Synthesis of two tripodal amine-phosphine ligands for the stabilization of Fe-P and Fe-V bonds

By: Sam Kenny

Under the supervision of Dr. Connie Lu and Alex Rudd

Abstract:

Bonds between metals and supporting elements are thought to play an important role in reactivity of catalysts and enzyme active sites. Iron catalysts are of particular interest, iron being cheap, abundant, and environmentally benign.[1] While natural iron-based enzymes such as MoFe-nitrogenase are known to facilitate small molecule activation, synthetic analogs are scarce, due in part to the lack of understanding of the role of supporting elements. To elucidate this role, attempts were made to synthesize and characterize molecules containing an iron atom bound to a supporting atom, held together by a tridentate ligand framework containing amine and phosphine binding sites. Of two ligand syntheses that were attempted, one was successful. Attempts were made to insert in this ligand both phosphorus and vanadium as the supporting element to iron. ^{1}H NMR and [1]P NMR spectra indicated that while formation of P-Fe and V-Fe complexes may have been successful, neither pure complex was isolated.

Introduction:

Synthesis of catalysts that improve the yield, rate, and selectivity of chemical reactions is a central goal of chemical research. Recent advancements in catalyst development have yielded promising results for a wide variety of organic transformations, including stereoselective hydrogenations, ketone and aldehyde reductions, and C-C bond formation to name a few.[1-3] Yet

challenges in catalyst development remain daunting, especially in the field of small molecule activation. The promise that catalysts hold to address pertinent issues of environmental and societal concern is directly at odds with the difficulty of activating small molecules such as carbon dioxide and dinitrogen. This difficulty stems partly from a lack of understanding of electronic interactions between the catalyst active site and small molecule substrate, which is compounded when ligand electronic effects or the effects of multiple metal centers are considered. Yet studying the complex biomolecules which can successfully facilitate small molecule transformations necessitates the consideration of both of these factors. Successful catalyst development, then, requires a deeper understanding of these interactions.

The goal of this study was to elucidate the role of metal-supporting atom interactions in affecting catalytic activity. Such metal-support interactions are common in small molecule activating enzymes such as molybdenum-iron (MoFe) nitrogenase (Fig. 1). This enzyme, found in certain microorganisms, can reduce atmospheric dinitrogen to ammonia at atmospheric pressure and room temperature (industrial ammonia production requires pressures over 200 atm and temperatures of 500 °C). The enzyme's active site consists of an iron-sulfur cluster with a single nearby molybdenum atom. The presence of iron makes this a particularly interesting molecule to study and emulate, since iron is cheap, abundant, and environmentally friendly when compared to existing heavy metal catalysts. There is a supporting element, E (now known to be carbon[4]) which is directly bound to the iron atom to which N_2 is thought to bind. The role of this supporting element may be essential in tuning the reactivity of the binding site. Synthesis of compounds containing an Fe-E bond (E=heteroatom) could establish trends which would allow for control of iron's catalytic activity.
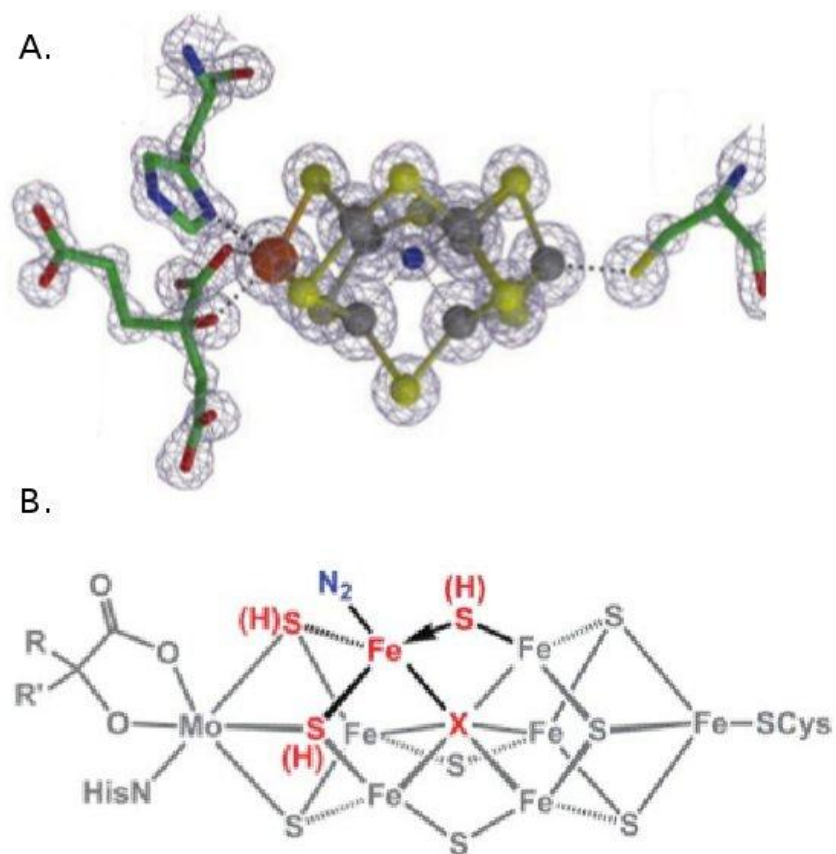
Figure 1: A. Experimentally determined crystal structure of the MoFe active site. B. Line drawing of active site, showing a possible dinitrogen binding site.

To investigate the role of the supporting element on iron's catalytic activity, two ligand frameworks were first targeted as frameworks for the Fe-X bond. One had been previously and successfully synthesized (Fig. 2A), while the other had not (Fig. 2B).[5,6] Structures for these ligands are given below.
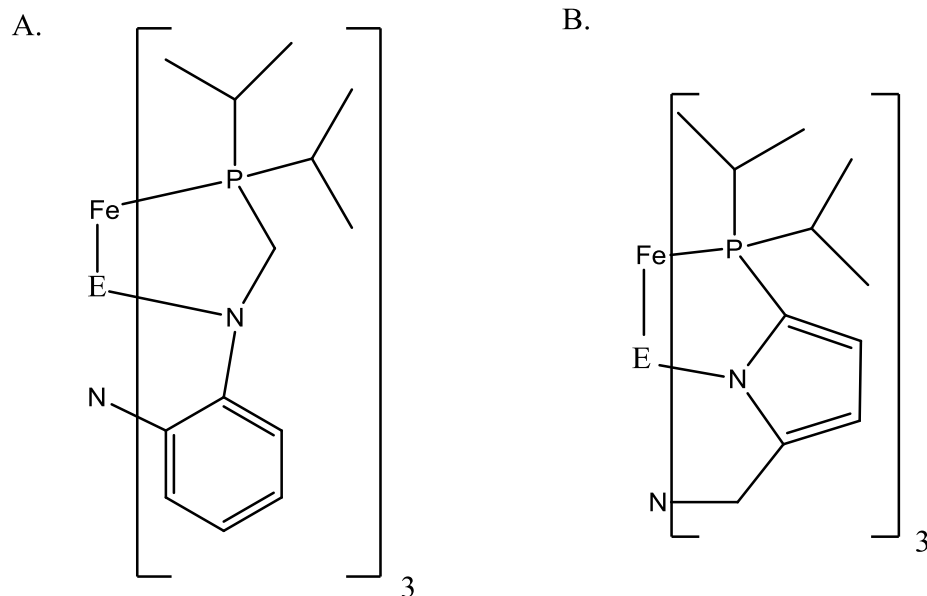
Figure 2: Structures of synthetic goals: E-Fe complexes stabilized by tridentate amine-phosphine ligands with (A) phenyl and (B) pyrrolyl backboes.


Both ligands consist of amine and phosphine metal binding sites, along with aromatic backbones which make A a strong electron donor and B a less strong donor. While ligand A had previously been successfully synthesized,[5] ligand B has only been partially synthesized as tris(pyrrolyl-α-methyl)amine (H_3tpa).[6] To our knowledge, no attempt in the literature has been made to this date to add phosphine arms to the H_3tpa ligand for the purpose of stabilizing a bimetallic complex. The purpose of selecting two ligand frameworks was to expand the number of possible synthetic routes towards creating Fe-X bonds. The ligands were chosen to be similar enough to facilitate similar experimental procedures, yet different enough (in terms of Fe-ligand and Fe-X bond lengths) to allow for varied energetics and reactivity.

Newly synthesized complexes were characterized by NMR spectroscopy. Additional methods such as UV-Vis spectroscopy, IR spectroscopy, X-ray crystallography, cyclic voltammetry, and Mössbauer spectroscopy have not yet been employed.

Procedure:

General considerations:

All manipulations of air-sensitive compounds were performed under a dinitrogen atmosphere in an MBraun Atmosphere glovebox or using standard Schlenk techniques. Dry solvents were obtained from an SG Water solvent purification system. Deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc. All dried solvents were stored over 4 Å molecular sieves. ^{1}H and ^{31}P NMR spectra were recorded using a Varian 300 MHz spectrometer at ambient temperature. Ligand syntheses and metallation with iron were adapted directly from literature procedures.[5,6] Metallations with phosphorus and vanadium were performed based on literature procedures for analogous reactions.[5] Aryl proton numberings for ^{1}H NMR analysis are shown below.
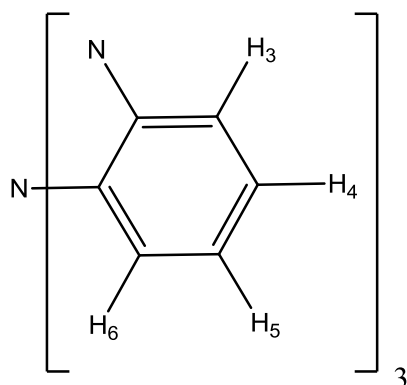
Figure 3: Proton numbering for NMR peak assignments

N(o-C$_6$H$_4$-NO$_2$)$_3$ (1)

A 250 mL round bottom flask was charged with a stir bar, potassium carbonate (30 g, 217 mmol), and 2-nitroaniline (5.1 g, 37 mmol). Enough DMSO was added to cover all solids (approx. 40 mL). The flask was fitted with a condenser and purged with nitrogen (15 mins). 2-fluoronitrobenzene (16.5 mL, 156 mmol) was added, and the resulting mixture was stirred at 145 °C for 72 hours. Upon cooling to

room temperature, the reaction mixture was then diluted with distilled water (200 mL) and filtered

through a coarse porosity frit. The resulting brown solid was rinsed liberally with acetone until washes

ran light yellow. This yielded a yellow solid, **1**, which was dried *in vacuo* (0.440 g, 3.1%); ^{1}H NMR (ppm,

$CDCl_3$, 300 MHz): δ 7.84 (dd, J=8, 1.5 Hz, 1H, 3-C_6H_4), 7.54 (td, J=7.8, 1.5 Hz, 1H, 5-C_6H_4), 7.31 (td, J=7.8

Hz, 1.3 Hz, 1H, 4-C_6H_4), and 7.22 (dd, J=8.2, 1.3 Hz, 1H, 6-C_6H_4)

$N(o\text{-}C_6H_4\text{-}NH_2)_3$ (2a)

A Parr high pressure vessel was charged with **1** (4.997 g, 13.1 mmol), Pd/C catalyst (10% Pd by

mass, 2.808 g), THF (40 mL), and a stir bar. The bomb was sparged three times with hydrogen, and was

then put under a hydrogen atmosphere (450 psi) for 24 hours with stirring. Subsequent workup was

performed in an air-free glovebox. The solution was filtered over Celite in a medium porosity frit. The

Pd/C residue was rinsed with additional THF. The filtrate was evaporated, and the resulting solid was

washed with ether in a medium porosity frit. Drying overnight yielded **2** as a white solid (3.11 g, 82%);

^{1}H NMR (ppm, $CDCl_3$, 300 MHz): δ 7.00 (td, J=7.3, 1.5 Hz, 1H, 4-C_6H_4), 6.92 (dd, J=7.5, 1.3 Hz, 1H, 6-C_6H_4),

6.72 (m, 2H, 3,5-C_6H_4), and 3.70 (s, 2H, NH_2)

Atmospheric pressure synthesis of $N(o\text{-}C_6H_4\text{-}NH_2)_3$ (2b)

A 250 mL Schlenk flask was charged with a stir bar, **1** (4.993 g, 7.338 mmol), and THF (80 mL).

The resulting solution was purged with nitrogen while stirring for 45 minutes. Pd/C (10% Pd by mass,

2.386 g) was then added. The mixture was stirred at room temperature under a hydrogen atmosphere

for 36 hours. The flask was then brought into the glovebox for workup. Solvent was evaporated,

yielding a black residue. This was redissolved in THF (50 mL) and filtered over celite through a frit.

Concentration of the filtrate yielded a sticky pink solid.

N(o-C$_6$H$_4$-NHCH$_2$P^{i}Pr$_2$)$_3$ (3)

This procedure was performed by Alex Rudd. A sample procedure is given below.[5]

Diisopropylphosphine was freshly distilled prior to use under a nitrogen atmosphere. Diisopropylphosphine was added dropwise to vial containing one equivalent of paraformaldehyde. The resulting slurry was stirred at 60 °C for four hours. The reaction, which yielded diisopropylphosphinomethanol, was determined to be complete by ^{31}P NMR spectroscopy. Four equivalents of this product were added to a solution of **2a** in DMSO (approx. 2 mL). The solution was sealed in a Schlenk flask and stirred overnight at 100 °C. Removal of solvent *in vacuo* at 65 °C was followed by collection of the resulting white solid on a medium porosity frit. The solid was washed with anhydrous DMSO and with acetonitrile (2 x 20 mL). **3** was isolated as a white powder (90 %). ^{1}H NMR (from lit.[5]) (C$_6$D$_6$, 300 MHz): δ 6.99 (t, J=9 Hz, 1H, 4-C$_6$H$_4$), 6.92 (d, J=9 Hz, 1H, 6-C$_6$H$_4$), 6.65 (d, J=9 Hz, 3-C$_6$H$_4$, 1H), 6.49 (s, J=9 Hz, 5-C$_6$H$_4$), 4.11 (s, NH, 1H), 3.10 (d, ^{2}J$_{HP}$ = 15 Hz, CH$_2$P^{i}Pr$_2$, 2H), 1.53 (br, CHMe$_2$, 1H), 1.30 (br, CH'Me$_2$, 1H), 0.94 and 0.84 (d, J=6 Hz, CH$_3$, 12H). ^{31}P NMR (from lit.[5]) (C$_6$D$_6$, 121 MHz): δ 3.05 (s)

Li$_3$N(o-C$_6$H$_4$-NCH$_2$P^{i}Pr$_2$)$_3$ (4)

3 (21.5 mg, 0.0316mmol) was dissolved in ether (3 mL) in a scintillation vial containing a stir bar. The solution was frozen at -196 °C, and n-butyllithium (2.5 M solution in hexanes, 39µL, 0.098mmol) was added. The solution was warmed to room temperature while stirring over a period of several minutes. Evaporation of volatiles *in vacuo* yielded **4** as a white solid.

VN(o-C$_6$H$_4$-NCH$_2$P^{i}Pr$_2$)$_3$ (5)

The previously prepared sample of **4** was used without further purification. **4** (assumed 0.0316 mmol) was dissolved in THF (3 mL) and frozen. VCl$_3$THF$_3$ (11.8 mg, 0.0316 mmol) was dissolved in THF (3

mL) and cooled to freezing. The solution of **4** was added dropwise while thawing to the frozen solution

of VCl_3THF_3. A stir bar was added to this mixture, which was allowed to stir overnight in a slowly

warming LN_2 coldwell. A yellow-brown solution was obtained. Lithium salts were removed by filtration

through celite. Removal of solvent in vacuo yielded **5** as a brown solid: 22.3 mg, 97%; ^{1}H NMR (ppm,

C_6D_6, 300 MHz): 9.39

VFeN(o-C_6H_4-$NCH_2P^iPr_2$)$_3$ (6)

The previously prepared sample of **5** (22.3 mg, 0.0306 mmol) was dissolved in THF (5 mL). This

was added to a suspension of $FeBr_2$ (6.6 mg, 0.0307 mmol) in THF (2 mL). The resulting mixture was

stirred for one hour. A suspension of KC_8 (4.5 mg, 0.0333 mmol) in THF (3 mL) was then added. The

resulting mixture was stirred for a few hours. Solution color changed from green-brown to yellow-

brown over the course of several minutes. Salts were removed by filtration through celite. Removal of

THF *in vacuo* yielded **6** as a brown solid. ^{1}H NMR (ppm, C_6D_6, 300 MHz): 17.6, 15.9, 12.6, 9.7, 6.8, 6.6,

6.3, 6.0, 5.2, 2.8, and 2.6

PN(o-C_6H_4-$NCH_2P^iPr_2$)$_3$ - synthesis with n-butyllithium (7a)

To a solution of **4** (0.035 mmol) in ether was added PCl_3 (5 μL, 0.06mmol). The resulting solution

was stirred for several hours at room temperature. The solution quickly turned from pale yellow to dark

orange in color. Removal of solvent *in vacuo* yielded **7** as a dark brown solid. ^{31}P NMR (C_6D_6, 121 MHz):

3.99 (d) and -113.99 (q)

PN(o-C_6H_4-$NCH_2P^iPr_2$)$_3$ - synthesis with Hünig's base (7b)

A solution of **3** (33.6 mg, 0.049mmol) in CH_2Cl_2 (3 mL) was added dropwise to a solution of N,N-

diisopropylamine (28 μL, 0.16 mmol) and PCl_3 (4 μL, 0.05 mmol) in CH_2Cl_2 (5 mL). The resulting solution

was stirred for one hour at room temperature. A yellow color developed after a few minutes.

Evaporation of solvent yielded **7** as a yellow solid. ^{31}P NMR (C_6D_6, 121 MHz): 134.25 (s)

H_3tpa (9)

Ammonium chloride (0.240 g, 4.49 mmol) and paraformaldehyde (0.406 g, 13.5 mmol) were

dissolved in a 2:1 solution of EtOH/H_2O (12 mL total) in a 100 mL round bottom flask. This solution was

degassed with nitrogen for 15 minutes. Pyrrole (0.95 mL, 13.7 mmol) was then added. The resulting

solution was stirred under a nitrogen atmosphere at 40 °C for three hours. Solvent was removed by

rotary evaporation. To the resulting residue were added 1:1 solution of THF and ether (10 mL) and 20%

NaOH solution (5 mL). The organic layer was separated. The aqueous layer was extracted with ether (2

x 6 mL). The organic layers were combined and concentrated to yield **9** as a white solid (2.03 g, 59%); ^{1}H

NMR (ppm, CDCl$_3$, 300 MHz): 6.78 (m, aryl H, 1H), 6.23 (m, aryl H, 1H), and 6.16 (m, aryl H, 1H)

## Results and Discussion:

1. Synthesis of ligand supports for P-Fe and V-Fe bonds

a. N(o-C$_6$H$_4$-NHCH$_2$P^{i}Pr$_2$)$_3$

Two ligands were targeted as potential frameworks for the formation of E-Fe bonds. The first,

N(o-C$_6$H$_4$-NHCH$_2$P^{i}Pr$_2$)$_3$, has been isolated and fully characterized in the literature.[5] This ligand has been

shown to successfully stabilize iron complexes including Al-Fe and Cr-Fe.[5,7] It was synthesized in three

steps, according to schemes 1, 2, and 3.

Product **1** was obtained in poor yield but good purity as evident by ^{1}H NMR (Fig. 4).
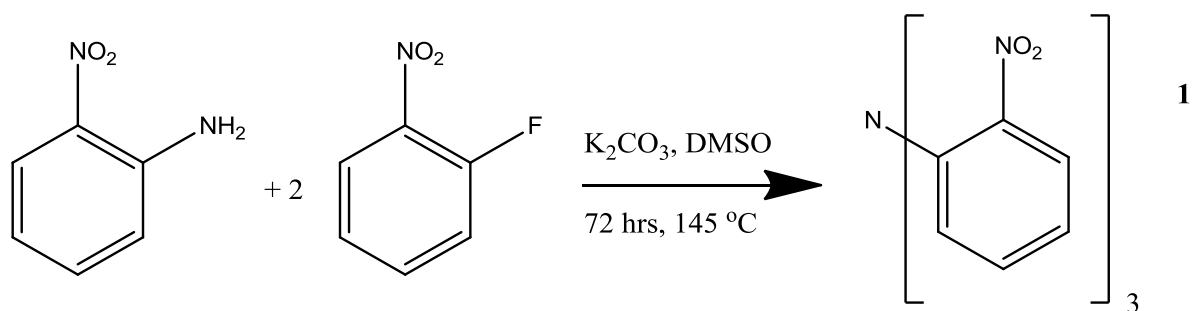
Scheme 1: Synthesis of N(o-C₆H₄-NO₂)₃ from o-nitroaniline and o-fluoronitrobenzene.
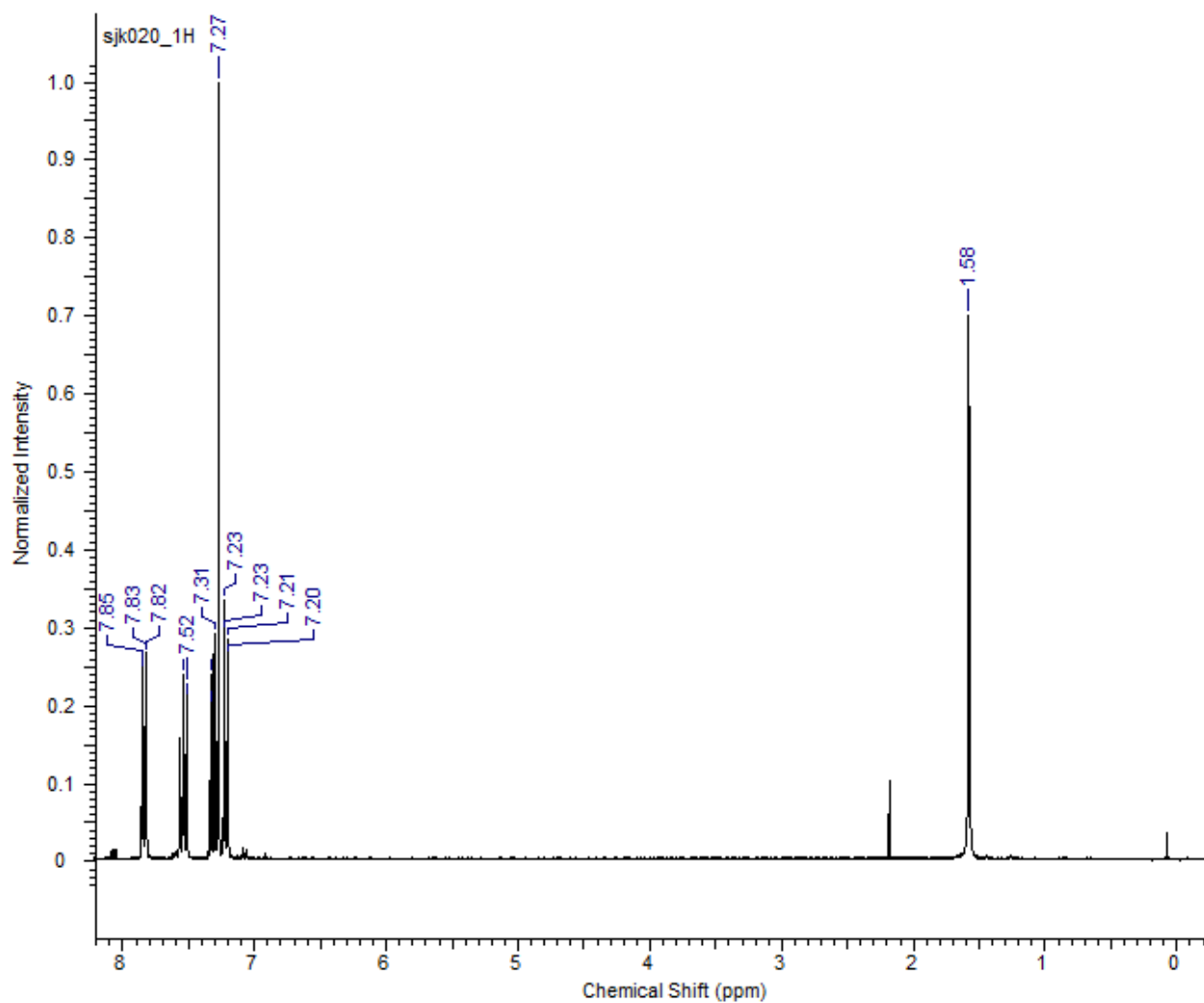
Figure 4: ¹H NMR of N(o-C₆H₄-NO₂)₃. Purity is indicated by the absence of any peaks from 0 to 7 ppm. Water (1.58) and acetone (2.07) are present.

Obtaining product **1** in good yield according to the aforementioned procedure seemed to be a trade-off between purity and yield, depending on the amount of acetone used in the rinse step. The crude product consists of the yellow, pure product immersed in a dark brown paste. The dark brown impurities can be rinsed away with acetone. However, the desired product is also sparingly soluble in acetone. A modified procedure might require less acetone use, and therefore less product loss. One additional step may be to stir the brown sludge with water for an extended period of time, breaking up the sludge and increasing the surface area accessible to the acetone for rinsing. Another may be to use cold acetone to minimize the solubility of the desired product. Other purification methods could be attempted with possibly better yields. Recrystallization could be attempted, which could separate off impurities with minimal product loss.

Two procedures were attempted for the synthesis of **2**: the proven method involving the Parr bomb as well as the atmospheric pressure method (Scheme 2).
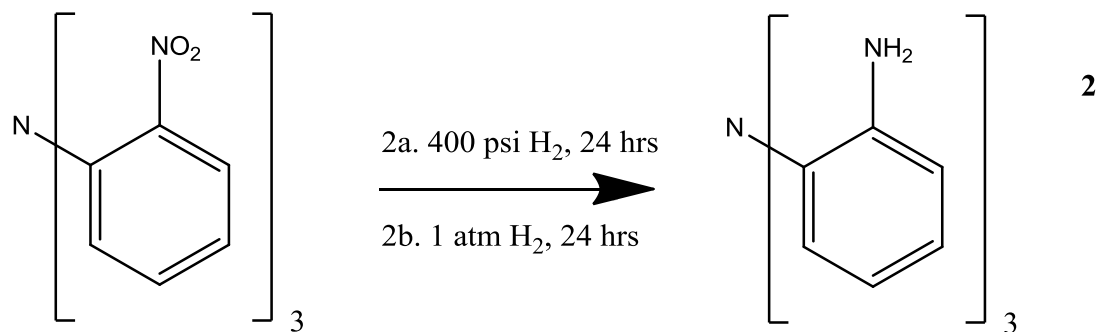
Scheme 2: Two schemes for the hydrogenation of N(o-C$_6$H$_4$-NO$_2$)$_3$ under high pressure (2a) and low pressure (2b).

The atmospheric pressure method was favored for its ease of use and scalability; the Parr bomb has a maximum volume of around 40 mL. Hydrogenation in the Schlenk flask resulted in an impure, pink product, as opposed to the pure white product obtained through bomb hydrogenation. This could be due to the bomb being a better air-free environment; it could also be that the slower reaction rate in

the standard pressure synthesis allows for oxidation to play a relatively greater role. Pure product **2** was

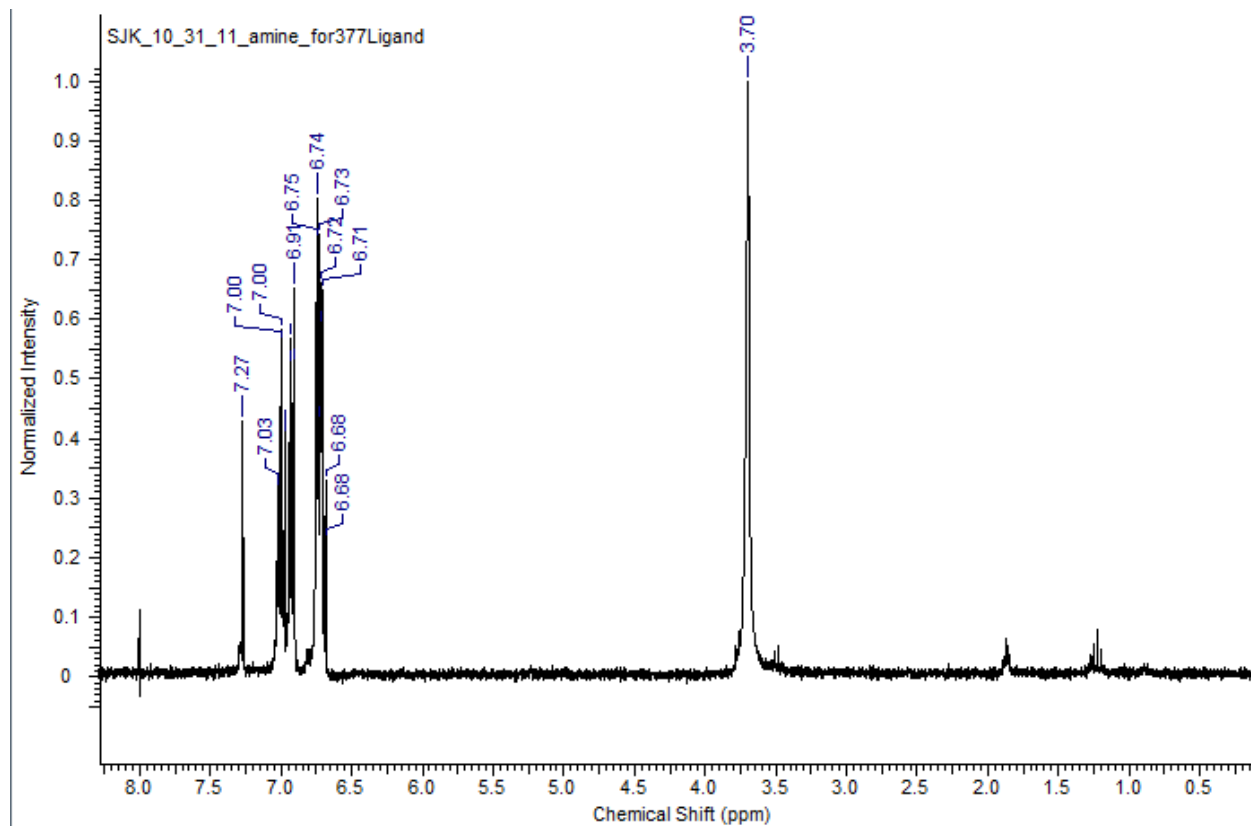only isolated using the high pressure method, as indicated by ^{1}H NMR (Fig. 5).

Figure 5: ^{1}H **NMR of N(o-C₆H₄-NH₂)₃. Proof of the reaction proceeding to completion is evident by the presence of an amine singlet at 3.70 and the absence of reactant peaks around 7.27.**

The final step in the synthesis of N(o-C₆H₄-NHCH₂P^{i}Pr₂)₃ was the addition of

diisopropylphosphine, as indicated by Scheme 3. This step was performed by Alex Rudd in order to

conserve the expensive diisopropylphosphine. This step usually proceeded with good yield and purity.
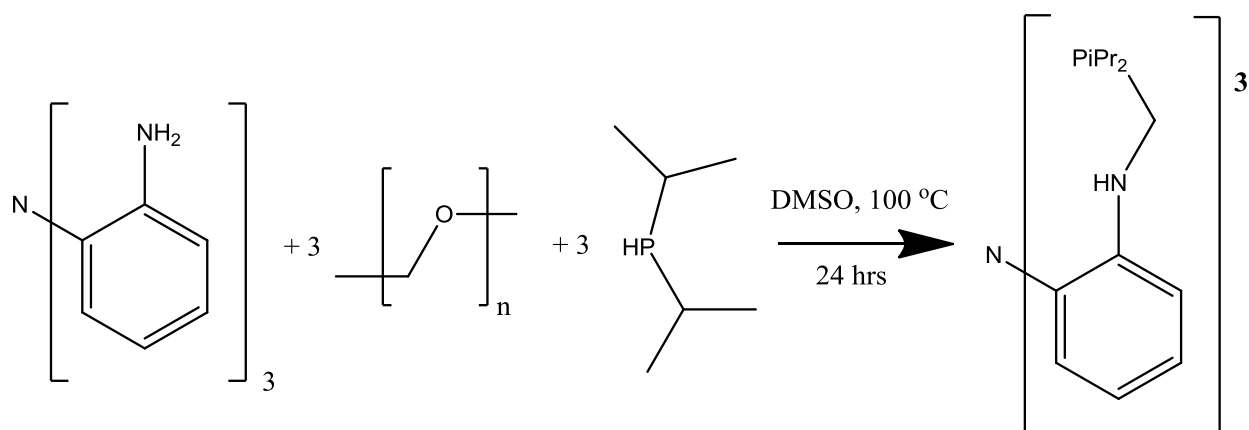
Scheme 3: Addition of diisopropylphosphine and paraformaldehyde resulted in the finished ligand N(o-C$_6$H$_4$-NHCH$_2$P^{i}Pr$_2$)$_3$.

b. Synthesis of H$_3$tpa

Literature reports of the tridentate pyrrole-based ligand H$_3$tpa for stabilizing a wide variety of transition metals,[6] as well as its similarity to N(o-C$_6$H$_4$-NO$_2$)$_3$ made it attractive as a building block for an alternate ligand framework. Efforts to synthesize H$_3$tpa by Scheme 4 were marginally successful; a white solid was obtained in one case which had similar ^{1}H NMR shifts to the literature values.
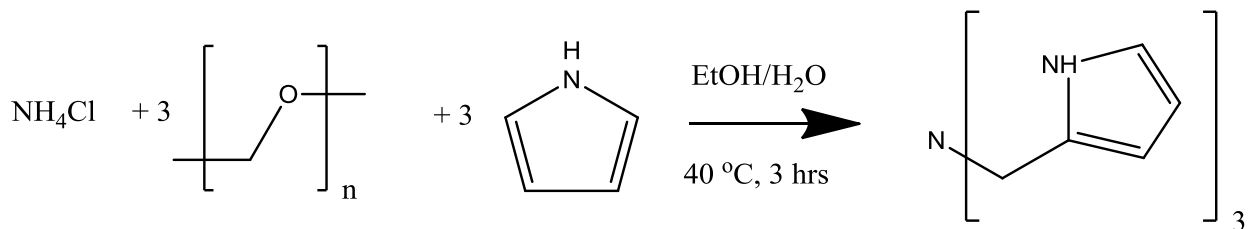
Scheme 4: Synthesis of H$_3$tpa from pyrrole, paraformaldehyde, and ammonium chloride according to a literature procedure.[6]
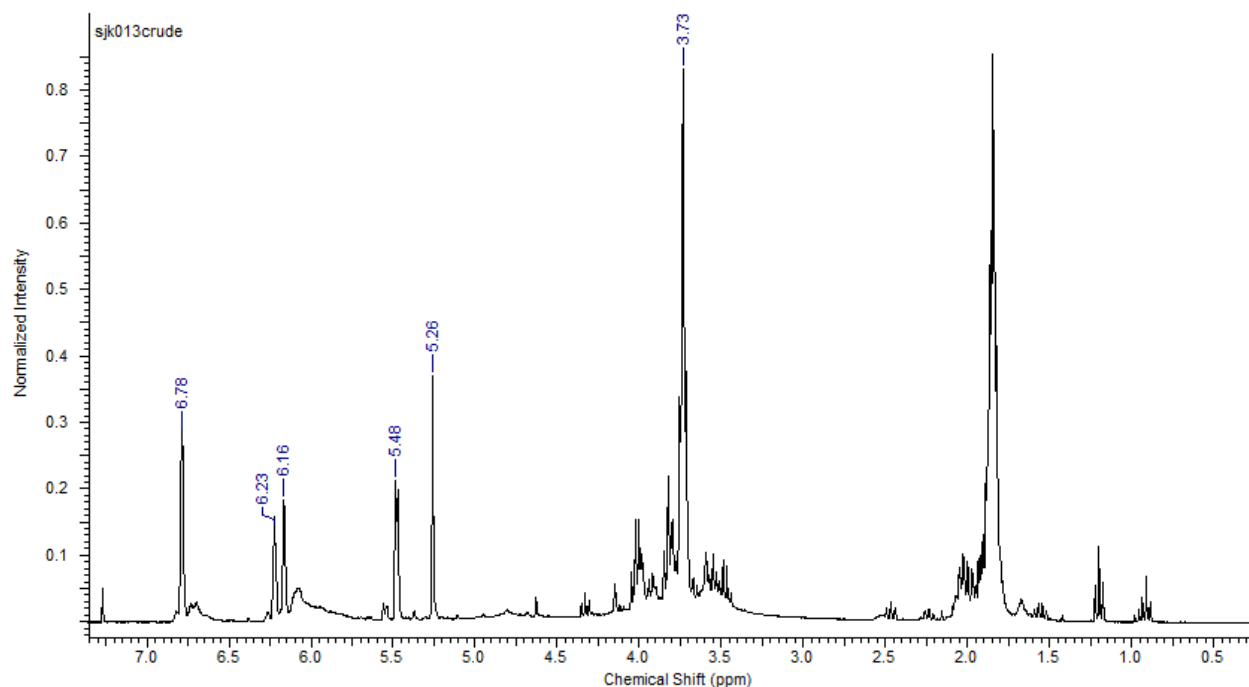
Figure 6: ^{1}H NMR spectrum of product 9, which may be impure H$_3$tpa.

Several peaks visible in the ^{1}H NMR spectrum indicate the presence of H$_3$tpa: multiplets at 6.78,

6.22, and 6.16 ppm correspond to the literature values of 6.70, 6.15, and 6.06, and a methylene singlet

at 3.73 corresponds to the literature value of 3.57.

An important experimental consideration for the attempted synthesis reported here is that the

pyrrole was not distilled prior to use. Time constraints prohibited the successive distillation,

preparation, synthesis, and workup required by including a distillation. As a result, NMR showed a mix

of products, likely due to side reactions involving polypyrrole impurities. Attempts were made to isolate

the H$_3$tpa product, including recrystallization (THF/pentane) and column chromatography (3:1

EtOAc:hexanes). Despite these efforts, H$_3$tpa was never isolated. A more straightforward approach

would be to distill the pyrrole prior to use.

2. Metallations

Metallations were performed for the $N(o\text{-}C_6H_4\text{-}NHCH_2P^iPr_2)_3$ ligand using procedures adapted from previous successful metallations.[5,7] Insertions of both phosphorus and vanadium were attempted. Insertion of iron was attempted for the synthesized $VN(o\text{-}C_6H_4\text{-}NHCH_2P^iPr_2)_3$ complex.

a. Synthesis of a new V-Fe complex

Insertion of vanadium in the form of VCl_3THF_3 was attempted according to Scheme 5. Deprotonation of the free ligand with n-butyllithium was followed by addition of VCl_3THF_3. Successful synthesis of the VL complex was indicated by paramagnetism (broad peak at 9.4 ppm) and lack of starting material in the ^1H NMR spectrum (Fig. 7). Presence of free ligand would have been indicated by multiplets between 6 and 7 ppm.
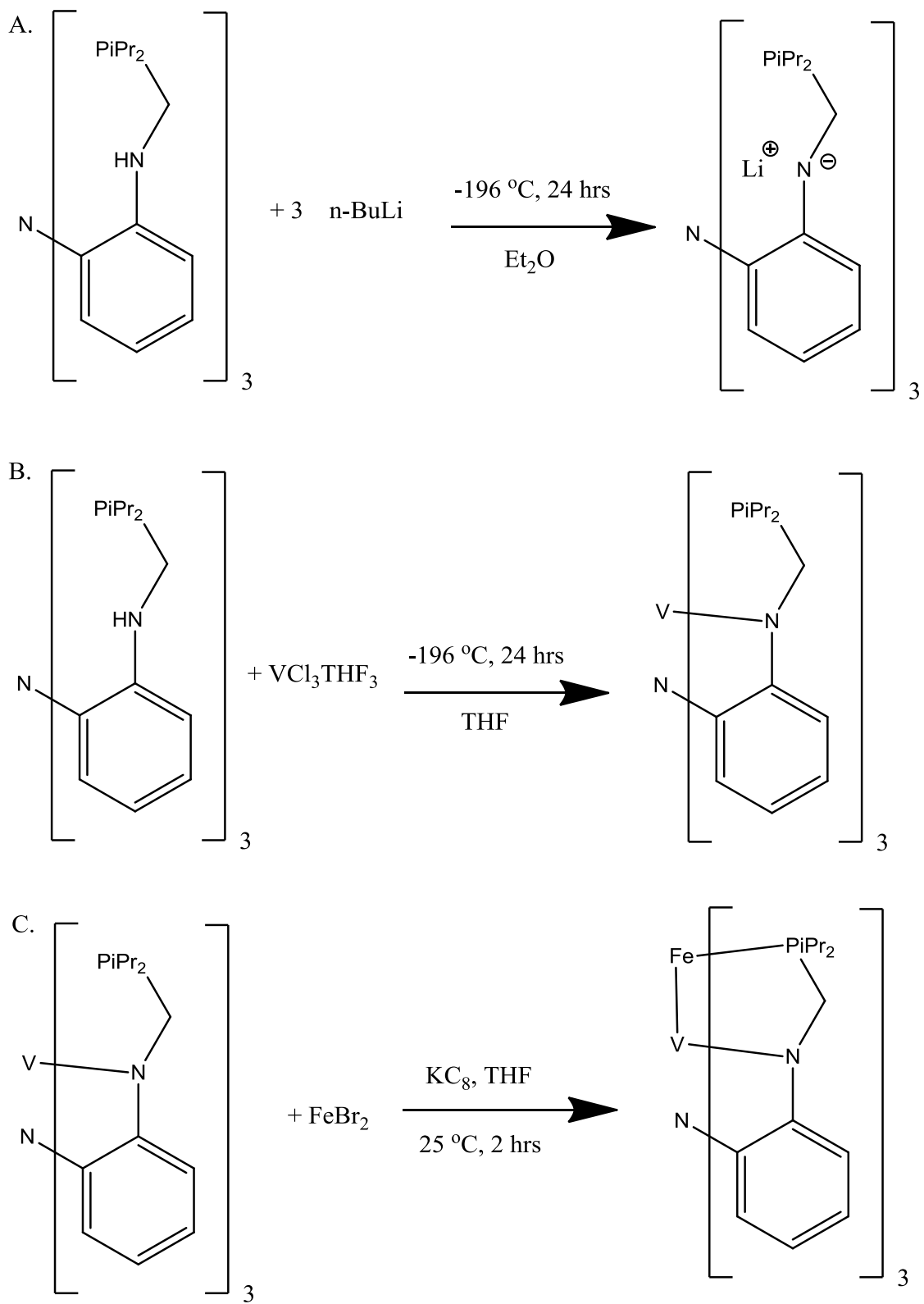
Scheme 5: Synthesis of a V-FeL complex by: A. deprotonation of free ligand, B. metallation with VCl₃THF₃, and C. addition of FeBr₂ and reduction by KC₈.
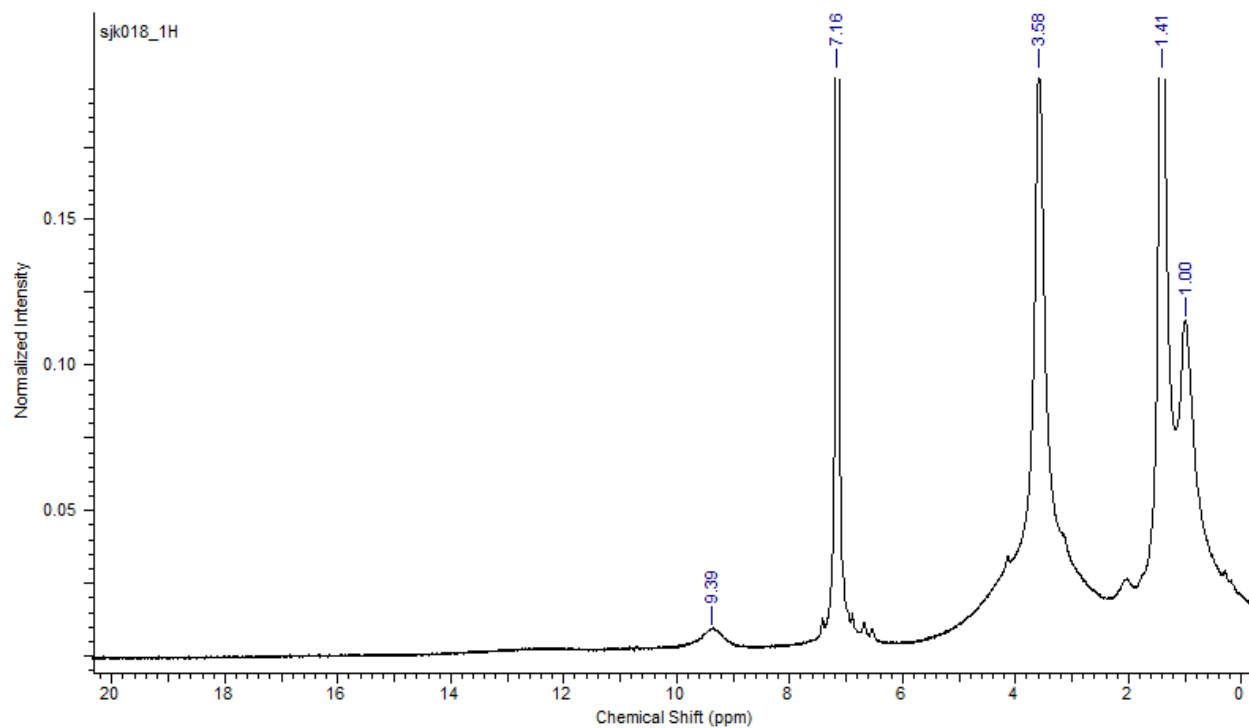
Figure 7: ^{1}H NMR spectrum of the VL complex. Paramagnetism is indicated by a broad peak at 9.39 ppm.

This complex may have been coordinated to THF, but this was difficult to determine due to the high degree of residual THF in the spectrum.

Comparison of NMR spectra supports the possibility that a new complex containing a V-Fe bond was synthesized. This is based on two observations. First, new peaks were observed in the FeVL spectrum when compared to the VL spectrum, indicating that a reaction occurred. None of the newly observed peaks in the FeVL complex corresponded to free ligand (which has shifts of 6.99, 6.62, 6.65, and 6.49 ppm). Paramagnetism was observed in the ^{1}H NMR spectrum of the FeVL product, with new paramagnetic peaks arising at 17.62, 15.86, 12.59, and 9.71 ppm.
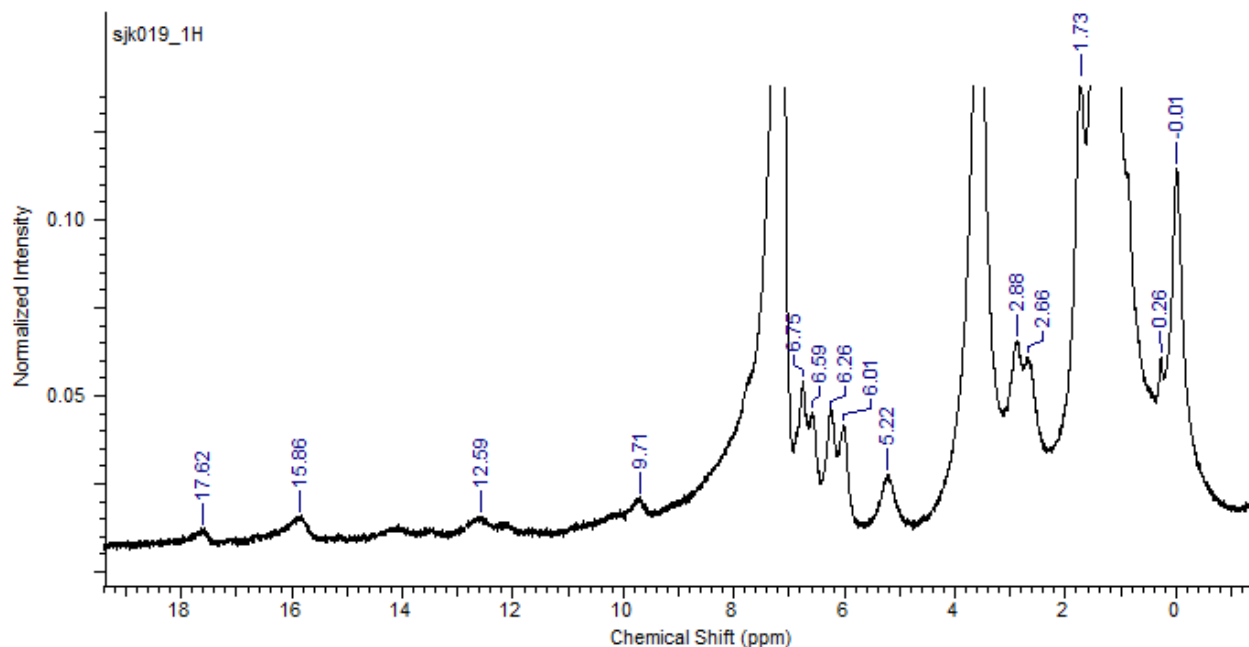
Figure 8: ^{1}H NMR spectrum of the proposed FeVL complex. Paramagnetic peaks can be seen from 9 to 18 ppm. Other new peaks (as compared to the VL spectrum) are visible between 2 and 7 ppm.

While comparison of NMR spectra supports the possibility of a new FeVL complex, it does not offer conclusive evidence. The numerous peaks may indicate side reactions and impurities. More characterization data is required to determine the outcome of this reaction. In particular, ^{31}P NMR would be a useful indicator of the number of products, and would easily determine (by a singlet peak at 3 ppm) if free ligand were present.

2. Phosphorus insertion in products 7a and 7b

Insertion of phosphorus was attempted in two ways: the first was analogous to metallation with vanadium (deprotonation with n-butyllithium followed by addition of PCl$_3$), while the other was an attempt at a soft metallation using an *in situ* deprotonation with Hünig's base. Both are outlined in Scheme 6.
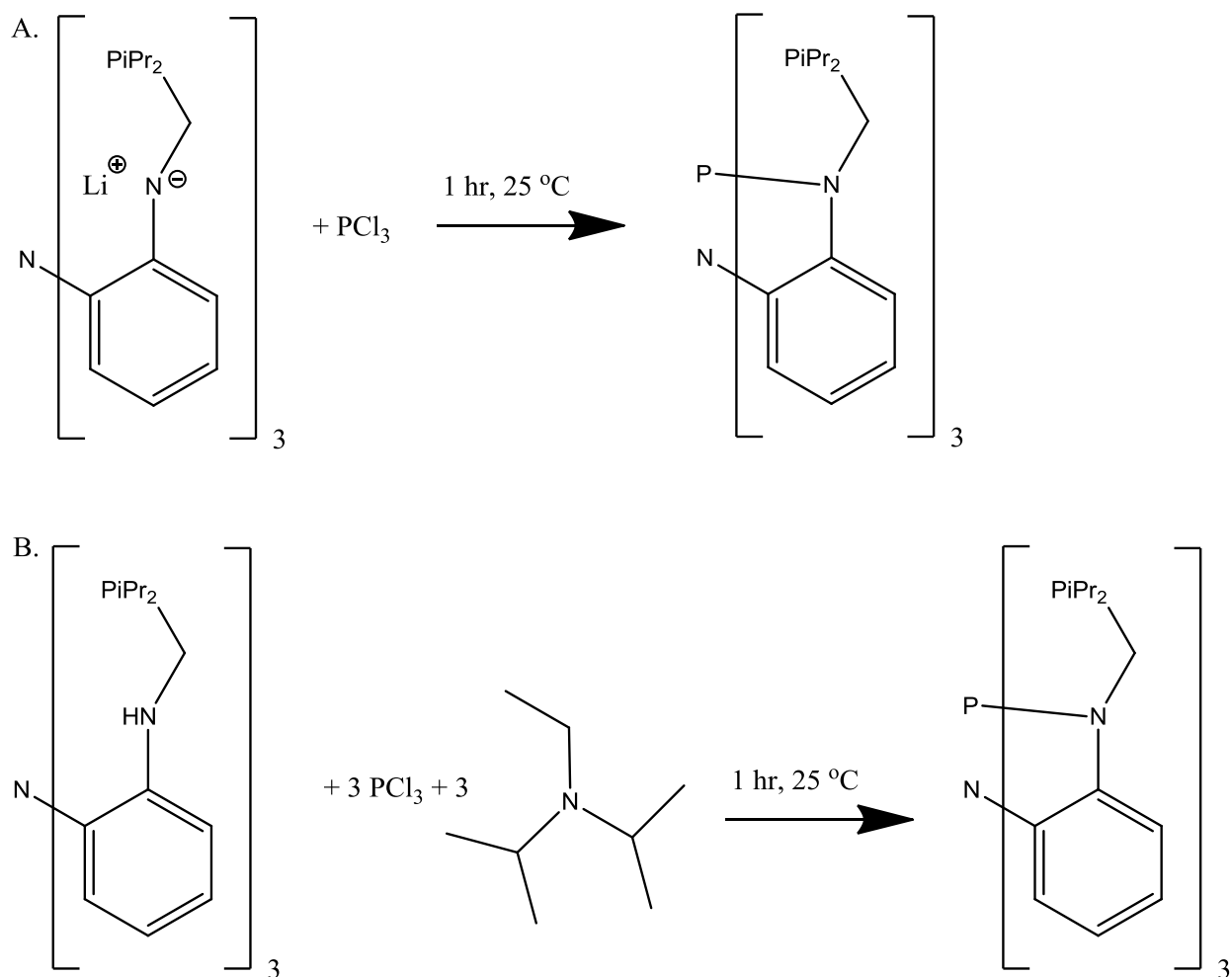
Scheme 6: Attempted insertion of phosphorus using two different deprotonation schemes: deprotonation by n-butyllithium (A) and an *in situ* deprotonation with Hünig's base (B).

Product **7** had a messy ^{31}P NMR spectrum with multiple peaks, indicating a messy reaction with numerous side products. However, it contains a doublet (4 ppm) and quartet (-114 ppm) that have identical splittings of 2.97 ppm (Fig. 9). This could be the result of a lithium-bridged P-Li-P coupling, which would indicate a successful, if messy, insertion of phosphorus.
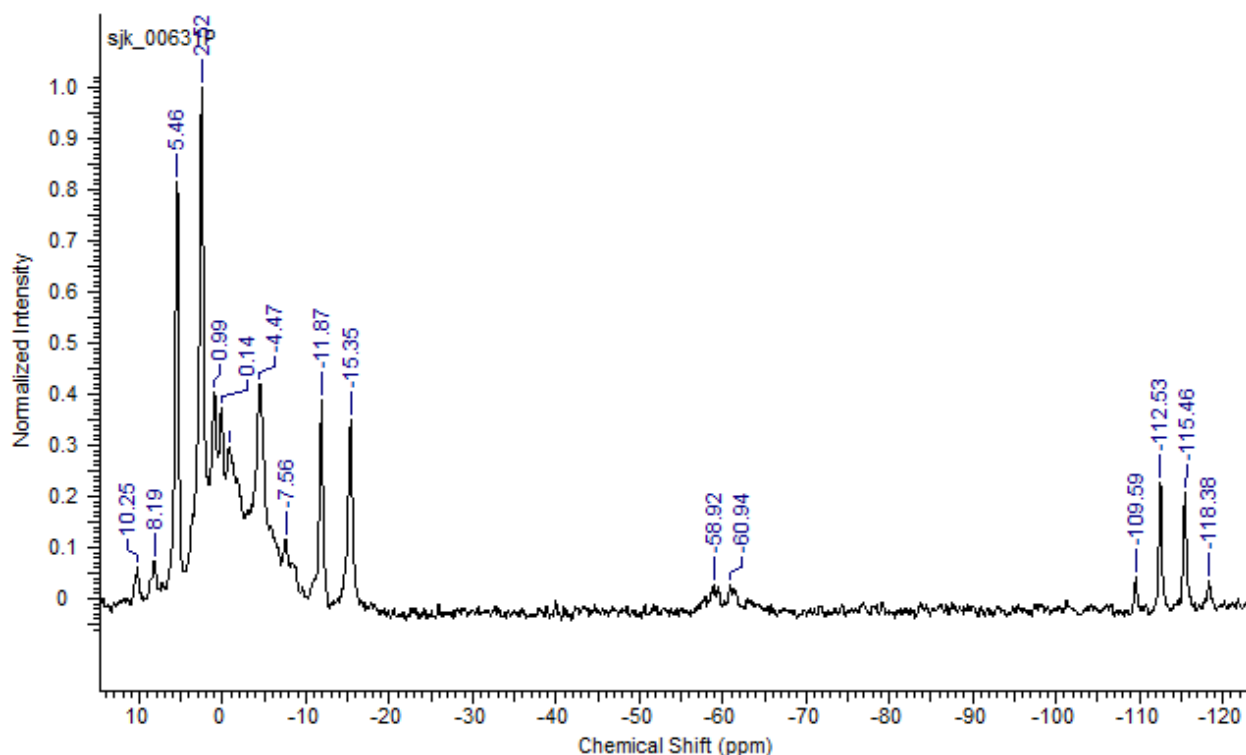
Figure 9: ^{31}P NMR spectrum of an attempted synthesis of a PL complex using n-butyllithium. A coupled doublet and quartet are visible at 4 and -114 ppm, respectively.

Such a coupling is supported by the fact that the chemical shift of the doublet (4 ppm) is very close to that of free ligand (3 ppm). The integration ratios also qualitatively support this conclusion; the doublet to quartet ratio should be 3:1, and while numerical integration isn't feasible with such a messy spectrum, the fact that the doublet is much more intense than the quartet is promising. Literature values for similar complexes of trivalent phosphorus bound to tridentate amine ligands undermine this conclusion; Verkade reported a chemical shift of 128 ppm (referenced to PPh_3) for his

$P[N(CH_2Ph)CH_2CH_2]_3N$ complex, placing it at the opposite end of the spectrum. [8]

Product **7b** showed one peak in the ^{31}P NMR spectrum (134 ppm) which indicates that the product may not have been soluble in the selected solvent. No free ligand peak was seen. The ^{1}H NMR spectrum was

similarly uninformative; no major peaks were seen in the aryl region. It is possible that this product existed as a salt, and was therefore insoluble in benzene.

Conclusion:

Attempts at synthesis of two ligands resulted in one being successfully synthesized (Fig. 2A). Insertion of phosphorus was attempted using procedures with conditions that were either too mild or too harsh to obtain an isolated PL complex. Insertion of vanadium likely succeeded as indicated by a relatively clean and paramagnetic ^{1}H NMR spectrum. Insertion of iron and formation of a FeVL complex may have succeeded as well, according to the presence of a complete reaction with a paramagnetic product.

Future Goals:

Procedures for the synthesis of both ligands can be improved upon. Alternative methods for the purification of **1** will be attempted in order to increase yield and to eliminate the tradeoff between yield and purity. Future attempts at the synthesis of H_3tpa will include the distillation of pyrrole prior to use. Additional characterization techniques will be employed to support the existence of an isolated FeVL complex.

References:

1. Enthaler, S.; Hagemann, B.; Erre, G.; Junge, K.; Beller, M. *Chem. Asian J.* **2006**, *4,* 598-604.

2. Andersson, P. G.; Church, T. L. *Coord. Chem. Rev.* **2008**, *252*, 513-531.

3. Miyaura, N.; Suzuki, K.; Yamada, K. *Tetrahedron Lett.* **1979**, *36*, 3437-3440.

4. Lancaster, K. M.; Roemelt, M.; Ettenhuber, P.; Hu, Y.; Ribbe, M. W.; Neese, F.; Bergmann, U.; DeBeer, S. *Science*. **2011**, *6058*, 974-977.

5. Rudd, P.A.; Liu, S.; Gagliardi, L.; Young Jr., V.G.; Lu, C.C. *J. Am. Chem. Soc.* **2011**, *133*, 20724-20727.

6. Shi, Y.; Changseng, C.; Odom, A. L. *Inorg. Chem.* **2004**, *43*, 275-281.

7. Rudd, P. A.; Liu, S.; Gagliardi, L.; Planas, N.; Eckhard, B.; Lu, C. C. *Multiple Metal-Metal Bonds in Heterobimetallic Chromium-Iron Complexes*

8. Laramay, M. A. H.; Verkade, J. G.; *Z. anorg. allg. Chem.* **1991**, *605*, 163-174.