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Reactivity of Iron Complexes containing Monodentate Aminophosphine Ligands - Formation of Four-Membered Carboxamido-Phospha-Metallacycles

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Abstract

Treatment of $[FeCp(CO)_2Cl]$ with 1 equiv of the amidophosphine ligands $Li[R_2PNR']$ (R = Ph, *i*Pr, R' = *i*Pr, *t*Bu, Cy) afforded complexes of the type $[FeCp(CO)(\kappa^2(C,P)\text{-}(C{=}O)\text{-}N\textit{i}Pr\text{-}PPh_2)]$ (**1a**), $[FeCp(CO)(\kappa^2(C,P)\text{-}(C{=}O)\text{-}N\textit{t}Bu\text{-}PPh_2)]$ (**1b**), and $[FeCp(CO)(\kappa^2(C,P)\text{-}(C{=}O)\text{-}NCy\text{-}P\textit{i}Pr_2)]$ (**1c**) in 40-50% yields. Complex **1a** was also formed when $[FeCp(CO)_2(PPh_2NH\textit{i}Pr)]^+$ (**2**) was reacted with 1 equiv of KO*t*Bu. These complexes feature a four-membered carboxamido-phospha-ferracycle as a result of an intramolecular nucleophilic attack of the amidophosphine ligand on coordinated CO. Upon treatment of **1a** with the electrophile $[Me_3O]BF_4$ the aminocarbene complex $[FeCp(CO)(\kappa^2(C,P)\text{=}C(OMe)\text{-}N\textit{i}Pr\text{-}PPh_2)]^+$ (**3**) was obtained bearing an aza-phospha-carbene moiety. Upon treatment of *cis,trans,cis*-$[Fe(CO)_2(Ph_2PNH\textit{i}Pr)_2(Br)_2]$ (**4a**) and *cis,trans,cis*-$[Fe(CO)_2(Ph_2PNH\textit{t}Bu)_2(Br)_2]$ (**4b**) with KO*t*Bu the carboxamido-phospha-ferracycles *trans*-$[Fe(CO)_2(\kappa^2(C,P)\text{-}(C{=}O)\text{-}N\textit{i}Pr\text{-}PPh_2)(Ph_2PNH\textit{i}Pr)Br]$ (**5a**) and *trans*-$[Fe(CO)_2(\kappa^2(C,P)\text{-}(C{=}O)\text{-}N\textit{t}Bu\text{-}PPh_2)(Ph_2PNH\textit{t}Bu)Br]$ (**5b**) were formed in moderate yield. Finally, representative structures were determined by X-ray crystallography.

Keywords: Iron, cyclopentadienyl, carbon monoxide, aminophosphines, nucleophilic attack, ferracycles

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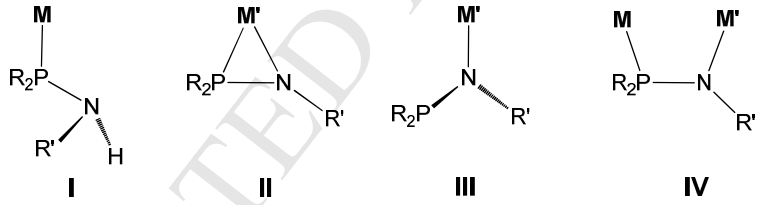
1. Introduction

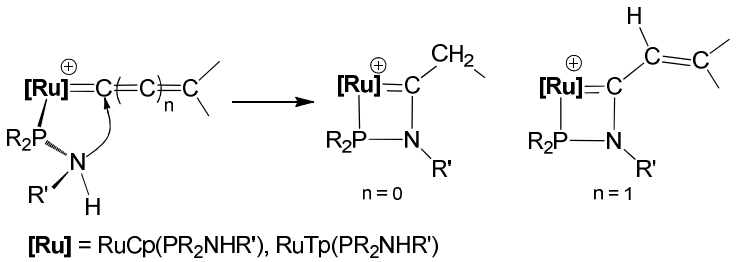
Aminophosphines of the type PR_2NHR' containing a direct polar P(III)-N bonds have received considerable attention in recent years as versatile ligands for transition metals [1].They are accessible in large quantities through the use of relatively simple condensation processes from inexpensive starting materials, i.e., primary amines and PR_2Cl compounds which contain dialkyl or diaryl substituents as well as achiral and chiral P-O and P-N containing phosphine units. Thus, variations of electronic, steric, and stereochemical parameters may be achieved in a very facile fashion. Due to their soft/hard donor atoms as well their acidic NH hydrogen, these polyfunctional ligands exhibit numerous coordination modes as illustrated in Scheme 1. As middle and late transition metals **M** are concerned PR_2NHR' ligands typically coordinate in $\kappa^1(P)$-fashion **I** [2],while $\kappa^1(N)$-coordination is unknown. Upon deprotonation of the PR_2NHR' ligands, anionic amidophosphines $[PR_2NR']^-$ are readily obtained which exhibit a higher affinity towards electropositive metals due to their increased nucleophilicity at the N-site. Thus, in conjunction with early transition metals **M'**, amidophosphine ligands were shown to display $\kappa^2(P,N)$ coordination **II**, and, albeit less common, also $\kappa^1(N)$-coordination **III**, while in the presence of both early and middle/late transition metals, amidophosphine ligands were shown to act as μ^2 bridging ligand thereby forming heterobimetallic complexes of the type **IV** [3,4].

Scheme 1



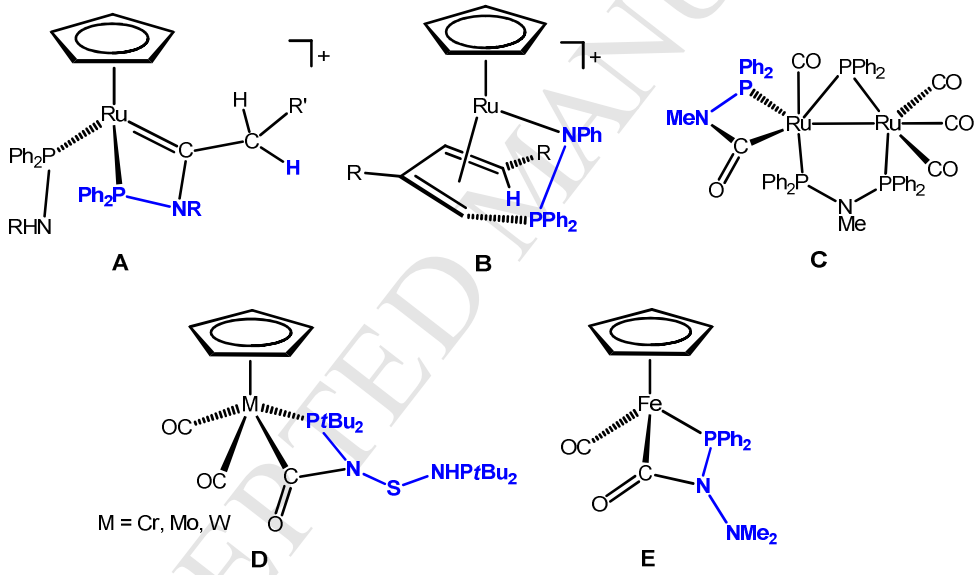
Besides interesting structural features, PR_2NHR' ligands display various reactivities opening up a range of synthetically useful transformations [5]. For instance, we have recently shown [6] that in vinylidene and allenylidene complexes $[RuCp(PPh_2NHR)_2(=C=(C)_n=CHR')]^+$ and $[RuTp(PPh_2NHR)_2(=C=(C)_n=CHR')]^+$ (n = 0, 1; R = Ph, *n*-Pr; R' = alkyl, aryl; Tp = trispyrazoloylborate) an intramolecular addition of the NHR' moiety to the α-carbon of the cumulene moiety takes place (Scheme 2) resulting in the formation of novel four-membered aza-phospha-carbenes (Scheme 3, **A**). Complexes of the types $[RuCp(PPh_2NHPh)(CH_3CN)_2]^+$ and $[RuCp^*(PR_2NHR')(CH_3CN)_2]^+$ (R = Ph, *i*-Pr, R' = Ph, C_6F_5) have been found to react with terminal alkynes and diynes to give amido butadiene complexes involving PR_2NHR' ligand migration (Scheme 3, **B**) [7,8]. Bunten *et al* reported [9] the synthesis of the dinuclear ruthenium complex $[Ru_2(CO)_3(\mu^2\text{-}PPh_2)(\mu^2\text{-}Ph_2PNMePPh_2)(\kappa^2(C,P)\text{-}C(=O)NMePPh_2)]$ containing a carboxamido-phospha-ruthenacyclic moiety (Scheme 3, **C**). Herberhold *et al* reported on the preparation of half sandwich complexes of the type $[MCp(CO)_2(C(=O)N(S\text{-}NHP\textit{t}Bu_2)P\textit{t}Bu_2)]$ (M = Cr, Mo, W) by reacting $[MCp(CO)_3H]$ with $P\textit{t}Bu_2PN=S=NP\textit{t}Bu_2$

Scheme 2



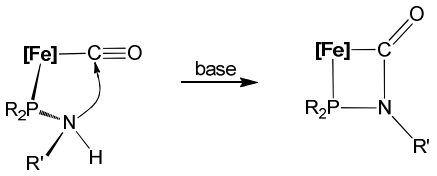
(Scheme 3, **D**) [10]. As iron complexes are concerned, $[FeCp(CO)_2(PPh_2NHNMe_2]^+$ bearing a hydrazinophosphine ligand, which is closely related to PR_2NHR' ligands, was shown to react with *n*BuLi to give the carboxamido-phospha-ferracycle $[FeCp(CO)(\kappa^2(C,P)$-(C=O)-$NNMe_2$-$PPh_2)]$ (Scheme 3, **E**) [11].

Scheme 3



In the present paper we report on the synthesis of iron(II) complexes containing aminophosphine ligands of the type PR_2NHR' with R = Ph, *i*Pr, R'= *i*Pr, *t*Bu, Cy. We describe the reactivity of these complexes yielding, upon treatment with strong bases, novel cyclic four-membered carboxamido-phospha-ferracycle formed via intramolecular addition of the amine moiety of the bifunctional aminophosphine ligand according to Scheme 4.

Scheme 4

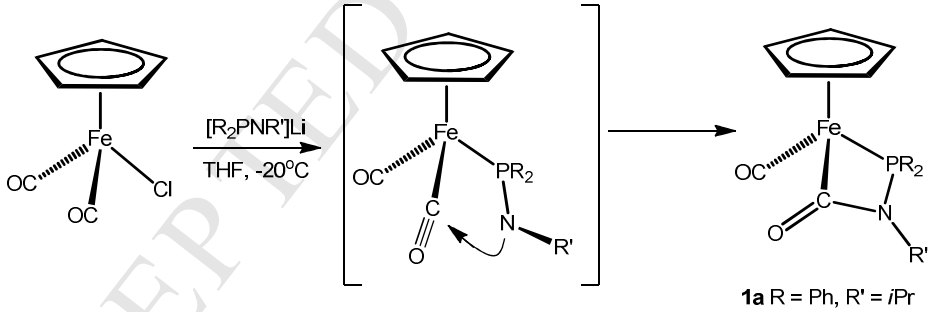


[Fe] = $[FeCp(CO)_2]^+$, $Fe(CO)_2(Br)_2(PR_2NHR')$

2. Results and discussion

Treatment of $[FeCp(CO)_2Cl]$ with 1 equiv of the amidophosphine ligands $[R_2PNR']^-$ (R = Ph, *i*Pr, R' = *i*Pr, *t*Bu, Cy), prepared *in situ* by the reaction of R_2PNHR' with *n*BuLi in THF at -20°C, afforded complexes of the type $[FeCp(CO)(\kappa^2(C,P)\text{-}(C{=}O)\text{-}N\textit{i}Pr\text{-}PPh_2)]$ (**1a**), $[FeCp(CO)(\kappa^2(C,P)\text{-}(C{=}O)\text{-}N\textit{t}Bu\text{-}PPh_2)]$ (**1b**), and $[FeCp(CO)(\kappa^2(C,P)\text{-}(C{=}O)\text{-}NCy\text{-}P\textit{i}Pr_2)]$ (**1c**) in reasonable isolated yields (40-50%) (Scheme 5). Although no intermediate could be detected spectroscopically, it is most likely that the deprotonated R_2PNHR' ligand first forms a complex with a $\kappa^1(P)$-bound rather than a $\kappa^1(N)$-bound amidophosphine. It has to be noted that $\kappa^1(N)$ coordinated $[PR_2NR']^-$ ligands to late transition metals are, according to our knowledge, unknown.

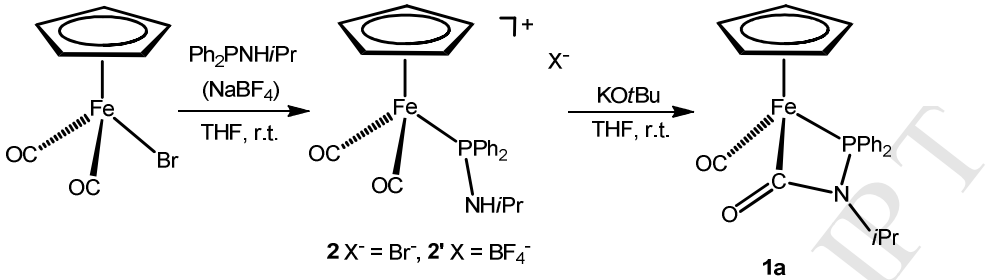
Scheme 5



1a R = Ph, R' = *i*Pr
1b R = Ph, R' = *t*Bu
1c R = *i*Pr, R' = Cy

Subsequently, intramolecular, chelate assisted, nucleophilic attack of the amido moiety of the PR_2NR' ligand at one of the two CO ligands took place resulting in the formation of novel four-membered carboxamido-phospha-ferracycle. This is also supported by the fact that **1a** is readily formed if the cationic dicarbonyl complex $[FeCp(CO)_2(PPh_2NH\textit{i}Pr)]^+$ with either Br^- (**2**) or BF_4^- (**2'**) as counterions was treated with KO*t*Bu as base according to Scheme 6. In the absence of base, even at elevated temperatures, no reaction took place. Complexes **2** and **2'** were readily obtained by the treatment of $[FeCp(CO)_2Br]$ with 1 equiv of the $PPh_2NH\textit{i}Pr$ ligand in the absence or presence of $NaBF_4$, respectively, in THF at room temperature (Scheme 6).

Scheme 6

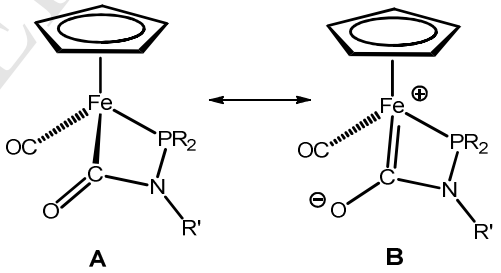


2 $X^- = Br^-$, **2'** $X = BF_4^-$ **1a**

All complexes are thermally robust orange solids that are air stable both in the solid state and in solution for several days. Their identity was unequivocally established by ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR, IR spectroscopy, and elemental analysis. In addition, the molecular structures of complexes **1a** and **2** were determined by X-ray crystallography. Structural views are depicted in Figures 1 and 2 with selected bond distances and angles reported in the captions.

Complexes **1a-c** display a single resonance in the $^{31}P\{^{1}H\}$ NMR at 111.6, 113.0, and 140.0 ppm, respectively. In the $^{13}C\{^{1}H\}$ NMR spectra, the Cp ring gives rise to a singlet in the range of about 80 - 82 ppm. The CO ligands exhibit a low-field doublet at 220.9, 221.0, and 221.0 ppm with coupling constants J_{PC} of 24.4 - 26.4 Hz, while the resonance of the carboxamido carbon atoms give rise to a doublet centered at 200.4 (J_{PC} = 39.0 Hz), 201.1 (J_{PC} = 45.8 Hz), and 199.8 ppm (J_{PC} = 37.8 Hz), respectively. In the IR spectrum, the characteristic CO stretching frequency of the CO ligand and the carboxamido unit was observed at 1937, 1919, and 1914 cm^{-1} and 1617, 1605, and 1618 cm^{-1}, respectively. For comparison, the IR stretching frequency of the carboxamido unit in [FeCp(CO)(κ^2(*C,P*)-(C=O)-$NNMe_2$-PPh_2)] was found at 1642 cm^{-1} [11].

Scheme 7



A **B**

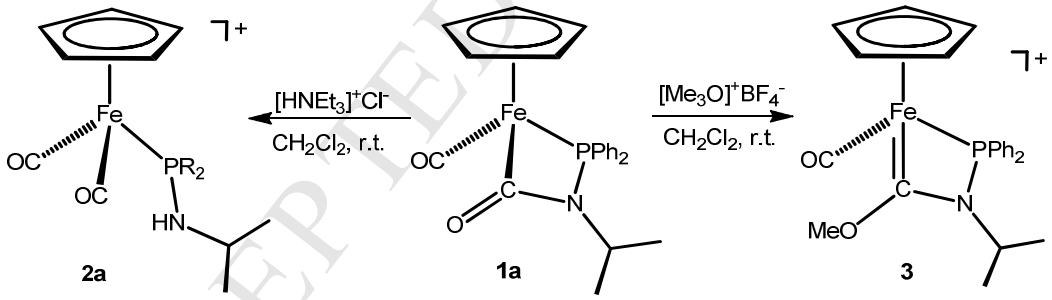
Complex **1a** adopts a typical three legged piano stool conformation with the C and P atoms of the C(=O)N*i*Pr-PPh_2 moiety and the C atom of the CO ligand as the legs (Figure 1). The Fe1-C(Cp) distance on average is 2.101(1) Å. The iron carbon bond distances Fe1-C6 and Fe1-C7 are 1.739(1) and 1.981(1) Å, respectively, the latter being typical for an iron carbon single bond. Thus, also in agreement with the NMR and IR spectroscopic data, **1a** is best described as a carboxamido complex (**A**) rather than an aminocarbene complex (**B**) (Scheme

7). The Fe1-P1 bond distance of 2.1773(3) Å is typical for iron phosphine complexes but slightly shorter than Fe1-P1 = 2.2223(4) Å in the parent complex **2** (Figure 2). The C7-Fe1-P1 bite angle of the chelating C(=O)N*i*Pr-PPh_2 ligand is 69.43(4)°. For comparison, in the related complex [FeCp(CO)(κ^2(*C,P*)-(C=O)-$NNMe_2$-PPh_2)] the bite angle is 70.5(1)°.

Since acyl and carbamoyl ligands are typically nucleophilic at the carbonyl oxygen, *i.e.*, resonance structure **B** may play a role, the reaction with carbon-based electrophiles may lead to amino carbene complexes. It has to be kept in mind however that an electrophilic attack may occur also at the N atom of the carboxamido moiety resulting in P-N bond cleavage with concomitant N-alkylation.

Treatment of **1a** with $[Me_3O]BF_4$ (1 equiv) at room temperature for 4 h in CH_2Cl_2 as the solvent results in the formation of the aza-phospha-carbene complex [FeCp(CO)(κ^2(*C,P*)=C(OMe)-N*i*Pr-PPh_2)]$^+$ (**3**) in 58% isolated yield (Scheme 8). This class of complexes belongs to a rare series of transition metal complexes in which the carbene moiety is part of a four-membered chelate ligand coordinated in a κ^2(*C,P*) mode [6,7,12]. Complex **3** was characterized by elemental analysis and by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. Characteristic features comprise, in the ^{13}C{^{1}H} NMR spectrum, a marked low-field doublet resonance at 238.0 ppm (d, J_{CP} = 34.8 Hz) assignable to the carbene carbon atom of the four-membered aza-phospha-carbene moiety. The carbonyl resonance gives rise to a doublet centered at 216.3 ppm (d, J_{CP} = 22.2 Hz). The ^{31}P{^{1}H} NMR spectrum of **3** reveals a singlet at 115.0 ppm (*cf*. 111.6 ppm in **1a**).

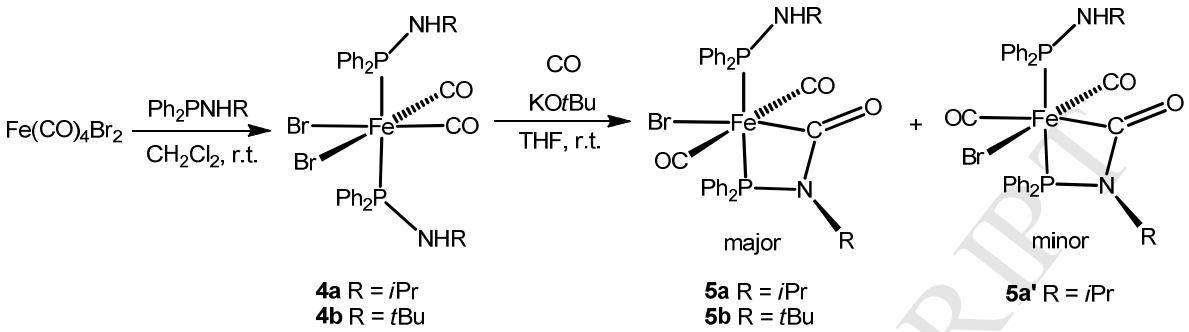
Scheme 8



On the other hand, protonation of **1a** with the Brønsted acid $[HNEt_3]^+$ led to clean formation of complex **2a** in 95% isolated yield (Scheme 8). Selective N-protonation took place which was associated with C-N bond cleavage and reformation of the CO and Ph_2PNH*i*Pr ligands.

In search of related iron systems where carboxamido-phospha-cycles may also be formed via nucleophilic attack of a κ^1(*P*)-coordinated PR_2NHR' ligand, we prepared complexes of the type *cis,trans,cis*-[$Fe(CO)_2(Ph_2PNHiPr)_2(Br)_2$] (**4a**) and *cis,trans,cis*-[$Fe(CO)_2(Ph_2PNHtBu)_2(Br)_2$] (**4b**). These compounds were readily obtained as red, air stable solids by reacting *cis*-[$Fe(CO)_4(Br)_2$] with 2 equivs of the respective PR_2NHR' ligands in 85 and 88% yield (Scheme 9) in CH_2Cl_2 at room temperature. In these complexes the CO and bromide ligands are in a mutual *cis* position, whereas the phosphine ligands are *trans* to one another.

Scheme 9



Treatment of **4a** with 2 equivs of KO*t*Bu in the presence of CO in THF at room temperature afforded the isomeric complexes *trans*-[Fe(CO)$_2$(κ^2(*C,P*)-(C=O)-N*i*Pr-PPh$_2$)(Ph$_2$PNH*i*Pr)Br] (**5a**) and *cis*-[Fe(CO)$_2$(κ^2(*C,P*)-(C=O)-N*i*Pr-PPh$_2$)(Ph$_2$PNH*i*Pr)Br] (**5a'**) in a roughly 5:1 ratio in 50% overall yield. In agreement with experimental data DFT/B3LYP calculations confirm that the isomer with a *trans* CO arrangement is slightly more stable by 2.5 kcal/mol (free energy) than the corresponding *cis* isomer. In the case of **4b** only one isomer, *viz trans*-[Fe(CO)$_2$(κ^2(*C,P*)-(C=O)-N*t*Bu-PPh$_2$)(Ph$_2$PNH*t*Bu)Br] (**5b**), was formed in 40% yield (Scheme 9). These reactions again involve attack of the amido moiety of a deprotonated PR$_2$NHR' ligand on coordinated CO. It has to be mentioned that the yields of **5a** and **5b** were independent of whether 1 or 2 equivs of KO*t*Bu were used, i.e., complexes such as [Fe(CO)$_2$(κ^2(*C,P*)-(C=O)-N*i*Pr-PPh$_2$)$_2$], were not observed. Complexes **5a** and **5b** are thermally robust red solids that are air stable in the solid state but slowly decompose in solution. Their identity was unequivocally established by ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR, IR spectroscopy, and elemental analysis.

In the ^{13}C{^{1}H} NMR spectrum of the major isomer **5a** the most noticeable resonances are a low-field signal of the two *trans* CO ligands observed as triplet centered at 212.4 ppm with a P-C coupling constants of 22.7 Hz. The resonance of the carboxamido moiety give rise to a doublet of doublets centered at 206.0 ppm with P-C couplings constant of 9.6 and 13.4 Hz. The ^{31}P{^{1}H} NMR spectrum of **5a** reveals two doublets centered at 95.6 and 85.8 ppm with a large coupling constant of 84.7 Hz which is indicative for the phosphorus atoms being in a mutual *trans* position. Most ^{1}H and ^{13}C{^{1}H} NMR of resonances of the minor isomer **5a'** could not be reliably assigned since they were superimposed by the signals of the major isomer **5a**. In the ^{31}P{^{1}H} NMR spectrum, however, **5a'** also exhibits two doublets centered at 94.8 (d, J_{PP} = 115.9 Hz) and 90.0 ppm (d, J_{PP} = 115.9 Hz). The large coupling constant again is consistent with a *trans*-P,P configuration. Similar NMR spectra were observed for **5b**, and are thus not discussed here. In the IR spectrum of **5a** and **5b** the two CO ligands give rise to two bands at 1966 and 1960 cm^{-1} (**5a**) and 1955 and 1950 cm^{-1} (**5b**) which can be assigned to the asymmetric CO stretching frequency (*cf* 2143 cm^{-1} in free CO). As expected the symmetric CO stretching frequency is IR inactive which is also confirmed by DFT/B3LYP calculations. The appearance of two the resonances, which are only 5-6 cm^{-1} apart, may be due to intermolecular interactions, e.g. C=O···HN bonds, in the solid state [13]. The CO vibration of the carboxamido phospha cycle is shifted to lower wavenumbers

observed at 1619 and 1616 and cm^{-1}, respectively. The scaled calculated frequencies ν_{CO} together with the experimentally observed values are given in Table 1 and show a reasonably good agreement.

Table 1. Comparison of the DFT/B3LYP calculated and experimental ν_{CO} absorptions of **5a**.

	$\nu_{CO\ sym}/cm^{-1}$	$\nu_{CO\ asym}/cm^{-1}$	$\nu_{NC=O}/cm^{-1}$
calcd.	2022	1980	1615
exptl.	not observed	1966/1960	1616

The molecular structure of complex **5a** was determined by X-ray crystallography. A structural view is depicted in Figure 3 with selected bond distances and angles reported in the caption. The geometry about the metal center is distorted octahedral with the two phosphorus and carbon atoms in *trans* position and the bromide and carbon atom of carboxamido moiety atoms in *cis* position (Figure 3). The C32-Fe1-C33 bond angle is 170.6(2)°.The chelate system Fe1-P1-N1-(C31=O1)-Fe1 resembles closely in bond lengths and bond angles the corresponding system in complex **1a**, except for the bond Fe1-P1, which is 2.1773(3) Å in **1a** while it is 2.2480(9) Å in **5a** due to the *trans*-influence of phosphorus P2 (Fe1-P2 = 2.2651(9) Å). The short intramolecular hydrogen bond N2-H2n···O1 in **5a** (N2···O1 = 2.839(4) Å) has no effect on the bond angle Fe1-C31-O1 = 134.2(2)° as evident from the correspondin g angle 133.8(1)° in complex **1a** which lacks this interaction.

3. Conclusion

In the present study iron(II) complexes featuring one or two aminophosphine ligands of the type PR_2NHR' with R = Ph, *i*Pr and R = *i*Pr, *t*Bu, Cy were synthesized. We demonstrated that upon treatment of $[FeCp(CO)_2X]$ (X = Cl, Br) with the anionic amidophosphine ligands $[R_2PNR']^-$, or upon deprotonation of the PR_2NHR' ligand in complexes $[FeCp(CO)_2(PR_2NHR'_2)]^+$ and *cis,trans,cis*-$[Fe(CO)_2(Ph_2PNHR')_2(Br)_2]$ complexes featuring four-membered carboxamido-phospha-ferracycles were obtained. In the course of these reactions the highly nucleophilic amido nitrogen atom reacted readily in an intramolecular fashion with the electrophilic carbon atom of a CO ligand. We have further demonstrated that the carboxamido-phospha-ferracycles react with the carbon-based electrophile $[Me_3O]^+$ to afford an aza-phospha-carbene. This is a relatively rare type of transition metal complexes in which the carbene moiety is part of a four-membered chelate ligand coordinated in a $\kappa^2(C,P)$ mode. In the presence of protons, the carboxamido-phospha-ferracycle underwent clean C-N bond cleavage thereby reforming the starting complex $[FeCp(CO)_2(PR_2NHR'_2)]^+$.

4. Experimental

4.1. General

All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. The solvents were purified according to standard procedures [14]. The ligands PPh_2NHiPr, PPh_2NHtBu, and PPh_2NHCy [15] and the complexes $[FeCp(CO)_2Cl]$, of $[FeCp(CO)_2Br]$ [16], and *cis*-$[Fe(CO)_4Br_2]$ [17] were prepared according to the literature. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker AVANCE-250 and AVANCE-300 DPX spectrometers and were referenced to $SiMe_4$ and H_3PO_4 (85%), respectively.

4.2. Syntheses

*[FeCp(CO)(κ²(C,P)-(C=O)-NiPr-PPh₂)] (**1a**)*

A solution of PPh_2NHiPr (300 mg, 1.23 mmol) in THF (20 mL) was cooled to -20°C and *n*BuLi (500 µL, 1.23 mmol, 2.5 M solution in *n*-hexane) was slowly added. The solution was stirred for 2h at -20°C and an additional hour at room temperature. After that, $[FeCp(CO)_2Cl]$ (262 mg, 1.23 mmol) was added and the mixture was stirred for 8h at room temperature. The solvent was then removed under reduced pressure. The residue was redissolved in toluene (10 mL) and the solution was filtered through Celite. After removal of the solvent under reduced pressure, an orange solid was obtained which was washed with *n*-pentane (10 mL) and dried under vacuum. Yield: 207 mg (40%). Anal. calcd. for $C_{22}H_{22}FeNO_2P$: C, 63.03; H, 5.29; N, 3.34. Found: C, 63.09; H, 5.12; N, 3.28. ^1H NMR (δ, $CDCl_3$, 20°C): 7.87 (m, 4H, Ph), 7.51 (m, 6H, Ph), 4.38 (s, 5H, Cp), 3.49 (m, 1H, C*H*$(CH_3)_2$), 1.29 (d, J = 5.8 Hz, 3H, CH(C*H*$_3)_2$), 0.99 (d, J = 6.7 Hz, 3H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 220.9 (d, J_{PC} = 26.0 Hz, *C*O), 200.4 (d, J_{PC} = 39.0 Hz, N*C*O), 137.2 (d, J_{PC} = 40.6 Hz, Ph), 133.8 (d, J_{PC} = 13.5 Hz, Ph), 131.8 (d, J_{PC} = 2.7 Hz, Ph), 130.7 (d, J_{PC} = 13.5 Hz, Ph), 130.4 (d, J_{PC} = 2.7 Hz, Ph), 128.6 (d, J_{PC} = 9.5 Hz, Ph), 128.4 (d, J_{PC} = 7.5 Hz, Ph), 82.1 (s, Cp), 50.7 (d, J_{PC} = 8.1 Hz, *C*H$(CH_3)_2$), 23.0 (s, CH(*C*H$_3)_2$), 21.4 (s, CH(*C*H$_3)_2$). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 111.6. IR (ATR, 25°C): 1937 ($\nu_{C=O}$), 1617 ($\nu_{C=O}$).

*[FeCp(CO)(κ²(C,P)-(C=O)-NtBu-PPh₂)] (**1b**)*

This complex was prepared analogously to **1a** with $[FeCp(CO)_2Cl]$ (400 mg, 1.55 mmol) and $Ph_2PNHtBu$ (400 mg, 1.55 mmol), and *n*BuLi (630 µL, 1.48 mmol, 2.5 M solution in *n*-hexane) as starting materials. Yield: 335 mg (50%). Anal. calcd for $C_{23}H_{24}FeNO_2P$: C, 63.76; H, 5.58; N, 3.23. Found: C, 63.66; H, 5.63; N, 3.19. ^1H NMR (δ, $CDCl_3$, 20°C): 7.90 (m, 4H, Ph), 7.48 (m, 6H, Ph), 4.39 (s, 5H, Cp), 1.20 (s, 9H, C(C*H*$_3)_3$). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 221.0 (d, J_{PC} = 24.4 Hz, *C*O), 201.1 (d, J_{PC} = 45.8 Hz, N*C*O), 136.4 (d, J_{PC} = 39.3 Hz, Ph), 133.8 (d, J_{PC} = 41.3 Hz, Ph), 132.7 (d, J_{PC} = 12.5 Hz, Ph), 131.2 (d, J_{PC} = 3.2 Hz, Ph), 130.7 (d, J_{PC} = 11.7 Hz, Ph), 130.3 (d, J_{PC} = 3.2 Hz, Ph), 128.6 (d, J_{PC} = 7.4 Hz, Ph), 128.4 (d, J_{PC} = 5.8 Hz,

Ph), 82.8 (s, Cp), 65.8 (s, *C*H(CH_3)$_2$), 29.5 (s, CH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 113.0. IR (ATR, 25°C): 1919 ($\nu_{C=O}$), 1605 ($\nu_{C=O}$).

*[FeCp(CO)(κ^2(C,P)-(C=O)-NCy-PiPR$_2$)] (**1c**)*

This complex was prepared analogously to **1a** with [FeCp(CO)$_2$Cl] (370 mg, 1.75 mmol), Ph_2PNHCy (376 mg, 1,75 mmol), and *n*BuLi (700 μL, 1.75 mmol, 2.5 M solution in *n*-hexane) as starting materials. Yield: 307 mg (45%). Anal. calcd for $C_{19}H_{30}FeNO_2P$: C, 58.48; H, 7.49; N, 3.59. Found: C, 58.53; H, 7.40; N, 3.62. ^1H NMR (δ, $CDCl_3$, 20°C): 4.61 (s, 5H, Cp), 2,93 (m, 1H, NC*H*), 2.54 (m, 1H, C*H*(CH_3)$_2$), 2.18 (m, 1H, C*H*(CH_3)$_2$), 1,69 (bs, 4H, Cy), 1,53 (bs, 6H, Cy), 1.32 (d, *J* = 11.0 Hz, 3H, CH(C*H*$_3$)$_2$), 1.30 (s, 1H, Cy), 1.25 (d, *J* = 7.3 Hz, 3H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 221.0 (d, J_{PC} = 26.4 Hz, *C*O), 199.8 (d, J_{PC} = 37.8 Hz, N*C*O), 80.8 (s, Cp), 58.5 (d, J_{PC} = 8.1 Hz, N*C*), 32.7 (d, J_{PC} = 71.9 Hz, *C*H(CH_3)$_2$), 30.6 (d, J_{PC} = 19.3 Hz, Cy), 27.9 (d, J_{PC} = 15.9 Hz, Cy), 26.8 (s, Cy), 25.3 (s, Cy), 20.4 (d, J_{PC} = 5.7 Hz, CH(*C*H$_3$)$_2$), 18.7 (s, Cy), 18.0 (d, J_{PC} = 5.74 Hz, CH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 140.0. IR (ATR, 25°C): 1914 ($\nu_{C=O}$), 1618 ($\nu_{C=O}$).

*[FeCp(CO)$_2$(Ph$_2$PNHiPr)]Br (**2**)*

To a solution of [FeCp(CO)$_2$Br] (1.00 g, 3.89 mmol) in THF (10 mL) Ph_2PNH*i*Pr (995 mg, 4.01 mmol) was added and the reaction mixture was stirred overnight at room temperature. Removal of the solvent afforded **2** as a yellow solid. Yield: 1.75 g (90%). Anal. calcd for $C_{22}H_{23}BrFeNO_2P$: C, 52.94; H, 4.44; N, 2.81. Found: C, 53.04; H, 4.39; N, 2.85. ^1H NMR (δ, $CDCl_3$, 20°C): 7.61-7.53 (m, 10H, Ph), 5.96 (d, *J* = 10.2 Hz, 1H, N*H*), 5.27 (s, 5H, Cp), 2.99 (bs, 1H, CH(C*H*$_3$)$_2$), 1.16 (d, *J* = 5.4 Hz, 6H, CH(C*H*$_3$)$_2$).). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 210.3 (d, J_{PC} = 27.1 Hz, *C*O), 135.0 (d, J_{PC} = 59.1 Hz, Ph), 131.7 (d, J_{PC} = 10.4 Hz, Ph), 131.3 (d, J_{PC} = 10.7 Hz, Ph), 129.0 (d, J_{PC} = 10. 9 Hz, Ph), 88.7 (s, Cp), 48.8 (d, J_{PC} = 9.6 Hz, *C*H(CH_3)$_2$), 24.8 (d, J_{PC} = 3.52 Hz, CH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 100.6. IR (ATR, 25°C): 2040 ($\nu_{C=O}$), 1993 ($\nu_{C=O}$).

*[FeCp(CO)$_2$(Ph$_2$PNHiPr)]BF$_4$ (**2'**)*

This complex was prepared analogously to **2** with [FeCp(CO)$_2$Br] (350 mg, 1.65 mmol) and Ph_2PNH*i*Pr (400 mg, 1.65 mmol) as starting materials but in the presence of $NaBF_4$ (182 mg, 1.65 mmol). Yield: 600 mg (72%). Anal. calcd for $C_{22}H_{23}BF_4FeNO_2P$: C, 52.11; H, 4.17; N, 2.76. Found: C, 52.14; H, 4.08; N, 2.80. NMR and IR spectra were identical to those of **2**.

*Reaction of [FeCp(CO)$_2$(Ph$_2$PNHiPr)]BF$_4$ with KOtBu. Formation of [FeCp(CO)(κ^2(C,P)-(C=O)-NiPr-PPh$_2$)] (**1a**)*

A solution of [FeCp(CO)$_2$(Ph_2PNH*i*Pr)]BF_4 (**2a'**) (220 mg, 0.44 mmol) in THF (10 mL) was treated with KO*t*Bu (55 mg, 0.48 mmol) and was stirred for 8 h. The solvent was removed under vacuum and the crude product was redissolved in toluene and filtered through Celite. After removal of the solvent under reduced pressure, **1a** was obtained which was washed with *n*-pentane (10 mL) and dried under vacuum. Yield: 87 mg (48%).

*[FeCp(CO)(κ^2(C,P)=C(OMe)-NiPr-PPh$_2$)]BF$_4$ (**3**)*

A solution of **1a** (500 mg, 1.19 mmol) in CH_2Cl_2 (10 mL) was treated with $[Me_3O]BF_4$ (177 mg, 1.19 mmol). After stirring for 4h, insoluble materials were removed by filtration through Celite. On removal of the solvent, **5** was obtained as an orange solid which was washed with *n*-hexane, and dried under vacuum. Yield: 360 mg (58%). Anal. calcd for $C_{35}H_{39}BBrF_4FeN_2O_3P$: C, 53.27; H, 4.98; N, 3.55. Found: C, 53.19; H, 4.89; N, 3.64. ^{1}H NMR (δ, $CDCl_3$, 20^{o}C): 7.58 (m, 10H, Ph), 4.80 (s, 5H, Cp), 4.33 (s, 3H, *OCH*$_3$), *3*.93 (m, 1H, C*H*(CH$_3$)$_2$), 1.40 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$), 0.92 (d, *J* = 6.4 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20^{o}C): 238.0 (d, J_{PC} = 34.8 Hz, Fe=*C*), 216.3 (d, J_{PC} = 22.2 Hz, *C*O), 134.7 (d, J_{PC} = 22.3 Hz, Ph), 134.4 (d, J_{PC} = 14.2 Hz, Ph), 134.2 (d, J_{PC} = 22.2 Hz, Ph), 132.8 (d, J_{PC} = 2.59 Hz, Ph), 131.9 (d, J_{PC} = 2.5 Hz, Ph), 131.3 (d, J_{PC} = 11.1 Hz, Ph), 129.9 (d, J_{PC} = 11.3 Hz, Ph), 83.1 (s, Cp), 64.9 (s, *OC*H$_3$), 55.8 (d, J_{PC} = 5.5 Hz, *C*H(CH$_3$)$_2$), 21.8 (s, CH(*C*H$_3$)$_2$), 20.8 (s, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20^{o}C): 115.0. IR (ATR, 25 ^{o}C): 2004 ($\nu_{C=O}$).

*Protonation of **1a** with [HNEt$_3$]Cl. Formation of **2***

A solution of **1a** (500 mg, 1.19 mmol) in CH_2Cl_2 (10 mL) was treated with [HNEt$_3$]Cl (165 mg, 1.19 mmol). After stirring for 4h, insoluble materials were removed by filtration through Celite. On removal of the solvent, **2** was obtained as a yellow solid which was collected on a glass frit, washed with *n*-hexane, and dried under vacuum. Yield: 514 mg (95%).

*cis,trans,cis-[Fe(CO)$_2$(Ph$_2$PNHiPr)$_2$(Br)$_2$] (**4a**)*

To a solution of *cis*-[Fe(CO)$_4$Br$_2$] (1.00 g, 3.05 mmol) in CH_2Cl_2 (10 mL) Ph$_2$PNH*i*Pr (1.52 g, 6.25 mmol) was added at 0^{o}C and the mixture was stirred overnight at room temperature. The solution was then filtered through Celite. After removal of the solvent under reduced pressure, an orange solid was obtained which was washed with diethyl ether (10 mL) and dried under vacuum. Yield: 1.96 g (85%). Anal. calcd for $C_{32}H_{36}Br_2FeN_2O_2P_2$: C, 50.69; H, 4.79; N, 3.69. Found: C, 50.69; H, 4.79; N, 3.69. ^{1}H NMR (δ, $CDCl_3$, 20^{o}C): 7.99 (bs, 8H, Ph), 7.48 (bs, 12H, Ph), 3.42 (bs, 2H, *NH),* 2.29 (m, 2H, C*H*(CH$_3$)$_2$), 0.91 (d, J_{PC} = 6.3 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20^{o}C): 212.7 (t, J_{PC} = 22.7 Hz, *C*O), 133.6 (d, J_{PC} = 25. Hz, Ph), 133.0 (dd, J_{PC} = 5.1 Hz, Ph), 131.7 (dd, J_{PC} = 5.4 Hz, Ph), 130.8 (s, Ph , 127.9 (dd, J_{PC} = 4.6 Hz, Ph), 46.4 (dd, J_{PC} = 4.9 Hz, *C*H(CH$_3$)$_2$), 24.7 (s, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20^{o}C): 80.6. IR (ATR, 25^{o}C): 2041 ($\nu_{C=O}$), 1986 ($\nu_{C=O}$).

*cis,trans,cis-[Fe(CO)$_2$(Ph$_2$PNHtBu)$_2$(Br)$_2$] (**4b**)*

This complex was prepared analogously to **4a** with *cis*-[Fe(CO)$_4$Br$_2$] (845 mg, 2.58 mmol) and Ph$_2$PNH*t*Bu (1.33 g, 5.16 mmol) as starting materials. Yield: 1.7 mg (88%). Anal. calcd for $C_{34}H_{40}Br_2FeN_2O_2P_2$: C, 51.94; H, 5.13; N, 3.56. Found: C, 52.04; H, 5.20; N, 3.46. ^{1}H NMR (δ, acetone-d$_6$, 20^{o}C): 8.36 (bs, 8H, Ph), 7.48 (bs, 12H, Ph), 3.7 (bs, 2H, *NH),* 0.87 (s, 18H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20^{o}C): 213.3 (t, J_{PC} = 24.0 Hz, *C*O), 134.2 (dd, J_{PC} = 25.7 Hz, Ph), 133.5 (dd, J_{PC} = 5.3 Hz, Ph), 130.7 (s, Ph), 127.7 (dd, J_{PC} = 4.7 Hz,

Ph), 55.5 (s, *C*(CH_3)$_3$), 31.7 (s, C(*C*H_3)$_3$). $^{31}P\{^1H\}$ NMR (δ, acetone-d_6, 20°C): 72.2. IR (ATR, 25°C): 2035 ($\nu_{C=O}$), 1980 ($\nu_{C=O}$).

*trans-[Fe(CO)$_2$(κ^2(C,P)-(C=O)-NiPr-PPh$_2$)(Ph$_2$PNHiPr)Br] (**5a**) and cis-[Fe(CO)$_2$(κ^2(C,P)-(C=O)-NiPr-PPh$_2$)(Ph$_2$PNHiPr)Br] (**5a'**)*

A Schlenk tube was charged with **4a** (400 mg, 0.53 mmol) and KO*t*Bu (122 mg, 1.06 mmol). Under a CO atmosphere THF (10 mL) was added and the mixture was stirred overnight at room temperature. The red solution was then filtered through Celite and the solvent was removed under reduced pressure. The residue was redissolved in CH_2Cl_2. Insoluble materials were removed by filtration. After evaporation of the solvent *in vacuo*, a red solid was obtained which was washed with *n*-pentane (10 mL) and dried under vacuum. Yield: 185 mg (50%). Anal. calcd for $C_{33}H_{35}BrFeN_2O_3P_2$: C, 50.69; H, 4.79; N, 3.69. Found: C, 50.72; H, 4.73; N, 3.73. Major isomer: ^1H NMR (δ, $CDCl_3$, 20°C): 7.85 (d, *J* = 6.79 Hz, 8H, Ph), 7.50 (d, *J* = 8.38 Hz, 8H, Ph), 7.43 (s, 4H, Ph), 4.70 (bs, 1H, *NH),* 3.46 (m, 1H, C*H*(CH_3)$_2$), 3.12 (m, 1H, C*H*(CH_3)$_2$), 1.31 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 0.94 (d, *J* = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 212.4 (t, J_{PC} = 22.7 Hz, *C*O), 206.0 (dd, J_{PC} = 9.6 Hz, J_{PC} = 13.4 Hz, N*C*O), 135.1 (d, J_{PC} = 37.5 Hz, Ph), 133.3 (d, J_{PC} = 12.1 Hz, Ph), 133.1 (d, J_{PC} = 13.5 Hz, Ph), 131.8 (s, Ph), 130.2 (s, Ph), 128.7 (d, J_{PC} = 11.1 Hz, Ph), 128.0 (d, J_{PC} = 11.1 Hz, Ph), 45.7 (t, J_{PC} = 12.7 Hz, Ph), 25.5 (s, *C*H(CH_3)$_2$), 22.0 (s, CH(*C*H_3)$_2$). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 95.6 (d, J_{PP} = 84.7 Hz), 85.8 (d, J_{PP} = 84.7 Hz). IR (ATR, 25°C): 1966 ($\nu_{C=O}$), 1960 ($\nu_{C=O}$), 1616 ($\nu_{C=O}$). Minor isomer *cis*-[Fe(CO)$_2$(κ^2(*C,P*)-(C=O)-N*i*Pr-PPh$_2$)(Ph$_2$PNH*i*Pr)Br] (**5a'**): Most ^1H and ^{13}C NMR resonances are superimposed by the signals of the major isomer and could not reliably assigned. $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 94.8 (d, J_{PP} = 115.9 Hz), 90.0 (d, J_{PP} = 115.9 Hz).

*trans-[Fe(CO)$_2$(κ^2(C,P)-(C=O)-NtBu-PPh$_2$)(Ph$_2$PNHtBu)Br] (**5b**)*

This complex was prepared analogously to **5a** with **4b** (0.70 g, 0.89 mmol) as starting material. Yield: 260 mg (40%). Anal. calcd for $C_{35}H_{39}BrFeN_2O_3P_2$: C, 57.32; H, 5.36; N, 3.82. Found: C, 57.40; H, 5.29; N, 3.79. ^1H NMR (δ, $CDCl_3$, 20°C): 7.98 (bs, 8H, Ph), 7.42 (bs, 12H, Ph), 4.84 (bs, 1H, *NH),* 3.46 (m, 1H, C*H*(CH_3)$_2$), 1.28 (s, 9H, C(C*H*$_3$)$_3$), 1.05 (s, 9H, C(C*H*$_3$)$_3$). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 213.3 (dd, J_{PC} = 23.4 Hz, J_{PC} = 22.9 Hz *C*O), 206.0 (dd, J_{PC} = 9.6 Hz, J_{PC} = 13.4 Hz, N*C*O), 136.2 (d, J_{PC} = 47.7 Hz, Ph), 136.1 (d, J_{PC} = 47.7 Hz, Ph), 134.5 (d, J_{PC} = 10.8 Hz, Ph), 132.8 (d, J_{PC} = 10.8 Hz, Ph), 132.6 (d, J_{PC} = 11.6 Hz, Ph), 131.4 (d, J_{PC} = 2.3 Hz, Ph), 129.9 (d, J_{PC} = 2.3 Hz, Ph), 128.5 (d, J_{PC} = 10.6 Hz, Ph), 127.6 (d, J_{PC} = 10.0 Hz, Ph), 62.3 (d, J_{PC} = 7.6 Hz, *C*(CH_3)$_3$), 55.9 (d, J_{PC} = 13.9 Hz, *C*(CH_3)$_3$), 32.1 (d, J_{PC} = 3.1 Hz, C(*C*H_3)$_3$), 29.5 (d, J_{PC} = 1.5 Hz, C(*C*H_3)$_3$). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20°C): 90.4 (d, J_{PP} = 79.3 Hz), 87.3 (d, J_{PP} = 79.3 Hz . IR (ATR, 25 °C): 1955 ($\nu_{C=O}$), 1950 ($\nu_{C=O}$),1619 ($\nu_{C=O}$).

2.3. X-ray Structure Determinations

Single crystals for X-ray diffraction were obtained as follows: [FeCp(CO)(κ^2(*C,P*)-(C=O)-N*i*Pr-PPh_2)] (**1a**), by vapour diffusion of *n*-pentane into a THF solution, [$FeCp(CO)_2(Ph_2PNHiPr)$]Br (**2**) by vapour diffusion of Et_2O into a CH_2Cl_2 solution; *trans/cis*-[$Fe(CO)_2$(κ^2(*C,P*)-(C=O)-N*i*Pr-PPh_2)($Ph_2PNHiPr$)Br] (**5a**/**5a'**) by vapour diffusion of Et_2O into a CH_2Cl_2 solution. The colour of the crystals varied from orange to red brown. X-ray diffraction data were collected at T = 100 K on a Bruker Kappa APEX-2 CCD diffractometer with an Oxford Cryosystems cooler using graphite-monochromatised Mo-Kα radiation (λ = 0.71073 Å) and fine sliced φ- and ω-scans covering complete spheres of the reciprocal space. After data integration with program SAINT corrections for absorption and detector effects were applied with the program SADABS [18] The structures were solved by direct methods (SHELXS97) and refined on F^2 with the program SHELXL97 [19] Non-hydrogen atoms were refined anisotropically. Most H atoms were placed in calculated positions and thereafter refined as riding. In (**5a**) Br was partly substituted by CO and vice versa (84% *trans*- and 16% in *cis*-dicarbonyl configuration), and the subordinately occupied sites were refined with distance and displacement parameter restraints. All crystal structures were checked with the program PLATON [20] Molecular graphics was generated with program MERCURY [21] Crystal data and experimental details are given in Table 2.

2.4. Computational Details

Calculations were performed using the GAUSSIAN 09 software package [22], and the B3LYP functional [23] without symmetry constraints. The optimized geometries were obtained with the Stuttgart/Dresden ECP (SDD) basis set [24] to describe the electrons of the iron atom. For all other atoms the 6-31g** basis set was employed [25]. Frequency calculations were performed to confirm the nature of the stationary points. A scaling factor of 0.9521 was applied for the CO frequencies [26].

Acknowledgements

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Table 2. Details for the crystal structure determinations of compounds **1a**, **2**, and **5a**.

	1a	**2**	**5a**
formula	$C_{22}H_{22}FeNO_2P$	$C_{22}H_{23}BrFeNO_2P$	$C_{33}H_{35}BrFeN_2O_3P_2$
fw	419.23	500.14	705.33
cryst.size, mm	0.45 x 0.26 x 0.14	0.59 x 0.20 x 0.18	0.25 x 0.20 x 0.18
color, shape	red plate	yellow prism	red prism
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a, Å	10.0648(3)	13.2697(2)	10.1667(4)
b, Å	14.5893(5)	17.5534(2)	17.7127(7)
c, Å	13.4024(4)	9.2565(2)	18.9313(8)
α, deg	90	90	90
β, deg	92.871(2)	92.768(2)	105.453(2)
γ, deg	90	90	90
V, Å^3	1965.52(11)	2153.59(6)	3285.9(2)
T, K	100(2)	100(2)	100(2)
Z	4	4	4
ρ_{calc}, g cm^{-3}	1.417	1.543	1.426
μ, mm^{-1} (MoKα)	0.865	2.647	1.807
F(000)	872	1016	1448
absorption corrections	multi-scan, 0.89-0.76	multi-scan, 0.65-0.43	multi-scan, 0.74-0.58
θ range, deg	2.06–30.11	1.93-30.00	2.08-27.50
no. of rflns measd	65996	39753	50035
R_{int}	0.034	0.023	0.076
no. of rflns unique	5771	6253	7526
no. of rflns I>2σ(I)	4787	5578	5356
no. of params /	246 / 0	258 / 0	387 / 136
R_1 (I > 2σ(I)) [a]	0.0253	0.0269	0.0406
R_1 (all data)	0.0366	0.0320	0.0742
wR_2 (I > 2σ(I))	0.0593	0.0682	0.0891
wR_2 (all data)	0.0642	0.0713	0.1081
Diff.Four.peaks min/max, eÅ^{-3}	-0.32 / 0.40	-0.45 / 0.82	-0.60 / 0.77

[a] $R1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{½}$, $\text{GooF} = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)\}^{½}$

Figure Captions

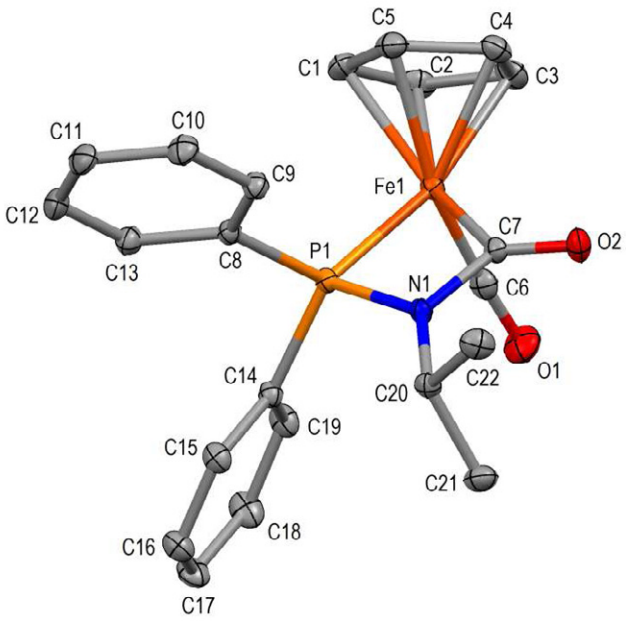


Figure 1. Molecular structure of [FeCp(CO)(κ^2(*C,P*)-(C=O)-N*i*Pr-PPh$_2$)] (**1a**) showing 50% displacement ellipsoids. Selected distances and angles (Å, °): < Fe1–C_{Cp}> = 2.101(1), Fe1–P1 2.1773(3), Fe1–C6 1.739(1), Fe1–C7 1.981(1), C6–O1 1.158(2), C7–O2 1.219(2), N1–C7 1.404(2), P1–N1 1.6915(10), C7-Fe1-P1 69.43(4), Fe1–C7–O2 133.8(1), Fe1–C7–N7 103.7(1), Fe1–P1–N1 86.95(3), P1–N1–C7 99.7(1).

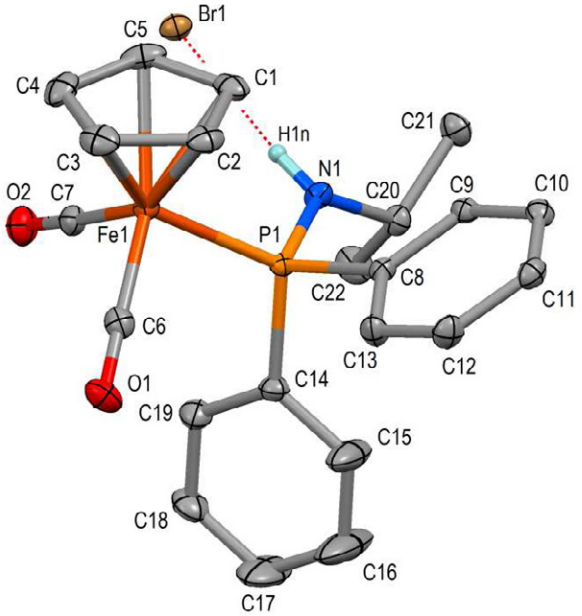


Figure 2. Molecular structure of **2** showing 50% displacement ellipsoids. Selected distances and angles (Å, °): <Fe1–C_{Cp}> = 2.104(2), Fe1–P1 2.2223(4), Fe1–C6 1.780(2), Fe1–C7 1.785(2), C6–O1 1.141(2), C7–O2 1.139(2), P1–N1 1.6473(13), N1–C20 1.477(2), P1–Fe1–C6 90.73(5), P1–Fe1–C7 93.83(5), C6–Fe1–C7 96.28(7), C20–N1–P1 125.14(10), N1···Br1 3.3854(13).

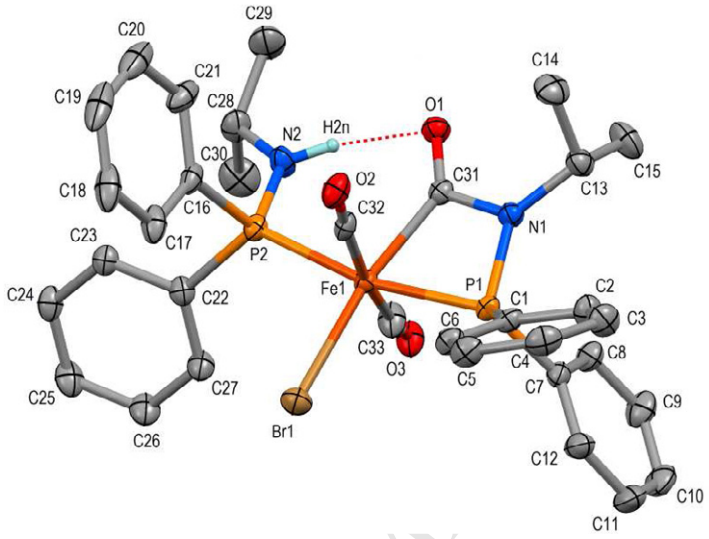
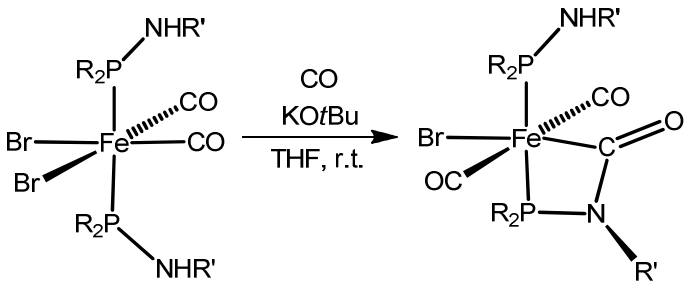
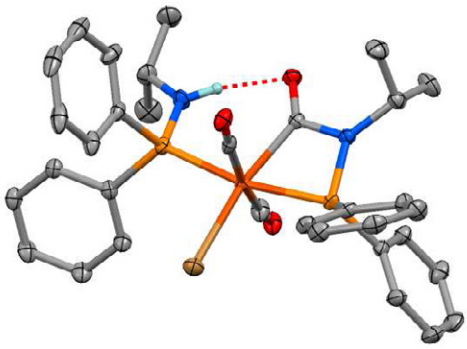


Figure 3. Molecular structure of *trans*-[Fe(CO)$_2$(κ^2(*C,P*)-(C=O)-N*i*Pr-PPh$_2$)(Ph$_2$PNH*i*Pr)Br] (**5a**) (major isomer) showing 40% displacement ellipsoids. Selected distances and angles (Å, °): Fe1–Br1 2.4752(6), Fe1–P1 2.2480(9), Fe1–P2 2.2651(9), Fe1–C33 1.799(3), Fe1–C32 1.826(3), Fe1–C31 1.997(3), P2–N2 1.650(3), P1–N1 1.694(3), C31–O1 1.221(4), C31–N1 1.409(4), C32-Fe1-C33 170.6(2), P1-Fe1-P2 167.1(1), P1–Fe1–C31 68.9(1), Fe1–P1–N1 85.3(1), Fe1–C31–O1 134.2(2), Fe1–C31–N1 103.6(2), O1–C31–N1 122.2(3), P1–N1–C31 101.5(2), P1–N1–C13 132.4(2), N2···O1 2.839(4).

Graphical Abstract

The synthesis of several iron(II) complexes featuring a four-membered carboxamido-phospha-ferracycle moiety as a result of an intramolecular nucleophilic attack of a deprotonated aminophosphine ligand on coordinated CO is described.





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Highlights

$FeCp(CO)_2Cl$ reacts with amidophosphine ligands to give complexes with four-membered carboxamido-phospha-ferracycles – these reaction involve an intramolecular nucleophilic attack of the amidophosphine ligand on coordinated CO - treatment with electrophiles affords aza-phospha-carbenes

Graphical Abstract

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