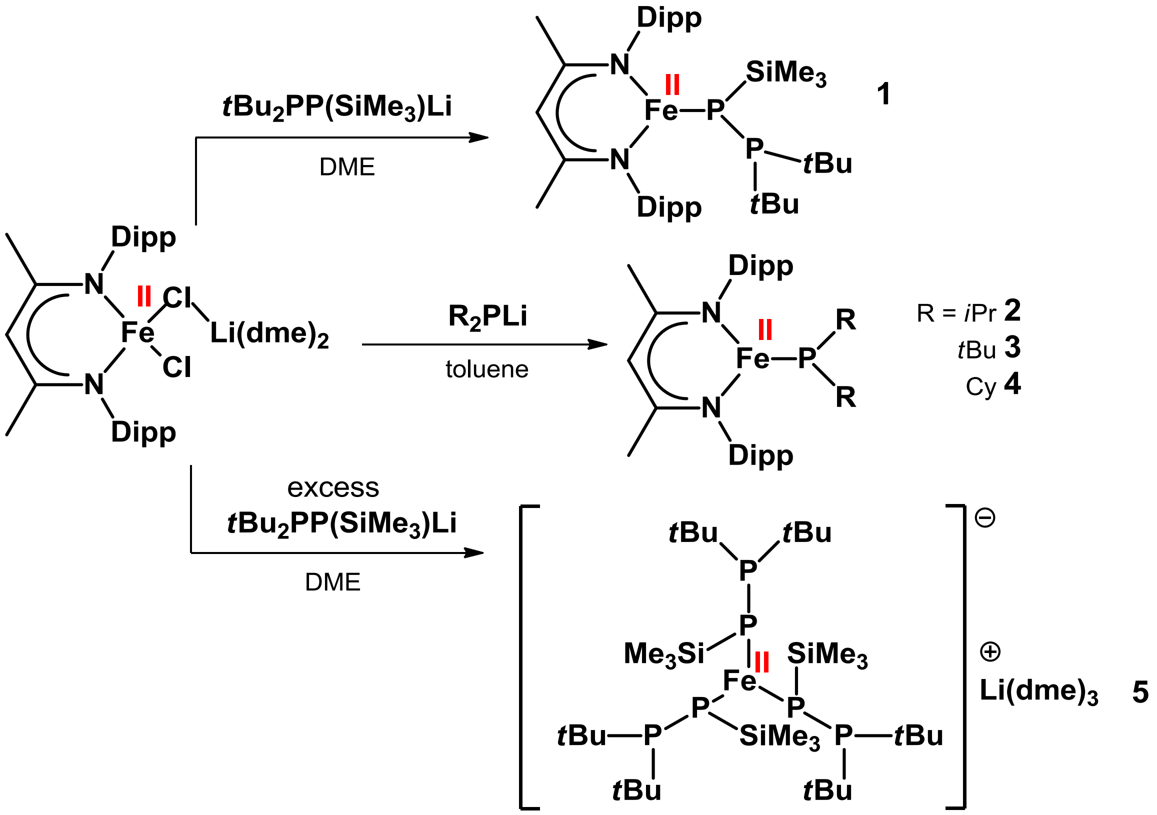


Figure 8. Syntheses of terminal phosphanido and phosphanylphosphanido iron(II) complexes from [(Dippnacnac)FeCl$_2$Li(dme)$_2$].

Three-coordinate neutral terminal phosphanido complexes of iron(II) (**2**–**4**) were obtained in equimolar reactions carried out in toluene. Their anionic four-coordinate analogs (**6**–**13**, Figure 16, Table 2) are discussed in the next chapter [39]. In the case of phosphanylphosphanido iron complexes with nacnac coligands, however, the steric effect of the R groups of R'$_2$P-P(SiMe$_3$)Li precursors has a substantial impact on obtaining the desirable products. Therefore, by tuning the steric hindrance by the choice of *i*Pr or *t*Bu groups, we were able to obtain a complex with a *side-on* bonded *i*Pr$_2$P-P(SiMe$_3$) moiety (**14**, four-coordinate, next chapter, Figure 10, Table 2) or terminal [(Dippnacnac)Fe(η^1-Me$_3$SiP-P*t*Bu$_2$)] (**1**) [48]. Moreover, utilization of an almost threefold excess of *t*Bu$_2$P-P(SiMe$_3$)Li led to the first homoleptic anionic phosphanylphosphanido complex in which the iron center is bonded to only three *t*Bu$_2$P-P(SiMe$_3$) groups. This reaction is accompanied by the unexpected exchange of the *β*-diketiminate to a phosphanylphosphanido ligand [80].

In all these coordinatively unsaturated compounds **1**–**5** (12 electrons), the geometry of the metallic center is trigonal planar (av. ΣFe 358.58°). Contrary to the pyramidal geometry of P in phosphanido complexes, the geometry of the phosphanido phosphorus in phosphanylphosphanido complexes is nearly planar. However, the Fe-P distance indicates essentially a single bond character. Notably, the P-P bonds in these complexes (2.168(2) and 2.167(2) for **1** and **5**, respectively) are shorter than typical single P-P bonds, determined to be 2.22 Å as a sum of phosphorus covalent radii. Based on this observation together with the planar phosphanido-P geometry, we may conclude that the lone electron pairs located on these P atoms interact with phosphanyl-P atoms, which increases the π-character of the P-P bonds in these complexes. Moreover, we have performed a series of DFT calculations, which permit discussion of the stereochemistry and electronic structure of the $R'_2P\text{-}P(SiMe_3)^-$ anions [48]. The obtained results showed that the phosphanylphosphanido ligands coordinate to the metal ions by adopting an anticlinal (nonchelate, monodentate) or a synclinal (chelate, bidentate) conformation, which mostly depends on steric hindrance of the ligand substituents (Figure 9). Furthermore, analysis of the neutral bond orbitals (NBOs) and canonical orbitals indicated, inter alia, that the negative charge is mainly located on the phosphanido moiety and confirmed the experimental examination that the P-P bond exhibits multiple-bond character.

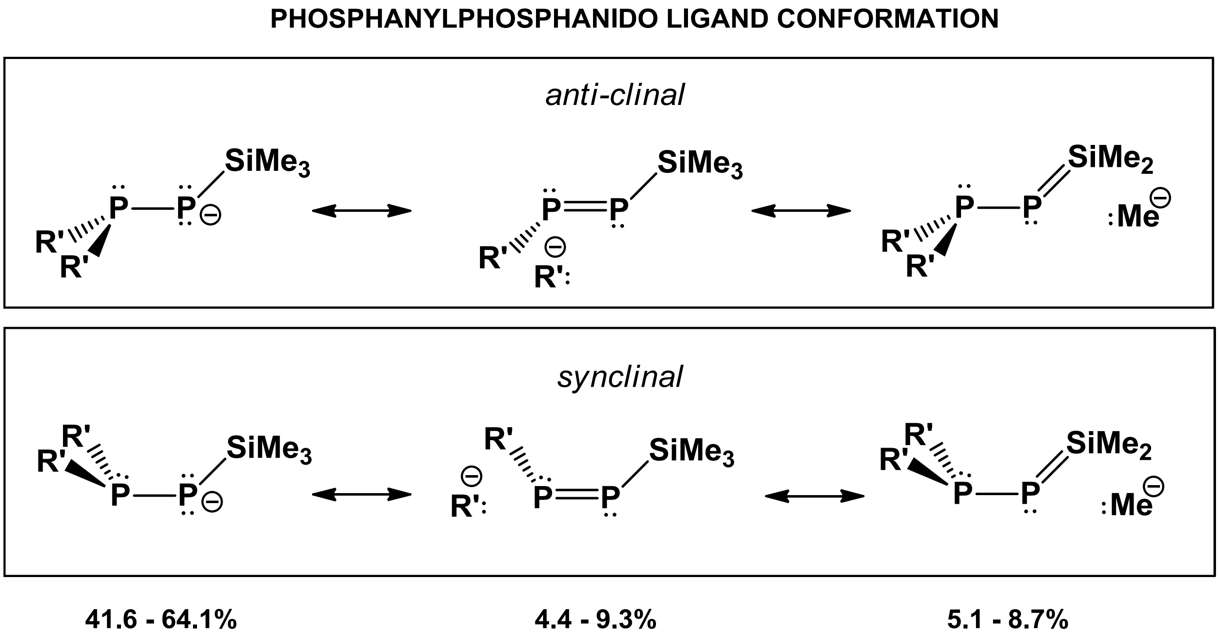


Figure 9. Lewis resonance structures of anticlinal and synclinal conformers of the phosphanylphosphanido anion with weights larger than 1.5%.

The stabilities in solution of complexes with *β*-diketiminate ligands presented in this chapter (Table 1) were confirmed by ^{1}H NMR spectroscopy. Moreover, the electronic structures were determined by ^{57}Fe Mössbauer spectroscopy (**1**–**4**) and EPR spectroscopic investigation, together with analysis of the magnetic susceptibility and magnetization data (**1** and **14** from the next chapter) revealing high-spin Fe(II) sites. Particular attention, however, should be paid to three-coordinate (**1**) and four-coordinate (**14**) complexes, which, despite the presence of the same kind of ligands in their structures, have different magnetic properties. Our DFT calculations have enabled us to better understand these differences and allowed us to rationalize their fine and hyperfine structure parameters. The calculations proved that in the ground state of the terminal complex (**1**), the z^2 orbital is doubly occupied, and the electronic configuration can be described as $|(z^2)^2(x^2-y^2)^\alpha(xy)^\alpha(xz)^\alpha(yz)^\alpha|$. Its ZFS is the result of a strong spin-orbit coupling of the ground state with the low-lying xz and yz orbital states ($\{z^2 \rightarrow xz\}$ i $\{z^2 \rightarrow yz\}$, Figure 10). For complex **14**, which is discussed in depth in the next chapter, the calculations showed that the doubly occupied orbital is yz and that electronic configuration of Fe(II) can be presented as $|(z^2)^\alpha(x^2-y^2)^\alpha(xy)^\alpha(xz)^\alpha(yz)^2|$. In this case, the observed ZFS is closely related to the strong spin-orbit interaction of two low-lying yz and z^2 orbitals ({yz → z^2}, Figure 10).

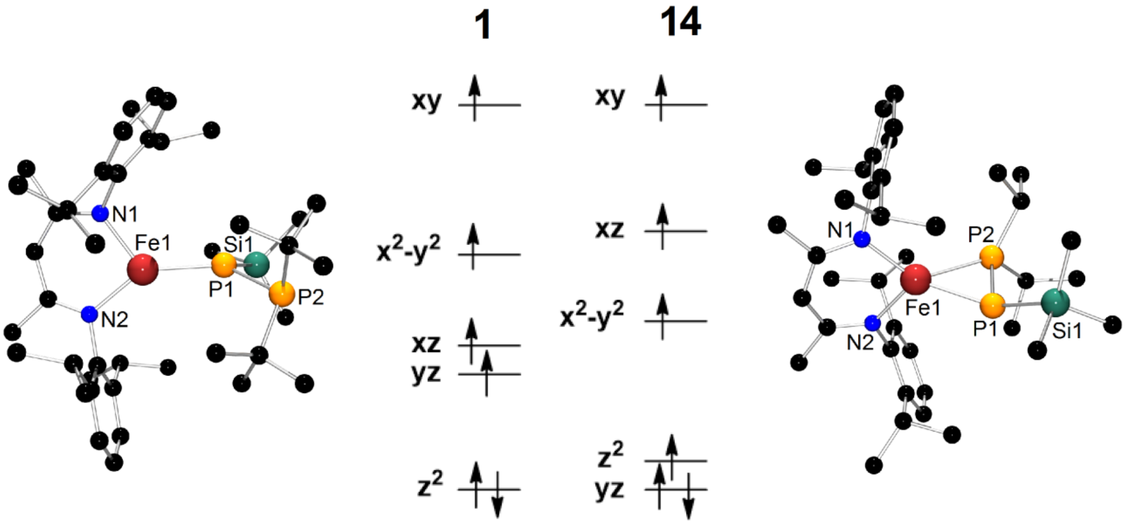


Figure 10. Diagram of the 3d orbitals of phosphanylphosphanido complexes of iron with their X-ray structures (**1** – left, **14** – right). **The drawings of the crystal structures were generated from the cif file obtained from the CSD. ORTEP software was used for illustration.**

Synthetic reagents and biologically active molecules based on functionalized phosphorus compounds are widely used in many different chemistry fields. An excellent example of such compounds is phosphanes, for which, among various methods for their synthesis, an appropriate way to form the P-C bonds seems to be hydrophosphination catalyzed by metal complexes, resulting in high yield and selectivity.

Webster *et al* reported the first examples of intermolecular [81] and intramolecular [82] hydrophosphination reactions using an iron complex stabilized by a *β*-diketiminate ligand [(Dippnacnac)$FeCH_2SiMe_3$] as a precatalyst (Figure 11). Based on the conducted experiments, kinetic studies and mechanistic interpretation, they presented a probable mechanism of intramolecular hydrophosphination of unactivated unsaturated C-C bonds. Unfortunately, due to the challenging synthesis of the starting material and the difficulty of further isolation or identification of presumed intermediates in the catalytic cycle, the proposed mechanism has not been fully confirmed. It was proposed that the reaction between the precatalyst mentioned above (used as a model) and the primary phosphinoalkene leads to the formation of an active catalyst the monomeric iron phosphanido complex which crystalizes in the form of a dimer [82] (Figure 11).

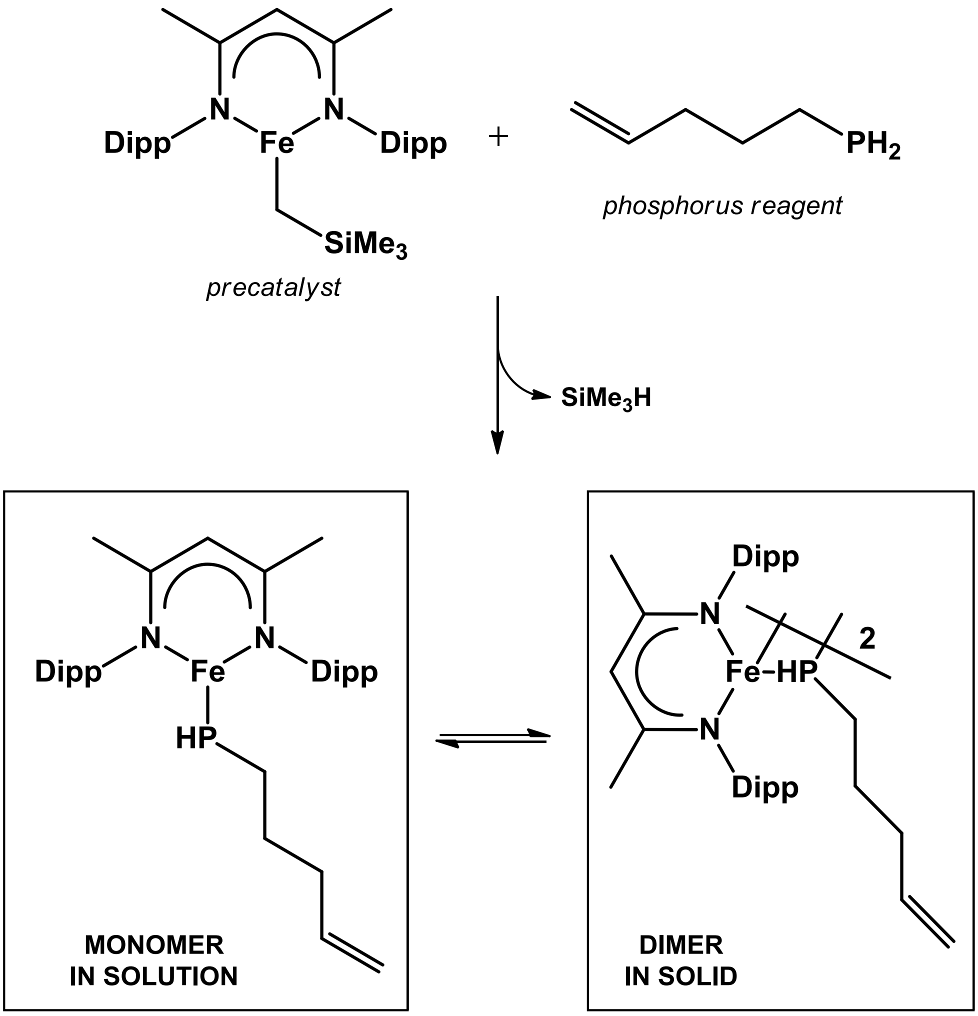


Figure 11. Formation of the phosphanido complex of iron considered an active catalyst in the intramolecular hydrophosphination reaction of unsaturated phosphinohydrocarbons [82]**.**

On the other hand, appropriate reaction conditions and the presence of dichloromethane CH_2Cl_2 as a solvent are required for intermolecular hydrophosphination. Moreover, Webster *et al* confirmed that [(Dippnacnac)$FeCH_2SiMe_3$] is also an excellent precatalyst in the dehydrocoupling (DHC) of various primary and secondary phosphanes. Currently, these reactions are considered the most efficient methods for P-P bond formation, in which gaseous hydrogen is the only reaction side-product. As in hydrophosphination, the formation of an active monomeric terminal iron phosphanido intermediate was presumed to be a result of the reaction of the starting iron compound with RPH_2 or R_2PH. Further interaction between the obtained transient complex with another phosphane molecule led to the elimination of the DHC product, which is diphosphane, and hydride iron complex. This in turn could further react with the starting phosphane, resulting in H_2 and phosphanido complex formation.

To verify the postulated hypothesis and gain an access to multigram quantities of this class of complexes, our research focused on the examination of the catalytic activity of three-coordinate (**2**–**4**, presented in this chapter) and four-coordinate (**6**–**13**, presented in the next chapter) neutral and anionic iron phosphanido complexes in dehydrocoupling reactions [39]. The conducted experiments included thermal stability studies, through testing the catalytic activity within different secondary phosphanes (Ph_2PH, *t*BuPhPH, *t*Bu_2PH, Cy_2PH, and (*i*$Pr_2N)_2PH$), DFT calculations, leading to the conclusion that terminal phosphanido Fe(II) complexes can act as a phosphanyl radical source and are good catalysts for the DHC of Ph_2PH. We stated that the most acceptable explanation for observed catalytic activity, which probably involves a radical-mediated mechanism, is the formation of iron dimeric species.

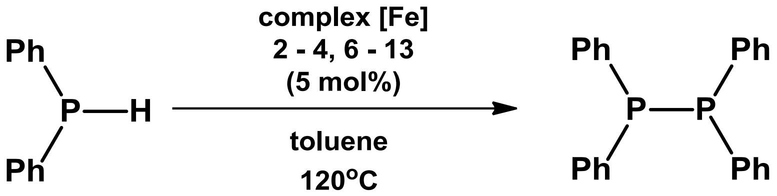
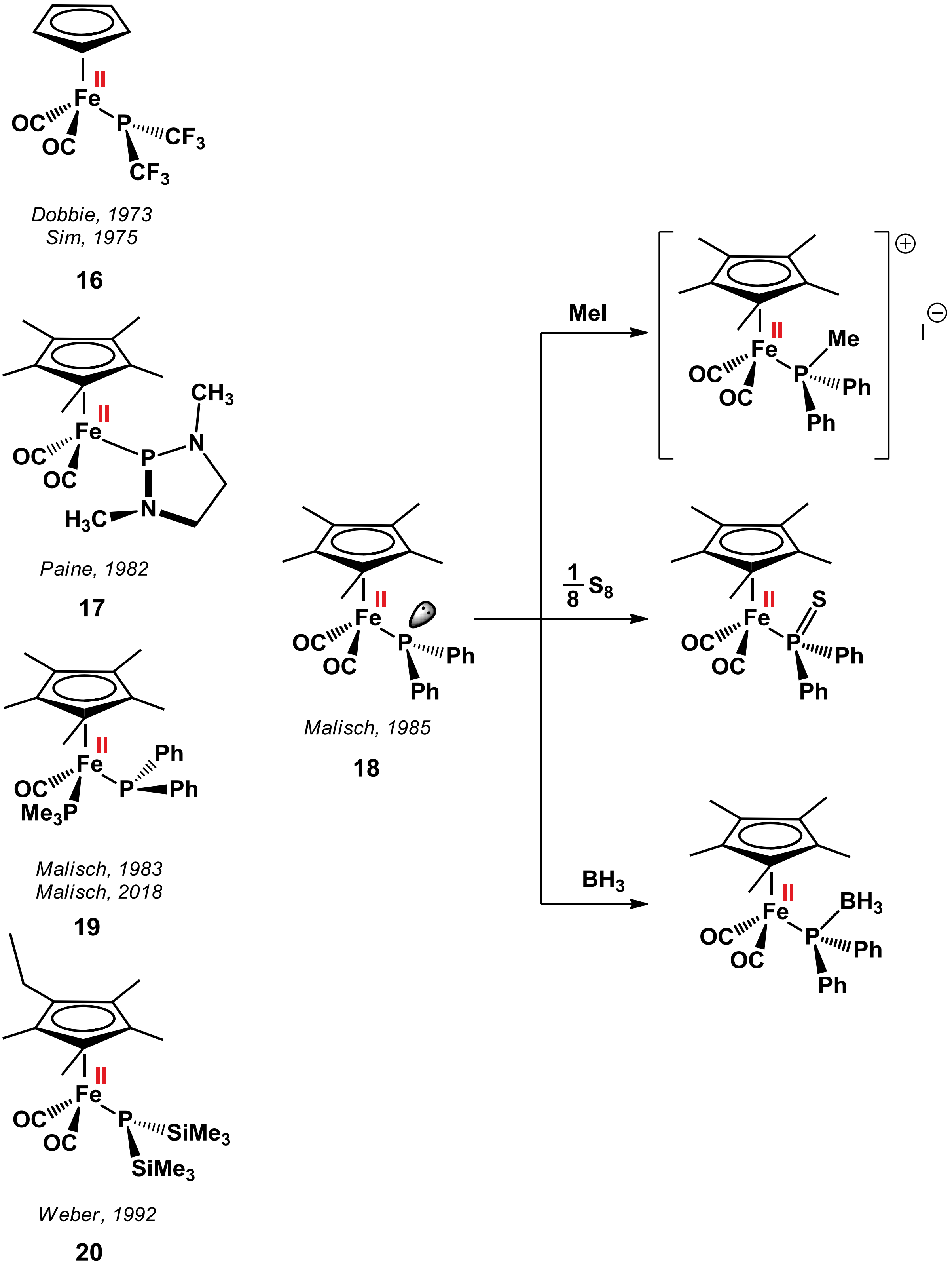


Figure 12. Dehydrocoupling of diphenylphosphane using phosphanido complexes of iron(II) stabilized by *β*-diketiminate ligands as catalysts [39].

3. Four-coordinate iron phosphanido complexes

The vast majority of terminal phosphanido iron complexes described in the literature contain well-known carbonyl and cyclopentadienyl coligands in their structures. To the best of our knowledge, the first iron terminal complex with the PR_2 moiety, reported by Cooke, Green and Kirkpatric in 1968, is $[(\eta^5\text{-Cp})(CO)_2Fe(P(C_6F_5)_2)]$ (**15**) [34]. This compound was obtained in the reaction between chlorophosphane $(C_6F_5)_2PCl$ and the carbonyl-stabilized anion $[(\eta^5\text{-Cp})Fe(CO)_2]^-$ formed from $[(\pi\text{-Cp})Fe(CO)_2]_2$ and sodium amalgam. The identity of this complex was determined by elemental analysis, IR, ^{1}H and ^{19}F NMR and mass spectrometry. However, the lack of structural data, the presence of highly electron-withdrawing C_6F_6 substituents at the P atom and the inability to synthesize this complex via the reaction between the lithium derivative $(C_6F_6)_2PLi$ and $[(\eta^5\text{-Cp})Fe(CO)_2Cl]$ led to some doubts with regarding correct assignment of this compound to either the phosphanido or phosphenium class. Insight into this interpretation was obtained in 1972 and the $[(\eta^5\text{-Cp})(CO)_2FeP(CF_3)_2]$ complex with electrophilic CF_3 groups (**16**, Figure 13) was fully characterized in 1975 [83]. This complex was synthetized by the reaction of diphosphane $P(CF_3)_2$ with $[(\eta^5\text{-Cp})Fe(CO)_2]_2$. Because the Fe-P bond distance is equal to 2.265(3) Å and the complex adopted pyramidal geometry (ΣP 309.23°), this complex is considered the first terminal phosphanido complex of iron structurally described in the literature.

In the 1980s and 1990s, the iron phosphanido chemistry developed mainly as the chemistry of complexes with cyclopentadienyls and carbonyls as ancillary ligands. The geometries of the iron centers were more or less distorted tetrahedral, also known as a distorted three-legged piano-stool arrangement. Unfortunately, most of these complexes were only spectroscopically identified. Two major synthesis methods were used: (a) the Schäfer method, which involves the reaction between halogen iron derivatives [33] and lithium phosphides, and (b) the reaction of nucleophilic iron carbonylates with halophosphanes. Both of these methods are used till now (Figure 4). All these complexes exhibits pyramidal geometry and the Fe-P bond length equal to av. 2.35 Å, which corresponds to the phosphanido moiety (complex **17** [30] presented in Figure 13 was recognized by the authors as a phosphenium complex, but according to Thomas *et al* [84], due to the geometry of the phosphorus atom, it should be considered a phosphanido compound). Moreover, high reactivity with electrophiles was observed. One example is the reactions between $[(\eta^5\text{-Cp*})(CO)_2FePPh_2]$ (**18**) and MeI, elemental sulfur and $BH_3{\cdot}THF$ described by Malisch *et al*, which led to methylation, thialation and borane addition products, respectively (Figure 13).



Dobbie, 1973
Sim, 1975

16

Paine, 1982

17

Malisch, 1985

18

Malisch, 1983
Malisch, 2018

19

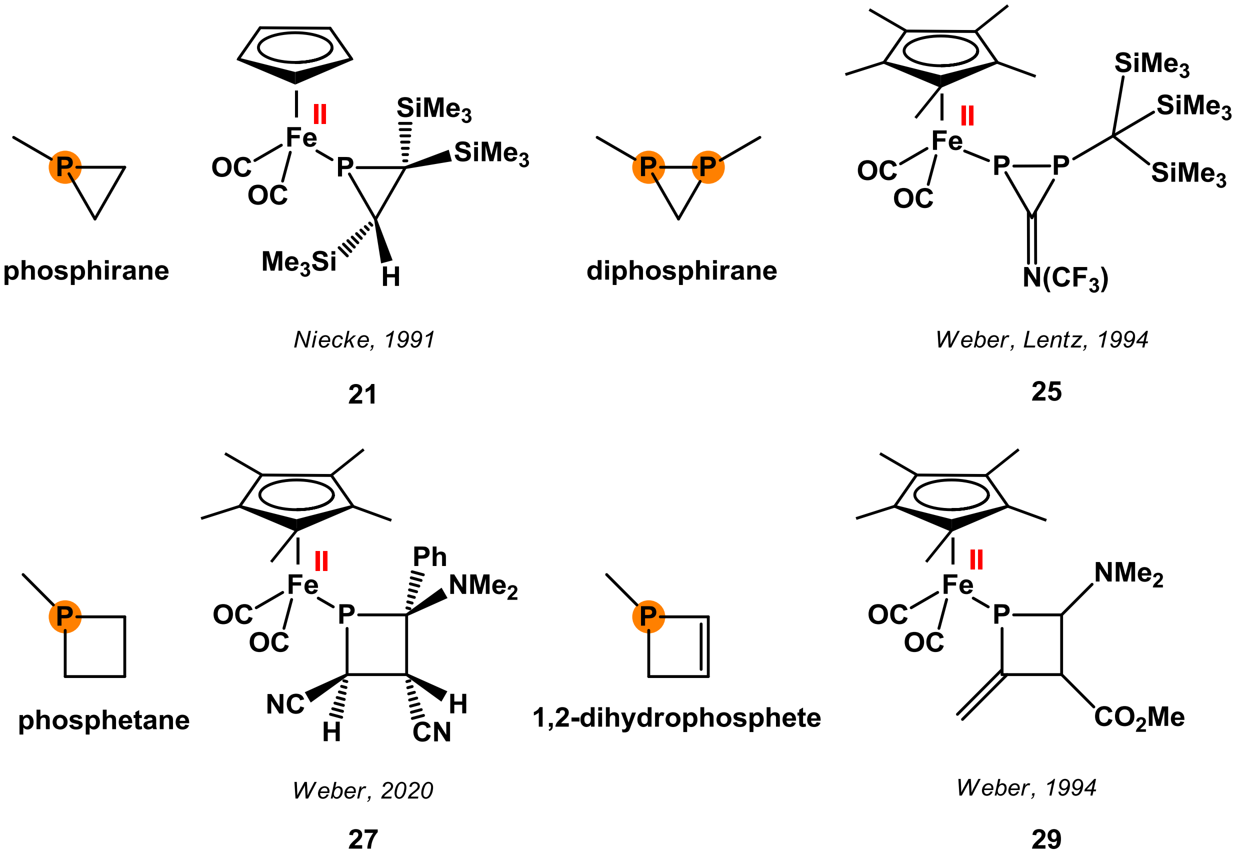
Weber, 1992

20

Figure 13. Examples of phosphanido iron complexes stabilized by cyclopentadienyls and carbonyls [36,83,85–87] **and their reactivity.**

Among the four-coordinate iron complexes with R_2P^- ligands, cyclic phosphorus systems such as metallophosphiranes (**21**–**26**), metallophosphetanes (**27**) and metallophosphetes (**28**, **29**) can be distinguished (Table 2, Figure 14). These compounds are mainly obtained from metallophosphaalkene [Fe]-P=CR and metallodiphosphene [Fe]-P=PR (Fe coordinated by cyclopentadienyls and carbonyls,

Figure 14). The structural analysis indicated Fe-P single bond character; however, the most interesting feature is the geometry of the phosphorus rings. Due to ring tension, the sum of the angles around P is mostly lower than 300° (one exception is complex **26**, where ΣP is equal to 316.75°. Additionally, in this complex, the Fe-P bond length is slightly shorter than those of the other complexes described here). The latter adopt a distorted three-legged piano stool configuration.



Niecke, 1991

21

Weber, Lentz, 1994

25

Weber, 2020

27

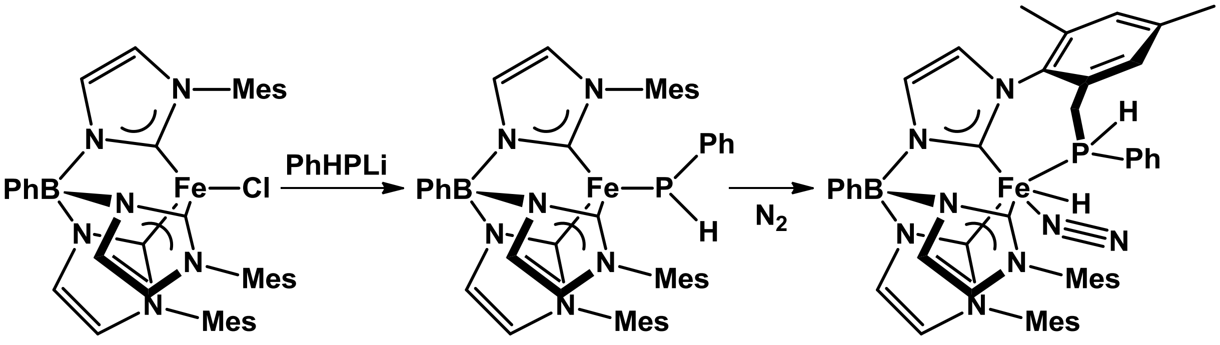
Weber, 1994

29

Figure 14. Examples of iron phosphiranes and phosphetanes and their derivatives [88–91].

Special attention is given to terminal phosphanido complexes because of the high possibility of their use as catalysts for the preparation of various types of phosphorus compounds. One group of the increasing importance is vinylphosphanes, which can serve as novel ligands in TM complexes or as intermediates in the synthesis of polyphosphanes. In 2016, Itazaki and Nakazawa *et al* reported a single hydrophosphination of terminal arylalkynes with secondary phosphanes catalyzed by an iron complex $[(\eta^5\text{-Cp*})(CO)Fe(py)(Me)]$ [92]. A resting state in the proposed catalytic cycle was the phosphino(phosphanido) iron complex $[(\eta^5\text{-Cp*})(CO)_2Fe(PHPh_2)(PPh_2)]$ (**30**), which was isolated from the reaction of $[(\eta^5\text{-Cp*})(CO)_2Fe(PHPh_2)(Me)]$ with diphenylphosphane. Moreover, the reaction between $[(\eta^5\text{-Cp*})(CO)_2Fe(PHPh_2)(PPh_2)]$ (**30**) and phenylacetylene led to planar metallaphosphacyclobutene, which is the result of regioselective insertion of PhC≡CH into the Fe-P bond in **30**.

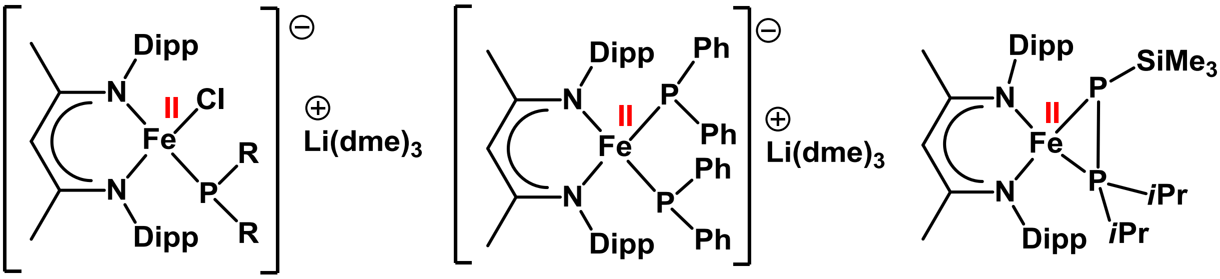
Another example of the utility of iron compounds for P-C bond formation is a phosphanido iron complex $[PhB(MesIm)_3FeP(H)Ph]$ (**31**, Figure 15) coordinated by a bulky tris(carbene)borate ligand [38]. This paramagnetic compound, whose structure was elucidated based on DFT calculations, is thermally unstable at room temperature and after a few hours in a nitrogen atmosphere is converted to a six-membered complex in which the insertion of a phosphanido group into an *o*-methyl C-H bond of borate ligand occurs. Intramolecular migration of the hydrogen atom takes place, leading to activation of the C-H bond to create a new P-C bond (Figure 15). The iron coordination sphere is completed by hydride and nitrogen molecules, which was confirmed by NMR and IR spectroscopy, respectively. This complex is also thermally unstable, and heating for 2 days led to a six-coordinate iron(II) complex formed during the cyclometalation reaction of the second *o*-methyl group in the starting ligand, which generated H_2. The structures of two analogous thermally stable high-spin iron(II) complexes $[PhB(tBuIm)_3FeP(H)Ph]$ (**32**) and $[PhB(Cy_2Im)_3FeP(H)Ph]$ (**33**), were confirmed by X-ray analysis. Interestingly complex **32** exhibits a planar geometry of the phosphanido ligand. However, the high Fe-P distance indicated a single bond character. Complex **33** displays typical features of a pyramidal R_2P^- ligand.



31

Figure 15. Synthesis of phosphanido iron complex $[PhB(MesIm)_3FeP(H)Ph]$ (31) and its intramolecular C-H bond insertion reaction [38]**.**

Over the last three years, our group has investigated chemistry of four-coordinate iron phosphanido complexes. As mentioned in an earlier chapter, the reaction between the starting metal complex $[(Dippnacnac)FeCl_2Li(dme)_2]$ and appropriate precursors of phosphanido and phosphanylphosphanido ligands led to the formation of four-coordinate analogs [39,48] (**6**–**13,** Figure 16, Table 2) in addition to low-coordinate compounds (**1**–**5**, Figure 8).



R = *i*-Pr **6**
Ph **8**
Cy **10**

11

14

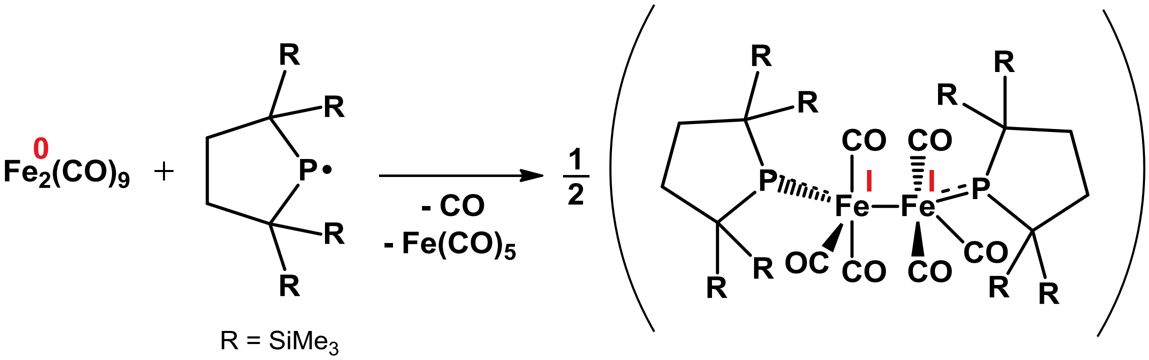
Figure 16. Four-coordinated phosphanido and phosphanylphosphanido complexes of iron(II) stabilized by a *β*-diketiminate ligand [39,48]**.**

Mono- and disubstituted phosphanido anionic complexes **6**–**13** [39] and phosphanylphosphanido complex **14** with a *side-on* bonded $iPr_2P\text{-}P(SiMe_3)^-$ moiety [48] can be distinguished. Disubstituted complex **12** was obtained in the reaction with a threefold excess of Ph_2PLi. The long Fe-P distances (even 2.454(2) Å in the case of **12**) with pyramidal geometry of phosphorus indicate single bond character. The *β*-diketiminate ligand plane is perpendicular to the Fe-Cl bond in monoanionic phosphanido complexes, whereas in the case of disubstituted phosphanido and phosphanylphosphanido, it is perpendicular to the plane determined by the two Ph_2P^- and *i*Pr_2P-$P(SiMe_3)^-$ ligands, respectively. The electronic structures of **6**, **8**, **10**, **11**, **13**, and **14** (for more details, see the chapter above) were interrogated by ^{57}Fe Mössbauer spectroscopy, and these studies revealed high-spin iron(II) complexes. Moreover, reactivity studies of the three-coordinate phosphanido complexes have shown that complexes **6**, **8**, **9**, **10**, **11**, and **13** are good catalysts for the dehydrocoupling of Ph_2PH (for more information, see the previous chapter).

4. Five-coordinate iron phosphanido complexes

Metal carbonyls, due to the presence of labile CO ligands in their molecules, are one of the most important precursors for the synthesis of other organometallic complexes. The reaction of $Fe(CO)_5$ with potassium phosphide Ph_2PK gave a spectroscopically determined phosphinocarbonyl adduct $[(CO)_4FeCOPPh_2]^-$, which decomposed at high temperatures to a five-coordinate phosphanido complex of iron $[(CO)_4Fe(PPh_2)]^-$, symmetrical diphosphane $(Ph_2P)_2$ and $[Fe_2(CO)_8]^{2-}$ [93]. Petz and Weller proposed that this reaction occurred via a radical mediated mechanism.

Twenty years later, in 2016, Suanada and Iwanoto *et al* reported the synthesis of coordinatively unsaturated dinuclear iron complex in the reaction between $Fe_2(CO)_9$ and a phosphinyl radical [94] (Figure 17). Phosphinyl radical underwent one-electron reduction, as revealed by the formation of the R_2P^- ligand, accompanied by one-electron oxidation of iron. Crystal structure examination showed that this compound $[Fe(CO)_3(2,2,5,5\text{-}(SiMe_3)\text{-}1\text{-phoshacyclopentane})]_2$ (**34**, Figure 17) can be considered the first iron complex with terminally bonded planar phosphanido ligands. The sum of the angles around the phosphorus atoms (358.55 and 358.71°) with short Fe-P bond distances (2.0934(12) and 2.1047(13) Å) indicates high planarity at P and, thus, strong π-donation to the metal. This complex is characterized by the presence of a quite long unsupported Fe-Fe bond of 2.7374(10) Å (longer than that described previously in the literature), where the geometry of each metal center is trigonal bypiramidal.



34

Figure 17. Synthesis of the first phosphanido iron complex with a planar phosphanido ligand [94].

Two iron centers can be considered iron(I), as stated by the authors, and intramolecular antiferromagnetic coupling between two neighboring centers results in diamagnetic complex, which allows confirmation of its molecular structure by NMR spectroscopy. The ^{31}P NMR spectrum consists of only one significantly downfield shifted signal at 425.9 ppm, characteristic of planar R_2P species, which supports the X-ray crystallography investigations. The ^{1}H NMR spectrum at higher temperatures shows one broad signal at 3-5 ppm in addition to signals corresponding to $SiMe_3$ and CH_2 groups. Due to the long Fe-Fe bond in this compound, the authors proposed the formation of paramagnetic species (Figure 18) *via* homolytic cleavage of the mentioned above bond. This hypothesis was supported by ESR spectroscopy and DFT calculations. Moreover, they performed reactions with organic radicals to obtain two additional iron complexes with planar phosphanido ligands (**35**, **36**, Figure 18, Table 3).

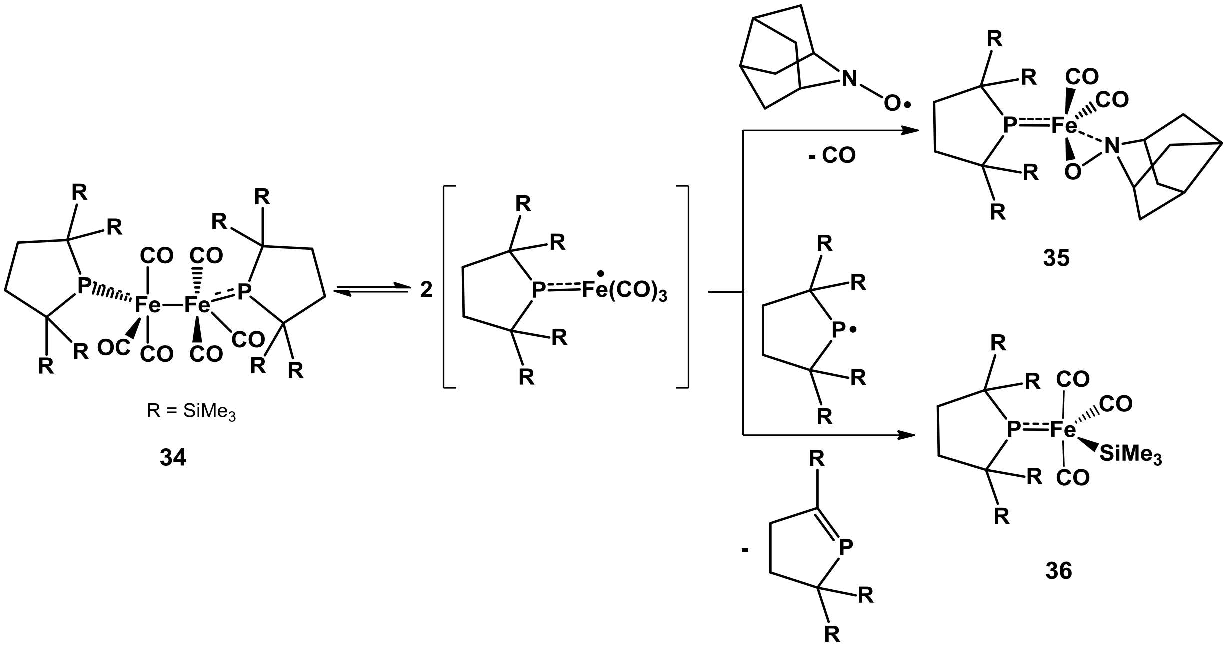


Figure 18. Formation of radical species from dinuclear iron complex with planar phosphanido ligands [94].

The last interesting example of a five-coordinate phosphanido iron complex is the phosphanido iron compound [$(CO)_4Fe(P(CPh_3)(NH\textit{i}Pr))$][K(18-crown-6)(dme)]$(thf)_2$] described by Ferao and Streubel *et al* in 2018 (**37**, Figure 19) [95,96]. This structurally characterized complex was obtained *via* deprotonation of the 1,1'-bifunctional aminophosphane $Fe(CO)_4$ complex (Figure 19). This in turn was synthesized from another starting material spectroscopically characterized as the phosphinidenoid iron(0) complex [$(CO)_4Fe-P(Cl)(CPh_3)$][Li(12-crown-4)] [95,96].

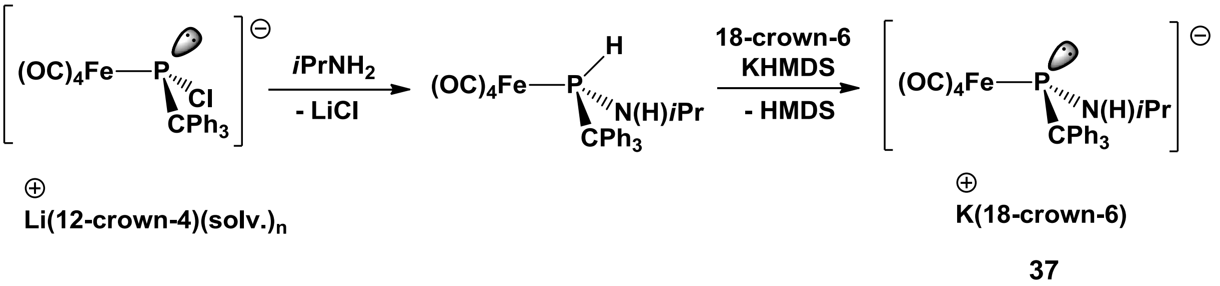
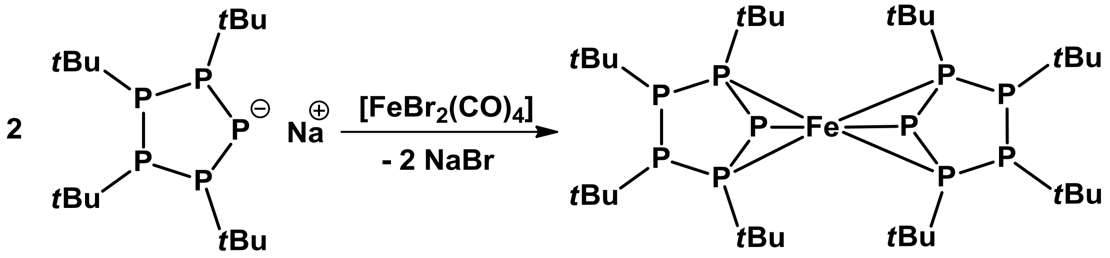


Figure 19. Synthesis of a phosphinidenoid iron(0) complex [95,96].

5. Six-coordinate iron phosphanido complexes

Only one example of a six-coordinate compound has been reported, namely, the crystallographically determined oligophosphanido iron complex [Fe{*cyclo*-(P_5tBu_4)}$_2$] (**38**, Figure 20) reported by Hey-Hawkins *et al* in 2014 [62]. It was obtained by a reaction of sodium oligophosphanide (Figure 7) with [$FeBr_2(CO_4)$]. Unlike other previously obtained similar complexes of Ni, Pd, Pt, Cu, Ag, Au, and Rh [56,59–61], this compound, as the first of its kind, was characterized by a tridentate coordination mode of the ligand to the metal center in accordance with the 18 electron rule [97]. The geometry of the iron, located on the inversion center, is distorted trigonal-antiprismatic. Two of the three Fe-P bonds of one oligophosphanido moiety are 0.2 Å shorter (2.2366(3) and 2.2056(3) Å) than the third bond (2.4028(4) Å). Moreover, due to delocalization of the lone electron pair at the anionic phosphorus atom into the LUMO at the nearest located P atom, the P-P bond lengths between phosphorus atoms bonded to the metal center of 2.1258(5) and 2.1588(5) Å are shorter than the others present the structure (av. 223.46 Å). These results indicate the multiple bond character of these bonds (the sum of single bond covalent radii for two P is 2.22 Å[98]). In addition to structural studies, further research on the reactivity of this complex is even more interesting. Because this complex is very rich in phosphorus, its thermogravimetry and differential thermal analysis (TG/DTA) were crucial, and thermolysis of the analyzed complex resulted in the formation of iron phosphide FeP_6 [62].



38

Figure 20. Synthesis of the homoleptic iron complex with cyclooligophosphanido ligands [62].

6. Conclusions

In this review, we underline the diverse chemistry of terminal phosphanido iron complexes, which adopt various coordination modes of the central iron atoms. In the 50 complexes studied, phosphorus mostly adopts a pyramidal geometry characterized by the occurrence of a stereochemically active lone electron pair. Only four examples are considered planar phosphanido iron complexes. Moreover, phosphanylphosphanido and oligophosphanido iron compounds were discussed. Nevertheless, in addition to the fascinating developments in the structural chemistry field, there are also further promising applications of iron-based systems in catalysis and materials science. Considering availability, price, toxicity, and environmental aspects, this review nicely shows the wide range of benefits of utilizing iron complexes in the synthesis of phosphorus-containing fine chemicals.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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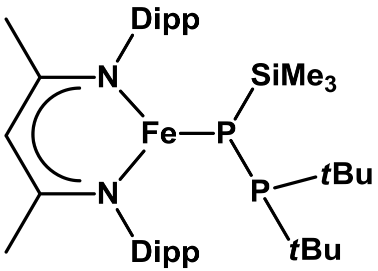
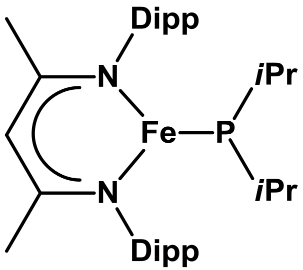
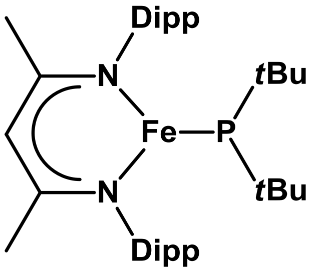
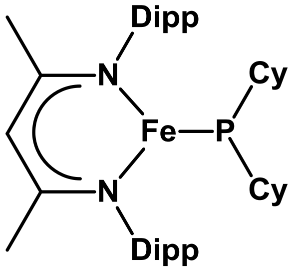
Table 1. Crystalographically determined three-coordinate iron complexes with nonbridging ligands (bond lengths and bond angles taken from the CSD cif file)

Number in the publication	CSD refcode	Publication year	Complex	Structure	Fe-P$_{\text{phosphanido}}$ bond length [Å]	Geometry of P$_{\text{phosphanido}}$ ΣP$_{\text{phosphanido}}$ [°]	Ref.
1	MAZHIH	2017	[(Dippnacnac)Fe(η^1-Me$_3$SiP-P*t*Bu$_2$)]		2.3144(17)	nearly planar 354.02	[48]
2	KIQLUU	2018	[(Dippnacnac)Fe(P*i*Pr$_2$)]		2.372(1)	pyramidal 333.73	[39]
3	KIQMEF	2018	[(Dippnacnac)Fe(P*t*Bu$_2$)]		2.366	pyramidal 345.34	[39]
4	KIQMIJ	2018	[(Dippnacnac)Fe(PCy$_2$)]		2.328(2)	pyramidal 327.68	[39]

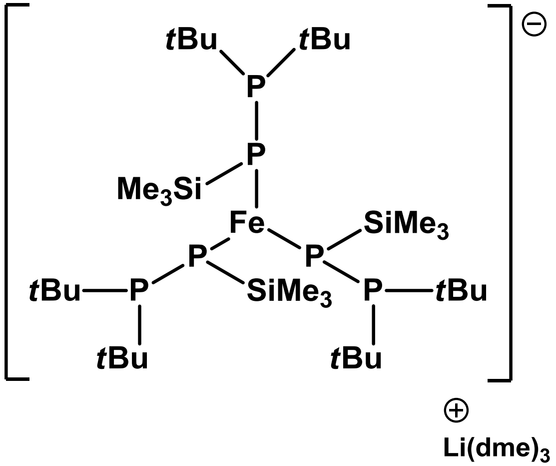
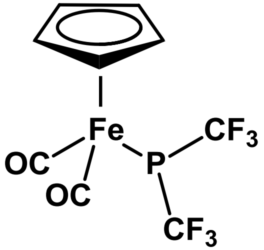
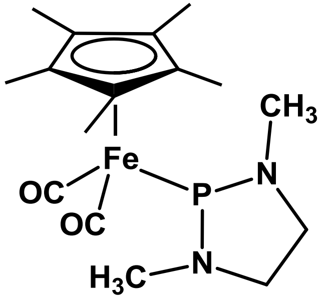
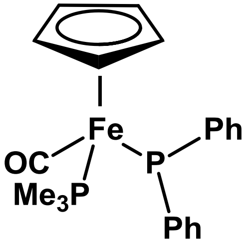
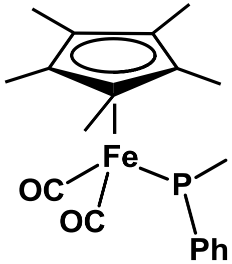
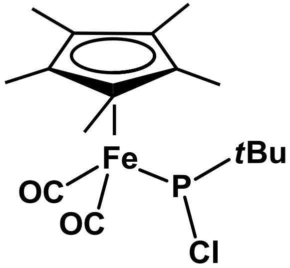
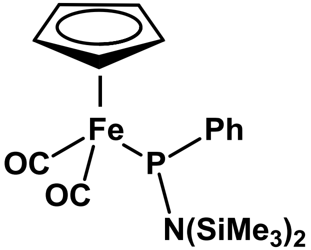
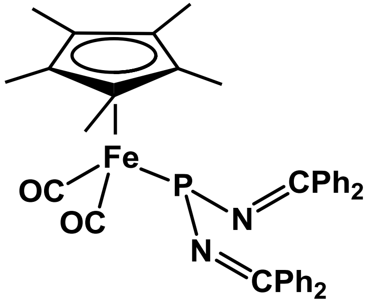
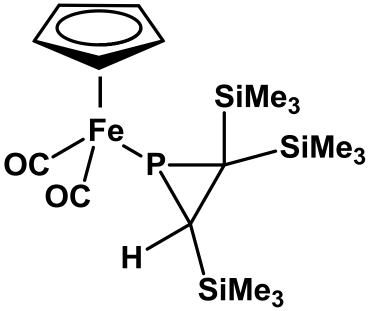
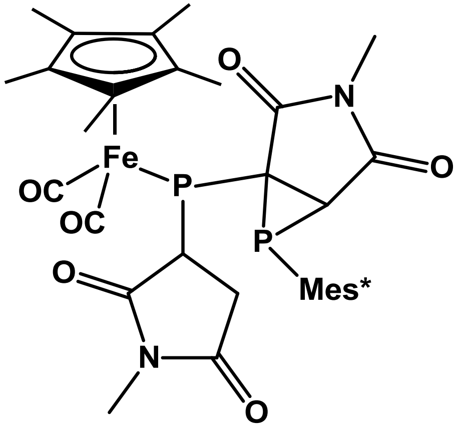
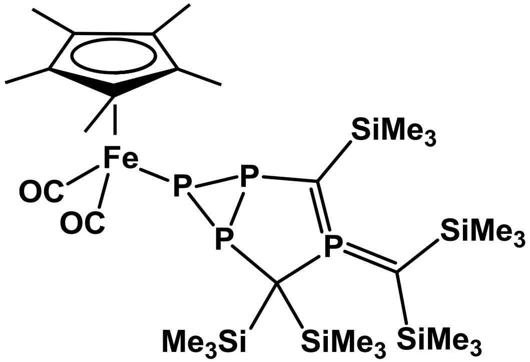
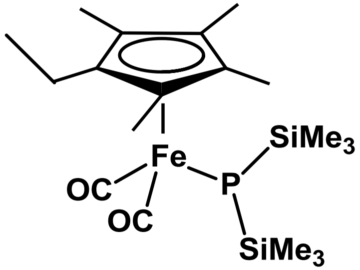
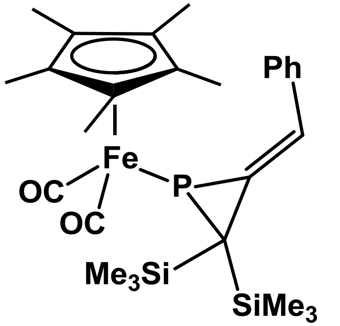
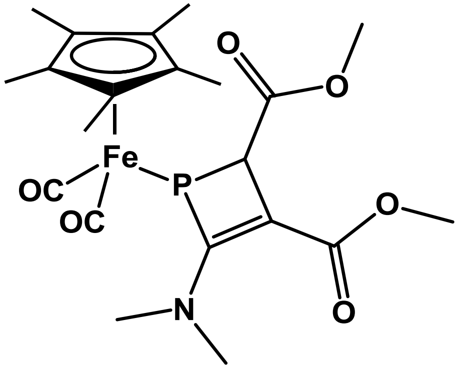
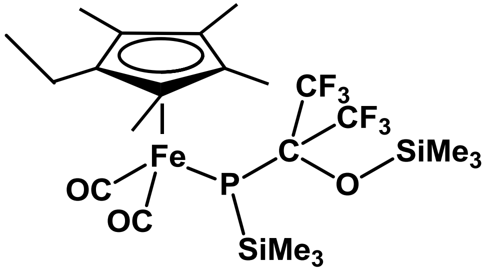
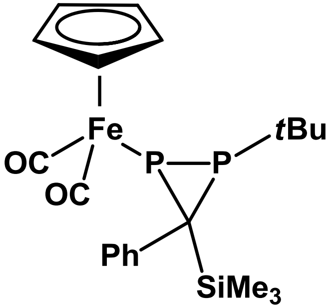
5	GUVMOC	2020	[Fe(η^1-Me_3SiP-P$t$$Bu_2$)$_3$][Li(dme)$_3$]		2.346(1) 2.345(1) 2.334(2)	nearly planar 356.59 354.13 357.78	[80]

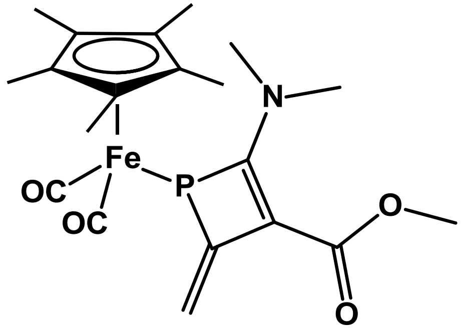
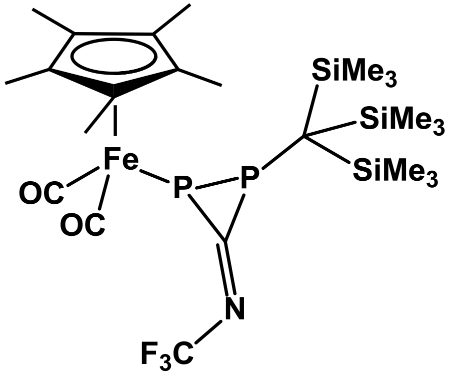
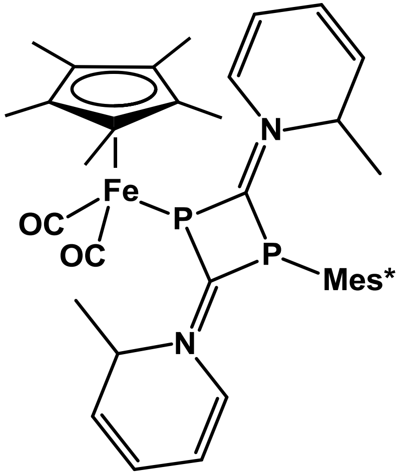
Table 2. Crystalographically determined four-coordinate iron complexes with non-bridging ligands (bond lengths and bond angles taken from the CSD cif file)

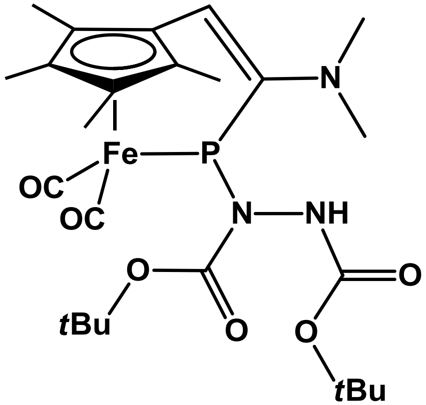
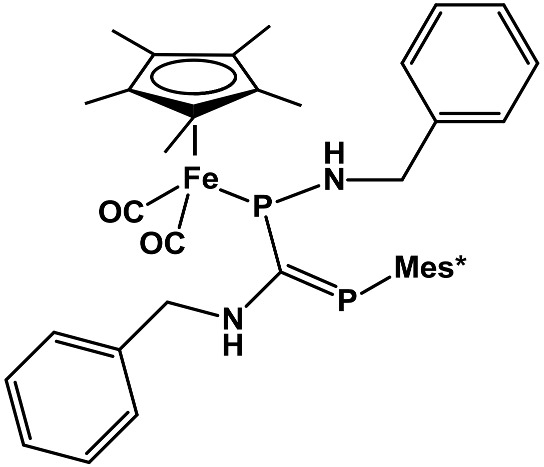
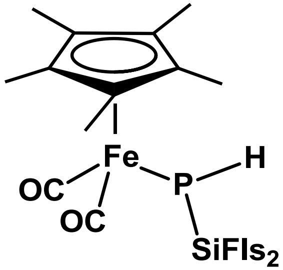
Number in the publiaction	CSD refcode	Publication year	Complex	Structure	Fe-P$_{phosphanido}$ bond length [Å]	Geometry of P$_{phosphanido}$ ΣP$_{phosphanido}$ [°]	Ref.
16	CPFMPI10	synthesis 1973 1974 structure 1975	[(η^5-Cp)(CO)$_2$Fe(P(CF_3)$_2$)]		2.265(3)	pyramidal 309.23	[85] [86] [83]
17	BODWOG	1982	[(η^5-Cp)(CO)$_2$Fe(PN(Me)CH_2CH_2NMe)]		2.340(2)	pyramidal 313.52	[30]

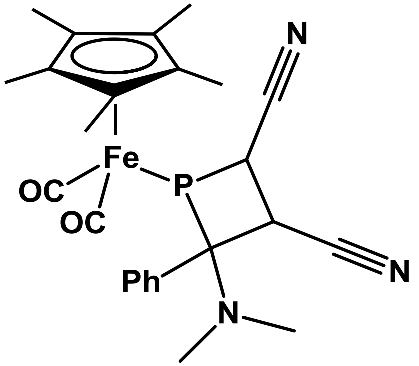
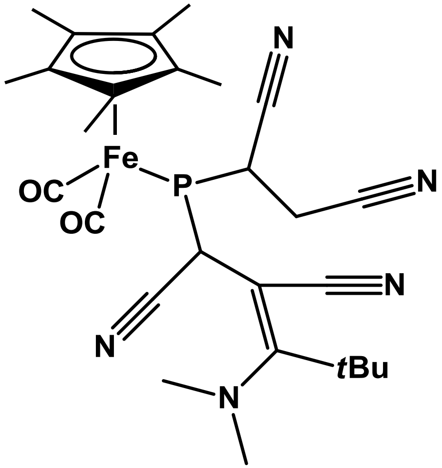
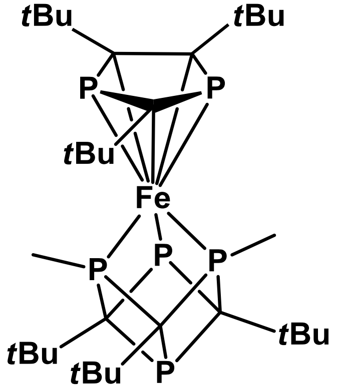
19	JIFWAZ	1983	[(η^5-Cp)(CO)Fe(PMe$_3$)(PPh$_2$)]		2.311(1)	pyramidal 316.55	[87]
18	DASJIQ	1985	[(η^5-Cp*)(CO)$_2$Fe(PPh$_2$)]		2.319(1)	pyramidal 318.77	[40] [35]
	DEJDUR	1985	[(η^5-Cp*)(CO)$_2$Fe(PCl(*t*Bu))]		2.285(1)	pyramidal 317.21	[41]
	GESWUW	1988	[(η^5-Cp)(CO) $_2$Fe(P(N(SiMe$_3$)$_2$)Ph)]		2.338(1)	pyramidal 330.59	[99]
	VISJUC	1991	[(η^5-Cp*)(CO)$_2$Fe(P(N=CPh$_2$)$_2$)]		2.306(1)	pyramidal 311.25	[42]

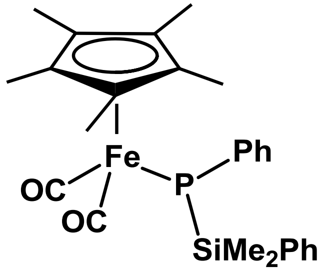
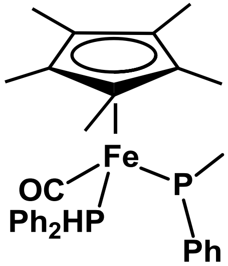
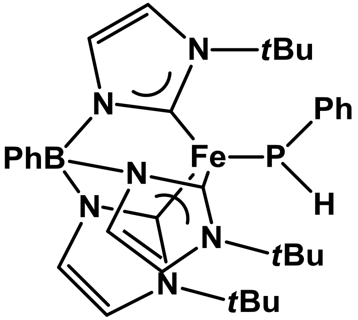
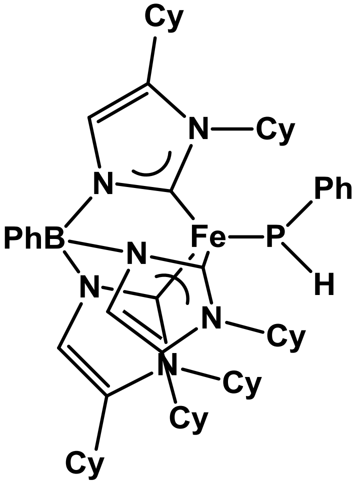
21	KONSUB	1991	$[(\eta^5\text{-Cp})(CO)_2FePC(SiMe_3)_2CSiMe_3H]$		2.331(2)	pyramidal 290.27	[88]
	KORNAG	1992	$[(\eta^5\text{-Cp*})(CO)_2Fe(P(3\text{-(1-Me-pyrrole-2,5-dione))(3-(3,4-}\eta^1\text{-P(1-Me-pyrrole-2,5-dione)(Mes*))}]$		2.318(2)	pyramidal 319.66	[100]
22	PADFIJ	1992	$[(\eta^5\text{-Cp*})(CO)_2Fe(P(\eta^2\text{-PC}(SiMe_3)P(=C(SiMe_3)_2)=C(SiMe_3)P))]$		2.321(3)	pyramidal 270.05	[101]
	PAHYUS	1992	$[(\eta^5\text{-C}_5Me_4Et)(CO)_2Fe(P(SiMe_3)_2)]$		2.359(2)	pyramidal 329.14	[36]

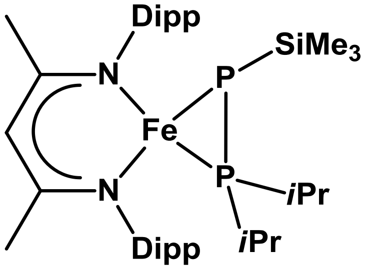
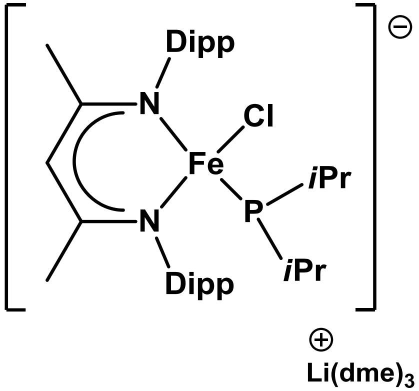
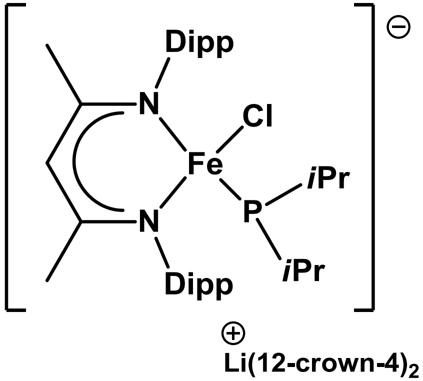
23	HASZUW	1993	$[(\eta^5\text{-Cp*})(CO)_2Fe\overline{PC(SiMe_3)_2C}=NPh]$		2.279(2)	pyramidal 283.54	[102]
28	HAZKOI	1993	$[(\eta^5\text{-Cp*})(CO)_2Fe\overline{PCH(CO_2Me)C(CO_2Me)=C}(NMe_2)]$		2.2983	pyramidal 294.48	[103]
	LIKXIM	1994	$[(\eta^5\text{-Cp*})(CO)_2Fe(PSiMe_3(C(CF_3)_2(OSiMe_3))]$		2.363(3)	pyramidal 333.51	[104]
24	POSVUO	1994	$[(\eta^5\text{-Cp})(CO)_2Fe\overline{PP(tBu)C}(Ph)(SiMe_3)]$		2.327(1)	pyramidal 281.17	[105]

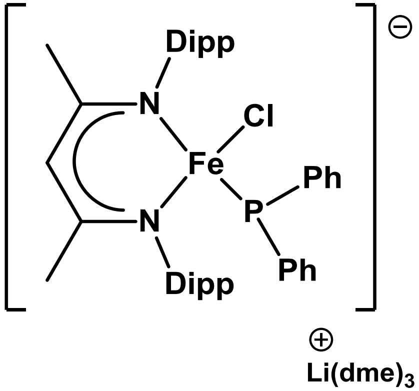
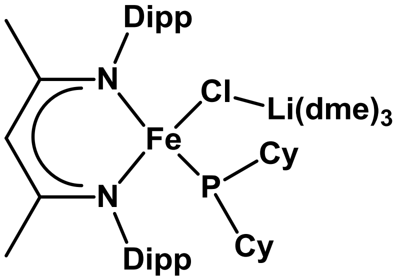
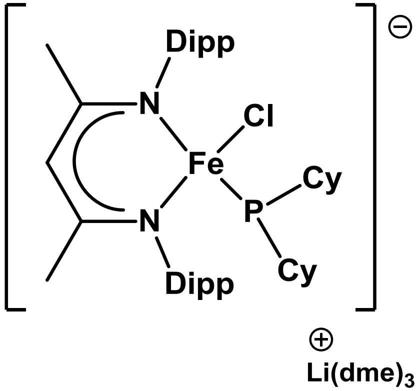
29	YIBVIO	1994	$[(\eta^5\text{-Cp*})(CO)_2Fe(\overline{PC(NMe_2)=C(CO_2Me)C}(=CH_2))]$		2.298(2)	pyramidal 298.28	[90]
25	YIFKED	1994	$[(\eta^5\text{-Cp*})(CO)_2Fe(\overline{PP(C(SiMe_3)_3)C}=NCF_3)]$		2.303(1)	pyramidal 271.45	[89]
26	YIFKIH	1994	$[(\eta^5\text{-Cp*})(CO)_2Fe\overline{PC(=N\text{-}o\text{-}Tol)P(Mes^*)C}(=N\text{-}o\text{-}Tol)]$		2.269(2)	pyramidal 316.75	[89]

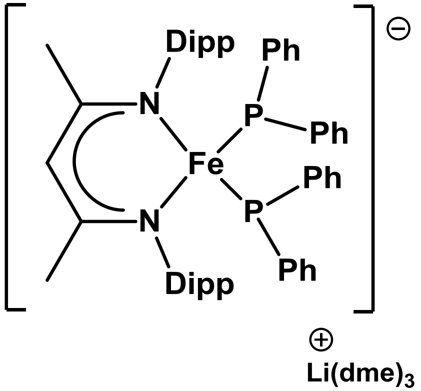
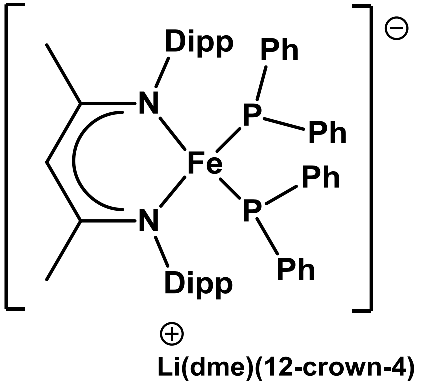
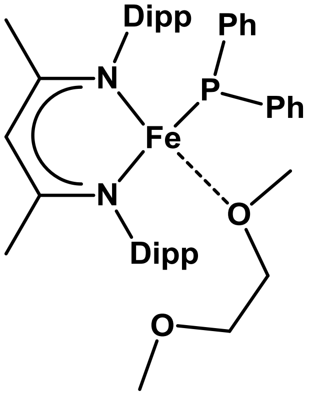
	YOJNOA	1995	$[((\eta^5\text{-}C_5Me_4CH=C(NMe)_2)P(N(CO_2\textit{t}Bu)NH(CO_2\textit{t}Bu))Fe]$		2.307(2)	pyramidal 311.97	[106]
	ZAHHUL	1995	$[(\eta^5\text{-}Cp^*)(CO)_2FeP(NHCH_2C_6H_5)(C(NHCH_2C_6H_5)=PMes^*)]$		2.3181(13)	pyramidal 319.15	[107]
	RUJQAO	1997	$[(\eta^5\text{-}Cp^*)(CO)_2FeP(H)SiFIs_2]$		2.323(2)	pyramidal 307.32	[37]

27	XOYKIF	2002	[(η^5-Cp*)(CO)$_2$Fe(PCH(CN)CH(CN)C(Ph)NMe$_2$)]		2.297(1)	pyramidal 302.62	[91]
	XOYKOL	2002	[(η^5-Cp*)(CO)$_2$Fe (P(CH(CN)CH$_2$CN)(CH(CN)C(CN)=C(*t*Bu)NMe$_2$)]		2.296(1)	pyramidal 314.84	[91]
	YAVDAB	2005	[(η^5-1,3-P$_2$C$_3$*t*Bu$_3$)Fe(P$_2$(PMe)$_2$(C*t*Bu)$_3$)]		2.3013(13)	pyramidal 272.45	[108]

	DORHEY	2008	[(η^5-Cp*)(CO)$_2$Fe(P(SiMe$_2$Ph)Ph)]		2.3284(11)	pyramidal 321.97	[109]
30	GUZCEL	2016	[(η^5-Cp*)(CO)Fe(PHPh$_2$)(PPh$_2$)]		2.3081(4)	pyramidal 321.85	[110]
32	DAKWOE	2017	[PhB(*t*BuIm)$_3$Fe(PHPh)]		2.4035(6)	planar 360	[38]
33	DAKWIY	2017	[PhB(Cy$_2$Im)$_3$Fe(PHPh)]		2.375(2)	pyramidal 311.52	[38]

14	MAZHON	2017	[(Dippnacnac)Fe(η^2-Me$_3$SiP-P*i*Pr$_2$)]		2.364(1)	pyramidal 332.28	[48]
6	KIQLII	2018	[(Dippnacnac)FeCl(P*i*Pr$_2$)][Li(dme)$_3$](dme)		2.4054(8)	pyramidal 316.50	[39]
7	KIQKIH	2018	[(Dippnacnac)FeCl(P*i*Pr$_2$)] [Li(12-crown-4)$_2$]		2.371(2)	pyramidal 321.49	[39]

8	KIQKON	2018	[(Dippnacnac)FeCl(PPh$_2$)][Li(dme)$_3$]		2.3827(6)	pyramidal 322.13	[39]
9	KIQKUT	2018	[(Dippnacnac)FeCl(PCy$_2$)Li(dme)$_2$](dme)		2.3770(9)	pyramidal 321	[39]
10	KIQLAA	2018	[(Dippnacnac)FeCl(PCy$_2$)][Li(dme)$_3$](dme)$_{1.5}$]		2.405(1)	pyramidal 322.79	[39]

11	KIQLEE	2018	[(Dippnacnac)Fe(PPh$_2$)$_2$][Li(dme)$_3$]		2.367(1) 2.473(1)	pyramidal 338.88 337.42	[39]
12	KIQLOO	2018	[(Dippnacnac)Fe(PPh$_2$)$_2$]$_2$ [Li(12-crown-4)(dme)][Li(dme)$_3$]		2.375(2) 2.454(2)	pyramidal 332.33 338.87	[39]
13	KIQMAB	2018	[(Dippnacnac)Fe(PPh$_2$)(dme)]		2.3663(6)	pyramidal 325.75	[39]

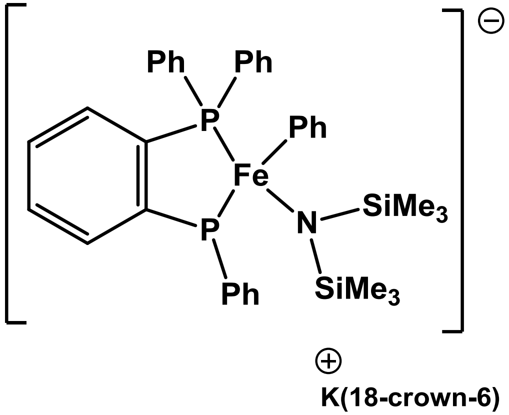
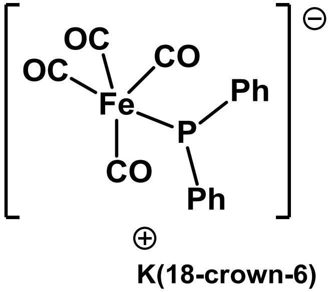
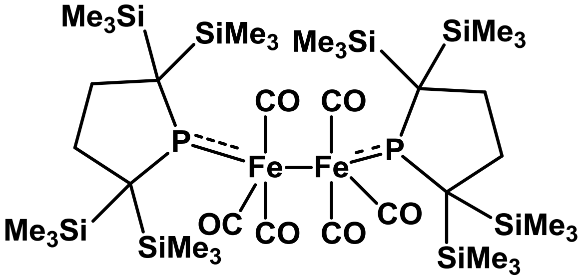
	FUGDUJ	2020	[Fe(Ph)(N(SiMe$_3$)$_2$)(ppbz*)][K(18-crown-6)](Et$_2$O)$_2$		2.4096(5)	pyramidal 324.25	[111]

Table 3. Crystalographically determined five-coordinate iron complexes with non-bridging ligands (bond lengths and bond angles taken from the CSD cif file)

Number in the publication	CSD refcode	Publication year	Complex		Fe-P$_{\text{phosphanido}}$ bond length [Å]	Geometry of P$_{\text{phosphanido}}$ ΣP$_{\text{phosphanido}}$ [°]	Ref.
	ZUYYIB	1996	[(CO)$_4$Fe(PPh$_2$)][K(18-crown-6)](thf)		2.359(2)	pyramidal 318.36	[93]
34	LITDUB	2016	[Fe(CO)$_3$(2,2,5,5-(SiMe$_3$)-1-phoshacyclopentane)]$_2$		2.0934(12) 2.1047(13)	planar 358.55 358.71	[94]

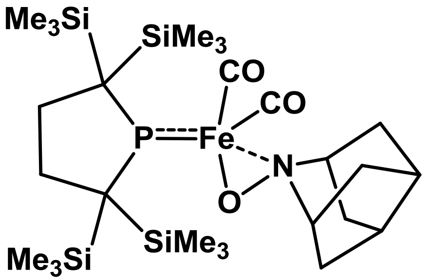
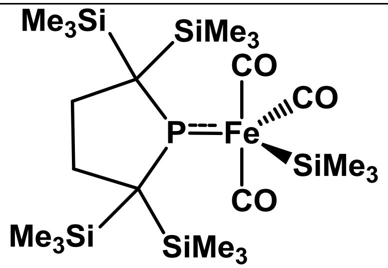
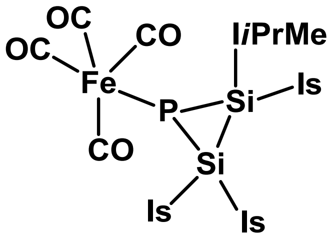
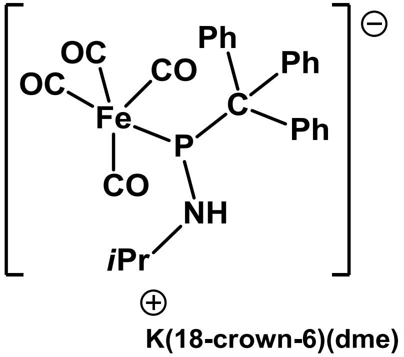
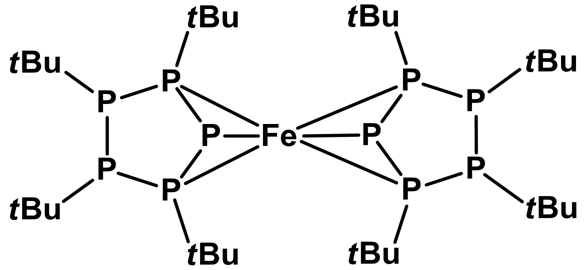
35	LITFAJ	2016	[Fe(CO)$_2$(κ^2-nor-AZADO)(2,2,5,5-(SiMe$_3$)-1-phoshacyclopentane)]		2.1205(4)	planar 358.10	[94]
36	LITFEN	2016	[(Me$_3$Si)Fe(CO)$_3$(2,2,5,5-(SiMe$_3$)-1-phoshacyclopentane)]		2.1009(7)	planar 359.92	[94]
	HIWZUL	2018	[(CO)$_4$Fe(PSi(Is)$_2$Si(Is)(I*i*PrMe))]		2.2874(4)	pyramidal 350.38	[112]
37	RISQAO	2018	[(CO)$_4$Fe(P(CPh$_3$)(NH*i*Pr))] [K(18-crown-6)(dme)](thf)$_2$		2.3895(8)	pyramidal 320.08	[95] [96]

Table 4. Crystalographically determined six-coordinate iron complexes with nonbridging ligands (bond lengths and bond angles taken from the CSD cif file)

Number in the publication	CSD refcode	Publication year	Complex		Fe-P$_{phosphanido}$ bond length [Å]	Geometry of P$_{phosphanido}$ ΣP$_{phosphanido}$ [°]	Ref.

38	JOHROP	2014	[Fe{*cyclo*-(P$_5$*t*Bu$_4$)}$_2$]		2.4028(4)	distorted pyramidal 198.98	[62]

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