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Dalton Trans

COMMUNICATION

An iron(II) complex featuring κ^3 and labile κ^2-bound PNP pincer ligands – striking differences between CH$_2$ and NH spacers
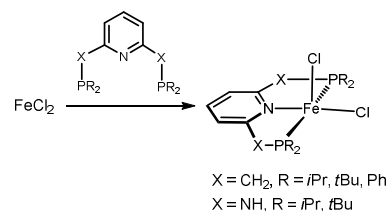
Bernhard Bichler,[a] Mathias Glatz,[a] Berthold Stöger,[b] Kurt Mereiter,[b] Luis F. Veiros,[c] and Karl Kirchner*,[a]

Treatment of anhydrous FeCl$_2$ with 2 equivs of the pincer ligand PNP-Ph afforded the diamagnetic cationic octahedral complex [Fe(κ^3-_P,N,P_-PNP)(κ^2-_P,N_-PNP)Cl]$^+$ featuring a κ^2-_P,N_-bound PNP ligand. Preliminary reactivity studies revealed that the κ^2-_P,N_-bound PNP ligand is labile reacting with CO to afford _trans_-[Fe(PNP-Ph)(CO)$_2$Cl]$^+$.
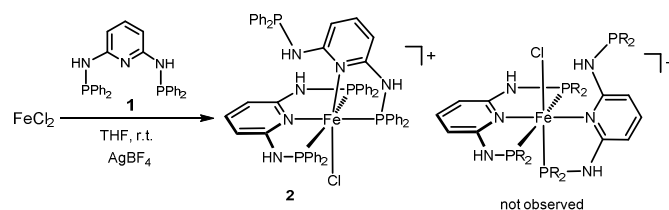
Tridentate PNP ligands based on a central pyridine donor with -CH$_2$PR$_2$, -OPR$_2$, or -NHPR$_2$ substituents in the two _ortho_ positions are widely utilized in transition metal chemistry (e.g., Fe, Ru, Rh, Ir, Pd, Pt).[1,2,3] Most of these PNP pincer complexes feature strongly electron donating and bulky phosphine donors such as _i_Pr or _t_Bu substituents, while complexes with less bulky and less electron donating Ph groups are, in comparison, less utilized.

As far as iron is concerned, coordinatively unsaturated 16e iron(II) complexes of the type [Fe(PNP)Cl$_2$] were prepared by reacting FeCl$_2$ with the pyridine-based PNP ligands PNP^{CH2}-_t_Bu, PNP^{CH2}-_i_Pr,[4] and also PNP^{CH2}-Ph,[5,6] featuring CH$_2$ spacers between the phosphine donors and the pyridine moiety (Scheme 1). The bulkiness and donor strengths of these ligands decrease in the order PNP-_t_Bu > PNP-_i_Pr > PNP-Ph and apparently seems to have no influence on these reactions. We have recently prepared similar complexes but with the bulky PNP ligands N,N'-bis(di-_iso_-propylphosphino)-2,6-diaminopyridine (PNP-_i_Pr) and N,N'-bis(di-_tert_-butylphosphino)-2,6-diamino-pyridine (PNP-_t_Bu) where the central pyridine ring contains NHPR$_2$ (R = _i_Pr, _t_Bu) substituents in the two _ortho_ positions (Scheme 1).[1g,7] In continuation of our studies on iron PNP complexes, we report here on the synthesis and reactivity of an unusual octahedral Fe(II) complex where two N,N'-bis(diphenylphosphino)-2,6-diaminopyridine (PNP-Ph) pincer ligands are coordinated both in κ^3(_P,N,P_)- and κ^2(_P,N_)-fashion.

Scheme 1 Formation of 16e iron(II) PNP pincer complexes of the type [Fe(PNP)Cl$_2$]

In sharp contrast to the reactions shown in Scheme 1, treatment of anhydrous FeCl$_2$ with PNP-Ph (**1**) in THF in the presence of AgBF$_4$ at room temperature for 4h afforded diamagnetic emerald green cationic octahedral complex [Fe(κ^3-_P,N,P_-PNP-Ph)(κ^2-_P,N_-PNP-Ph)Cl]$^+$ (**2**) in essentially quantitative yield (Scheme 2). In the absence of Ag$^+$ salt as halide scavanger, the respective chloride complex **2Cl** was formed. The formation of these complexes is independent of whether 1 or 2 equivs of ligand are used.

Scheme 2 Formation of [Fe(κ^3-_P,N,P_-PNP)(κ^2-_P,N_-PNP)Cl]$^+$ (**2**) featuring a κ^2-_P,N_ bound PNP ligand.

However, in the first case substantial amounts of unreacted FeX$_2$ remained which form the paramagnetic haloferrate counterion

$[FeCl_4]^{2-}$. The reaction of $FeCl_2$ with the related ligand PNP^{CH2}-Ph yields the pentacoordinate complex $[Fe(PNP^{CH2}-Ph)Cl_2]$ revealing striking differences between CH_2 and NH spacers in pyridine-based PNP pincer ligands (Scheme 1).[5,6] The formation of **2** is very selective and only one isomer was observed where the pyridine moiety of the κ^2-*P,N* bound PNP ligand is *trans* to the halide ligand. There was no evidence for the formation of an isomer where the pyridine moiety of the κ^2-*P,N* bound PNP ligand is *cis* to the halide ligand. DFT calculations for the two possible isomers of **2** in agreement with the experiment indicate that the unobserved isomer is less stable by 6.9 kcal/mol. That stability difference is essentially due to steric effects (for details see ESI).

Complex **2** is fully characterized by a combination of ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, and elemental analysis. While the ^{1}H NMR spectra were not very informative, the ^{31}P{^{1}H} NMR spectrum revealed a characteristic A_2B pattern.[8] The spectrum gives rise to multiplets centered at $\delta_A = 108.7$ (κ^3-PNP) and $\delta_B = 100.9$ (κ^2-PNP) with a coupling constant J_{PP} of 50 Hz, which can be assigned to the two phosphorus atoms of the κ^3-PNP-bound ligand, and one phosphorous atom of κ^2-PNP-bound ligand. In addition, the pendant PR_2-NH-arm of the κ^2-bound PNP ligand gives rise to a singlet at 47.0 ppm. The solid state structure of **2**, determined by single-crystal X-ray diffraction is depicted in Fig. 1 with selected bond distances given in the caption. This complex adopts a severely distorted octahedral geometry with the P1-Fe1-P2, N1-Fe1-P3, and N4-Fe1-Cl1 angles deviating from the ideal 180° being 170.02(6), 163.33(3), and 172.36(6)^o, respectively.

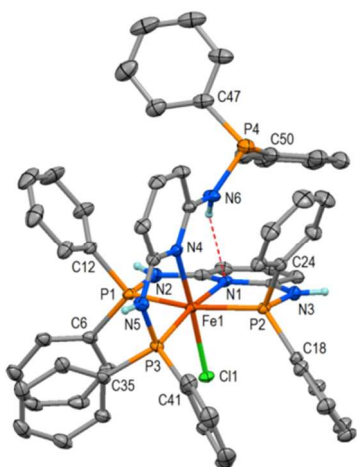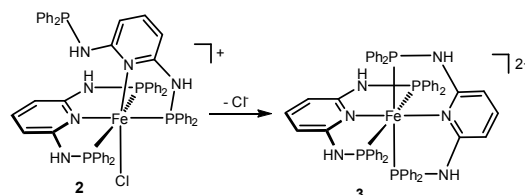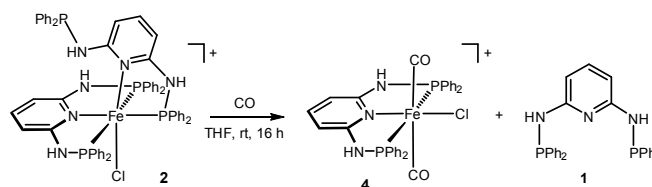**Fig. 1** Structural diagram of $[Fe(\kappa^3$-*P,N,P*-PNP-Ph)(κ^2-*P,N*-PNP-Ph)Cl]BF$_4$·2THF·Et$_2$O (**2**·2THF·Et$_2$O) showing only N-bonded H-atoms and 40%-ellipsoids (solvent molecules and BF$_4^-$ counterion are omitted for clarity). Selected bond distances and angles (Å, deg): Fe1-N1 2.064(2), Fe1-N4 2.084(2), Fe1-P3 2.1845(7), Fe1-P1 2.2439(7), Fe1-P2 2.2530(7), Fe1-Cl1 2.3330(7); P1-Fe1-P2 163.33(3), N1-Fe1-P3 170.02(6), N4-Fe1-Cl1 172.36(6), C34-N6-P4 120.3(3); hydrogen bond N6···N1 2.941(3).

Complex **2** is stable in THF for several days, but readily rearranges in CH_3CN (within a few minutes) and CH_2Cl_2 (within a few hours) to give the known complex $[Fe(\kappa^3$-*P,N,P*-PNP-Ph)$_2]^{2+}$ (**3**) (Scheme 3). In the presence of halide scavengers this reaction proceeds within a few minutes. Complex **3** was already prepared by an alternative method recently.[7a] It has to be noted that an analogous complex $[Fe(PNP^{CH2}-Ph)]_2^{2+}$ bearing CH_2-spacers between the pyridine ring and the PPh_2 moieties was reported.[9]

Scheme 3 Formation of $[Fe(\kappa^3$-*P,N,P*-PNP)$_2]^{2+}$ (**3**) featuring two κ^3-*P,N,P* bound PNP ligands.

In a preliminary study we investigated the reactivity of $[Fe(\kappa^3$-*P,N,P*-PNP-Ph)(κ^2-*P,N*-PNP-Ph)Cl]$^+$ (**2**) towards the addition of CO. Treatment of **2** with CO at room temperature resulted in the dissociation of the κ^2-*P,N*-bound PNP ligand and formation of the cationic dicarbonyl complex *trans*-$[Fe(\kappa^3$-*P,N,P*-PNP-Ph)(CO)$_2$Cl]$^+$ (**4**) as shown in Scheme 4.

Scheme 4 Reaction of $[Fe(\kappa^3$-*P,N,P*-PNP-Ph)(κ^2-*P,N*-PNP-Ph)Cl]$^+$ (**2**) with carbon monoxide

Complex **4** is a thermally robust red solid that is air stable both in the solid state and in solution for several days. In the ^{13}C{^{1}H} NMR spectrum the two CO ligands exhibit a single low-intensity triplet resonance 207.2 ppm with a coupling constant J_{CP} of 25.8 Hz, thus, clearly revealing that the two CO ligands are *trans* to one another. Accordingly, **4** gives rise to only one band 2031 cm^{-1} in the IR spectrum for the mutually *trans* CO ligands which can be assigned to the asymmetric CO stretching frequency. The symmetric CO stretching band is IR inactive and thus not observed. For comparison, in the related complex *trans*-$[Fe(PNP-iPr)(CO)_2Cl]^+$ the CO stretch is shifted to lower wave numbers observed at 2015 cm^{-1}, clearly showing that PNP-*i*Pr is a stronger electron donor than PNP-Ph.[7e]

In summary we prepared the octahedral Fe(II) complex $[Fe(\kappa^3$-*P,N,P*-PNP-Ph)(κ^2-*P,N*-PNP-Ph)Cl]$^+$ (**2**) where the PNP pincer ligands are coordinated both in κ^3-*P,N,P*- and κ^2-*P,N*-fashion. This complex adopts a strongly distorted octahedral geometry as established by X-ray crystallography. Obviously related to these distortions is the reactivity of **2** undergoing,

upon halide dissociation, a facile rearrangement reaction to give the dicationic complex $[Fe(\kappa^3-P,N,P-PNP-Ph)_2]^+$ (**3**) where now both PNP-Ph ligands are bound in κ^3-P,N,P-fashion. Moreover, preliminary reactivity studies revealed that the κ^2-P,N-bound PNP-Ph ligand is substitutionally labile resulting in dissociation of the κ^2-P,N-bound PNP ligand in the presence of CO to afford the cationic dicarbonyl complex *trans*-$[Fe(\kappa^3-P,N,P-PNP-Ph)(CO)_2Cl]^+$ (**4**) and free PNP-Ph ligand. In order to answer the question whether these reactions are sterically or electronically driven, investigations are currently underway utilizing PNP ligands with both weakly and strongly electron donating substituents which however are sterically non-demanding. These results will be reported in due course.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental and computational details, spectroscopic characterization, CCDC 1005379 for **2**. For ESI and crystallographic data in CIF or other electronic format see DOI:. 10.1039/c000000x/

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Graphical Abstract

An iron(II) complex featuring κ^3 and labile κ^2-bound PNP pincer ligands – striking differences between CH$_2$ and NH spacers

By changing the spacer between the pyridine and the PPh$_2$ unit from CH$_2$ to NH the cationic octahedral complex $[Fe(\kappa^3\text{-}P,N,P\text{-PNP})(\kappa^2\text{-}P,N\text{-PNP})Cl]^+$ featuring a $\kappa^2\text{-}P,N$ bound PNP ligand instead of $Fe(\kappa^3\text{-}P,N,P\text{-PNP})Cl_2$ is formed when FeCl$_2$ is reacted with a PNP-Ph ligand.