Synthesis and characterization of an unsaturated PNPFe complex.

Submitted by:
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In partial fulfillments of
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Caulton Group

Introduction:

The design of highly electron rich metal complexes is one of the main themes of modern organometallic chemistry. Such complexes have the potential to be novel catalysts, allow modeling of inaccessible biochemical pathways, and even to bring a greater understanding of the forces behind metal ligand binding. The key to creating unsaturated metal complexes is the design of the ligand, requiring the protection of the active metal site while still allowing the molecules of interest close enough passage to react with the metal. Fryzuk et al. in the early eighties developed a class of ligand which has been especially fruitful in creating complexes both novel and interesting.
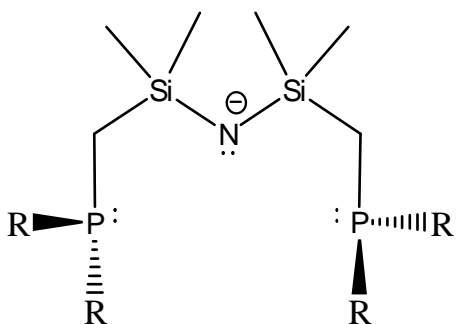
Figure 1. – The PNP ligand

Fryzuk first published on the usefulness of the PNP pincer ligand in 1982[2]. His creation of low-coordinate electron-rich complexes with group 10 metals[3] served to stimulate interest in PNP's potential for high reactivity complexes. Over the next 20 years more than 100 papers were published involving some derivative of the PNP ligand[4]. The usefulness of this ligand lies in the two different chemical moieties which can compete for

[2] Fryzuk, Michael D. and MacNeil, Patricia A., *J. Am. Chem. Soc.* **1981**, *103*, 3592-3593
[3] Ibid.
[4] Search of Scifinder Scholar Database and the ACS Web Archives

the attentions of the central metal atom. The phosphorous atoms with their 'soft'

behavior and readily available lone pairs allows for binding behavior reminiscent of those

organometallic staples, the alkyl phosphines. The nitrogen with its anionic charge and

'hard' nature allows for a strong bond to a positive metal ion, while its lone pairs might

also help bind the metal center datively. These properties guarantee tricoordinate bonding

between the ligand and metal as shown in figure 2, as well as a meridional geometry motif.

In general ligands of this type are referred to as 'PNP' or 'Fryzuk'

ligands of the general class 'pincer ligands', of which many are now in common use[5].


$M = Fe\text{-}Ni^{n+}$
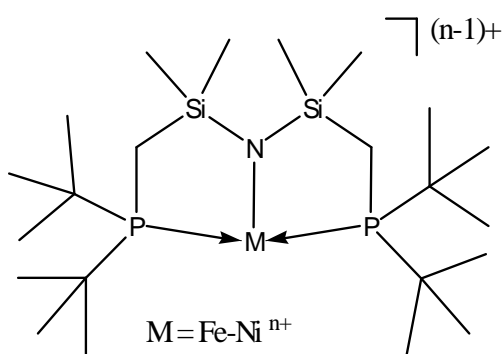
Figure 2. – PNP ligand (Caulton Group)

The Caulton group has brought new reactivity to this research by choosing R = t-

butyl groups in place of Fryzuk's use of phenyl rings, thereby adding additional steric bulk

to the molecule. This additional bulk in the Caulton version of the Fryzuk ligand prevents

the systemic problem of dimerization[6], allowing the complex to remain at extremely low

oxidation state and high reactivity.

[5] Watson, L.; Caulton, K. G. et al. *New Journal of Chemistry*, 2003, 27, 2632.
[6] Watson, Lori A.; Ozerov, Oleg V.; Pink, Maren; and Caulton K. G.; *J. Am. Chem. Soc.;* 2003; *125*(28); 8426-8427

One metal complex of interest to the Caulton group is PNPFe (figure 3). This complex is sought due to the wide range of potential reactivity available from the combination of the parent ligand's diverse range of electron donating ability and iron's many available oxidation states. As the diagram below shows, one electron reduction is quite possible in the formation of this complex, raising the possibility for facile one electron reduction of incoming molecules once PNPFe is formed.
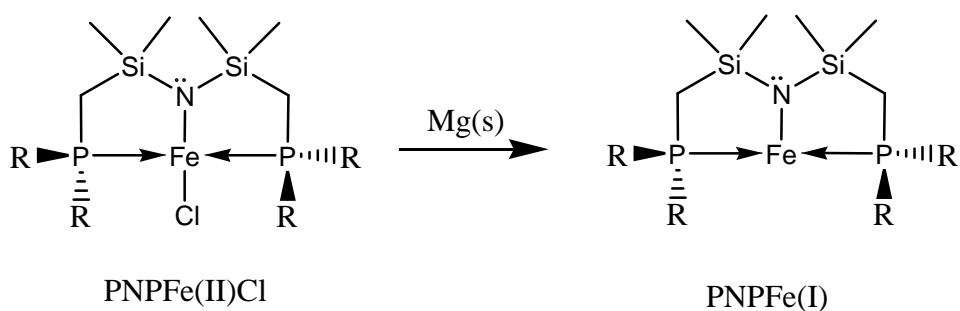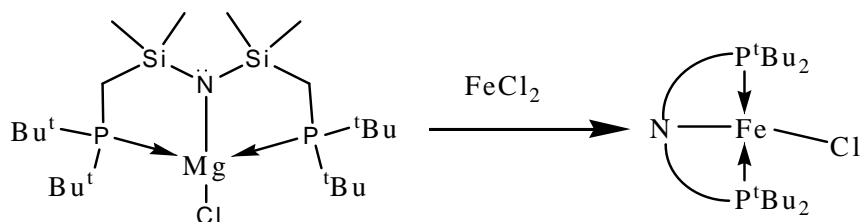

Scheme 1.

Using the electron counting formalism PNPFeCl is a 14 electron compound, making PNPFe a 13 electron Fe(I) compound possibility possessing the highly unusual quality of being stable with respect to dimerization. Exploring the reactivity of PNPFe with regard to olefins, small diatomic molecules and other electron rich species is the aim of this research. Most interestingly, how will H_2, N_2, CO, NO, and the other small molecule probes react to an intrinsically paramagnetic low coordinate metal? The answers will be found by ^1H, ^{31}P, and variable temperature NMR as well as x-ray crystallography.

Results and Discussion:

The reaction of an equimolar ratio of PNPMgCl (the commonly used storage compound

for PNP⁻) with $FeCl_2$ anhydrous powder in THF resulted in a clean conversion to

PNPFeCl as shown in scheme 2. Crystals of the product were obtained quite easily (see

Methods) allowing crystallographic structure determination (figure 4) along with pure [1]H

(figure 5) and ^{31}P (figure 5 inset) NMR analysis.
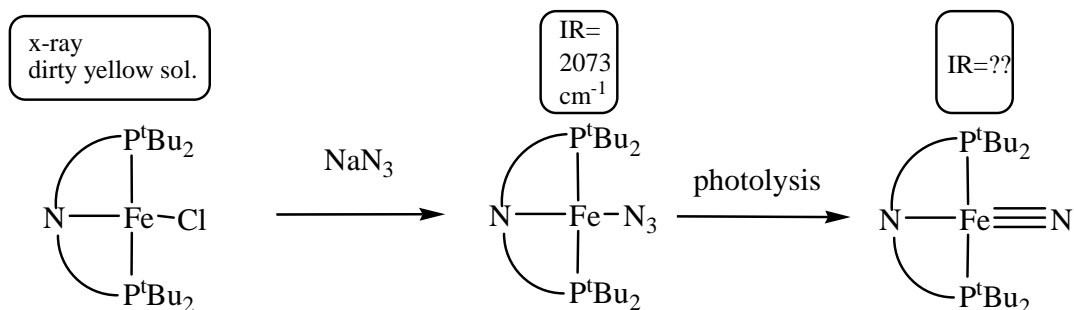

Scheme 2.
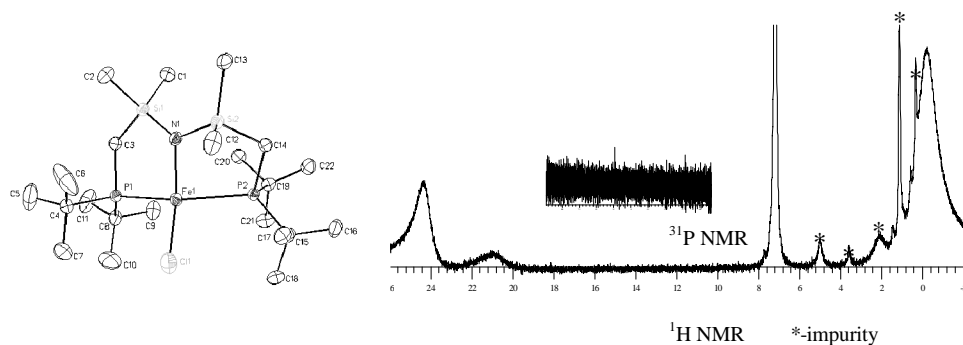
Figures 4 (FePNPCl) and 5 (^{1}H and ^{31}P NMR).

The NMR spectra show that PNPFeCl is effectively C_{2v} in solution, most likely due

to fluxional movement of the various carbon chains. The lack of peaks in the phosphorous

spectrum reveals that the phosphorous atoms are still directly bound to what must be a

paramagnetic iron core. The real surprise comes from the crystallographic data which

shows that the chloride has risen out of the plane of the complex forming a tetrahedral

geometry. This combined with the observed symmetry implies that the chloride rapidly shifts position resulting in a time averaged spectrum. On the basis of these results, a magnetic moment test was performed and confirmed the complex to be high spin with four unpaired electrons.

With the structure determined, the reactivity of this complex was tested. With H_2 and N_2 no color change was noted upon addition, with the NMR spectra showing only a slight broadening of peak width, possibly due to poor NMR shimming. This reactivity was reversible on removal of overpressure of the added gas and did not show any further NMR change even with low temp NMR. With CO a very slight color change from yellow-brown to green-brown was seen after an extended period (>12 hours), but was not further investigated due to the lack of new NMR peaks in the spectrum, and PNPFe's greater reactivity. When the complex was reacted with NaN_3, a strong reaction was noted as an IR peak was observed at 2073 cm^{-1}. This IR region has been noted by the Caulton group as indicative of the formation of the azide-complex per scheme 3. This azide complex has great potential for forming a nitride complex of iron which would be unique in organometallic chemistry. Investigations were attempted to form this nitride by photolysis, but were frustrated by PNPFeN$_3$'s extreme air sensitivity and remain unfinished.

Scheme 3.

It should be noted that in all of the complexes described ^{1}H NMR is used as a diagnostic tool only because of the tendency of the iron complex to form paramagnetic highly broadened peaks across an extreme range of chemical shifts (e.g. 0 ppm to 35 ppm).

Synthesis and Reactivity of PNPFe

The reaction of a large excess of magnesium powder with PNPFeCl resulted in an incomplete reduction to PNPFe even over 48 hours stirring in THF. While ^{1}H and ^{31}P NMR spectra were taken and new peaks identified, it was decided a better method must be found. On the advice of Dr. Michael Ingleson the reducing solution sodium naphthalide[7] was prepared. Reaction of equimolar amounts of this solution with PNPFeCl resulted in the fast (<12 hours) formation of PNPFe as verified by the ^{1}H and ^{31}P NMR described above. Once the resulting material had been crystallized[8], a crystal structure

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[7] See Methods

[8] Crystallization was carried out by taking a saturated sample of FePNP in pentane, placing in a -40 ℃ refrigerator which was left over two days, and once crystals had formed, the solvent was rapidly removed in vacuuo.

was determined as well as a set of pure NMR spectra taken from a single crystal (figures 6 and 7).
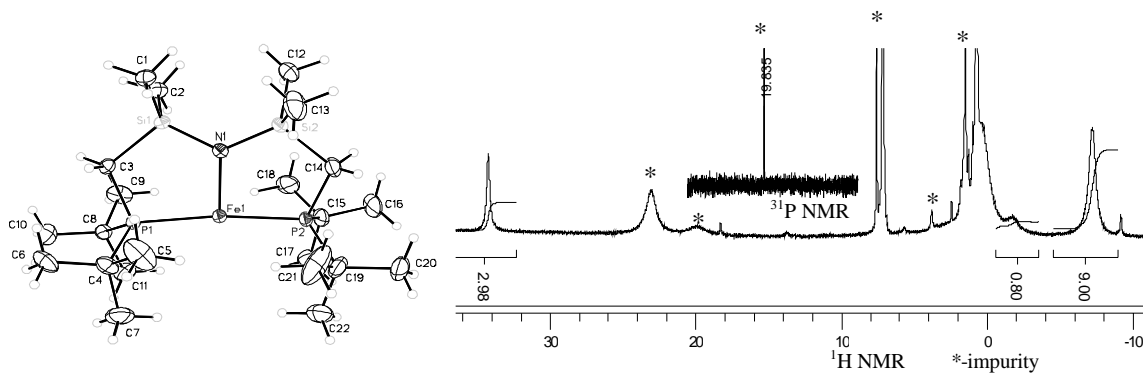

Figures 6 (FePNP) and 7 (^{1}H and ^{31}P NMR).

The crystal structure again reveals the complex to be C_{2v} as also shown by the NMR with the existence of only three different hydrogen groups, those being the CH_2, Si-Me, and P-t-Butyl groups. PNPFe is the most reactive of the PNP iron complexes yet synthesized. The +1 oxidation state of the central metal suggested by the crystal structure was confirmed by magnetic moment analysis. The magnetic moment test showed the complex to have three unpaired electrons confirming a d^7 high spin state Fe^+. The T-shape of the complex center is quite rigorous implying strong donation from the nitrogen along with the necessary donation from the two opposing phosphorous atoms.

The reactivity found so far with PNPFe has been interesting with regard to small molecules due to the available cavity that can be seen in the crystal structure (figure 7). While no reactivity has been seen with N_2 (including low temperature studies), H_2 has been shown a very peculiar behavior. The addition of H_2 gas in equimolar quantities to

134

dissolved PNPFe shows no shift in the ^{1}H NMR peaks of PNPFe. While normally this would indicate no reaction, it is an anomaly that dissolved H_2 does not appear in the ^{1}H NMR spectrum either. The proposed explanation is that H_2 binds in a weak equilibrium with PNPFe resulting in a complex (shown in scheme 4) which broadens the H_2 signal to immeasurability while never existing in sufficient quantity to cause a noticeable shift in the PNPFe peaks. That this equilibrium remains undetectable even at high overpressures of H_2 and in low temperature experiments remains one of the mysteries of the paramagnetic coupling of PNPFe at the moment.
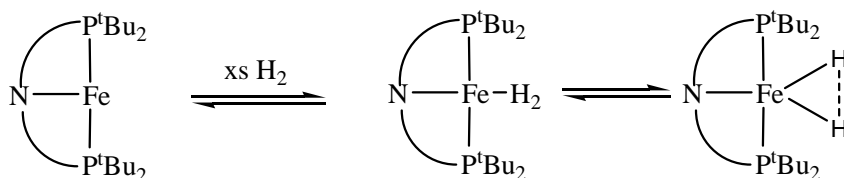
Scheme 4.

When PNPFe was mixed with a sample of CO_2, a reaction was observed. Upon investigation two different compounds were found in the reacted sample which were separated by partial solubility. A ^{31}P NMR with peaks at 19 ppm revealed one compound to be the protonated form of PNP$^-$ often formed by exposure to water and the other to be PNPFe(CO)$_2$. Analysis of the CO_2 tank revealed possible H_2O and CO contamination. For this reason study of the CO_2 was discontinued while focus was turned to CO gas.

Synthesis and Reactivity of PNPFe(CO)$_2$

The reaction of PNPFe with a large excess of pure CO gas effected complete conversion to $PNPFe(CO)_2$ as shown indirectly by the disappearance of ^{1}H NMR peaks for PNPFe. Simultaneously two new peaks appeared in the IR spectrum (foreground-figure 9) compared to the IR spectrum of the solvent, pentane (background) with the two peaks being within the region commonly expected of CO bound to metals. That two peaks appeared, strongly suggested two CO groups were present. After purification, crystals of $PNPFe(CO)_2$ were grown form pentane as per FePNP for crystallographic study. The results are shown in figure 8 with two CO, one axial, one equatorial, clearly bound. The NMR spectra were of unintelligible, with the ^{31}P being featureless and the ^{1}H only showing only one new peak and the disappearance of PNPFe. While this absence of identifiable peaks in the ^{1}H NMR is unexpected, even more so since it remains even at low temperature NMR studies, it is not unheard of when dealing with paramagnetic metal centers. In any case, with the crystallographic evidence of figure 8 the synthesis of this complex is unequivocal.
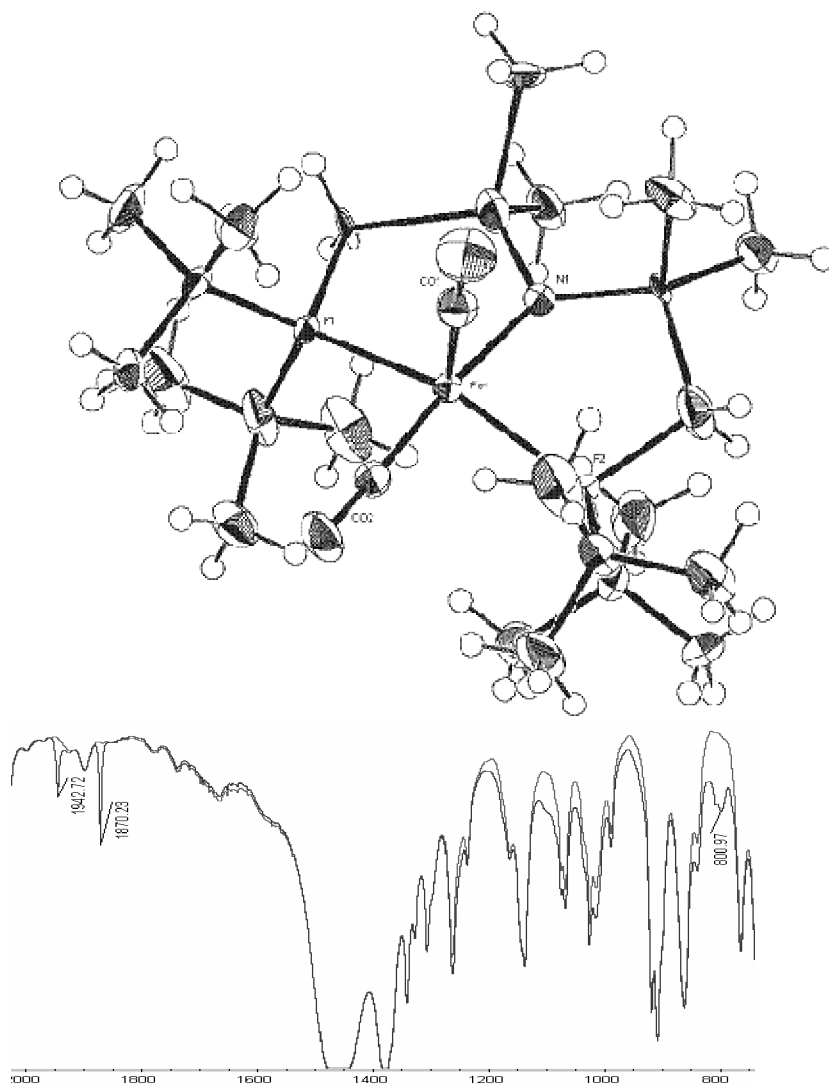
Figures 8 (PNPFe(CO)$_2$) and 9 (IR Spectrum).

Once the structure of this compound was known to be C$_s$ possessing two

nonequivalent CO groups, it was decided to test its magnetic moment for orbital splitting.

Evans' method revealed a magnetic moment indicating a single unpaired electron as

opposed to PNPFe's three unpaired electrons. This clearly shows the CO has had a strong

field effect on the complex separating the high lying orbitals so that a d^7 low-spin state is

now preferred over PNPFe's high spin state. Not surprisingly PNPFe(CO)$_2$ is quite stable

with regard to reaction with other small molecules due both to the formal 17 electron count of the complex and the complete inaccessibility of the metal center. As a further example of this stability, the complex is completely stable to vacuum with no loss of CO after 8 hours of vacuum.

Conclusion:

The successful synthesis of the starting materials of PNPFeCl and PNPFe gives this line of inquiry great promise. PNPFe has shown itself to be quite resistant to dimerization as had been hoped. The extreme reactivity of PNPFe has created problems with isolation as described above, but this reactivity shows the great promise for small molecule activation once proper handling protocols are established.

While the PNPFeCl's reactivity with small molecules, excluding the formation of PNPFeN$_3$, has been disappointing, the fascinating reactivity of PNPFe has more than compensated. The NMR reactivity of PNPFe with H$_2$ has many opportunities for further study in order to find the cause of the H$_2$ peak disappearance and to determine the strength of the reversible binding. Work by other members of the Caulton group have shown that binding H$_2$ even weakly can lead to interesting reactivity with further incoming molecules. My most exciting result to date has been the PNPFe(CO)$_2$ complex which fits well in the trend of carbonyl complexes formed by the work of other members of the Caulton group.

With the reactivity of PNPFe established the next line of effort will be to test the ability of the complex to bind and activate organic small molecules rather than the classical inorganic molecules used so far. Amy Groves work with PNPRu has had

amazing results with small organic molecules, which PNPFe should replicate and with

luck, expand upon.

Experimental:

General Considerations:

Literature preparations were used to synthesize starting materials. Standard techniques for inert atmosphere (Argon) conditions were used for air sensitive manipulations. All solvents, including deuterated NMR solvents, were dried and stored under argon. ^{1}H and ^{31}P NMR spectra were recorded on Varian spectrometers, either a Gemini XL300 or a Unity I400 instrument, with chemical shifts reported in ppm and referenced to each specific solvent, with the exception of ^{31}P which was externally referenced to H_3PO_4 (neat).

Synthesis and referencing of starting materials:

PNPMgCl.Dioxane synthesis:

(PNPtBu) ligand was synthesized according to the procedure described by Caulton et al.[9] This procedure gave 2.51 g of a fluffy white solid, for ~30% yield. This low yield is common with this procedure. ^{1}H NMR (C_6D_6): δ 3.35 (s, 8H, dioxane) 1.15 (d, 36H, t-Butyl), 0.40 (d, 4H, P-CH_2-Si), 0.30 (s, 12H, Si-CH_3). ^{31}P NMR (C_6D_6): δ 18.8 (s).

PNPFeCl synthesis:

This unsaturated paramagnetic metal compound was synthesized via procedure set forth in the supporting material for a publication by Caulton et al.[10] Commercial

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[9] Watson, L.; Caulton, K. G. et al. *New Journal of Chemistry*, 2003, 27, 2632.
[10] Ibid.

anhydrous $FeCl_2$ (s) was purchased from Alfa Aesar, heated at 120 ºC for two days under vacuum then further dried by vacuum overnight. IR analysis was performed on the $FeCl_2$ in a Nujol mull to verify that no water was present. 0.045g (3.5mmol) of $FeCl_2$ was reacted with 0.200g of PNPMgCl.Dioxane (3.4mmol) in 30 mL of dry THF. The heterogeneous mixture was stirred overnight resulting in a homogenous clear yellow-brown solution. This was dried under vacuum, dissolved in pentane and filtered. Purple and colorless crystals totaling approximately 0.025g (0.63mmol) were collected for an 18% yield. The best were set aside for x-ray analysis as detailed below. The two color sets of crystals were shown to have the same composition with the varying colors the result of dichroism.

^{1}H NMR (C_6D_6): δ 24 (br s, 12H, Si-CH_3) 21 (br s, 4H, P-CH_2-Si) -0.8 (br s, 36H, t-Butyl). ^{31}P NMR (C_6D_6): 19.7 (s, amine contamination)

PNPFe synthesis:

This compound was synthesized by two different methods. In both cases strict anhydrous and inert atmosphere conditions were observed. In the first method, PNPFeCl was stirred with a 100 fold excess of magnesium metal powder in 50 mL of THF overnight. This method resulted in an incomplete conversion of PNPFeCl to PNPFe with side products. In order to verify the NMR peaks found in the Mg synthesis, PNPFe was synthesized from the reducing agent NaNaphthalide. 0.004g (0.031mmol) of Naphthalene was dissolved in ~20 mL THF with a suspended excess of Na metal and allowed to stir for several hours until the solution had turned an intensely dark green. This solution was then taken and added drop wise to a solution of 0.017g (0.031mmol) of PNPFeCl in 30 mL

THF. After stirring overnight the solution had turned an intense dark brown. Solution was evacuated to dryness under vacuum, extracted with pentane and filtered. The filtrate was then crystallized from pentane for an approximately 20% yield, 0.0003g. The single dark brown crystal formed was used for x-ray crystallography, discussed below, while the remaining powder was used for NMR analysis.

^{1}H NMR (C_6D_6): δ 34 (br s, 12H, Si-CH_3) -9.0 (br s, 4H, P-CH_2-Si) -7.8 (br s, 36H, t-Butyl). ^{31}P NMR (C_6D_6): 19.7 (s, amine contamination)

PNPFe(CO)$_2$ synthesis:

This compound was synthesized by the addition of one atmosphere of CO gas to a solution of .05g (0.1mmol) of PNPFe in benzene. This resulted in an instantaneous color change in the solution from dark brown/yellow to a dark forest green. A sample was taken and NMR run. These NMR were unintelligible except for the disappearance of the PNPFe peaks. For this reason an IR was run by drying a sample of the solution and dissolving in pentane. The IR showed new peaks, when compared to pentane, at 1872 and 1945 cm^{-1}. On the strength of these IR peaks, it was undertaken to grow intensely blue crystals were grown by cooling overnight at -40 ºC, with the resulting crystals being analyzed by x-ray crystallography as discussed below.

Crystallographic Data:

The structures of the three crystals described above were determined by the Indiana University Molecular Structure Center according to a procedure described in detail for PNPFeCl below, quoting from an internal communication from Dr. Maren Pink.

A light brown crystal (approximate dimensions $0.25 \times 0.23 \times 0.20$ mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a SMART6000 (Bruker).

Data collection

The data collection was carried out using Mo K radiation (graphite monochromator) with a frame time of 10 seconds and a detector distance of 5.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of a sphere. Four major sections of frames were collected with 0.30º steps in at different settings and a detector position of $-43°$ in 2 . An additional set of 50 frames was collected in order to model decay. Data to a resolution of 0.84 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 6987 strong reflections from the actual data collection after integration (SAINT).[11] The intensity data were corrected for absorption (SADABS).[12] **Structure solution and refinement**

The space group P-1 was determined based on intensity statistics and the lack of systematic absences. The structure was solved using SIR-92[13] and refined with SHELXL-

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[11] SAINT, Bruker Analytical X-Ray Systems, Madison, WI, current version.

[12] An empirical correction for absorption anisotropy, R. Blessing, Acta Cryst. A51, 33 - 38 (1995).

[13] SIR-92, A. Altomare, G. Cascarno, C. Giacovazzo, A. Gualardi, J. Appl. Cryst. 26, 343-350 (1993).

97.[14] A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0331 and wR2 = 0.0863 (F^2, all data). The remaining electron density is located around the metal.

The remaining crystal structures were determined in a like fashion with Dr. Pink solving PNPFe also, while Dr. John Huffman solved the structure of FePNP$(CO)_2$. The key angles and bond distances for each complex are provided below, numbered as in the graphics within the document.

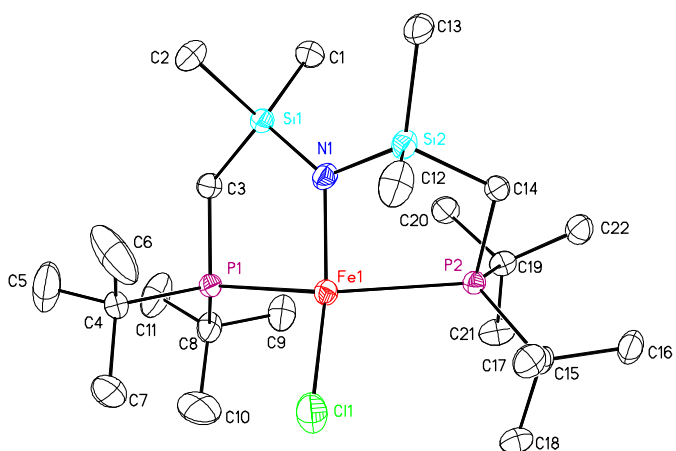Figure 10 – PNPFeCl – IUMSC #05190

Bond Distances (Å)

Fe1-N1	1.9824(18)	
Fe1-Cl1	2.2708(7)	
Fe1-P1	2.4943(6)	
Fe1-P2	2.5824(6)	
Si1-N1	1.7077(18)	
Si2-N1	1.7077(19)	

Bond Angles (°)

N1-Fe1-Cl1	139.98(6)

P1-Fe1-P2	137.07(2)
N1-Fe1-P1	92.50(5)
N1-Fe1-P2	88.22(5)
Cl1-Fe1-P1	103.59(2)
Cl1-Fe1-P2	103.01(2)

Figure 11 – PNPFe – IUMSC #05210

Bond Distances (Å)

Fe1-N1	2.0265(19)
Fe1-P1	2.2490(8)
Fe1-P2	2.264(8)
Si1-N1	1.6995(19)
Si2-N1	1.6950(19)
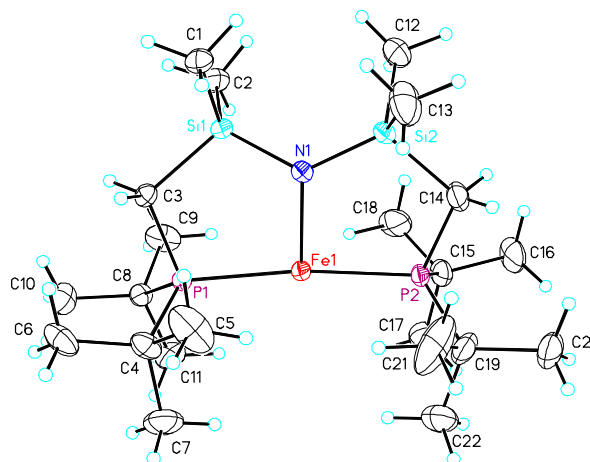
Bond Angles (°)

N1-Fe1-P1	94.14(6)
N1-Fe1-P2	93.0(6)
P1-Fe1-P2	172.7(5)

Figure 12 – PNPFe(CO)$_2$ – IUMSC #05234

Bond Distances (Å)

Fe(1)-N(1)	**2.039(2)**
Fe(1)-P(1)	**2.299(4)**
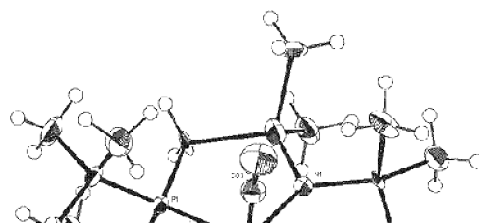
Fe(1)-P(2)	**2.331(4)**
Fe(1)-C(23)	**1.814(5)**
Fe(1)-C(24)	**1.738(4)**
Si(1)-N(1)	**1.707(6)**
Si(2)-N(1)	**1.722(4)**
O(1)-C(23)	**1.141(6)**
O(2)-C(24)	**1.171(5)**

Bond Angles (º)

N(1)Fe(1)P(1)	87.10(13)
N(1)Fe(1)P(2)	90.67(11)
P(1)Fe(1)P(2)	156.02(16)
C(24)Fe(1)P(1)	89.06(19)
C(23)Fe(1)P(1)	99.49(18)
C(24)Fe(1)P(2)	89.05(18)
C(23)Fe(1)P(2)	104.48(17)
C(24)Fe(1)N(1)	169.89(16)
C(23)Fe(1)N(1)	93.97(15)
C(24)Fe(1)C(23)	95.9(2)
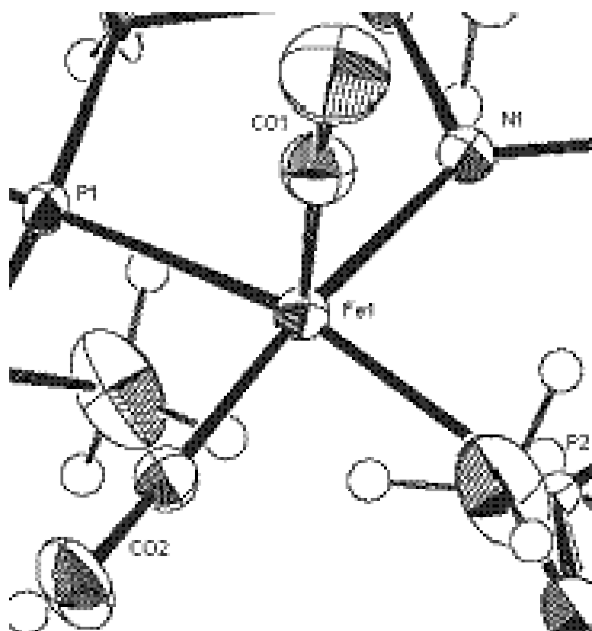
zoom of figure 12
metal center

Magnetic Moment Determination Procedure:

A modified version of Evans' method[15] for magnetic susceptibility determination was used

on pure crystals of each compound. The procedure used will be described in detail for

PNPFeCl with the other two complexes being analyzed in a similar fashion.

Magnetic Moment of PNPFeCl:

A J-Young tube and a flame sealed capillary tube with deuterated benzene were

placed in a glovebox with a vial of PNPFeCl which had been drying overnight under

vacuum. Also taken in was a syringe for the accurate addition of 0.500 mL of deuterated

benzene. Exactly 0.0109g (0.0202 mmol) of PNPFeCl was added to the J-Young tube

followed by 0.490 mL of d_6-benzene for a concentration of 0.0222g/mL. Finally the flame

sealed capillary was placed in the Young's tube and the tube sealed. The Young's tube

was removed from the glovebox and a ^{1}H NMR run. The NMR showed a peak shift of -

432 Hz. Using the Evans' method equation, at a temperature of 298 K with a 300 MHz

(Gemini 300) NMR spectrometer:

$\mu_{obs}= \text{sqrt}(\ \chi_{spin\text{-}only}\ {}^* \chi_{ligand}\ )$;

where $\chi_{spin\text{-}only} = 2.344 \times 10^3$ at 298 K

and $\chi_{ligand} = \chi_{obs}$ - ligand-effect

and $\chi_{obs} = -3/4\ {}^*\ (-432Hz\ /\ (\pi^*300MHz^*.0222g/mL))$

so that for PNPFeCl

$\mu_{obs}= \text{sqrt}(\ 2.344 \times 10^7\ {}^*\ 8.73 \times 10^{-3}) =$ **4.6 μ_B**

which when compared to the spin-only magnetic moment of $\mu = 2^*\text{sqrt}(S(S+1))$,

assuming a **high spin state d^6** complex (S=2)

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[15] D. F. Evans, *J. Chem. Soc.,* 2003 (1959)

$\mu_B = 2*\text{sqrt}(S(S+1)) = 2*\text{sqrt}(2(3)) = 4.9 \ \mu_B$

seems in good agreement with the data.

Magnetic Moment of PNPFe:

Concentration = 0.0116g / 0.490 mL

NMR peak shift = -497 Hz

At 298 K, μ_{obs}= **4.53 μ_B**

Spin only for S=0.5, μ= 1.7 μ_B

Spin only for S=1.5, μ= 3.9 μ_B

If **high spin d^7** then S=1.5 in agreement with data,

if low spin d^7 S=0.5 in contradiction to the data.

Magnetic Moment of PNPFe(CO)$_2$:

Concentration = 0.012g / 0.490 mL

(Previous FePNP sample gassed with excess CO)

NMR peak shift = -105 Hz

At 298 K, μ_{obs}= **2.33 μ_B**

Spin only for S=0.5, μ= 1.73 μ_B

Spin only for S=1.5, μ= 3.9 μ_B

If **low spin d^7** then S=0.5 in agreement with data.