MODELING THE ACTIVE SITE OF [NIFE]-HYDROGENASE

BY

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THESIS

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Abstract

The hydrogenases are metalloenzymes that act to catalytically interconvert dihydrogen with protons and electrons. Although there are three classes of hydrogenases that are known, the focus of this research will be on the first hydrogenase to be evolved, the [NiFe]-hydrogenase, which contains a heterobimetallic NiFe active site. The [NiFe]- hydrogenase is a heterodimeric enzyme, and it is composed of a large subunit and a small subunit, inside the large subunit is buried the active site deep within the protein, while the small subunit contains a series of [Fe-S] clusters that controls the electron transfer system of the enzyme. The active site is heterobimetallic, and contains an octahedral $Fe(CN)_2(CO)$ center. This ferrous center is coordinated to a $Ni(S\text{-}cys)_4$ center via two cysteine thiolates.

Previous work has shown that Ni(dppe)(pdt) reacts with $Fe_2(CO)_9$ in dichloromethane to form (CO_3)Fe(pdt)Ni(dppe). The Fe(I)Ni(I) complex, $(CO)_3$Fe(pdt)Ni(dppe), was readily protonated with HBF_4 to give the corresponding bridging hydride. This complex served as the first example of a nickel-iron thiolato hydride. Isolation of the first nickel iron-thiolato hydride, as well as a series of nickel-iron- bridging chloride complexes, led to the investigation of different pathways to similar compounds.

Attempts to isolate similar [$(CO)_3$Fe(dithiolate)Ni(diphosphine)] complexes by reaction of the mononuclear Ni^{II}(diphosphine)(dithiolate) with $Fe_2(CO)_9$ were unsuccessful with this original route, except for [$(CO)_3$Fe(pdt)Ni(dppe)]. The reaction of $FeI_2(CO)_4$ followed by reduction with cobaltocene with different L type ligands can generate the corresponding substituted compounds, thus this reagent was investigated as a source of the $Fe(CO)_3$ fragment for our $(CO)_3$Fe(dithiolate)Ni(diphosphine) models. The preparation and successful isolation of novel $(CO)_3$Fe(dithiolate)Ni(diphosphine) compounds (that were previously unsuccessful via the $Fe_2(CO)_9$ route) and the catalytic activity of their corresponding hydrides was the primary focus of this research.

The reactions with the $Ni(SR)_2$(diphosphine) and $FeI_2(CO)_4$ appear to proceed through the intermediacy of the cations $[(CO)_3Fe(SR)_2(\mu\text{-}I)NiL_2]^+$. IR spectra of these

intermediates resemble those for the corresponding μ-hydrides but are shifted to higher energies. Also the spectra tend to be more complex, possibly because of decomposition reactions. Addition of cobaltocene to these solutions produced greenish colored intermediates $(CO)_3Fe(pdt)Ni(diphosphine)$, which in some cases could be further identified by IR and ^{31}P NMR spectroscopy. The reductive process was optimized for $(CO)_3Fe(pdt)Ni(dppe)$, which was obtained in yields competitive with the $Fe_2(CO)_9$ + Ni(pdt)(dppe) route. In most cases, such reduced intermediates were converted to the hydrides by protonation with strong acids.

The reactions of Ni(pdt)(dppbz) and Ni(pdt)(dcpe) with $FeI_2(CO)_4$ followed the expected patterns: stable μ-iodo intermediates were observed, which reduced to the corresponding Fe(I)Ni(I) compound. Protonation of the reduced species with ether-HBF_4 gave the targeted hydride $[(CO)_3Fe(pdt)(\mu\text{-}H)Ni(dppbz)]BF_4$ and $[(CO)_3Fe(pdt)(H)Ni(dcpe)]BF_4$, and the latter compound was characterized crystallographically.

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Chapter 1

Synthesis of New $Ni(SR)_2$(diphosphine) Complexes and a New Reduction Route to $(CO)_3Fe(SR)_2Ni$(diphosphine) and Their Hydrides

Introduction

Hydrogenases are found in an abundance of organisms. For example, methanogenic, acetogenic, nitrate and sulfate reducing bacteria, and anaerobic archae are only a small portion of the types of organisms that contain hydrogenases.[1] The metal-sulfur clusters of hydrogenases catalyze the interconversion of protons and dihydrogen by the following reversible reaction:

$$2H^+ + 2e^- \rightleftharpoons H_2 \qquad (1.1)$$

Hydrogenases can sustain particularly high turnover rates, and this makes them attractive candidates to study in the technological frame as alternatives to precious metals in hydrogen production/fuel cell applications.[1]

There are three classes of hydrogenases, whose names stem from the metals contained in their active sites: [FeFe]-hydrogenase, [NiFe]-hydrogenase, and [Fe]-hydrogenase. Hydrogenases containing only iron are bi-directional, meaning they catalyze both the forward and reverse reaction (equation 1.1). However iron- only containing hydrogenases are generally associated with hydrogen production, or the reduction of protons to dihydrogen. Nickel-iron hydrogenases are generally involved in the oxidation of hydrogen, they are also the most abundant class of these enzymes[2], and will be the focus of this thesis.

The crystal structures from five periplasmic [NiFe]-hydrogenases have been reported, all from sulfate-reducing bacteria.[3] The [NiFe]- hydrogenase is a heterodimeric enzyme, and it is composed of a large subunit and a small subunit, inside the large subunit is buried the active site deep within the protein, while the small subunit contains a series of [Fe-S] clusters that controls the electron transfer system of the enzyme. The active site (Figure 1.1) is heterobimetallic, and contains an octahedral

$Fe(CN)_2(CO)$ center. This ferrous center is coordinated to a $Ni(S\text{-}cys)_4$ center via two cysteine thiolates. The identity of the third bridging site depends on the state of the [NiFe]-hydrogenase, and it varies from a bridging hydroxide, peroxide, oxide, hydride, or empty site. The nickel atom is redox active, and the oxidation state of the metal depends on the state of the [Ni-Fe]-hydrogenase, ranging from Ni(I), Ni(II), or Ni(III).

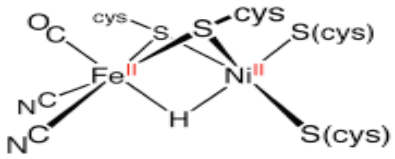


Figure 1.1. The active site of the [NiFe]-hydrogenase, Ni-R state.

The [NiFe]- hydrogenase active site has a plethora of states, whose names are derived from whether they are active or inactive (Figure 1.2). Within the inactive states, which are paramagnetic, some states are quickly converted to active states, referred to as “ready”, while others take longer time to reductively activate, these are called “unready”. Within the active forms of the enzyme, there are two states that contain a Ni(III) intermediate: Ni-A “unready oxidized” and Ni-B “ready oxidized”. However, when these states are reduced to Ni(II), they give rise to the Ni-SU “unready reduced” and Ni-Si_r “ready reduced” states. After which these states loose H_2O or H_2O_2 to give the most catalytically active state, Ni-Si_a.[4]

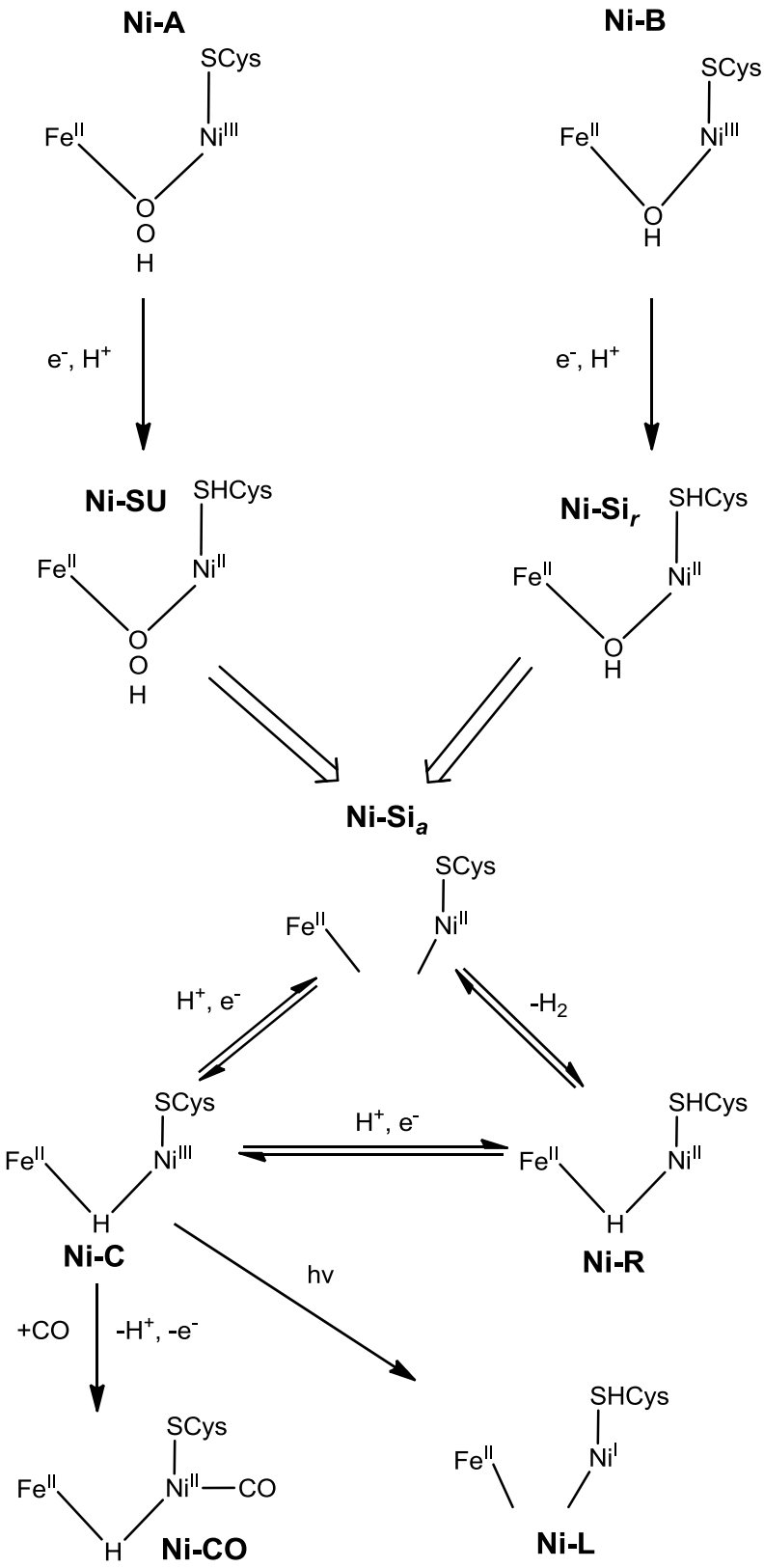


Figure 1.2. States of the [NiFe]-hydrogenases.

In order to produce a useful model for the [NiFe]-hydrogenase from nickel and iron building blocks, some key features of the active site must be emulated. First, the model must contain a heterobimetallic center, composed of a redox-active nickel and a redox-inactive iron. Two-bridging cysteine thiolate ligands hold the bimetallic site intact to ~2.6 Å, this spacing between nickel and iron again depends on the state of the enzyme.[3] A key feature of any useful [NiFe]-hydrogenase model is the presence of a bridging hydride.

After the publication of the first structure of [NiFe]-hydrogenase from Volbeda and Fonticella-Camps, there was a large interest in the synthesis of heterobimetallic nickel and iron complexes. One of these first compounds was published by Darensbourg and co-workers, and featured a [{NiL-S}Fe(CO)$_4$] (L= *N,*N'-bis(ethane-thiol)-1,5-diazacylooctane] complex, where the nickel and iron were bridged by the two thiolates in the N_2S_2 "bme-daco" ligand.[5] Siegfried Pohl's group also published an early [NiFe] hydrogenase model that featured iron, nickel, two nitrosyl ligands and the N_2,S_2 ligand = *N,N'*- diethyl-3,7-diazanonane-1,9-dithiol (Figure 1.3).[6] Although pioneers at the time, neither of these models featured both a bis(thiolate) bridging ligand or an iron atom saturated with carbonyls, as was found to be contained in the [NiFe]-hydrogenase active site.

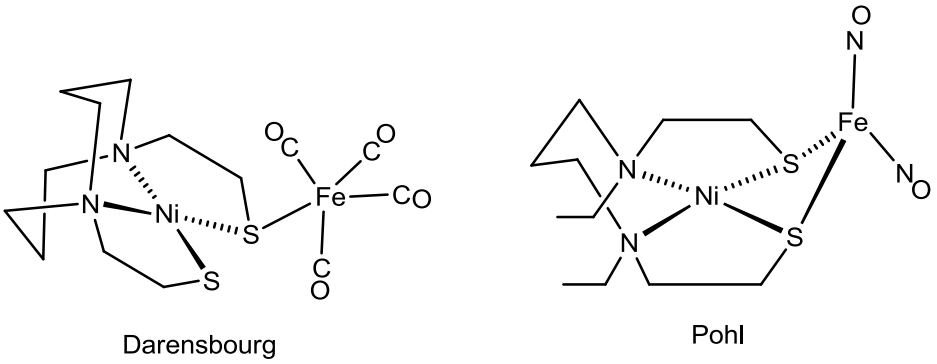
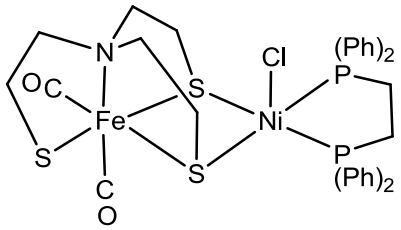


Figure 1.3. Early models of the [NiFe]- hydrogenase from Marcetta Darensbourg and Siegfried Pohl.

David Evans and co-workers showed that an anionic iron complex containing the NS_3 [NS_3 = $N(CH_2CH_2S)_3^{3-}$] ligand reacts with $NiCl_2$dppe under a CO atmosphere to give a dinuclear [NiFe]-complex (Figure 1.4).[7,8] The Ni-Fe distance for this model complex, 3.31 Å, was longer than reported distances for different states of the enzyme. Evans' group also made a similar compound with nitrosyl ligands replacing the CO ligands, and found the Ni…Fe distance, 3.02 Å, for this complex was smaller than the CO adduct, but still significantly longer than that reported for the enzyme.



Evans

Figure 1.4. Evans and co-workers' [NiFe] model featuring the tripodal NS_3 ligand, [NS_3 = $N(CH_2CH_2S)_3^{3-}$].

Sellmann and co-workers synthesized the first heterobimetallic [NiFe] complex in which the nickel is coordinated by four thiolates (Figure 1.5a).[9,10] The reaction of $[Fe(CO)_2(`S_3')]_2$ ($`S_3'^{2-}$ = bis(mercaptoethyl)sulfide^{2-} with $Nibdt(PMe_3)_2$ (bdt = 1,2 benzenedithiol) gave [{$Fe(`S_3')(CO)(PMe_3)_2$-*S,S'*}Ni(bdt)] and the formation of other by-products. Another noteworthy compound from the Sellmann group featured a mononuclear anionic iron complex, with a dicyanide and carbonyl ligand environment around iron that is similar to that found in the enzyme.

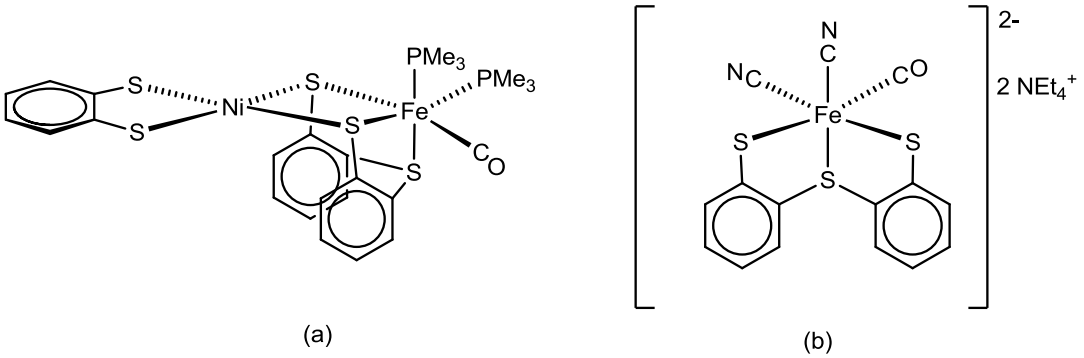
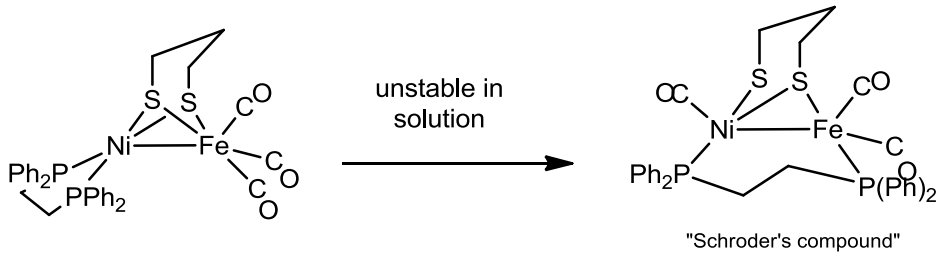


Figure 1.5. Sellmann and co-worker's [NiFe] complex, the first dinuclear [NiFe]-hydrogenase model complex with nickel coordinated to four thiolates (a). Sellmann's mononuclear anionic iron complex featuring similar ligand environment around iron to that found in the enzyme (b).

Other noteworthy contributions to the synthesis of [NiFe]-hydrogenase model complexes came from the Schröder group. The reaction of Ni(dppe)(pdt) (dppe = diphenylphosphinoethane, pdt-H_2 = 1,3 propanedithiol) with $Fe_3(CO)_{12}$ formed (CO_3)Fe(pdt)Ni(dppe) in low yield, and other by-products.[11] Schroder and co-workers found that the same mononuclear nickel starting reagent reacted with Fe(bda)$(CO)_3$ (bda = benzylideneacetone) to give (CO_3)Fe(pdt)Ni(dppe), which was unstable in solution and isomerized to form $(CO)_2$Fe(pdt)(dppe)Ni(CO) (Scheme 1.1), hereby referred to as "Schroder's compound."



Scheme 1.1. Isomerization of (CO_3)Fe(pdt)Ni(dppe) to form "Schroder's compound," $(CO)_2$Fe(pdt)(dppe)Ni(CO).

Previous work in the Rauchfuss group has shown that Ni(dppe)(pdt) reacts with $Fe_2(CO)_9$ in dichloromethane at 25 °C, to form (CO_3)Fe(pdt)Ni(dppe), and the product was isolated from other by-products by column chromatography.[12] The Fe(I) complex,

$(CO)_3Fe(pdt)Ni(dppe)$ was readily protonated with $HBF_4 \cdot Et_2O$ in CH_2Cl_2 solution to give the corresponding bridging hydride. This complex served as the first example of a nickel-iron thiolato hydride (Figure 1.6).

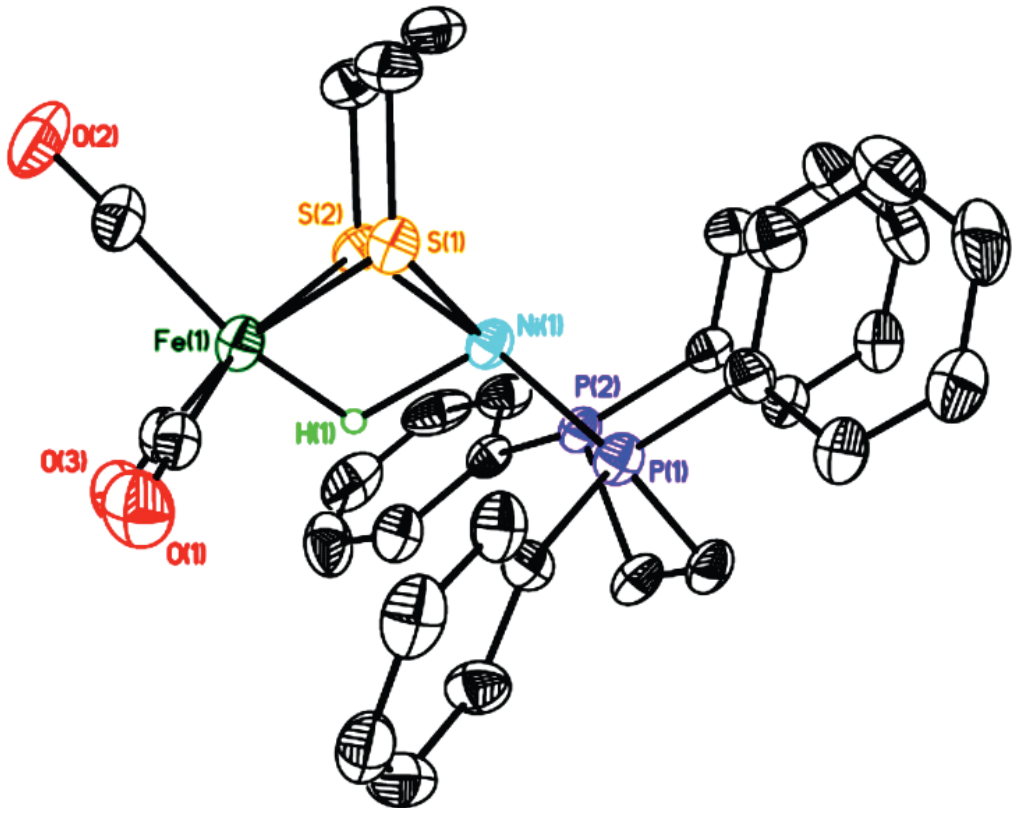


Figure 1.6. Structure of $[(CO)_3Fe(pdt)(\mu\text{-}H)Ni(dppe)]BF_4$, the first example of a nickel-iron thiolato hydride.

Several attempts to isolate other $[(CO)_3Fe(dithiolate)Ni(diphosphine)]$ compounds by reaction of the Ni(dithiolate)(diphosphine) monomers with $Fe_2(CO)_9$ were investigated (Table 1.1a). The reaction of Ni(pdt)(dppe) with $Fe_2(CO)_9$ resulted in the successful isolation of the $(CO)_3Fe(dithiolate)Ni(diphosphine)$ complex. Attempts to isolate three new Ni(dithiolate)(disphosphine) monomers were unsuccessful because the Ni(diphosphine)(dichloride) precursors polymerized when reacted with 1,3 propanedithiol in the presence of triethylamine (Table 1.1b). This result was evident from the precipitation of a black substance ($Ni(pdt)_2$ polymer) from the reaction solution, as well as evidence of the free diphosphine ligand in the ^{31}P NMR spectrum.

Table 1.1a. Attempts to isolate $(CO)_3Fe$(dithiolate)Ni(diphosphine) complexes by reaction of the Ni(dithiolate)(diphosphine) compounds with $Fe_2(CO)_9$.

Ni(dithiolate)(diphosphine)	Results of Reaction with $Fe_2(CO)_9$
Ni(pdt)(dppe)	Successful Isolation of $[(CO)_3Fe(pdt)Ni(dppe)]$
Ni(pdt)(dmpe)	Inconclusive, too many carbonyl stretches in IR spectrum
Ni(pdt)(dppbz)	Successful Isolation of $[(CO)_3Fe(pdt)Ni(dppbz)]$
Ni(pdt)(dcpe)	Successful Isolation of $[(CO)_3Fe(pdt)Ni(dcpe)]$
Ni(edt)(dmpe)	Inconclusive, too many carbonyl stretches in IR spectrum
$Ni(SPh)_2$(dmpe)	Inconclusive, too many carbonyl stretches in IR spectrum
$Ni(SPh)_2$(dppe)	Evidence in IR spectrum of formation of dimeric product $[(CO)_3Fe(SPh)_2Ni(dppe)_2]_2$
$Ni(SPh)_2$(dppv)	Evidence in IR spectrum of formation of dimeric product $[(CO)_3Fe(SPh)_2Ni(dppv)_2]_2$
$Ni(SPh)_2$(dppbz)	Evidence in IR spectrum of formation of dimeric product $[(CO)_3Fe(SPh)_2Ni(dppbz)_2]_2$

Previous work in the Rauchfuss group has also shown that the reaction of [(dppe)(CO)Fe(pdt)] with $Ni(dppe)(Cl)_2$ in hot acetone generated a single isomer of $[(dppe)(CO)Fe(pdt)(\mu\text{-}Cl)Ni(dppe)][BF_4]$.[12] A series of four complexes of the type [(disphosphine)(CO)Fe(dithiolate)(μ-Cl)Ni(diphosphine)][BF_4] were prepared in a similar manner.[13] The four complexes are $[(dppe)(CO)Fe(pdt)(\mu\text{-}Cl)Ni(dppe)][BF_4]$, $[(dppe)(CO)Fe(edt)(\mu\text{-}Cl)Ni(dppe)][BF_4]$, $[(dppe)(CO)Fe(pdt)(\mu\text{-}Cl)Ni(dppf)][BF_4]$, and $[(PMe_3)_2(CO)\ Fe(edt)(\mu\text{-}Cl)Ni(dppe)][BF_4]$. Electronic differences due to the dithiolate strap were not apparent. However, attempts to isolate $[(dppe)(CO)Fe(xdt)(\mu\text{-}Cl)Ni(dppe)][BF_4]$ (where "xdt" = xylenedithiol) were unsuccessful. This is most likely due to the larger bite angle of the xdt ligand as well as the unfavorable steric interactions between the dithiolate strap and the dppe ligands.

Isolation of the first nickel iron-thiolato hydride as well as this series of nickel-iron- bridging chloride complexes led us to investigate different pathways to similar

compounds. Attempts to isolate similar [$(CO)_3$Fe(dithiolate)Ni(diphosphine)] complexes by reaction of the mononuclear Ni^{II}(diphosphine)(dithiolate) with $Fe_2(CO)_9$ were unsuccessful with this original route, except for [$(CO)_3$Fe(pdt)Ni(dppe)]. Marcetta Darensbourg and co workers have shown that reaction of $FeI_2(CO)_4$ with different L type ligands can generate the corresponding substituted compounds[14], thus this reagent was investigated as a source of the $Fe(CO)_3$ fragment for our $(CO)_3$Fe(dithiolate)-Ni(diphosphine) models.

Results and Discussion

$Ni(SR)_2$(diphosphine). With the goal of examining variations in the nature of the diphosphine, we prepared several new examples of this general type of complex. The procedures entailed the initial formation of $NiCl_2$(diphosphine), which were subsequently converted to the dithiolates. Early experiments on the Fe-Ni compounds suggested problems with the SPh derivatives. The alkyl thiolates are known to be somewhat labile, so we focused on 1,3-propanedithiolates and to a lesser extent, 1,2-ethanedithiolates. These derivatives were prepared by salt-forming processes. All isolable derivatives proved to be diamagnetic and hence square planar. We were unable to prepare Ni(pdt)(dppf), Ni(pdt)(dppp), and Ni(pdt)($Ph_2Si(CH_2PPh2)_2$) owing to the formation of polymeric Ni(pdt). The highly rigid diphosphine dppn did allow the formation of a square planar complex. The following new derivatives were prepared in analytical purity Ni(pdt)(dppbz), Ni(pdt)(dppn), and Ni(pdt)(dppv).

Table 1.1b. New $Ni(SR)_2$(diphosphine) compounds and related results.

Ni(pdt)(dppn)	Successful isolation of Ni(pdt)(dppn)
Ni(pdt)(dppf)*	*These Ni(dithiolate)(diphosphine) compounds could not be formed because the Ni(diphosphine)$(Cl)_2$ precursors polymerized with pdt.
Ni(pdt)(dppp)*	
Ni(pdt)$(Ph_2Si(CH_2PPh2)_2)$ *	
Ni(dp^Fpe)Cl_2	*$NiCl_2 \cdot 6H_2O$ did not react with dp^Fpe, even if the reaction was refluxed in EtOH or toluene.

Being a rare example of a stable nickel dithiolate with a wide bite angle, Ni(pdt)(dppn) was investigated by X-ray crystallography, shown in Figure 1.7. The key bond distances (Å) are : Ni1-P1, 2.1455(13); Ni-S(1), 2.2039(12) and the key bond angles (°) are : P(2)-Ni(1)-P(1), 93.27(4); P(2)-Ni(1)-S(2), 172.02(5).

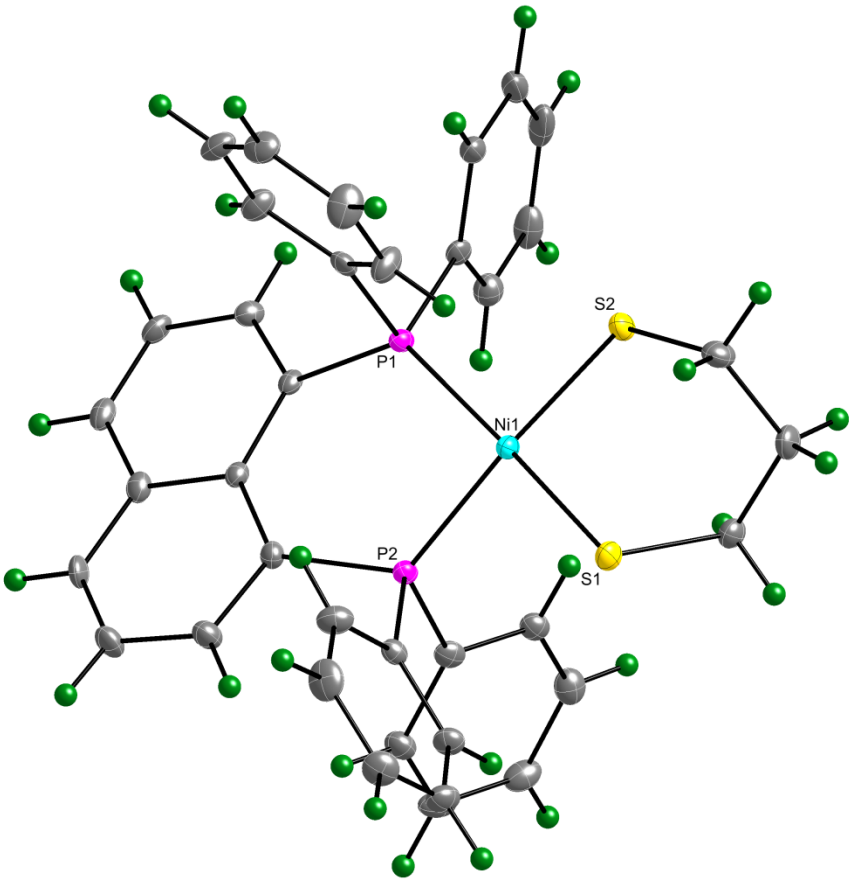


Figure 1.7. Structure of Ni(pdt)(dppn). Key distances (Å): Ni1-P1, 2.1455(13); Ni-S(1), 2.2039(12). Key bond angles (°): P(2)-Ni(1)-P(1), 93.27(4); P(2)-Ni(1)-S(2), 172.02(5).

Complexes containing Ni(pdt) and alkyl-substituted diphosphines were unknown prior to this work. The following new derivatives were prepared, Ni(pdt)(dmpe), Ni(edt)(dmpe), and Ni(pdt)(dcpe). Only the latter proved fruitful however in forming a robust $(CO)_3Fe(SR)_2Ni$(diphosphine) complex.

Synthesis of $Fe(CO)_3(SR)_2Ni$(diphosphine) Compounds. In a test case, $(CO)_3Fe^{I}(pdt)Ni^{I}(dppe)$ was prepared in good yield via the multistep, one-pot reaction of $FeI_2(CO)_4$ and Ni(pdt)(dppe), followed by treatment of this mixture with 2 equiv of cobaltocene. The yield is comparable or better than the $Fe_2(CO)_9$ method described in the Introduction.

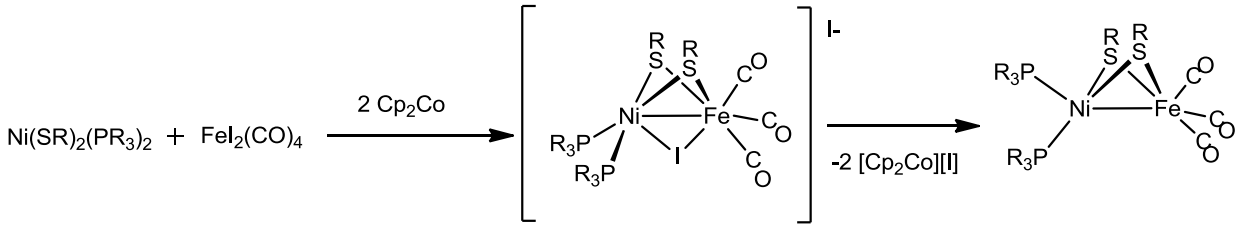
The aforementioned $Ni(SR)_2$(diphosphine) compounds were tested using our new reduction route (Scheme 1.2). These attempts are summarized in Table 1.2.

Table 1.2 The results from the synthetic reduction route to new $(CO)_3Fe(SR)_2Ni$(diphosphine) compounds and in some cases their corresponding hydrides.

$(PR_3)_2$ Thiolate	**$[(CO)_3Fe(SR)_2(I)Ni(PR_3)_2]^+$ ν_{CO} (cm^{-1}, CH_2Cl_2)**	**Monomeric $[(CO)_3Fe(SR)_2Ni(PR_3)_2]$ and dimeric product(s) $[(CO)_3Fe(SR)_2Ni(PR_3)_2]_2$ from Cp_2Co reduction ν_{CO} (cm^{-1}, CH_2Cl_2)**	**Hydride(s) $[(CO)_3Fe(SR)_2(H)Ni(PR_3)_2]^+$ ν_{CO} (cm^{-1}, CH_2Cl_2) $\mu_{hydride}$**
dppe, $S_2C_3H_6$	2096, 2054, 2023	monomer 2028, 1952	2082, 2024 (δ -3.53)
dppe, $(SPh)_2$	(unstable) 2082, 2032	monomer 2035, 1970 dimer 2001, 1942	
dppn, $(SPh)_2$	(unstable) 2094, 2075, 2048, 2040	monomer 2031, 1963 dimer 1997, 1936	
dmpe, $S_2C_3H_6$	2095, 2052, 2024	(unstable) monomer 2016, 1941	(unstable) 2078, 2018 (δ -3.63)
dmpe, $S_2C_2H_4$	2094, 2049, 2026	(unstable) monomer 2018, 1943	(unstable) 2079, 2018 (δ -3.71)

Table 1.2(cont.)

dppbz, $S_2C_3H_6$	2096, 2053, 2027	monomer 2030, 1954	2082, 2023 (δ-3.42)
dppn, $S_2C_3H_6$	2090, 2075, 2054, 2024	(unstable) dimer 1996, 1936	
dcpe, $S_2C_3H_6$	2095, 2053, 2021	monomer 2014, 1940	2078, 2017 (δ -3.00)



Scheme 1.2. General reduction route to new $[(CO)_3Fe(SR)_2Ni(diphosphine)]$ complexes.

The reactions with the $Ni(SR)_2(diphosphine)$ and $FeI_2(CO)_4$ appear to proceed through an intermediate, containing a bridging iodide ligand (Scheme 1.2). IR spectroscopy is consistent with such a $(CO)_3Fe(SR)_2(\mu\text{-}I)NiL_2$ intermediate. This intermediate forms after the mixing of $FeI_2(CO)_4$ and the $Ni(SR)_2(diphosphine)$, even at low T. Attempts to isolate these μ-iodide intermediates were unsuccessful. The IR spectra all show three bands in the carbonyl region around 2090, 2050, and 2025 cm^{-1}. An example of this spectrum is shown in Figure 1.7 for the reaction of Ni(pdt)(dmpe) with $FeI_2(CO)_4$.

Having generated the labile μ-iodide intermediate, addition of 2 equiv of cobaltocene at –78 °C (Figure 1.7) gave greenish colored products. After generating the reduced compound, $[(CO)_3Fe(pdt)Ni(dmpe)]$ was protonated with a solution of HCl in diethyl ether to the corresponding hydride, $[(CO)_3Fe(H)(pdt)Ni(dmpe)][Cl]$. This

protonation was also conducted at –78 °C. Evidence of the formation of this hydride was observed in the IR spectrum (Figure 1.8), in the hydride region of the ^{1}H NMR spectrum, showing a broad signal at δ -3.63 (Figure 1.9), and in the ^{31}P-NMR spectrum (Figure 1.10). As with generating the neutral $(CO)_3Fe(pdt)Ni(dmpe)$ compound, the hydride could only be generated cleanly if the protonation occurred at -78 °C, once the compound was allowed to warm it would quickly decompose to a species with a single carbonyl stretch at 2330 cm^{-1} that could not be further characterized.

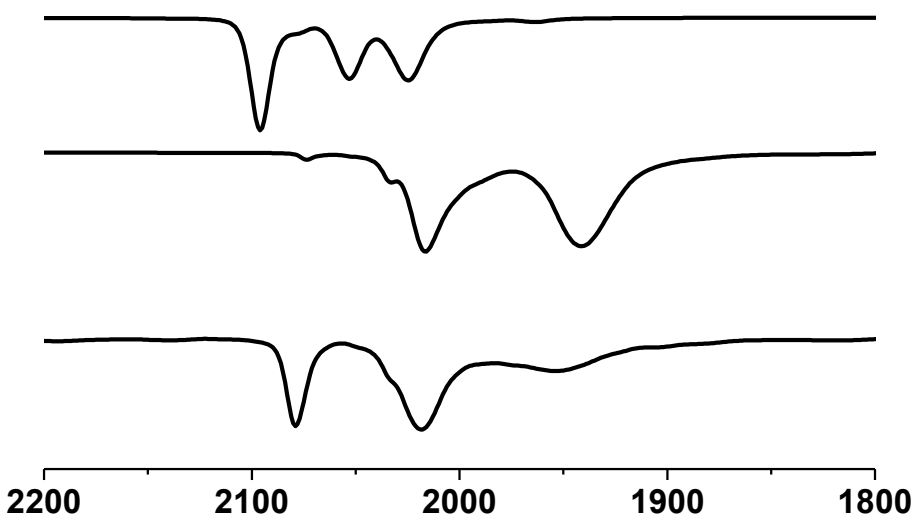


Figure 1.8. IR spectra (CH_2Cl_2 solution) of $[(CO)_3Fe(pdt)(I)Ni(dmpe)]I$ (top), $(CO)_3Fe(pdt)Ni(dmpe)$ (middle), and $[(CO)_3Fe(pdt)Ni(dmpe)]Cl$ (bottom).

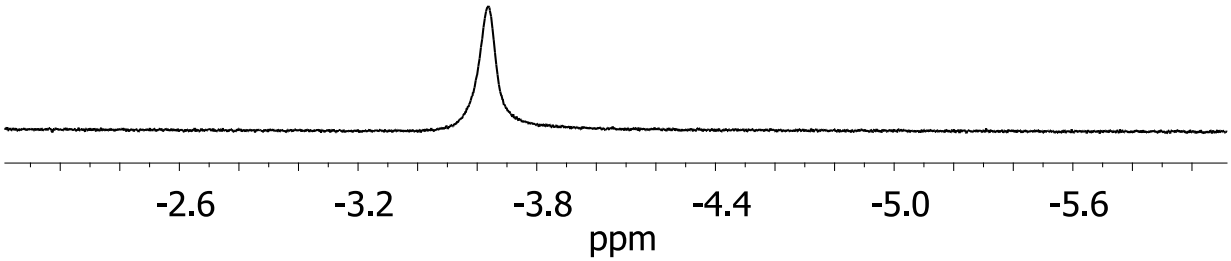


Figure 1.9. ^{1}H NMR spectrum (CD_2Cl_2 solution) of $[(CO)_3Fe(H)(pdt)Ni(dmpe)][Cl]$, showing the hydride species at δ -3.63.

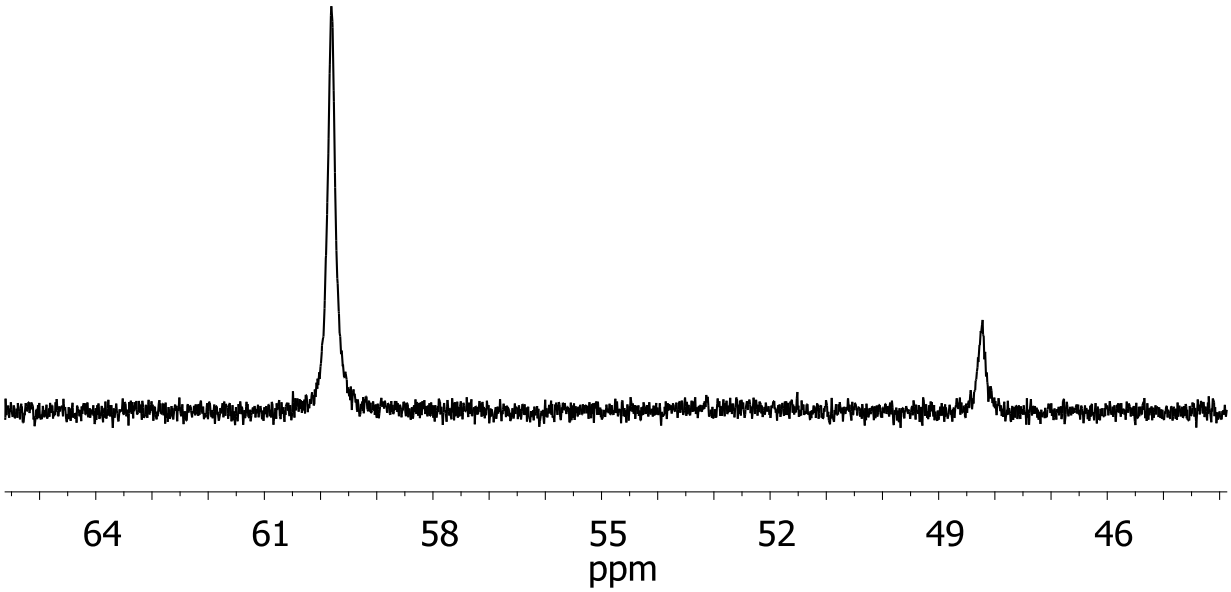


Figure 1.10. ^{31}P-NMR spectrum (CD_2Cl_2 solution) of a mixture of $[(CO)_3Fe(H)(pdt)Ni(dmpe)]Cl$ (left) and $(CO)_3Fe(pdt)Ni(dmpe)$ (right).

The reaction of Ni(pdt)(dppbz) with $FeI_2(CO)_4$ initially produced the expected bridging iodide species, which reduced to the corresponding Fe(I)Ni(I) compound. Protonation of the reduced species with $HBF_4 \cdot Et_2O$ gave the hydrido complex, which was obtained in analytical purity. IR spectra for the μ-I intermediate, the reduced species, and the hydride product are shown in Figure 1.11.

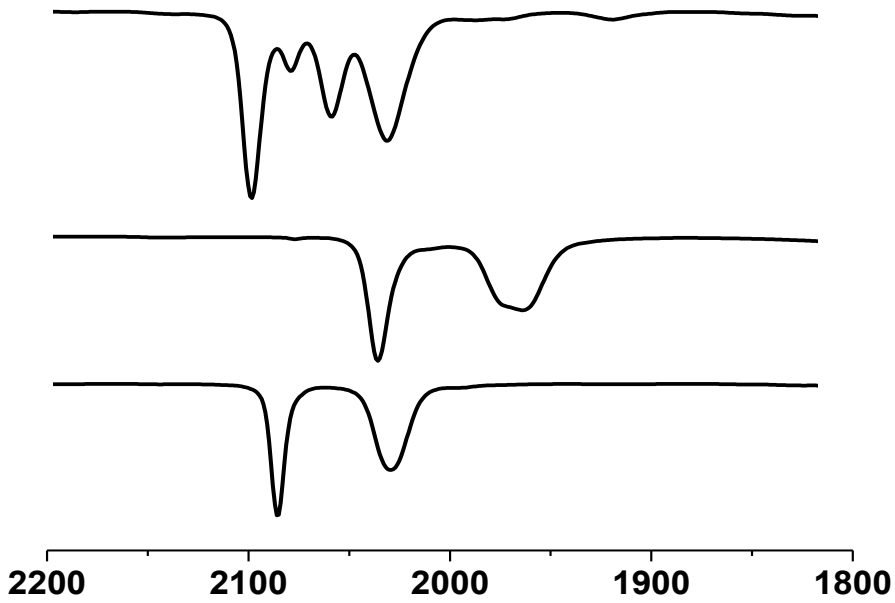


Figure 1.11. IR spectra (CH_2Cl_2 solution) of $[(CO)_3Fe(pdt)(I)Ni(dppbz)]I$ (top), $(CO)_3Fe(pdt)Ni(dppbz)$ (middle), and $[(CO)_3Fe(pdt)(H)Ni(dppbz)][BF_4]$ (bottom).

The reaction of Ni(pdt)(dcpe) with $I_2Fe(CO)_4$ followed the sought-for pattern: a thermally robust μ-iodide species underwent reduction with cobaltocene to form what appears to be a Fe(I)Ni(I) derivative. Protonation of this Fe(I)Ni(I) compound with a $HBF_4 \cdot Et_2O$ solution gave the bridging hydride complex. This is another example of a nickel-iron thiolato hydride, and this compound was characterized crystallographically (Figure 1.12). Unlike similar compounds that are electron rich at nickel, such as $(CO)_3Fe(pdt)Ni(dmpe)$ and $[(CO)_3Fe(pdt)(H)Ni(dmpe)][BF_4]$, the dcpe compound and its immediate precursor are thermally stable. IR spectra for the bridging iodide species, the Fe(I)Ni(I) compound, and the bridging hydride complex are presented in Figure

1.13. ^{1}H NMR spectrum revealed a hydride signal at δ -3.00, shown in Figure 1.14. The ^{31}P NMR spectrum also revealed a broad signal at δ 89.5, shown in Figure 1.15.

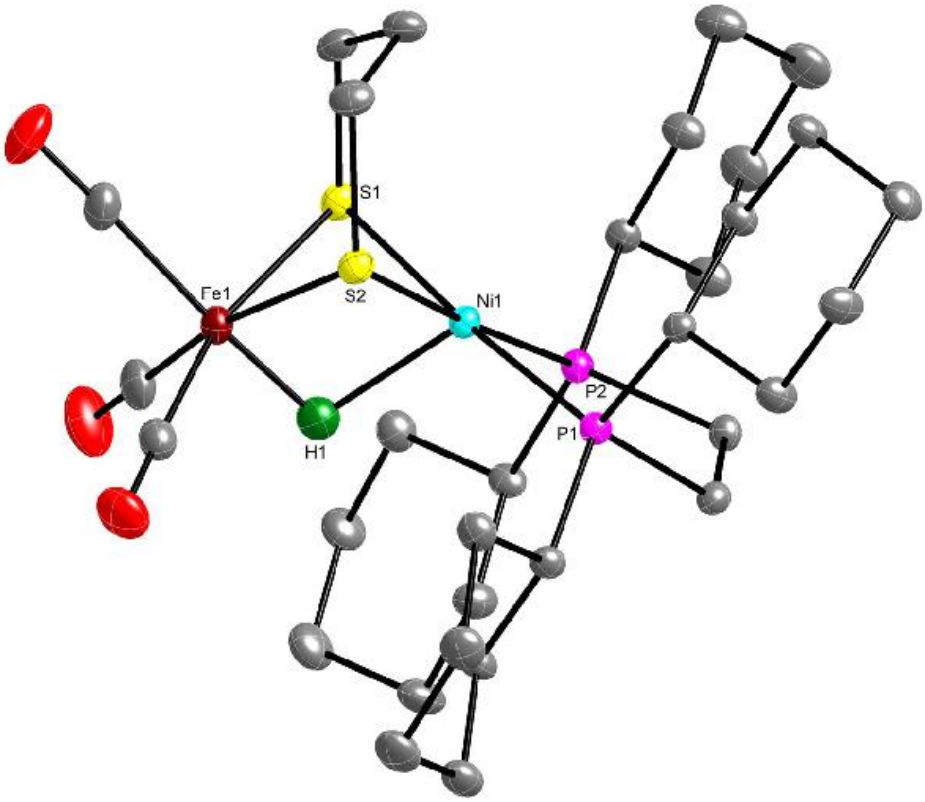


Figure 1.12. Molecular structure of the cation in $[(dcpe)Ni(pdt)(H)Fe(CO)_3]BF_4$. Hydrogen atoms and BF_4 have been omitted for clarity. Key distances (Å): Ni-Fe, 2.6843(5); Ni-S(1), 2.2274(7); Ni-S(2), 2.2307(7); Fe-S(1), 2.3208(8); Fe-S(2), 2.3169(8); Ni-H, 1.90(2); Fe-H, 1.53(2).

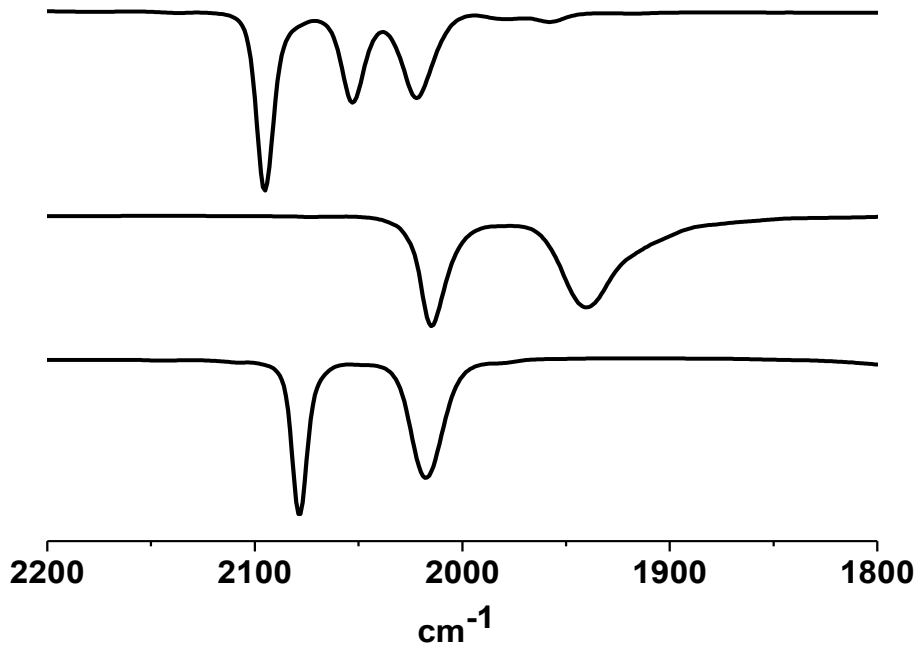


Figure 1.13. IR spectra (CH_2Cl_2 solution) of $[(CO)_3Fe(pdt)(I)Ni(dcpe)]I$ (top), $(CO)_3Fe(pdt)Ni(dcpe)$, and $[(CO)_3Fe(pdt)(H)Ni(dcpe)]BF_4$.

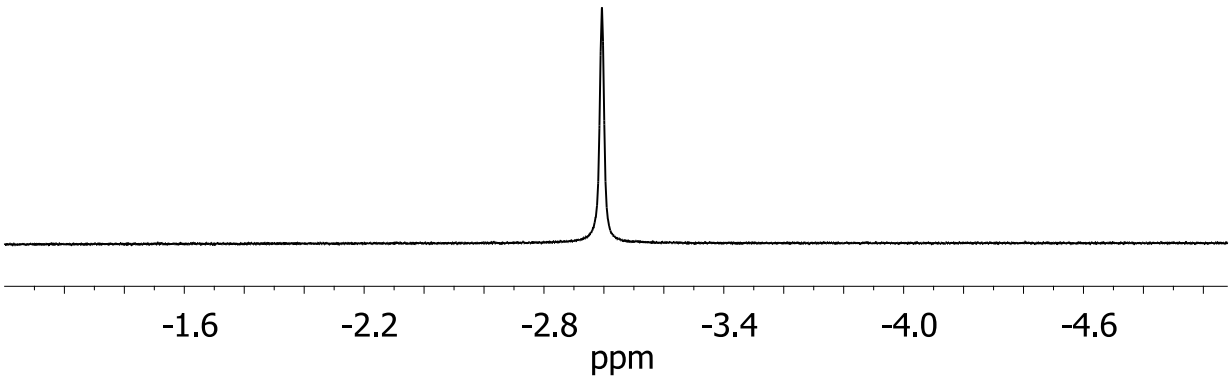


Figure 1.14. ^1H NMR spectrum (CD_2Cl_2 solution) of $[(CO)_3Fe(H)(pdt)Ni(dcpe)][BF_4]$, showing the hydride species at δ -3.00.

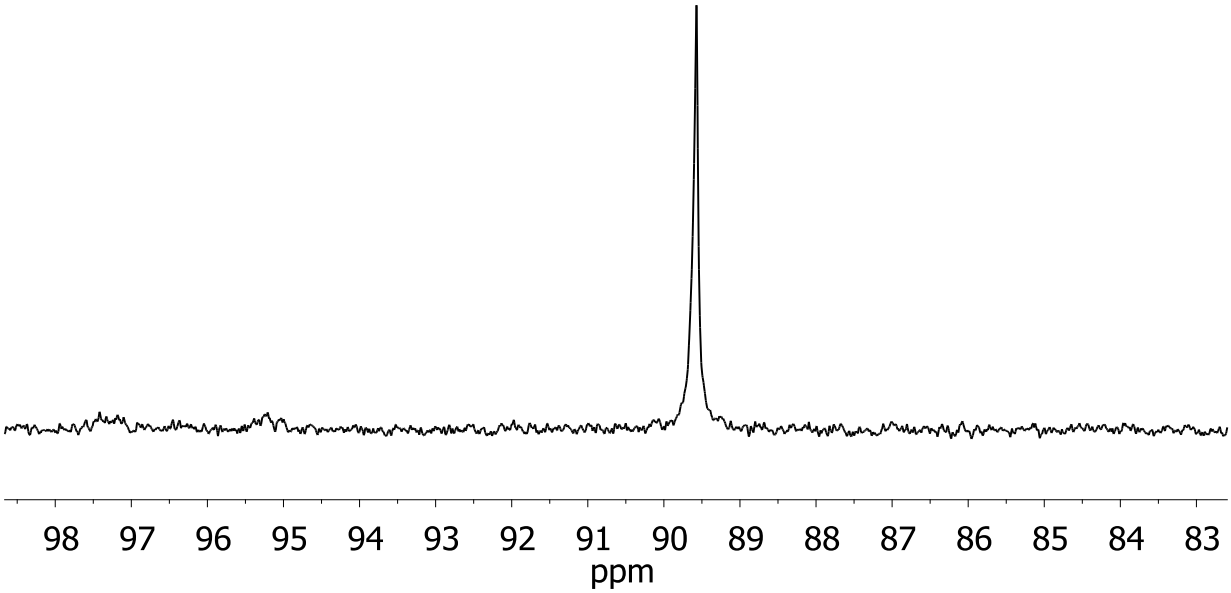


Figure 1.15. ^{31}P-NMR spectrum (CD_2Cl_2 solution) of $[(CO)_3Fe(H)(pdt)Ni(dcpe)]BF_4$.

Extension to Thiolato Building Blocks Other than $Ni(SR)_2L_2$. Previous work from the Millar group inspired us to synthesize another known nickel monomer to test our reduction to new $NiFe(CO)_3$-thiolate complexes. Millar and co-workers originally synthesized the nickel monomer $(NBu)_4[Ni(PS_3*)(CO)]$ (Figure 1.16) as a means to form a new Ni(II)-CO complex, which had little literature precedence (The synthesis of this compound is presented in the experimental section of chapter 3). The synthesis of this nickel monomer was not trivial, and was modified from the original procedure in order to obtain the bright green complex in a moderate yield.

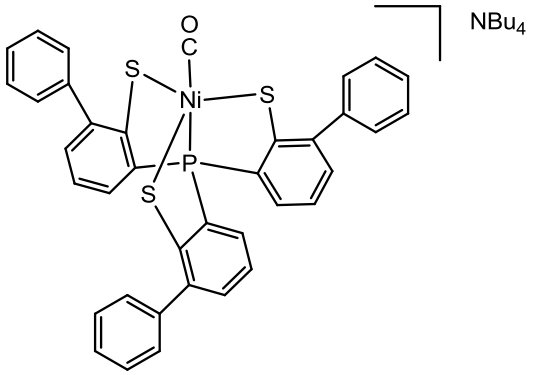


Figure 1.16 Millar's nickel monomer, $(NBu_4)[Ni(PS_3*)(CO)]$.

The reaction of $(NBu)_4[Ni(PS_3*)(CO)]$ and $FeI_2(CO)_4$ in CH_2Cl_2, followed by reduction with two equivalent of cobaltocene produced a bright pink solution that had a single CO band in the infrared spectrum. The single CO band in the FT-IR spectrum at 1940 cm^{-1} had shifted from the starting nickel complex at 2046 cm^{-1}. The isotope pattern from the ESI-MS of the resulting bright pink compound indicated a mononuclear iron complex. We believe that the $(NBu)_4[Ni(PS_3*)(CO)]$ monomer exchanged the nickel atom for iron, resulting in $(NBu)_4[Fe(PS_3*)(CO)]$ and possibly formation of $Ni(CO)_4$. Nearly identical results were seen from the reaction of $(NBu)_4[Ni(PS_3*)(CO)]$ with $Fe_2(CO)_9$.

In an attempt to make a more electron-rich [NiFe]-hydrogenase model, Pd(pdt)(dppe) was synthesized. The reaction of Pd(pdt)(dppe) with $FeI_2(CO)_4$ followed by reduction with cobaltocene did not clearly form a $(CO)_3Fe(pdt)Pd(dppe)$ complex. The initial reaction seemed to form a possible bridging iodide intermediate species (indicated by IR spectroscopy). However after reduction with cobaltocene, the resulting solution IR spectrum revealed a complicated CO band pattern, which changed at room temperature indicating decomposition.

Experimental Section

Unless otherwise noted, all reactions were conducted using Schlenk techniques at room temperature using cannula filtration techniques.

Spectroscopy. NMR spectra were recorded on a Varian 500 MHz or Varian 400 MHz spectrometer. NMR chemical shits are quoted in ppm; spectra are referenced to

residual solvent for ^{1}H and 85% H_3PO_4 for $^{31}P\{^{1}H\}$ spectra. FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer.

Compounds. Chemicals were purchased from Aldrich, and solvents were HPLC-grade and dried by passing through an alumina filtration system or distilled under nitrogen over an appropriate drying agent. Ni(pdt)(dppe)[15], $Ni(SPh)_2$(dppe)[16], $Ni(SPh)_2$(dmpe)[16], $(CO)_3Fe$(pdt)Ni(dppe)[12] were all prepared according to modified literature procedures. The following were also examined in our unsuccessful efforts $NidppfCl_2$[17], $NidpppCl_2$,[18] and $NidppbzCl_2$.[19]

Ni(pdt)(dmpe). A suspension of $NiCl_2$dmpe (0.875 g, 3.13 mmol, 1 equiv) and 1,3-propanedithiol (0.34g, 3.13 mmol, 1 equiv) in CH_2Cl_2 (10 mL) was treated with a solution of NaOMe (0.34 g, 6.25 mmol, 2 equiv) in MeOH (8 mL), slowly over the course of 15 min. After the addition of the NaOMe/MeOH solution, the reaction was stirred for an additional 30 min. Removed all solvent under reduced pressure, then dissolved substance in CH_2Cl_2 (15 mL). The reaction mixture was filtered through a pad of Celite to remove NaCl. Evaporation of solvent afforded a bright orange powder. Yield: 0.80 g (81 %). ^{31}P-NMR (CD_2Cl_2, 23 °C): δ 40.2 (s). Anal. Calcd for $C_9H_{22}NiP_2S_2$ (found): %C 34.31 (34.67), %H 7.04 (7.11).

Ni(edt)(dmpe). Ni(edt)(dmpe) was prepared analogously to the method for Ni(pdt)(dmpe). ^{31}P-NMR: (CD_2Cl_2, 23 °C): δ 42.8 (s). Anal. Calcd for $C_8H_{20}NiP_2S_2$ (found): %C 31.92 (32.12), %H 6.70 (6.81).

Ni(pdt)(dppn). A suspension of $NiCl_2$(dppn) (0.78 g, 1.25 mmol, 1 equiv) in CH_2Cl_2 (20 mL) was treated with 1,3 propanedithiol (0.13 mL, 1.25 mmol) followed by triethylamine (0.69 mL, 5 mmol, 4 equiv). The reaction turned a brown/green color. The solution was concentrated under reduced pressure, and hexanes (30 mL) was added to the concentrate, causing precipitation of a red/orange powder. This solid was washed with hexanes, EtOH, and then finally Et_2O. Single crystals suitable for x-ray diffraction were obtained by layering a CH_2Cl_2 solution with diethyl ether. Yield: 0.63 g (76 %). Unlike related compounds, this species required storage in a glovebox. ^{31}P-NMR (CD_2Cl_2, 23 °C): δ 23.9 (s). Anal. Calcd for $C_{37}H_{32}NiP_2S_2$ (found): %C 67.19 (66.91), %H 4.88 (4.81).

Ni(pdt)(dppbz). A solution of $NiCl_2$(dppbz)ref (1.59 g, 2.76 mmol, 1 equiv) in CH_2Cl_2 (20 mL) was treated with 1,3 propanedithiol (0.28 mL, 2.76 mmol) followed by triethylamine (1.53 mL, 11.04 mmol, 4 equiv), which immediately caused the solution to turn a darker brown/red. The solution was stirred for 20 minutes, and then most of the solvent was removed under reduced pressure. When 3 mL of CH_2Cl_2 remained, diethyl ether (50 mL) was added to the solution to precipitate out an orange fluffy powder. This powder was dissolved in CH_2Cl_2(5 mL) and ethanol (100 mL) was added and the entire reaction mixture was placed in the freezer at -30 °C. After 30 min., orange crystals were washed with ethanol. Yield 1.00 g (59 %). ^{31}P-NMR (CD_2Cl_2, 23 °C): δ 61.1). Anal. Calcd for $C_{33}H_{33}NiP_2S_2$ (found): %C 64.83 (64.52), %H 4.95 (4.74).

Ni(dcpe)Cl_2. Synthesis of this compound is reported in the literature, but there is no information provided on the ^{31}P-NMR or ^{1}H NMR spectroscopy. ^{31}P-NMR (CD_2Cl_2, 23 °C): δ 81.1).

Ni(pdt)(dcpe). A solution of $NiCl_2$(dcpe) (3.5 g, 6.34 mmol, 1 equiv) in CH_2Cl_2 (30 mL) was treated with 1,3-propanedithiol (0.685 g, 6.34 mmol, 1 equiv) followed by a solution of NaOMe (1.37 g, 25.3 mmol, 4 equiv) in MeOH (10 mL). The mixture was stirred for 15 minutes. The solution became deeper orange in color. Solvent was removed under reduced pressure, and the residue was washed with CH_2Cl_2. The slurry was filtered over a pad of Celite to remove NaCl. The dark orange solution was concentrated to dryness. Yield: 3.61 g (97 %). ^{31}P-NMR (500 MHz, CD_2Cl_2): δ 72.31. Anal. Calcd for $C_{29}H_{54}NiP_2S_2$ (found): %C 59.29 (59.57), %H 9.26 (9.33).

$Fe(CO)_3$(pdt)Ni(dppbz). A 100-mL Schlenk flask was charged with a Teflon-coated stir bar, $FeI_2(CO)_4$ (0.53 g, 1.27 mmol, 1 equiv), and Ni(pdt)(dppbz) (0.776 g, 1.27 mmol, 1 equiv). The flask was cooled to –78 °C. To the cooled mixture of solids was added CH_2Cl_2 (10 mL), resulting in a dark brown homogeneous solution. A 0.5 mL sample was removed (into an ambient temperature syringe) and checked by FT-IR to confirm the formation of the proposed μ-I intermediate (Table 1.2). The cold reaction solution was then treated with a pre-cooled (–78 °C) solution of Cp_2Co (0.48 g, 2.54 mmol, 2 equiv) in CH_2Cl_2 (5 mL), which was transferred via cannula. The reaction solution turned brown-green and was allowed to warm to room temperature. After the solution stirred for 1 h at room temperature, the solvent was removed under reduced

pressure, concentrated in CH_2Cl_2 (5 mL) and the solution run over a silica gel column, eluting with CH_2Cl_2 to remove unreacted Ni(pdt)(dppbz) which remained on the silica gel column. The green solution was then concentrated under reduced pressure and hexanes (50 mL) was added to precipitate the product as a light green powder. Yield = 0.600 g (62.9 %). IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2030, 1954. ^{31}P-NMR (CD_2Cl_2, 23 °C): δ 60.1. ESI-MS: m/z 750 ($[M]^+$). Anal. Calcd for $C_{36}H_{30}FeNiO_3P_2S_2$ (found): %C 57.56 (54.89), %H 4.03 (4.01).

$[Fe(CO)_3(pdt)(H)Ni(dppbz)]BF_4$. To a solution of $(CO)_3Fe(pdt)Ni(dppbz)$ (0.030 g, 0.039 mmol, 1 equiv) in CH_2Cl_2 (10 mL) was added $HBF_4{\cdot}Et_2O$ (0.050 mL, 0.345 mmol, 8.6 equiv). The reaction mixture immediately changed from dark green to light orange. The solution was concentrated, and Et_2O (20 mL) was added to precipitate a light orange powder. Yield: 0.083 g (32%). IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2082, 2023. ^{31}P-NMR (CD_2Cl_2, 23 °C): δ 69.6. ^{1}H-NMR (CD_2Cl_2, 23 °C): δ –3.42 (s, 1H, hydride). Anal. Calcd for $C_{36}H_{31}BF_4FeNiO_3P_2S_2$ (found): C 51.53 (48.02), H 3.72 (3.60).

$Fe(CO)_3(pdt)Ni(dcpe)$. A 100-mL Schlenk flask was charged with a Teflon-coated stir bar, $FeI_2(CO)_4$ (0.350 g, 0.85 mmol, 1 equiv), and Ni(pdt)(dcpe) (0.500 g, 0.85 mmol, 1 equiv). The flask was cooled to –78 °C. To the cooled mixture of solids was added CH_2Cl_2 (10 mL), resulting in a dark brown homogeneous solution. A 0.5 mL sample was removed (into an ambient temperature syringe) and checked by FT-IR to confirm the formation of the proposed μ-I intermediate (Table 1.2). The cold reaction solution was then treated with a pre-cooled (–78 °C) solution of Cp_2Co (0.320 g, 1.70 mmol, 2 equiv) in CH_2Cl_2 (5 mL), which was transferred via cannula. The reaction solution turned brown-green and was allowed to warm to room temperature. After the solution stirred for 1 h at room temperature, the solvent was removed under reduced pressure, and the dark brown residue was washed with MeCN (3 x 15 mL) until the washings were colorless. The brown residue was extracted into CH_2Cl_2 (5 mL), and the dark brown product was precipitated by addition of hexanes (30 mL). Yield: 0.21 g (34%). IR (CH_2Cl_2): ν_{CO} 2014, 1940. ^{31}P NMR (500 MHz, CD_2Cl_2): δ 79.3.

$[Fe(CO)_3(pdt)(H)Ni(dcpe)]BF_4$. To a solution of $(CO)_3Fe(pdt)Ni(dcpe)$ (0.150 g, 0.207 mmol, 1 equiv) in CH_2Cl_2 (10 mL), was injected a solution of $HBF_4{\cdot}Et_2O$ (100 □L, 0.691 mmol, 3.35 equiv), which caused an immediate color change from green-brown to

dark orange. The solution was concentrated under reduced pressure to about 5 mL and diluted with hexanes (30 mL) to precipitate a dark orange powder. Crystals suitable for x-ray diffraction were grown from slow diffusion of ether into a solution of the compound in dichloromethane. Yield: 0.090 g (53%). IR (CH_2Cl_2): ν_{CO} 2078, 2017. ^{31}P NMR (500 MHz, CD_2Cl_2): δ 89.5. ^{1}H NMR (500 MHz, CD_2Cl_2): δ -3.00 (br. s, 1H, hydride). Anal. Calcd for $C_{32}H_{55}BF_4FeNiO_3P_2S_2 \cdot 2CH_2Cl_2$ (found): C 41.46 (41.59), H 6.04 (6.41). ESI-MS: m/z 727 ($[M]^+$).

$Fe(CO)_3$(pdt)Ni(dmpe). A 100-mL Schlenk flask was charged with a Teflon-coated stir bar, $FeI_2(CO)_4$ (0.053 g, 0.127 mmol, 1 equiv), and Ni(pdt)(dmpe) (0.040 g, 0.127 mmol, 1 equiv). The flask was cooled to –78 °C. To the cooled mixture of solids was added CH_2Cl_2 (10 mL), resulting in a dark brown homogeneous solution. A 0.5 mL sample was removed (into an ambient temperature syringe) and checked by FT-IR to confirm the formation of the proposed μ-I intermediate (Table 1.2). The cold reaction solution was then treated with a pre-cooled (–78 °C) solution of Cp_2Co (0.320 g, 1.70 mmol, 2 equiv) in CH_2Cl_2 (5 mL), which was transferred via cannula. The addition of the Cp_2Co induced a color change from bright red to bright green. A sample of the cold (-78 °C) reaction solution was withdrawn and injected into an ambient temperature IR cell, and the spectrum was recorded within a few minutes. The spectrum corresponded to that expected for $Fe(CO)_3$(pdt)Ni(dmpe) (see Table 1.2). If however the reaction solution was allowed to warm to room temperature, the resulting spectrum was complex and indicative of decomposition. IR (CH_2Cl_2, cm^{-1}, cold): ν_{CO} 2016, 1941. ^{31}P-NMR (CD_2Cl_2): δ 46.6.

$Fe(CO)_3$(edt)Ni(dmpe). This compound was prepared in the same manner and behaved in a similar fashion to $Fe(CO)_3$(pdt)Ni(dmpe). IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2018, 1943. ^{31}P-NMR (CD_2Cl_2): δ 48.2.

[$Fe(CO)_3$(H)(pdt)Ni(dmpe)]Cl]. A 1.90 M solution of HCl in Et_2O (0.33 mL, 0.635 mmol, 5 equiv) was added to a cold (-78 °C) solution of $Fe(CO)_3$(pdt)Ni(dmpe) prepared as described above . The [$Fe(CO)_3$(H)(pdt)Ni(dmpe)][Cl] compound was also thermally unstable and could only be observed via IR spectroscopy if the solution remained cold. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2078, 2018. ^{1}H-NMR (CD_2Cl_2): δ -3.63 (s, 1H, hydride). ^{31}P-NMR (CD_2Cl_2): δ 61.3.

$[Fe(CO)_3(H)(edt)Ni(dmpe)]Cl$. This compound was prepared in the same manner and behaved in a similar fashion to $[Fe(CO)_3(H)(pdt)Ni(dmpe)][Cl]$. IR ($CH_2Cl_2$, cm^{-1}): ν_{CO} 2079, 2018. ^{1}H-NMR (CD_2Cl_2): δ –3.71(s, 1H, hydride). ^{31}P-NMR (CD_2Cl_2): δ 59.8

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Chapter 2

Modifications to Known Inorganic Syntheses Relevant to [FeFe] and [NiFe] Hydrogenases

Part One: Synthesis of $(NEt_4)_2[Fe(tdt)(CN)_2(CO)]$ and $(NEt_4)_2[Fe(bdt)(CN)_2(CO)]$

Iron in biological systems is studied by Nuclear Resonance Vibrational Spectroscopy (NRVS). Cramer and co-workers have studied Fe^{IV}=O complexes that are models of the intermediates in a large number of mononuclear non-heme iron enzymes.[1] A sample is excited with a 1 meV bandwith beam near a Mossbauer resonance, and the delayed fluorescence is recorded as a function of excitation energy. NRVS is only sensitive to vibrations involving motion of 57-Fe, thus a few model complexes containing the key features of the [Ni-Fe] hydrogenase enzyme have been synthesized and enriched with 57-Fe isotopes, to be studied using this synchrotron radiation technique.

Previous work in the Rauchfuss group has shown that there are two methods for preparing the compound $(NEt_4)_2[Fe(bdt)(CN)_2(CO)]$.[2] The first method is a primordial route in which anhydrous ferrous chloride reacts with Na_2bdt (generated from NaH and 1,2-benzenedithiol dissolved in MeOH) in MeCN under a CO atmosphere. Two equivalents of NEt_4CN are added to the solution and the entire solution purged with N_2 for three hours to generate $(NEt_4)_2[Fe(bdt)(CN)_2(CO)]$. However, several attempts to repeat this method were unsuccessful and only lead to the isolation of the 18 electron dicarbonyl adduct: $(NEt_4)_2[Fe(bdt)(CN)_2(CO)_2]$.

A second method was reported for the synthesis of the 16 electron compound in which $Fe(bdt)(CO)_6$ reacts with two equivalents of NEt_4CN in MeCN and after purging the solution for 6 h with N_2, the $(NEt_4)_2[Fe(bdt)(CN)_2(CO)]$ can be isolated. Repetition of this method with a few modifications was successful. In order to generate 57-Fe labeled compounds for NRVS studies, the primordial method first for generating $Fe_2(tdt)(CO)_6$ with anhydrous 57-$FeCl_2$ was employed, followed by the reaction with two equivalents of NEt_4CN to generate $(NEt_4)_2[(57\text{-}Fe)(tdt)(CN)_2(CO)]$. The modifications to these known procedures are reported in this thesis. Also, the synthesis of new analogous anionic

iron(dithiolate)(dicyanide)(carbonyl) compounds using 4-toluene 1,2 dithiol is also reported in this thesis. It appears that the synthesis of the 16 electron species with the 4-toluene 1,2 dithiol ligand results in the formation of $(NEt_4)_2[(Fe(tdt)(CN)_2(CO)]$, which has fewer impurities by IR spectroscopy than the analogous compound $(NEt_4)_2[Fe(bdt)(CN)_2(CO)]$. The $(NEt_4)_2[(Fe(tdt)(CN)_2(CO)]$ also has greater solubility than the $(NEt_4)_2[Fe(bdt)(CN)_2(CO)]$.

Synthesis of $Fe_2bdt(CO)_6$ from the Primordial Route using Ferrous Chloride:

This procedure was modified from *Inorganic Chemistry*, **2008,** 47, 7002-7008. Dissolved $FeCl_2$ (0.400 g, 3.16 mmol, 1.95 equiv) in acetone (45 mL), the solution was a light orange color. Purged the solution with CO for 30 minutes, then injected NEt_3 (0.45 mL, 3.24 mmol, 1 equiv) and the solution immediately turned a grayish color. Then injected 1,2 benzenedithiol into the solution, which immediately turned black. Added the Zn (0.132 g, 2.02 mmol, 2.02 equiv) directly to the reaction flask, and allowed the solution to stir while purging with CO for 10 h. There was no observable change. In air, filtered the black slurry over Celite, and continually washed the Celite with acetone until the filtrate was clear. Then took the dark black filtrate and removed all solvent under reduced pressure, and extracted the black substance into CH_2Cl_2 (15 mL), and ran the solution over a silica gel column, eluting with hexanes. Collected the first band, which was a dark orange/red band. Then removed all CH_2Cl_2, and extracted the dark brown/red substance into hexanes. Ran the hexane solution over a silica gel column, and collected the bright orange band, which was identified by IR spectroscopy to be $Fe_2bdt(CO)_6$ (0.222 g, 32.6 % Yield). IR (hexanes) ν_{CO}: 2079, 2044, 2006, 1992, 1967, 1958 cm^{-1}.

Synthesis of $[NEt_4]_2[Febdt(CN)_2(CO)]$:

This procedure was modified from *Journal of the American Chemical Society,* **2001,** 123, 6933. $Fe_2bdt(CO)_6$ (0.22 g, 0.53 mmol, 1 equiv) was dissolved in MeCN (10 mL). In a separate flask, NEt_4CN (0.16 g, 1.06 mmol, 2 equiv) was dissolved in MeCN (10 mL). The solution of NEt_4CN was transferred via cannula into the orange solution of $Fe_2bdt(CO)_6$. This solution was purged under Argon (or nitrogen) for 12 h.

After 12 h, the solution was a dark brown red. All of the MeCN was removed under reduced pressure, leaving a dark brown residue. The brown residue was washed with THF (10 mL), then filtered via cannula (The filtrate was dark red). Redissolved the remaining substance in a small amount of MeCN (~3 mL) and added diethyl ether (30 mL), to attempt to precipitate out the product. The product first came out as an oil, so this procedure was repeated three times until the product precipitated out as a fine dark purple powder. This powder was washed with THF continuously until the filtrate was clear. After final filtration, the dark purple powder was dried under vacuum and isolated in the glovebox. Isolated 0.09 g of dark purple powder. IR (solid state using ATR) ν_{CO}: 1886 cm^{-1}; ν_{CN}: 2071, 2078 cm^{-1} (Figure 2.1).

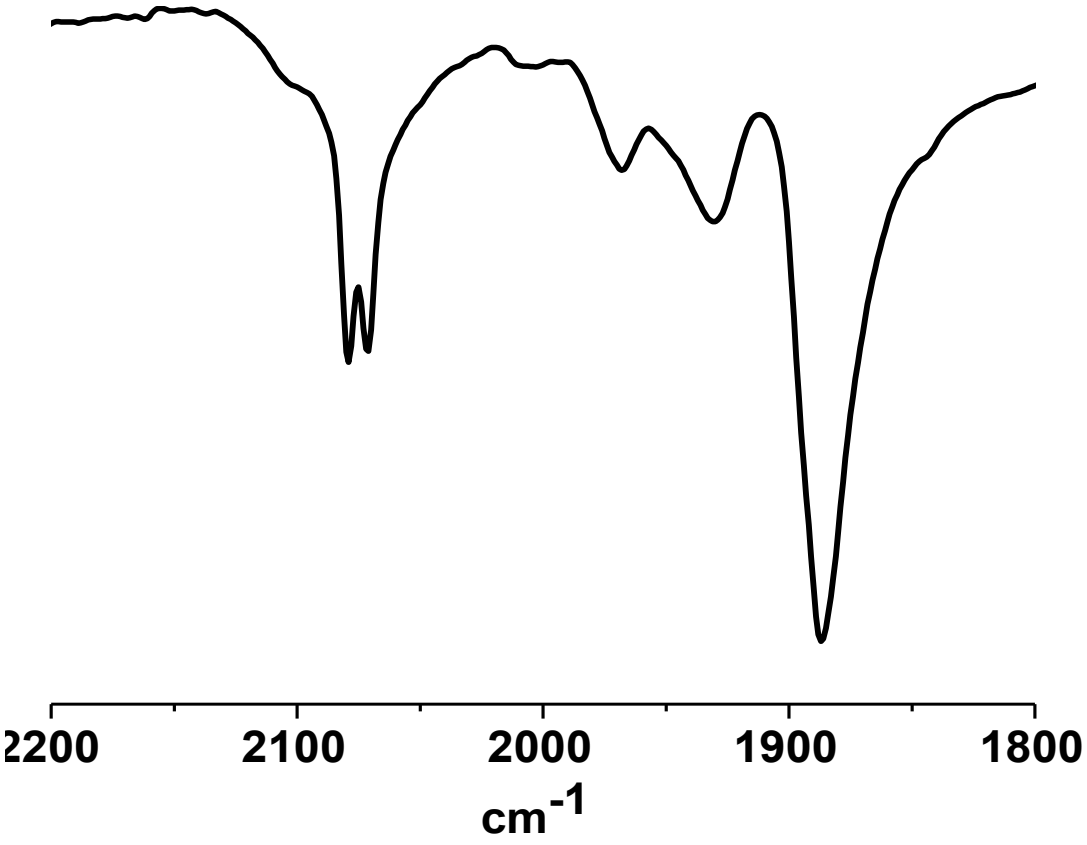


Figure 2.1 Solid State IR Spectrum for $[NEt_4]_2[Febdt(CN)_2(CO)]$.

Synthesis of $Fe_2tdt(CO)_6$:

This procedure was modified from *Comptes Rendues Chimie*¸**2008,** *11,* 875. $Fe_3(CO)_{12}$ (1.45 g, 2.88 mmol, 1 equiv) was dissolved in toluene (30 mL). To this dark green solution was added 4-toluene 1,2 dithiol (0.44 g, 2.88 mmol, 1 equiv). This dark green solution was heated at reflux for 1.5 h. Then all of the solvent was removed under reduced pressure leaving a dark red substance. This substance was dissolved in ~ 10 mL of hexanes, and was run on a silica gel column eluting with hexanes. The product was the first band which was a red-orange color. There was also a second dark green band that was later determined to be excess $Fe_3(CO)_{12}$. Isolated 0.97 g (Yield = 77.6 %). of flaky red-orange material that was determined by IR spectroscopy to be $Fe_2tdt(CO)_6$.

Synthesis of $Fe_2tdt(CO)_6$ from the Primordial Route using Ferrous Chloride:

This procedure was modified from *Inorganic Chemistry*, **2008,** 47, 7002-7008. Dissolved $FeCl_2$ (0.400 g, 3.16 mmol, 1.95 equiv) in acetone (45 mL), the solution was a light orange color. Purged the solution with CO for 30 minutes, then injected NEt_3 (0.45 mL, 3.24 mmol, 1 equiv) and the solution immediately turned a grayish color. Then injected 3,4 toluenedithiol** (0.250 g, 1.62 mmol, I equiv) into the solution, which immediately turned black. Added the Zn (0.210 g, 3.27 mmol, 2.02 equiv) directly to the reaction flask, and allowed the solution to stir while purging with CO for 10 h. There was no observable change. In air, filtered the black slurry over Celite, and continually washed the Celite with acetone until the filtrate that poured through was clear. Then took the dark black filtrate and removed all solvent under reduced pressure, and extracted the dark red brown substance into CH_2Cl_2 (15 mL), and ran the solution over a silica gel column, eluting with hexanes. Collected the first band, which was a dark orange/red band. Then removed all CH_2Cl_2, and extracted the dark brown/red substance into hexanes. Ran the hexane solution over a silica gel column, and collected the bright orange band, which was identified by IR spectroscopy to be $Fe_2tdt(CO)_6$ (0.326 g, 48.2 % Yield).

Synthesis of $(NEt_4)_2[Fe(tdt)(CN)_2(CO)]$:

This procedure was modified from *Journal of the American Chemical Society* ,**2001,** 123, 6933. Dissolved $Fe_2tdt(CO)_6$ (0.400 g, 0.922 mmol, 1 equiv) in 35 mL of MeCN. Then dissolved NEt_4CN (0.288 g, 1.84 mmol, 2 equiv) in a separate flask, and transferred this into the solution of $Fe_2tdt(CO)_6$. Stirred this solution for 10 h under argon, which turned a dark black/grey solution. Removed all solvent under reduced pressure, the substance was a dark brown/red oil. Washed this oil with 30 mL of THF, the filtrate was a dark red color, and a dark red oil remained in the flask. Then concentrated the red oil substance in MeCN (~ 3 mL) and added 30 mL ether, and filtered via cannula. Repeated this process until the substance that crashed out was a dark purple crystalline powder. Isolated 0.070 g of purple crystalline powder that was determined to be $(NEt_4)_2[Fetdt(CN)_2(CO)]$. IR (Solid State using ATR): v(CN): 2081, 2074 v(CO): 1886 cm^{-1} (Figure 2.2).

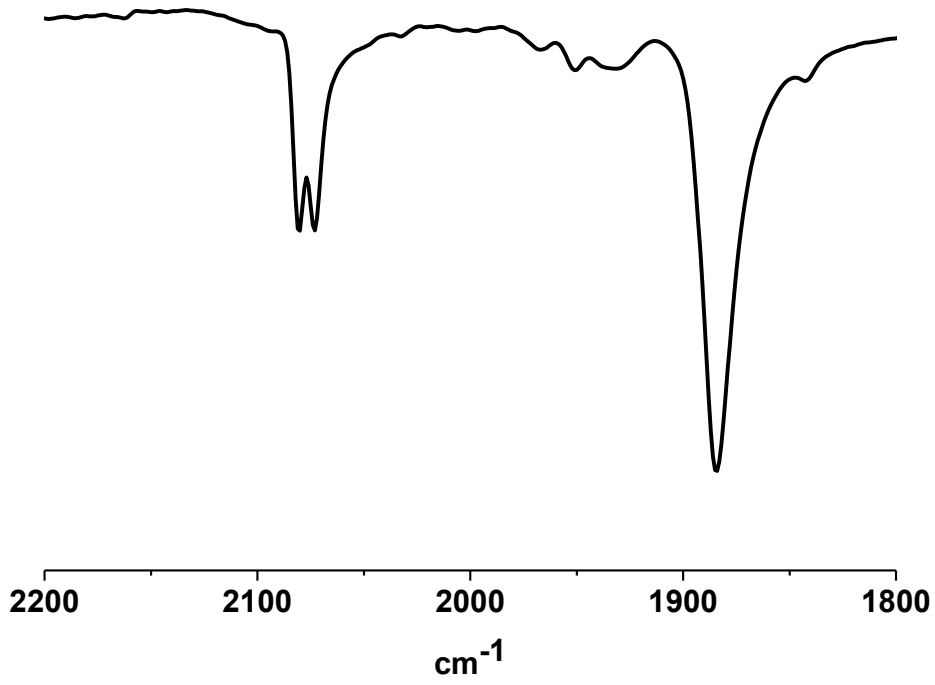
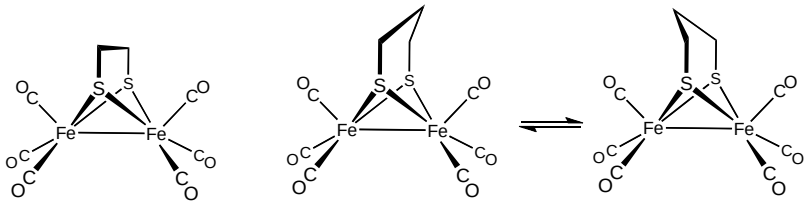


Figure 2.2 Solid State IR Spectrum for $(NEt_4)_2[Fetdt(CN)_2(CO)]$.

Part Two: Revisiting Synthesis of $(NEt_4)_2[Fe_2(pdt)(CN)_2(CO)]$ and $(NEt_4)[HFe_2(pdt)(CN)_2(CO)]$

Dithiolatodiiron hexacarbonyl complexes were first reported by Reihlen and then Hieber and are generally prepared from the reaction of the thiols with iron carbonyls.[3] $Fe_2(S_2C_nH_{2n})(CO)_6$ derived from ethanedithiol (n = 2) and 1,3-propanedithiol (n = 3) were described by Huttner and coworkers by the reaction of $Fe_3(CO)_{12}$ with the respective dithiols.[4] Extensive work had been reported for the related methanthiolates $Fe_2(SCH_3)_2(CO)_6$, which exist in solution as two isomers, depending on the relative orientation of the methyl groups.[5] The ethanedithiolate is more amenable to analysis because it exists exclusively as a single isomer of C_{2v} symmetry. The propanedithiolate is structurally more complex owing to the folded conformation of the $Fe_2S_2C_3$ core.[4] In solution the two conformers rapidly interconvert.



Scheme 2.1: Models of $Fe_2(S_2C_nH_{2n})(CO)_6$, the propanedithiolate is more complex owing to folding conformation of the $Fe_2S_2C_3$ core.

The hexacarbonyls $Fe_2(S_2C_nH_{2n})(CO)_6$ readily undergo substitution by cyanide,[6,7] phosphines,[8] isocyanides,[9] *N*-heterocyclic carbenes,[10] and other donor ligands. With monodentate ligands, disubstitution proceeds efficiently to afford derivatives $Fe_2(S_2C_nH_{2n})(CO)_4L_2$ (L = RNC, NHC) and, for cyanide, $[Fe_2(S_2C_nH_{2n})(CO)_4(CN)_2]^{2-}$.[11] Monosubstitution can be complicated by competitive disubstitution reactions, but this problem can be circumvented by in situ generation of the labile acetonitrile complex, which undergoes rapid monosubstitution as illustrated in a procedure given below.[11] In contrast to the parent hexacarbonyls, substituted derivatives undergo many electrophilic reactions, including protonation to afford hydrides. The hydrides are efficient catalysts for hydrogen evolution.[12]

Synthesis of $Fe_2(pdt)(CO)_6$:

A 250-mL round-bottomed Schlenk flask containing a Teflon-covered magnetic stirring bar is charged with benzene (20 mL). The benzene is sparged with nitrogen for a few minutes and then 1,3 propanedithiol (0.79 mL, 7.95 mmol) and solid $Fe_3(CO)_{12}$ (3.2 g, 6.36 mmol) are added. The flask is fitted with a reflux condenser, and the mixture is heated at vigorous reflux under nitrogen for 1.5-2 h. During the reaction, the solution changes a color from green to red. The reaction solution was allowed to cool to room temperature, and the contents were evaporated to an oily red solid. The solid is dissolved in 5 mL of hexane and chromatographed on a 15 in x 1 in column, eluting with hexanes. The main band is red and is collected and evaporated to dryness, leaving red-orange crystals. The yield is 2.26 g (92 %). Anal. Calcd for $C_9H_6Fe_2O_6S_2$ (found): %C 28.00 (28.03), %H 1.55(1.37) % N 0.00 (0.12). IR (hexanes): 2076, 2035, 2006, 1993, 1982 cm^{-1}. ^1H NMR (400 MHz, acetone-d_6, 25°C): δ 2.26 (t, 4H), 1.86 (m, 2H).

Properties: The product is air-stable for extended periods. It is soluble in a variety of organic solvents. The product is best characterized by its infrared spectrum. The same procedure can be used to prepare the ethanedithiolate. IR (hexanes): 2077, 2037, 2007,1995, 1984 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ 2.38 (s, 4H).

Synthesis of $(NEt_4)_2[Fe_2(pdt)(CN)_2(CO)_4]$:

A 100-mL round-bottomed Schlenk flask containing a magnetic stirring bar is charged with $Fe_2(S_2C_3H_6)(CO)_6$ (0.56 g, 1.45 mmol, 1 equiv) and acetonitrile (20 mL). The red-orange solution is treated with a solution of NEt_4CN (0.45 g, 2.9 mmol) in 10 mL acetonitrile, and stirred for 1 h. The resulting dark red solution was evaporated to dryness, and the remaining red solid was washed with 3 x 5 mL hexanes and dried in vacuum. The yield is 0.86 g (95%). Anal. Calcd for $C_{24}H_{46}Fe_2N_4O_4S_2$ (found): %C 45.72 (45.97), %H 7.35 (7.33), %N 8.89 (8.98), %S 10.17 (10.34), %Fe 17.72 (17.59). ^1H NMR (400 MHz, CD_3CN, 25°C): δ 1.21 (t, 24H, $NCH_2\mathit{CH_3}$), 1.67 (m, 2H, $CH_2\mathit{CH_2}CH_2$),

1.85 (t, 4H, SCH_2), 3.18 (q, 16H, NCH_2CH_3). IR (MeCN): 2072, 2036, 1961, 1913, 1879 cm^{-1}.

Properties: The compound is soluble in water, methanol, and acetonitrile. Both the solid and especially its solutions are unstable in air. $(NEt_4)_2[Fe_2(S_2C_3H_6)(CN)_2(CO)_4]$ is unreactive toward other ligands, including cyanide. It has been characterized crystallographically.[6] The reaction of the ethanedithiolate $Fe_2(S_2C_2H_4)(CO)_6$ with NEt_4CN under the same conditions afforded $(NEt_4)_2[Fe_2(S_2C_3H_6)(CN)_2(CO)_4]$. ^1H NMR (400 MHz, CD_3OD, 25°C): δ 3.28 (q, 16H, NCH_2CH_3), 1.96 (s, 4H, SCH_2), 1.21 (t, 24H, NCH_2CH_3). IR (MeCN): 2078, 2029, 1961, 1917, 1880 cm^{-1}.

Synthesis of $(NEt_4)[Fe_2(pdt)(CN)(CO)_5]$

A solution of 0.25 g of (0.65 mmol) of $Fe_2(S_2C_3H_6)(CO)_6$ in 10 mL of MeCN is treated with a solution of 0.049 g (0.65 mmol) of Me_3NO in 10 mL of MeCN. The infrared spectrum of the resulting dark brown solution indicates formation of the acetonitrile adduct [IR(MeCN): ν_{CO} = 2050, 2040, 1990, 1962, 1932 cm^{-1}]. The dark brown solution is then cooled to -40 °C and is treated with a solution of 0.10 g (0.65 mmol) of NEt_4CN in 10 mL of MeCN. The solution changes to dark red within minutes. The cooling bath is removed and the reaction mixture is allowed to warm to room temperature. The dark red solution is evaporated to dryness under vacuum. The resulting red oil is extracted into 10 mL of THF, and this extract is filtered. The filtrate is reduced to approximately 1 mL, and the product is precipitated upon addition of 20 mL of hexanes and washed with additional hexanes to leave an oily residue. The crude red product is dried under vacuum for 1 h, leaving a red solid. Yield: 0.29 g (87%). Anal. Calcd for $C_{17}H_{26}Fe_2N_2O_5S_2$ (found): %C 39.71 (39.43), %H 5.10 (5.06), %N 5.45 (5.43), %S 12.47 (12.47). IR (THF): ν_{CN} = 2091; ν_{CO} = 2030, 1975, 1955, 1941, 1914 cm^{-1}. ^1H NMR (500 MHz, CD_3CN): δ 3.16 (q, 8H, NCH_2CH_3), 2.18 and 1.77 (br, 6H, $S(CH_2)_3S$), 1.19 (t, 12H,NCH_2CH_3).

Properties: The compound is soluble in water, methanol, and acetonitrile. Both the solid and especially its solutions are unstable in air. The product is most easily obtained as a

glassy solid, but single crystals can be obtained by recrystallization from THF-hexanes. The salt has been characterized crystallographically.[11] The acetonitrile complex is stable for minutes in acetonitrile solution. It undergoes substitution by a variety of ligands under mild conditions.[11]

Part Three: Improved Synthesis of $Fe(pdt)(dppv)_2(CO)_2$

Previous work in the Rauchfuss group has shown that $Fe_2(pdt)(dppv)_2(CO)_2$ can be synthesized from photolyzing a solution of $Fe_2(pdt)(dppv)(CO)_4$ in toluene in the presence of one equivalent of dppv over the course of 12 hours. However, the IR spectrum in CH_2Cl_2 of the resulting product always revealed an unexplainable impurity near 1950 cm^{-1}. The original synthesis involved photloyzing the toluene solution of the $Fe_2(pdt)(dppv)(CO)_4$ with a 100 W UV immersion lamp, with a 365 nm maximum wavelength. It was thought that this powerful polychromatic UV source may be over-photolyzing the compound, resulting in degradation. Replacing the UV source with a single wavelength 365 nm LED resulted in isolation of the $Fe_2(pdt)(dppv)_2(CO)_2$ with a greatly reduced presence of the impurity as shown by IR spectroscopy. This modification will be shown in this thesis.

Synthesis of $Fe_2(pdt)(dppv)_2(CO)_2$ using a new photoloysis source:

$Fe_2(pdt)(dppv)_2(CO)_4$ (500 mg, 0.720 mmol, 1 equiv) and dppv (280 mg, 0.720 mmol, 1 equiv) were dissolved in toluene (20 mL). The toluene solution was photolyzed for 20 h with a single wavelength 365nm LED to produce a dark green solution. All of the solvent was removed under reduced pressure and the dark black substance was extracted into CH_2Cl_2 (5 mL) and the product precipitated upon addition of hexanes (50 mL). The product was redissolved in CH_2Cl_2 (5 mL) and precipitated again upon the addition of MeOH (50 mL). An olive green powder was isolated. Yield = 0.61 g (83 %).

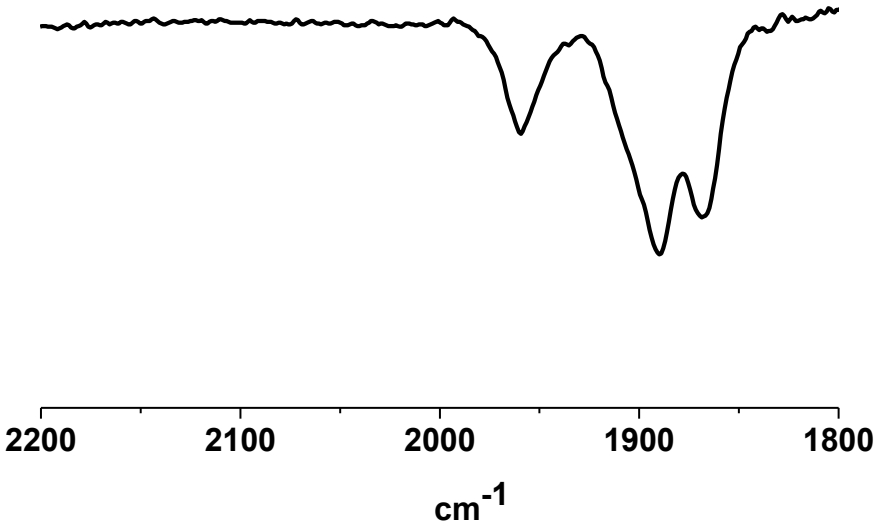


Figure 2.3a IR Spectrum of $Fe_2(pdt)(dppv)_2(CO)_2$ in CH_2Cl_2, using previous method with more powerful polychromatic UV photolysis source.

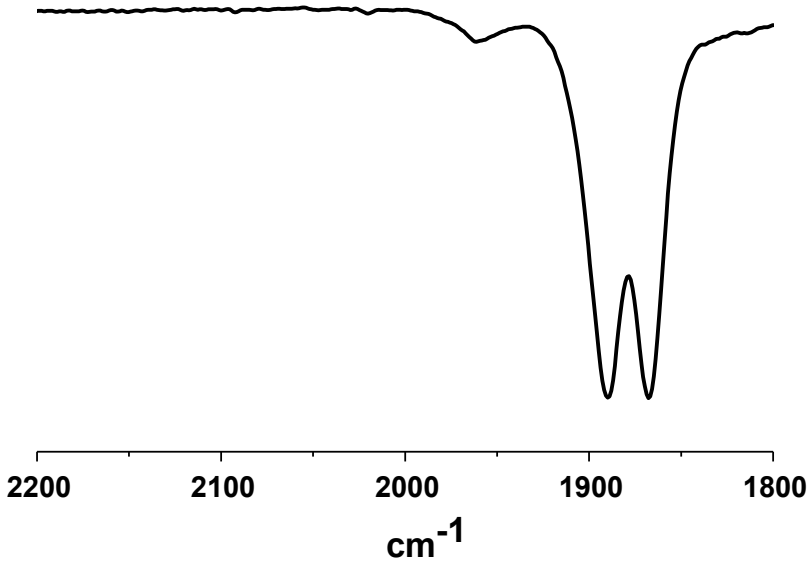


Figure 2.3b IR Spectrum of $Fe_2(pdt)(dppv)_2(CO)_2$ in CH_2Cl_2, using new method with a 365 nm single wavelength LED as photolysis source. IR shows greatly reduced presence of impurity at 1960 cm^{-1}.

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Chapter 3

Modifications to Syntheses of Thiophenol Phosphine Ligands and Millar's $[NBu_4][Ni(PS_3*)(CO)]$ Complex

Synthesis of 2-(diphenylphosphino)thiophenol (PPh_2S)

This procedure was modified from the literature.[1] Degassed cyclohexane (100 mL); then degassed TMEDA (22 mL, 0.142 mol, 2.2 equiv) and added the TMEDA to the cyclohexane. Slowly added 1.6 M solution of n-butyllithium in hexanes (88.8 mL, 0.142 mol, 2.2 equiv) into the cyclohexane/TMEDA (by transferring via cannula directly from Sure Seal Aldrich bottle). Cooled the entire pale yellow solution in an ice bath, and added thiophenol (6.99 g (6.5 mL), 0.064 mol, 1 equiv) in cyclohexane (10 mL), dropwise through an addition funnel. Allowed the solution to warm to room temperature overnight, the white solid di-lithiated species had settled to the bottom.

Decanted off the supernatant yellow liquid, using a filter cannula. Washed the white solid with 3 x 50 mL hexanes, also using a filter cannula. In a separate flask, cooled THF (100 mL) to -78 ^{o}C and added this to the pre-cooled white solid (also at -78 ^{o}C). While keeping the solution at - 78 ^{o}C, slowly added neat PPh_2Cl (9.99 g (8.13 mL), 0.045 mol, 0.7 equiv) dropwise into the mixture. Allowed the solution to warm to room temperature overnight. Treated this solution with an ice cold 2.0 M solution of H_2SO_4 (100 mL), initially added the solution dropwise as the reaction was exothermic. The entire mixture was then concentrated in vacuum, and the residue was taken up into ether. Cannula transferred the bottom aqueous layer, leaving the product in ether. Extracted more product from the aqueous layer into ether. Finally combined all of the ether layers and removed solvent under reduced pressure. Isolate 12.0 g of crude material. Attempted to crystallize by "dissolving" in ether, although the product was not very soluble, then added hexanes. Isolated the white solid by cannula filtration. Yield = 9.0 g (70 %). ^{1}H-NMR (500 MHz, CD_2Cl_2): δ 7.3 – 6.6 (m, 14 H, Ph rings), 4.07 (d, 1 H, SH). ^{31}P NMR ($CDCl_2$): δ -13.8.

Synthesis of tris(2-thiophenol)phosphine (PS_3)

This procedure was modified from the literature.[1] Degassed cyclohexane (100 mL); then degassed TMEDA (22 mL, 0.142 mol, 2.2 equiv) and added the TMEDA to the cyclohexane. Slowly added 1.6 M solution of n-butyllithium in hexanes(88.8 mL, 0.142 mol, 2.2 equiv) into the cyclohexane/TMEDA (by transferring via cannula directly from Sure Seal Aldrich bottle). Cooled the entire pale yellow solution in an ice bath, and added thiophenol (6.99 g (6.5 mL), 0.064 mol, 1 equiv) in cyclohexane (10 mL), dropwise through an addition funnel. Allowed the solution to warm to room temperature overnight, the white solid di-lithiated species had settled to the bottom.

Decanted off the supernatant yellow liquid, using a filter cannula. Washed the white solid with 3 x 50 mL hexanes, also using a filter cannula. In a separate flask, cooled THF (100 mL) to -78 ^{o}C and added this to the pre-cooled white solid (also at -78 ^{o}C). While keeping the solution at - 78 ^{o}C, slowly added neat PCl_3 (1.87 mL, 0.021 mol, 0.33 equiv) dropwise into the mixture over the course of 1 h. Allowed the solution to warm to room temperature overnight. The solution was brown-red the following day. Treated the solution with an ice cold 2.0 M solution of H_2SO_4 (100 mL), initially added the solution dropwise as the reaction was exothermic. Then concentrated the entire reaction mixture under reduced pressure, some white precipitate began to form. Then extracted all of the precipitate into diethyl ether, separated the aqueous from the ether layer, and washed the aqueous layer with more diethyl ether. Combined all of the ether layers and removed solvent under reduced pressure, isolated 4.3 g of crude product. 'Dissolved' (not very soluble) crude product into diethyl ether (10 mL), then added hexanes (50 mL) which caused white crystalline material to precipitate out of solution. Filtered, and isolated white crystalline powder. Yield = 2.5 g (33.2 %). ^{1}H-NMR (500 MHz, CD_2Cl_2): δ 7.4 - 6.7 (m, 12 H, Ph rings), 4.07 (d, 3 H, SH). ^{31}P-NMR (500 MHz, CD_2CL_2): δ -27.1.

Synthesis of 2-phenylthiophenol

This procedure was modified from the literature.[2] Dissolved biphenyl (10.04 g, 66.8 mmol, 1.02 equiv) in *dry* THF (~150 mL). Added lithium wire (cut into 0.5 cm pieces) (1.00 g, 148 mmol, 2.26 equiv) to the solution of biphenyl in THF. The color immediately turned from clear to dark blue. In a separate flask dissolved dibenzothiophene (12.28 g, 65.2 mmol, 1 equiv) in THF (100 mL) and ether (50 mL). Cooled the solution of biphenyl/lithium/THF to 0 °C, then added the dibenzothiophene solution slowly over the course of 30 minutes. The mixed solution was very viscous (perhaps too concentrated), allowed to stir vigorously overnight and warm to room temperature. After 20 h, the solution was quenched slowly with a 0.6 M solution of HCl (200 mL). The color slowly changed from a tinted red solution to clear. HCl was continuously added until the aqueous layer was acidic. The organic layer was separated from the aqueous layer and the solvent was removed under reduced pressure to leave a colorless oil. The oil was dissolved in toluene and mixed with a 0.6 M NaOH solution. The layers were separated and the organic layer was discarded. The basic aqueous layer was re-acidified and the resulting white slurry was extracted with toluene. The organic layer was separated, dried over $MgSO_4$, and the solvent was removed under reduced pressure to leave a yellow oil. The yellow oil was dissolved in a minimal amount of toluene, and eluted through a plug of silica gel with toluene. Then the solvent was removed under reduced pressure to leave a colorless oil, which was placed in the freezer to crystallize. After 24 h, isolated white crystalline powder. Yield = 6.3 g (52 %). ^{1}H NMR (500 MHz, d_6-acetone): δ 7.26 (d, 2H); 7.15 -6.97 (m, 5H); 6.90-6.80 (m, 2H); 3.09 (s, 1H, *S*-H).

Synthesis of tris(2-phenylthiophenol)phosphine (PS_3*)

This procedure was modified from the literature.[3] To a three neck roundbottom flask, injected TMEDA (3.67 mL, 24.6 mmol, 2.2 equiv) into degassed cyclohexane (50 mL). Slowly added 1.6 M solution of n-butyllithium in hexanes(15.36 mL, 24.6 mmol, 2.2 equiv) into the cyclohexane/TMEDA (by transferring via cannula directly from Sure Seal Aldrich bottle). Dissolved the 2-phenylthiophenol (2.08 g, 11.2 mmol, 1 equiv) into degassed cyclohexane (30 mL), then added this dropwise over the course of 30

minutes to the cooled mixture of TMEDA/n-butyllithium/cyclohexane at 0 °C. Allowed this to stir overnight.

Pre-cooled THF (100 mL) to -78 °C in a separate flask. Filtered the reaction mixture, isolating a white precipitate. Cooled the white precipitate to -78 °C. Then added the pre-cooled THF to the pre-cooled flask containing the white precipitate via plastic cannula transfer. (It is crucial to make sure the THF is *dry* and pre-cooled before dissolving the white precipitate. Failure to do so will result in a dramatic loss of yield). Once the white precipitate was mostly dissolved, began adding PCl_3 (0.33 mL, 3.73 mmol, 0.33 equiv) dissolved in THF (20 mL) slowly through an addition funnel over the course of 1 h. The entire reaction flask was still kept at -78 °C. The flask was kept cold an additional hour, then allowed to warm to room temperature and stirred overnight. After 18 hours, began concentrating the entire reaction mixture under reduced pressure, and a white crystalline solid began to precipitate out. Filtered off the supernatant liquid *while keeping the reaction flask cold* (failure to do this will result in a dramatic loss of white crystalline solid collected at the end of the synthesis).
Yield = 2.91 g (44.3 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-6.77 (m, 24H); 4.09 (br, 3H). ^{31}P NMR (500 MHz, $CDCl_3$): δ -23.1.

Synthesis of Millar's $[NBu_4][Ni(PS_3*)(CO)]$

This procedure was modified from the literature.[3] To a Schlenk flask added PS_3* (0.586 g, 0.99 mmol, 1 equiv) along with MeOH (15 mL). To the cloudy-white slurry, added Lithium wire (0.028 g, 4.0 mmol, 4 equiv). The slurry quickly became a clear yellow solution. In a separate flask, dissolved the $Ni(acac)_2$ (0.254 g, 0.99 mmol, 1 equiv) in MeOH (6 mL). This made a light green slurry. Transferred the light green slurry of $Ni(acac)_2$ into the solution of deprotonated PS_3*. Instantly, the solution turned a dark brown color. Allowed the solution to stir at room temperature for about 40 minutes, then began to purge under CO. After 30 minutes of purging with CO, the solution was a very deep/bright green color. Layered the solution with a solution of NBu_4Br (0.960 g, 2.96 mmol, 3 equiv) in MeOH (5 mL), then placed in a freezer at -30 °C to crystallize. After 24 hours, isolated bright green crystals. Yield = 0.762 g (83.6 %). IR (CH_2Cl_2): 2046 cm^-

[1]. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.72 (d, 3H); 7.33-7.02 (m, 15H); 7.13 (d, 3H); 6.96 (t, 3H); 2.65 (br, 8H); 1.17 (br, 8H); 0.88 (br, 8H); 0.72 (br, 12H).

References

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