

**Iron Chemistry of Hemilabile SNS Ligands: Synthesis,
Reactivity, and Catalytic Applications**

by

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Abstract

The development of abundant and economical first-row transition metal-based catalysts is an appealing area of research for efficient and selective chemical transformations. In this context, iron complexes are highly desirable as they feature a range of accessible oxidation states allowing for transfer of one or two electrons to or from a substrate. Therefore, over the past two decades, many iron-based catalysts have been developed, extensively studied, and exploited for catalysis ranging from oxidation and reduction to C-C bond forming reactions.

In homogeneous transition metal catalysis, the ligand plays a vital role in determining activity and selectivity of the above stated catalytic reactions. Some key features of ligands that support both stoichiometric and catalytic reactions of metal complexes include: 1) strong chelation ability to metals, 2) tunability of donor atoms, 3) strong field ligands such as phosphine, phosphite, CO, and hydride favoring low-spin complexes, 4) hemilability allowing substrate activation via reversible dissociation of one donor atom, and 5) redox-activity enabling donation or accepting of electrons, thus avoiding a change of metal oxidation state. To this end, *bifunctional ligands* containing the above described properties have emerged as important elements in chemical synthesis and in catalysis. Iron and other transition metal complexes containing multidentate bifunctional ligands have recently been shown to activate small molecules and catalyze a number of chemical transformations with activity and selectivity typical of more well-studied precious metals.

The objective of this *thesis* is to further advance the field of *bifunctional ligands* by preparing new sterically svelte tridentate ligands with a mixture of hard nitrogen and soft sulfur donors and to investigate their iron chemistry. The overall goal is to then explore the utility of these iron complexes as potential bifunctional catalysts. Chapter 2 describes a one-step synthesis of a new $S^{Me}N^HS$ ligand in excellent yield that undergoes ring-opening on treatment with $Fe(OTf)_2$ affording a thiolate-bridged, trinuclear iron complex, $[Fe_3(\mu_2-S^{Me}NS^-)_4](OTf)_2$. The structure, spectroscopic, magnetic, and computational studies of this iron complex are provided along with its solvent-dependent reactivity towards monodentate donor ligands that yields both dinuclear and

mononuclear derivatives. Chapter 3 describes the formation of an electron-rich Fe(II) thiolate complex, $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_3](\text{OTf})$ and its substitution reactivity with both mono- and bidentate donor ligands. On heating this complex, an oxidative thioether $\text{C}_{\text{aryl}}\text{-S}$ bond cleavage is observed, leading to a cationic Fe(III)-CNS thiolate analog. Reduction of this Fe(III) species with cobaltocene yielded a neutral Fe(II)-CNS thiolate complex. To investigate the bifunctional activity of these Fe(II) complexes, both Fe(II)-SNS and -CNS species were assessed as precatalysts for amine-borane dehydrogenation. Chapter 4 employs the $\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}$ ligand in formation of a neutral, imine-coupled Fe- N_2S_2 complex that serves as an efficient and selective aldehyde hydroboration catalyst using pinacolborane. A reaction profile kinetic analysis implicates the hemilability and redox-active properties of this complex. Chapter 5 introduces the new unsymmetrical amine ligand, $\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}^{\text{Me}}$, and details its iron chemistry with formation of a pseudooctahedral Fe(II) bis(amido) complex. The Mössbauer spectra, MCD study, and DFT calculations support formation of a minor five-coordinate isomer in solution due to the hemilability of the six-membered ring thioether group. Reactivity studies of this Fe(II) species with a variety of donor ligands confirmed this lability and protonation at nitrogen yielded a cationic Fe(II) amine-amido complex. Reaction of the latter with the tridentate phosphine, triphos, gave a $16e^-$, low-spin, square-pyramidal Fe(II) complex that proved to be a robust precatalyst that is more active for dehydrogenation of dimethylamine-borane vs. ammonia-borane. Formation of a monohydride catalyst resting state under these reaction conditions is suggestive of a bifunctional activation pathway. Finally, Chapter 6 concludes the outcomes of the iron chemistry of hemilabile SNS ligands and discusses future directions and opportunities to extend these ligand systems to other transition metals.

The knowledge gained by the stoichiometric and catalytic reactivity of iron-SNS complexes presented herein contributes to our understanding of bifunctional catalysis. With the increasing demand for base metal catalysts in chemical industry for efficient and selective synthesis of value-added chemicals, iron SNS complexes could offer economical, active, and selective catalyst precursors.

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Abbreviations

AB	Ammonia-borane
ATR	Attenuated total reflection
a.u.	Atomic unit
BM	Bohr magneton
BTB	1,3-bis(trifluoromethyl)benzene
CH ₃ CN	Acetonitrile
CHCl ₃	Chloroform
CNAr/CNxylyl	2,6-dimethylphenyl isocyanide
ca.	circa, approximately
DCM/CH ₂ Cl ₂	Dichloromethane
DEE	Diethyl ether
DFT	Density functional theory
DMAB	<i>N,N</i> -Dimethylamine-borane
dmpe	1,2-bis(dimethylphosphino)ethane
EI-MS	Electron impact mass spectrometry
e.g.	For example
et al.	And others
ESI-MS	Electrospray ionization mass spectrometry
Eq./Equiv.	Equivalent
h	Hour(s)
HS	High-spin
HOMO	Highest occupied molecular orbital
i.e.	It is
IR	Infrared
L	Ligand
LS	Low-spin
LUMO	Lowest unoccupied molecular orbital
MCD	Magnetic circular dichroism
Me/CH ₃	Methyl
MHz	Megahertz
MLCT	Metal to ligand charge transfer
MPA	Mulliken population analysis
NIR	Near infrared
NMR	Nuclear magnetic resonance
NPA	Natural population analysis
NTf	<i>N</i> -(trifluoromethyl sulfonyl)
ORTEP	Oak Ridge thermal-ellipsoid plot
OTf	Trifluoromethanesulfonate
RB	Round-bottom
RT	Room temperature
TMAB	Trimethylamine-borane
TMS	Trimethylsilyl
THF	Tetrahydrofuran
triphos	Bis(2-diphenylphosphinoethyl)phenylphosphine
UV-Vis	Ultraviolet-visible spectrometry

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List of Contributions

Publications resulting from the chapters of this Thesis:

1. Das, U. K.; Daifuku, S. L.; Gorelsky, S. I.; Korobkov, I.; Neidig, M. L.; Le Roy, J. J.; Murugesu, M.; Baker, R. T. Mononuclear, Dinuclear, and Trinuclear Iron Complexes Featuring a New Monoanionic SNS Thiolate Ligand. *Inorg. Chem.* **2016**, 55, 987-997 (Full article, most read article in January and February 2016).
2. Das, U. K.; Daifuku, S. L.; Iannuzzi, T. E.; Gorelsky, S. I.; Korobkov, I.; Gabidullin, B.; Neidig, M. L.; Baker, R. T. Iron(II) Complexes of a Hemilabile SNS Amido Ligand: Synthesis, Characterization, and Reactivity. *Inorg. Chem.* **2017**, 56, 13766-13776 (Full article).
3. Das, U. K.; Higman, C. S.; Gabidullin, B.; Hein, J. E.; Baker, R. T. Efficient and Selective Iron-Complex-Catalyzed Hydroboration of Aldehydes. *ACS Catal.* **2018**, 8, 1076-1081 (Letter).
4. Das, U. K.; Ghostine, K.; Gabidullin, B.; Baker, R. T. Iron-SNS and -CNS complexes: Synthesis, reactivity and amine-borane dehydrogenation catalysis (manuscript in preparation).

Publication as a contribution to knowledge of science (not included in this Thesis):

1. Das, U. K.; Clement, R.; Johannes, C. W.; Robins, E. G.; Jong, H.; Baker, R. T. One-pot Suzuki-Heck relay to prepare industrially valuable intermediates using the Pd-Cy*Phine catalyst system. *Catal. Sci. Technol.* **2017**, 7, 4599-4603 (Communication, featured on front cover and hot article in 2017).

Presentations:

1. **Uttam K. Das**, R. Clément, R. T. Baker, *A one-pot Suzuki-Heck relay to prepare industrially valuable intermediates using the Pd-Cy*Phine catalyst*, CCRI Technical Seminar Series, Dept. of Chemistry, University of Ottawa, Ottawa, ON, October 2016. (TALK)
2. **Uttam K. Das**, K. Ghostine, B. Gabidullin, R. T. Baker, *Iron SNS complexes as efficient catalysts for selective hydroboration of aldehydes and ammonia borane dehydrogenation*, Inorganic Chemistry Gordon Research Seminar and Conference 2016, University of New England, Maine, USA, July 2016. (POSTER)
3. **Uttam K. Das**, K. Ghostine, B. Gabidullin, R. T. Baker, *Iron SNS complexes as efficient catalysts for selective hydroboration of aldehydes and ammonia borane dehydrogenation*, Boron in the Americas 2016 (BORAM XV), Queen's University, Kingston, ON, July 2016. (POSTER)
4. **Uttam K. Das**, K. Ghostine, B. Gabidullin, R. T. Baker, *Iron SNS complexes as efficient catalysts for selective hydroboration of aldehydes and ammonia borane dehydrogenation*, Canadian Symposium on Catalysis (CANCAT16), University of Ottawa, Ottawa, ON, May 2016. (POSTER, 2nd place graduate poster award)
5. **Uttam K. Das**, I. Korobkov, R. T. Baker, *Iron casting call: Fe(II) NHC complexes featuring hemilabile SNS pincer-type ligands*, 98th Canadian Chemistry Conference and Exhibition (CSC 2015), Ottawa, ON, June 2015. (TALK)

6. **Uttam K. Das**, M. L. Neidig, S. I. Gorelsky, I. Korobkov, R. T. Baker, *Fe(II) amido SNS pincer complexes*, Ottawa-Carleton Chemical Institute Symposium day (OCCI 2014), Carleton University, Ottawa. ON, May 2014. (POSTER)
7. **Uttam K. Das**, M. L. Neidig, S. I. Gorelsky, I. Korobkov, R. T. Baker, *Fe(II) amido SNS pincer complexes*, 97th Canadian Chemistry Conference and Exhibition (CSC 2014), Vancouver, BC, June 2014. (POSTER, 'Honorable Mention' graduate poster award)
8. **Uttam K. Das**, M. L. Neidig, S. I. Gorelsky, I. Korobkov, R. T. Baker, *Fe(II) amido SNS pincer complexes*, Symposium Annuel de Chimie Inorganique du Québec 2014 (SACIQ-2014), La Mauricie National Park, Shawinigan, QC, August 2014. (POSTER, 1st place graduate poster award)
9. **Uttam K. Das**, S. L. Daifuku, S. I. Gorelsky, I. Korobkov, M. L. Neidig, R. Tom Baker, *Nuclearity control at Iron(II) with hemilabile SNS pincer-types ligands: facile C-S bond activation and imine coupling to redox-active N₂S₂ ligand*, Inorganic Discussion Weekend (IDW 2014), University of Montreal, Montreal, QC, November 2014. (TALK)
10. **Uttam K. Das**, S. L. Daifuku, S. I. Gorelsky, I. Korobkov, M. L. Neidig, R. Tom Baker, *New Fe SNS Pincer Complexes as Potential Bifunctional Catalysts*, Ottawa-Carleton Chemical Institute Symposium day (OCCI 2013) University of Ottawa, Ottawa, ON, May 2013. (POSTER)
11. **Uttam K. Das**, S. I. Gorelsky, I. Korobkov, M. L. Neidig, R. Tom Baker, *Hey Iron... Are You Listening? Synthesis and characterization of new Fe SNS pincer complexes as potential bifunctional catalysts*, 96th Canadian Chemistry Conference and Exhibition, CSC 2013, Quebec City, QC, May 2013. (POSTER, awarded poster prize)
12. **Uttam K. Das**, I. Korobkov, R. Tom Baker, *Conversion of Biomass to Fuel: Development of Robust, Water-tolerant Iron Hydrogenation Catalysts*, Summer School on Green Chemistry and Sustainable Energy 2012, Denver, CO, USA, June 2012. (POSTER)
13. **Uttam K. Das**, I. Korobkov, R. Tom Baker, *Conversion of Biomass to High Energy Density Fuel: Towards Development of Robust, Water-tolerant Iron Hydrogenation Catalysts*, Symposium Annuel de Chimie Inorganique du Québec 2012 (SACIQ-2012), La Mauricie National Park, Shawinigan, QC, August 2012. (POSTER, 2nd place graduate poster award)
14. **Uttam K. Das**, I. Korobkov, R. Tom Baker, *Conversion of Biomass to High Energy Density Fuel: Towards Development of Robust, Water-tolerant Iron Hydrogenation Catalysts*, Inorganic Discussion Weekend (IDW 2012), University of Ottawa, Ottawa, ON, November 2012. (POSTER)

Chapter 1. Introduction

1.1 Iron: An Overview

Iron is an essential element (${}_{26}\text{Fe}$: $[\text{Ar}]3d^64s^2$) for plants and animals as well as for human life. It is relatively abundant in the universe, found in the sun and other stars. It is the 4th most abundant element, by weight, in the Earth's crust due to its high production through fusion in dying stars and supernovae. Being the first group 8 transition metal in the periodic table, iron exists in a wide range of oxidation states from $-II$ to $+VI$ of which $+II$ and $+III$ are most common. It shows a variety of electronic spin states with all possible spin quantum number values for a d-block element from 0 (diamagnetic) to 5/2 (5 unpaired electrons).^{1,2}

Iron is a lustrous, silvery-gray metal and oxidizes in air to give hydrated iron oxides, commonly known as rust. The most common ores of iron are *hematite* (Fe_2O_3) and *magnetite* (Fe_3O_4) or *black sands*. Pure iron is very reactive, pyrophoric when dissolved in dilute acids, and corrodes rapidly either in moist air or at elevated temperatures. It exists in four allotropic forms, known as α , γ , δ , and ϵ . Since pure iron is soft, it is usually alloyed with carbon and other elements in varied proportions to make pig iron (often called cast iron), wrought iron and carbon steel.^{1,2}

Being a prehistoric element, the use of iron is known from the ancient world. It is now one of the most widely used metals in the world contributing over 90% of worldwide metal production. With its low cost and high strength, it is indispensable in engineering applications such as the construction of machinery and machine tools, automobiles, the hulls of large ships, and structural components for buildings. Iron catalysts are commonly used in chemical industry to catalyze various chemical processes.²

1.2 Iron Catalysis: ‘*From Rust to a Rising Star*’

With its exponentially growing population, the world is facing a number of technological challenges to overall sustainable growth. The challenges are: (i) to utilize renewable alternatives as we are consuming more of our natural resources, (2) to produce sufficient clean energy, and (3) to

solve the environmental issues connected to our chemical needs.³ As a result, solutions to tackle these tasks are continuously being warranted. As an important principle of ‘green chemistry’, catalysis can be one smart solution since it is a key proven technology to minimise waste and optimise various chemical processes in both academic research as well as industry.^{4,5} The use of abundant and readily accessible catalysts that are preferably not obtained from expensive and/or potentially toxic (transition) metals is the basis of economical and sustainable progress for a chemical industry. In this context, iron is undoubtedly the best candidate since it represents an earth abundant and versatile metal, and its oxides and salts are readily available, inexpensive (price for 1 ounce (28.3 g) palladium: US\$ 1087, platinum: US\$ 1000⁶ whereas one metric ton of iron ore is US\$ 72⁷). In the pharmaceutical industry, iron is considered a “metal with minimum safety concern” (i.e., 1300 ppm residual iron is acceptable in drug substances when compared with ≤ 10 ppm prescribed for most other transition metals)⁵. As a matter of fact, being the 2nd most abundant metal after aluminium, and spanning *formal* oxidation states from $-II$ to $+VI$, iron can be applied in both reductive and oxidative processes. The affinity of iron cations to bind strongly with many inexpensive N- or O- and S-based ligands as well as with N-heterocyclic carbenes and similar donors can save additional cost, labor and time in lieu of using expensive phosphines and related ligands.⁵ Iron can be found in a number of metalloenzymes that play prominent roles in metabolism. In addition, these iron-dependent enzymes show redox chemistry which allows noble metal-type two electron processes.⁸ With landmark contributions by heterogeneous iron catalysts in the Haber-Bosch and Fischer-Tropsch processes, iron catalysis has also gained massive importance in homogeneous catalysis in recent years.^{4,9-11} While high-valent iron catalysts have proven to be active in many oxidation reactions,⁴ low- and sub-zero valent iron complexes show their activity and selectivity in small molecule and H-E bond (E = H, O, N, S, Si, B, C) activation processes^{10,12-16} and coupling reactions.^{11,17} Moreover, bifunctional iron catalysis has lately seen exciting applications in the area of asymmetric hydrogenation and transfer hydrogenation of polar bonds, achieving precious metal catalyst type activity under mild conditions.^{15,18} Several milestones of iron

catalysis are highlighted in Figure 1. Nonetheless, iron catalysis, along with organometallic and coordination chemistry of iron, still remains a wide-open field of research with enormous opportunities for discovery and innovation.

1884	Fenton oxidation chemistry published	1971	Further investigations on iron-catalyzed cross-coupling reactions by Kochi
1910	Haber-Bosch process patented	1979	Iron porphyrin complexes catalyze epoxidation reactions
1925	Fischer-Tropsch process developed	1983	Enantioselective epoxidation catalysis with chiral iron-porphyrin complexes
1944	First iron-catalyzed cross-coupling reported	1998	Efficient iron catalysts for ethylene polymerization
1951	First organometallic compound ferrocene prepared	2000	Research in iron-catalyzed cross-coupling reactions and enantioselective transfer hydrogenations
1953	Reppe carbonylation of ethylene by a homogeneous iron catalyst	2010	Rapid development of iron catalysis in all areas of organic synthesis
1959	Structure of Hemoglobin determined	2013	Bifunctional iron-catalyzed asymmetric transfer hydrogenations and direct hydrogenations developed

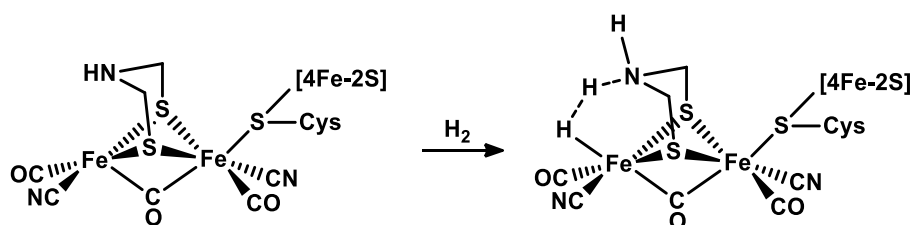
Figure 1.1 Historical timeline of iron catalysis⁹

1.3 Bifunctional Ligands

The design and use of new ligands for developing efficient and sustainable metal catalysts are ubiquitous parts of chemical research. In homogeneous transition metal catalysis, the neighbouring ligand scaffold plays a key role with the metal in executing transformations such as small molecule activation, functionalization and selective conversion of challenging substrates. Some key properties of modern ligands include: 1) strong chelation ability to metals, 2) tunability of donor atoms, 3) inclusion of strong field donor atoms such as P,C,S to favor low-spin complexes, 4) hemilability to allow substrate activation via reversible dissociation of one donor atom, and 5) redox-activity enabling donation or accepting of electrons, thus avoiding a change of metal oxidation state.¹⁹ In this context, bifunctional ligands, comprising the above described properties, have emerged as an important class of ligands in chemical synthesis and in catalysis. Iron and other transition metal complexes containing multidentate bifunctional ligands have recently been shown to activate small molecules and catalyze a number of chemical transformations^{15,20-23} with activity and selectivity typical of more well-studied precious metals.

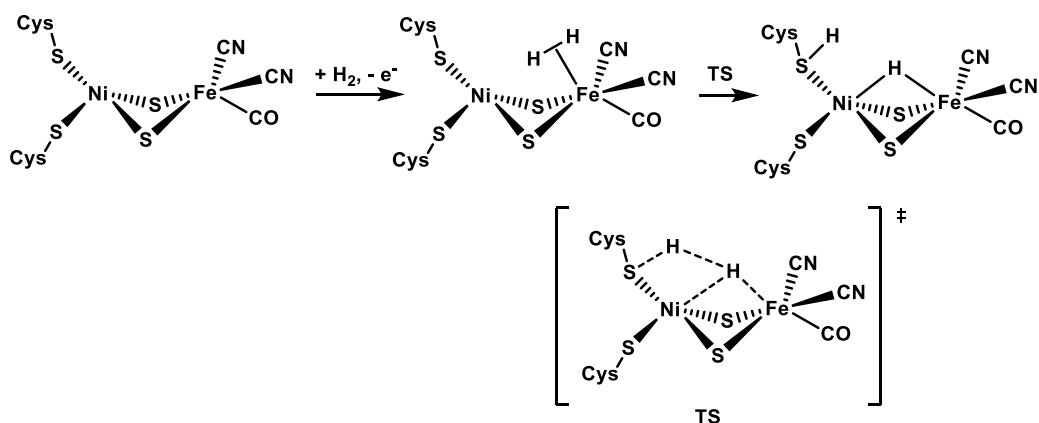
Nature utilizes perfect examples of *bifunctional activation* in enzymatic catalytic processes. In these biological systems, the modes of action of enzymes are often based on cooperative effects induced by the ligand scaffolds around the metal active site. For instance, the enzyme [FeFe]-hydrogenase catalyzes reversible formation of dihydrogen from electrons and protons ($2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$) at its active site that contains a thiolate-bridged dinuclear iron unit (Scheme 1.1).²⁴⁻²⁷ Both experimental and theoretical studies have demonstrated that the pendant amine motif of the bridging thiolate ligand is essential for heterolytic H_2 activation.²⁸⁻³¹

Scheme 1.1 H_2 Activation at [FeFe]-Hydrogenase



A similar type of bifunctional reactivity is shown by the heterobimetallic [NiFe]-hydrogenase enzyme which is capable of oxidizing H_2 to H^+ . It has been proposed that the Ni and Fe-bound thiolates are directly involved in the H_2 splitting step (Scheme 1.2).^{32,33}

Scheme 1.2 H_2 Activation at [NiFe]-Hydrogenase



Many metalloenzymes use such multimetallic cooperative effects for selective transformations including nonheme iron enzymes (e.g., nitrile hydratases, superoxide reductases, and cysteine dioxygenases), copper-based oxidases and oxygenases, dinuclear nickel-containing systems, and

many mixed-metal biocatalysts. Some of these enzymatic processes also involve multi-electron redox events and proton-coupled electron-transfer phenomena.²⁰ Subsequently, numerous mono- and multinuclear iron and other metal complexes have been developed as synthetic enzyme mimics as well as potential electrocatalysts for proton reduction and hydrogen evolution.³⁴⁻³⁷

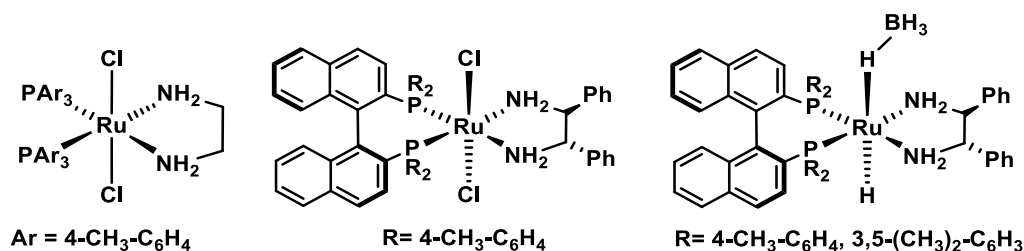
1.3.1 Nitrogen and Phosphorus-Based Bifunctional Ligands

Metal-coordinated multidentate N- and P-donor ligands are the most thoroughly studied bifunctional systems to date in homogeneous catalysis. The pioneering work by Fryzuk et al. on the first example of heterolytic splitting of H₂ by Rh and Ir amido phosphine complexes^{38,39} created a firm basis for the development of metal-ligand bifunctional reactivity. Shvo et al. discovered a bifunctional Ru catalyst supported by a tetraphenyl-substituted hydroxycyclopentadienyl ligand, which heterolytically splits H₂, and serves as a stable precatalyst for both hydrogenation and dehydrogenation catalysis.^{40,41}

1.3.1.1 Bidentate Ligands

Noyori disclosed benchmark Ru catalysts containing diamine and bisphosphine ligands that enabled a conceptually new enantioselective hydrogenation process with unprecedented activity in the reduction of prochiral ketones and imines.^{42,43} For instance, Noyori's Ru complex, [RuCl₂(PPh₃)₃] in combination with ethylenediamine and KOH, was found to be an effective catalyst for acetophenone hydrogenation.^{44,45} Several highly active Noyori-type Ru bifunctional catalysts for enantioselective ketone hydrogenation are depicted in Scheme 1.3.

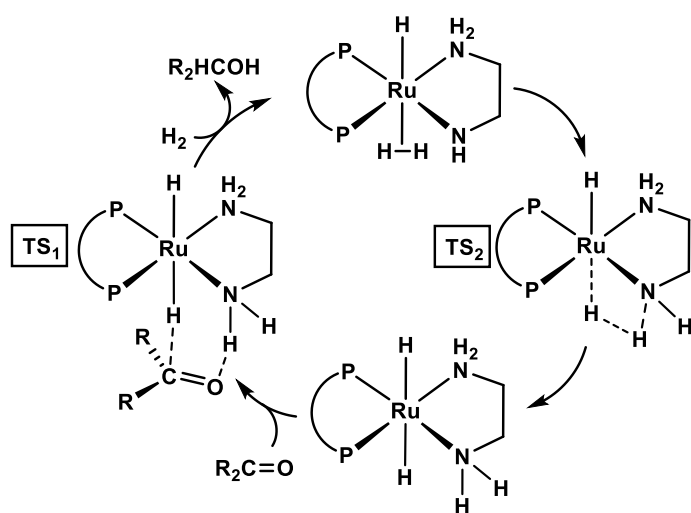
Scheme 1.3 Bisphosphine Diamine Bifunctional Ru Catalysts for Ketone Hydrogenation²¹



Usually a primary or secondary amine group is present in the ligand scaffold to accelerate the hydrogenation. The high catalyst performance observed with Noyori's Ru catalyst in the

asymmetric direct hydrogenation of ketones to alcohols reveals the importance of the “NH effect” in the ligand structure, while the absence of such “NH effect” (*i.e.*, N-Me analogs such as TMEDA) is found to be inefficient under analogous conditions.²¹ The classical Noyori mechanism of asymmetric ketone hydrogenation is proposed to occur in an outer-sphere manner via a six-member pericyclic transition state (TS₁, Scheme 1.4) in which the proton from the nitrogen undergoes hydrogen-bonding to the oxygen of the ketone and orients it for attack by the metal hydride. However, comprehensive mechanistic investigations with both experimental and theoretical supports in recent years by Dub, Gordon and co-workers have shown that the nature of proton and hydride transfer is likely to be a two-step process as opposed to a concerted one and the exact role of the NH group in metal-ligand cooperativity has been revised.^{43,46-48}

Scheme 1.4 Catalytic Cycle for the Hydrogenation of Ketones under Basic Conditions⁴⁶

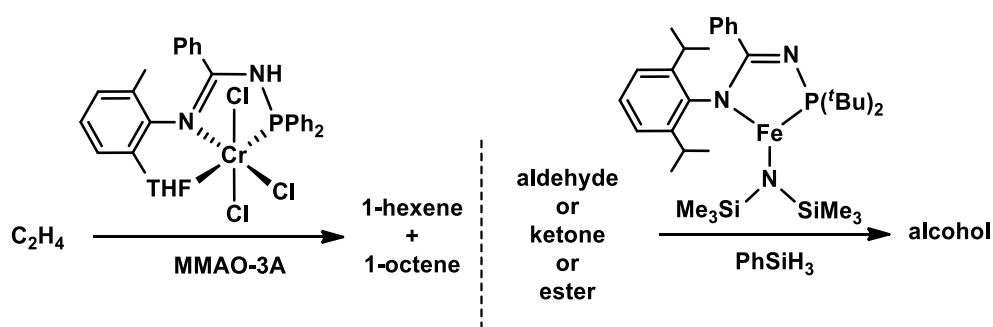


Inspired by the importance of cooperative amino/amido ligands in bifunctional Ru catalysis, a large variety of transition metal complexes have been designed to incorporate this “NH effect” in the ligand scaffolds. For example, Noyori, Ikariya et al. developed Ru-arene complexes, $[\{\text{RuCl}_2(\eta^6\text{-arene})\}_2]$ which catalyze transfer hydrogenation of ketones in the presence of ethanolamine containing at least one primary or secondary amine (“NH effect”).⁴⁹ Similar P- and

N-donor bifunctional ligands have been reported by Fagnou,⁵⁰ Schneider,^{51,52} and Baker^{53,54} for ammonia-borane dehydrogenation catalysis.

N-phosphinoamidine has been introduced as another modular P,N-ligand system which provides more steric and electronic flexibility compared to bisphosphine and diamine ligands. Both neutral and anionic forms of this ligand were complexed to Cr, Fe, and Co. A Cr(III) complex with *N*-phosphinoamidine ligands was found to be a highly active precatalyst for ethylene tri-/tetramerization⁵⁵ while a low-coordinate Fe(II) (*N*-phosphinoamidinate) complex is an efficient precatalyst for room temperature hydrosilylation of aldehydes, ketones, and esters to alcohols, at remarkably low catalyst loading (Scheme 1.5).⁵⁶

Scheme 1.5 (*N*-Phosphinoamidine)CrCl₃(THF) and (*N*-Phosphinoamidinate)Fe[N(TMS)₂] Complexes Utilized in Catalysis^{55,56}

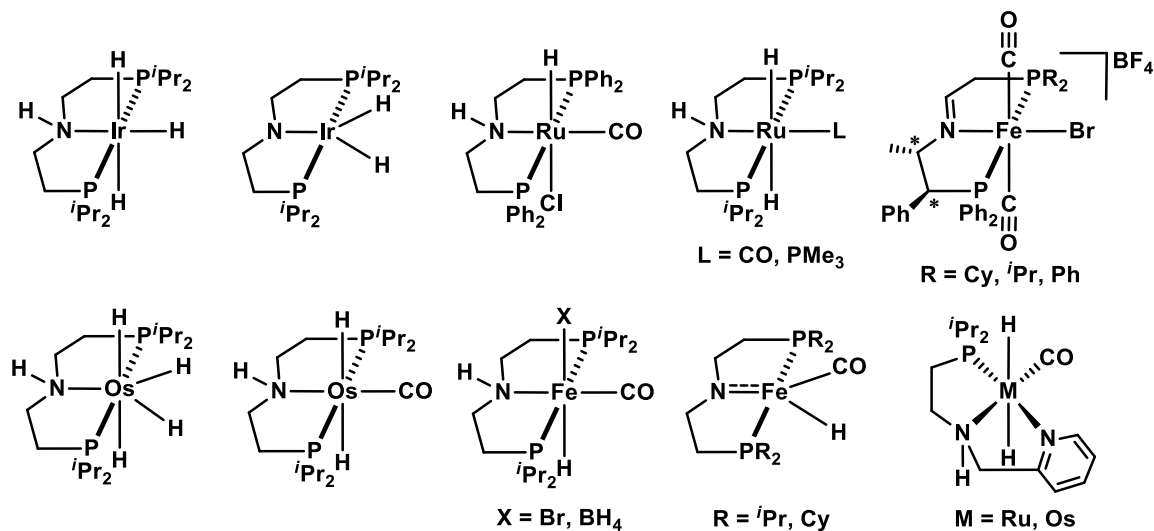


1.3.1.2 Tridentate Ligands

The aliphatic tridentate “pincer” ligands with a central amide/amine/imine N-donor and terminal P-/N-donors are the most extensively studied bifunctional ligand systems in homogeneous catalysis since their inception in the 1970’s by Shaw.⁵⁷ A plethora of aliphatic PNP and PNN pincer ligands have been designed and many well-defined transition metal complexes containing these ligands have been reported (Scheme 1.6).²¹ These pincer complexes have been successfully exploited in synthesis, bond activation, and catalytic processes including direct hydrogenation and transfer hydrogenation of ketones and imines, hydrogenation of CO₂ to formate, hydrogenation of esters and amides, and dehydrogenation of alcohols and amine-boranes. Experimental and computational

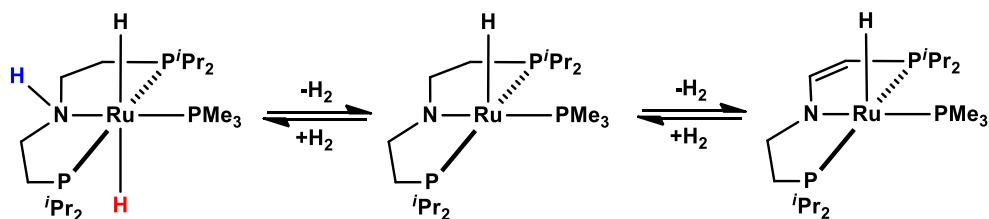
studies suggest that metal-ligand cooperativity through a metal–amide/metal–amine bond plays an important role in these reactions.

Scheme 1.6 Bifunctional Complexes with Aliphatic PNP and PNN Pincer Ligands^{21,58}



In particular, Schneider et al. reported Ru(II) complexes of aliphatic PNP amido chelate ligands, which undergo reversible hydrogenation/dehydrogenation reactions both at the amide nitrogen and the ethylene backbone (i.e., bifunctional behaviour of the PNP amido ligand, Scheme 1.7).⁵⁹

Scheme 1.7 Hydrogenation/Dehydrogenation Equilibria Between Ru(II) Amino, Amido, and Eneamido Complex⁵⁹

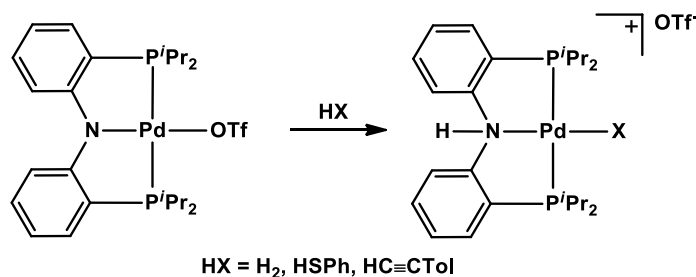


The Ru(II) PNP amido complex demonstrated unprecedented activity and turnover numbers in the catalytic dehydrogenation of ammonia-borane under mild conditions with low catalyst loadings. Notably, the influence of hydrogen bonding of borane-amine adducts to the amine functional group (“NH effect”) of the PNP pincer ligand makes $\text{Ru}(\text{H})_2(\text{PN}^{\text{H}}\text{P})(\text{PMe}_3)$ a better catalyst than

$\text{Ru}(\text{H})_2(\text{PN}^{\text{Me}}\text{P})(\text{PMe}_3)$ as demonstrated by thorough mechanistic studies.⁵² Morris et al. recently reported chiral cationic Fe(II) complexes supported by unsymmetrical aliphatic PNP pincer ligands which were found to be active for asymmetric hydrogenation of ketones and imines under mild conditions. The chiral Fe(II) precatalysts were activated by reaction with hydride reagent and alcohol to produce Fe(II) hydride amine catalysts with the bifunctional HN-FeH group known to efficiently reduce polar double bonds.⁵⁸

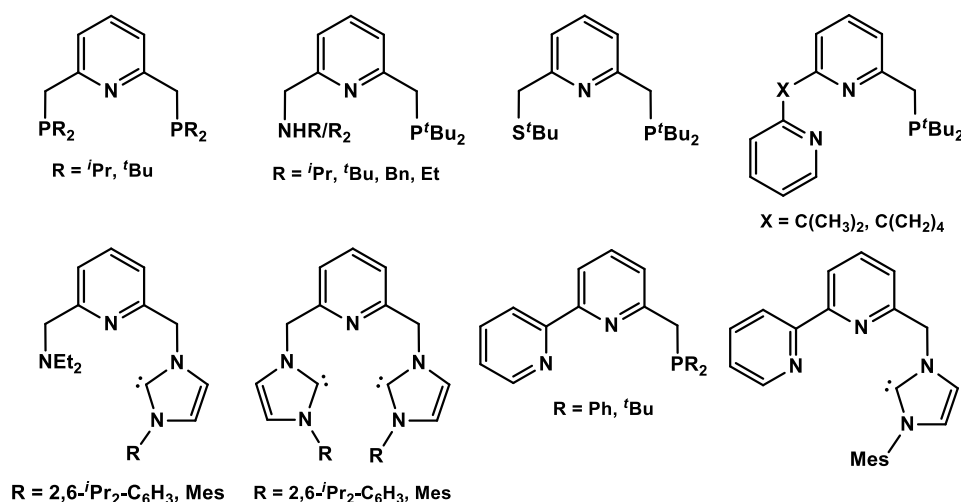
Aside from aliphatic PNP ligands, bifunctional aryl-based PNP ligands are also known. For example, the Ozerov group reported a Pd complex bearing diarylamide PNP ligand, which heterolytically activates H-X bonds ($\text{HX} = \text{H}_2$, terminal alkyne, thiol; Scheme 1.8). The H_2 activation by this complex occurs through initial coordination of H_2 to the Pd center to give $[(\text{PNP})\text{Pd}(\text{H}_2)]^+$ followed by an intermolecular proton transfer from coordinated H_2 to the amide nitrogen by means of an external Brønsted base (triflate or solvent).⁶⁰

Scheme 1.8 H-X Bond Activation by the Pd Diarylamide Complex⁶⁰



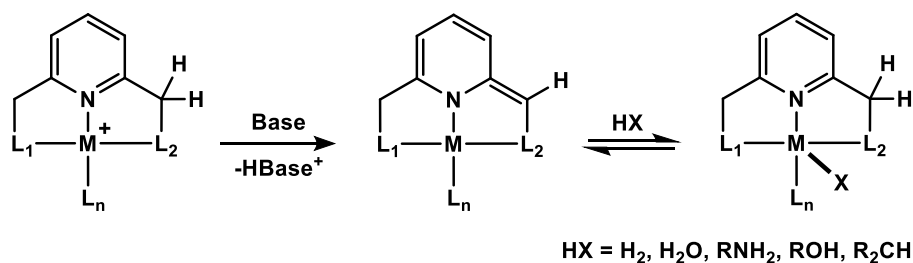
Substituted lutidine- and 2-picoline-based neutral, aromatic tridentate pincer ligands are another class of bifunctional ligands which have become popular in the last decades, originally developed and extensively studied by the Milstein group and others (Scheme 1.9).^{21,23,61,62} These ligands contain a central pyridine unit with one or two CH_2 groups in the ortho- position of pyridine, and both arms are occupied by heteroatom donor groups (e.g., P-, N-, S-, and C-functionalities).

Scheme 1.9 Lutidine- and Picoline-Based Pincer Ligands²¹



A unique feature of this ligand is that deprotonation of a pyridinyl-methylene proton by strong bases can lead to dearomatization of the central pyridine ring with formation of an exocyclic double bond. The dearomatized complex can then activate a chemical bond (H-Y, where Y = H, OR, NR₂, C etc.) by cooperation between the metal and the ligand, thereby regaining aromatization (Scheme 1.10).^{21,61} The overall process does not involve a change in the metal oxidation state.

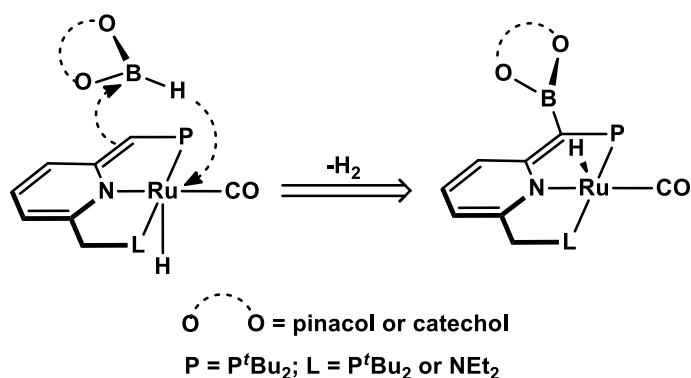
Scheme 1.10 Aromatization-De aromatization and Bond Activation by Lutidine-Based Pincer Complex²¹



A variety of transition metal pincer complexes of lutidine- and picoline-derived ligands have been reported and many of these complexes have shown diverse reactivity, activated many small molecules, and catalyzed challenging chemical reactions with high activities under relatively mild conditions.²¹ Metal-ligand cooperation by means of aromatization-dearomatization of the ligand plays a key role in these processes. For instance, Milstein et al. demonstrated the activation of a

borane B-H bond across the metal center and the ligand in a dehydrogenative manner by reaction of simple boranes with dearomatized ruthenium pincer complexes based on lutidine-based PNP or PNN ligands (Scheme 1.11). The isolated Ru(II) dearomatized boryl pincer complex acts as a potential catalyst for dehydrogenative B-B and B-C coupling reactions.⁶³

Scheme 1.11 B-H Bond Cleavage by Dearomatized Ru Pincer Complexes⁶³



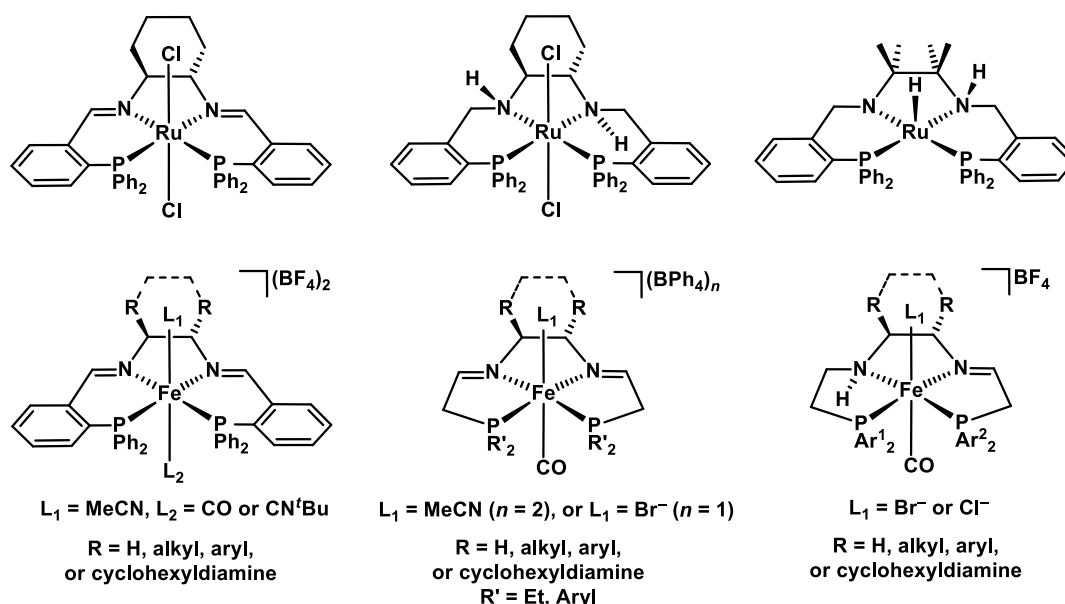
Similar to the above described lutidine-based ligands, pincer ligands based on 2-aminopyridine, 2,6-diaminopyridine and diaminosubstituted N-heterocycles have also been reported.²¹ These ligands contain an NH spacer, which is generally more acidic than the CH₂ group of the lutidine-based pincer ligands. Therefore, the deprotonation of the NH moiety is relatively easier as is dearomatization of the pyridine ring. The deprotonated species can then participate in a range of bond activation processes through metal-ligand cooperation by reversible aromatization/dearomatization of the 2-aminopyridine system.

1.3.1.3 Tetradentate Ligands

The tetradentate imino- and aminophosphine PNNP ligands have received much attention as chiral bifunctional ligand platforms for asymmetric hydrogenation (AH) and asymmetric transfer hydrogenation (ATH) catalysis of ketone and imines.^{15,64} These two catalytic reduction processes provide enantiopure alcohols and imines which are highly valuable precursors for pharmaceutical, fragrance, agrochemical and relevant fine chemical industries.^{18,65} The tetradentate ligands can be prepared by Schiff base condensation of phosphine aldehydes and amines. The commercially

available *ortho*-diphenylphosphinobenzaldehyde and dialkyl/diaryl-phosphinoacetaldehyde have both become popular as ligand synthons in combination with appropriate enantiopure amines to generate chiral tridentate, and tetradentate ligands. Some of the previously reported Ru and Fe bifunctional catalysts containing PNNP tetradentate ligands are depicted in Scheme 1.12.⁶⁴

Scheme 1.12 Bifunctional Ru and Fe Precatalysts with Tetradentate Ligands for Asymmetric Transfer Hydrogenation and Asymmetric Hydrogenation Catalysis⁶⁴



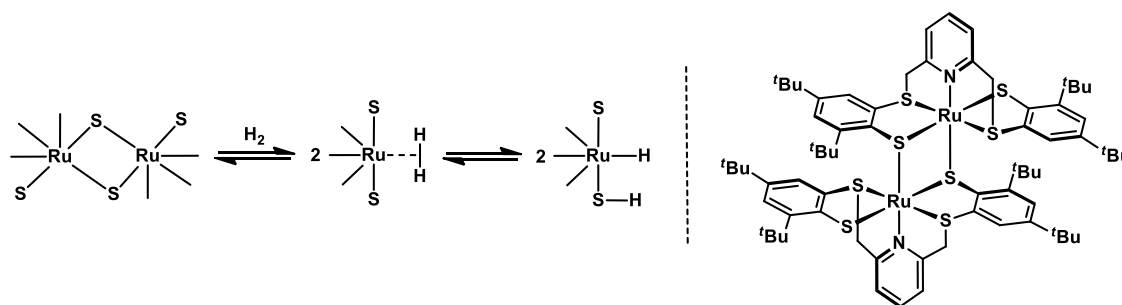
Gao, Ikariya, and Noyori disclosed early examples of Ru bifunctional systems based on tetradentate PNNP ligands. They synthesized (*S,S*)-*trans*-RuCl₂(PNNP) and (*S,S*)-*trans*-RuCl₂(PNHNHP) complexes as active precatalysts for the asymmetric transfer hydrogenation (ATH) of ketones in basic isopropanol.⁶⁴ Later, the Morris group developed Ru(II)-hydrido amido complex using a similar PNNP ligand scaffold for efficient asymmetric ketone hydrogenation. In 2008, the Morris group first discovered monocarbonyl iron complexes with tetradentate PNNP ligands which showed good activity for ATH, when treated with base in isopropanol.⁶⁶ With this initial discovery of the iron-based homogeneous system, Morris et al. extensively studied iron-catalyzed ATH and AH processes and successively uncovered more active and enantioselective iron catalysts. The most efficient Fe(II) complexes which contain the amine(imine)diphosphine

PN^HNP ligand (Scheme 1.12) catalyze both the AH and ATH reactions under mild conditions. Both of these reactions proceed through the formation of an iron hydride intermediate by reaction of the amido(ene-amido) Fe(II) complex with either dihydrogen or 2-propanol.^{15,64}

1.3.2 Sulfur-Based Bifunctional Ligands

Sulfur-containing bifunctional ligands are of great interest in biomimetic studies, metalloenzyme catalysis, as well as fundamental metal-ligand cooperative reactivity and catalysis.^{22,37,67,68} These sulfur-derived ligands usually contain only thiolate donors or mixed donors including thiolate, thioether, amine, phosphine, aryl/alkoxo groups. The thiolate group may behave as both σ - and π -donor and can serve as terminal or bridging ligands. Additionally, metal-bound thiolates have reactive lone-pair electrons available for bifunctional substrate activation. For example, Sellmann et al. showed the heterolytic cleavage of H₂ by a thiolate-bridged dinuclear Ru complex containing a pentadentate mixed N, S-donor ligand. The H₂ activation is proposed to occur via a transient η^2 -H₂ species which undergoes heterolytic cleavage by the concerted action of Lewis acidic Ru and Brønsted basic sulfur centers to give the protonated thiolate hydride complex (Scheme 1.13).⁶⁹

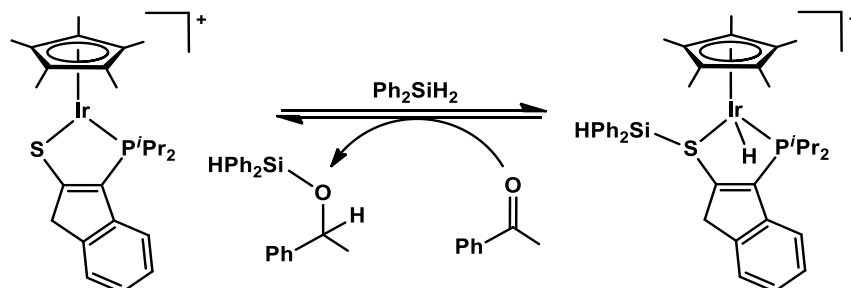
Scheme 1.13 Heterolytic H₂ Cleavage by Dinuclear Ru(II) Thiolate Complex⁶⁹



In seminal work to uncover unusual modes of metal-ligand cooperative substrate activation, the Stradiotto group demonstrated reversible activation of the H-Si bond of organosilanes by a coordinatively unsaturated, cationic Ir complex, [Cp*Ir(κ^2 -P,S)]⁺ B(C₆F₅)₄⁻ supported by bidentate LX-type indene ligand (Scheme 1.14). Although the isolated Ir hydride species is capable of

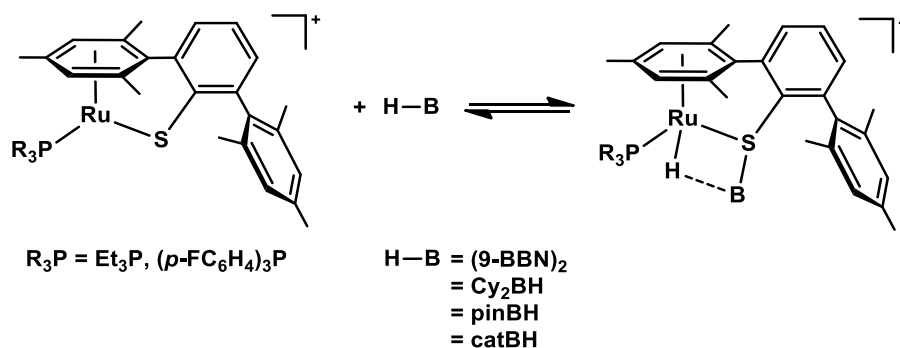
transferring the bound fragments of the activated silane to acetophenone in a stoichiometric fashion, it was not found to be effective as a catalyst for hydrosilylation of ketones.⁷⁰

Scheme 1.14 Si–H Bond Activation by a Thiolate-Coordinated Ir Complex⁷⁰



Recent work by Oestreich and co-workers has shown that metal-ligand cooperative activation of the B–H bond is possible by a coordinatively unsaturated cationic Ru(II) thiolate complex bearing a tethered thiolate ligand (Scheme 1.15).²² The group has characterized stable adducts formed by the heterolytic cleavage of the B–H bond of boranes using NMR spectroscopy as well as by single crystal X-ray diffraction. They have also reported that this unsaturated Ru thiolate complex served as an effective catalyst for the electrophilic borylation and C–H silylation of indoles, and hydrodefluorination of C(sp³)-F bonds.⁷¹

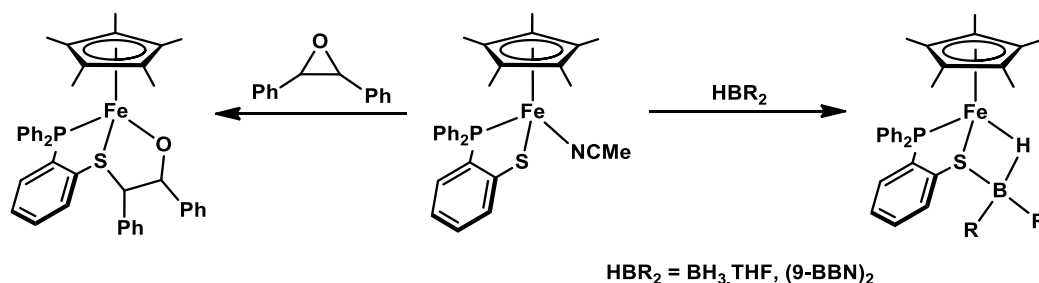
Scheme 1.15 B–H Bond Activation by a Tethered Ru(II) Thiolate Complex⁷²



Most recently, Liao and Wang et al. developed an Fe(II) thiolate complex, Cp*Fe(κ^2 -P,S)(NCMe), containing an arylphosphine-thiolate chelating ligand, which acts as an efficient catalyst for regioselective hydroboration of aryl epoxides by pinacolborane (HBpin). This Fe(II) species activates epoxides rather than the B–H bond of HBpin through the iron-thiolate

cooperation. The resulting ferrous–alkoxide compounds are found to be the key intermediates in this catalytic process (Scheme 1.16).⁷³ The ferrous–alkoxide intermediate was isolated from the reaction of the Fe(II) species with *trans*-2,3-diphenyloxirane and characterized by X-ray crystallography. Although no reaction was observed with HBpin, this Fe(II) thiolate species activates more Lewis acidic boranes such as $\text{H}_3\text{B}\cdot\text{THF}$ and 9-H-BBN (BBN = borabicyclononane). The resulting iron–borane adducts, that are relevant in the context of this *Thesis*, feature an agostic $\text{Fe}\cdots\text{H}-\text{B}$ interaction.

Scheme 1.16 B–H Bond and Epoxide Activation by a Cooperative Fe(II) Thiolate Complex⁷³



Apart from the above described sulfur-based cooperative ligands, a handful of sulfur-containing amido and thiolate ligands are reported in the literature, many of which are summarized in chapters 2 and 6 of this *Thesis*. In addition, relevant sulfur-derived ligands featuring hemilabile and redox non-innocent behavior are described below.

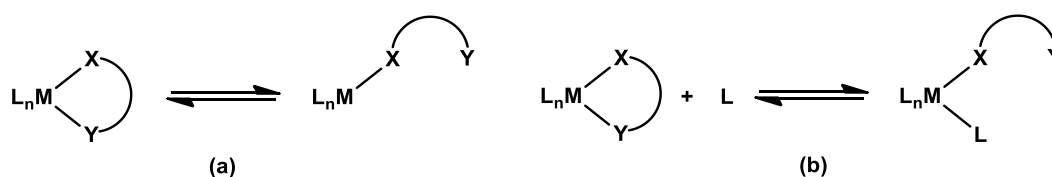
1.4 Hemilabile Ligands

The transition metal coordination chemistry of *hemilabile* ligands plays a pivotal role in homogeneous catalysis. The synthesis of metal complexes using potential ligand hemilability is a useful approach to induce both stoichiometric and catalytic reactions and create new ligand systems for homogeneous catalysis and functional materials.^{74,75} Metal complexes with hemilabile ligands have been found to be catalytically active in a range of reactions including hydrogenation, carbonylation, hydroformylation of olefins and epoxides, allylation, epoxidation, olefin metathesis and copolymerization, and ring-opening metathesis polymerization (ROMP).⁷⁴ Ligand hemilability

is also important in self-assembly,⁷⁶ switching processes,^{77,78} molecular sensing,⁷⁹ and for the function of many metalloenzymes.⁸⁰

In transition metal complexes, multidentate hybrid ligands bearing labile and/or pendant donor groups typically display hemilabile character. Based on the different strengths of the metal-heteroatom bonds, the metal complex may undergo a ring-opening process by the preferential cleavage of the weakest coordinate bond. When the weak donor is recoordinates, the process becomes reversible (Scheme 1.17a).⁷⁵ This type of reversible de-coordination behavior exhibited by the weakly bonding moiety is referred to as hemilability and the overall ligand can therefore be named as ‘half labile’ or hemilabile.⁸¹

Scheme 1.17 (a) Hemilability of a Bifunctional Ligand X-Y, (b) Substitution Reaction in the Complex with a Hemilabile Ligand⁷⁵

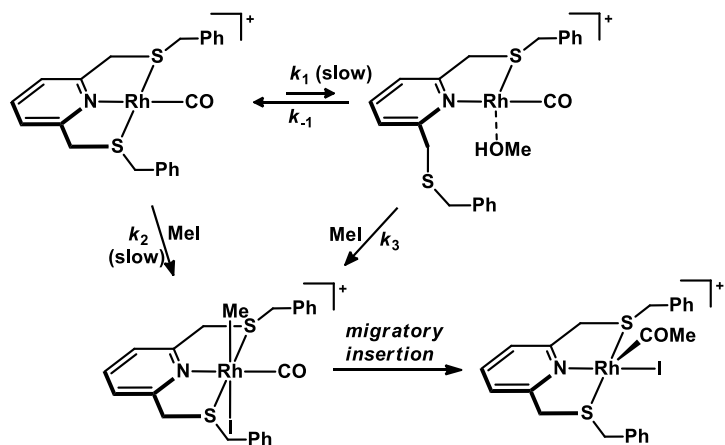


Two significant features often exhibited by hemilabile bifunctional ligands are (1) fluxional behavior arising from the mixed bonding characteristics by intramolecular ligand exchange processes (Scheme 1.17b), and (2) the facility to undergo ligand displacement reactions with external donors, in which a monodentate ligand, a small molecule, or an organic substrate coordinates to the metal ion via the arm opened by the substitutionally labile group.⁷⁵ The latter feature is particularly relevant to this *thesis*. With its first inception by Jeffrey and Rauchfuss from their early reports of hemilability shown by phosphine-amine and phosphine-ether type bifunctional ligands, transition metal complexes of a large variety of hemilabile ligands have been elegantly studied and previously reported.^{74,75}

One of the promising labile donors is the thioether group which has been implicated as a potential hemilabile ligand component in synthesis and catalysis. The thioether S atom usually has a low affinity to coordinate to transition metals; however, under suitable conditions, thioether can

bind quite efficiently since it can also behave as a π -accepting ligand. The hemilability of thioether groups has previously been demonstrated in connection with N-heterocyclic carbenes,⁸² functionalized phosphines,^{83,84} and mixed donors chelate ligands.⁸⁵⁻⁸⁷ For instance, Bassetti et al. reported the hemilability of a thiobenzyl group through a kinetic study of the oxidative addition of methyl iodide to the cationic Rh(I) complex bearing lutidine-derived tridentate S^RNS^R ligand (Scheme 1.18).⁸⁸ The reaction of four-coordinate Rh(I) species with MeI proceeds via reversible decooordination of one thiobenzyl arm generating an equilibrium between the substrate and a transient three-coordinate 14e species which can be stabilized by solvent. This unstable species either recoordinates the pendant arm or rapidly reacts with MeI to form the Rh(III) methyl complex and CO migratory insertion yields the corresponding acetyl complex. The dissociative process of the thiobenzyl group is the rate-determining step (k_1) of this oxidative addition reaction.

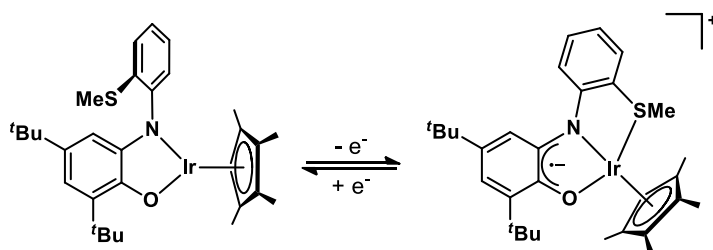
Scheme 1.18 Reaction of Cationic Rh(I) Carbonyl Complex with MeI⁸⁸



In exemplary work highlighting hemilability of the thioether group, Kaim and co-workers reported that while the four-coordinate cationic Cu(I) complex with a potentially tridentate NNS^{Me} ligand does not display any bonding interaction between the thioether ligand and the metal, its corresponding oxidized Cu(II) analogue binds to a thiomethyl group of one of the two NNS^{Me} ligands as evidenced by X-ray crystallography and electrochemical studies.⁸⁹ In contrast to this metal-centered oxidation, reversible, intramolecular, single-electron oxidative addition of a neutral

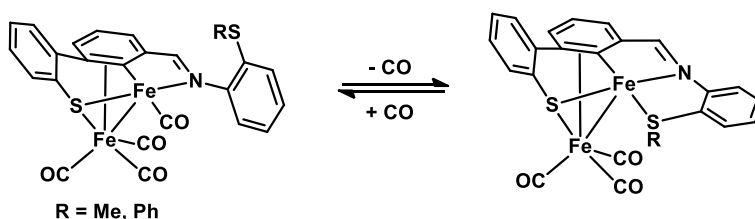
Ir(III) complex was reported by the Kaim group as a ligand-based oxidation. In this case, a non-innocent ligand L (L = 4,6-di-*tert*-butyl-2-(2-methylthio) amidophenolate with a thioether group as potential hemilabile moiety induced the oxidative addition of the [IrCp*L] complex via structural rearrangement (i.e., catecholato $\rightarrow$ semiquinonato transition coupled with reversible S $\rightarrow$ Ir coordination) which led to a cationic Ir(III) species (Scheme 1.19).⁹⁰ Recently, the same authors reported similar ligand-induced oxidative addition reactions with Ru- and Os-arene complexes.⁸⁷

Scheme 1.19 Intramolecular Oxidative Addition Involving a Hemilabile Non-Innocent Ligand⁹⁰



Most recently, Kinoshita et al. demonstrated hemilability of a thioether group by reversible CO/thioether substitution in dinuclear Fe(II) carbonyl complexes using an NCS pincer ligand with a pendant thioether group. The hemilabile thioether moiety binds to iron reversibly in the complex by replacing the carbonyl ligand, allowing for interconversion between the tridentate NCS ligand and tetradentate SNCS ligand. The bonding between the thioether and the iron remains stable during the reaction of the dinuclear Fe(II) carbonyl species with Lewis bases such as dimethylphenylphosphine and 4-(dimethylamino)pyridine, which afforded mononuclear and thiolate-bridged dinuclear complexes, respectively (Scheme 1.20).⁹¹

Scheme 1.20 Reactions of Diiron Carbonyl Complexes Containing an NCS Pincer Ligand with a Hemilabile Thioether Arm⁹¹

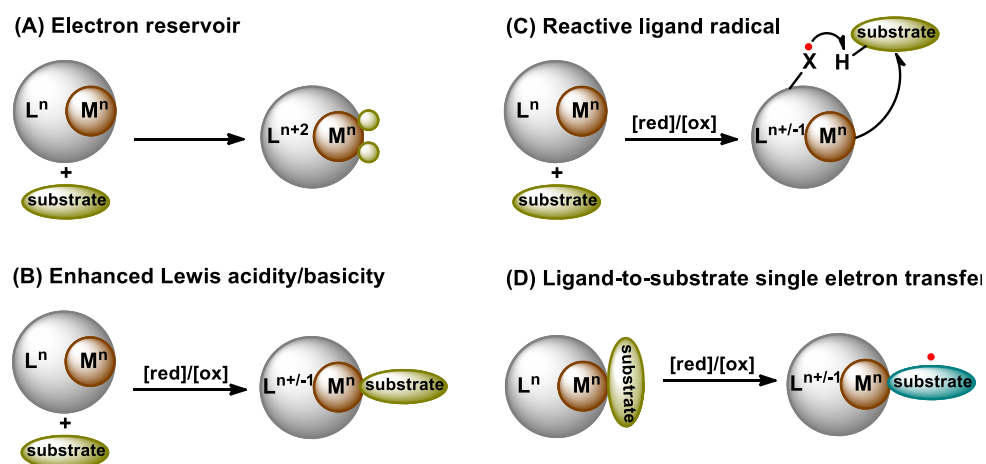


1.5 Redox-Active Ligands

Redox-active or ‘non-innocent’ ligands have been recognized as a distinctive class of ligands in coordination chemistry. The application of redox-active ligands in synthetic chemistry as well as in catalysis to induce new reactivity of transition and main group metal complexes is a flourishing field of research.^{8,92-95} These ligands can be oxidized or reduced by one or more electrons and thus can serve as electron reservoirs to allow multi-electron transformations that are otherwise reluctant to proceed. Furthermore, these ligands have more energetically accessible levels that allow redox reactions by altering their charge states. The higher energy HOMO (or alternatively a low-lying LUMO) of these ligands as compared to those of traditional innocent ligands facilitates these redox events. This specificity can expand the scope of the redox-active ligands to be used with base metals (one-electron redox changes occur more frequently), and are thus able to mimic noble metals (which typically favor two electron redox changes) in catalysis.⁹⁵

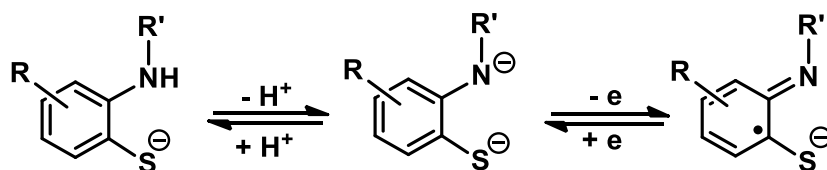
The true pioneer of redox-active ligands to be used with metals is Nature. Redox-active ligands can be found in the active sites of many metalloenzymes that work in synergy with a metal ion, enabling multi-electron reactions to occur near thermodynamic potential, avoiding undesirable and deleterious radical reactions.⁹⁴ Four different ways the redox-active ligands can affect (transition) metal reactivity include (A) acting as an electron reservoir, (B) enhancing the Lewis acidity/basicity of the metal, (C) generating reactive ligand-centered radicals, and (D) undergoing ligand-to-substrate single electron transfer (Scheme 1.21).⁹⁵

Scheme 1.21 Reactivity of Transition Metal Complex with Substrate Affected by Redox-Active Ligands⁹⁵

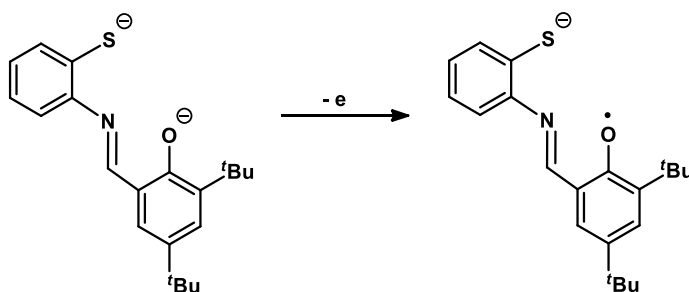


Introduced by Jørgensen in 1966, redox non-innocent ligands were mainly considered as spectroscopic curiosities in early days but lately redox-active ligands have emerged as synthetically useful and attractive ligand scaffolds in coordination and organometallic chemistry and catalysis.⁹² In this light, various classes of redox-active ligands have been developed, investigated and reviewed.^{8,92,93,95} Some well-known examples include quinones, dithiolenes, α -diimines, bis(imino)pyridines, diphenylamines, and polypyridines.

Sulfur-containing redox non-innocent ligands have received much attention in recent years due to their resemblance to numerous biological systems and their potential to display intriguing redox activity by coordinating to metals, and serving in catalytic reactions.^{86,87,89,96-101} Although sulfur is less electronegative than oxygen, it can retain significant spin density which enables these ligands to exhibit their redox activity. A vast array of polydentate [N,S]- or [N,S,E]-type redox-active ligands (E = O, Se) have been developed and their rich redox chemistry has previously been reported.^{86,87,96-99} For example, Wieghardt et al. developed diverse coordination chemistry of iron-containing redox-active *o*-aminothiophenolate ligands that can exist in different protonation levels (amine vs. imine) and in three different redox states (Scheme 1.22).⁹⁸

Scheme 1.22 Redox and Protonation Levels for Aminobenzenethiolate Ligands⁹⁸


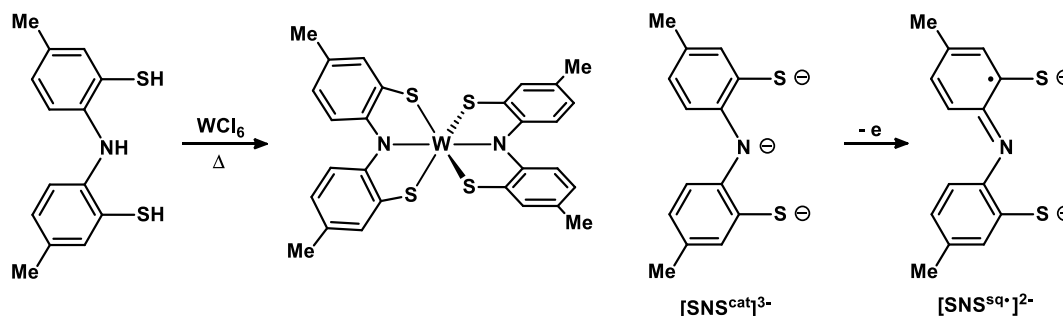
The redox non-innocence of the Schiff base ligand has also been reported by Wieghardt and co-workers. A tridentate [N,O,S] donor ligand (H_2L), reacts with $FeBr_2$ in presence of trimethylamine to afford a paramagnetic mononuclear complex, $[Fe^{III}(L-L)Br]$, where $(L-L)^{2-}$ is a pentacoordinate, N_2O_2S -donor ligand which is formed by oxidative dimerization of the tridentate ligand via formation of a disulfide bridge. In contrast, $RuCl_3 \cdot H_2O$ forms a diamagnetic dimer, $[Ru^{III}_2(L)_2Cl_2(MeCN)_2]$ with a Ru-Ru single bond. Two successive reversible one-electron oxidations are observed with the diamagnetic Ru(III) species yielding $[Ru^{III}_2(L')(L)Cl_2(MeCN)_2]^+$, ($S = 1/2$), and $[Ru^{III}_2(L')_2Cl_2(MeCN)_2]^{2+}$, ($S = 0$) ions (Scheme 1.23).⁹⁷ Spectro-electrochemical and electron paramagnetic resonance measurements along with DFT calculations identified that these are ligand-centered redox processes with formation of *O*-coordinated phenoxyl radicals.

Scheme 1.23 Tridentate Redox-Active [N,O,S] Schiff Base Ligand⁹⁷


Heyduk et al. recently developed a tridentate redox-active bis(thiophenolato)amido ligand, $[SNS]^{3-}$ and compared the redox properties of this ligand with the well-established $[ONO]^{3-}$ redox-active ligand by preparing their homoleptic tungsten complexes, $W(SNS)_2$ and $W(ONO)_2$. Both complexes show two reversible reductions and two partially reversible oxidations. Interestingly, while the hard oxygen and nitrogen donors of $[ONO]$ ligand favor a $W^{VI}[ONO^{cat}]_2$ electronic structure, the soft sulfur donor atoms of the $[SNS]$ platform seem to increase $S \rightarrow W$ π covalency,

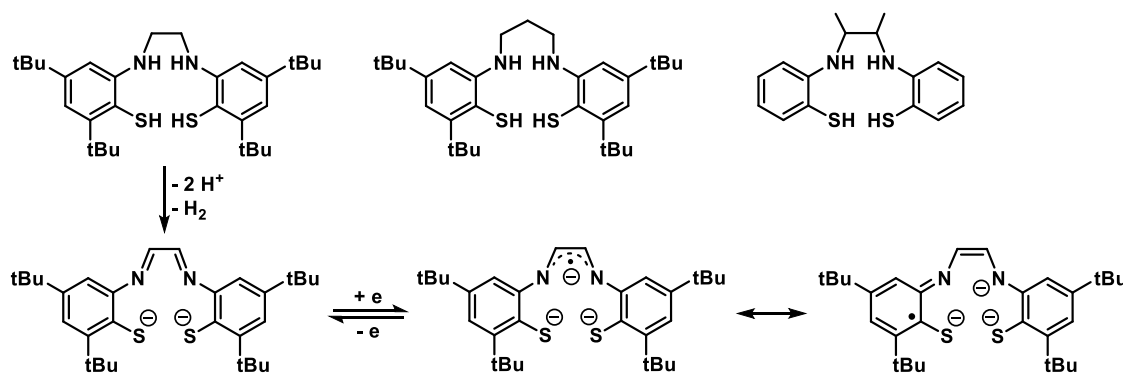
giving the $W(SNS)_2$ complex a non-innocent feature that can be described as a tungsten(IV) metal center coordinated to two $[SNS^{sq}]^{2-}$ ligands (Scheme 1.24).¹⁰²

Scheme 1.24 Synthesis of $W(SNS)_2$ Complex and Non-Innocent Behavior of Redox-Active [SNS] Pincer Ligand¹⁰²



The coordination chemistry of iron bearing tetradentate, redox non-innocent *o*-aminothiophenolate-based $[N_2S_2]$ ligands has also been demonstrated. Wieghardt and co-workers reported a handful of iron complexes of bis(aminothiophenolate) N_2S_2 ligands and investigated thoroughly their diverse coordination modes, spin states and electronic structures by means of experimental (X-ray crystallography, Mössbauer spectroscopy, electron paramagnetic resonance, magnetic measurements and spectroelectrochemistry) and theoretical (DFT study) analysis. A few such tetradentate N_2S_2 ligands and their different oxidation levels are depicted in Scheme 1.25.^{98,99}

Scheme 1.25 Tetradentate Bis(Aminothiophenolate) N_2S_2 Ligands and Their Oxidation States^{98,99}



Redox-active metal-ligand complexes have received popularity as a result of significant advancement in spectroscopic techniques and methods including high-resolution X-ray crystallography.⁹² These physical and spectroscopic techniques support not only identification of ligand-centered radicals but also help determine their electronic structures. Computational chemistry (e.g., DFT) has also become an indispensable tool in this regard in order to compare and contrast the experimental and/or simulated data with the theoretical data.

Although many redox-active ligands have been reported to be capable of catalyzing various reactions when coordinated to (transition) metals, there are not that many catalytic applications of metal complexes bearing sulfur-derived redox-active ligands.

1.6 Scope of Thesis Work

The work described in this *thesis* aims to advance the field of *bifunctional ligands* by introducing new sterically svelte tridentate ligands with a mixture of hard nitrogen and soft sulfur donors. A number of iron complexes are prepared with these ligands. The reactivity of the well-defined iron complexes is investigated, and their utility as potential bifunctional catalysts is explored. The ligands used in these studies are produced in one or two steps in excellent yield from commercially available sources. Specifically, Chapter 2 details a one-step synthesis of a new $S^{Me}N^H S$ ligand in excellent yield that undergoes ring-opening on treatment with $Fe(OTf)_2$ affording a thiolate-bridged, trinuclear iron complex, $[Fe_3(\mu_2-S^{Me}NS^-)_4](OTf)_2$. The structure, spectroscopic, magnetic, and computational studies of this iron complex are shown along with its solvent-dependent reactivity towards monodentate donor ligands that yields both dinuclear and mononuclear derivatives. Chapter 3 entails the formation of $[Fe(S^{Me}NS)(PMe_3)_3]^+$ and its substitution reactivity along with an oxidative thioether $C_{aryl}-S$ bond cleavage reaction which led to a cationic Fe(III)-CNS thiolate analog. The Fe(II)-SNS and -CNS species were assessed as precatalysts for amine-borane dehydrogenation as a complement for bifunctional iron catalysis. Chapter 4 highlights our efforts to prepare neutral $Fe(SNS)_2$ which led instead to the synthesis of neutral, imine-coupled $Fe-N_2S_2$ complexes that serve as efficient and selective catalytic aldehyde

hydroboration catalysts using pinacolborane at room temperature. Chapter 5 introduces the new unsymmetrical amine ligand, $S^{Me}N^H S^{Me}$, and details its iron chemistry including hemilability of the ligand and reactivity studies with a variety of donor ligands. A tridentate phosphine ligand, triphos, afforded a 16e, low-spin, square-pyramidal Fe(II) amido complex that proved to be a robust precatalyst for dehydrogenation of dimethylamine-borane vs. ammonia-borane; preliminary results are indicative of a bifunctional activation pathway. Finally, Chapter 6 concludes the outcomes of the iron chemistry of hemilabile SNS ligands and future directions and opportunities are identified to extend these ligand systems to other transition metals.

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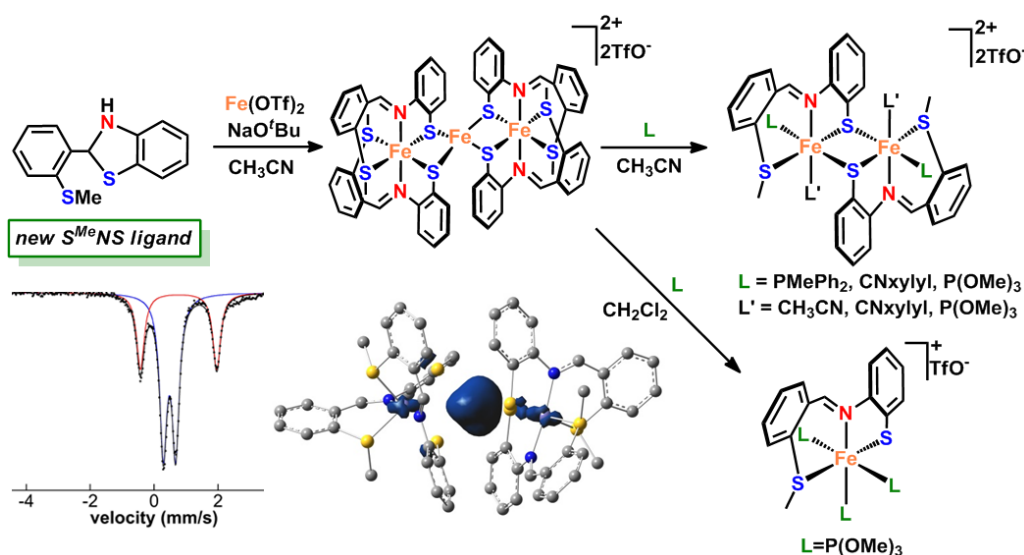
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Chapter 2. Mononuclear, dinuclear, and trinuclear iron complexes featuring a new monoanionic SNS thiolate ligand

2.1 Published Contributions

Mononuclear, Dinuclear, and Trinuclear Iron Complexes Featuring a New Monoanionic SNS Thiolate Ligand

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Author Contributions

Uttam and Prof. Baker wrote the manuscript. Uttam performed all experiments presented. Stephanie collected all Mössbauer spectra and explained the data under the supervision of Prof. Neidig. Serge was responsible for DFT studies presented. Jennifer performed magnetic measurements under the supervision of Prof. Murugesu. Ilia was responsible for X-ray diffraction studies.

Abstract

The new tridentate ligand $S^{Me}N^HS = 2-(2\text{-methylthiophenyl})\text{benzothiazolidine}$, prepared in a single step from commercial precursors in excellent yield, undergoes ring-opening on treatment with $Fe(OTf)_2$ in the presence of base affording a trinuclear iron complex, $[Fe_3(\mu_2-S^{Me}NS^-)_4](OTf)_2$

(1) which is fully characterized by structural and spectroscopic methods. X-ray structural data reveal that **1** contains four $S^{Me}NS^-$ ligands meridionally bound to two pseudooctahedral iron centers each bridged by two thiolates to a distorted tetrahedral central iron. The combined spectroscopic (UV-vis, Mössbauer, NMR), magnetic (solution and solid-state) and computational (DFT) studies indicate that **1** includes a central, high-spin Fe(II) ($S = 2$) with two low-spin ($S = 0$) peripheral Fe(II) centers. Complex **1** reacts with excess $PMePh_2$, $CNxylyl$ (2,6-dimethylphenyl isocyanide), and $P(OMe)_3$ in CH_3CN to form diamagnetic, thiolate-bridged dinuclear Fe(II) complexes $\{[Fe(\mu-S^{Me}NS^-)L_2]_2\}(OTf)_2$ (**2-4**). These complexes are characterized by elemental analysis, 1H NMR, IR, UV-vis and Mössbauer spectroscopy and single crystal X-ray diffraction. Interestingly, addition of excess $P(OMe)_3$ to complex **1** in CH_2Cl_2 produces primarily the diamagnetic, mononuclear Fe(II) complex, $\{Fe(S^{Me}NS^-)[P(OMe)_3]_3\}(OTf)$ (**5**).

2.2 Introduction

Iron complexes containing N- and S-donor ligands have garnered much attention due to their stunningly diverse structural features and intriguing reactivity as well as their prominent roles in biological catalysis.¹⁻¹² For example, sulfur-bridged dinuclear iron clusters have been found in the active site of metalloenzymes such as [FeFe]-hydrogenases which are capable of catalyzing reversible formation of dihydrogen from electrons and protons ($2H^+ + 2e^- \rightleftharpoons H_2$).^{3, 5, 7, 12, 13} The nitrogenase enzyme, which contains [Fe-S] clusters in its active site (*e.g.*, MoFe-cofactor) efficiently catalyzes biological N_2 reduction to ammonia.^{4, 11} It has been demonstrated that the structural and dynamic features of these Fe-S cores (*e.g.*, [2Fe-2S] cluster in [FeFe]-hydrogenase, P cluster in nitrogenase, and [4Fe-3S] cluster in oxygen-tolerant [NiFe]-hydrogenase) are important in their enzymatic activities.¹⁴⁻¹⁹ Subsequently, numerous dinuclear iron complexes of the type $[Fe_2(\mu-S)_2(CO)_{6-x}L_x]$ and $[Fe_2(\mu-SR)_2(CO)_{6-x}L_x]$ ($L = CN, NO, P$ -donor ligands, *etc.*) have been developed as synthetic hydrogenase mimics as well as potential electrocatalysts for hydrogen evolution.²⁰⁻²⁸ Kinoshita and co-workers recently demonstrated that a new class of carbon- and

sulfur-bridged dinuclear iron carbonyl complexes containing an unsymmetrical $S^-C^-N^R$ pincer ligand can serve as electrocatalysts for proton reduction.²⁹

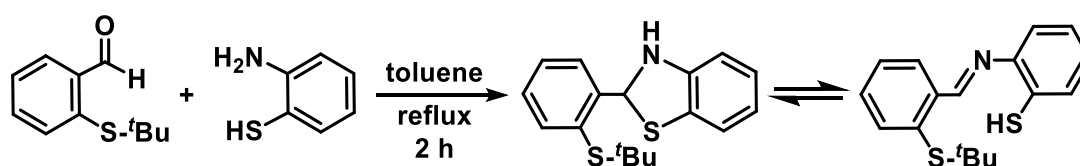
Non-heme iron enzymes (*e.g.*, nitrile hydratases,^{2, 30-33} superoxide reductases,^{2, 8, 34, 35} and cysteine dioxygenases^{9, 36}) contain mononuclear iron-bound thiolates with N-donor ligands in their active sites which are responsible for catalyzing many biologically important reactions including hydration of nitriles to their corresponding amides, reduction of superoxide to hydrogen peroxide and oxidation of L-cysteine to cysteine sulfinic acid. Most recently, Goldberg *et al.* developed both thiolate- and thioether-ligated mononuclear iron complexes bearing N_3PyS^- and N_3PyS^R ligand scaffolds, respectively. They demonstrated that these complexes function as biomimetic models, mimicking certain structural and functional features of non-heme iron enzymes.^{37, 38}

We are interested in preparing new tridentate ligands featuring hard nitrogen and soft sulfur donors capable of stabilizing a range of metal oxidation states,^{29, 33, 37-54} and hemilabile arms to allow substrates to coordinate for potential applications in catalysis.⁵⁵ To this end, we have been investigating mixed N,S-donor ligands and their iron complexes. Thioether ligands usually bind weakly to transition metals^{45, 47, 51, 56-58} and their hemilability has been previously demonstrated.^{47, 59, 60} Thiolate groups typically form stronger bonds to metals, can serve as terminal or bridging ligands and thus can form mononuclear or biologically relevant multimetallic compounds (*vide supra*). Additionally, metal-bound thiolates have reactive lone-pair electrons available for bifunctional substrate activation. For the nitrogen portion of the ligand, we have targeted neutral (*e.g.*, imine) or charged (*e.g.*, amido) donors, with the goal of obtaining ligands/complexes for broader applicability in biomimetic studies or molecular catalysis.

A variety of tridentate mixed-donor ligands containing nitrogen and sulfur are known, including $[S^R N^R S^R]$,^{47, 50, 52, 55, 61} $[S^R N^- S^R]$,^{49, 50, 54} $[S^- N^R S^-]$,³⁹ $[S^- N^- S^-]$,⁵³ $[N^R N^R S^R]$,⁶⁰ $[N^R N^R S^-]$,^{42, 62} $[N^R N^- S^-]$,⁶³ $[N^- S^R N^-]$,^{41, 51} $[O^- N^R S^-]$,⁴⁸ $[O^- N^- S^R]$,^{45, 59} $[N^R C^- S^-]$,²⁹ and many complexes of iron and other transition metals have been reported, but only in rare cases has catalytic activity been demonstrated. For instance, mononuclear ruthenium complexes bearing $[S^R N^R S^R]$ ligands have been

shown to catalyze the transfer hydrogenation of ketones and oxidation of alcohols.⁵⁰ Mononuclear chromium complexes containing $[S^R N^R S^R]$ ligands efficiently trimerized ethylene to 1-hexene⁵⁵ while zinc complexes with bis-triazole based $[S^R N^R S^R]$ ligands catalyzed reduction of electron-poor aldehydes to alcohols in the presence of a hydrogen donor.⁵² Similarly, iron compounds featuring a $[N^R S^R N^R]$ ligand are active catalysts for the hydrogenation of benzonitrile to benzylamine.⁴¹ Moreover, some of the above complexes exhibited hemilabile character, specifically for pincer ligands with thioether arms.^{47, 59, 60} Interestingly, nearly all of the metal complexes of the aforementioned tridentate ligands are mononuclear, with only two exceptions reported by Mikuriya and co-workers⁶² who synthesized and characterized thiolate-bridged di- and trinuclear iron complexes employing $[N^R N^R S^-]$ ligand although no reactivity studies were described. The ability to access both mono- and multinuclear species is desirable considering the preponderance of multimetallic enzymatic sites in nature. In 1998 Bouwman *et al.* reported⁶⁴ a simple $[S^{t-Bu} N^H S]$ heterocycle prepared from functionalized aldehyde and aniline (Scheme 2.1) which exists in equilibrium with the imine isomer in chloroform. While

Scheme 2.1 Previously Reported $[S^{t-Bu} N^H S]$ Heterocycle



treatment of this heterocycle with nickel acetate afforded a mononuclear Ni(II) complex of the ring-opened isomer, reaction of the same ligand with nickel tetrafluoroborate yielded a dinuclear $[S^- NS^-]$ -ligated Ni(II) complex upon loss of the *tert*-butyl group.

Herein we describe a more stable version of the $S^R N^H S$ ligand wherein $R = Me$, synthesized in high yield from commercially available precursors in a single step. We have prepared a trinuclear iron complex bearing four of these new ligands and investigated its reactions with donor ligands to give a series of mono- and dinuclear iron complexes which were fully characterized by elemental analysis, 1H NMR, IR, UV/vis, Mössbauer spectroscopy and single crystal X-ray diffraction. These

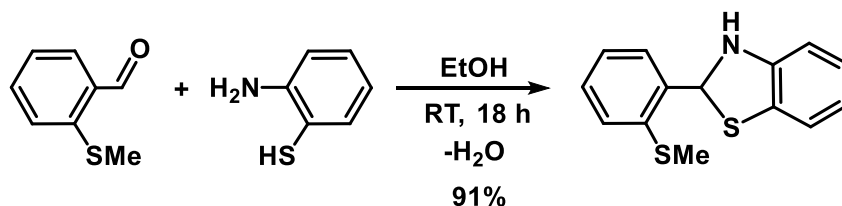
complexes form the basis for our current studies of bifunctional catalysis that will appear in future publications.

2.3 Results and Discussion

2.3.1 Synthesis of [$S^{Me}N^H S$] Ligand

We have targeted ligands that can be synthesized rapidly in one or two steps from inexpensive precursors, in contrast to many of the previously reported tridentate N,S-donor ligands.^{29, 39, 41, 49-52, 54, 63} The tridentate ligand 2-(2-methylthiophenyl)benzothiazolidine, [$S^{Me}N^H S$] was prepared in a single step from commercially available precursors, 2-(methylthio)benzaldehyde and 2-aminothiophenol (Scheme 2.2). Condensation reaction of these two starting materials at room temperature in ethanol afforded the ligand as an off-white solid in excellent yield. The ligand was fully characterized by elemental analysis, 1H NMR, $^{13}C\{^1H\}$ NMR, UV/vis, IR, and high-resolution mass spectrometry (EI-MS). Spectroscopic measurements confirmed the benzothiazolidine structure with a strong N-H stretch observed in the infrared spectrum at 3339 cm^{-1} , and the absence of an imine signal in the 1H NMR spectrum (Figure A1). The ^{13}C NMR spectrum of the benzothiazolidine contains a peak at δ 66.73 which can be assigned to the benzylic carbon atom (Figure A2). In contrast to the previously reported S^tBu analog,⁶⁴ no trace of the ring-opened imine isomer was observed by NMR spectroscopy.

Scheme 2.2 Synthesis of [$S^{Me}N^H S$] Ligand

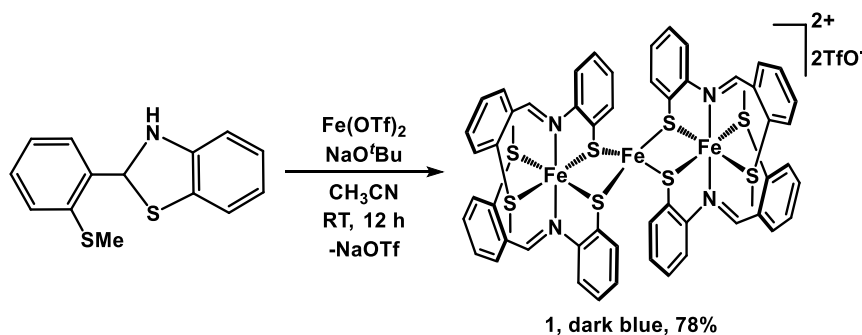


2.3.2 Synthesis and Structure of Trinuclear Iron Complex

The thiolate-bridged trinuclear iron complex $[Fe_3(\mu_2-S^{Me}NS^-)_4](OTf)_2$ (**1**) was obtained upon treatment of $Fe(OTf)_2$ with one equiv. of the [$S^{Me}N^H S$] ligand in the presence of NaO^tBu base (Scheme 2.3). The 1H NMR spectrum of **1** exhibits paramagnetically shifted resonances spanning a

chemical shift range of 22 to -55 ppm, suggestive of a high-spin complex (Figure A5). The ^{19}F NMR spectrum shows a broad singlet at -78.05 ppm, consistent with the presence of triflate anion in the outer coordination sphere (Figure A6).

Scheme 2.3 Synthesis of Trinuclear Iron Complex **1**



Single-crystal X-ray diffraction studies established the molecular structure of **1** which contains a linear array of three iron atoms connected to each other by the thiolate groups of four $[\text{S}^{\text{Me}}\text{NS}^-]$ ligands (Figure 2.1). None of the $[\text{S}^{\text{Me}}\text{NS}^-]$ ligands in **1** can be described as planar and, in fact, this non-planarity is observed in all of the iron complexes reported herein (*vide infra*). The distorted tetrahedral central iron (S-Fe-S angles range from $88.81(5)$ to $122.59(6)^\circ$) is coordinated to two bidentate dithiolate groups of the pseudooctahedral $[\text{Fe}(\text{mer-}\text{S}^{\text{Me}}\text{NS}^-)_2]$ units. The Fe-S_{thiolate} distances and S-Fe-S angles (Table 2.1) are comparable to those found in related O_h - T_d - O_h iron complexes.^{62, 66-68} In spite of its lower coordination number, the thiolate bonds to the central iron atom are significantly longer than those to the peripheral (chelated) iron atoms [*e.g.*, $2.3807(16)$ Å for Fe(2)-S(3) vs. $2.3349(15)$ Å for Fe(1)-S(3)]. The $\text{Fe}(\mu\text{-S})_2\text{Fe}(\mu\text{-S})_2\text{Fe}$ substructure is bent, resulting in shorter Fe $\cdots$ Fe distances (avg. 3.191 Å) vs. those in planar dinuclear complexes **2-4** ($3.412 - 3.473$ Å, *vide supra*). The longer central Fe-S_{thiolate} bonds and bent $\text{Fe}(\mu\text{-S})_2\text{Fe}(\mu\text{-S})_2\text{Fe}$ core suggest that dissociation of the central Fe-S_{thiolate} bonds should be feasible using strong donor ligands (*vide infra*). The Fe-S_{thioether} and Fe-N_{imine} distances (Table 2.1) also compare well to those found in related iron^{38, 62, 67, 69, 70} and ruthenium^{43, 50} complexes. The shorter Fe-S_{thioether} (avg. $2.270(2)$ Å) vs. Fe-S_{thiolate} (avg. $2.336(2)$ Å) bond distances may result from π -back donation from a

peripheral iron occupied d orbital into the thioether C-S σ^* orbitals.⁵⁶ It is worth noting that trinuclear complex **1** could not be synthesized using 3 equivalents of $\text{Fe}(\text{OTf})_2$ and 4 equivalents of $[\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}]$ ligand in presence of base.

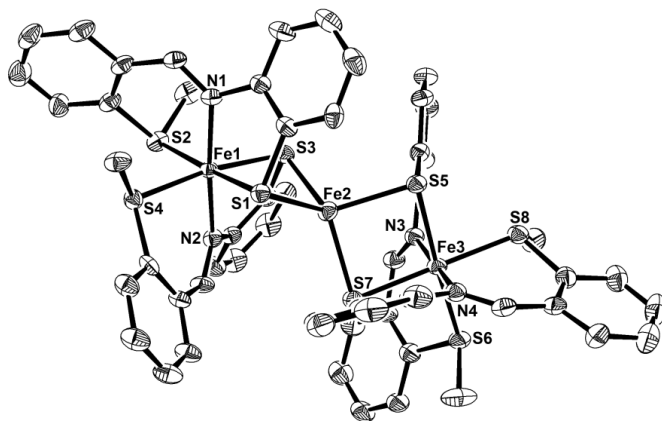


Figure 2.1 ORTEP diagram of $[\text{Fe}_3(\mu_2\text{-S}^{\text{Me}}\text{NS}^-)_4](\text{OTf})_2$ (**1**). Thermal ellipsoids are shown at 40% probability. Hydrogen atoms, disordered CHCl_3 molecules and triflate anions are omitted for clarity. Selected bond lengths and angles can be found in Table 2.1.

Table 2.1 Selected bond distances (Å) and angles (deg) for $[\text{Fe}_3(\mu_2\text{-S}^{\text{Me}}\text{NS}^-)_4](\text{OTf})_2$ (**1**)

Bond Distances (Å)		Bond Angles (deg)	
Fe-S _{thiolate}			
Fe(1)-S(1)	2.3316(14)	S(2)-Fe(1)-S(1)	173.87(6)
Fe(1)-S(3)	2.3349(15)	S(4)-Fe(1)-S(3)	170.51(6)
Fe(2)-S(1)	2.3543(15)	N(1)-Fe(1)-N(2)	173.80(18)
Fe(2)-S(3)	2.3807(16)	S(3)-Fe(2)-S(5)	109.67(6)
Fe(2)-S(5)	2.3556(17)	S(1)-Fe(2)-S(7)	116.87(6)
Fe(2)-S(7)	2.3542(17)	S(1)-Fe(2)-S(3)	88.81(5)
Fe(3)-S(5)	2.3264(16)	S(3)-Fe(2)-S(7)	130.75(6)
Fe(3)-S(7)	2.3542(17)	S(7)-Fe(2)-S(5)	91.55(6)
Fe-S _{thioether}		S(5)-Fe(2)-S(1)	122.59(6)
Fe(1)-S(2)	2.2760(15)	S(6)-Fe(3)-S(5)	174.76(6)
Fe(1)-S(4)	2.2777(15)	S(8)-Fe(3)-S(7)	178.54(6)
Fe(3)-S(6)	2.2619(16)	N(3)-Fe(3)-N(4)	174.1(2)
Fe(3)-S(8)	2.2638(17)		
Fe-N			
Fe(1)-N(1)	1.966(4)		
Fe(1)-N(2)	1.972(4)		
Fe(3)-N(3)	1.972(5)		
Fe(3)-N(4)	1.956(5)		

Further investigations shed additional light on the electronic structure of **1**. The blue color of complex **1** rapidly turns brown upon exposure to air. Electrochemical studies revealed two quasireversible oxidations at -0.03 and 0.33 V vs. ferrocene in CH_2Cl_2 solution (Figure A38). The electronic structure of **1** was evaluated further using Mössbauer spectroscopy, SQUID magnetometry, and DFT calculations. The 5 K Mössbauer spectrum of **1** (Figure 2.2; Table 2.4) exhibits two major doublets, consistent with the presence of two distinct iron sites in a $\sim 1:2$ ratio, with $\delta = 0.77$ mm/s and $\Delta E_Q = 2.39$ mm/s ($\sim 35\%$, red component) for the central iron center and $\delta = 0.48$ mm/s and $\Delta E_Q = 0.36$ mm/s ($\sim 65\%$, blue component) for the peripheral Fe centers. The larger ΔE_Q observed for the central Fe compared to the peripheral Fe sites is consistent with a high-spin, four-coordinate geometry for the central Fe(II) and a low-spin, six-coordinate geometry for the peripheral Fe(II) centers (see X-ray crystal data for geometries, *vide infra*). No change in the Mössbauer spectrum within the error of the fit analysis was observed up to 130 K demonstrating no change in spin state within this temperature range (Figure A8). Magnetic measurements in the solid state gave an effective magnetic moment of 6.4 BM (Figures A9 and A10), which matched well the solution magnetic moment (6.4 BM) at room temperature estimated by the Evans' method.⁶⁵ The observed magnetic moment is consistent with $S = 2$ spin-state with the significant deviation of the effective magnetic moment from the spin-only value (4.90 BM) arising presumably from spin-orbit coupling.

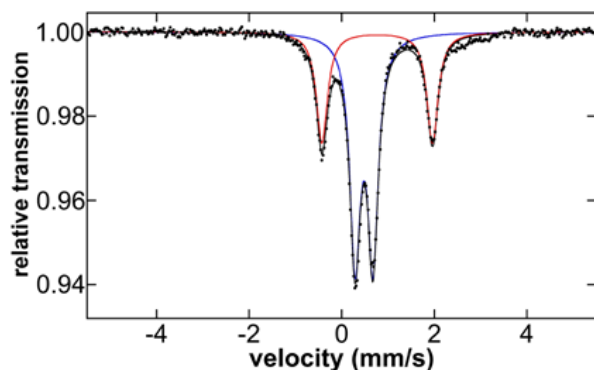


Figure 2.2 5 K Mössbauer spectrum of $[\text{Fe}_3(\mu_2\text{-S}^{\text{Me}}\text{NS}^-)_4](\text{OTf})_2$ (**1**). Data (black dots) and total fit (black lines) are shown. Individual component fits are shown and described in the text.

In order to more rigorously confirm the valence and spin state description of the trinuclear complex, DFT calculations were performed at the PBE/TZVP level of theory. Geometry optimization of the complex with the $\text{Fe}^{\text{II}}(\text{LS})\text{—Fe}^{\text{II}}(\text{HS})\text{—Fe}^{\text{II}}(\text{LS})$ description ($S_{\text{total}} = 2$) resulted in a structure with very close agreement to the X-ray structure. The calculated Fe1-N1,2 and Fe3-N3,4 distances were 1.97-1.98 Å (the X-ray values are in the 1.956-1.972 Å range), the calculated Fe1-S2,4 and Fe3-S6,8 distances were 2.29-2.30 Å (the X-ray values are in the 2.262-2.278 Å range), the calculated Fe1-S1,3 and Fe3-S5,7 distances were 2.33-2.34 Å (the X-ray values are in the 2.326-2.335 Å range), and the calculated Fe2-S1,3,5,7 distances were 2.35-2.38 Å (the X-ray values are in the 2.354-2.381 Å range). The latter Fe-S distances are the longest in the set due to weak covalent bonding between high-spin Fe(II) and the bridging thiolate S atoms (*vide infra*). The calculated geometry confirms that the Fe1,3 atoms with their distorted octahedral coordination environment correspond to the low-spin Fe(II) and the Fe2 atom with its distorted tetrahedral coordination environment corresponds to the high-spin Fe(II). The spin density distribution for this complex is shown in Figure 2.3. Most of the spin density, as expected, is localized on the high-spin Fe^{II} (the NPA and MPA derived atomic spin density values of 3.31 a.u. and 3.38 a.u., respectively), with a small spin delocalization to the Fe1 and Fe3 atoms (the NPA and MPA derived atomic spin density values between 0.04 and 0.07 a.u.). The bridging thiolate S atoms also carry a spin density of ~0.07-0.09 a.u. (MPA) or 0.09-0.11 a.u. (NPA).

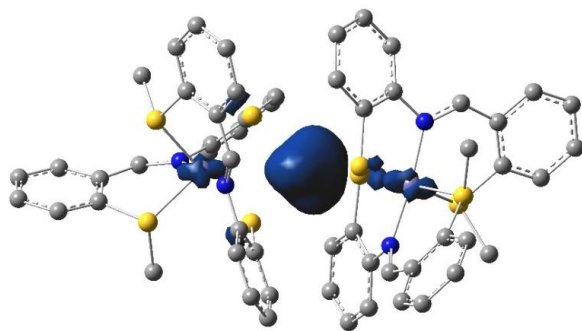


Figure 2.3 Spin density distribution for $[\text{Fe}_3(\mu_2\text{-S}^{\text{Me}}\text{NS}^-)_4](\text{OTf})_2$ (**1**) (the isosurface contour value of 0.005 a.u.). H atoms are not shown for clarity.

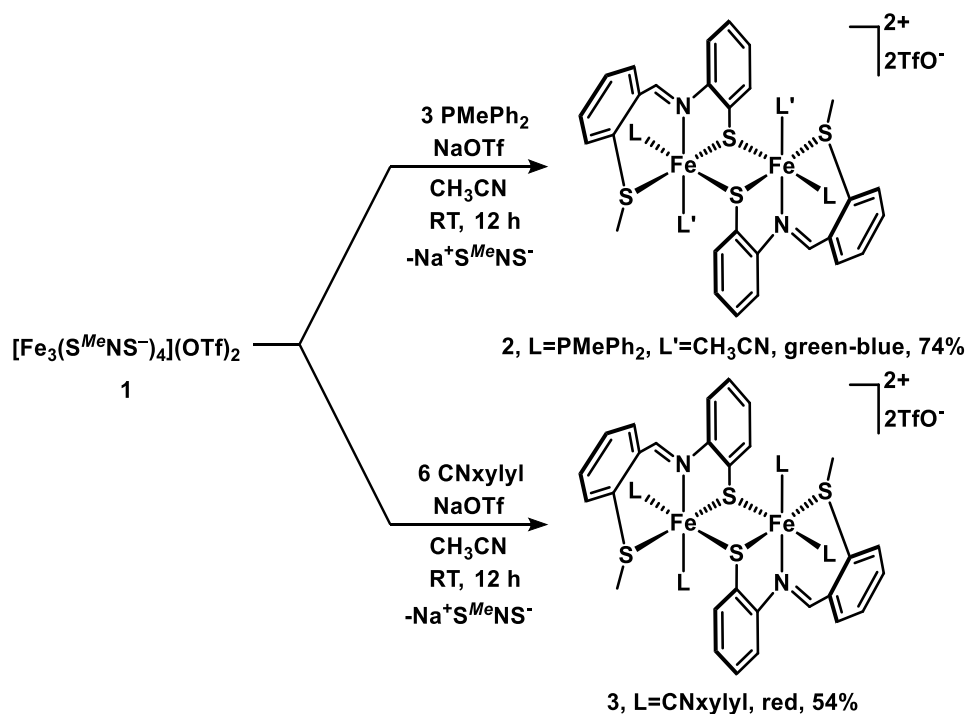
The Mayer bond orders⁷¹ can be used to quantify metal-ligand covalency in this structure. The Fe^{II}(LS)-N bonds have bond order values of 0.62-0.63 while Fe^{II}(LS)-S bonds have the bond order values of 0.71-0.73 and 0.74-0.77 for thiolate and thioether bonds, respectively. These higher values for the Fe-S bonds reflect the additional contribution of π -donation to the metal-ligand covalency relative to mostly sigma-covalent Fe-N bonds. Since the d-orbitals have the same alpha and beta-spin electron occupancy for the low-spin Fe ions, alpha- and beta-spin d-orbitals contribute equally to the metal-ligand covalency (50% of the bond order for each manifold). Relative to the Fe^{II}(LS)-S bonds, the Fe^{II}(HS)-S bonds have slightly weaker covalency, with bond orders of 0.70-0.73, with alpha-spin molecular orbitals contributing 0.29-0.30 and beta-spin molecular orbitals contributing the remaining 0.41-0.44. The larger contribution of the beta-spin orbitals reflects the fact that the beta-spin d-orbitals in high-spin Fe^{II} are empty and available for additional ligand-to-metal donation from the bridging S atoms while alpha-spin d-orbitals in high-spin Fe^{II} are occupied and cannot contribute to ligand-to-metal donation.

2.3.3 Formation of Thiolate-Bridged Dinuclear Iron Complexes

Reactions of the trinuclear complex **1** with several donor ligands afforded thiolate-bridged iron dimers. While no coordination was observed with PPh₃, treatment of **1** in acetonitrile with 3 equivalents of PMePh₂ yielded a thiolate-bridged iron dimer, {[Fe(μ -S^{Me}NS⁻)(PMePh₂)(CH₃CN)]₂}(OTf)₂ (**2**) (Scheme 2.4). The ¹H NMR spectrum of **2** displays diamagnetic resonances and the ³¹P{¹H} NMR spectrum shows a sharp singlet at 25.0 ppm indicative of a low-spin (*S* = 0) complex (Figures A11-S12). It should be noted that a stoichiometric amount of NaOTf was added to the reaction in order to balance the counter anion (TfO⁻) of the iron dimer. Addition of 6 equivalents of CNxylyl (2,6-dimethylphenyl isocyanide) to a mixture of **1** and NaOTf in acetonitrile generated the bis(ligand) iron dimer, {[Fe(μ -S^{Me}NS⁻)(CNxylyl)₂]₂}(OTf)₂ (**3**). Similar to complex **2**, the ¹H NMR spectrum exhibits well-resolved resonances in the diamagnetic region suggestive of a low-spin (*S* = 0) species and the data indicate effective *C*₂ symmetry in solution. The IR spectrum of **3** in solid state shows two sharp strong signals at 2098 cm⁻¹ and 2124

cm^{-1} , which are assigned to the C-N stretching vibrations of isocyanides coordinated to iron (Figure A17). Further attempt to synthesize **2** and **3** not using complex **1** but from the mixture of $\text{Fe}(\text{OTf})_2$, $[\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}]$ ligand, base and either phosphine or isocyanide ligand led to very low yield of these complexes. Complexes **2** and **3** were characterized further by X-ray crystallography (Figures 2.4 and 2.5).

Scheme 2.4 Preparation of Dinuclear Iron Complexes **2** and **3**



Single crystals of **2** for X-ray diffraction were grown from saturated acetonitrile solutions and crystals of **3** were obtained by layering diethyl ether over a concentrated acetonitrile solution (Figures 2.4 and 2.5, respectively). The two structures are very similar: each asymmetric unit consists of two iron centers with slightly distorted octahedral geometry with one $[\text{S}^{\text{Me}}\text{NS}^-]$ ligand and two neutral monodentate donors (phosphine and acetonitrile in **2**, and two isocyanides in **3**) per iron atom. The $\text{Fe}-\text{S}_{\text{thiolate}}$, $\text{Fe}-\text{S}_{\text{thioether}}$ and $\text{Fe}-\text{N}_{\text{imine}}$ distances in **2** and **3** (Table 2.2) are similar to those of the trinuclear iron complex **1** and are comparable to analogous bond distances previously observed in related iron complexes.^{38, 62, 67, 69, 70} As seen in the trinuclear species **1**, the $\text{Fe}-\text{S}_{\text{thioether}}$

distances in both of these structures are shorter than the Fe-S_{thiolate} distances. The Fe(μ -S)₂Fe substructure in all of these dinuclear species is planar which is in marked contrast to the trinuclear complex **1** where the Fe(μ -S)₂Fe(μ -S)₂Fe core is bent (*vide supra*). In **2** the Fe-P bond lengths of 2.2852(4) Å and 2.1862(11), respectively are in good agreement with typical Fe(II) phosphine complexes.⁶⁹

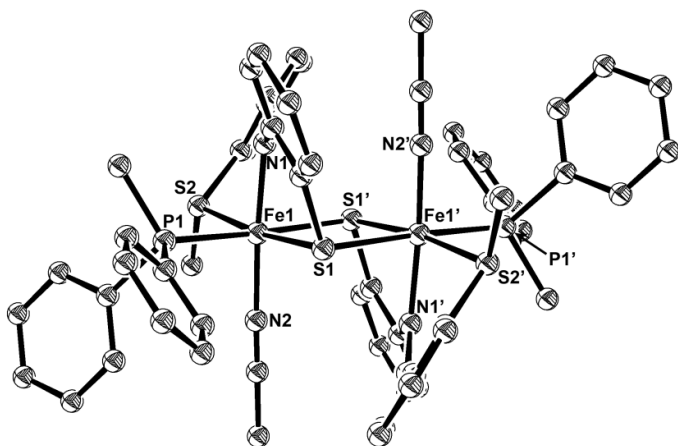


Figure 2.4 ORTEP diagram of $\{[\text{Fe}(\mu\text{-S}^{\text{Me}}\text{NS}^-)(\text{PMePh}_2)(\text{CH}_3\text{CN})]_2\}(\text{OTf})_2$ (**2**). Thermal ellipsoids are shown at 40% probability. Hydrogen atoms, CH_3CN solvate molecules and triflate anions are omitted for clarity. Selected bond lengths and angles are given in Tables 2.2 and 2.3.

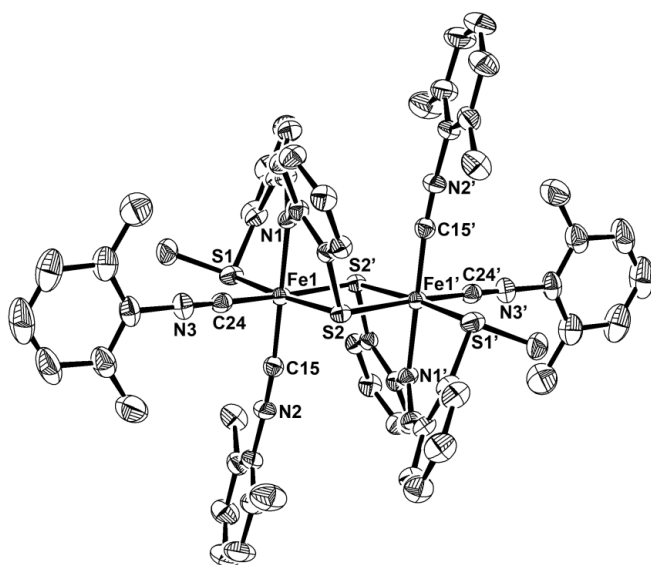


Figure 2.5 ORTEP diagram of $\{[\text{Fe}(\mu\text{-S}^{\text{Me}}\text{NS}^-)(\text{CNxylyl})_2]_2\}(\text{OTf})_2$ (**3**). Thermal ellipsoids are shown at 40% probability. Hydrogen atoms, CH_3CN solvate molecules and triflate anions are omitted for clarity. Selected bond lengths and angles are given in Tables 2.2 and 2.3.

Table 2.2 Selected bond distances (Å) for dinuclear complexes **2**, **3** and **4a**

	Bond Distances (Å)		
	[2]	[3]	[4a]
Fe-S_{thiolate}			
Fe(1)-S(1)	2.2759(4)	2.2515(7)	2.2776(10)
Fe(1)-S(1')	2.3522(4)	2.3318(7)	2.3716(11)
Fe(1')-S(1)	2.3522(4)	2.3318(7)	2.3716(11)
Fe(1')-S(1')	2.2759(4)	2.2515(7)	2.2776(10)
Fe-S_{thioether}			
Fe(1)-S(2)	2.2735(4)	2.2748(7)	2.2560(12)
Fe(1')-S(2')	2.2735(4)	2.2748(7)	2.2560(12)
Fe-N_{imine}			
Fe(1)-N(1)	1.9581(13)	1.9990(2)	1.964(3)
Fe(1')-N(1')	1.9581(13)	1.9990(2)	1.964(3)
Fe-P/N/C			
Fe(1)-P(1)	2.2852(4)	N/A	2.1862(11)
Fe(1')-P(1')	2.2852(4)	N/A	2.1862(11)
Fe(1)-N(2)	1.9116(14)	N/A	1.925(3)
Fe(1')-N(2')	1.9116(14)	N/A	1.925(3)
Fe(1)-C(15)	N/A	1.848(3)	N/A
Fe(1')-C(15')	N/A	1.848(3)	N/A
Fe(1)-C(24)	N/A	1.849(3)	N/A
Fe(1')-C(24')	N/A	1.849(3)	N/A

Table 2.3 Selected bond angles (deg) for dinuclear complexes **2**, **3** and **4a**

	Bond Angles (deg)		
	[2]	[3]	[4a]
S(2)-Fe(1)-S(1)	172.72(18)	173.89(3)	173.73(5)
N(1)-Fe(1)-N(2)	176.24(6)	N/A	176.44(12)
P(1)-Fe(1)-S(1')	175.68(17)	N/A	177.35(4)
N(1)-Fe(1)-C(15)	N/A	178.49(11)	N/A
C(24)-Fe(1)-S(2')	N/A	174.94(8)	N/A
S(2)-Fe(1)-P(1)	86.92(16)	N/A	90.71(5)
S(1)-Fe(1)-S(1')	82.90(15)	N/A	83.34(4)
P(1)-Fe(1)-S(1)	94.56(16)	N/A	94.10(4)
S(1')-Fe(1)-S(2)	95.17(16)	N/A	91.80(5)
S(2)-Fe(1)-S(2')	N/A	84.44(3)	N/A
S(1)-Fe(1)-C(24)	N/A	93.48(8)	N/A
S(2)-Fe(1)-C(24)	N/A	92.10(8)	N/A
S(1)-Fe(1)-S(2')	N/A	89.83(3)	N/A

Complex **2** is also air-sensitive in solutions turning from blue-green to brown. In spite of the two phosphine donor ligands, complex **2** is oxidized at a higher potential (0.37 V) than **1** (Figure A39). The variable temperature (5 K to 80 K) Mössbauer spectra of **2** (Figure 2.6A; Table 2.4; Figure A18) is well-described by a single quadrupole doublet, consistent with equivalent iron sites in the symmetrical dimer and no change in spin state was observed within this temperature range. The observed Mössbauer parameters of $\delta = 0.45$ mm/s and $\Delta E_Q = 0.35$ mm/s are consistent with low-spin, six-coordinate Fe(II).⁷² The 80 K Mössbauer spectrum of **3** (Figure 2.6B; Table 2.4) also exhibits a single doublet with $\delta = 0.18$ mm/s and $\Delta E_Q = 0.44$ mm/s, consistent with low-spin, six-coordinate Fe(II).

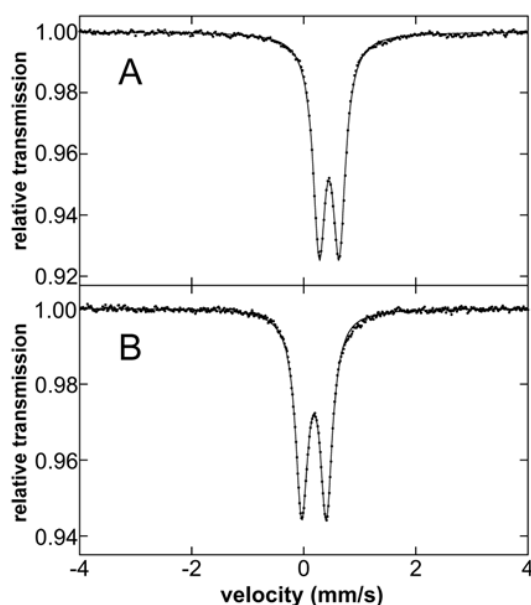


Figure 2.6 80 K Mössbauer spectra of (A) $\{[\text{Fe}(\mu\text{-S}^{\text{Me}}\text{NS}^-)(\text{PMePh}_2)(\text{CH}_3\text{CN})]_2\}(\text{OTf})_2$ (**2**) and (B) $\{[\text{Fe}(\mu\text{-S}^{\text{Me}}\text{NS}^-)(\text{CNxylyl})_2]_2\}(\text{OTf})_2$ (**3**). Data (black dots) and total fit (black lines) are shown.

Table 2.4. Experimentally determined 80 K ^{57}Fe Mössbauer parameters iron complexes **1-4**

Complex	δ (mm/s)	ΔE_Q (mm/s)
$[\text{Fe}_3(\mu_2\text{-S}^{\text{Me}}\text{NS}^-)_4](\text{OTf})_2$ (1)	0.76 (central Fe ^{II}) 0.48 (terminal Fe ^{II})	2.37 (central Fe ^{II}) 0.39 (terminal Fe ^{II})
$\{[\text{Fe}(\mu\text{-S}^{\text{Me}}\text{NS}^-)(\text{PMePh}_2)(\text{CH}_3\text{CN})]_2\}(\text{OTf})_2$ (2)	0.45	0.35
$\{[\text{Fe}(\mu\text{-S}^{\text{Me}}\text{NS}^-)(\text{CNxylyl})_2]_2\}(\text{OTf})_2$ (3)	0.18	0.44
$\{[\text{Fe}(\mu\text{-S}^{\text{Me}}\text{NS}^-)[\text{P}(\text{OMe})_3]_2]_2\}(\text{OTf})_2$ (4)	0.28	0.59

2.3.4 Synthesis of Mononuclear Iron Complex with a Terminal Thiolate

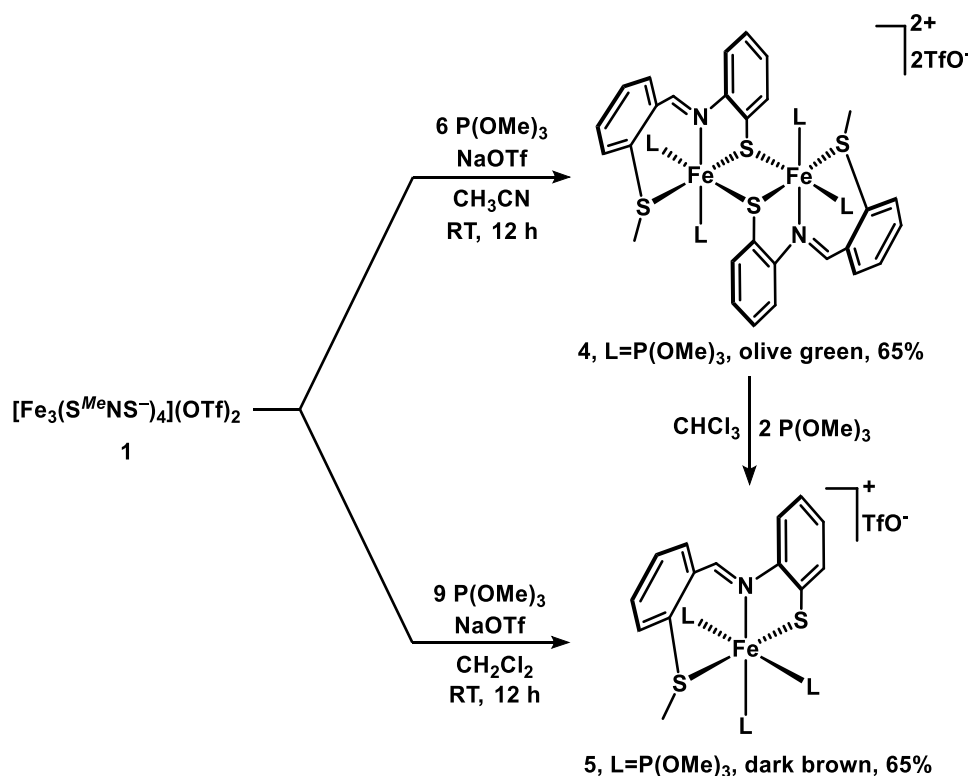
Reactions of P(OMe)_3 with the trinuclear complex **1** afforded both mono- and dinuclear iron complexes depending on the solvent. Addition of 6 equivalents of P(OMe)_3 to a mixture of complex **1** and NaOTf in acetonitrile resulted in an olive green solution of the bis(ligand) dimer, $\{[\text{Fe}(\mu\text{-S}^{\text{Me}}\text{NS}^-)[\text{P(OMe)}_3]_2]_2\}(\text{OTf})_2$ (**4**) (Scheme 2.5) as characterized by ^1H , $^{31}\text{P}\{^1\text{H}\}$ and ^{19}F NMR spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Figure A21) contains two doublets at 153.3 and 164.0 ppm ($^2J_{\text{PP}} = 168$ Hz) consistent with *cis* P(OMe)_3 ligands.⁶⁹ However, the ^1H NMR spectrum shows resonances due to more than one diamagnetic iron species with the predominant species **4** exhibiting effective C_2 symmetry in solution (Figure A20). Interestingly, the imine C-H resonance is a doublet due to long range H-P coupling ($^4J_{\text{HP}} = 3.5$ Hz) not observed in the mixed ligand dimer **2**. Surprisingly, recrystallization of **4** from a saturated acetonitrile solution at -35°C afforded the mixed-ligand, thiolate-bridged iron dimer, $\{[\text{Fe}(\mu\text{-S}^{\text{Me}}\text{NS}^-)[\text{P(OMe)}_3](\text{CH}_3\text{CN})]_2\}(\text{OTf})_2$ (**4a**) (see Figure A23 for X-ray structure), which is structurally similar to **2**. However, we were not able to observe **4a** via solution NMR spectroscopy as the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the dissolved crystals consisted primarily of the bis(ligand) dimer **4** (Figures A24-S25). Similar results were obtained by addition of a deficiency of P(OMe)_3 to **1** and NaOTf. Addition of excess P(OMe)_3 (9 equiv.) to a mixture of complex **1** and NaOTf in acetonitrile again yielded mostly dimer **4** along with a minor amount of a new mononuclear iron complex **5** (Figures A26-S27). Consistent with these results, the 80 K Mössbauer spectrum of the isolated solid from the 6 equiv. P(OMe)_3 reaction (Figure A19) shows a major iron species ($\sim 72\%$) with parameters of $\delta = 0.28$ mm/s and $\Delta E_{\text{Q}} = 0.59$ mm/s, consistent with a symmetrical dimer of low-spin, six-coordinate Fe(II) ($S = 0$) along with two additional minor iron species ($\sim 28\%$ of total iron combined).

In contrast, treatment of complex **1** and NaOTf with excess P(OMe)_3 in dichloromethane resulted in a color change from dark blue to brown due to the mononuclear complex, $[\text{Fe}(\text{S}^{\text{Me}}\text{NS}^-)\{\text{P(OMe)}_3\}_3](\text{OTf})$ (**5**) (Scheme 2.5). Although we were unable to obtain X-ray quality crystals for complex **5**, its structure in solution was confirmed by NMR spectroscopy; the $^{31}\text{P}\{^1\text{H}\}$

NMR spectrum shows a pseudotriplet and doublet at 164.1 and 140.1 ppm (integration ratio: 1:2), respectively, with ${}^2J_{\text{pp}} \approx 133$ Hz (Figure A29). In addition, the phosphite $-\text{OCH}_3$ groups show doublet and pseudotriplet resonances in the ${}^1\text{H}$ NMR spectrum, typical of meridional FeP_3 coordination.^{73, 74} In this case the observed quartet imine proton resonance reflects coupling to all three phosphites (${}^4J_{\text{HP}} = 5$ Hz in CD_3CN). Moreover, the molecular cation, $[\text{Fe}(\text{S}^{\text{Me}}\text{NS}^-)\{\text{P}(\text{OMe})_3\}_3]^+$, was observed by electrospray-mass spectrometry with the expected isotopic distribution (Figure A31). The mononuclear species **5** can also be formed by adding 2 equivalent of $\text{P}(\text{OMe})_3$ to dimer **4** in less polar solvents such as chloroform, dichloromethane or tetrahydrofuran.⁷⁵ The electronic structure of **5** was characterized using DFT calculations with geometry optimization performed at the PBEPBE/TZVP level. The resulting structure has an Fe(II) coordination environment with Fe-N bond distance of 2.02 Å, the two Fe-S bonds of 2.31 Å, and the Fe-P bonds of 2.22-2.28 Å. The B3LYP/TZVP calculations with the PCM solvent model (CH_2Cl_2 was solvent) were used to calculate the MO descriptors and the electronic absorption spectrum. The Mayer bond orders⁷¹ for Fe-N, Fe-S_{thiolate}, Fe-S_{thioether} and Fe-P bonds are 0.51, 0.83, 0.72 and 0.86-0.98, respectively. Thus, the least covalent metal-ligand bond is the Fe-N bond and the most covalent bonds are the three Fe-phosphite bonds. The energies and compositions of the frontier molecular orbitals are shown in the Supporting Information (Table S1). The HOMO is the antibonding orbital for the π interaction between the S_{thiolate} $p\pi$ and Fe(II) d_{xz} orbitals with S_{thiolate} and metal atomic contributions of 52% and 11%, respectively (Figure A32 and Table S1). The HOMO-2 is the mixed Fe/S^{Me}NS⁻ ligand orbital which features weak σ interaction between the S_{thiolate} $p\pi$ and the Fe(II) d_{xy} with the S_{thiolate} and metal atomic contributions of 9% and 35%, respectively (Figure A34 and Table S1). The LUMO is the π^* orbital of the S^{Me}NS⁻ ligand (Figure A33). TD-DFT calculations (Table S2) indicate that the first principal band, with energy of 16,500 cm^{-1} ($f = 0.059$), in the absorption spectrum of the complex arises from the HOMO-LUMO excitation. As a result, this transition has mostly S^{Me}NS⁻ intraligand character with a small metal-to-ligand charge transfer (MLCT) contribution. Similarly, the most intense band in the near-UV region of the

spectrum also corresponds to an excitation (HOMO-2 $\rightarrow$ LUMO) with mixed intraligand/MLCT character, calculated at 27,800 cm^{-1} ($f = 0.15$).

Scheme 2.5 Synthesis of Mono- and Dinuclear Iron Trimethylphosphite Complexes 4 and 5



In order to understand the solvent effect in the above stated reactions, we investigated the reactivity of **1** with PMe_3 in both acetonitrile and dichloromethane. Addition of excess PMe_3 to a mixture of **1** and NaOTf in CD_3CN yielded a dimer analogous to **4**, as confirmed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy [two doublets at 20.3 and 14.7 ppm ($^2J_{\text{PP}} = 64$ Hz) consistent with *cis* PMe_3 ligands] along with two unidentified by-products (singlets at 23.0 and 7.8 ppm; Figure A35). Interestingly, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the analogous reaction of **1** and PMe_3 in CDCl_3 shows two broad resonances at 12.3 and -0.6 ppm in a 1:2 ratio for the major product (Figure A36). Cooling this solution to -20°C converts these resonances into a doublet and pseudotriplet ($^2J_{\text{PP}} \approx 50$ Hz; Figure A37) similar to mononuclear, terminal thiolate complex **5**. Isolation and further characterization of this complex are currently in progress and will be published in due course.

Table 2.5 X-ray diffraction data collection and refinement parameters for **1**, **2**, **3** and **4a**

	[1]·1.5CHCl ₃	[2]·2CH ₃ CN	[3]·2CH ₃ CN	[4a]
Formula	C _{59.5} H _{49.5} Cl _{4.5} F ₆ Fe ₃ N ₄ O ₆ S ₁₀	C ₆₄ H ₆₂ F ₆ Fe ₂ N ₆ O ₆ P ₂ S ₆	C ₇₀ H ₆₆ F ₆ Fe ₂ N ₈ O ₆ S ₆	C ₇₀ H ₆₆ F ₆ Fe ₂ N ₈ O ₆ S ₆
Formula weight	1678.21	1491.22	1533.39	1256.83
Color	dark blue	dark greenish blue	Red	green
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	P-1	P2(1)/c	P 21/n	P-1
<i>a</i> /Å	10.1391(3)	11.4900(3)	12.5719(5)	10.6895(5)
<i>b</i> /Å	15.2828(4)	21.1626(5)	18.9447(7)	11.2318(5)
<i>c</i> /Å	22.8885(7)	14.9493(4)	15.7164(6)	11.5933(5)
<i>α</i> /deg	94.993(2)	90	90	74.390(3)
<i>β</i> /deg	98.271(2)	90.0760(10)	104.8256(18)	85.483(3)
<i>γ</i> /deg	98.650(2)	90	90	75.255(3)
<i>V</i> /Å ³	3448.38(17)	3635.04(16)	3618.6(2)	1296.35(10)
<i>Z</i>	2	4	2	2
<i>D_c</i> /Mg m ⁻³	1.616	1.437	1.407	1.610
<i>μ</i> /mm ⁻¹	1.168	0.686	0.646	0.946
<i>F</i> (000)	1702	1624	1584	644
Crystal size/mm	0.15 × 0.11 × 0.01	0.20 × 0.18 × 0.12	0.19 × 0.14 × 0.12	0.13 × 0.05 × 0.04
Reflections collected/unique	69142/17133	44276/8846	10539/7950	16057/6380
<i>θ</i> range/deg	1.54 to 28.43	1.67 to 28.31	1.718 to 26.433	1.82 to 28.42
Index range	−13 ≤ <i>h</i> ≤ 13, −20 ≤ <i>k</i> ≤ 20, −30 ≤ <i>l</i> ≤ 30	−15 ≤ <i>h</i> ≤ 15, −28 ≤ <i>k</i> ≤ 28, −19 ≤ <i>l</i> ≤ 19	−15 ≤ <i>h</i> ≤ 15, 0 ≤ <i>k</i> ≤ 23, 0 ≤ <i>l</i> ≤ 19	−14 ≤ <i>h</i> ≤ 14, −15 ≤ <i>k</i> ≤ 14, −15 ≤ <i>l</i> ≤ 15
<i>R</i> (int)	0.0668	0.0290	'twinned'	0.0755
Completeness to <i>θ</i>	28.43, 98.6%	28.31, 97.8 %	25.242, 98.9%	28.42, 97.7 %
Max. and min. transmission	0.9884 and 0.8443	0.9222 and 0.8749	0.745373 and 0.446069	0.9632 and 0.8869
Data/restraints/parameters	17133/166/856	8846/0/445	7950/21/444	6380/282/335
Goodness-of-fit on <i>F</i> ²	1.044	1.012	1.024	1.019
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0788, 0.2090	0.0321, 0.0811	0.0451, 0.1171	0.0655, 0.0959
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1373, 0.2473	0.0456, 0.0891	0.0611, 0.1291	0.1591, 0.1167

2.4 Conclusions

In summary, a new tridentate ligand, 2-(2-methylthiophenyl)benzothiazolidine, [S^{Me}N^HS], readily prepared in high yield from commercially available starting materials, was used to synthesize a new trinuclear thiolato-bridged Fe(II) complex, **1**. Reactivity studies of **1** with several donor ligands afforded a series of mono- and dinuclear thiolato-bridged Fe(II) complexes. Reactions in different solvents showed that mononuclear complexes with terminal thiolate ligands are stabilized (vs. dimerization) in less polar solvents. Because the [S^{Me}N^HS] ligand is readily accessible in good yields, and since metalation is straightforward, it should receive considerable attention for the preparation of new coordination complexes in which thiolate-bridging, meridional

binding, and softer donor atoms are desirable. Given the importance of sulfur-based ligands in metalloenzymes, the $[S^{Me}NS^-]$ ligand offers a new platform for pursuing reactivity models for hydrogenases, nitrile hydratases, and oxygen-atom transferases.

2.5 Experimental Section

2.5.1 General considerations. Experiments were conducted under nitrogen, using Schlenk techniques or an MBraun glove box unless otherwise stated. All solvents were deoxygenated by purging with nitrogen. Toluene, hexanes, diethyl ether and THF were dried on columns of activated alumina using a J. C. Meyer (formerly Glass Contour®) solvent purification system. Benzene- d_6 (C_6D_6) was dried by standing over activated alumina (*ca.* 10 wt. %) overnight, followed by filtration. Acetonitrile (CH_3CN), acetonitrile- d_3 (CD_3CN), dichloromethane, dichloromethane- d_2 (CD_2Cl_2), chloroform ($CHCl_3$), chloroform- d ($CDCl_3$) were dried by refluxing over calcium hydride under nitrogen. After distillation, CH_3CN , dichloromethane, $CHCl_3$, $CDCl_3$ and CD_3CN were further dried by filtration through activated alumina (*ca.* 5-10 wt. %). CD_2Cl_2 was vacuum-transferred before use. Ethanol (EtOH) was dried by refluxing over Mg/I₂ under nitrogen, followed by distillation. All solvents were stored over activated (heated at *ca.* 250°C for >10 h under vacuum) 4 Å molecular sieves except ethanol which was stored over activated 3 Å molecular sieves. Glassware was oven-dried at 150 °C for > 2 h. The following chemicals were obtained commercially, as indicated: 2-(methylthio)benzaldehyde (Aldrich, 90%), 2-aminothiophenol (Alfa Aesar, 98%), Fe(OTf)₂ (Strem, 98%), NaO^tBu (Aldrich, 97%), NaOTf (Aldrich, 98%) PMePh₂ (Aldrich, 99%), P(OMe)₃ (Strem, 97%), 2,6-dimethylphenyl isocyanide (CNxylyl, Aldrich 96%). ¹H, ¹⁹F and ³¹P NMR spectra were recorded on either a 300 MHz Bruker Avance or a 300 MHz Bruker Avance II instrument at room temperature (21-25 °C). ¹³C{¹H} NMR spectra were recorded on a 400 MHz Bruker Avance instrument. NMR spectra were referenced to the residual proton peaks associated with the deuterated solvents (for ¹H NMR, C_6D_6 : 7.16 ppm; CD_3CN : 1.96 ppm, CD_2Cl_2 : 5.32 ppm, $CDCl_3$: 7.26 ppm and for ¹³C{¹H} NMR C_6D_6 : 128.06 ppm, CD_3CN : 1.32 and

118.26 ppm). ^{19}F NMR spectra were referenced to internal 1,3-bis(trifluoromethyl)benzene (BTB) (Aldrich, 99%, deoxygenated by purging with nitrogen, stored over activated 4 Å molecular sieves), set to -63.5 ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR data were referenced to external H_3PO_4 (85% aqueous solution), set to 0.0 ppm. UV-vis spectra were recorded on a Varian Cary 50 Bio UV-Visible spectrophotometer, using sealable quartz cuvettes (1.0 cm path length) and dry CH_2Cl_2 or CH_3CN . IR data were collected on a Thermo Scientific Nicolet 6700 FT-IR spectrometer. Elemental analyses were performed by Canadian Microanalytical Service Ltd. (Delta, British Columbia, Canada) and by Elemental Analysis Service, Université de Montréal, Montréal, Québec. Mass spectra were recorded on an AB Sciex Q1MS mass spectrometer with electrospray ionization (ESI-MS) in positive mode (ion spray voltage: 5000.0 V, TEM: 400 °C, declustering potential: 11.00 V and focusing potential: 300.0 V) with samples prepared to *ca.* 0.05 mg/mL in acetonitrile or in dichloromethane. For electron impact (EI), solid samples were prepared by drying products under vacuum and a Kratos Concept S1 (Hres 7000-10000) mass spectrometer was used. Magnetic susceptibility measurements were obtained on a Quantum Design SQUID magnetometer MPMS-XL7 operating between 1.8 K and 300 K for dc applied fields ranging from -7 T to 7 T. The spin-only magnetic moment in solution at room temperature was obtained by the Evans' method.⁶⁵ Cyclic voltammetry was performed using a Princeton Applied Research Versastat3 potentiostat controlled by Versastudio software. A conventional single compartment 3-electrode configuration with Pt working and counter electrodes and a silver pseudoreference electrode was employed. The measurements were carried out on dichloromethane solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (Aldrich) as supporting electrolyte with a scan rate of 100 mV/s. The experiments were subsequently referenced to the Fc/Fc^+ redox couple of ferrocene.

2.5.2 Synthesis of 2-(2-methylthiophenyl)benzothiazolidine, [$\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}$]. 2-(methylthio)benzaldehyde (1.5 mL, 11.83 mmol) and 2-aminothiophenol (1.4 mL, 13.01 mmol) were added to a 100 mL Schlenk flask charged with a stir bar under nitrogen. 25 mL of EtOH were added and the resulting pale yellow solution was stirred at room temperature overnight under nitrogen. The color of the

reaction mixture changed from pale yellow to off-white and the product precipitated as an off-white solid. Finally, the off-white product was filtered, washed with cold EtOH and dried *in vacuo*. Yield: 3.80 g, 91% based on 2-(methylthio)benzaldehyde. ^1H NMR (300 MHz, CD_3CN) δ 2.52 (s, 3H, S–Me), 5.40 (br s, 1H, N–H), 6.58 (d, 1H, C–H), 6.69 (td, 1H, Ar–H), 6.78 (d, 1H, Ar–H), 6.94 (dd, 1H, Ar–H), 6.98 (dd, 1H, Ar–H), 7.18 (td, 1H, Ar–H), 7.29 (td, 1H, Ar–H), 7.35 (d, 1H, Ar–H), 7.57 (d, 1H, Ar–H). ^{13}C NMR (101 MHz, CD_3CN) δ 16.85 (CH_3), 66.73 (C–NH), 111.03 (Ar–C), 121.25 (Ar–C), 122.95 (Ar–C), 126.58 (Ar–C), 126.73 (Ar–C), 126.88 (Ar–C), 126.89 (Ar–C), 128.06 (Ar–C), 129.90 (Ar–C), 136.66 (Ar–C), 142.60 (Ar–C), 148.65 (Ar–C). UV-vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$): 255 (34,100), 283 (14,500), 311 (11,400). IR (ATR, cm^{-1}): 3339 (N–H), 694 (S–Me). HRMS (EI): Calcd. for $\text{C}_{14}\text{H}_{13}\text{N}_1\text{S}_2$ m/z 259.0490 ($[\text{M}]^+$), found 259.0483. Anal. Calcd. for $\text{C}_{14}\text{H}_{13}\text{NS}_2$: C, 64.83; H, 5.05; N, 5.40; S, 24.72. Found: C, 64.53; H, 5.00; N, 5.40; S, 24.51. Figures S1–S4 for the ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR, UV-vis and EI mass spectra.

2.5.3 Synthesis of $[\text{Fe}_3(\mu_2\text{-S}^{\text{Me}}\text{NS}^-)_4](\text{OTf})_2$ (1). $\text{Fe}(\text{OTf})_2$ (1.00 g, 2.82 mmol), $[\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}]$ (0.731 g, 2.82 mmol) and KO^tBu (0.349 g, 3.11 mmol) were added to a 100 mL round-bottomed Schlenk flask charged with a stir bar and CH_3CN (20 mL), giving a dark blue solution/suspension. The mixture was allowed to stir at room temperature for 12 hours after which time the solution turned dark teal blue. The CH_3CN was removed under vacuum, and the resulting residue was washed with benzene (3×10 mL) and diethyl ether (3×5 mL). The resulting dark residue was concentrated to dryness under vacuum and the residue was extracted into dichloromethane (30 mL), filtered and evaporated *in vacuo*. Finally, the resulting dark blue product was dried *in vacuo*. Yield: 1.10 g, 78% based on $\text{Fe}(\text{OTf})_2$ (> 4 trials). Single crystals suitable for X-ray diffraction were grown from a concentrated chloroform solution at room temperature. UV-vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$): 300 (41,300), 600 (5,500). ^1H NMR (300 MHz, CD_2Cl_2) δ 22.02 (br s, $\Delta\nu_{1/2} = 88$ Hz), 17.70 (br s, $\Delta\nu_{1/2} = 58$ Hz), 15.93 (br s, $\Delta\nu_{1/2} = 95$ Hz), 12.69 (br s, $\Delta\nu_{1/2} = 48$ Hz), 8.34 (br s, $\Delta\nu_{1/2} = 32$ Hz), 5.91 (br s, $\Delta\nu_{1/2} = 32$ Hz), 3.38 (br s, $\Delta\nu_{1/2} = 61$ Hz), -42.07 (br s, $\Delta\nu_{1/2} = 80$ Hz), -54.96 (br s, $\Delta\nu_{1/2} = 323$ Hz). ^{19}F NMR (282 Hz, CD_2Cl_2) δ -78.1 (br s, $\Delta\nu_{1/2} = 56$ Hz, OTf). μ_{eff} (CD_2Cl_2) = $6.4 \mu_{\text{B}}$. Anal.

Calc. for $C_{59.5}H_{49.5}Cl_{4.5}F_6Fe_3N_4O_6S_{10}$: C, 42.55; H, 3.06; N, 3.34. Found: C, 42.42; H, 3.10; N, 3.38.

Figures S5-S7 for the 1H , ^{19}F and UV-vis spectra.

2.5.4 Synthesis of $\{[Fe(\mu-S^{Me}NS^-)(PMePh_2)(CH_3CN)]_2\}(OTf)_2$ (2). Complex **1** (100 mg, 0.07 mmol) and NaOTf (14 mg, 0.08 mmol) were placed in a 20 mL scintillation vial with a stir bar. CH_3CN (5 mL) was added to the vial yielding a teal blue solution, which was vigorously stirred for 15 min. PPh_2Me (40 mg, 0.21 mmol, 37 μ L) was then added dropwise to the vial and the reaction mixture turned to greenish-blue. The mixture was allowed to stir at room temperature for 12 h after which time the solution was filtered and the CH_3CN was removed under vacuum. The resulting dark residue was washed with diethyl ether (3×5 mL) and dried *in vacuo*. Finally, the product was redissolved in CH_3CN , concentrated to *ca.* 2 mL and cooled at $-35^\circ C$ overnight to yield dark greenish-blue crystals of **2**. The crystals were recovered by filtration, washed with cold CH_3CN (*ca.* 3×1 mL) and dried *in vacuo*. Yield after crystallization: 105 mg, 74%. UV-vis (CH_3CN): λ_{max}/nm ($\epsilon/M^{-1} cm^{-1}$): 313 (19,950), 472 (3,100), 572 (1,700). 1H NMR (300 MHz, CD_3CN) δ 1.17 (s, br, 3H, S-Me), 1.65 (s, br, 3H, Me), 1.98 (s, 3H, CH_3CN), 6.54 (s, br, 1H, Ar-H), 6.69 (d, br, 1H, Ar-H), 6.89 (s, br, 2H, Ar-H), 7.33 (m, 11H, Ar-H), 7.72 (s, br, 2H, Ar-H), 7.94 (s, br, 1H, Ar-H), 8.91 (s, br, 1H, N=C-H). $^{31}P\{^1H\}$ NMR (121 MHz, CD_3CN) δ 25.10 (s, PPh_2Me). ^{19}F NMR (282 MHz, CD_3CN) δ -77.9 (br s, $\Delta\nu_{1/2} = 191$ Hz, OTf). Anal. Calc. for $C_{60}H_{56}F_6Fe_2N_4O_6P_2S_6$: C, 51.14; H, 4.01; N, 3.98. Found: C, 50.58; H, 4.19; N, 3.92. Figures S11-S13 for the 1H , $^{31}P\{^1H\}$ and ^{19}F NMR spectra.

2.5.5 Synthesis of $\{[Fe(\mu-S^{Me}NS^-)(CNxylyl)]_2\}(OTf)_2$ (3). Complex **1** (100 mg, 0.07 mmol) and NaOTf (14 mg, 0.08 mmol) were dissolved in 5 mL CH_3CN and vigorously stirred for 15 min after which a solution of CNxylyl (53 mg, 0.40 mmol) was slowly added dropwise, giving a red-brown solution. After stirring for 12 h the reaction mixture was filtered with suction and CH_3CN was removed under vacuum. The resulting dark residue was washed with diethyl ether (3×5 mL) and dried *in vacuo*. THF (5 mL) was then added to the residue yielding a brown solution (not further

characterized) and a red precipitate of **3**. The latter was isolated by filtration, washed with diethyl ether (2×3 mL) and dried *in vacuo*. Yield: 50 mg, 54%. Single crystals suitable for X-ray crystallography were obtained by layering ether over a concentrated CH₃CN solution of **3** at room temperature. UV-vis (CH₃CN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$): 461 (60). ¹H NMR (300 MHz, CD₃CN) δ 1.77 (s, 6H, Me), 2.07 (s, 6H, Me), 2.34 (s, 3H, S–Me), 6.93 (d, 2H, Ar–H), 7.05 (dd, 1H, Ar–H), 7.22 (d, 2H, Ar–H), 7.34 (m, 4H, Ar–H), 7.79 (m, 4H, Ar–H), 8.00 (dd, 1H, Ar–H), 9.17 (s, 1H, N=C–H). ¹³C{¹H} NMR (75 MHz, CD₃CN) δ 18.28 (CH₃), 19.19 (CH₃), 26.18 (CH₃), 68.22 (N=C), 120.53 (Ar–C), 124.24 (Ar–C), 126.16 (Ar–C), 128.25 (Ar–C), 128.80 (Ar–C), 128.92 (Ar–C), 128.99 (Ar–C), 129.12 (Ar–C), 129.28 (Ar–C), 129.80 (Ar–C), 129.91 (Ar–C), 130.94 (Ar–C), 132.51 (Ar–C), 132.76 (Ar–C), 135.06 (Ar–C), 135.44 (Ar–C), 135.80 (Ar–C), 136.16 (Ar–C), 159.53 (Ar–C≡N), 168.94 (Ar–C≡N). ¹⁹F NMR (282 MHz, CD₃CN) δ –79.3 (s, OTf). IR (ATR, cm^{–1}): 2124 (C≡N), 2098 (C≡N). Anal. Calc. for C₆₆H₆₀F₆Fe₂N₆O₆S₆: C, 54.62; H, 4.17; N, 5.79; S, 13.25. Found: C, 54.41; H, 4.22; N, 5.60; S, 13.48. Figures **S14–S17** for the ¹H, ¹³C{¹H}, ¹⁹F NMR, and IR spectra.

2.5.6 Synthesis of {[Fe(μ -S^{Me}NS[–])[P(OMe)₃]₂]₂}(OTf)₂ (4**).** Complex **1** (200 mg, 0.13 mmol) and NaOTf (28 mg, 0.16 mmol) were placed in a 20 mL scintillation vial with 8 mL of CH₃CN and vigorously stirred for 15 min. P(OMe)₃ (97 mg, 0.78 mmol, 92 μ L) was then added dropwise to the vial affording an olive-green solution. After stirring at room temperature for 12 h the reaction mixture was filtered with suction and CH₃CN was removed under vacuum. The resulting dark olive-green residue was washed with diethyl ether (3×5 mL) and dried *in vacuo*. Yield: 180 mg, 65%. UV-vis (CH₃CN): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$): 313 (1,400), 472 (200), 572 (100). ¹H NMR (300 MHz, CD₃CN) δ 1.96 (s, 3H, CH₃CN), 2.17 (s, 3H, S–Me), 3.37 (d, 9H, $J_{\text{HP}} = 9.5$ Hz, P(OMe)₃), 3.81 (d, 9H, $J_{\text{HP}} = 9.5$ Hz, P(OMe)₃), 6.87 (td, 1H, Ar–H), 6.96 (td, 1H, Ar–H), 7.32 (dd, 1H, Ar–H), 7.48 (dd, 1H, Ar–H), 7.54 (td, 1H, Ar–H), 7.66 (td 1H, Ar–H), 7.79 (td, 2H, Ar–H), 8.96 (d, 1H, N=C–H). ³¹P{¹H} NMR (121 MHz, CD₃CN) δ 153.26 (d, $J_{\text{PP}} = 168$ Hz, P(OMe)₃), 164.01 (d,

$J_{PP} = 168$ Hz, $P(OMe)_3$. ^{19}F NMR (282 MHz, CD_3CN) δ -77.6 (br s, $\Delta\nu_{1/2} = 328$ Hz, OTf). Anal. Calc. for $C_{42.5}H_{60.75}F_6Fe_2N_{2.25}O_{18}P_4S_6$: C, 35.62; H, 4.27; N, 2.20; S, 13.42. Found: C, 36.94; H, 4.66; N, 2.10; S, 12.39. Figures S20-S22 for the 1H , $^{31}P\{^1H\}$ and ^{19}F NMR spectra.

2.5.7 Synthesis of $\{Fe(S^{Me}NS^-)[P(OMe)_3]_3\}(OTf)$ (5). Complex **1** (100 mg, 0.07 mmol) and NaOTf (14 mg, 0.08 mmol) were dissolved in 5 mL of dichloromethane in a 20 mL scintillation vial and $P(OMe)_3$ (71 mg, 0.63 mmol, 71 μ L) was added dropwise, yielding a green solution. After stirring at room temperature for 12 h the reaction mixture was filtered with suction and the solvent was removed under vacuum. Diethyl ether (15 mL) and benzene (15 mL) were then added to the resulting dark green residue giving a dark brown oily product and a green solution (not characterized further). The dark brown solid was washed with diethyl ether (3×5 mL) and dried *in vacuo*, giving complex **5** as a dark brown powder. Yield: 100 mg, 65%. UV-vis (CH_2Cl_2): λ_{max}/nm ($\epsilon/M^{-1} cm^{-1}$): 292 (20,600), 396 (3,800), 632 (1,200). 1H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, br, 3H, S-Me), 3.54 (t, br, 18H, $P(OMe)_3$), 3.81 (d, 9H, $J_{HP} = 9.5$ Hz, $P(OMe)_3$), 6.93 (m, br, 3H, Ar-H), 7.32-7.63 (m, br, 5H, Ar-H), 8.90 (s, br, 1H, Ar-H). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ 140.10 (d, $J_{PP} = 133$ Hz, $P(OMe)_3$), 164.10 (t, $J_{PP} = 133$ Hz, $P(OMe)_3$). ^{19}F NMR (282 MHz, $CDCl_3$) δ -77.8 (br s, $\Delta\nu_{1/2} = 104$ Hz, OTf). ESI-MS: Calcd. for $C_{23}H_{39}FeNO_9P_3S_2$ m/z 686.06 ($[M]^+$), found 686.08. Anal. Calc. for $C_{24}H_{39}F_3FeNO_9P_3S_2$: C, 34.50; H, 4.71; N, 1.68; S, 11.51. Found: C, 37.73; H, 4.53; N, 3.14; S, 12.17. Figures S28-S31 for the 1H , $^{31}P\{^1H\}$, ^{19}F NMR and ESI mass spectra.

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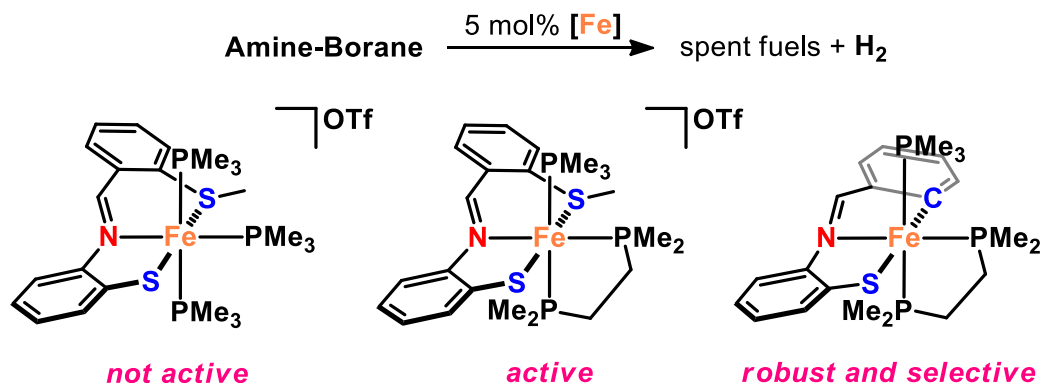
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- 75. Formation of **5** is accompanied by small amounts of diamagnetic and paramagnetic side products.

Chapter 3. Iron-SNS and -CNS complexes: Synthesis, reactivity and amine-borane dehydrogenation catalysis

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3.1 Authors Contributions

Uttam wrote the chapter and conducted preliminary experimental studies and catalysis. Karine optimized and performed all experiments under the supervision of Uttam Das. Gabidullin is responsible for X-ray diffraction studies.

3.2 Abstract

The synthesis, structure and reactivity of an electron-rich Fe(II) thioether-imine-thiolate complex, $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_3](\text{OTf})$ (**1**), prepared by reaction of $(\text{PMe}_3)_4\text{Fe}(\text{OTf})_2$ ($\text{Tf} = \text{SO}_2\text{CF}_3$) with the $\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}$ ligand in THF, are reported. Substitution reactions of **1** with mono- and bidentate donor ligands afforded $[\text{LFe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_2](\text{OTf})$ (**2-6**; $\text{L} = \text{P}(\text{OMe})_3$, CO, CNxyl) and $[(\text{dmpe})\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)](\text{OTf})$ [**7**; $\text{dmpe} = 1,2\text{-bis}(\text{dimethylphosphino})\text{ethane}$]. Heating **1** in THF at 60 °C gave trivalent aryl-imine-thiolate complex, $[\text{Fe}(\text{CNS})(\text{PMe}_3)_3](\text{OTf})$ (**8**) via selective $\text{C}_{\text{aryl}}\text{-S}$ bond cleavage. Reduction of **8** with cobaltocene yielded divalent $[\text{Fe}(\text{CNS})(\text{PMe}_3)_3]$ (**9**), which adds dmpe to give $[(\text{dmpe})\text{Fe}(\text{CNS})(\text{PMe}_3)]$ (**10**). Assessment of dmpe complexes **7** and **10** as precatalysts for amine-borane dehydrogenation catalysis in THF at 60 °C shows that **10** forms a selective and robust bifunctional catalyst system.

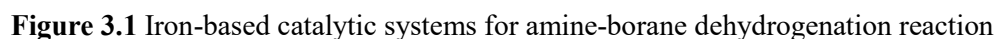
3.3 Introduction

Bifunctional metal complexes are ubiquitous in homogeneous catalysis due to their prominent role in E-H bond (E = H, N, S, Si, C, B) activation reactions¹⁻³ as well as in cooperative catalysis.⁴⁻⁸ Many bifunctional systems including metal-amido,^{5,9} -nacnac,¹⁰⁻¹² -unsaturated pincer linker backbone,^{9,13,14} -phosphinoamidinate,¹⁵ -proximate pendant amine,^{16,17} have been reported which activate different types of E-H bonds via heterolytic splitting. A variety of hard and/or soft donors in the supporting ligands allow for bifunctional E-H bond activation by acting as proton acceptors (i.e., bases) in cooperation with Lewis acidic metals. In this regard, metal-thiolate motifs have gained much attention as potential bifunctional systems. The thiolate group may behave as both σ - and π -donor, typically forms strong bonds to metals, and can serve as terminal or bridging ligands. In addition, metal-bound thiolates have reactive lone-pair electrons available for bifunctional substrate activation. For example, M. Oestreich and co-workers developed cationic Ru(II) thiolate complexes, $[(\text{DmpS})\text{Ru}(\text{PR}_3)]^+\text{BAr}^{\text{F}}_4^-$ (DmpS = 2,6-dimesitylphenyl thiolate, Ar^{F} = 3,5-bis(trifluoromethyl)phenyl) which enable reversible heterolytic splitting of E-H bonds (E = H, Si, and B) across the polar ruthenium-thiolate bond, generating metal hydrides and sulfur-stabilized E^+ cations.⁸ These bifunctional Ru(II) thiolate species were applied to many catalytic applications including dehydrogenative couplings [Si-C, Si-O, Si-N, and B-C],^{18,19} chemoselective hydrogenation and hydrosilylation,¹⁸ and hydrodefluorination reactions.²⁰ Recently, Liao and Wang et al. reported a seminal iron-based bifunctional complex, $\text{Cp}^*\text{Fe}(\kappa^2\text{-P,S})(\text{NCMe})$, containing an arylphosphine-thiolate chelating ligand, which is an active catalyst for regioselective hydroboration of aryl epoxides using pinacolborane.²¹ Many biologically relevant bifunctional metal-thiolate complexes and a variety of synthetic mimics are also known.²²⁻²⁹ We recently reported Fe(II) SNS complexes containing sterically svelte, thioether-imine-thiolate³⁰ and bis (thioether)-amido³¹ ligands as potential bifunctional catalysts. An imine-coupled Fe(II) complex, $[\text{Fe}(\text{N}_2\text{S}_2)]_2$ using the SNS thiolate ligand has also been reported by our group and found to be an efficient and selective

precatalyst for hydroboration of aromatic and aliphatic aldehydes.³² In this work, we show that new electron-rich iron analogs undergo selective C_{aryl}-S bond cleavage, allowing us to compare several Fe-SNS and -CNS complexes as bifunctional catalysts for amine-borane dehydrogenation.

The C-S bond activation of thioether groups by transition metal complexes is a powerful approach in synthetic chemistry for functionalizing sulfur-containing compounds.³³⁻³⁵ This approach has been employed in many catalytic reactions including cross-coupling, alkyne insertion, cyclization, and borylation reactions.³³⁻³⁷ In the petroleum industry, the C-S bond cleavage of thiophene and its derivatives is a key reaction of the hydrodesulfurization (HDS) process by which sulfur is removed from hydrocarbons during petroleum refining. To date, a large array of mid- and late transition metals have been reported for oxidative cleavage of C-S bonds by stoichiometric and catalytic manners under various conditions.^{35,38-41} In some of these cases, cleavage of successive C-S bonds was also observed.³⁵ Selective C_{aryl}-S bond cleavage was recently reported by M. Hirotsu et al. via thermal reactions of quinolyl-substituted thiophenes with iron carbonyls. The addition of a coordinating N-donor group adjacent to the C-S bond of dibenzothiophene moiety facilitates the selective C_{aryl}-S bond cleavage to generate a [NCS]²⁻ ligand.⁴¹ C_{alkyl}-S bond cleavage has also been reported with low-valent iron⁴² and nickel⁴³ complexes. Herein we demonstrate a selective C_{aryl}-S bond cleavage of an electron-rich Fe(II) SNS species that leads to an Fe(III) CNS complex.

Catalytic dehydrocoupling of amine-boranes has become a vibrant area of research because of their potential for utilization as chemical hydrogen-storage materials.⁴⁴⁻⁴⁸ For example, ammonia-borane (NH₃BH₃, AB) has a hydrogen content of 6.5, 13.1 and 19.6% for the step-wise release of the first, second and third equivalents of H₂, respectively.⁴⁸ It has high thermal stability and can release H₂ under mild conditions relative to metal hydrides such as NaAlH₄.^{44,48} Additionally, the dehydrogenation of AB affords valuable B-N bonded inorganic oligomers and/or polymer.^{49,50} The presence of both protic N-H and hydridic B-H bonds makes amine-borane dehydrogenation an ideal test reaction for potential bifunctional catalysts. As a result, a myriad of precious and inexpensive



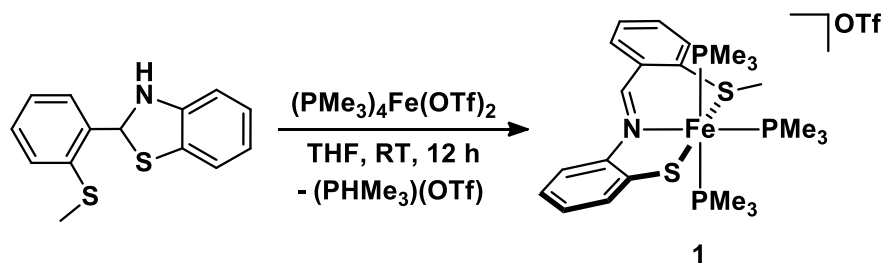
complexes supported by a POCOP pincer ligand. The stable pincer complexes released 2.3-2.5 equivalents of H₂ per AB at 60 °C in 24 h, which is so far the highest amount of hydrogen using iron-based catalytic systems.⁵⁴ Herein, we prepared and characterized several Fe-SNS and -CNS complexes of thioether-imine-thiolate SNS ligand and assessed these complexes as precatalysts for amine-borane dehydrogenation.

3.4 Results and Discussion

3.4.1 Synthesis and Structure of Fe(II) Thiolate Complex, **1**

Treatment of an *in situ* prepared Fe(II) complex, (PMe₃)₄Fe(OTf)₂ with one equiv. of S^{Me}N^HS ligand in THF at room temperature afforded the title complex, [Fe(S^{Me}NS)(PMe₃)₃](OTf) **1** as a dark purple solid in 64% yield (Scheme 3.1). The ¹H NMR spectrum of **1** shows broad resonances at room temperature that sharpen on cooling to -40 °C. Singlets at δ 2.8 due to SMe and δ 9.6 for the imine proton, along with multiplets in the aromatic region confirm coordination of the S^{Me}NS ligand. Similarly, two broad ³¹P{¹H} NMR resonances at room temperature appeared at -40 °C as a triplet and doublet in a 1:2 ratio at 11.1 and -0.35 ppm (²J_{pp} = 50 Hz), respectively, presumably due to facile PMe₃ ligand exchange in solution. We were unable to observe the high-temperature limiting ³¹P NMR spectrum of **1** due to its subsequent reaction at 60 °C (see below).

Scheme 3.1 Synthesis of Fe(II) Thiolate Complex



The molecular structure of **1** confirms the pseudo-octahedral coordination of the meridional S^{Me}NS thiolate and three PMe₃ ligands (Figure 3.1). The Fe-S_{thioether} distance [2.254(1) Å] is shorter than the Fe-S_{thiolate} distance [2.2865(6) Å]. The Fe(1)-P(3) distance *trans* to the imine N [2.255(9)

Å] is longer than those to the *trans* PMe₃'s [Fe(1)-P(1) = 2.384(7) Å; Fe(1)-P(2) = 2.3117(6)] as expected due to the latter's stronger *trans* influence.

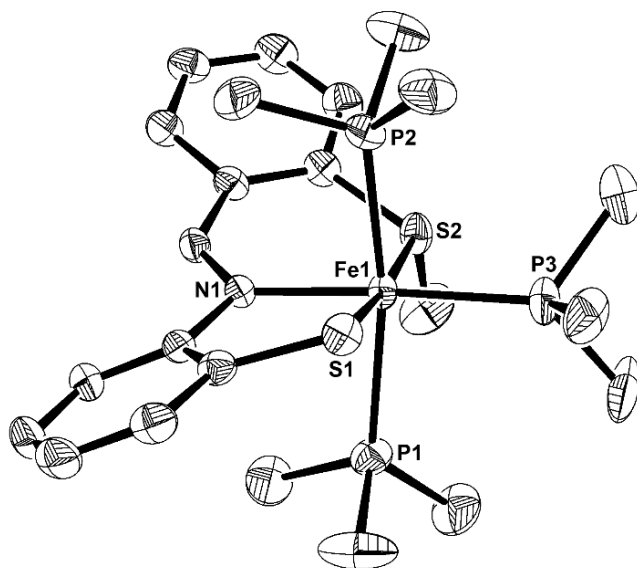
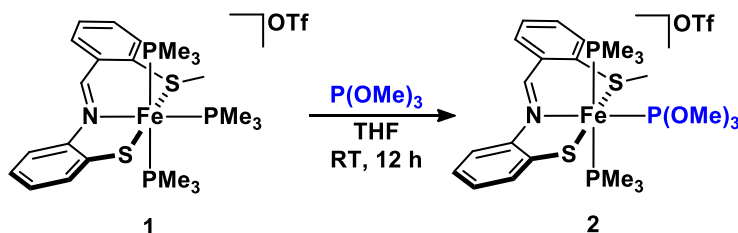


Figure 3.2 Molecular structure of [Fe(S^{Me}NS)(PMe₃)₃](OTf) **1** with 35% thermal probability ellipsoids. Hydrogen atoms and triflate anion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)-S(1) 2.2865(6), Fe(1)-S(2) 2.2544(11), Fe(1)-N(1) 2.0059(16), Fe(1)-P(1) 2.384(7), Fe(1)-P(2) 2.3117(6), Fe(1)-P(3) 2.255(9), N(1)-Fe(1)-S(1) 85.88(5), N(1)-Fe(1)-S(2) 93.44(5), N(1)-Fe(1)-P(2) 87.54(5), N(1)-Fe(1)-P(3) 175.2(2), S(2)-Fe(1)-S(1) 172.45(5), P(2)-Fe(1)-P(1) 168.51(15), P(3)-Fe(1)-P(2) 94.2(2), P(3)-Fe(1)-P(1) 93.8(3).

3.4.2 Reactivity Studies of Fe(II) SNS Thiolate Complex, **1**

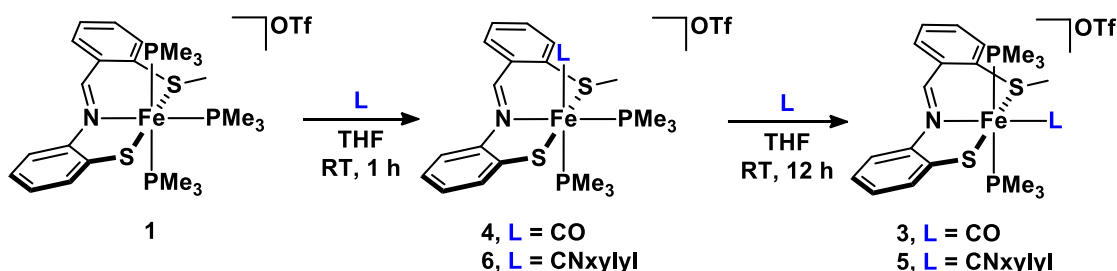
Reactivity studies of complex **1** with several mono- and bidentate neutral donor ligands were performed. Addition of one equiv. trimethylphosphite, P(OMe)₃ to **1** in THF gave an instant color change from purple to purple-brown with formation of a cationic iron complex, [Fe(S^{Me}NS)(PMe₃)₂{P(OMe)₃}]⁺(OTf)⁻ (**2**) in 79% yield (Scheme 3.2). The ³¹P{¹H} NMR spectrum of **2** shows a sharp triplet and doublet in a 1:2 ratio at 165.5 and 4.2 ppm (²J_{PP} = 88 Hz). The ¹H NMR spectrum shows a doublet at δ 4.0 due to phosphite –OCH₃ and a typical pseudotriplet at δ 1.1 due to *trans* phosphine –CH₃ groups. The imine proton appeared as an apparent quartet at δ 9.4 due to phosphorus coupling (⁴J_{HP} = 5 Hz in acetone-d₆).

Scheme 3.2 Synthesis of Cationic Fe(II) Thiolate Complex



Addition of CO to **1** in THF resulted in an instant color change from purple to dark green yielding $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_2(\text{CO})](\text{OTf})$ (**3**) in 90% yield (Scheme 3.3). The ^1H NMR spectrum of **3** shows well-resolved resonances in the diamagnetic region, and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at 6.2 ppm due to the two *trans*- PMe_3 ligands. The IR spectrum of **3** in the solid state shows a sharp strong signal at 1959 cm^{-1} , which is assigned to CO stretching vibration of iron-coordinated carbonyl ligand. Although attempts to substitute more than one phosphine ligand from **1** using CO were unsuccessful, monitoring the reaction by ^{31}P NMR spectroscopy allowed for identification of the expected kinetic *cis*-(PMe_3)₂ isomer **4** (doublets at 20.9 and -1.0 ppm with $^2J_{\text{PP}} = 70$ Hz).

Scheme 3.3 Synthesis of Cationic Fe(II) Thiolate Complexes



Treatment of **1** with one equiv. of 2,6-dimethylphenyl isonitrile (CNxylyl) in THF gave an initial color change to brown and finally to dark maroon overnight, affording $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_2(\text{CNxylyl})](\text{OTf})$ (**5**) in 89% yield (Scheme 3.3). The phosphine $-\text{CH}_3$ groups appeared as a pseudotriplet and the imine proton as a triplet ($^3J_{\text{HP}} = 4$ Hz in acetone- d_6) in the ^1H NMR spectrum. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays a singlet at 8.6 ppm due to the two *trans*- PMe_3 ligands. The IR spectrum of **5** in the solid state shows a sharp strong signal at 2065 cm^{-1} assigned to the $\text{C}\equiv\text{N}$ stretching vibration of iron-coordinated isonitrile. Like CO, the kinetic *cis*-

(PMe₃)₂ isomer **6** (doublets at 18.2 and –3.5 ppm with ²J_{PP} = 64 Hz) was observed by ³¹P NMR spectroscopy. The substitution of more than one phosphine ligand from **1** using excess CNxylyl was unsuccessful.

The molecular structure of **5** (Figure 3.2) confirms formation of the *trans*-(PMe₃)₂ isomer with similar Fe-S and Fe-P distances to those for **1** (see above). The Fe(1)-C(22) distance [1.810(5) Å] is in good agreement with typical Fe(II) isonitrile complexes.⁵⁵⁻⁵⁷

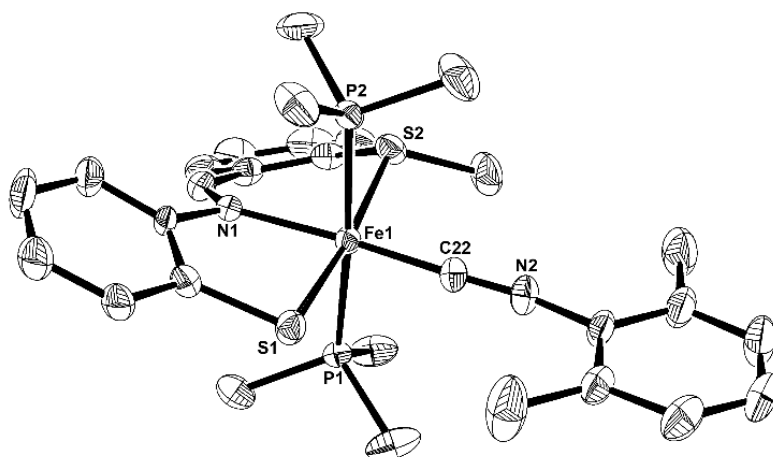
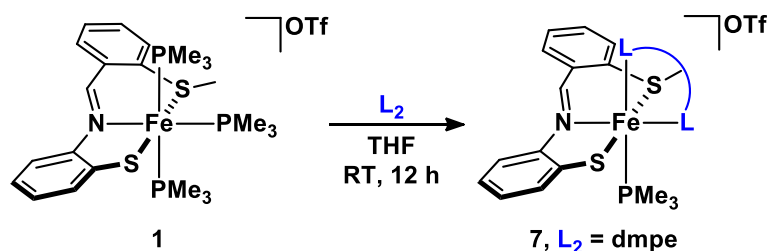


Figure 3.3 Molecular structure of [Fe(S^{Me}NS)(PMe₃)₂(CNxylyl)](OTf) (**5**) with 35% thermal probability ellipsoids. Hydrogen atoms and triflate anion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)-S(1) 2.2902(16), Fe(1)-S(2) 2.2317(15), Fe(1)-N(1) 2.003(4), Fe(1)-P(1) 2.272(4), Fe(1)-P(2) 2.336(8), Fe(1)-C(22) 1.810(5), N(1)-Fe(1)-S(1) 85.73(12), N(1)-Fe(1)-S(2) 89.88(12), N(1)-Fe(1)-C(22) 174.2(4), S(2)-Fe(1)-S(1) 172.70(7), P(2)-Fe(1)-P(1) 175.41(15), C(22)-Fe(1)-S(2) 95.5(5), C(22)-Fe(1)-S(1) 88.7(5).

Next, we examined the reactivity of **1** towards a bidentate phosphine ligand. Addition of one equiv. of dmpe (1,2-bis(dimethylphosphino)ethane) to a THF solution of **1** resulted in an immediate color change from purple to dark maroon. Removal of solvent *in vacuo* yielded [Fe(S^{Me}NS)(dmpe)-(PMe₃)](OTf) (**7**) in 91% yield (Scheme 3.4). The ¹H NMR spectrum of **7** displays doublet resonances at δ 1.0 (²J_{HP} = 9 Hz), 1.1 (²J_{HP} = 8 Hz), 1.4 (²J_{HP} = 9 Hz), and 1.6 (²J_{HP} = 8 Hz) attributed to four inequivalent dmpe CH₃ groups. Another doublet due to the CH₃ groups of PMe₃ is at δ 1.3 (²J_{HP} = 8 Hz) and the inequivalent dmpe backbone methylene protons appeared as overlapping multiplets centred at δ 2.0. The imine proton shows an apparent quartet resonance (⁴J_{HP}

= 4 Hz) due to coupling with PMe_3 and dmpe ligands. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7** shows three doublet of doublets at 56.8 ($^2J_{\text{PP}} = 43, 29$ Hz), 54.8 ($^2J_{\text{PP}} = 163, 29$ Hz), and 3.4 ppm ($^2J_{\text{PP}} = 163, 43$ Hz). The molecular structure of **7** was further established by X-ray crystallography (Figure 3.3).

Scheme 3.4 Synthesis of Cationic Fe(II) Thiolate Complex



The molecular structure of **7** confirms the lack of symmetry observed in the NMR spectra with arms of the dmpe ligand *trans* to P and N (Figure 3.3). The Fe(1)-P(1) distance [2.3025(11) Å] is longer than both Fe(1)-P(2) and Fe(1)-P(3) distances [2.2661(11) and 2.237(2) Å] of the dmpe ligand.

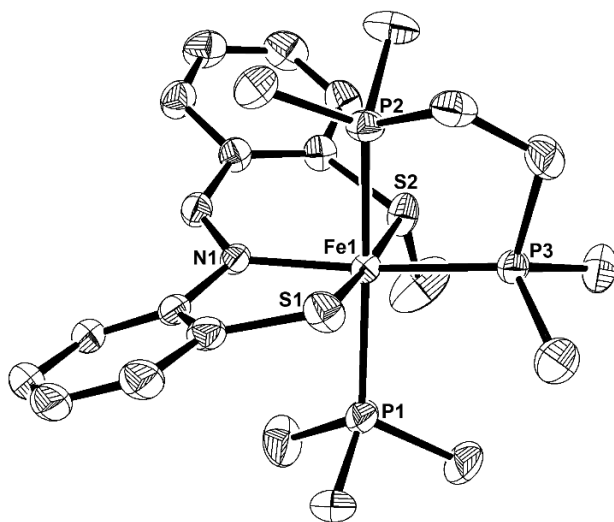
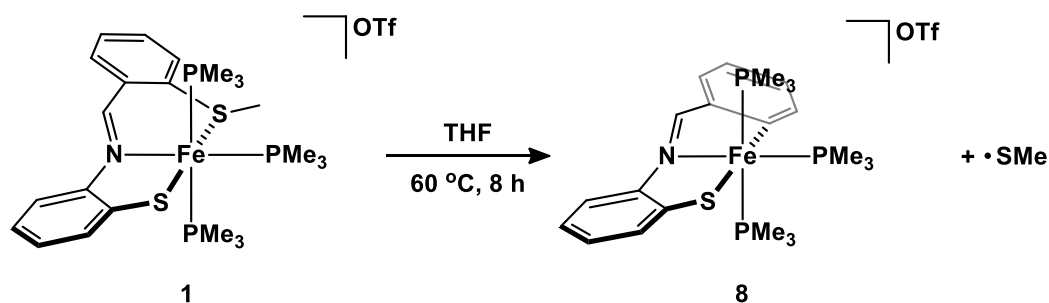


Figure 3.4 Molecular structure of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{dmpe})(\text{PMe}_3)](\text{OTf})$ (**7**) with 35% thermal probability ellipsoids. Hydrogen atoms and triflate anion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)-S(1) 2.2928(11), Fe(1)-S(2) 2.2223(10), Fe(1)-N(1) 1.984(3), Fe(1)-P(1) 2.3025(11), Fe(1)-P(2) 2.2661(11), Fe(1)-P(3) 2.237(2), N(1)-Fe(1)-S(1) 86.10(8), N(1)-Fe(1)-S(2) 94.13(8), N(1)-Fe(1)-P(3) 172.13(11), S(2)-Fe(1)-S(1) 173.38(4), P(2)-Fe(1)-P(1) 170.46(4), P(3)-Fe(1)-P(2) 82.81(8), P(3)-Fe(1)-S(1) 89.02(7), P(3)-Fe(1)-S(2) 90.00(7), P(3)-Fe(1)-P(1) 96.20(8).

3.4.3 Formation of Fe(III) CNS Thiolate Complex, **8**: Selective C_{aryl}-S Bond Cleavage

Thermolysis of the Fe(II) SNS thiolate complex **1** at 60 °C in THF produced a color change from purple to green due to formation of the Fe(III) CNS thiolate complex, [Fe(CNS)(PMe₃)₃](OTf) (**8**) isolated in 65% yield (Scheme 3.5). The molecular structure of **8** was established by single-crystal X-ray diffraction (Figure 3.4).

Scheme 3.5 Synthesis of Fe(III) CNS Thiolate Complex



The molecular structure of **8** shows formation of a new meridional aryl-imine-thiolate CNS ligand resulting from oxidative cleavage of the C_{aryl}-S bond (Figure 3.4). In contrast to the S^{Me}NS thiolate ligand, the dianionic CNS thiolate ligand is planar. The iron center adopts a distorted octahedral geometry. The Fe(1)-N(1) distance [1.9716(17) Å] is shorter than those in complexes **1**, **5** and **7** and the Fe-C bond is typical for those found in Fe(III) aryl complexes.⁵⁸ It should be noted that the mechanism of the oxidative C_{aryl}-S bond cleavage of **1** is unknown as no evidence of expected dimethyl disulphide by-product formation was observed by ¹H NMR spectroscopy during thermolysis of **1**. Attempted •SMe radical trapping experiments using several trapping reagents were also inconclusive. However, ³¹P NMR spectroscopy (Figure A14) and GC-MS revealed the formation of trimethylphosphine sulfide (Me₃P=S). Interestingly, while thermolysis of **1** afforded **8** through oxidative cleavage of the C_{aryl}-S bond, thermal reactions of **2**, **3**, **5** and **7** did not yield such Fe(III) derivatives, indicating that lability of an ancillary PMe₃ ligand in **1** plays a key role in the C-S bond cleavage reaction.

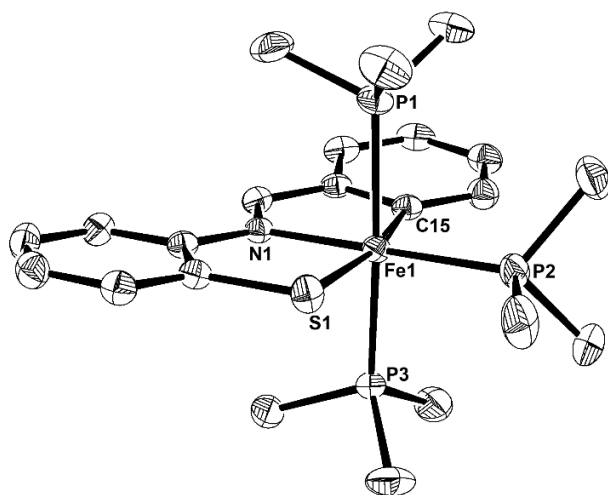


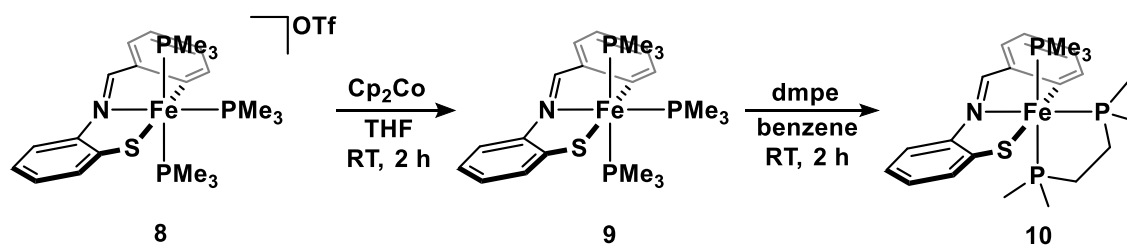
Figure 3.5 Molecular structure of $[\text{Fe}(\text{CNS})(\text{PMe}_3)_3](\text{OTf})$ (**8**) with 35% thermal ellipsoids. Hydrogen atoms and triflate anion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)-S(1) 2.2193(6), Fe(1)-C(15) 1.976(2), Fe(1)-N(1) 1.9716(17), Fe(1)-P(1) 2.3206(6), Fe(1)-P(2) 2.2703(6), Fe(1)-P(3) 2.3142(6), N(1)-Fe(1)-S(1) 85.49(5), N(1)-Fe(1)-C(15) 81.96(8), N(1)-Fe(1)-P(2) 177.75(5), C(15)-Fe(1)-S(1) 167.44(6), P(3)-Fe(1)-P(1) 171.29(2), P(2)-Fe(1)-C(15) 100.07(6), P(2)-Fe(1)-S(1) 92.46(2).

3.4.4 Reactivity Studies of Fe(III) CNS Thiolate Complex, **8**

Addition of one equiv. of Cp_2Co to a THF solution of **8** at room temperature gave an instant color change from green to olive-green, affording the neutral diamagnetic complex, $[\text{Fe}(\text{CNS})(\text{PMe}_3)_3]$ (**9**) as a dark olive-green powder in 88% yield (Scheme 3.6). The ^1H NMR spectrum of **9** shows doublet and pseudotriplet resonances at δ 1.1 and 0.9 ppm due to $-\text{CH}_3$ groups of PMe_3 , typical of meridional FeP_3 coordination. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **9** shows a sharp triplet and doublet in a 2:1 ratio at 23.2 and 9.9 ppm ($^2J_{\text{PP}} = 61$ Hz).

Treatment of **9** with one equiv. of dmpe in THF gave an immediate color change from olive-green to purple. Removal of solvent *in vacuo* yielded $[\text{Fe}(\text{CNS})(\text{dmpe})(\text{PMe}_3)]$ (**10**) in 88% yield (Scheme 3.6). The ^1H NMR spectrum of **10** displays four overlapped doublet resonances at δ 1.2 attributed to the four inequivalent dmpe CH_3 groups. Another doublet attributed to the PMe_3 CH_3 groups was observed at δ 1.0 ppm ($^2J_{\text{HP}} = 8$ Hz). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **10** shows three doublet of doublets at 66.9 ($^2J_{\text{PP}} = 58, 41$ Hz), 60.0 ($^2J_{\text{PP}} = 115, 41$ Hz), and 11.8 ($^2J_{\text{PP}} = 115, 58$ Hz) ppm.

Scheme 3.6 Synthesis of Fe(II) CNS Thiolate Complexes



3.4.5 Amine-Borane Dehydrogenation Catalysis

In order to explore the potential bifunctional behavior of Fe(II) thiolate complexes, the Fe(II) SNS cationic and neutral CNS thiolate complexes were assessed as precatalysts for amine-borane dehydrogenation. The Fe(II) SNS cationic species **1-6** and Fe(II) CNS neutral complex **9** showed no catalytic activity for the dehydrogenation of ammonia-borane (AB, 20 equiv.) at 60° C with formation of a black precipitate indicating decomposition. However, dmpe complexes **7** and **10** were both catalytically active. For instance, immediate gas evolution was observed when a solution of **7** in THF was mixed with AB (20 equiv.) at 60° C. The reaction mixture changed color from maroon to red, accompanied by formation of an off-white precipitate of polyaminoborane.⁴⁹ After 2 h, the ¹¹B NMR spectrum (Figure A19) of soluble materials showed a doublet at 30.7 ppm and a broad resonance at 25.8 ppm due to the formation of borazine and polyborazylene, respectively. Other observable boron resonances between -5 to -15 ppm are assigned to linear and branched aminoborane oligomers.^{44,51} The ¹H NMR spectrum (Figure A25) displayed a few multiplet hydride resonances, suggesting bifunctional AB activation. Most importantly, multiplets at -36.4 and -37.5 ppm in the ¹¹B{¹H} NMR spectrum (Figure A19) can be assigned to BH₃•PMe₃ and BH₃•PMe₂CH₂CH₂PMe₂[L] where L could be BH₃ or the Fe center. Precatalyst **10** gave improved selectivity yielding only the branched cyclic aminoborane tetramer (Figure A23) in addition to borazine and polyborazylene. Although the high field multiplets are again observed in the ¹¹B NMR spectrum, the catalyst derived from **10** remained active and could be reused several times although longer reaction times were required to consume the second and third batches of AB. The above

observations are indicative of slow catalyst degradation. Intrigued by this promising result, complexes **7** and **10** were further assessed as precatalysts for dehydrogenation of methylamine-borane (MeAB), *N,N*-dimethylamine-borane (DMAB) and trimethylamine-borane (TMAB). The precatalysts **7** and **10** show similar catalytic activity with both MeAB and DMAB (20 equiv. in THF at 60 °C for 2 h) as observed with AB. However, TMAB shows no reaction (Figure A22) with these complexes even at 60 °C for 24 h, suggesting that activation of both protic N-H and hydridic B-H bonds of amine-boranes is occurring in a bifunctional manner. The isolation and characterization of intermediate iron hydride complexes is currently in progress to check for formation of B-S bonds.

3.5 Conclusions

In summary, we have demonstrated the synthesis, structure and reactivity of an electron-rich Fe(II) thioether-imine-thiolate complex, $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_3](\text{OTf})$ (**1**) which is prepared by reaction of $(\text{PMe}_3)_4\text{Fe}(\text{OTf})_2$ ($\text{Tf} = \text{SO}_2\text{CF}_3$) with the $\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}$ ligand in THF. Substitution reactions of **1** with mono- and bidentate donor ligands afforded a series of Fe(II) SNS cationic complexes, $[\text{LFe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_2](\text{OTf})$ (**2-6**; $\text{L} = \text{P}(\text{OMe})_3$, CNxyl , CO) and $[\text{L}_2\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)](\text{OTf})$ [**7**; $\text{L}_2 = 1,2\text{-bis}(\text{dimethylphosphino})\text{ethane (dmpe)}$]. Thermolysis of **1** in THF yielded trivalent aryl-imine-thiolate complex, $[\text{Fe}(\text{CNS})(\text{PMe}_3)_3](\text{OTf})$ (**8**) via selective $\text{C}_{\text{aryl}}\text{-S}$ bond cleavage. Reduction of **8** with cobaltocene followed by addition of dmpe afforded divalent neutral complex, $[(\text{dmpe})\text{Fe}(\text{CNS})(\text{PMe}_3)]$ (**10**). Assessment of dmpe complexes **7** and **10** as precatalysts for amine-borane dehydrogenation catalysis in THF at 60 °C reveals that whereas the cationic dmpe complex **7** is active in dehydrogenating amine-borane, the neutral dmpe species **10** forms a selective and robust bifunctional catalyst system. In previous work with iron SNS amido complexes we demonstrated Fe-S_{thioether} bond lability that was selective to the 6-membered ring.³¹ With iron SNS thiolato complexes, imine coupling of two SNS ligands afforded a redox active N_2S_2 ligand.³² In this work, we show that electron-rich iron SNS thiolate complex selectively cleave the $\text{C}_{\text{aryl}}\text{-S}$ bond

affording a new aryl-imine-thiolate CNS ligand. Although the location of the aryl donor in a non-central position of the tridentate chelate may eventually lead to a bidentate NS ligand in some catalytic applications, preliminary spectroscopic analysis of the electron-rich iron complexes reported herein suggests some stability in dehydrocoupling reactions that need not involve a reductive elimination step.

3.6 Experimental Section

3.6.1 General considerations. Experiments were conducted under nitrogen, using Schlenk techniques or an MBraun glove box unless otherwise stated. Hexanes, diethyl ether and THF were collected from solvent purification system. Acetone ($\text{CH}_3)_2\text{CO}$ was dried by refluxing over activated Mg turnings. Acetone- d_6 ($(\text{CD}_3)_2\text{CO}$), acetonitrile (CH_3CN), CD_3CN , dichloromethane, dichloromethane- d_2 (CD_2Cl_2) and THF- d_8 ($\text{C}_4\text{D}_8\text{O}$) were dried by refluxing over calcium hydride under nitrogen. After distillation, CH_3CN and dichloromethane were further dried by filtration through activated alumina (*ca.* 5-10 wt. %). CD_2Cl_2 , $(\text{CD}_3)_2\text{CO}$ and $\text{C}_4\text{D}_8\text{O}$ were vacuum-transferred before use. All solvents were stored over activated (heated at *ca.* 250 °C for >10 h under vacuum) 4 Å molecular sieves except acetone and acetone- d_6 . Glassware was oven-dried at 150 °C for >2 h. The following chemicals were obtained commercially, as indicated: $\text{Fe}(\text{OTf})_2$ (Strem, 98%), PMe_3 (Strem, 99%), $\text{P}(\text{OMe})_3$ (Strem, 97%), 2,6-dimethylphenyl isocyanide (CNxyl yl, Aldrich 96%), 1,2-bis(dimethylphosphino)ethane (dmpe, Strem, 98%), Ammonia-borane (AB, Scitix, 91%), cobaltocene (CoCp_2 , Strem, 98%). ^1H and ^{31}P NMR spectra were recorded on either a 300 MHz Bruker Avance or a 300 MHz Bruker Avance II instrument at room-temperature (21-25 °C). $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a 400 MHz Bruker Avance instrument. NMR spectra were referenced to the residual proton peaks associated with the deuterated solvents (for ^1H NMR CD_2Cl_2 : 5.32 ppm, $(\text{CD}_3)_2\text{CO}$: 2.05 ppm, $\text{C}_4\text{D}_8\text{O}$: 1.72 and 3.58 ppm). $^{31}\text{P}\{^1\text{H}\}$ NMR data were referenced to external H_3PO_4 (85% aqueous solution), set to 0.0 ppm. IR data were collected on a Thermo Scientific Nicolet 6700 FT-IR spectrometer. Elemental analyses were performed by

Elemental Analysis Service, Université de Montréal, Montréal, Québec. The $S^{Me}N^H S$ ligand was prepared using a previously reported procedure.³⁰

3.6.2 Synthesis of $[Fe(S^{Me}NS)(PMe_3)_3](OTf)$ (1). A 250 mL Schlenk flask was charged with $Fe(OTf)_2$ (1.00 g, 2.82 mmol), $S^{Me}N^H S$ ligand (0.731 g, 2.82 mmol, 1 equiv.) and 60 mL of THF giving an off-white solution/suspension. The resulting solution was vigorously stirred for half an hour. A dropping funnel was charged with PMe_3 (1.72 mg, 22.6 mmol, 2.32 mL, 4 equiv.) and in 10 mL of THF and connected to the 250 mL Schlenk flask. The THF solution of PMe_3 was then added dropwise to the off-white solution/suspension. Upon addition of PMe_3 , the color of the reaction mixture slowly turned to dark purple. The resulting solution was stirred overnight at room temperature, THF was removed under vacuum, and the resulting dark purple residue was extracted into THF (50 mL) and filtered through Celite. Finally, the resulting solution was concentrated and cooled at $-35\text{ }^{\circ}\text{C}$ overnight to yield dark purple crystals of **1**. The crystals were recovered by filtration, washed with cold diethyl ether (*ca.* $3 \times 5\text{ mL}$) and THF ($3 \times 5\text{ mL}$) and dried *in vacuo*. Yield after crystallization: 2.5 g, 64% based on $Fe(OTf)_2$. ^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$ at $-40\text{ }^{\circ}\text{C}$) δ 1.2 (s, 18H, PMe_3), 1.6 (s, 3H, PMe_3), 2.8 (s, 3H, S-Me), 7.0 (d, 2H, Ar-H), 7.4 (s, 1H, Ar-H), 7.7 (s, 2H, Ar-H), 8.0 (t, 3H, Ar-H), 9.6 (s, 1H, N=C-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, $(\text{CD}_3)_2\text{CO}$ at $-40\text{ }^{\circ}\text{C}$) -0.35 (d, $^2J_{\text{PP}} = 50\text{ Hz}$, PMe_3), 11.1 (d, $^2J_{\text{PP}} = 50\text{ Hz}$, PMe_3) ppm. Anal. Calc. for $\text{C}_{24}\text{H}_{39}\text{F}_3\text{FeNO}_3\text{P}_3\text{S}_3$: C, 41.68; H, 5.68; N, 2.03; S, 13.91. Found: C, 41.62; H, 5.82; N, 2.03; S, 14.11. See Figures A1-A2 for the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra.

3.6.3 Synthesis of $[Fe(S^{Me}NS)(PMe_3)_2\{P(OMe)_3\}](OTf)$ (2). $[Fe(S^{Me}NS)(PMe_3)_3](OTf)$ (**1**) (48 mg, 0.07 mmol) was placed in a 20 mL scintillation vial. THF (10 mL) was added to the vial yielding a dark purple solution. $P(OMe)_3$ (9 mg, 0.07 mmol, 8.2 μL , 1 equiv.) was added dropwise to the vial and the color of the reaction mixture instantly changed to purple brown. The mixture was allowed to stir at room temperature for 2 h, THF was removed under vacuum, and the resulting dark residue was washed with diethyl ether ($3 \times 3\text{ mL}$) and dried *in vacuo*. Yield: 41 mg, 79%. ^1H

NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$) δ 1.1 (t, 18H, $J_{\text{HP}} = 4$ Hz, PMe_3), 2.8 (s, 3H, S–Me), 4.0 (d, 9H, $^3J_{\text{HP}} = 10$ Hz, $\text{P}(\text{OMe})_3$), 6.95 (d, 1H, Ar–H), 7.03 (dt, 2H, Ar–H), 7.40 (d, 1H, Ar–H), 7.64 (dd, 2H, Ar–H), 7.79 (m, 2H, Ar–H), 8.05 (m, 1H, Ar–H), 9.4 (q, 1H, $^4J_{\text{HP}} = 5$ Hz, N=C–H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, $(\text{CD}_3)_2\text{CO}$) 4.2 (d, $^2J_{\text{PP}} = 88$ Hz, PMe_3), 165.5 (t, $^2J_{\text{PP}} = 88$ Hz, $\text{P}(\text{OMe})_3$) ppm. Anal. Calc. for $\text{C}_{24}\text{H}_{40}\text{F}_3\text{FeNO}_6\text{P}_3\text{S}_3$: C, 38.93; H, 5.44; N, 1.89; S, 12.99. Found: C, 38.72; H, 5.44; N, 1.80; S, 13.25. See Figures A3–A4 for the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra.

3.6.4 Synthesis of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_2(\text{CO})](\text{OTf})$ (3). A 50 mL ampoule was charged with complex **1** (72 mg, 0.10 mmol) and 10 mL THF yielding a dark purple solution that was freeze-pump-thawed (two times) using liquid nitrogen and then exposed to CO gas (10 psi) under vacuum. The resulting dark green solution was stirred overnight at room temperature by which time no further color change was observed. THF was removed under vacuum, the resulting dark residue was washed with diethyl ether (3×3 mL) and dried *in vacuo*. Yield: 60 mg, 90%. ^1H NMR (300 MHz, CDCl_3) δ 1.3 (s, 18H, PMe_3), 2.9 (s, 3H, S–Me), 7.1 (m, 2H, Ar–H), 7.4 (m, 1H, Ar–H), 7.7 (m, 2H, Ar–H), 7.6 (dd, 2H, Ar–H), 7.9 (m, 2H, Ar–H), 8.2 (m, 1H, Ar–H), 9.1 (s, 1H, N=C–H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CDCl_3) 6.2 (s, PMe_3) ppm. IR (ATR, cm^{-1}): 1959 (CO). Anal. Calc. for $\text{C}_{22}\text{H}_{30}\text{F}_3\text{FeNO}_4\text{P}_2\text{S}_3$: C, 41.06; H, 4.70; N, 2.18; S, 14.95. Found: C, 40.81; H, 5.08; N, 2.03; S, 14.41. See Figures A5–A7 and A26 for the ^1H , $^{31}\text{P}\{^1\text{H}\}$ NMR and IR spectra.

3.6.5 Synthesis of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_2(\text{CNxyllyl})](\text{OTf})$ (5). A 20 mL scintillation vial was charged with $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_3](\text{OTf})$ (**1**) (50 mg, 0.07 mmol), CNxyllyl (9 mg, 0.07 mmol, 1 equiv.) and THF (10 mL). The resulting brown mixture was allowed to stir at room temperature overnight by which time the color further changed to dark maroon. THF was removed under vacuum and the product was dissolved in THF, concentrated to ca. 2 mL and left at room temperature overnight to yield dark maroon crystals of **5**. The crystals were recovered by filtration, washed with cold diethyl ether (ca. 3×2 mL) and dried *in vacuo*. Yield after crystallization: 48 mg, 89%. ^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$) 60.3 mg, 90%. ^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$) δ 1.3 (t, $J_{\text{HP}} = 4$ Hz, 18H, PMe_3),

2.5 (s, 6H, CH₃-CNAr), 3.1 (s, 3H, S-Me), 7.00 (td, 1H, Ar-H), 7.09 (td, 1H, Ar-H), 7.24 (m, 3H, Ar-H), 7.42 (dd, 1H, Ar-H), 7.69 (m, 2H, Ar-H), 7.79 (m, 1H, Ar-H), 7.88 (m, 1H, Ar-H), 9.3 (t, $J_{\text{HP}} = 4$ Hz, 1H, N=C-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, (CD₃)₂CO) 8.6 (s, PMe₃) ppm. IR (ATR, cm⁻¹): 2065 (C≡N). Anal. Calc. for C₃₀H₃₉F₃FeN₂O₃P₂S₃: C, 48.26; H, 5.26; N, 3.75; S, 12.88. Found: C, 48.47; H, 5.58; N, 3.60. See Figures A8-A11 and A27 for the ^1H , $^{31}\text{P}\{^1\text{H}\}$ NMR and IR spectra.

3.6.6 Synthesis of [Fe(S^{Me}NS)(PMe₃)(dmpe)](OTf) (7). [Fe(S^{Me}NS)(PMe₃)₃](OTf) (**1**) (50 mg, 0.07 mmol) was placed in a 20 mL scintillation vial. THF (10 mL) was added to the vial yielding a dark purple solution. 1,2-bis(dimethylphosphino)ethane, dmpe (11 mg, 0.20 mmol, 12 uL, 1 equiv.) was added dropwise to the vial and the color of the reaction mixture instantly changed to dark maroon. The mixture was allowed to stir at room temperature for 2 h. Finally, the resulting maroon solution was concentrated to *ca.* 2 mL and left at room temperature overnight to yield dark maroon crystals of **7**. The crystals were recovered by filtration, washed with cold diethyl ether (*ca.* 3 × 2 mL) and dried *in vacuo*. Yield after crystallization: 45 mg, 91%. ^1H NMR (300 MHz, THF-d₈) δ 1.0 (d, $^2J_{\text{HP}} = 9$ Hz, 3H, CH₃), 1.09 (d, $^2J_{\text{HP}} = 8$ Hz, 3H, CH₃), 1.28 (d, $J_{\text{HP}} = 8$ Hz, 9H, PMe₃), 1.42 (d, $^2J_{\text{HP}} = 9$ Hz, 3H, CH₃), 1.64 (d, $^2J_{\text{HP}} = 9$ Hz, 3H, CH₃), 2.01 (m, 4H, CH₂), 2.55 (s, 3H, S-Me), 6.93 (m, 2H, Ar-H), 7.30 (dd, 1H, Ar-H), 7.58 (q, 2H, Ar-H), 7.68 (d, 1H, Ar-H), 7.85 (m, 1H, Ar-H), 8.02 (m, 1H, Ar-H), 9.32 (q, 1H, $^4J_{\text{HP}} = 4$ Hz, N=C-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, THF-d₈) 3.4 (dd, $^2J_{\text{cis PMe}_3\text{-P(dmpe)}} = 43$ Hz, $^2J_{\text{trans PMe}_3\text{-P(dmpe)}} = 163$ Hz, PMe₃), 54.8 (dd, $^2J_{\text{trans P(dmpe)-PMe}_3} = 163$ Hz, $^2J_{\text{PP(dmpe)}} = 29$ Hz, dmpe), 56.8 (dd, $^2J_{\text{cis P(dmpe)-PMe}_3} = 43$ Hz, $^2J_{\text{PP(dmpe)}} = 29$ Hz, dmpe) ppm. Anal. Calc. for C₂₅H₄₀F₃FeNO₃P₃S₃: C, 42.62; H, 5.72; N, 1.99; S, 13.65. Found: C, 42.50; H, 5.80; N, 1.86; S, 14.03. Figures A12-A13 for the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra.

3.6.7 Synthesis of trivalent [Fe(S^{Me}NC)(PMe₃)₃](OTf) (8). A 50 mL ampoule was charged with complex **1** (51 mg, 0.09 mmol) and 10 mL THF yielding a dark purple solution. The ampoule was heated to 60 °C for 8 hr by which time the colour of the reaction mixture changed from dark purple to green. THF was removed under vacuum and the resulting solution was extracted with CH₂Cl₂

(15 mL) and filtered to give a green solution. CH_2Cl_2 was removed under vacuum and the resulting green residue was dissolved in THF (*ca.* 2 mL) and cooled to $-35\text{ }^\circ\text{C}$ to yield green crystals of **8**. The crystals were recovered by filtration, washed with cold diethyl ether (*ca.* $3 \times 2\text{ mL}$) and dried *in vacuo*. Yield after crystallization: 44 mg, 65%. Anal. Calc. for $\text{C}_{23}\text{H}_{36}\text{F}_3\text{FeNO}_3\text{P}_3\text{S}_2$: C, 42.87; H, 5.63; N, 2.17; S, 9.95. Found: C, 42.88; H, 5.86; N, 2.07; S, 10.53.

3.6.8 Synthesis of $[\text{Fe}(\text{S}^{\text{Me}}\text{NC})(\text{PMe}_3)_3](\text{OTf})$ (9**).** A 15 mL scintillation vial was charged with complex **8** (22 mg, 0.04 mmol, 1 equiv.), bis(cyclopentadienyl)cobalt(II) (Cp_2Co) (14 mg, 0.08 mmol, 2 equiv.) and 4 mL THF yielding a dark green solution. The mixture was allowed to stir at room temperature for 2 hr resulting in an olive-green solution. THF was removed under vacuum. The resulting green powder was dissolved in benzene and filtered. Solvent was removed from the filtrate and the resulting olive-green powder was dried *in vacuo*. Yield: 14 mg, 88%. ^1H NMR (300 MHz, C_6D_6) δ 0.9 (t, 18H, $J_{\text{HP}} = 3\text{ Hz}$, PMe_3), 1.1 (d, $J_{\text{HP}} = 7\text{ Hz}$, 9H, PMe_3), 6.6 (td, 1H, Ar-H), 6.7 (td, 1H, Ar-H), 6.8 (t, 2H, Ar-H), 6.9 (d, 1H, Ar-H), 7.2 (m, 1H, Ar-H), 7.4 (m, 1H, Ar-H), 7.6 (dd, 1H, Ar-H), 8.4 (td, 1H, $J_{\text{HP}} = 3\text{ Hz}$, $\text{N}=\text{C}-\text{H}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6) 9.9 (d, $^2J_{\text{PP}} = 61\text{ Hz}$, PMe_3), 23.2 (t, $^2J_{\text{PP}} = 61\text{ Hz}$, PMe_3) ppm. See Figures A15-A16 for the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra.

3.6.9 Synthesis of $[\text{Fe}(\text{SNC})(\text{PMe}_3)(\text{dmpe})]$ (10**).** $[\text{Fe}(\text{S}^{\text{Me}}\text{NC})(\text{PMe}_3)_3]$ (**9**) (14 mg, 0.03 mmol, 1 equiv.) was placed in a 15 mL scintillation vial. Benzene (4 mL) was added to the vial yielding an olive-green solution. 1,2-bis(dimethylphosphino)ethane, dmpe (5 mg, 0.03 mmol, 6 μL , 1 equiv.) was added to the vial and the colour of the reaction mixture changed to dark purple. The mixture was allowed to stir at room temperature for 2 h. Solvent was removed, and the resulting purple powder was dried *in vacuo*. Yield: 12 mg, 88%. ^1H NMR (300 MHz, C_6D_6) δ 0.95 (d, $^2J_{\text{HP}} = 8\text{ Hz}$, 9H, PMe_3), 1.2 (m, 12H, CH_3), 1.35 (m, 4H, CH_2), 6.67 (t, 1H, Ar-H), 6.83 (m, 3H, Ar-H), 7.08 (d, 1H, Ar-H), 7.25 (d, 1H, Ar-H), 7.31 (d, 1H, Ar-H), 7.69 (d, 1H, Ar-H), 8.49 (td, 1H, $J_{\text{HP}} = 3\text{ Hz}$, $\text{N}=\text{C}-\text{H}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6) 11.8 (dd, $^2J_{\text{cis PMe}_3-\text{P}(\text{dmpe})} = 58\text{ Hz}$, $^2J_{\text{trans PMe}_3-\text{P}(\text{dmpe})} = 115$

Hz, PMe₃), 60.0 (dd, $^2J_{\text{trans P(dmpe)-PMe}_3} = 115$ Hz, $^2J_{\text{PP(dmpe)}} = 41$ Hz, dmpe), 66.9 (dd, $^2J_{\text{cis P(dmpe)-PMe}_3} = 58$ Hz, $^2J_{\text{PP(dmpe)}} = 41$ Hz, dmpe) ppm. See Figures A17-A18 for the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra.

3.6.10 Procedure for amine-borane dehydrogenation catalysis. In a J. Young NMR tube, 5 mg of ammonia-borane (AB, 20 equiv.) was mixed with 5.5 mg crystals of **7** or 4 mg solid of **10** in THF (0.3 mL). The NMR solution was then heated at 60 °C for 2 h over which time the color of the solution changed from purple to brown-red for **7** and purple to red for **10**. The progress of the reaction was monitored by ^{11}B , $^{11}\text{B}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. After 2 h, the resulting solution was filtered, and THF was removed using vacuum. The resulting solid was further characterized by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. For dehydrogenation catalysis using methylamine-borane (MeAB) and dimethylamine-borane (DMAB), in a J. Young NMR tube, 5 mg of MeAB (20 equiv.) or DMAB (20 equiv.) was mixed with required amount of **7** or **10** in THF (0.3 mL). The NMR solution was then heated at 60 °C for 2 h. The progress of the reaction was monitored by ^{11}B , $^{11}\text{B}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. After 2 h, the resulting solution was filtered, and THF was removed using vacuum. The resulting solid was then characterized by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. For dehydrogenation catalysis using trimethylamine-borane (TMAB), a J. Young NMR tube was charged with 10 mg TMAB (20 equiv.) and 5 mg of **7** or 3 mg of **10** in THF (0.3 mL). The NMR solution was then heated at 60 °C for 24 h after which time no color change was observed and the resulting solution was characterized by ^{11}B and $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy.

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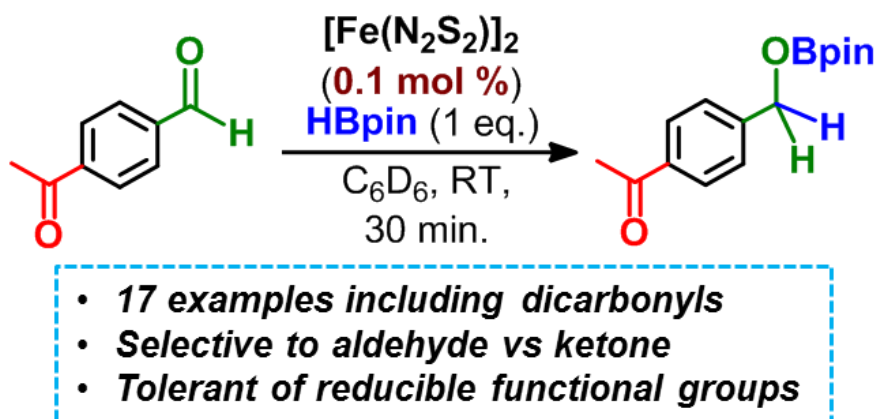
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Chapter 4. Efficient and selective iron complex-catalyzed hydroboration of aldehydes

4.1 Published Contributions

Efficient and Selective Iron Complex-Catalyzed Hydroboration of Aldehydes

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Author Contributions

Uttam and Prof. Baker wrote the manuscript. Uttam performed all experiments presented. Carolyn carried out reaction progress kinetic studies and described the studies under the supervision of Prof. Hein. Bulat was responsible for X-ray diffraction studies.

Abstract

An imine-coupled $[\text{Fe}-\text{N}_2\text{S}_2]_2$ complex, prepared from a readily-available benzothiazolidine ligand, catalyzes selectively the hydroboration of aliphatic and aromatic aldehydes at low catalyst loadings (0.1 mol %) using pinacolborane. Both mono- and disubstituted aromatic and aliphatic aldehydes are hydroborated selectively in the presence of ketones, nitriles, alkenes, amines, and halides. Reaction of the $[\text{Fe}-\text{N}_2\text{S}_2]_2$ complex with CO and preliminary reaction progress kinetic studies point to a complex mechanism.

4.2 Introduction

Catalytic hydroboration of carbonyl compounds using pinacolborane (HBpin) represents an attractive strategy in organic synthesis¹ not only for synthesizing widely used borate ester intermediates,^{2,3} but also for conversion into the corresponding alcohols.⁴ Since the Bpin group can serve as a versatile directing and protecting group, this catalytic process enjoys further advancement in synthetic chemistry.⁵⁻⁸ Intrigued by recent reports from C. Gunanathan and co-workers of selective aldehyde (vs. ketone) hydroboration catalysed by a simple Ru precursor,⁹ we disclose herein an efficient and strictly selective iron-based catalyst containing an imine-coupled, redox-active N₂S₂ ligand.

To date, hydroboration catalysts for carbonyl compounds based on transition metals (Ti,¹⁰⁻¹⁴ Mo,¹⁵ Fe,¹⁶ Ru,⁹ Co,¹⁷ and Cu¹⁸), main group metals (Li,¹⁹ Mg,²⁰⁻²² Ca,²³ Al,^{24,25} Ga,²⁶ Zn,²⁷⁻³⁰ Ge and Sn³¹), and main group elements (P),³² are known. Recently, rare-earth metal catalysts,^{33,34} and a silica-supported Zr catalyst³⁵ have also been reported. Selective hydroboration of aldehyde over ketone, however, has only recently been reported using Fe(acac)₃,¹⁶ aluminum monohydride,²⁵ diazaphosphine,³² and [(*p*-cymene)RuCl₂]₂⁹ catalysts. In these cases, ketones can also be hydroborated by increasing either the catalyst loading, reaction temperature or reaction time.

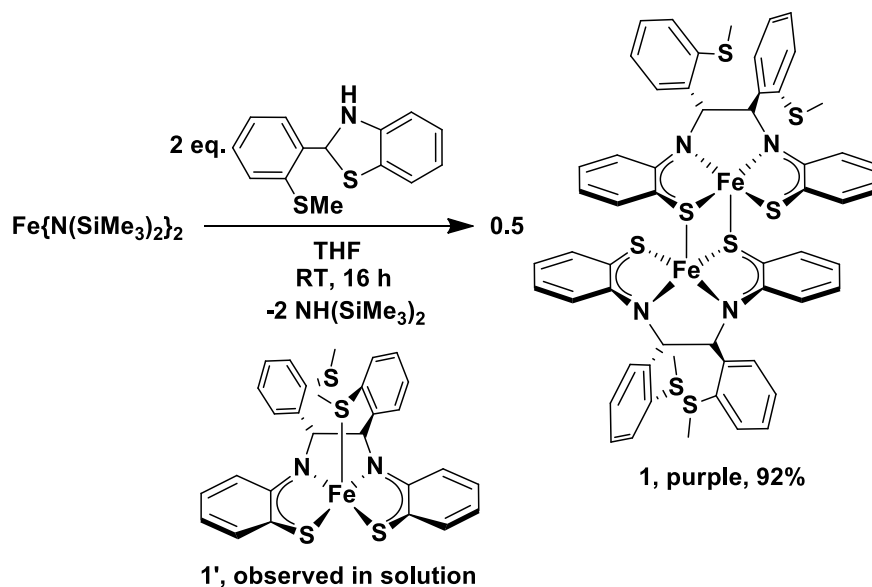
Herein we report the synthesis of a paramagnetic, imine-coupled Fe(II) complex, [Fe(N₂S₂)]₂ **1** and its application to selective hydroboration catalysis of various aliphatic and aromatic aldehydes at low catalyst loading (0.1 mol %) at room temperature using HBpin. In this unique example of iron-catalysed carbonyl hydroboration, the reaction tolerates a variety of reducible functional groups, including nitriles, amines, alkenes, halides, and ketones even at elevated temperatures.

4.3 Results and Discussion

4.3.1 Synthesis and Structure of $[\text{Fe}(\text{N}_2\text{S}_2)]_2$, **1**

We recently reported an easily-prepared benzothiazolidine ligand, $[\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}]$ containing a potentially labile thioether donor, that undergoes facile ring-opening to afford a series of mono-, di- and trinuclear Fe(II) complexes containing the anionic thioether-imine-thiolate $[\text{S}^{\text{Me}}\text{NS}]$ ligand.³⁶ During the course of this study, we observed that treatment of the low-coordinate iron complex, $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2]$ with two eq. of $[\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}]$ in THF at room temperature afforded the title complex, **1** as a purple solid in 92% yield (Scheme 4.1). Complex **1** was characterized by ^1H NMR and UV-vis spectroscopy, ESI-MS, and single-crystal X-ray diffraction. The ^1H NMR spectrum shows broadened and shifted resonances spanning the range from δ 88.03 to -14.42 , indicative of a paramagnetic complex.

Scheme 4.1 Synthesis of $[\text{Fe}(\text{N}_2\text{S}_2)]_2$, **1**



Single crystals of **1** for X-ray diffraction were grown from a saturated THF solution. Interestingly, the solid-state structure of **1** shows formation of a thiolate-bridged dimer containing imine-coupled N_2S_2 ligands (Figure A7 in the Supporting Information). One of the two thiolates in each monomer binds to an iron centre in the other, linking the two.

Moreover, the imine groups of two tridentate $S^{Me}NS$ ligands have been transformed into a diamido unit, forming the redox-active $(N_2S_2)^{2-}$ ligand with two uncoordinated thioether groups.

While **1** is dimeric in the solid-state, in solution (CD_2Cl_2 , THF- d_8 and C_6D_6 ; Figures A1-A3) it exists solely as a monomer that retains the square pyramidal coordination about iron (Scheme 4.1). The monomeric structure in solution is confirmed by a broad paramagnetic singlet (3H) at δ 88.03 in the 1H NMR spectrum due to coordination of one of the thioether groups to the paramagnetic iron centre; the methyl resonance of the uncoordinated S–Me is observed at δ 2.21. The dimeric structure of **1** was not observed in any solvent. The identity of **1'** [$Fe(N_2S_3)$] was further confirmed by electrospray mass spectrometry (Figures A5-A6). The solution magnetic moment of **1'** at room temperature (measured by Evans' method³⁷) is $2.7 \mu_B$, consistent with two unpaired spins.

4.3.2 Hydroboration Catalysis

We commenced our catalytic study using complex **1'** as a catalyst for the reduction of carbonyl compounds. While poor results were obtained using H_2 or Et_3SiH , treatment of 1 eq. of benzaldehyde, with 1 eq. of HBpin and 10 mol % of **1'** in C_6D_6 at room temperature gave the hydroboration product in quantitative yield in one hour (Table 4.1, entry 1) as observed by both 1H and ^{11}B NMR spectroscopy. While the purple solution of **1'** was unchanged upon addition of benzaldehyde, once HBpin was added, the colour changed quickly to light beige or colorless, showing that complex **1'** acts as a precatalyst. Reducing the catalyst loading to 0.1 mol % still gave excellent yields (> 80%) within 15 minutes (entry 2) that were essentially quantitative after 30 minutes (entry 3) at room temperature. In contrast, use of alternate Fe(II) precatalysts (*i.e.*, $FeCl_2$, $Fe(OTf)_2$, and $Fe\{N(SiMe_3)_2\}_2$) gave much lower yields of the hydroboration product along with dark precipitates (entries 4-6), underscoring the uniqueness of **1'**.

A similar test with the $[S^{Me}N^H S]$ ligand alone (entry 7) failed to give more than 5% hydroboration product. Surprisingly, reaction of equimolar acetophenone and HBpin using 0.1 mol

% of **1'** at room temperature afforded less than 5% of the hydroboration product. Even with high catalyst loading (10 mol %) at 60 °C for 16 h, less than 10% of the corresponding borate ester was

Table 4.1 Optimization of reaction conditions^a

Entry	Catalyst (mol %)	Solvent	Time (h)	Yield (%) ^b
1	1' (10)	C ₆ D ₆	1	> 99
2	1' (0.1)	C ₆ D ₆	0.25	> 80
3	1' (0.1)	C₆D₆	0.5	> 99
4	Fe{N(TMS) ₂ } ₂ (0.5)	C ₆ D ₆	0.5	20
5	FeCl ₂ (0.5)	C ₆ D ₆	0.5	35
6	Fe(OTf) ₂ (0.5)	C ₆ D ₆	0.5	51
7	[S ^{Me} N ^H S] ligand (1)	C ₆ D ₆	0.5	< 5
8	1' (0.1)	THF- <i>d</i> ₈	0.5	95
9	1' (0.1)	CD ₃ CN	0.5	> 99
10	None	C ₆ D ₆	2	< 5
11	2 (0.1)	C ₆ D ₆	0.5	86

^aReaction conditions: benzaldehyde (0.436 mmol), HBpin (0.436 mmol), solvent (0.3 ml), catalyst loading relative to benzaldehyde. ^bYields were determined by ¹H NMR spectroscopy using mesitylene as an internal standard.

detected, indicating that precatalyst **1'** is selective toward aldehydes (vs. ketones). A brief screening of solvents showed that both tetrahydrofuran and acetonitrile gave comparable yields of the hydroboration product (Table 4.1, entries 8 and 9). Without precatalyst **1'** less than 5% of the hydroboration product was formed in two hours (entry 10).

With the optimized reaction conditions in hand, the scope of the hydroboration was examined with a variety of aldehydes. Precatalyst **1'** showed remarkable efficiency with excellent selectivity in hydroboration reactions of both aliphatic and aromatic aldehydes (Table 4.2). Cyclic aliphatic aldehyde, electron-rich 1-pentanal and 2-(methylthio) benzaldehyde all afforded high yields of their corresponding borate esters (entries 1, 2 and 15). The α , β -unsaturated aldehyde yielded a single product (entry 3). Aromatic aldehydes containing electron-withdrawing as well as reducible functional groups showed excellent tolerance (entries 7-12, 14) yielding > 99% of the hydroboration products under these conditions. Interestingly, electron-donating aromatic aldehydes gave low to moderate yields (entries 5 and 13), in contrast to 1-pentanal, suggesting that both steric

and electronic factors are at play in this system. Significantly, terephthalaldehyde was cleanly converted into the bis(borate ester) derivative with 2 eq. of HBpin (entry 16). However, when 1 eq. of HBpin was treated with equimolar terephthalaldehyde at room temperature, as well as heating at 50 °C for 4 h, only the monohydroborated product was observed, indicating insignificant activation by the para-CH₂OBpin group. Importantly, 4-acetylbenzaldehyde underwent selective hydroboration only at the aldehyde group (entry 17) demonstrating the synthetic utility of this system. As ketone substrates are not hydroborated even at elevated temperatures, this is a rare example of exclusive aldehyde selectivity over ketone when compared, for example, to Fe(acac)₃-catalyzed chemoselective hydroboration of aldehydes over ketones in which poor selectivity was achieved with 3-acetylbenzaldehyde.¹⁶ To compare the efficiency of **1'** with a closely related derivative, we prepared and fully characterized the diamagnetic phosphite complex, [Fe(N₂S₂)P(OMe)₃], **2** (Scheme 4.2).³⁸ Treatment of 1 eq. of benzaldehyde with 1 eq. of HBpin catalyzed by 0.1 mol % of **2** afforded 86% of the corresponding borate ester in 30 minutes (Table 4.1, entry 11).

Scheme 4.2 Synthesis of [Fe(N₂S₂)P(OMe)₃], **2**

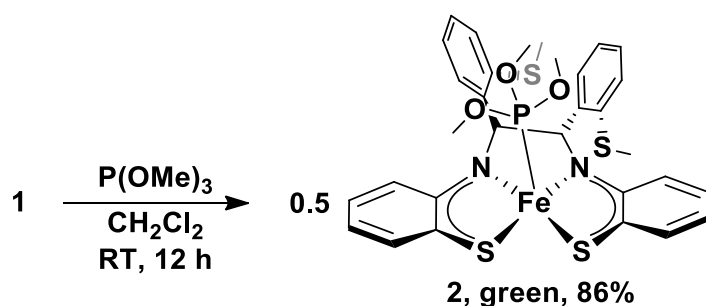


Table 4.2 Scope of hydroboration of aldehydes

Entry	Aldehyde	Product	Yield (%) ^a	Entry	Aldehyde	Product	Yield (%) ^a
1			> 99	10			> 99
2			> 99	11			> 99
3			85	12			> 99
4			> 99	13			26
5			70	14			> 99
6			> 99	15			> 99
7			> 99	16 ^c			> 99
8			> 99 (87)	17			> 99
9 ^b			39				

^aConditions: Aldehyde (0.436 mmol) was added to **1'** (0.1 mol %) in C₆D₆ (0.3 ml) followed by HBpin (0.436 mmol) at room temperature. All reactions afforded a single product and yields were calculated vs. mesitylene internal standard (0.058 mmol), average of at least 2 runs. ^bCD₃CN (0.4 ml) was used. ^c2 equiv. of HBpin were used. Isolated yield in parentheses using 1 mol % of **1'**.

In order to gain insight about potential catalytic intermediates or resting states in this hydroboration system, catalytic hydroboration of 4-(trifluoromethyl) benzaldehyde was scaled up using 1 mol % of **1'**, and of benzaldehyde using 2.5 mol % of **2**. The remaining brown liquid of the catalytic species, obtained from catalytic hydroboration using 1 mol % of **1'**,³⁹ showed a mix of

diamagnetic and paramagnetic resonances in the ^1H NMR spectrum due to unidentified species with no evidence of precatalyst **1'** (Figure A38). Nonetheless, this mixture further efficiently converted a portion of fresh substrate/HBpin mixture into the borate ester product, confirming the presence of active catalyst. Likewise, the ^1H NMR spectrum of the remaining green solid resulting from catalytic hydroboration using 2.5 mol % of diamagnetic species **2** was also inconclusive, showing a mix of resonances from both diamagnetic and paramagnetic species (Figure A39). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum taken during the reaction displays two singlets due to free $\text{P}(\text{OMe})_3$ and an unidentified species along with a broad singlet due to precatalyst **2** (Figure A40). The stoichiometric reaction of **2** with excess HBpin at room temperature also provided little insight into the catalyst resting state, affording small amounts of borohydride, observed previously in reactions of catecholborane and phosphorus ligands⁴⁰ (Figures A41-A42).

4.3.3 Kinetic Studies

To gain further mechanistic insight into this efficient iron catalysis, we performed kinetic studies to identify the resting state and substrate dependence of the catalytic process. We initially carried out analysis using the Reaction Progress Kinetic Analysis (RPKA) technique.^{41,42} Using this technique, the kinetic order of the aldehyde and HBpin can be solved by carrying out a series of experiments in which the initial concentrations of each component are varied.

Using less reactive 4-methylbenzaldehyde, we were able to validate that the observed reaction rate is indeed sensitive to both the initial concentration of aldehyde and HBpin. Increasing initial concentration of either aldehyde or HBpin results in a commensurate increase in the observed rate of reaction, suggesting that the catalytic system bears a positive order in both components. However, extracting a meaningful integer value for the order in each component was not straightforward, as both the percent conversion and shape of the reaction progress curve changed dramatically depending on if the reaction was performed with equimolar (blue) or excess (red and yellow) starting materials (Figure 4.1).

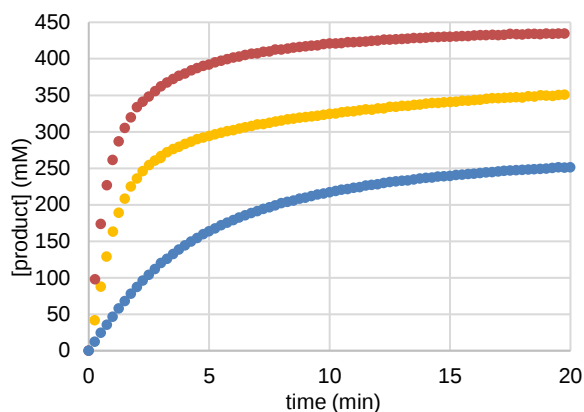


Figure 4.1 Effect of concentration on rate of formation of product in the hydroboration of 4-methylbenzaldehyde by precatalyst **1'** ($[1'] = 0.44$ mM, 23 °C, C_6H_6 ; blue $[CHO] = [HBpin] = 450$ mM; red $[CHO] = 450$ mM, $[HBpin] = 675$ mM; yellow $[CHO] = 675$ mM, $[HBpin] = 450$ mM).

When utilizing the RPKA method to extract information, analysis of the data is simplified because the difference in initial concentration of the two components (designated the reaction excess) is maintained for each experiment. However, for hydroboration using Fe precatalyst **1'**, analysis by ReactIR revealed that in a typical experiment, the rate of consumption of HBpin was greater than that for the aldehyde (Figure 4.2). This results in incomplete reduction of the aldehyde at short reaction times, unless more than one equivalent of HBpin is present.

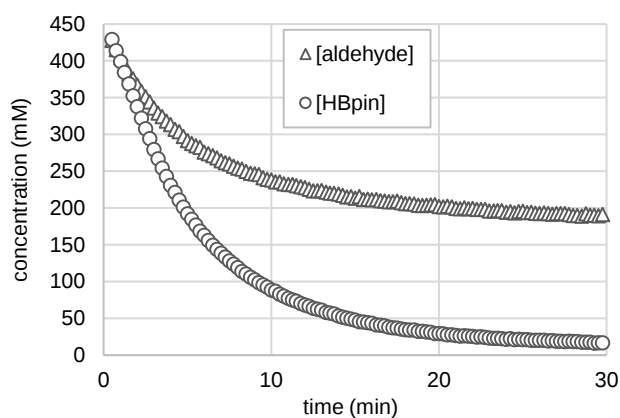


Figure 4.2 Unequal rates of consumption of aldehyde and HBpin in the hydroboration of *p*-methylbenzaldehyde by precatalyst **1'** ($[1'] = 0.44$ mM, 23 °C, C_6H_6 , $[CHO] = [HBpin] = 450$ mM).

Analysis of the reaction revealed no obvious by-products to account for the extra consumption of HBpin.⁴³ Due to this observation, we hypothesized that HBpin was being utilized to activate the initial iron catalyst. Consistent with this, a dramatic colour change was observed upon addition of

substrates to a solution of **1'** (from deep purple to either beige or colourless). Kinetic evidence for catalyst activation could be gleaned by carrying out a series of reductions where aliquots of both aldehyde and HBpin are added, allowing the reaction to proceed to completion between each subsequent addition. These experiments revealed several key features. First, conversion to product is lowest after the first equimolar addition of aldehyde and HBpin and increases in all subsequent doses (~65% conversion *cf.* ~90% for latter cycles; Figure 4.3). In addition, the rate of reaction appears to increase after the first aliquot addition. This is observed from the reaction profile for the concentration of HBpin for a series of sequential additions (Figure 4.3, cycle 1 vs. 2-4).

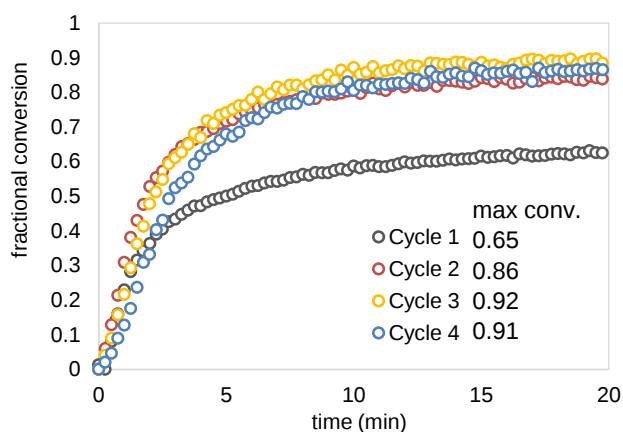


Figure 4.3 Comparing process efficiency for the first substrate addition and subsequent additions. See also Figure 4.4, and SI, Figure A44 for concentration profiles.

These observations revealed conclusively that the iron catalyst needs to undergo irreversible activation through reaction with HBpin to form the active complex. Furthermore, once activated, this catalyst is both exceptionally active (capable of producing ca. 40 mmol product/min) and very long-lived. In our studies, we demonstrated that a TON of ca. 5200 was easily achieved; note that this is by no means the limit of the activity. Importantly, reaction of the iron complex with HBpin in the absence of aldehyde appears to be detrimental. In experiments where the order of reagent addition was reversed, that is HBpin was added before aldehyde (Figure 4.4, cycle 5), we see a net decrease in the rate of reduction in the subsequent experiment (Figure 4.4, cycle 6).

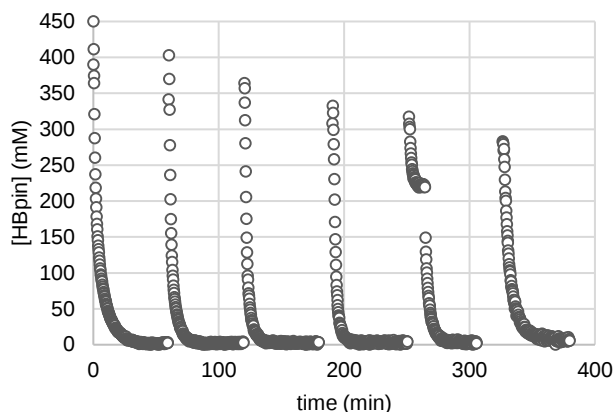
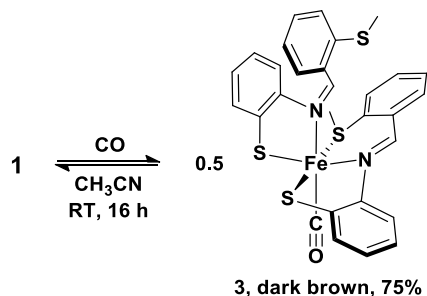


Figure 4.4 Concentration of HBpin throughout the multi-dose experiment. The experiment was initiated by the addition of HBpin (0.45 mmol), and aldehyde (0.45 mmol) to a solution of **1'** (0.44 μ mol) in C_6H_6 at 23 $^{\circ}C$. Cycles (2-4, 6) were triggered by the addition of HBpin (0.45 mmol), followed by aldehyde (0.45 mmol), ca. 15 s later. In Cycle 5, the order of addition of the reagents was reversed.

4.3.4 Synthesis of $[Fe(\kappa^3-SNS)(\kappa^2-SNS)CO]$, **3**

As no reaction of precatalyst **1'** was observed with aldehydes, we investigated its reaction with the more reactive carbonyl moiety, carbon monoxide. Treatment of complex **1** with CO in acetonitrile afforded an iron complex, $[Fe(\kappa^3-SNS)(\kappa^2-SNS)CO]$, **3** (Scheme 4.3) which was characterized by IR, 1H NMR and X-ray crystallography. The IR spectrum (Figure A13) of **3** in the solid state shows a strong and sharp CO stretching vibration at 1952 cm^{-1} , confirming the addition of a CO ligand to the iron centre. The X-ray data show that carbonylation of **1'** cleaves the diamido C-C bond, generating a pseudooctahedral iron centre occupied by one CO and two SNS ligands (Figure A14). Interestingly, the 1H NMR spectrum of diamagnetic complex **3** dissolved in CD_2Cl_2 shows also the paramagnetic resonances of complex **1'**, indicating that CO addition to iron is reversible in solution.

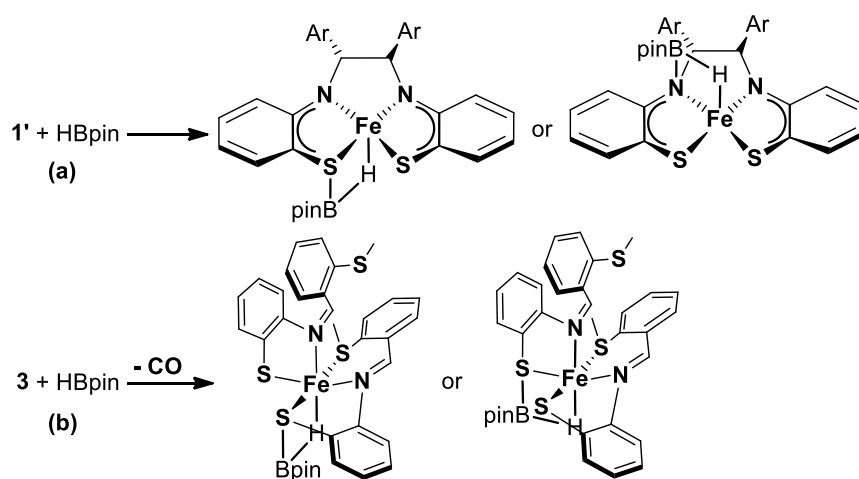
Scheme 4.3 Synthesis of $[Fe(\kappa^3-SNS)(\kappa^2-SNS)CO]$, **3**



4.3.5 B-H Bond Activation Pathway

Metal-catalyzed hydroboration of carbonyl compounds typically proceeds through either Lewis acid substrate activation or B-H bond activation.⁴ In the latter case formation of an iron hydride could be accompanied by boryl transfer to either the nitrogen or sulphur (Scheme 4.4a).⁴⁴⁻⁴⁶ In light of the reversible reaction of precatalyst **1'** with CO, however, one may also have to consider reaction pathways that involve bifunctional Fe SNS catalysts (Scheme 4.4b).

Scheme 4.4 Potential B-H Bond Activation Pathways for Aldehyde Hydroboration Catalysis using **1' (a, top) and **3** (b, bottom)**



Finally, our observations highlighting the robust and efficient nature of the iron catalyst led us to push the limits of stability for this system. Thus, we could demonstrate that this catalyst is tolerant of many common species that would typically deactivate such a metal catalyst. This includes running the reaction with crude aldehyde (contaminated with 5% 4-methylbenzoic acid) and even performing the reduction in open air (see SI, Figures A45–A46). Further kinetic studies are ongoing with catalysts **1** and **2** and their stable redox partners, i.e., $(1')^+$ and $(1')^-$.

4.4 Conclusions

In summary, we have prepared and characterized a five-coordinate, paramagnetic imine-coupled iron complex, $[\text{Fe}(\text{N}_2\text{S}_2)]_2$ that demonstrates excellent efficiency and selectivity in hydroboration catalysis of various aldehydes. The key advantages of this process are its exclusive aldehyde

selectivity over ketone, wide reducible functional group tolerance, mild reaction conditions and catalyst lifetime. This simple iron catalysed hydroboration system will therefore be attractive for synthetic, medicinal and fine chemical catalysis.

4.5 Experimental Section

4.5.1 General considerations. All experiments were conducted under nitrogen, using Schlenk techniques or an MBraun glovebox unless otherwise stated. Hexanes, diethyl ether, and THF were dried on columns of activated alumina using a J. C. Meyer (formerly Glass Contour) solvent purification system. Benzene and benzene- d_6 (C_6D_6) was dried by standing over activated alumina (ca. 10 wt %) overnight, followed by filtration. Acetonitrile (CH_3CN), acetonitrile- d_3 (CD_3CN), dichloromethane, and dichloromethane- d_2 (CD_2Cl_2) were dried by refluxing over calcium hydride under nitrogen. After distillation, CH_3CN , CD_3CN , and dichloromethane were further dried by filtration through activated alumina (ca. 5–10 wt %). CD_2Cl_2 was vacuum-transferred before use. $[d_8]$ -THF was dried by refluxing over benzophenone/ketyl, and vacuum-transferred before use. All solvents were stored over activated (heated at ca. 250 °C for >10 h under vacuum) 4 Å molecular sieves. Glassware was oven-dried at 150 °C for >2 h or overnight. Aldehydes, pinacolborane (HBpin), and trimethyl phosphite, $[P(OMe)_3]$ were obtained commercially and their purity confirmed by NMR spectroscopy prior to use. *p*-methylbenzaldehyde was purchased (Sigma-Aldrich, 97%), and either used as received or fractionally distilled. All kinetics experiments used distilled *p*-methylbenzaldehyde, unless otherwise noted. 1H , ^{19}F , and ^{31}P NMR spectra were recorded on either a 300 MHz Bruker Avance or a 300 MHz Bruker Avance II instrument at room temperature (21–25 °C). ^{11}B and $^{11}B\{^1H\}$ NMR spectra were recorded on a 300 MHz Bruker Avance II instrument at room temperature (21–25 °C). NMR spectra were referenced to the residual proton peaks associated with the deuterated solvents (for 1H NMR, C_6D_6 , 7.16 ppm; CD_3CN , 1.96 ppm; CD_2Cl_2 , 5.32 ppm; $[d_8]$ -THF, 1.72 ppm and 3.58 ppm. ^{19}F NMR spectra were referenced to internal 1,3- bis(trifluoromethyl)benzene (BTB) (Aldrich, 99%, deoxygenated by purging with nitrogen, stored over activated 4 Å molecular sieves), set to –63.5 ppm. $^{31}P\{^1H\}$ NMR

data were referenced to external H_3PO_4 (85% aqueous solution), set to 0.0 ppm. ^{11}B NMR data were referenced to external pinacolborane (29.3 and 27.5 ppm) in C_6D_6 . UV-vis spectra were recorded on an Agilent Cary 7000 Universal Measurement Spectrophotometer in dry THF or dichloromethane using sealable quartz cuvettes (1.0 cm path length). Elemental analyses were performed by Elemental Analysis Service, Université de Montréal, Montréal, Québec. Mass spectra were recorded on an Advion Expression^s mass spectrometer with electrospray ionization (ESI-MS) in positive mode with samples prepared to ca. 0.02 mg/ml in dichloromethane. For high-resolution mass spectra, a Micromass Global QTOF mass spectrometer (CsI cluster was used as a calibrant) was utilized with electrospray ionization (ESI-MS) in positive mode with samples prepared to ca. 0.01 mg/ml in dichloromethane. The spin-only magnetic moment in solution at room temperature was obtained by Evans' method.³⁷ 2-(2-Methylthiophenyl) benzothiazolidine, $[\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}]^{36}$ and $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2]^{47}$ were prepared by literature methods.

4.5.2 Synthesis of $[\text{Fe}(\text{N}_2\text{S}_2)]_2$ 1. Working under nitrogen, a 100 ml Schlenk flask was charged with the benzothiazolidine $\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}$ ligand (1.00 g, 3.85 mmol) and 30 ml THF, yielding an off-white solution. A dropping funnel was charged with $\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2$ (0.73 g, 1.94 mmol, 1 equiv.) and 10 ml hexane giving a green solution which was then added dropwise to the ligand solution. The resulting dark purple solution was stirred for 16 h at room temperature and then concentrated to ca. 20 ml under vacuum. 10 ml of hexanes were slowly added and the Schlenk flask left overnight at room temperature during which time purple crystalline product deposited in the flask. The light purple supernatant was decanted off and the resulting dark purple product was filtered, washed with benzene (4×5 ml) and hexanes (5×10 ml), and dried *in vacuo*. Yield: 1.02 g, 92% based on $\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2$. Single crystals suitable for X-ray diffraction were obtained from a concentrated THF solution of the purple powder at room temperature. ^1H NMR (300 MHz, CD_2Cl_2 at 25°C) δ 88.03 (br s, $\Delta\nu_{1/2} = 133$ Hz, 3H, S–Me), 43.09 (br s, $\Delta\nu_{1/2} = 94$ Hz), 16.50 (s), 14.64 (br s), 14.25 (br s), 12.60 (s), 12.43 (s), 10.05 (d), 9.73 (s), 7.49 (s), 6.17 (t), 5.65 (d), 2.21 (s, 3H, S–Me), 0.71

(s), -4.17 (s), -4.70 (s), -7.19 (s), -12.62 (s), -14.42 (s). μ_{eff} (CD_2Cl_2) = $2.7 \mu_{\text{B}}$. UV-vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$): 295 (10,950), 367 (4,000), 498 (6,000), 570 (9,900), 682 (7,300). HRMS (ESI-QTOF, CH_2Cl_2): Calcd for $\text{C}_{28}\text{H}_{24}\text{FeN}_2\text{S}_4$ m/z 572.0172 ($[\text{M}]^+$). Found m/z 572.0169. Figures **S1-S6** contain the ^1H NMR, UV-vis and ESI-MS spectra.

4.5.3 Synthesis of $[\text{Fe}(\text{N}_2\text{S}_2)\text{P}(\text{OMe})_3]$ **2.** A 20 ml scintillation vial was charged with complex **1** (0.25 g, 0.44 mmol) and 10 ml CH_2Cl_2 yielding a purple solution after stirring for 15 minutes. $\text{P}(\text{OMe})_3$ (52 μl , 0.44 mmol, 1 equiv.) was then added dropwise giving a green solution of **2**. The vial was stirred for 12 h at room temperature, concentrated and left overnight at room temperature over which time green crystals were formed. The supernatant was decanted off and the remaining dark green crystals washed with cold CH_2Cl_2 (3×3 ml). The CH_2Cl_2 washing was added to the supernatant solution from which a 2nd crop of dark green crystals of **2** were isolated. Total yield: 0.26 g, 86%. Single crystals were grown from a concentrated acetonitrile solution at room temperature. ^1H NMR (300 MHz, CD_2Cl_2 at 25°C) δ 2.68 (s, 3H, S–Me), 2.73 (s, 3H, S–Me), 2.90 (br s, 9H, $\text{P}(\text{OMe})_3$) 4.81 (d, 1H, $J = 7.8$ Hz, C–H), 6.31 (t, 1H, Ar–H), 6.73 (s, 1H, Ar–H), 6.96 (m, 6H, Ar–H), 7.33 (dd, 2H, Ar–H), 7.54 (d, 1H, $J = 7.8$ Hz, C–H), 7.59 (d, 2H, Ar–H), 7.78 (d, 1H, Ar–H), 8.02 (t, 2H, Ar–H), 8.13 (s, 1H, Ar–H). ^{31}P NMR (121 MHz, CD_2Cl_2) 90.0 ppm (s). UV-vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$): 293 (13,450), 499 (4,600), 568 (7,200), 682 (6,600). Anal. Calc. for $\text{C}_{31}\text{H}_{33}\text{FeN}_2\text{O}_3\text{PS}_4$: C 53.44, H 4.77, N 4.02, S 18.41; found: C 53.22, H 4.85, N 4.57, S 18.23. Figures **S8-S10** contain the ^1H , $^{31}\text{P}\{^1\text{H}\}$ NMR and UV-vis spectra.

4.5.4 Synthesis of $[\text{Fe}(\kappa^3\text{-SNS})(\kappa^2\text{-SNS})\text{CO}]$ **3.** A 100 ml ampoule was charged with complex **1** (0.1 g, 0.18 mmol) and 15 ml CH_3CN yielding a purple solution. The purple solution was freeze-pump-thaw and under vacuum CO (8 psi) gas was exposed to the purple solution at -78°C . During addition of CO, no initial color change was observed. The ampoule was finally stirred for 16 h at room temperature, over which time color of the reaction mixture was changed to dark brown along with the formation of dark brown crystals. The supernatant was decanted off and the remaining

dark brown crystals washed with cold CH_2Cl_2 (3×2 ml). Yield: 0.08 g, 75%. ^1H NMR (300 MHz, CD_2Cl_2 at 25°C) δ 88.03 (br s, $\Delta\nu_{1/2} = 133$ Hz, 3H, S–Me), 43.09 (br s, $\Delta\nu_{1/2} = 94$ Hz), 16.50 (s), 14.64 (br s), 14.25 (br s), 12.60 (s), 12.43 (s), 10.05 (d), 9.73 (s), 7.49 (s), 6.17 (t), 5.65 (d), 2.21 (s, 3H, S–Me), 0.71 (s), -4.17 (s), -4.70 (s), -7.19 (s), -12.62 (s), -14.42 (s). IR (ATR, cm^{-1}): 1952 (CO). Figures S12, S13 contain the ^1H NMR and IR spectra.

4.5.5 General catalytic procedure. In the glovebox, a precatalyst stock solution of **1'** was prepared by dissolving $[\text{Fe}(\text{N}_2\text{S}_2)]_2$ **1** (10 mg, 0.017 mmol) in C_6D_6 (12 ml). The vial was stirred for few hours giving a purple solution. Then 0.3 ml (0.436 μmol) of the precatalyst stock solution was transferred either to NMR tubes or to vials with stir bars. The aldehyde substrate (0.436 mmol) and then HBpin (0.436 mmol, 1 equiv.) were added to the NMR tubes or to the reaction vials. The reaction vial was then stirred for 30 minutes or the NMR tubes were left for 30 minutes at room temperature in which time the color changed from purple to either light beige, yellow or colorless. Finally, internal standard (mesitylene, 8 μl , 0.058 mmol) was added to the NMR tube. ^1H and ^{11}B NMR spectra were taken to monitor reaction progress, conversion and yield of the hydroboration product. All of these reactions are very clean and yielded a single hydroborated product. The yield is therefore determined by a comparison of the integrations of relevant resonances of the substrate (^1H NMR) with those of the RCH_2OBpin resonance of the hydroborated products. The spectroscopic data for products (entries 1, 4-7, 10, 13, 16 and 17 in Table 2) were identical to those reported in the literature.^{18,31,32} The hydroborated product in entry 8 (4-trifluoromethyl phenyl borate ester) is isolated and characterized. Due to the difficulties associated with flash chromatography separation in air to isolate all of the remaining hydroborated products, the NMR yields of those are calculated and both ^1H and ^{11}B NMR spectra of these catalytic reactions are shown (see below). All catalytic reactions were performed multiple times and yields were reproduced to within $\pm 2\%$.

4.5.6 General procedure for kinetic experiments. In a glovebox, gas-tight syringes containing the following reagents were prepared: *p*-methylbenzaldehyde (53 μ L, 0.45 mmol), HBpin (65 μ L, 0.450 mmol), stock solution of catalyst **1'** (600 μ L of a 0.727 mM solution in C₆H₆, 0.436 μ mol) and benzene (282 μ L). Each syringe was capped by piercing into a septum and removed from the glovebox. On a Schlenk line, a hot flask was assembled, with a stir bar and the ReactIR probe in place. After three evacuate/refill cycles, the flask was left under a constant flow of Ar. The syringes containing a solution of **1**, and benzene were expelled into the flask, and a background spectrum was collected. Data acquisition was then commenced. After ca. 1 minute, aldehyde was added, followed by HBpin ca. 1 minute later. Spectra were collected using an iC IR 15 from Mettler Toledo using the iC 10 software package. Spectra were collected over 15 s, every 15 s, for ca. 2 h. See Figure S40 for key peaks used in analysis.

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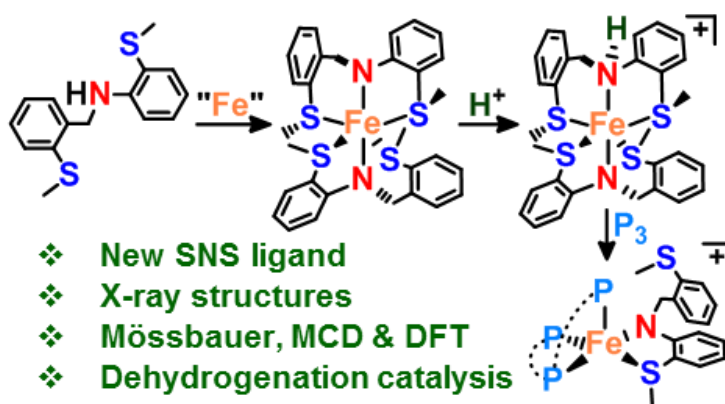
- (43) The data reveal consumption of a quantity of HBpin in excess of the equimolar quantity needed solely for stoichiometric catalyst activation or reaction with aldehyde. This does point to an as-yet-unidentified pathway for the consumption of HBpin. Products arising from dehydrocoupling (B_2pin_2) or diborylation of substrate were not observed.
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Chapter 5. Iron(II) complexes of a hemilabile SNS amido ligand: Synthesis, characterization and reactivity

5.1 Published Contributions

Iron(II) Complexes of a Hemilabile SNS Amido Ligand: Synthesis, Characterization and Reactivity

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Author Contributions

Uttam and Prof. Baker wrote the manuscript. Uttam conducted all experiments presented. Stephanie and Theresa performed Mössbauer and MCD experiments under the supervision of Prof. Neidig. Serge was responsible for TD-DFT studies. Korobkov and Gabidulin were responsible for X-ray diffraction studies.

Abstract

We report an easily prepared bis(thioether) amine ligand, $S^{Me}N^HMe$, along with the synthesis, characterization and reactivity of the paramagnetic iron(II) bis(amido) complex, $[Fe(\kappa^3-S^{Me}NS^{Me})_2]$ (**1**). Binding of the two different thioethers to Fe generates both five- and six-membered rings with Fe-S bonds in the five-membered rings (avg. 2.54 Å) being significantly shorter than those in the six-membered rings (avg. 2.71 Å), suggesting hemilability of the latter thioethers. Consistent with this hypothesis, magnetic circular dichroism (MCD) and computational (TD-DFT) studies indicate that **1** in solution contains a five-coordinate component $[Fe(\kappa^3-S^{Me}NS^{Me})(\kappa^2-S^{Me}NS^{Me})]$ (**2**). This

ligand hemilability was demonstrated further by reactivity studies of **1** with 2,2'-bipyridine, 1,2-bis(dimethylphosphino)ethane and 2,6-dimethylphenyl isonitrile to afford iron(II) complexes $[\text{L}_2\text{Fe}(\kappa^2\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2]$ (**3-5**). Addition of a Brønsted acid, HNTf_2 , to **1** produces the paramagnetic, iron(II) amine-amido cation, $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})(\kappa^3\text{-S}^{\text{Me}}\text{N}^{\text{H}}\text{S}^{\text{Me}})](\text{NTf}_2)$ (**6**; $\text{Tf} = \text{SO}_2\text{CF}_3$). Cation **6** readily undergoes amine ligand substitution by triphos, affording the 16e⁻ complex $[\text{Fe}(\kappa^2\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})(\kappa^3\text{-triphos})](\text{NTf}_2)$ (**7**; triphos = bis(2-diphenylphosphinoethyl)phenylphosphine). These complexes are characterized by elemental analysis, ¹H NMR, Mössbauer, IR and UV/vis spectroscopy and single crystal X-ray diffraction. Preliminary results of amine-borane dehydrogenation catalysis using complex **7** are reported.

5.2 Introduction

Iron amido complexes have attracted much interest in recent years as a result of their utility in many catalytic processes including asymmetric hydrogenation,^{1,2} dehydrogenation,³⁻⁵ hydroamination,^{6,7} and cross-coupling⁸ reactions. For example, in asymmetric hydrogenation and transfer hydrogenation catalysis, an iron amido complex is the key intermediate in some catalytic cycles, reacting with isopropanol (in asymmetric transfer hydrogenation) or dihydrogen (in asymmetric hydrogenation) to generate an iron hydride and a secondary amine in a bifunctional mechanism.² Iron-mediated chemical transformations such as dinitrogen reduction,⁹⁻¹² C-H bond amination,^{13,14} and olefin hydroamination^{15,16} also involve iron amido species. Moreover, iron amido complexes are fundamentally important due to their diverse structural features,¹⁷⁻²⁰ unusual reactivity^{21,22} and interesting magnetic properties.²³⁻²⁶ To date, numerous iron amido and imido complexes have been isolated and structurally characterized with a wide range of iron oxidation states from +I to +V.^{5,17,19,20,24,27-30} In general, sterically bulky amido ligands are used to stabilize low-coordinate iron amido complexes whereas multidentate chelating amido ligands are able to stabilize coordinatively saturated compounds.

The proliferation of bifunctional catalysts has been largely due to the popularity of pincer ligands that allow for tight binding and a variety of donors including P, S, N and C.³¹⁻³³ In our efforts to develop new bifunctional iron catalysts, we are investigating sterically svelte tridentate ligands with a mixture of hard nitrogen and soft sulfur donors capable of stabilizing a range of metal oxidation states,³⁴⁻⁴⁸ and hemilabile arms that allow for substrate coordination.⁴⁹ Recently, we reported a series of mono-, di- and trinuclear iron(II) complexes containing an easily prepared tridentate thiolate ligand with thioether and imine donors, $[S^{Me}NS^-]$.⁵⁰ In this work, reduction of a similar $[S^{Me}NS^{Me}]$ ligand affords an amine derivative that is used to prepare new iron amido complexes containing hemilabile thioether donors. Thioether ligands usually bind weakly to first row transition metals^{38,42,48,51-54} and their hemilability has been demonstrated previously.^{38,54-56} Amido groups typically form strong bonds to metals, may serve as terminal or bridging ligands, and can thus form mononuclear or multimetallic compounds. Additionally, late metal-bound amido groups have reactive lone-pair electrons available for bifunctional substrate activation.

A variety of tridentate sulfur-containing amido ligands are known, including $[S^R N^- S^R]$,^{40,41,47} $[S^- N^- S^-]$,⁴⁴ $[O^- N^- S^R]$,^{48,56} $[N^R N^- S^-]$,⁵⁷ and $[N^- S^R N^-]$ examples^{42,58} (see corresponding secondary amines in Figure 5.1). It is surprising that nearly all of these sulfur-based amido ligands have been studied with transition metals other than iron: Deng's group reported a few high- and low-spin iron(II) complexes employing the bulky *N,N'*-dimesityl-2,2'-diamidophenyl sulfide ligand, $[N^- S^R N^-]$ ⁴² and Mascharak and co-workers prepared and characterized an iron(III) complex bearing the *N*-2-mercaptophenyl-2'-pyridinecarboxamide ligand, $[N^R N^- S^-]$, which served as a structural model for nitrile hydratases.⁵⁷ Gusev *et al.* reported highly efficient ruthenium catalysts using pincer-type SNS ligand, $HN(C_2H_4SEt_2)$ for bifunctional ester hydrogenation.⁵⁹ Given the importance of sulfur-based amido ligands and the well-known hemilability of thioether groups in synthetic and biological coordination chemistry as well as in bifunctional catalysis, we describe herein the synthesis and characterization of a series of iron(II) amido complexes derived from an easily prepared, unsymmetrical bis(thioether) amine ligand.

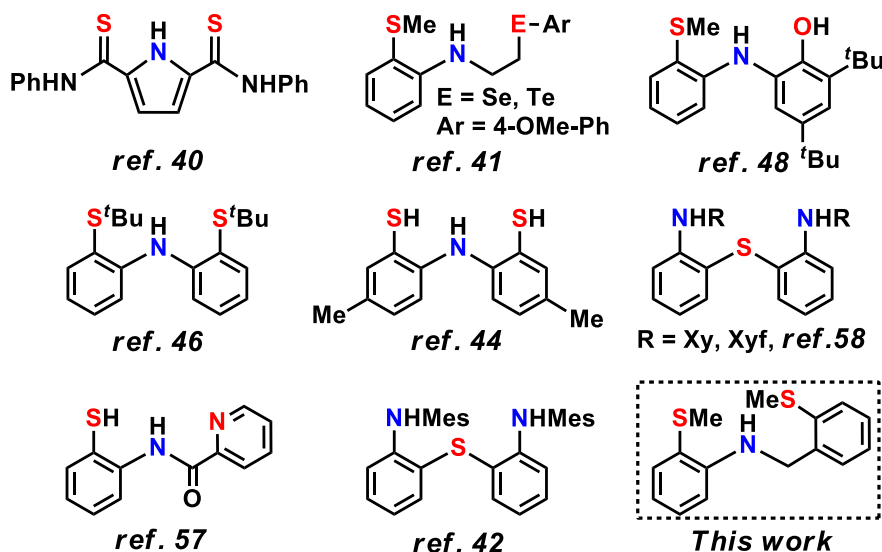


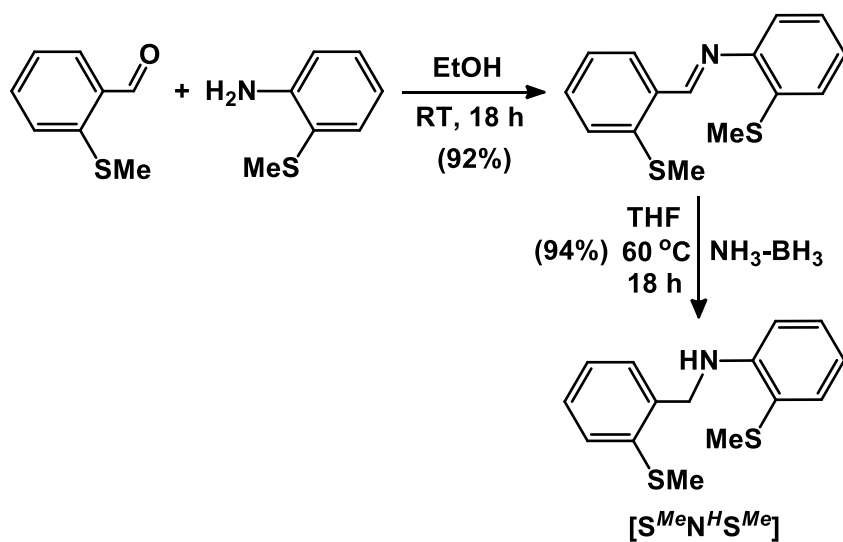
Figure 5.1 Sulfur containing amines.

5.3 Results and Discussion

5.3.1 Synthesis of the $[\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}^{\text{Me}}]$ ligand

We have targeted ligands that can be synthesized rapidly in one or two steps from inexpensive materials, in contrast to many of the previously reported tridentate N,S-donor ligands.^{40-44,47,57,58} The tridentate ligand 2-(2-methylthiobenzyl)methylthioaniline, $[\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}^{\text{Me}}]$ was prepared in two steps. Condensation of commercially available 2-(methylthio)benzaldehyde and 2-(methylthio)aniline in ethanol at room temperature afforded an imine ligand that was subsequently reduced to the amine in excellent yield using an excess of ammonia-borane (Scheme 5.1). Formation of the pure ligand was confirmed by ^1H , ^{13}C NMR, UV/vis and IR spectroscopy, EI-MS, and elemental analysis.

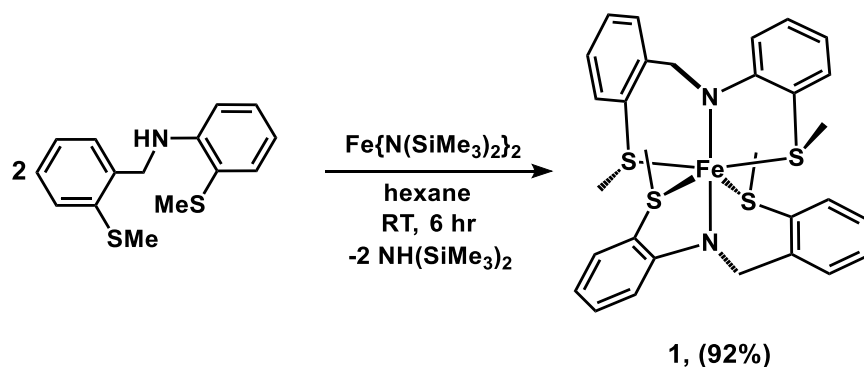
Scheme 5.1 Preparation of $[S^{Me}N^H S^{Me}]$ Ligand



5.3.2 Synthesis and Characterization of Iron(II) Bis(amido) Complex, **1**

The iron complex $[\text{Fe}(\kappa^3\text{-}S^{Me}N^H S^{Me})_2]$ (**1**) was prepared by a transamination reaction of the $[S^{Me}N^H S^{Me}]$ ligand with the low-coordinate bis(trimethylsilyl)amido iron complex, $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (Scheme 5.2). Slow addition of solid $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2]$ to a hexane suspension containing two equiv. of the $[S^{Me}N^H S^{Me}]$ ligand at room temperature afforded **1** as a yellow solid in 92% yield. The ^1H NMR spectrum of **1** shows broadened and shifted resonances ranging from 118.1 to -43.4 ppm, consistent with a paramagnetic iron center. The spectrum exhibits one set of resonances for the unsymmetrical $[S^{Me}N^H S^{Me}]$ amido ligand resulting from a dynamic exchange process in solution (*vide infra*). Room temperature magnetic measurement in solution (Evans' method)⁶⁰ gave an effective magnetic moment, μ_{eff} of $4.80 \mu_B$ consistent with an $S = 2$ ground state.

Scheme 5.2 Synthesis of Bis(amido) Iron(II) Complex



The molecular structure of **1** was determined by single-crystal X-ray diffraction (Figure 5.2). Crystals of **1** were grown from a saturated toluene solution at -35°C . The structure contains two $[\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}}]$ amido ligands meridionally bound to the iron center. The iron center adopts a distorted octahedral geometry with *trans*-N donors. The sum of angles about N(1) and N(2) are 356.38° and 356.45° , respectively, consistent with the near planarity of the amido ligands. The Fe-S distances in **1** (avg. Fe-S = 2.62 Å) are longer than those observed previously in high-spin iron(II) complexes with thioether ligation.^{42,46,61,62} More importantly, the Fe-S distances of the six-membered metallacycle rings are significantly longer than those of the five-membered rings [*e.g.*, 2.7156(7) and 2.7014(8) Å for Fe(1)-S(2) and Fe(1)-S(4) vs. 2.5389(7) and 2.5431(7) Å for Fe(1)-S(1) and Fe(1)-S(3)]. In spite of their *trans* arrangement, the Fe-N_{amido} bond lengths (avg. 2.02 Å) are comparable to those found in related iron(II) amido complexes.^{17-19,42} The S(1)-Fe(1)-S(2) and S(3)-Fe(1)-S(4) angles of $166.63(2)^{\circ}$ and $160.67(3)^{\circ}$ show significant deviation from 180° for an ideal octahedral geometry.

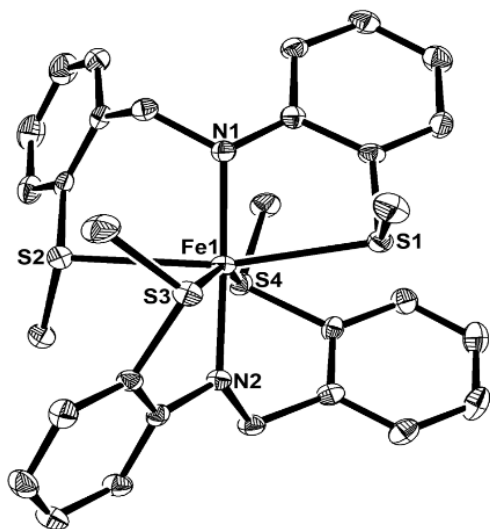


Figure 5.2 Molecular structure of $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2]$ (**1**) with 40% thermal ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)-S(1) 2.5389(7), Fe(1)-S(2) 2.7156(7), Fe(1)-S(3) 2.5431(7), Fe(1)-S(4) 2.7014(8), Fe(1)-N(1) 2.015(2), Fe(1)-N(2) 2.031(2), S(1)-Fe(1)-S(2) 166.63(2), S(3)-Fe(1)-S(4) 160.67(3), N(1)-Fe(1)-N(2) 177.60(8), N(1)-Fe(1)-S(1) 80.72(6), N(1)-Fe(1)-S(2) 86.80(6), N(2)-Fe(1)-S(3) 78.48(6), N(2)-Fe(1)-S(4) 95.63(6).

In order to further evaluate the electronic structure of complex **1**, Mössbauer spectroscopic and electrochemical studies were performed. Upon exposure to air, the yellow color of **1** turns initially to purple and finally to brown. The electrochemical study of **1** reveals an irreversible oxidation at 0.59 V versus ferrocene in dichloromethane solution (Figure A10). The 80 K Mössbauer spectrum of solid **1** exhibits a single quadrupole doublet with observed parameters of $\delta = 0.87$ mm/s and $\Delta E_Q = 0.95$ mm/s, where the isomer shift is consistent with a high-spin iron(II) species (Figure 5.3).⁶³⁻⁶⁵

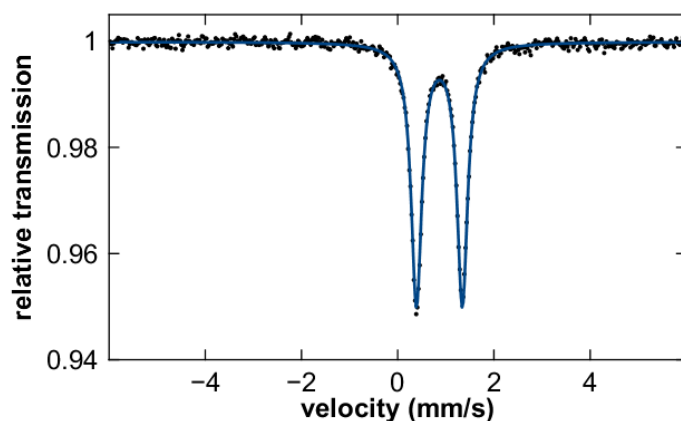


Figure 5.3 80 K Mössbauer spectrum of $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2]$ (**1**).

In order to probe the potential hemilability of the six-membered ring thioether donors, DFT optimizations of four-, five- and six-coordinate structures of **1** were performed at the PBE/TZVP level of theory with Grimme's dispersion corrections (GD3) in the gas phase. The Gibbs free energies of five- and six-coordinate structures of **1** are very similar, with the five-coordinate structure being 0.8 kcal mol⁻¹ higher in energy. The four-coordinate structure was found to be 2.5 kcal mol⁻¹ higher in energy. The structural parameters for the six-coordinate structure of **1** obtained from DFT are similar to those from the X-ray structure [e.g., 2.74 and 2.73 Å for Fe(1)-S(2) and Fe(1)-S(4), 2.500 and 2.539 Å for Fe(1)-S(1) and Fe(1)-S(3)]. The calculated Mayer bond orders for Fe-S bonds are 0.25-0.27 and 0.43-0.48 for the longer and shorter bonds, respectively. Thus, the covalency of the Fe(1)-S(2) and Fe(1)-S(4) bonds is very weak. In comparison, the Fe-N bonds have bond orders of 0.61 and 0.63. As can be expected, the metal-ligand bond distances in the optimized five-coordinate structure of **1** show small contractions relative to the six-coordinate structure, with Fe-N distances being reduced from 2.033 and 2.038 Å to 1.98 and 2.00 Å. The Fe-S distances show smaller contractions to 2.491, 2.514 and 2.74 Å. Overall, the loss of one weak covalent Fe-S bond does not cause major changes in the lengths of the remaining metal-ligand bonds. The Mayer valence index for the Fe atom in the five- and six-coordinate structures remains virtually the same (5.99 vs. 6.01).

Since the solid-state structural parameters and DFT-obtained relative energies of five- and six-coordinate structures were suggestive of possible hemilability of the SNS ligand in **1**, near-infrared magnetic circular studies (NIR MCD) of **1** in frozen solution were performed. The 5 K, 7T NIR MCD spectrum of **1** in 1:1 THF:2-Me-THF (Figure 5.4) contains ligand-field (LF) transitions at ~ 7000 cm⁻¹ and ~ 14900 cm⁻¹.

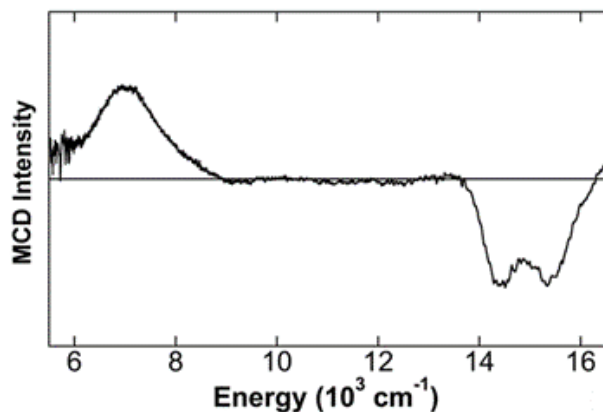


Figure 5.4 5 K, 7 T NIR MCD spectrum of $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2]$ (**1**) in 1:1 THF:2-MeTHF.

The observed transition energies are indicative of the presence of a distorted square pyramidal five-coordinate (5C) high-spin iron(II) component being present in solution,^{66,67} consistent with TD-DFT calculations for 5C which predict electronic transitions at 8300 cm^{-1} and 14200 cm^{-1} . Thus, it is clear that **1** can exist as square pyramidal complex **2**, $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})(\kappa^2\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})]$ in solution, consistent with hemilability of the SNS ligand (Figure 5.5). However, it should be noted that since five-coordinate (5C) species generally exhibit much larger $\Delta\epsilon$ values in MCD than distorted six-coordinate (6C) species, combined with the potential overlap of 6C LF transitions in the $14000\text{--}16000\text{ cm}^{-1}$ region (from TD-DFT calculations), the presence of a 6C component as well as the relative amounts of 5C versus 6C species in solution cannot be unambiguously determined.

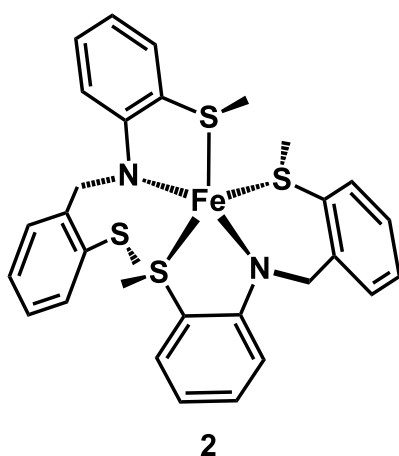


Figure 5.5 Proposed structure of $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})(\kappa^2\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})]$ (**2**) present in solution.

To further address the amount of 5C vs. 6C species that might be present in solution, frozen-solution Mössbauer studies of ^{57}Fe -enriched **1** in 1:1 THF/2-MeTHF were performed. While a reasonable fit to a single species with Mossbauer parameters nearly identical to **1** in the solid-state was possible (Figure A28), the increased broadness in solution, slight doublet asymmetry and reduced quality fit overall is consistent with the presence of a second, minor component at < 3 % of the total iron. Thus, combined with the MCD studies, the majority of **1** is 6C in solution though a minor, 5C species is also present. Even though both the MCD and TD-DFT calculations are most consistent with the square pyramidal complex **2**, we don't observe this species in the ^1H NMR (*vide supra*) as exchange is presumably too fast at room temperature and cooling the solution just gives the complex **1**.

5.3.3 Reactivity Studies of Iron(II) Bis(amido) Complex, **1**

Reactivity studies of complex **1** with a variety of mono- and bidentate neutral donor ligands further confirmed the hemilability of the six-membered ring thioethers. While no reaction was observed with acetonitrile, addition of 1 equiv. of 2,2'-bipyridine (bpy) to **1** in THF gave an instant color change from yellow to red-brown with formation of mononuclear iron complex, $[\text{Fe}(\kappa^2\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2(\text{bpy})]$ (**3**) in 80% yield (Scheme 5.3). The ^1H NMR spectrum of **3** displays broad resonances spanning a chemical shift range of 119 to -32 ppm, confirming a high-spin iron center. The room temperature magnetic measurement in solution showed an effective magnetic moment of $\mu_{\text{eff}} = 4.33 \mu_{\text{B}}$ consistent with an $S = 2$ ground state. The 80 K Mössbauer spectrum of **3** is characterized by a single quadrupole doublet with observed parameters of $\delta = 0.96 \text{ mm/s}$ and $\Delta E_{\text{Q}} = 2.81 \text{ mm/s}$, consistent with a high-spin iron(II) complex (Figure 5.6).⁶³⁻⁶⁵

Scheme 5.3 Synthesis of Paramagnetic Iron(II) Bis(SNS) Complex

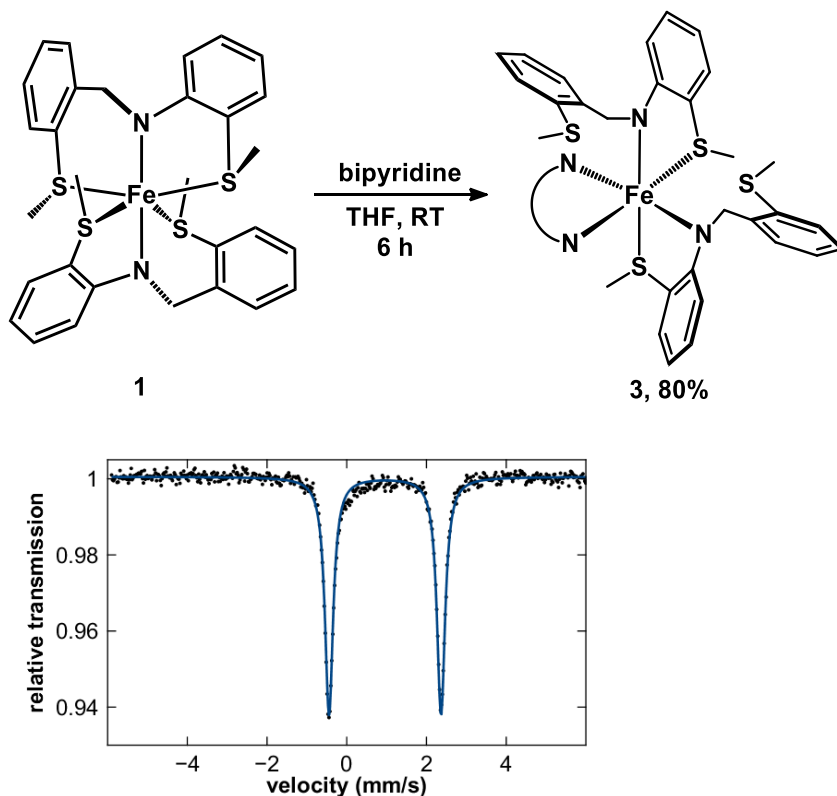


Figure 5.6 80 K Mössbauer spectrum of $[\text{Fe}(\kappa^2\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2(\text{bpy})]$ (**3**).

Crystals of **3** suitable for X-ray diffraction were grown from a saturated THF solution at room temperature. The structure contains two $[\kappa^2\text{-S}^{\text{Me}}\text{NS}^{\text{Me}}]$ amido ligands and a κ^2 -bipyridine ligand (Figure 5.7) in a distorted octahedral geometry about the iron. The Fe-S distances of the five-membered metallacycle rings are longer than those observed in **1** [e.g., 2.6146(4) Å for Fe(1)-S(1) and 2.6158(5) Å for Fe(1)-S(3) in **3** vs 2.5389(7) Å for Fe(1)-S(1) and 2.5431(7) Å for Fe(1)-S(3) in **1**] as well as in previously reported high-spin Fe(II) complexes with thioether ligation.^{42,46,62} In contrast to **1**, the amido nitrogens in **3** are in a cis arrangement and the two Fe-N_{amido} distances (Fe(1)-N(1) = 2.0678(13) and Fe(1)-N(2) = 2.0597(13) Å) are also slightly longer than those observed in **1** and other related iron(II) amido complexes.^{17,19,42,68} The Fe-N_{bpy} distances (2.2534(1) and 2.203(1) Å), on the other hand, are comparable to those previously reported for other high-spin iron(II) bipyridine complexes.⁶⁹⁻⁷¹ The N(2)-Fe(1)-N(3) and S(1)-Fe(1)-N(4) angles of 156.58(5)°

and 159.88(4)° respectively, deviate significantly from the ideal octahedral geometry similar to that observed in **1**. The sum of the angles about N(1) and N(2) of the amido ligands are 359.85° and 353.68°, respectively.

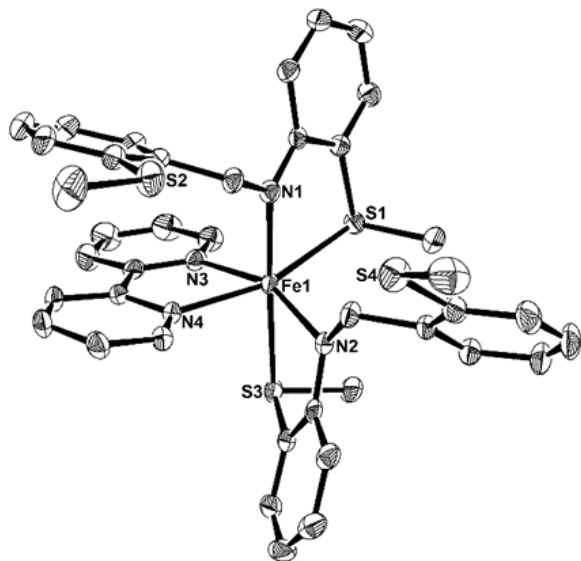


Figure 5.7 Molecular structure of $[\text{Fe}(\kappa^2\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2(\text{bpy})]$ (**3**) with 40% thermal ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)-S(1) 2.6146(4), Fe(1)-S(3) 2.6158(5), Fe(1)-N(1) 2.0678(13), Fe(1)-N(2) 2.0597(13), Fe(1)-N(3) 2.2539(13), Fe(1)-N(4) 2.2030(13), N(1)-Fe(1)-S(3) 175.95(4), N(2)-Fe(1)-N(3) 156.58(5), N(4)-Fe(1)-S(1) 159.88(4), N(2)-Fe(1)-S(1) 105.08(4), N(2)-Fe(1)-N(1) 104.27(5), S(1)-Fe(1)-S(3) 97.154(14), N(2)-Fe(1)-N(4) 94.95(5), N(3)-Fe(1)-S(1) 88.95(4).

Next, we examined the reactivity of **1** towards CNxyllyl (2,6-dimethylphenyl isonitrile) and a chelating phosphine (1,2-bis(dimethylphosphino)ethane, dmpe). Addition of 2 equiv. of CNxyllyl to a THF solution of **1** resulted in an immediate color change from yellow to brown. Removal of solvent *in vacuo* yielded a mononuclear complex, $[\text{Fe}(\kappa^2\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2(\text{CNxyllyl})_2]$ (**4**) in 80% yield (Scheme 5.4). The ^1H NMR spectrum of **4** only has resonances in the diamagnetic region, consistent with the formation of a low-spin iron(II) complex. Furthermore, the IR spectrum of **4** in the solid state shows two strong, sharp signals at 2054 and 2104 cm^{-1} which are assigned to the C-N stretching vibrations from the two cis-disposed isonitrile ligands. The 80 K Mössbauer spectrum of **4** exhibits a single doublet with observed parameters of $\delta = 0.14$ mm/s and $\Delta E_{\text{Q}} = 0.67$ mm/s consistent with a low-spin, six-coordinate iron(II) complex (Figure 5.8).^{63,72-74}

Scheme 5.4 Synthesis of Diamagnetic Iron(II) Bis(SNS) Complexes

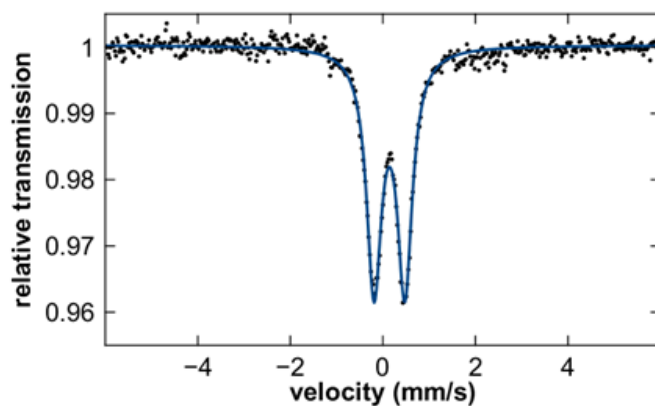
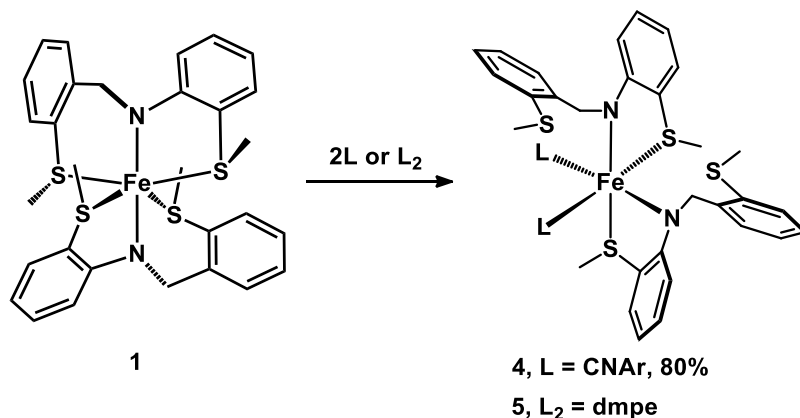


Figure 5.8 80 K Mössbauer spectrum of $[\text{Fe}(\kappa^2\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2(\text{CNxylyl})_2]$ (**4**).

However, addition of 1 equiv. of dmpe to a THF solution of **1** resulted no color change at room temperature. The ^1H NMR spectrum exhibited paramagnetically shifted resonances of the starting material and $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed resonances of free dmpe. Upon cooling to -40°C , the color of the reaction mixture changed from yellow to red-brown. The ^1H NMR spectrum of **5** at -40°C showed resonances in the diamagnetic region and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displayed two doublets at 56.1 and 44.4 ppm ($^2J_{\text{PP}} = 30\text{ Hz}$), which disappeared on warming the solution to room temperature accompanied by changing color back to yellow suggesting the reversible coordination of dmpe ligand to **1**.

5.3.4 Formation of the Iron(II) Amine-Amido Cation, 6

Deprotonated amines are usually strong bases, and therefore one would expect the basic amido donors of **1** to react with Brønsted acids. When 1 equiv. of bis(trifluoromethane)sulfonimide, HNTf₂, was added to a solution of **1** in dichloromethane, the color changed instantly from yellow to red, yielding a cationic iron(II) complex, [Fe(κ^3 -S^{Me}NS^{Me})(κ^3 -S^{Me}N^HS^{Me})](NTf₂) (**6**) in 82% yield (Scheme 5.5). The ¹H NMR spectrum shows the paramagnetically shifted resonances of a high-spin Fe(II) complex. The ¹⁹F NMR spectrum consisted of a broad singlet at -66.8 ppm assigned to the NTf₂ anion in the outer coordination sphere. The IR spectrum of **6** in the solid state shows a broad signal at 3488 cm⁻¹ which can be attributed to an N-H stretching vibration supportive of the protonation of the amide group. Attempts to further protonate **6** were unsuccessful. The 80 K Mossbauer spectrum is also consistent with a high-spin iron(II) complex with observed parameters of $\delta = 0.96$ mm/s and $\Delta E_Q = 1.92$ mm/s (Figure 5.9).⁶³⁻⁶⁵

Scheme 5.5 Synthesis of Cationic Iron(II) Amine-Amido Complex

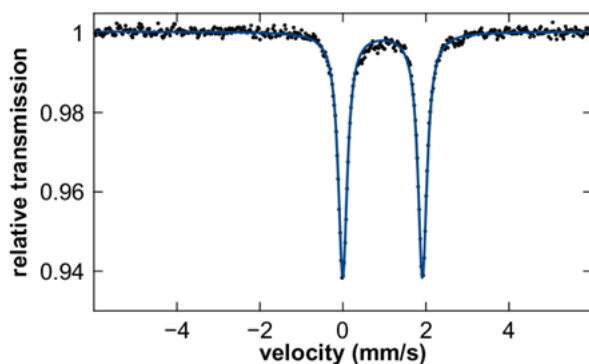
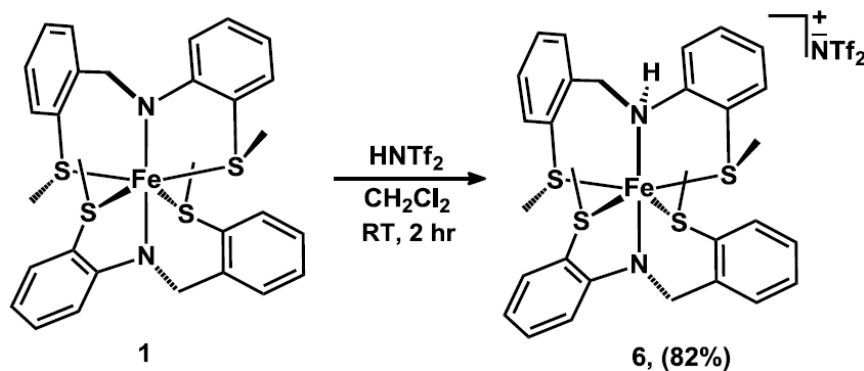


Figure 5.9 80 K Mössbauer spectrum of [Fe(κ^3 -S^{Me}NS^{Me})(κ^3 -S^{Me}N^HS^{Me})](NTf₂) (**6**).

Crystals of **6** suitable for X-ray diffraction were grown from a saturated dichloromethane solution at $-35\text{ }^{\circ}\text{C}$. The molecular structure consists of meridional κ^3 -amido and κ^3 -amine SNS ligands in a distorted octahedral geometry about iron (Figure 5.10). The Fe-S bond lengths of the amine ligand are longer than those of the amido ligand [*e.g.*, 2.6047(6) Å for Fe(1)-S(1) and 2.6573(5) Å for Fe(1)-S(2) vs 2.5200(5) Å for Fe(1)-S(3) and 2.5387(5) Å for Fe(1)-S(4)]. However, both Fe-S distances of the amido [$\text{S}^{\text{Me}}\text{N}^{\text{S}^{\text{Me}}}$] ligand in **6** are shorter than those found in complexes **1** and **3** (*vide supra*). The Fe-N_{amine} distance of 2.2763(15) Å is expectedly longer than the Fe-N_{amido} distance, 1.9974(16) Å. The coordination angles of the amine nitrogen in [$\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}^{\text{Me}}$] are consistent with the anticipated sp^3 hybridization (average of all four angles around N atom being 111.21°). The S(3)-Fe(1)-S(4) and S(1)-Fe(1)-S(2) angles of $163.40(19)^{\circ}$ and $154.92(19)^{\circ}$ deviate significantly from the ideal octahedral geometry. The elongated Fe-S and Fe-N_{amine} bonds of the [$\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}^{\text{Me}}$] moiety in **6** suggests that this ligand could be easily displaced by stronger donor ligands (*vide infra*).

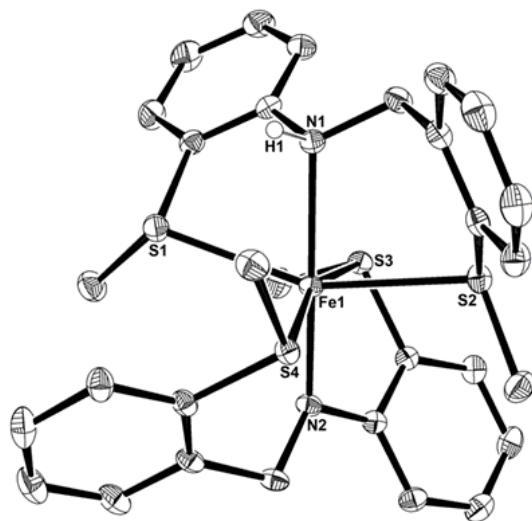
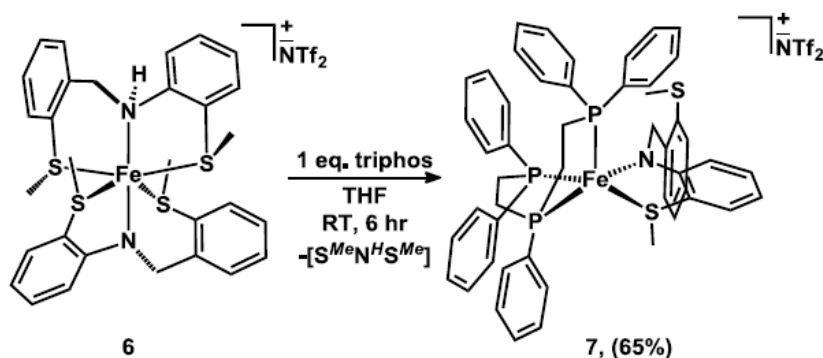


Figure 5.10 Molecular structure of $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})(\kappa^3\text{-S}^{\text{Me}}\text{N}^{\text{HS}^{\text{Me}}})](\text{NTf}_2)$ (**6**) with 40% thermal ellipsoids. H atom in the amine is shown and other H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)-S(1) 2.6047(6), Fe(1)-S(2) 2.6573(5), Fe(1)-S(3) 2.5200(5), Fe(1)-S(4) 2.5387(5), Fe(1)-N(1) 2.2763(15), Fe(1)-N(2) 1.9974(16), S(3)-Fe(1)-S(4) $163.40(19)^{\circ}$, N(1)-Fe(1)-S(4) $100.24(4)^{\circ}$, N(2)-Fe(1)-S(1) $108.18(5)^{\circ}$, S(3)-Fe(1)-S(1) $103.93(18)^{\circ}$, N(3)-Fe(1)-S(1) $88.95(4)^{\circ}$, S(1)-Fe(1)-S(2) $154.92(19)^{\circ}$, N(1)-Fe(1)-N(2) $173.25(6)^{\circ}$.

5.3.5 Reactivity Studies of Iron(II) Amine-Amido Complex, **6**

Treatment of cation **6** with 3 equiv. of P(OMe)_3 or CNxyl yl failed to give the expected diamagnetic iron SNS amido complex. Addition of 1 equiv. of bis(2-diphenylphosphinoethyl)phenyl phosphine (triphos) to a THF solution of **6** at room temperature, however, gave an instant color change from red to magenta. From this reaction a $16e^-$ diamagnetic iron amido complex, $[\text{Fe}(\kappa^2\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})(\kappa^3\text{-triphos})](\text{NTf}_2)$ (**7**) was isolated in 65% yield (Scheme 5.6). The ^1H NMR spectrum shows two singlets at δ 2.21 and 2.39 due to iron-bound and unbound thiomethyl groups of the SNS amido ligand. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a broad singlet and triplet at δ 75.6 and 83.2 (integration ratio: 2:1), respectively, with $^2J_{\text{pp}} \approx 22$ Hz. On cooling to -40°C , the spectrum shows three different signals: two doublet of doublets at 81.5 and 74.7 ppm ($^2J_{\text{pp}} = 21$ Hz, 28 Hz) and a parent triplet at 74.1 ppm ($^2J_{\text{pp}} = 21$ Hz). It should be noted that the spectrum also contains resonances due to free triphos (10%). The 80 K Mössbauer spectrum of **7** shows a single doublet with parameters of $\delta = 0.22$ mm/s and $\Delta E_{\text{Q}} = 1.77$ mm/s consistent with a low-spin, five-coordinate iron(II) complex (Figure A29).^{63,72-74}

Scheme 5.6 Synthesis of Iron(II) Amido SNS Complex



The molecular structure of the cation **7** was determined by X-ray diffraction (Figure 5.11). Crystals of **7** were grown from a saturated benzene solution layered with hexane at room temperature. The molecular structure contains a κ^2 -SNS amido and a κ^3 -triphos ligand in a distorted square pyramidal geometry about iron. Both Fe-N [1.921(4) Å] and Fe-S bond lengths [Fe(1)-S(1)

2.2506(18) Å] to the amido ligand are significantly shorter than those found in complexes **1**, **3** and **6** (*vide supra*). The Fe-N distance of 1.921(4) Å is also shorter than those in complexes **1**, **3** and **6**. The sum of three angles around N in SNS amido ligand is 357.88° (average of all three angles being 119.29°). The S(1)-Fe(1)-P(3) and N(1)-Fe(1)-P(2) angles of 158.13(7)° and 169.35(14)° deviate distinctly from the ideal square pyramidal geometry. Among three Fe-P bond distances, the apical Fe-P bond [Fe(1)-P(1) 2.1665(18) Å] is shorter than those in the basal plane [*i.e.*, Fe(1)-P(2) 2.2205(18) and Fe(1)-P(3) 2.2395(19) Å].

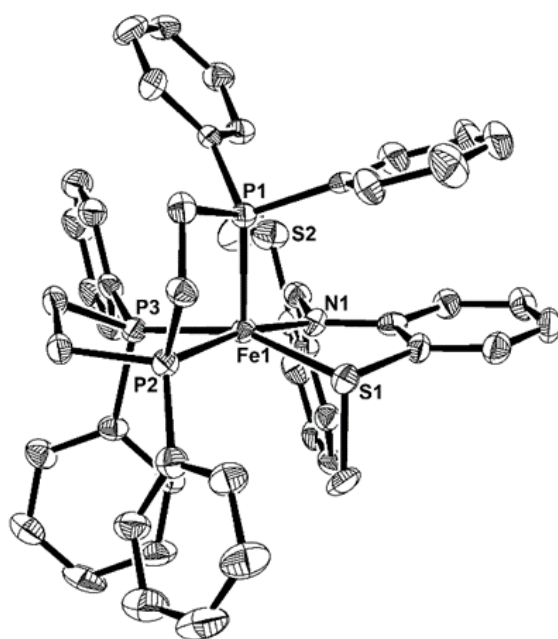


Figure 5.11 Molecular structure of $[\text{Fe}(\kappa^2\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})(\kappa^3\text{-triphos})](\text{NTf}_2)$ (**7**) with 35% thermal ellipsoids. H atoms and NTf_2 anion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)-S(1) 2.2506(18), Fe(1)-N(1) 1.921(4), Fe(1)-P(1) 2.1665(18), Fe(1)-P(2) 2.2205(18), Fe(1)-P(3) 2.2395(19), N(1)-Fe(1)-P(2) 169.35(14), S(1)-Fe(1)-P(3) 158.13(7), S(1)-Fe(1)-P(1) 96.78(7), N(1)-Fe(1)-P(1) 103.76(15), P(3)-Fe(1)-P(1) 101.48(7), P(2)-Fe(1)-P(1) 84.74(7), S(1)-Fe(1)-P(2) 87.83(7), S(1)-Fe(1)-N(1) 84.83(14), N(1)-Fe(1)-P(3) 102.22(14), P(2)-Fe(1)-P(3) 82.00(7).

5.3.6 Amine-Borane Dehydrogenation Catalysis

In order to explore the relevance of the hemilability of the $[\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}^{\text{Me}}]$ ligand and potential bifunctional behavior of the iron(II) amido complexes, complex **7** was assessed as a precatalyst for amine-borane dehydrogenation catalysis. At 60 °C, gas evolution was observed when a solution of

7 in THF was mixed with ammonia-borane (AB; 32 equiv.). The reaction mixture changed color from magenta to orange accompanied by formation of an off-white precipitate of polyaminoborane.⁷⁵ After 23 h of heating at 60 °C, the ¹¹B NMR spectrum (Figure A22) still shows unreacted AB confirming that the dehydrogenation is slow. Product resonances include a doublet at δ 30.7 ppm (borazine) and a doublet, triplet and quartet from –5 to –25 ppm which are assigned to the aminoborane tetramer, B-(cyclotriborazanyl) amine-borane (BCTB).⁴ Interestingly, the ³¹P{¹H} NMR spectrum displays only a doublet and a triplet at δ 88.7 and 144.6 ppm, respectively, with ²J_{pp} $\approx$ 30 Hz. These resonances are correlated (gated proton decoupled ³¹P NMR spectrum; Figure A23) with a quartet hydride resonance at δ –24.5 (³J_{HP} $\approx$ 58 Hz) in the ¹H NMR spectrum (Figure A24), suggestive of bifunctional AB activation. In contrast, complex **7** shows improved catalytic activity with *N,N*-dimethylamine-borane (DMAB; 20 equiv. in THF at 60 °C) affording predominately the aminoborane cyclic dimer. While the ¹H NMR spectrum of the resulting orange solution again showed the quartet resonance at δ –24.1, the ³¹P{¹H} NMR spectra showed a number of multiplet resonances, indicating less stability of the catalyst resting state with the DMAB substrate (Figure A26).

Table 5.1 Experimentally determined 80 K ⁵⁷Fe Mössbauer parameters^a for Fe(II) complexes **1–7**.

Fe(II) complexes	δ (mm/s)	ΔE_Q (mm/s)	γ (mm/s)
[Fe(κ^3 -S ^{Me} NS ^{Me}) ₂] (1)	0.87	0.95	0.27
[Fe(κ^2 -S ^{Me} NS ^{Me}) ₂ (bpy)] (3)	0.96	2.81	0.25
[Fe(κ^2 -S ^{Me} NS ^{Me}) ₂ (CNxylyl) ₂] (4)	0.14	0.67	0.39
[Fe(κ^3 -S ^{Me} NS ^{Me})(κ^3 -S ^{Me} N ^H S ^{Me})](NTf ₂) (6)	0.96	1.92	0.26
[Fe(κ^2 -S ^{Me} NS ^{Me})(κ^3 -triphos)](NTf ₂) (7)	0.22	1.77	0.30

^a The error bars for the fit analyses were $\delta \pm 0.02$ mm/s and $\Delta E_Q \pm 3\%$.

5.4 Conclusions

In summary, an unsymmetrical amine, 2-(2-methylthiobenzyl)methylthioaniline, [S^{Me}N^HS^{Me}], is readily prepared in excellent yield in two steps from commercially available starting materials. The derived pseudooctahedral Fe(II) bis(κ^3 -amido) complex, **1**, is shown by X-ray diffraction to contain two meridional tridentate ligands in the solid state with *trans*-nitrogens and two long Fe-S distances

associated with six-membered metallacycle rings. Further studies using MCD and DFT calculations support the presence of a five-coordinate isomer, **2**, in solution containing one κ^2 -amido ligand due to cleavage of one of the six-membered rings. Reactivity studies of **1** with a variety of donor ligands such as 2,2'-bipyridine, CNxylyl and dmpe produced a series of high- and low-spin iron(II) bis(κ^2 -amido) SNS complexes, **3-5** due to cleavage of both six-membered rings. Interestingly, stable products are only formed with those ligands that can accept electron density from the iron center; the dmpe analog is only stable at low temperatures.

Protonation of **1** with the Brønsted acid, HNTf₂, afforded a cationic iron(II) amine-amido complex, [Fe(κ^3 -S^{Me}NS^{Me})(κ^3 -S^{Me}N^HS^{Me})](NTf₂) (**6**) which readily undergoes amine ligand displacement upon interaction with the tridentate phosphine ligand, triphos, yielding a low-spin, square pyramidal iron(II) complex, [Fe(κ^2 -S^{Me}NS^{Me})(κ^3 -triphos)](NTf₂) (**7**). Finally, complex **7** was shown to be more active as a precatalyst for dehydrogenation of dimethylamine-borane vs. ammonia-borane at 60 °C and formation of a monohydride catalyst resting state is suggestive of a bifunctional activation pathway.

Since the [S^{Me}N^HS^{Me}] ligand is readily accessible in excellent yield and metalation is straightforward, this ligand and its analogues are well suited for the preparation of new coordination complexes in which selective hemilability, and coordination of mixed hard-soft donor groups are desirable. Given the importance of sulfur-containing amido ligands in reactivity studies and in catalysis, the [S^{Me}NS^{Me}] ligand offers a new platform for developing base-metal bifunctional catalysts.

5.5 Experimental Section

5.5.1 General considerations. Unless otherwise stated all experiments were conducted under nitrogen, using Schlenk techniques or an MBraun glovebox. All solvents were deoxygenated by purging with nitrogen. Toluene, hexanes, diethyl ether, and THF were obtained from solvent purification system. [d₆]-benzene (C₆D₆) was dried by standing over activated alumina (ca. 10

wt %) overnight, followed by filtration. Dichloromethane, [d₂]-dichloromethane (CD₂Cl₂), chloroform and d-chloroform (CDCl₃) were dried by refluxing over calcium hydride under nitrogen. After distillation, CDCl₃ and dichloromethane were further dried by filtration through activated alumina (*ca.* 5–10 wt %). CD₂Cl₂ was vacuum-transferred before use. Ethanol (EtOH) was dried by refluxing over Mg/I₂ under nitrogen, followed by distillation. All solvents were stored over activated (heated at *ca.* 250 °C for >10 h under vacuum) 4 Å molecular sieves except ethanol which was stored over activated 3 Å molecular sieves. Glassware was oven-dried at 150 °C for >2 h. The following chemicals were obtained commercially, as indicated: 2-(methylthio)benzaldehyde (Aldrich, 90%), 2-methylthioaniline (Alfa Aesar, 98%), ammonia borane (NH₃-BH₃, Scitix, 91%), dimethylamine-borane ((CH₃)₂NH-BH₃, Aldrich, 97%), bipyridine (bpy, Aldrich, 98%), 2,6-dimethylphenyl isonitrile (CNxylyl, Aldrich, 96%), 1,2-bis(dimethylphosphino)ethane (dmpe, Strem, 98%) and trimethylphosphite [P(OMe)₃, Strem, 97%]. ¹H, ¹⁹F, and ³¹P NMR spectra were recorded on either a 300 MHz Bruker Avance or a 300 MHz Bruker Avance II instrument at room temperature (21–25 °C). ¹³C{¹H} NMR spectra were recorded on a 400 MHz Bruker Avance instrument. NMR spectra were referenced to the residual proton peaks associated with the deuterated solvents (for ¹H NMR, C₆D₆, δ 7.16; CDCl₃, δ 7.26; CD₂Cl₂, δ 5.32 and for ¹³C{¹H} NMR, C₆D₆, δ 128.06 ppm). ¹⁹F NMR spectra were referenced to internal 1,3-bis(trifluoromethyl)benzene (BTB) (Aldrich, 99%, deoxygenated by purging with nitrogen, stored over activated 4 Å molecular sieves), set to δ –63.5 ppm. ³¹P NMR data were referenced to external H₃PO₄ (85% aqueous solution), set to δ 0.0 ppm. UV–vis spectra were recorded on an Agilent Cary 7000 Universal Measurement Spectrophotometer, using sealable quartz cuvettes (1.0 cm path length) and dry CH₂Cl₂ or THF. IR data were collected on a Thermo Scientific Nicolet 6700 FT-IR spectrometer. Elemental analyses were performed by Elemental Analysis Service, Université de Montréal, Montréal, Québec, and by CENTC Elemental Analysis Facility, University of Rochester, Rochester, NY 14627 USA. For electron impact (EI), solid samples were prepared by drying

products under vacuum, and a Kratos Concept S1 (Hres 7000–10000) mass spectrometer was used. $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2]$ was prepared by following a previously reported literature.⁷⁶ The spin-only magnetic moment in solution at room temperature was obtained by the Evans' method.⁶⁰

5.5.2 Synthesis of the $[\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}^{\text{Me}}]$ ligand

5.5.2.1 1st step: Synthesis of 2-(2-methylthiobenzylidene) methylthioaniline. 2-(methylthio)benzaldehyde (1.7 mL, 13.14 mmol) and 2-(methylthio)aniline (1.8 mL, 14.45 mmol, 1.1 equiv.) were added to a 100 mL round bottom Schlenk flask, followed by addition of 20 mL of dry EtOH. The resulting brown solution was refluxed for 18 h under dynamic nitrogen (vented to an oil bubbler) after which no further color change was observed. The reaction mixture was cooled at $-35\text{ }^\circ\text{C}$ overnight after which the product precipitated as a yellow solid. Finally, the yellow product was filtered, washed with cold EtOH and dried *in vacuo*. Yield: 3.30 g, 92% based on 2-(methylthio)benzaldehyde. The product was used directly in the 2nd step without further purification. ^1H NMR (300 MHz, C_6D_6 at 25°C) δ 1.88 (s, 3H, S–Me), 2.02 (s, 3H, S–Me), 6.84–7.01 (m, 7H, Ar–H), 8.41 (d, 1H, Ar–H), 9.02 (s, 1H, N=C–H). ^{13}C NMR (101 MHz, C_6D_6) δ 14.54 (CH_3), 16.71 (CH_3), 117.90 (Ar–C), 125.03 (Ar–C), 125.38 (Ar–C), 125.84 (Ar–C), 126.64 (Ar–C), 127.97 (Ar–C), 129.61 (Ar–C), 131.49 (Ar–C), 135.05 (Ar–C), 135.29 (Ar–C), 141.12 (Ar–C), 150.14 (Ar–C), 157.62 (N=C). Figures S1–S2 contain the ^1H and ^{13}C NMR spectra.

5.5.2.2 2nd step: Synthesis of 2-(2-methylthiobenzyl) methylthioaniline. 2-(2-methylthiobenzylidene) methylthioaniline (1.00 g, 3.66 mmol) was added to a 100 mL ampoule charged with a stir bar. 20 mL THF was added to form a yellow solution, followed by 0.45 g (14.64 mmol, 4 equiv.) $\text{NH}_3\text{-BH}_3$. The ampoule was sealed, and the resulting yellow solution was heated to $65\text{ }^\circ\text{C}$ for 24 h over which time the color of the reaction mixture turned from yellow to colorless. THF was removed using vacuum and the residue was purified using column chromatography (hexane:ethyl acetate, 4:1) to afford a white solid. Yield: 0.950 g, 94% based on 2-(2-methylthiobenzylidene) methylthioaniline. ^1H NMR (300 MHz, C_6D_6 at 25°C) δ 1.96 (s, 3H, S–

Me), 2.00 (s, 3H, S–Me), 4.29 (d, 2H, $^3J = 5.9$ Hz, $-\text{CH}_2$), 5.46 (t, 1H, $^3J = 5.9$ Hz, N–H), 6.53 (dd, 1H, Ar–H), 6.59 (td, 1H, Ar–H), 6.89 (m, 1H, Ar–H), 6.99 (m, 3H, Ar–H), 7.23 (dq, 1H, Ar–H), 7.48 (dd, 1H, Ar–H). ^{13}C NMR (101 MHz, C_6D_6) δ 15.36 (CH_3), 18.13 (CH_3), 46.12 (N–C), 110.94 (Ar–C), 117.67 (Ar–C), 120.32 (Ar–C), 125.29 (Ar–C), 125.99 (Ar–C), 127.88 (Ar–C), 127.94 (Ar–C), 130.04 (Ar–C), 134.89 (Ar–C), 137.24 (Ar–C), 137.51 (Ar–C), 148.71 (Ar–C). IR (ATR, cm^{-1}): 3390 (N–H), 752 (S–Me). UV-vis (THF): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$): 291 (4,300), 313 (6,900). HRMS (EI, 70 eV): Calcd. for $\text{C}_{15}\text{H}_{17}\text{NS}_2$ m/z 275.0802 [M^+], found 275.0815 [M^+]. Anal. Calc. for $\text{C}_{15}\text{H}_{17}\text{NS}_2$: C 65.41, H 6.22, N 5.09, S 23.28; found: C 64.89, H 6.46, N 5.04, S 23.13. Figures S3-S7 contain the ^1H , ^{13}C NMR, UV/vis, EI-MS and IR spectra.

5.5.3 Synthesis of $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2]$ (1**).** A 100 mL round bottom Schlenk flask was charged with 2-(2-methylthiobenzyl) methylthioaniline, $[\text{S}^{\text{Me}}\text{N}^{\text{H}}\text{S}^{\text{Me}}]$ (1.00 g, 3.63 mmol) and 15 mL hexane, yielding a white suspension. A graduated dropping funnel was charged with $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (0.684 g, 1.815 mmol, 0.5 equiv.) and 10 mL hexane giving a clear green solution. The dropping funnel was then connected to the Schlenk flask and the green solution was added dropwise to the white suspension. Upon addition of $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2]$, the color of the reaction mixture instantly turned to lime yellow. The resulting solution was stirred for 6 h at room temperature over which period a yellow solid deposited in the bottom of the flask. After decanting the supernatant lime yellow solution, the yellow precipitate of the title complex **1** was collected by filtration using a frit followed by washing with hexane (*ca.* 3×10 mL) and diethyl ether (3×5 mL) and drying *in vacuo*. Yield: 1.09 g, 92% based on $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2]$. Crystals of **1** suitable for X-ray crystallography were obtained from a concentrated toluene solution at -35°C . ^1H NMR (300 MHz, C_6D_6 at 25°C) δ -43.45 (br s, $\Delta\nu_{1/2} = 117$ Hz), -6.35 (br s, $\Delta\nu_{1/2} = 251$ Hz), -0.80 (br s, $\Delta\nu_{1/2} = 89$ Hz), $6.53\text{--}6.69$ (br m), 17.50 (br s, $\Delta\nu_{1/2} = 451$ Hz), 33.35 (br s, $\Delta\nu_{1/2} = 249$ Hz), 43.50 (br s, $\Delta\nu_{1/2} = 145$ Hz), 66.42 (br s, $\Delta\nu_{1/2} = 622$ Hz), 118.30 (br s, $\Delta\nu_{1/2} = 790$ Hz). UV/vis (THF): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$): 314 (14,100), 365 (2,200), 444 (1,000). $\mu_{\text{eff}}(\text{C}_6\text{D}_6) = 4.80 \mu_{\text{B}}$. Anal. Calc. for $\text{C}_{30}\text{H}_{32}\text{FeN}_2\text{S}_4$:

C 59.59, H 5.33, N 4.63, S 21.21; found: C 58.48, H 5.38, N 4.53, S 20.43. It should be noted that the elemental analysis data for **1** are <2% low due to its high air sensitivity. Figures **S8-S9** contain the ^1H NMR and UV/vis spectra.

5.5.4 Synthesis of $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2(\text{bpy})]$ (3**).** A 20 mL scintillation vial was charged with $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2]$ (**1**) (0.200 g, 0.33 mmol), 2,2'-bipyridine (0.051 g, 0.33 mmol, 1 equiv.) and THF (10 mL) affording instantly a red brown solution. The solution was then stirred for 6 h at room temperature over which period no further color change was observed. The solution was concentrated using vacuum and let stand at room temperature overnight to yield dark red-brown crystals (1st crop) of **3**. The red-brown filtrate was further concentrated which gave a 2nd crop of the crystals. Finally, the dark red crystals were collected by filtration, washed with cold THF (*ca.* 3×5 mL) and diethyl ether (*ca.* 3×5 mL) and dried *in vacuo*. Combined yield was 0.201 g, 80% based on $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2]$ (**1**). ^1H NMR (300 MHz, C_6D_6 at 25°C) δ -43.20 (br s), -37.20 (br s) -13.70 (br s), -6.32 (br s), 0.25 (br s), 8.70 (br s), 17.10 (br s), 32.10 (br s), 43.73 (br s), 66.72 (br s), 118.70 (br s). UV-vis (THF): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$): 218 (45,200), 247 (39,900), 252 (37,800), 283 (15,900), 313 (8,300). μ_{eff} (C_6D_6) = 4.33 μ_{B} . Anal. Calc. for $\text{C}_{40}\text{H}_{40}\text{FeN}_4\text{S}_4$: C 63.14, H 5.30, N 7.36; found: C 63.31, H 5.98, N 6.60. Figure **S11** shows the ^1H NMR spectrum.

5.5.5 Synthesis of $[\text{Fe}(\kappa^2\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2(\text{CNxylyl})_2]$ (4**).** A 20 mL scintillation vial was charged with $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2]$ (**1**) (0.200 g, 0.33 mmol), 2,6-dimethylphenyl isonitrile, CNxylyl (0.087 g, 0.66 mmol, 2 equiv.) and THF (10 mL) yielding instantly a brown solution. The solution was stirred for 6 h at room temperature over which period no further color change was observed. THF was removed under vacuum and the resulting brown residue was washed with cold diethyl ether (*ca.* 3×5 mL) and dried *in vacuo* to give **4**. Yield: 0.229 g, 80% based on $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2]$ (**1**). ^1H NMR (300 MHz, C_6D_6 at 25°C) δ 1.72-2.43 (m, 24H, S-Me and Me-CNxylyl), 4.29 (d, 1H, -CH₂), 4.55-4.75 (m, 2H, -CH₂), 5.31-5.45 (m, 1H, -CH₂), 6.23-7.98 (m, 22H, Ar-H). ^{13}C NMR (75 MHz, C_6D_6) δ 14.38 (CH₃), 15.34 (CH₃), 15.61 (CH₃), 18.13 (CH₃), 18.60 (CH₃), 18.89 (CH₃), 46.11 (N-

C), 65.92 (N–C), 109.82 (Ar–C), 110.13 (Ar–C), 110.93 (Ar–C), 115.33 (Ar–C), 117.66 (Ar–C), 120.32 (Ar–C), 123.96 (Ar–C), 124.13 (Ar–C), 125.29 (Ar–C), 124.28 (Ar–C), 125.27 (Ar–C), 125.94 (Ar–C), 126.04 (Ar–C), 126.17 (Ar–C), 127.12 (Ar–C), 127.17 (Ar–C), 127.35 (Ar–C), 127.55 (Ar–C), 127.87 (Ar–C), 127.92 (Ar–C), 127.94 (Ar–C), 128.23 (Ar–C), 130.05 (Ar–C), 132.41 (Ar–C), 134.89 (Ar–C), 135.04 (Ar–C), 135.39 (Ar–C), 135.49 (Ar–C), 136.42 (Ar–C), 136.73 (Ar–C), 137.19 (Ar–C), 137.49 (Ar–C), 139.55 (Ar–C), 140.39 (Ar–C), 148.69 (Ar–C≡N), 164.33 (Ar–C≡N). UV/vis (THF): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$): 230 (56,300), 239 (53,600), 249 (49,200), 285 (15,700), 310 (1,700), 396 (3,400). IR (ATR, cm^{-1}): 2054 (C≡N), 2107 (C≡N). Anal. Calc. for $\text{C}_{48}\text{H}_{50}\text{FeN}_4\text{S}_4$: C 66.49, H 5.81, N 6.46; found: C 65.78, H 5.98, N 6.50. It is noted that due to high air sensitivity, the elemental analysis data of **4** are <2% low. Figures **S12–S14** contain the ^1H NMR, ^{13}C NMR and IR spectra.

5.5.6 Synthesis of $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2(\text{dmpe})]$ (5**).** A J-young NMR tube was charged with $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2]$ (**1**) (0.020 g, 0.033 mmol) and 0.5 mL of CD_2Cl_2 affording a yellow solution. 5.5 μL of 1,2-bis(dimethylphosphino) ethane, dmpe (0.005 g, 0.033 mmol, 1 equiv.) was added to the yellow solution using a glass microsyringe. Upon addition of dmpe, no color change was observed which was confirmed by both ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR experiments at room temperature. Upon cooling to -40°C , the color of the reaction mixture turned to brown. However, attempts to isolate and characterize the expected brown product by recrystallization at lower temperatures were unsuccessful. As a result, we could not obtain its elemental analysis. However, both ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra clearly demonstrate formation of **5** at low temperature in solution. ^1H NMR (300 MHz, CD_2Cl_2 at -40°C) δ 1.11 (br t, 12H, $-\text{CH}_3$ dmpe), 1.97 (ov s, 3H, S–Me), 1.99 (ov s, 3H, S–Me), 2.10 (s, 3H, S–Me), 2.47 (s, 3H, S–Me), 2.99 (d, 1H, $^2J = 18 \text{ Hz}$, $-\text{CH}_2$ dmpe), 3.58 (d, 1H, $^2J = 18 \text{ Hz}$, $-\text{CH}_2$ dmpe), 3.85 (d, 1H, $^2J = 18 \text{ Hz}$, $-\text{CH}_2$ dmpe), 4.21 (d, 1H, $^2J = 18 \text{ Hz}$, $-\text{CH}_2$ dmpe), 5.71 (br s, 1H, $-\text{CH}_2$), 6.01 (br m, 3H, $-\text{CH}_2$), 6.52 (br s, 1H, Ar–H), 6.69 (br s, 2H, Ar–H), 6.88 (br d, 4H, Ar–H), 7.02 (br d, 4H, Ar–H), 7.16 (br s, 2H, Ar–H), 7.34 (br d, 2H, Ar–H). $^{31}\text{P}\{^1\text{H}\}$ NMR

(121 MHz, CD₂Cl₂ at –40°C) δ 44.36 (d, $^2J_{\text{PP}} = 30$ Hz, dmpe) 56.07 (d, $^2J_{\text{PP}} = 30$ Hz, dmpe). Figures **S15-S16** contain the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra.

5.5.7 Synthesis of $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})(\kappa^3\text{-S}^{\text{Me}}\text{N}^{\text{H}}\text{S}^{\text{Me}})](\text{NTf}_2)$ (6**).** A 50 mL round bottom Schlenk flask was charged with $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2]$ (**1**) (0.300 g, 0.496 mmol) and 10 mL of dichloromethane, yielding a yellow solution. A graduated dropping funnel (10 mL) was charged with bis(trifluoromethane)sulfonimide, HNTf₂ (0.139 g, 0.496 mmol, 1 equiv.) and 5 mL of dichloromethane giving a clear colorless solution. The dropping funnel was then connected to the Schlenk flask and the HNTf₂ solution was added dropwise to **1** affording a brick red solution. The resulting solution was stirred for 2 h at room temperature and the solvent was removed under vacuum. The remaining red solid was then washed with diethyl ether (*ca.* 5 × 5 mL) and dried *in vacuo*. Yield: 0.360 g, 82% based on $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2]$. Crystals of **7** suitable for X-ray crystallography were obtained from a concentrated dichloromethane solution at –35 °C. ^1H NMR (300 MHz, CD₂Cl₂ at 25°C) δ –69.22 (br s), –42.56 (br s) –12.02 (br s), –11.05 (br s), –7.31 (br s), 0.45 (br s), 2.32 (br s), 4.30 (br s), 7.07 (br s), 8.63 (br s), 10.54 (br s), 13.68–14.58 (br m), 22.08 (br s), 25.55 (br s), 36.58 (br s), 40.96 (br s), 54.19 (br s), 81.70 (br s), 86.40 (br s), 125.70 (br s), 132.10 (br s), 152.70 (br s). ^{19}F NMR (282 MHz, CDCl₃) δ –66.80 (br s, $\Delta\nu_{1/2} = 215$ Hz, Tf). UV/vis (CH₂Cl₂): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{ cm}^{-1}$): 312 (6,800), 351 (2,000). IR (ATR, cm^{–1}): 3488 (N–H). μ_{eff} (CDCl₃) = 5.37 μ_{B} . Anal. Calc. for C₃₂H₃₃F₆FeN₃O₄S₆: C 43.39, H 3.75, N 4.74; found: C 42.92, H 3.54, N 4.32. Figures **S17-S18** contain the ^1H and ^{19}F NMR spectra.

5.5.8 Synthesis of $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})(\kappa^3\text{-triphos})]$ (7**).** A 20 mL scintillation vial was charged with $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})(\kappa^3\text{-S}^{\text{Me}}\text{N}^{\text{H}}\text{S}^{\text{Me}})](\text{NTf}_2)$ (**6**) (0.060 g, 0.068 mmol) and triphos (0.036 g, 0.068 mmol, 1 equiv.). Upon addition of 5 mL of THF, the color of the reaction mixture instantly turned to magenta. The resulting solution was stirred for 6 h at room temperature over which period no further color change was observed. THF was removed under vacuum and the remaining dark solid was washed with benzene (*ca.* 4 × 5 mL) and diethyl ether (3 × 5 mL) and dried *in vacuo*. Yield:

0.051 g, 65% based on $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})(\kappa^3\text{-S}^{\text{Me}}\text{N}^{\text{H}}\text{S}^{\text{Me}})](\text{NTf}_2)$. Crystals of **7** suitable for X-ray crystallography were obtained from a concentrated benzene solution layered with hexane at room temperature. ^1H NMR (300 MHz, THF- d_8 at 25°C) δ 2.20 (s, 3H, S–Me), 2.39 (s, 3H, S–Me), 3.11 (br m, 6H, –CH₂ triphos), 4.10 (br s, 2H, –CH₂ triphos), 5.89 (br s, 1H, –CH₂), 6.15 (d, 1H, –CH₂), 6.48–7.25 (m, 26H, Ar–H), 7.38–7.74 (m, 7H, Ar–H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, THF- d_8 at 25°C) 75.60 (br s, triphos), 83.15 ppm (t, $^2J_{\text{PP}} \approx 22$ Hz, triphos); at –40°C 81.54 (dd, $^2J_{\text{PP}} = 21$ Hz, 28 Hz, triphos), 74.74 (dd, $^2J_{\text{PP}} = 21$ Hz, 28 Hz, triphos), 74.12 (t, $^2J_{\text{PP}} = 21$ Hz, triphos). ^{19}F NMR (282 MHz, THF- d_8) δ –78.50 (br s, $\Delta\nu_{1/2} = 140$ Hz, Tf). UV/vis (THF): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$): 251 (22,000), 311 (6,600), 519 (2,400). Anal. Calc. for $\text{C}_{54}\text{H}_{52}\text{F}_6\text{FeN}_2\text{O}_4\text{P}_3\text{S}_4$: C, 54.78; H, 4.43; N, 2.37. Found: C, 54.63; H, 4.42; N, 2.29. Figures **S19–S21** contain the ^1H , $^{31}\text{P}\{^1\text{H}\}$ and ^{19}F NMR spectra.

5.5.9 Procedure for amine-borane dehydrogenation catalysis. In a J. Young NMR tube, 3 mg of ammonia-borane (AB, 32 equiv.) was mixed with 3.5 mg of **7** in THF (0.3 mL). The NMR solution was then heated at 60 °C in which time the color of the solution changed from magenta to orange. The progress of the reaction was monitored by ^{11}B , $^{11}\text{B}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. After 23 h, the resulting solution was filtered and THF was removed using vacuum. The resulting solid was further characterized by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. For dehydrogenation catalysis using dimethylamine-borane (DMAB), in a J. Young NMR tube, 7.7 mg of DMAB (20 equiv.) was mixed with 7.5 mg of **7** in THF (0.3 mL). The NMR solution was then heated at 60 °C in which time the color of the NMR solution changed from magenta to orange. The progress of the reaction was monitored by ^{11}B , $^{11}\text{B}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. After 23 h, the resulting solution was filtered and THF was removed using vacuum. The resulting solid was then characterized by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

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Chapter 6. Conclusions and Future Outlook

Development of efficient and sustainable metal catalysts depends on judicious choice of metal and ligand. In catalysis, either the metal or both the metal and a ligand acting cooperatively, activate substrates, functionalize, and allow selective conversion into products. However, today's industrial synthesis of chemicals still relies heavily on metal catalysts based on precious, non-abundant and toxic metals, and expensive ligands. Although these precious metal catalysts are quite active and selective, and sometimes benefit from low catalyst loadings, leaching traces of these toxic metals may cause environmental and health impacts during separation and purification of chemicals. This is particularly true for the pharmaceutical industry. In this context, earth abundant, inexpensive, and environmentally benign metals have gained significant attention in recent years. Iron-based catalysts are undoubtedly the best choice in this regard since iron is earth-abundant, inexpensive, and non-toxic. Both homo- and heterogeneous iron catalysts have been used in reactions ranging from oxidation and reduction to C-C bond-forming reactions. In addition, bifunctional iron catalysts have lately emerged as remarkable catalysts for asymmetric hydrogenation and transfer hydrogenation of polar bonds, achieving precious metal catalyst type activity under mild conditions.

In homogeneous transition metal catalysis, the supporting ligand plays a significant role with the metal in executing important tasks such as small molecule activation, functionalization and selective conversion of challenging substrates. Bifunctional ligands are attractive in this context since they have shown potential for small molecule activation and for catalyzing a number of chemical transformations with activity and selectivity typical of more well-studied precious metal-based catalysts. We aimed to improve the field of bifunctional ligands by preparing new sterically svelte tridentate ligands with a mixture of hard nitrogen and soft sulfur donors and to investigate their iron chemistry. The ultimate goal is to explore the utility of these iron complexes as potential bifunctional catalysts. This *Thesis* covered progress towards the synthesis of new hemilabile

tridentate mixed sulfur and nitrogen donor ligands, studied iron chemistry with these ligands, and explored several applications of these iron complexes as potential bifunctional catalysts.

Iron complexes with ‘hard’ nitrogen and ‘soft’ sulfur donor ligands are of increasing interest because of their diverse structural features and intriguing reactivity as well as their important role in biological catalysis. Many mono- and multimetallic iron complexes containing the mixed N,S-donor ligands have been developed in previous years. These complexes function as biomimetic models and show their ability as potential electrocatalysts for hydrogen evolution. In order to develop bifunctional iron catalysts containing mixed N,S-donor ligands, we set out to design new sterically svelte tridentate mixed S,N-donor ligands which can easily be synthesized using commercially available starting materials, and to then investigate their iron chemistry.

Chapter 2 unveiled the preparation of a new tridentate mixed N,S-donor ligand, $S^{Me}N^HS = 2-(2\text{-methylthiobenzylidene})\text{aminothiophenol}$ in a single step from commercial precursors in excellent yield. Spectroscopic measurements confirmed the $S^{Me}N^HS$ ligand is a closed ring heterocycle. No trace of the ring-opened imine isomer was observed by NMR spectroscopy. Treatment of this ligand with $Fe(OTf)_2$ in the presence of base afforded a trinuclear iron complex, $[Fe_3(\mu_2-S^{Me}NS^-)_4](OTf)_2$ in which two pseudooctahedral $Fe(SNS)_2$ units are coordinated to a central tetrahedral iron center via thiolate bridges. In our attempts to isolate mononuclear $Fe(SNS)$ complexes, we uncovered an unusual solvent dependence in which addition of $P(OMe)_3$ in acetonitrile afforded the thiolate-bridged, dinuclear dicationic product whereas use of less polar chlorinated solvents gave mononuclear $[Fe(\kappa^3-SNS)\{P(OMe)_3\}_3](OTf)$ with a terminal thiolate. Future work may be directed at the preparation of a series of mixed-metal trinuclear species by exchange of the central iron with other divalent or trivalent metals (including lanthanides), with a view to incorporating a Lewis acid site for bifunctional substrate activation.

Use of more electron-rich ancillary ligands in Chapter 3 revealed a propensity for selective oxidative $C_{aryl}\text{-S}$ bond cleavage associated with the thioether donor, forming a *trivalent* iron complex of the dianionic thiolate-imine-aryl tridentate ligand. Although we were only able to trap

the expected methylthioradical by its reaction with PMe_3 to give $\text{Me}_3\text{P}=\text{S}$, the inability of the electron-rich bis(phosphine) analog, $[\text{Fe}(\text{SNS})(\text{PMe}_3)(\text{dmpe})](\text{OTf})$, to effect the C-S bond cleavage suggests that the lability of the thioether S-donor must be accompanied by phosphine dissociation in order for this transformation to proceed. Reduction of this Fe(III) species with cobaltocene afforded the divalent complex, which adds dmpe to give $[\text{Fe}(\text{CNS})(\text{PMe}_3)(\text{dmpe})]$, allowing us to assess the similar SNS and SNC complexes as catalysts. Conducting amine-borane dehydrogenation catalysis in THF at 60 °C showed that the Fe(II) SNC dmpe complex serves as a selective and robust bifunctional catalyst system. While we speculated that the location of the aryl donor in a non-central position of the tridentate chelate may eventually lead to a bidentate NS ligand in some catalytic applications, preliminary spectroscopic suggests retention of the Fe-aryl linkage in dehydrocoupling reactions. Future work should be directed to exploring the potential bifunctional behavior of the CNS thiolate dmpe complex in other applications, including isolation and characterization of intermediate iron hydride complexes to check for formation of B-S bonds.

In chapter 4 we attempted to synthesize neutral $\text{Fe}(\text{SNS})_2$ using the low-coordinate iron complex, $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2]$. Interestingly, the reaction yielded instead the imine-coupled $[\text{Fe}-\text{N}_2\text{S}_2]_2$ complex. Experimental characterization and DFT studies confirmed formation of the redox-active $(\text{N}_2\text{S}_2)^{2-}$ ligand with two uncoordinated thioether groups in the thiolate-bridged dimer. Interestingly, in solution the dimer totally dissociates into the monomer which retains the square pyramidal coordination about iron by coordinating one of the two thioether groups. Spectroelectrochemical and DFT studies indicated two additional stable redox states localized primarily at the iron center, i.e., Fe(I, II, III). The Fe(II) complex was found to an efficient and selective aldehyde hydroboration catalyst at room temperature using pinacolborane. The key advantages of this catalyst are its exclusive aldehyde selectivity over ketone, wide reducible functional group tolerance and extraordinary catalyst lifetime. To gain mechanistic insight, kinetic studies were performed using the Reaction Progress Kinetic Analysis (RPKA) technique which revealed complex dependence on the substrate, borane and catalyst concentrations. Unusual rate

enhancement by specific concentrations of ketones that are not reduced, combined with reversible formation of the CO complex, $[\text{Fe}(\kappa^3\text{-SNS})(\kappa^2\text{-SNS})\text{CO}]$ presumable furnish clues as to this complex reaction mechanism. Further experimental and theoretical studies are in progress using all three redox states in order to better understand the mechanism of this catalytic system.

While synthesizing the imine-coupled iron complex, reaction of one equivalent of $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2]$ with one equivalent of $[\text{S}^{\text{Me}}\text{N}^{\text{HS}}]$ ligand in THF at room temperature afforded a paramagnetic, thiolate-bridged Fe(II) dimer, $[\text{Fe}(\kappa^2\text{-SNS}^{\text{Me}})\text{N}(\text{SiMe}_3)_2]_2$ which has been characterized by ^1H NMR and X-ray crystallography. Although this complex is not included in this *Thesis*, its reactivity with a variety of E-H compounds and mono- and bidentate donor ligands will be explored in the future along with their roles as bifunctional homogeneous catalysts.

One goal of our bifunctional catalysis research was to prepare analogous thiolate and amido complexes in order to assess when a ‘soft’ vs ‘hard’ donor would be optimal for a given bifunctional catalytic application. In chapter 5, we prepared a new unsymmetrical tridentate bis(thioether) amine ligand, $\text{S}^{\text{Me}}\text{N}^{\text{HS}}\text{S}^{\text{Me}}$, and the corresponding paramagnetic, pseudo-octahedral $\text{Fe}(\kappa^3\text{-SNS})_2$ bis(amido) complex, that exhibits short Fe-S bond distances in the 5-membered rings and long ones in the 6-membered rings. Using a combination of magnetic circular dichroism and TD-DFT calculations, we provided evidence for both 6- and square-pyramidal 5-coordinate iron species in solution due to the hemilability of the $\text{Fe-S}_{\text{thioether}}$ bonds in the 6-membered rings. We also prepared pseudo-octahedral $\text{FeL}_2(\kappa^2\text{-SNS})_2$ bis(ligand) bis(amido) complexes (paramagnetic for L_2 = bipyridine and diamagnetic for L = arylisonitrile) in which both 6-membered rings have been opened by treatment of $\text{Fe}(\kappa^3\text{-SNS})_2$ with suitable donor ligands. Addition of a Brønsted acid, HNTf_2 , produced the paramagnetic, iron(II) amine-amido cation, $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})(\kappa^3\text{-S}^{\text{Me}}\text{N}^{\text{HS}}\text{S}^{\text{Me}})](\text{NTf}_2)$ that readily undergoes amine ligand substitution by triphos affording the 16e- complex $[\text{Fe}(\kappa^2\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})(\kappa^3\text{-triphos})](\text{NTf}_2)$. The latter was shown to be more active as a precatalyst for dehydrogenation of dimethylamine-borane vs. ammonia-borane at 60 °C and

formation of a monohydride catalyst resting state is suggestive of a bifunctional activation pathway. Future studies in this area will benefit from the isolation and characterization of this iron hydride complex to check for formation of the N-H bond.

Preliminary attempts to prepare electron-rich Fe(SNS) amido complexes led again to selective C_{aryl}-S and benzylic C-H bond activation with formation of divalent Fe(SNC)(PMe₃)₃ that now features a monoanionic thioether-imine-aryl (S^{Me}NC) tridentate ligand. The Fe-SNS and -SNC dmpe derivatives will soon be compared with their thiolate analogs as precatalysts for amine-borane dehydrogenation, providing additional insight into the performance of these four bifunctional tridentate ligands.

As the work presented in this *thesis* was being carried out over the past six years, incredible progress was made in many different areas of inorganic and organometallic chemistry. The knowledge gained from iron chemistry of hemilabile SNS ligands presented here is now being extended successfully to other transition metals such as Mn, Co, Ni and Cu in the Baker lab. Studies focused on furthering the understanding of transition metal SNS chemistry will undoubtedly aid the further development of bifunctional catalysis.

Appendices

Chapter 2:

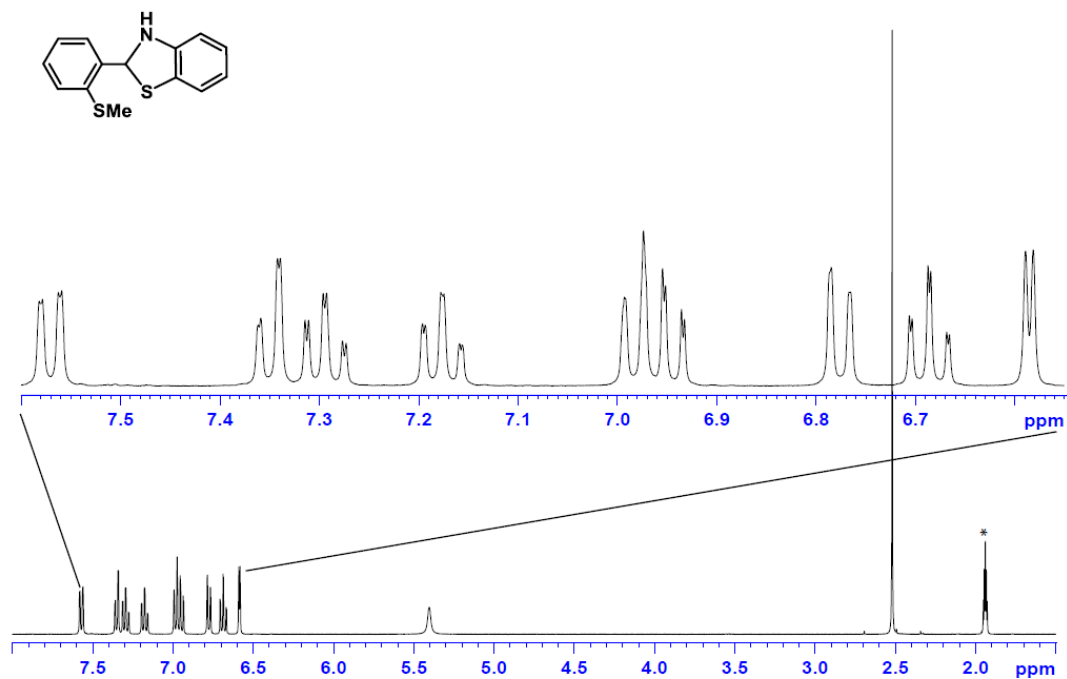


Figure A1. 1H NMR spectrum (300 MHz, CD_3CN) of $[S^{Me}N^H S]$ ligand.

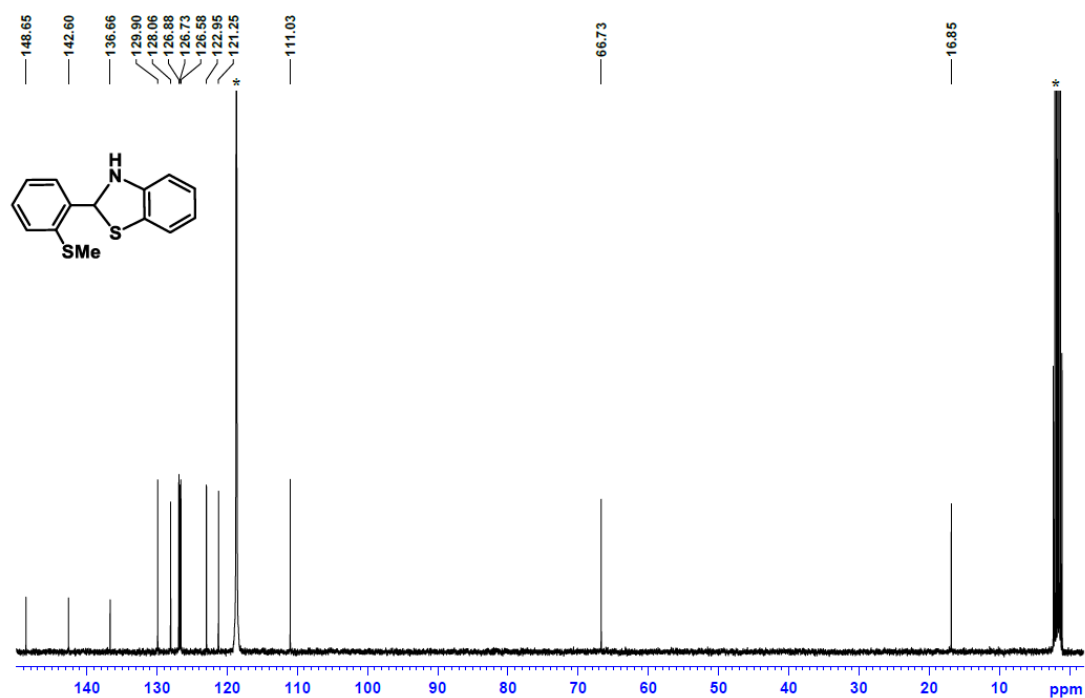


Figure A2. $^{13}C\{^1H\}$ NMR spectrum (101 MHz, CD_3CN) of $[S^{Me}N^H S]$ ligand.

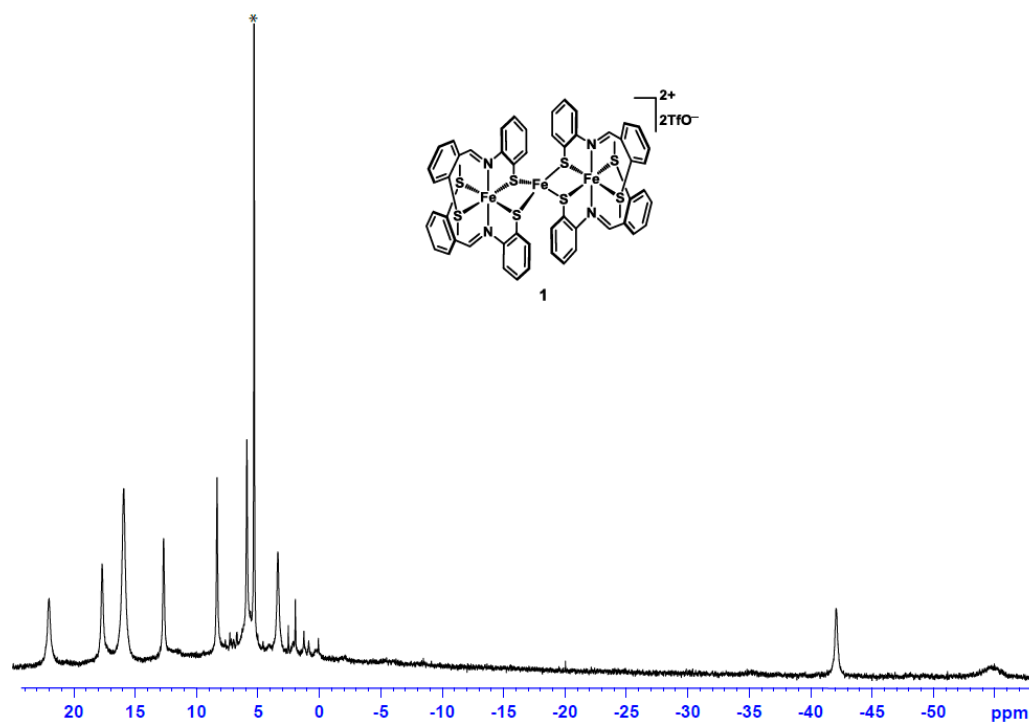


Figure A5. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of $[\text{Fe}_3(\mu^2\text{-S}^{\text{Me}}\text{NS}^-)_4](\text{OTf})_2$ (1).

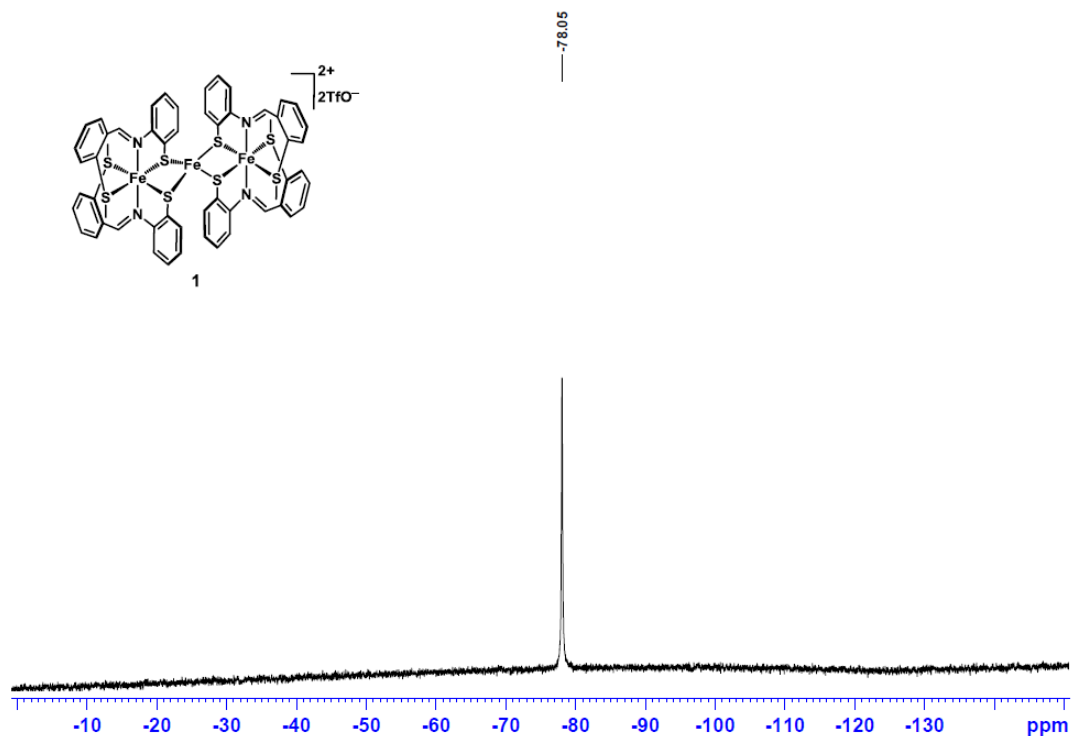


Figure A6. ^{19}F NMR spectrum (282 MHz, CD_2Cl_2) of $[\text{Fe}_3(\mu^2\text{-S}^{\text{Me}}\text{NS}^-)_4](\text{OTf})_2$ (1).

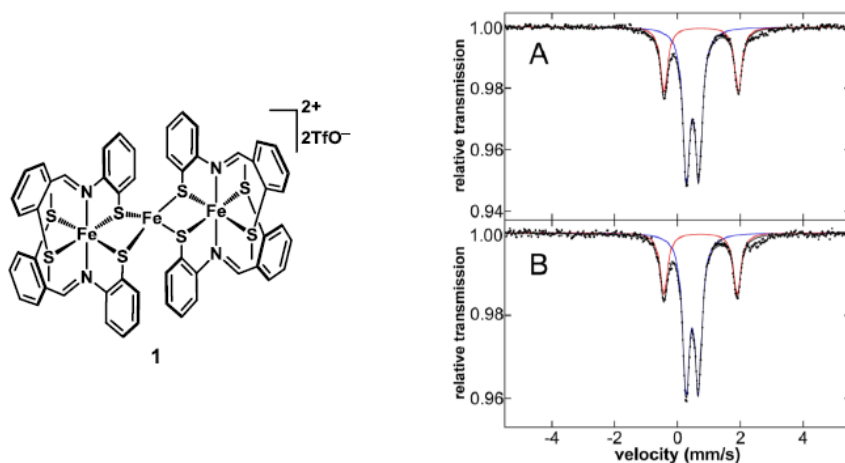


Figure A8. VT Mössbauer spectrum of $[\text{Fe}_3(\mu^2\text{-S}^{\text{Me}}\text{NS}^-)_4](\text{OTf})_2$ (**1**). (A) 80 K and (B) 130 K Mössbauer spectra. Data (black dots) and total fit (black lines) are shown. The Individual component parameters are the following. T = 80 K: $\delta = 0.48$, $\Delta\text{EQ} = 0.39$ (blue, 65%) and $\delta = 0.76$, $\Delta\text{EQ} = 2.37$ (red, 35%). T = 130 K: $\delta = 0.47$, $\Delta\text{EQ} = 0.39$ (blue, 69%) and $\delta = 0.76$, $\Delta\text{EQ} = 2.33$ (red, 31%).

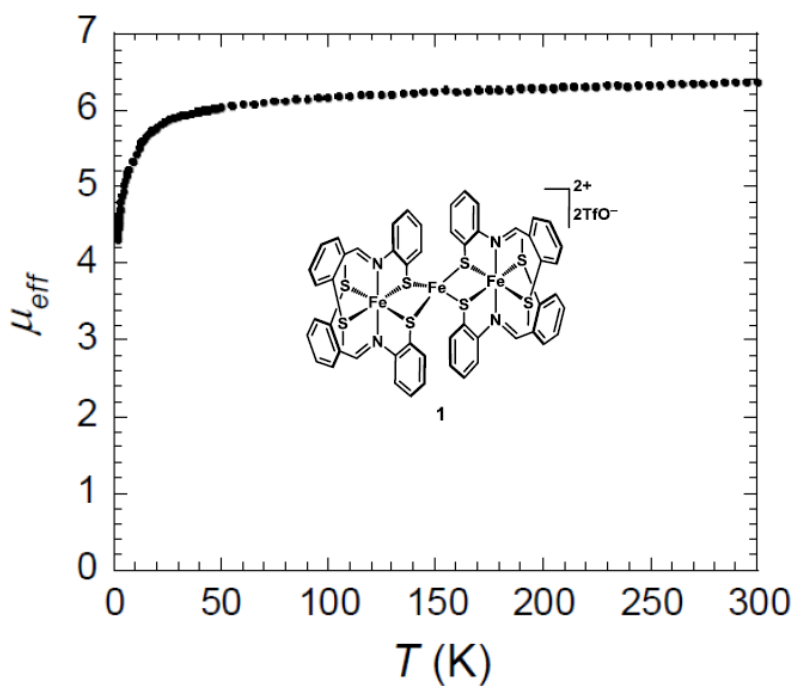


Figure A9. Variable temperature magnetic moment of $[\text{Fe}_3(\mu^2\text{-S}^{\text{Me}}\text{NS}^-)_4](\text{OTf})_2$ (**1**) under an applied dc field of 0.1 T.

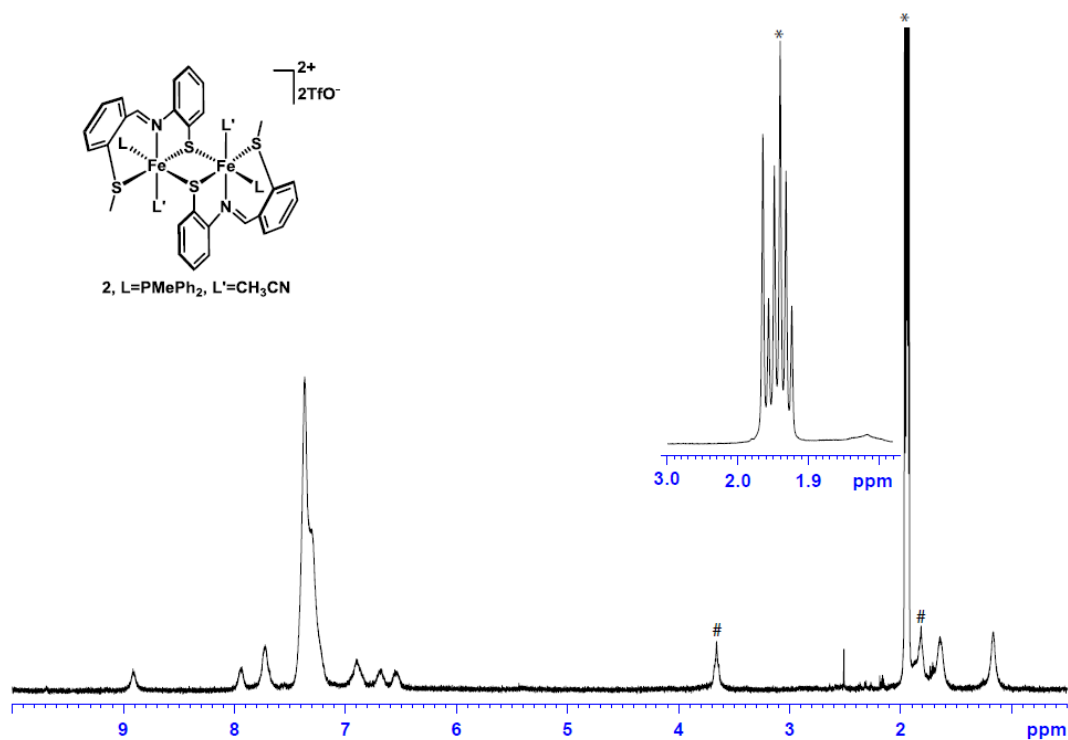


Figure A11. ^1H NMR spectrum (300 MHz, CD_3CN) of $\{[\text{Fe}(\mu\text{-S}^{\text{Me}}\text{NS}^-)(\text{PMePh}_2)(\text{CH}_3\text{CN})]_2\}(\text{OTf})_2$ (**2**). [*NMR solvent; #THF]

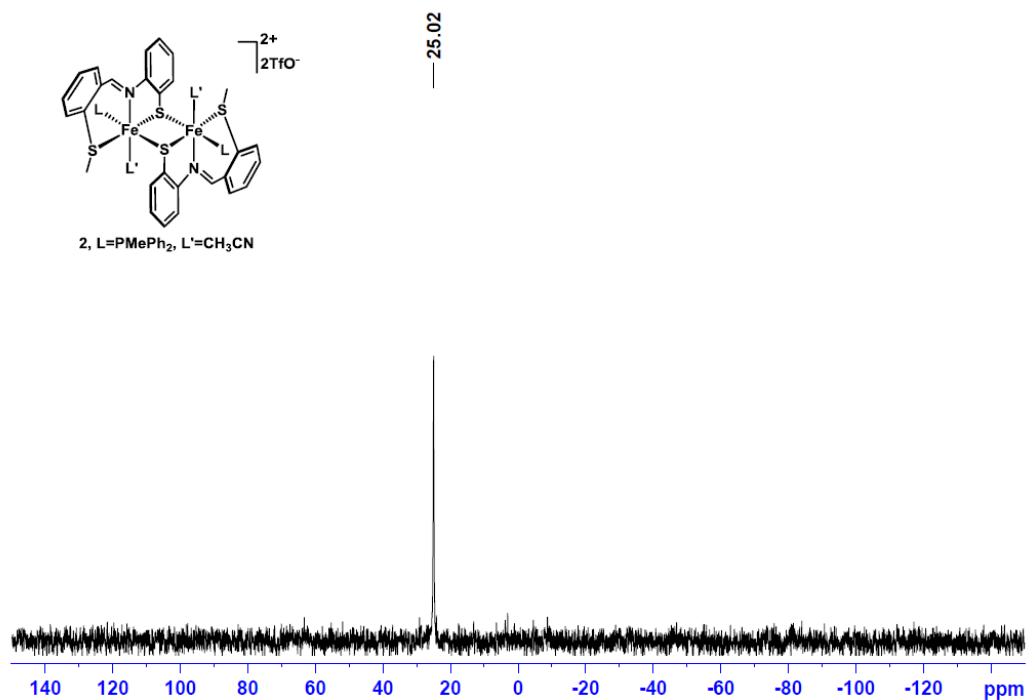


Figure S12. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121 MHz, CD_3CN) of $\{[\text{Fe}(\mu\text{-S}^{\text{Me}}\text{NS}^-)(\text{PMePh}_2)(\text{CH}_3\text{CN})]_2\}(\text{OTf})_2$ (**2**). (LB = 3Hz)

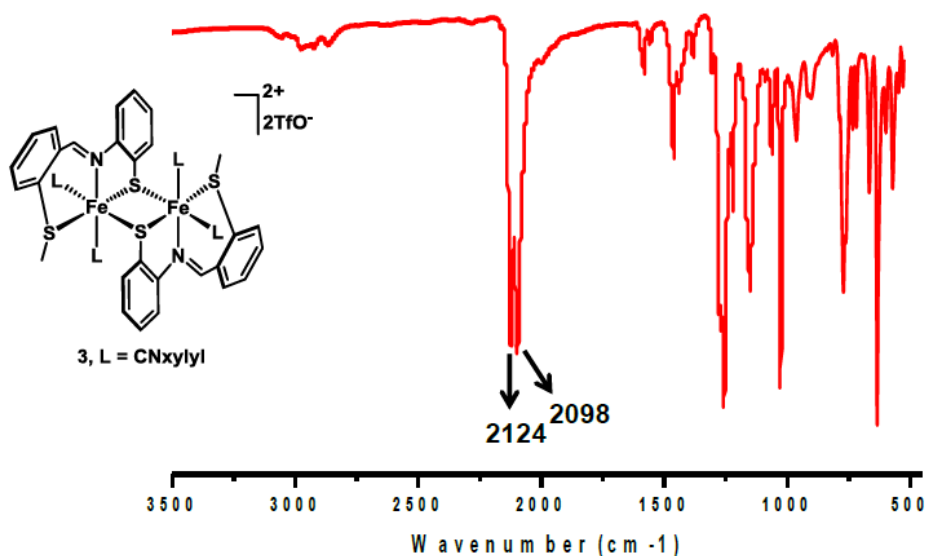


Figure A17. IR (ATR) spectrum of $\{[\text{Fe}(\mu\text{-S}^{\text{Me}}\text{NS}^-)(\text{CNxylyl})_2]_2\}(\text{OTf})_2$ (**3**).

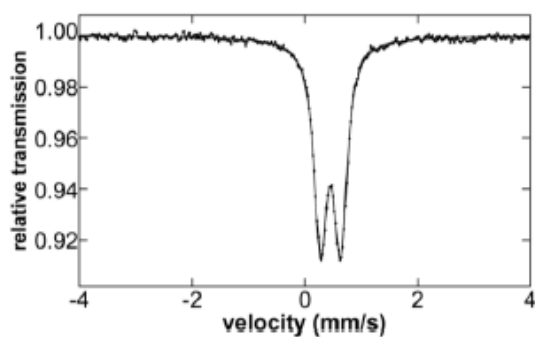


Figure A18. 5 K Mössbauer spectrum of $\{[\text{Fe}(\mu\text{-S}^{\text{Me}}\text{NS}^-)(\text{PMePh}_2)(\text{CH}_3\text{CN})]_2\}(\text{OTf})_2$ (**2**). The doublet is well-fit to the Mössbauer parameters $\delta = 0.45$ and $\Delta\text{EQ} = 0.35$.

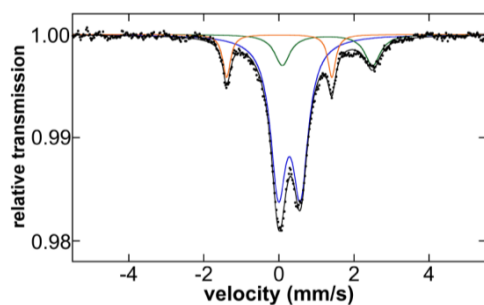


Figure A19. 80 K Mössbauer spectrum of $\{[\text{Fe}_2(\mu\text{-S}^{\text{Me}}\text{NS}^-)[\text{P}(\text{OMe})_3]_2\}(\text{OTf})_2$ (**4**). The major species is fit to $\delta = 0.28$ and $\Delta\text{EQ} = 0.59$ (blue, 72%). Two additional components are observed with $\delta = 1.29$, $\Delta\text{EQ} = 2.40$ (green, 16%) and $\delta = 0.01$, $\Delta\text{EQ} = 2.80$ (orange, 11%).

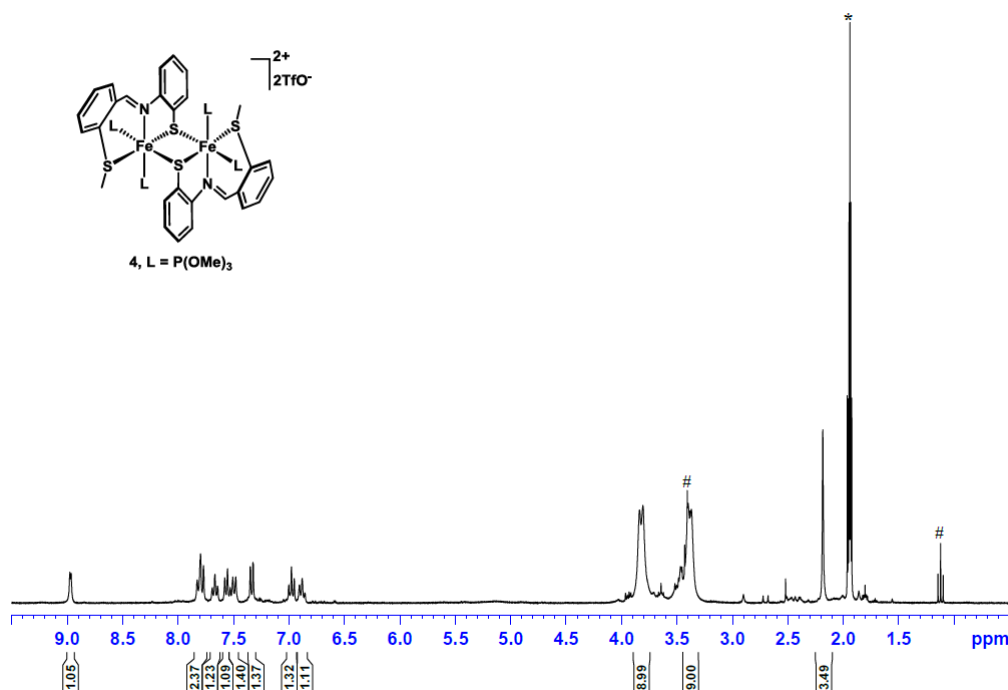


Figure A20. ^1H NMR spectrum (300 MHz, CD_3CN) of $\{[\text{Fe}(\mu\text{-S}^{\text{Me}}\text{NS}^-)[\text{P}(\text{OMe})_3]_2]_2\}(\text{OTf})_2$ (**4**). [*NMR solvent; #diethyl ether]

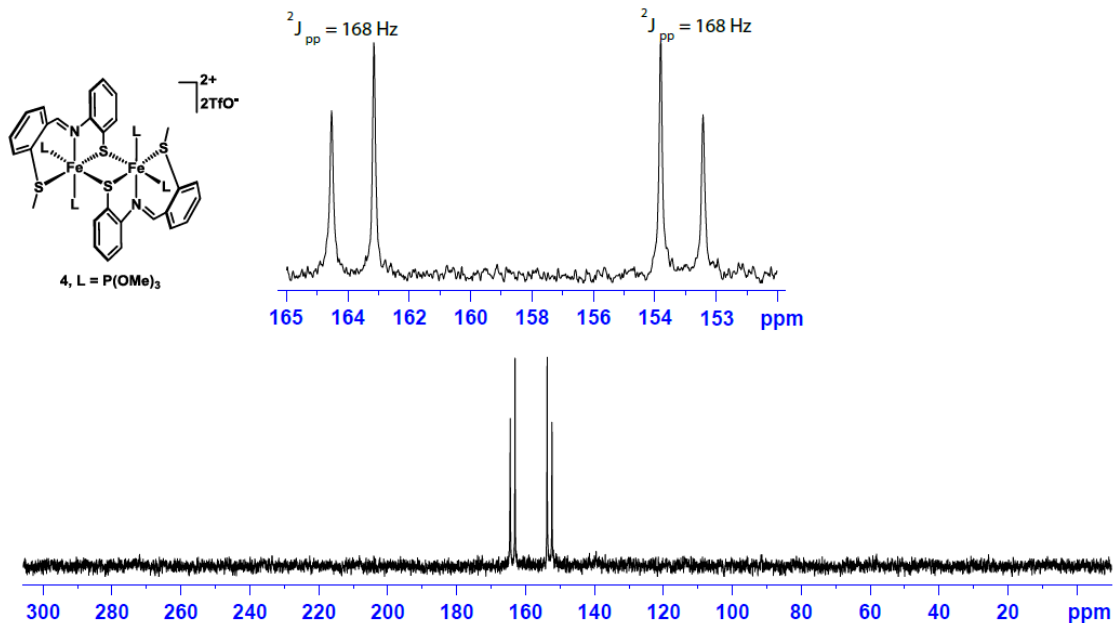


Figure A21. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121 MHz, CD_3CN) of $\{[\text{Fe}(\mu\text{-S}^{\text{Me}}\text{NS}^-)[\text{P}(\text{OMe})_3]_2]_2\}(\text{OTf})_2$ (**4**). (LB = 5Hz)

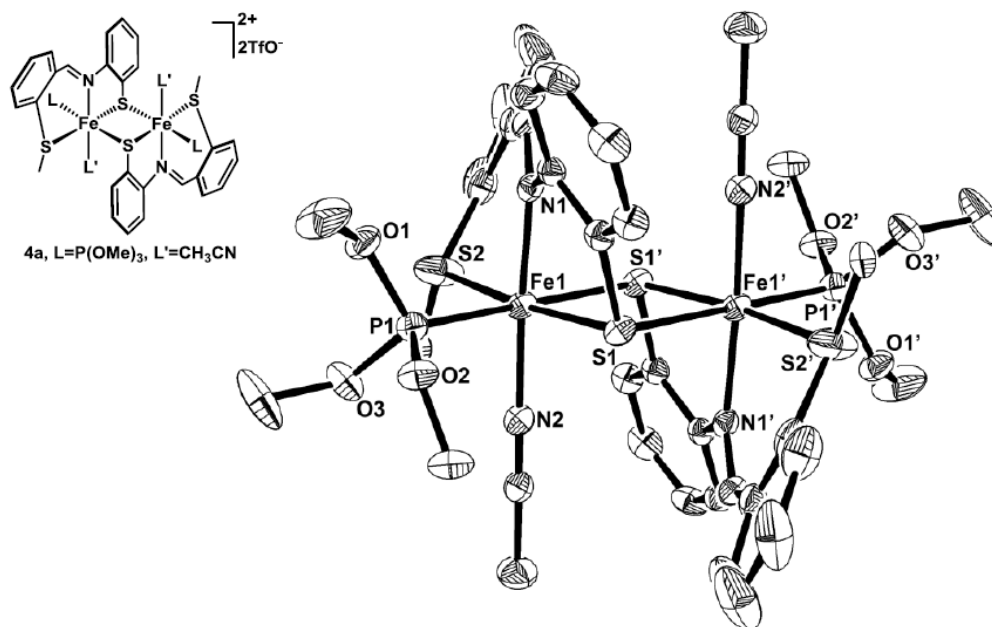


Figure A23. ORTEP diagram of $\{[\text{Fe}(\mu\text{-S}^{\text{Me}}\text{NS}^-)(\text{CH}_3\text{CN})[\text{P}(\text{OMe})_3]]_2\}(\text{OTf})_2$ (**4a**). Thermal ellipsoids are shown at 40% probability. Hydrogen atoms, CH₃CN molecules and triflate anions are omitted for clarity.

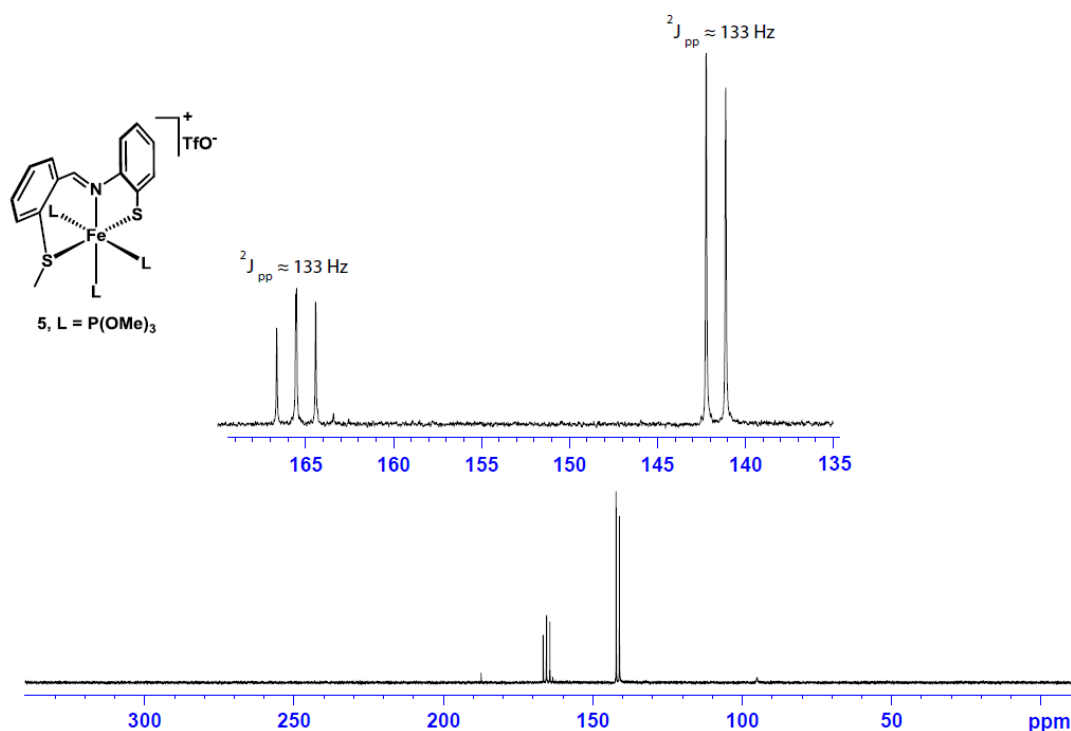


Figure A29. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121 MHz, CDCl₃) of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS}^-)\{\text{P}(\text{OMe})_3\}_3](\text{OTf})$ (**5**).

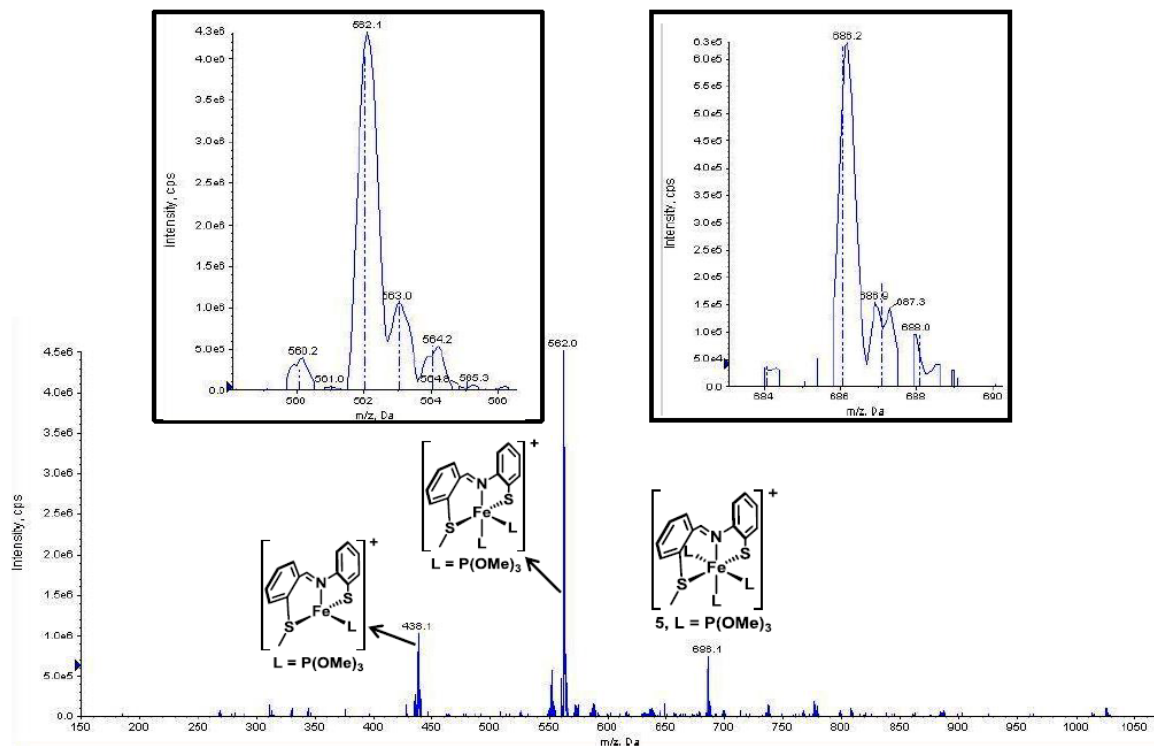


Figure A31. ESI-MS spectrum of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS}^-)\{\text{P}(\text{OMe})_3\}_3](\text{OTf})$ (5). Inset figures: comparison of experimental isotopic patterns of $[\text{M}]^+ = 686.1$ and 562.0 with simulated isotopic patterns.

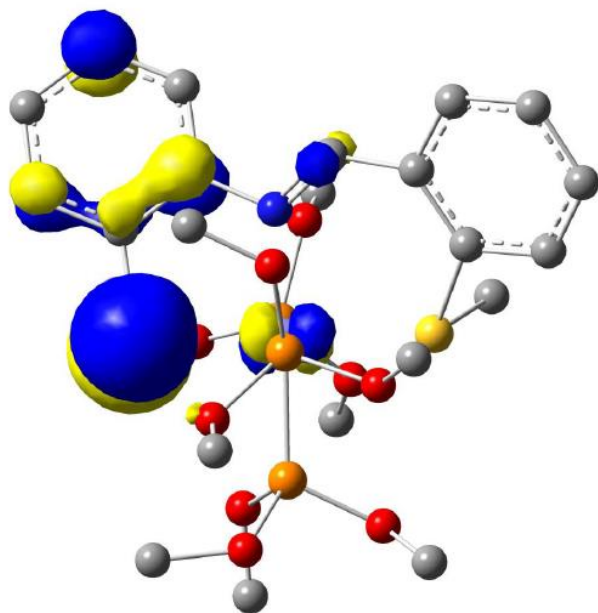


Figure A32. The HOMO of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS}^-)\{\text{P}(\text{OMe})_3\}_3](\text{OTf})$ (5). The orbital is shown with the isosurface value of 0.05 a.u. H atoms are omitted for clarity.

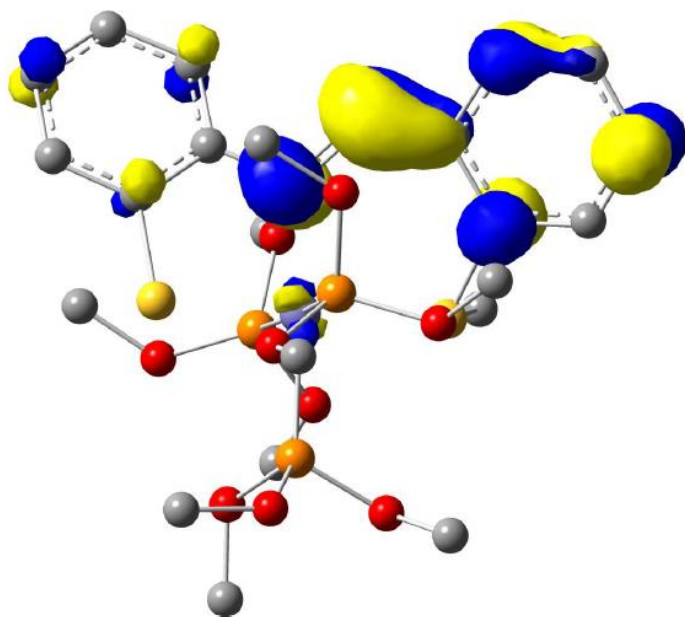


Figure A33. The LUMO of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS}^-)\{\text{P}(\text{OMe})_3\}_3](\text{OTf})$ (5). The orbital is shown with the isosurface value of 0.05 a.u. H atoms are omitted for clarity.

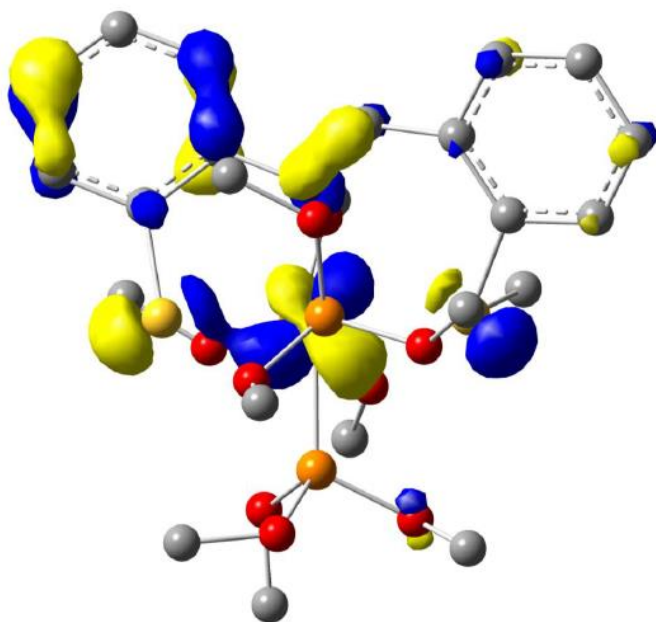


Figure A34. The HOMO-2 of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS}^-)\{\text{P}(\text{OMe})_3\}_3](\text{OTf})$ (5). The orbital is shown with the isosurface value of 0.05 a.u. H atoms are omitted for clarity.

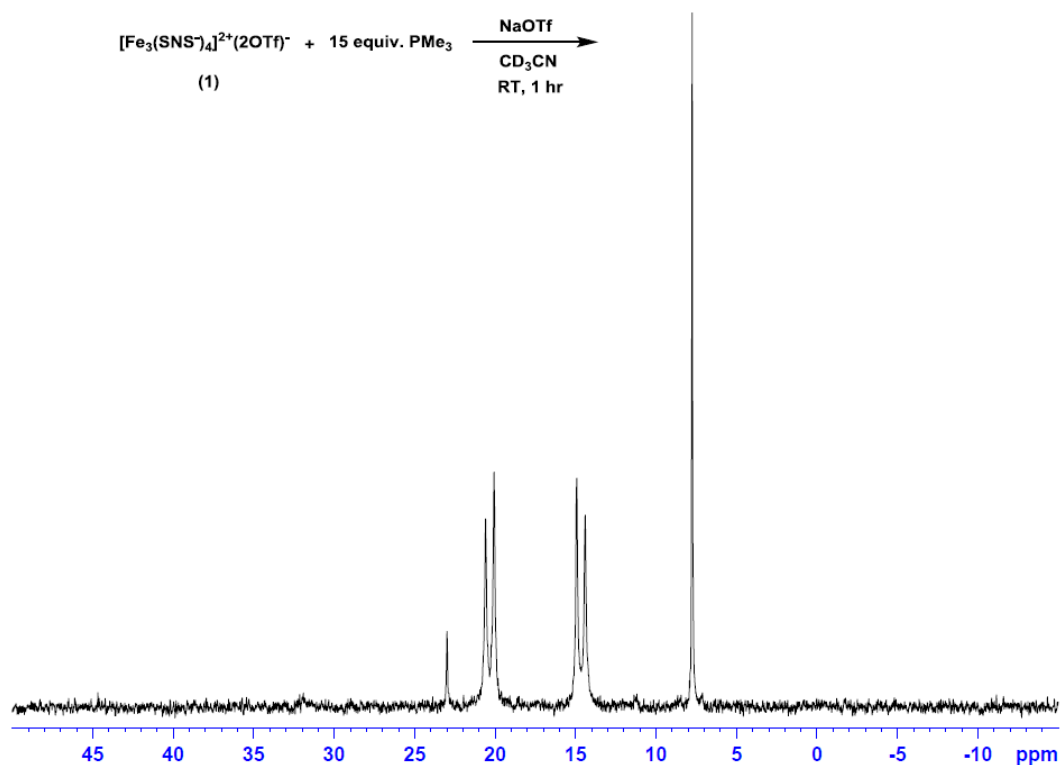


Figure A35. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121 MHz, CD_3CN) of the reaction of $[\text{Fe}_3(\mu^2\text{-S}^{\text{Me}}\text{NS}^-)_4](\text{OTf})_2$ (**1**) and NaOTf with PMe_3 .

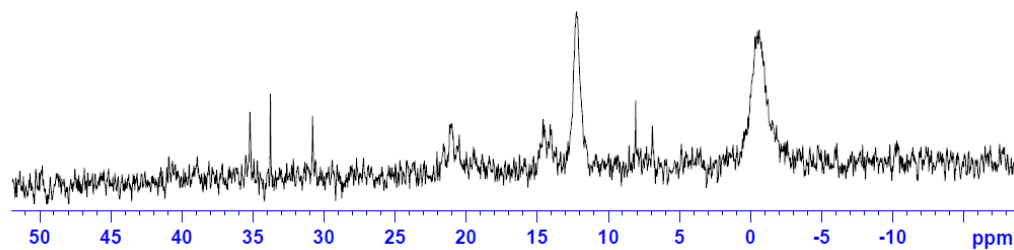
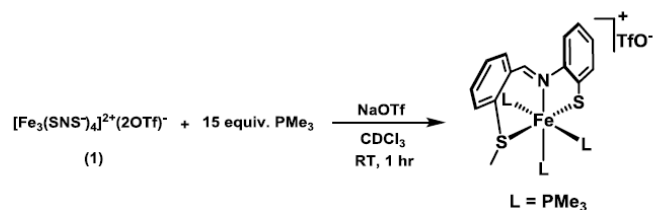


Figure A36. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121 MHz, CDCl_3) of the reaction of $[\text{Fe}_3(\mu^2\text{-S}^{\text{Me}}\text{NS}^-)_4](\text{OTf})_2$ (**1**) and NaOTf with excess PMe_3 .

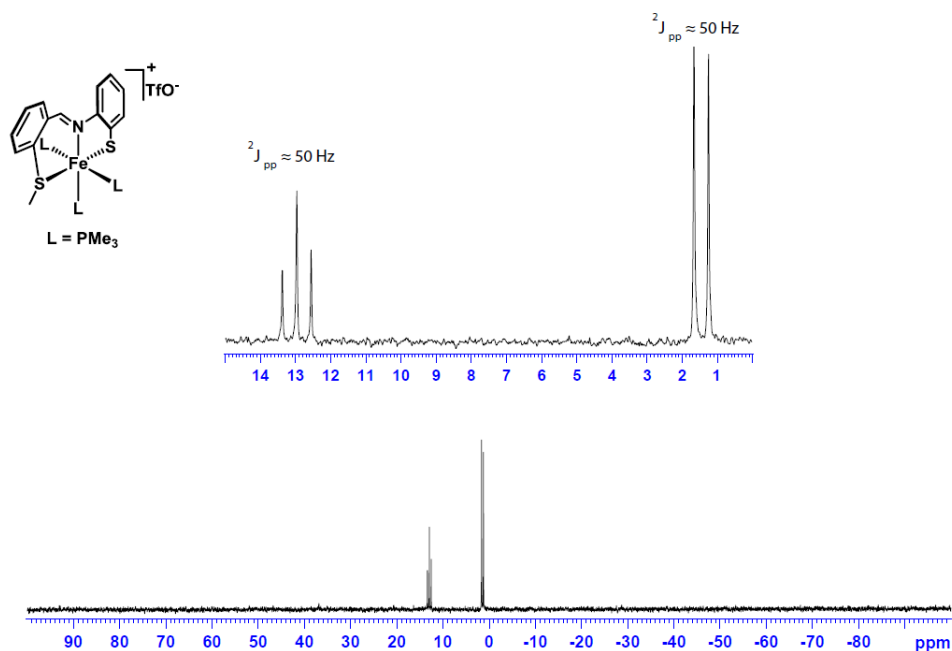


Figure A37. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum {121 MHz, $(\text{CD}_3)_2\text{CO}$ } of the reaction of $[\text{Fe}_3(\mu^2\text{-S}^{\text{Me}}\text{NS}^-)_4](\text{OTf})_2$ (**1**) and NaOTf with excess PMe_3 at -20°C .

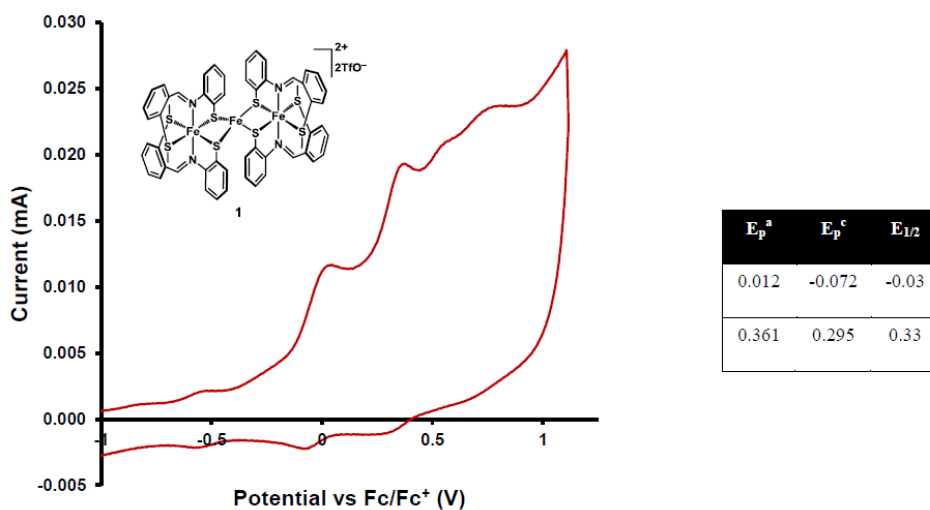


Figure A38. Cyclic voltammogram of $[\text{Fe}_3(\mu^2\text{-S}^{\text{Me}}\text{NS}^-)_4](\text{OTf})_2$ (**1**) in CH_2Cl_2 under N_2 atmosphere ([complex] 0.5 mM, at 100 mV scan rate in 0.1M n-Bu₄NPF₆).

Remaining appendices for Chapter 2 of this thesis can be found in the supporting information of the following published article:

Chapter 2: Das, U. K.; Daifuku, S. L.; Gorelsky, S. I.; Korobkov, I.; Neidig, M. L.; Le Roy, J. J.; Murugesu, M.; Baker, R. T. Mononuclear, Dinuclear, and Trinuclear Iron Complexes Featuring a New Monoanionic SNS Thiolate Ligand. *Inorg. Chem.* **2016**, 55, 987-997.

Chapter 3:

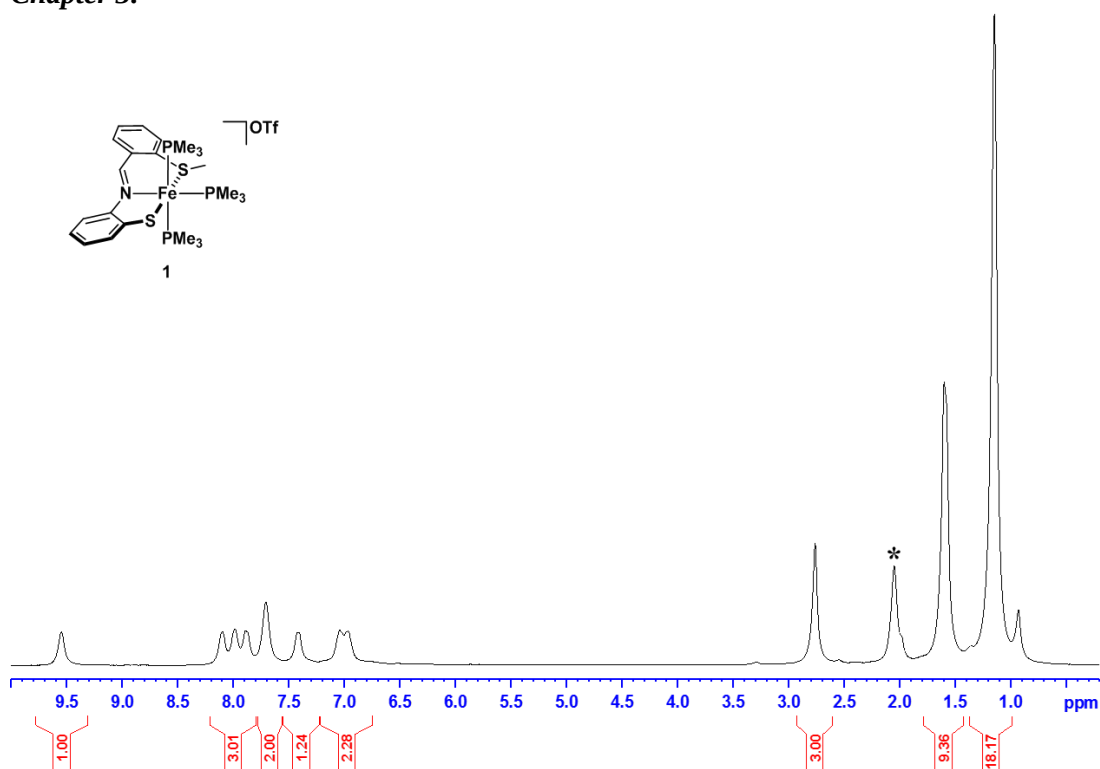


Figure A1. ^1H NMR (300 MHz, acetone- d_6) spectrum of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_3](\text{OTf})$ (**1**) at $-40\text{ }^\circ\text{C}$.

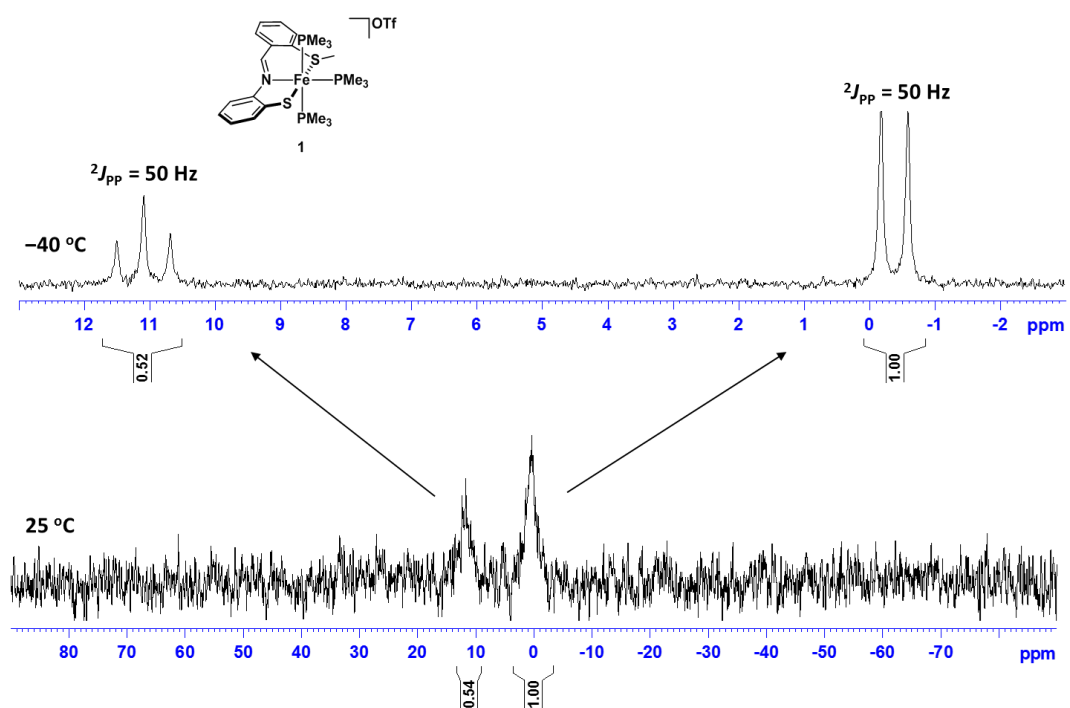


Figure A2. ^{31}P $\{^1\text{H}\}$ NMR (121 MHz, acetone- d_6) spectrum of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_3](\text{OTf})$ (**1**) at room temperature (bottom) and at $-40\text{ }^\circ\text{C}$ (top).

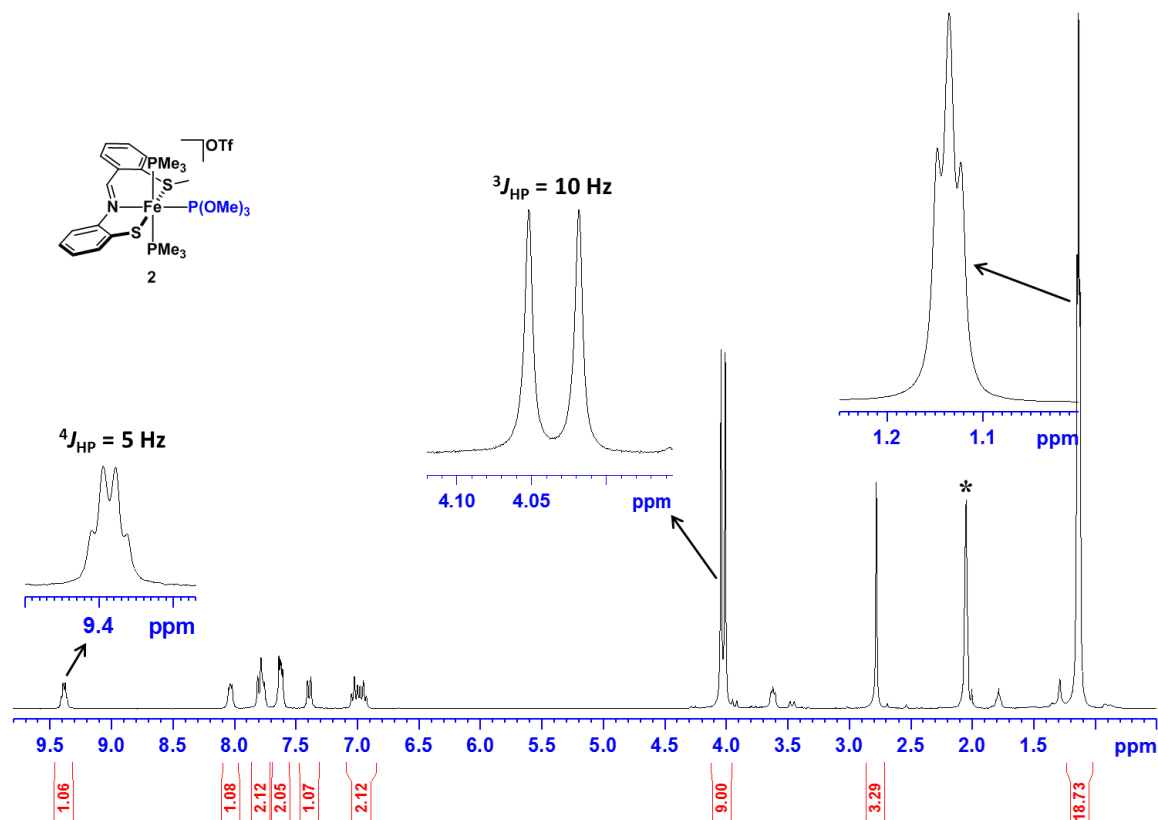


Figure A3. ^1H NMR (300 MHz, acetone- d_6) spectrum of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_2\{\text{P}(\text{OMe})_3\}](\text{OTf})$ (**2**).

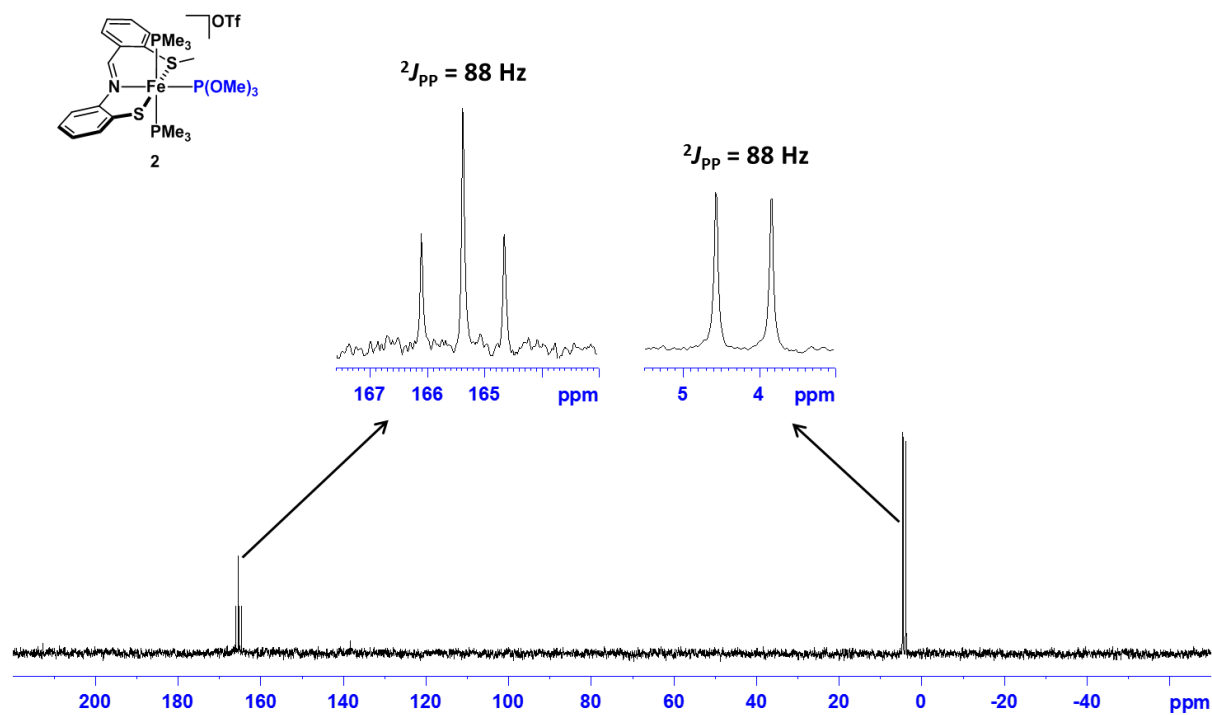


Figure A4. ^{31}P $\{^1\text{H}\}$ NMR (121 MHz, acetone- d_6) spectrum of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_2\{\text{P}(\text{OMe})_3\}](\text{OTf})$ (**2**).

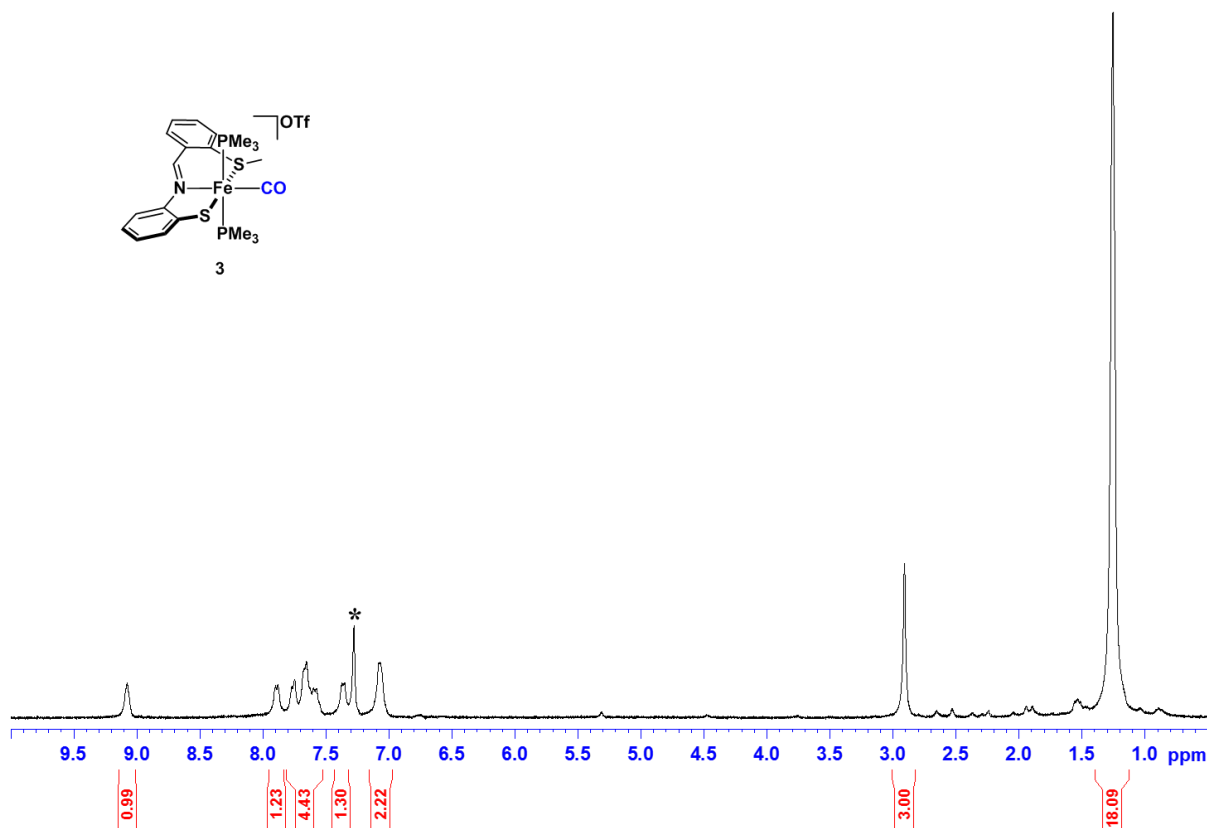


Figure A5. ^1H NMR (300 MHz, CDCl_3) spectrum of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_2(\text{CO})](\text{OTf})$ (**3**).

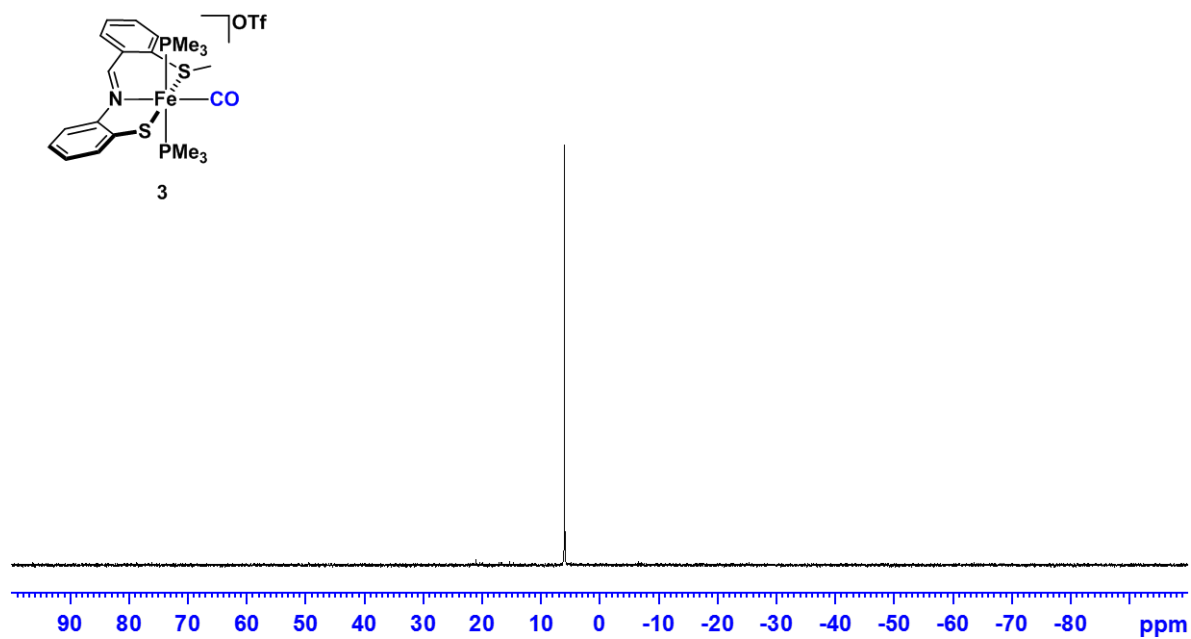


Figure A6. $^{31}\text{P} \{^1\text{H}\}$ NMR (121 MHz, CDCl_3) spectrum of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_2(\text{CO})](\text{OTf})$ (**3**).

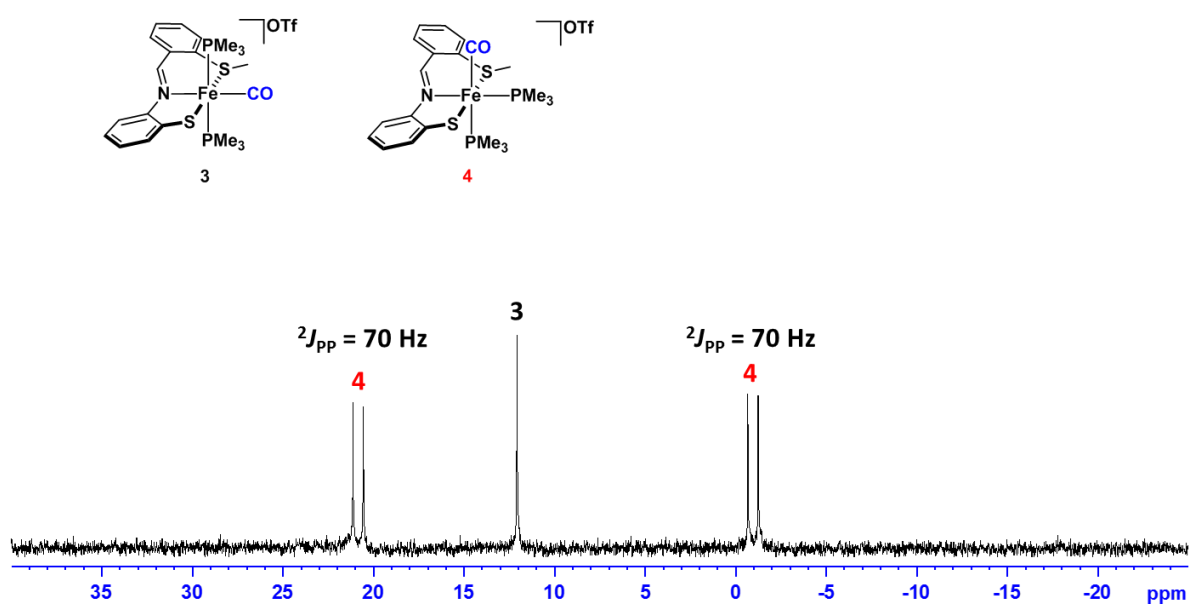


Figure A7. ^{31}P $\{^1\text{H}\}$ NMR (121 MHz, CDCl_3) spectrum of *trans*-(PMe_3)₂ isomer **3** and kinetic *cis*-(PMe_3)₂ isomer **4**.

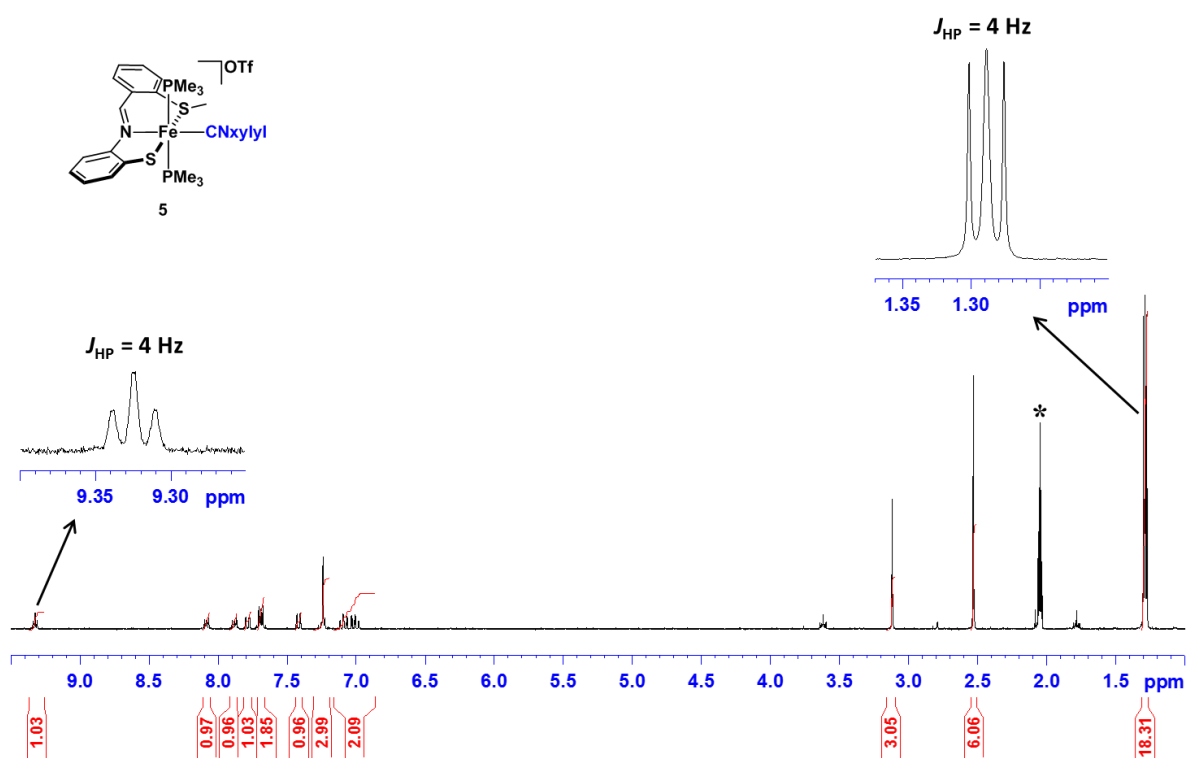


Figure A8. ^1H NMR (300 MHz, acetone-d_6) spectrum of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_2(\text{CNxylyl})](\text{OTf})$ (**5**).

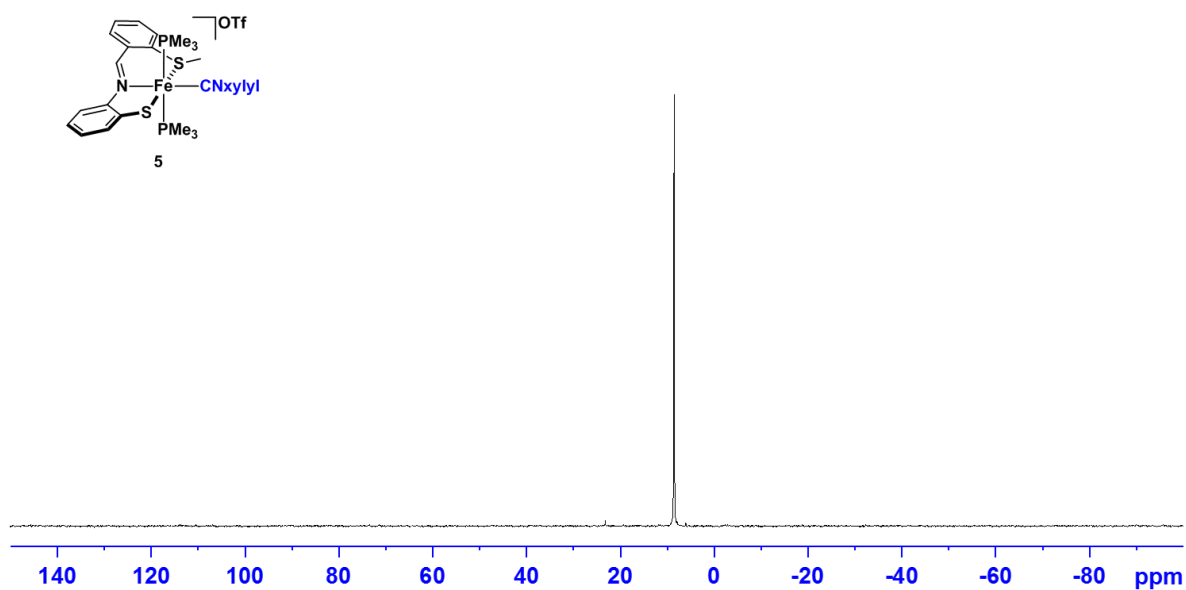


Figure A9. ^{31}P { ^1H } NMR (121 MHz, acetone- d_6) spectrum of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_2(\text{CNxylyl})](\text{OTf})$ (**5**).

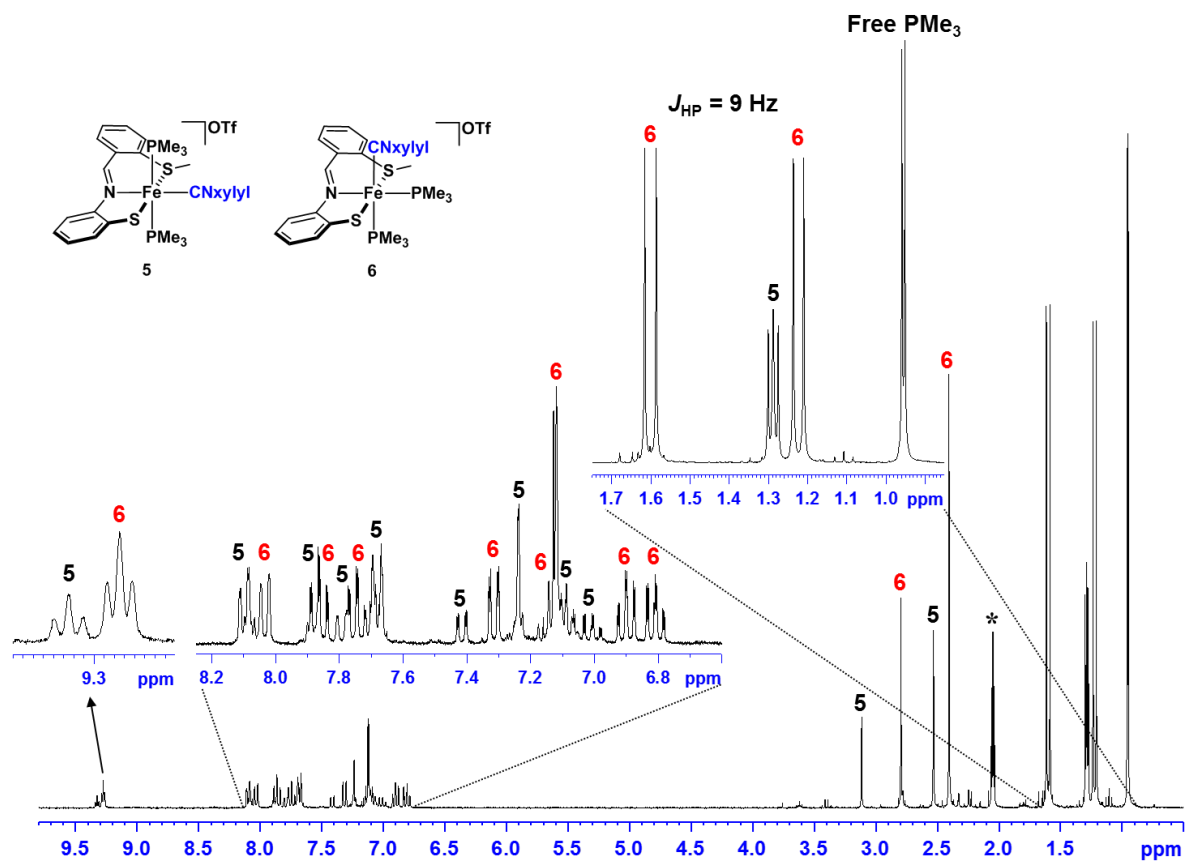


Figure A10. ^1H NMR (300 MHz, acetone- d_6) spectrum of *trans*-(PMe_3) $_2$ isomer **5** and kinetic *cis*-(PMe_3) $_2$ isomer **6**.

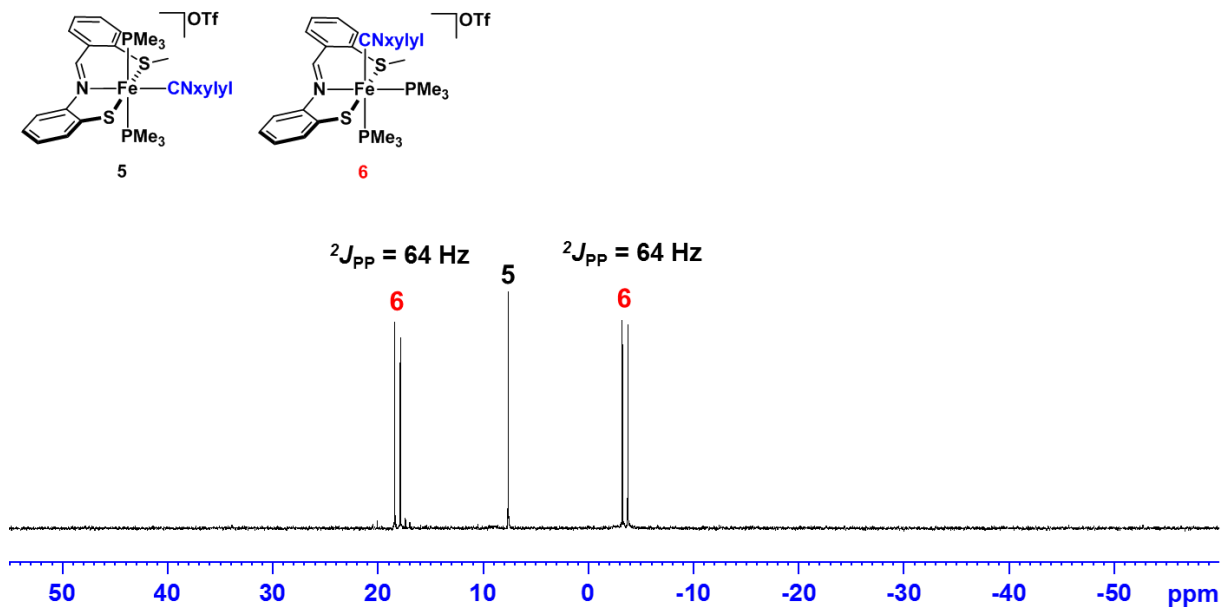


Figure A11. ^{31}P $\{^1\text{H}\}$ NMR (121 MHz, acetone- d_6) spectrum of *trans*-(PMe₃)₂ isomer **5** and kinetic *cis*-(PMe₃)₂ isomer **6**.

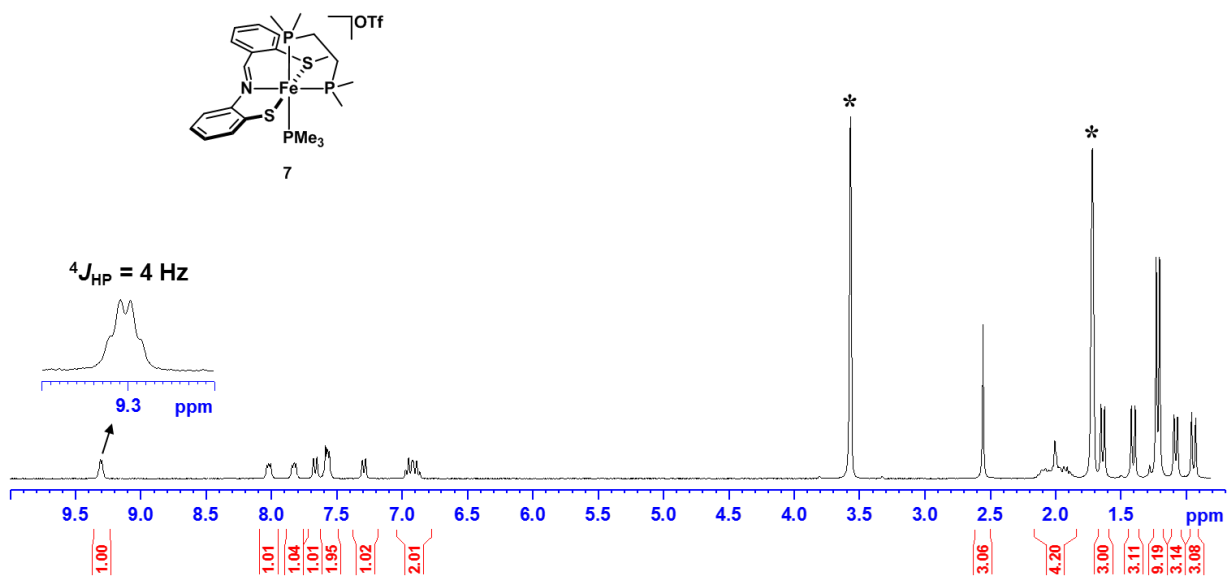


Figure A12. ^1H NMR (300 MHz, THF- d_8) spectrum of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{dmpe})(\text{PMe}_3)](\text{OTf})$ (**7**).

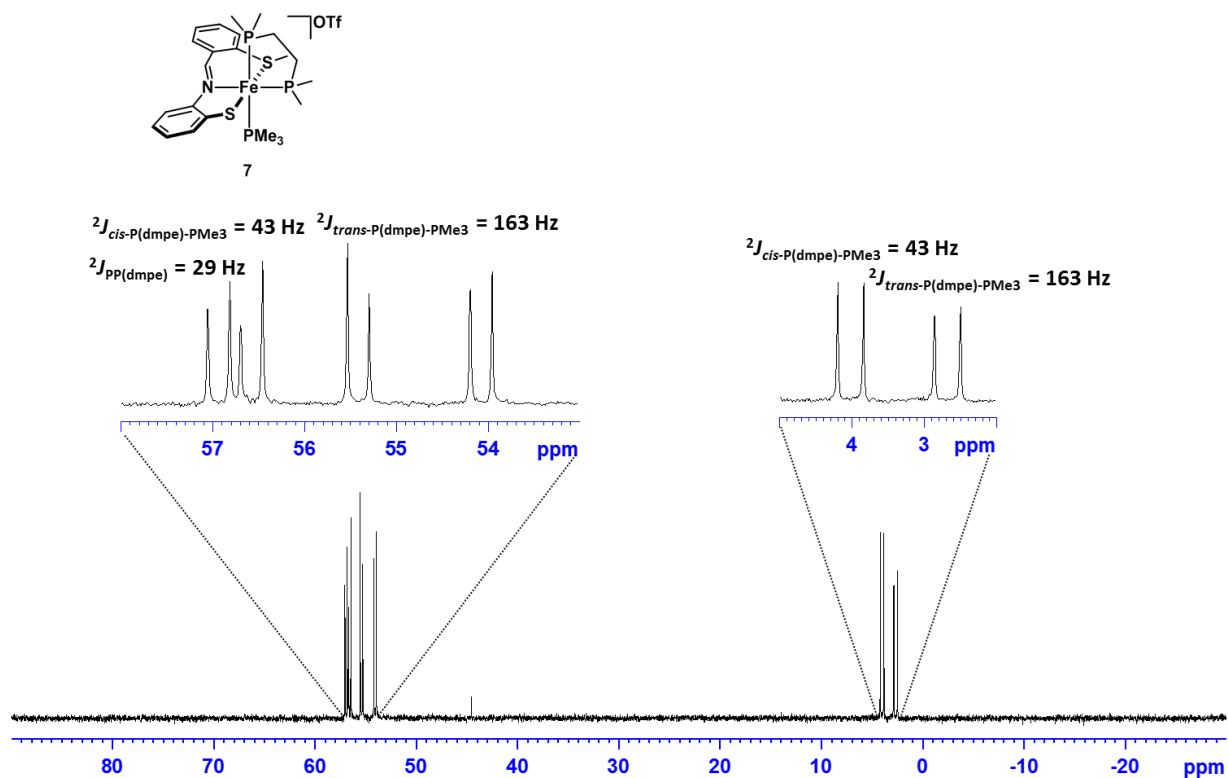


Figure A13. ^{31}P $\{^1\text{H}\}$ NMR (121 MHz, THF-d_8) spectrum of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{dmpe})(\text{PMe}_3)](\text{OTf})$ (**7**).

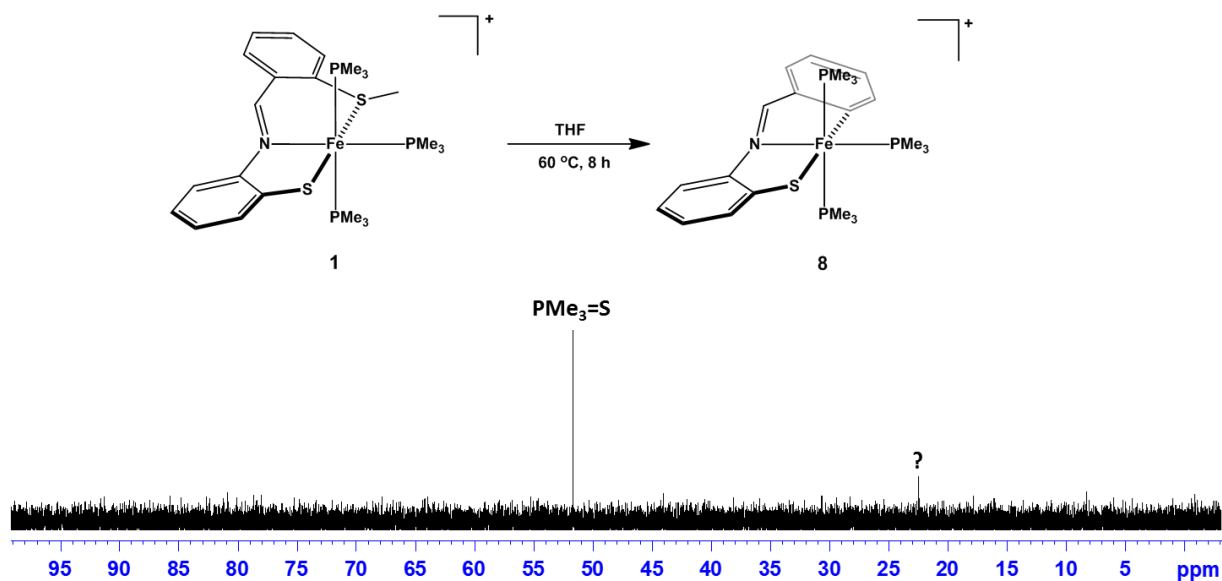


Figure A14. ^{31}P $\{^1\text{H}\}$ NMR (121 MHz, THF) spectrum of thermolysis of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_3](\text{OTf})$ (**1**) in THF.

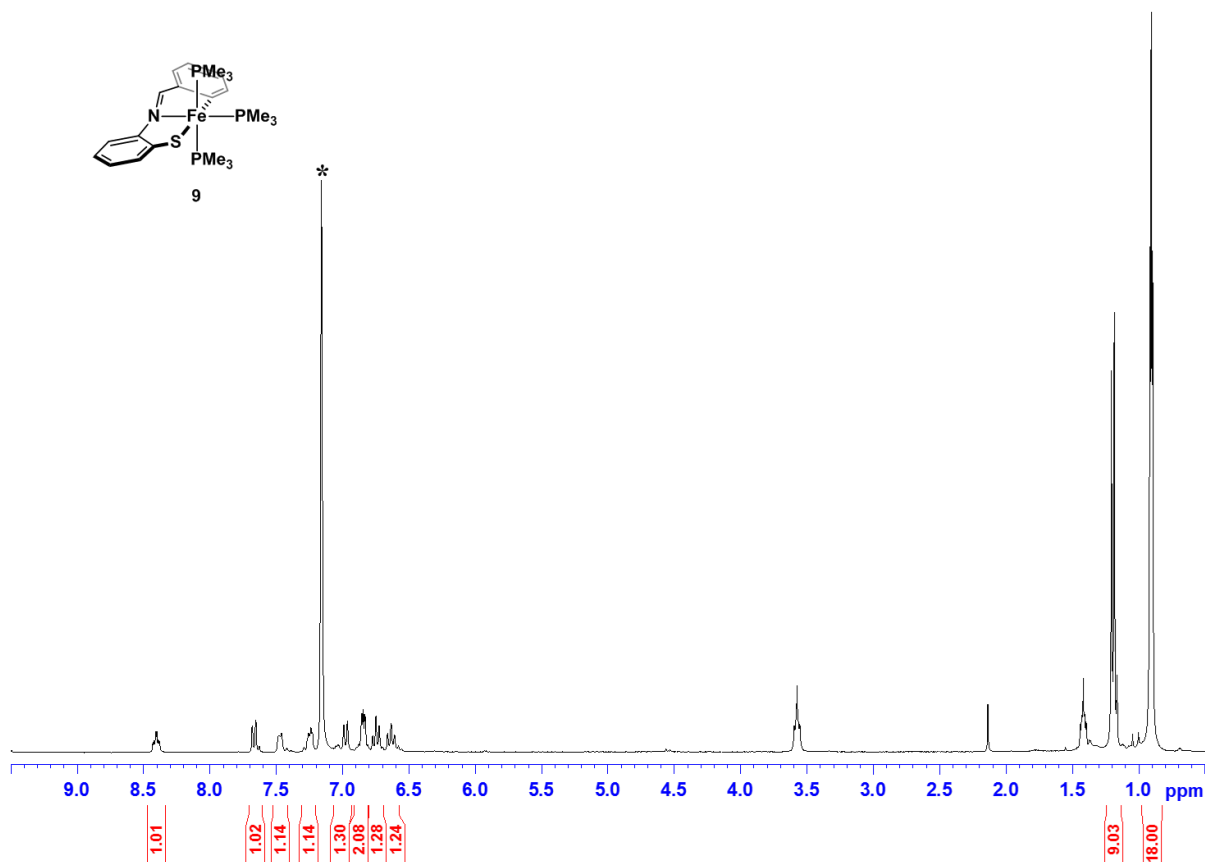


Figure A15. ¹H NMR (300 MHz, C₆D₆) spectrum of [Fe(CNS)(PMe₃)₃] (**9**).

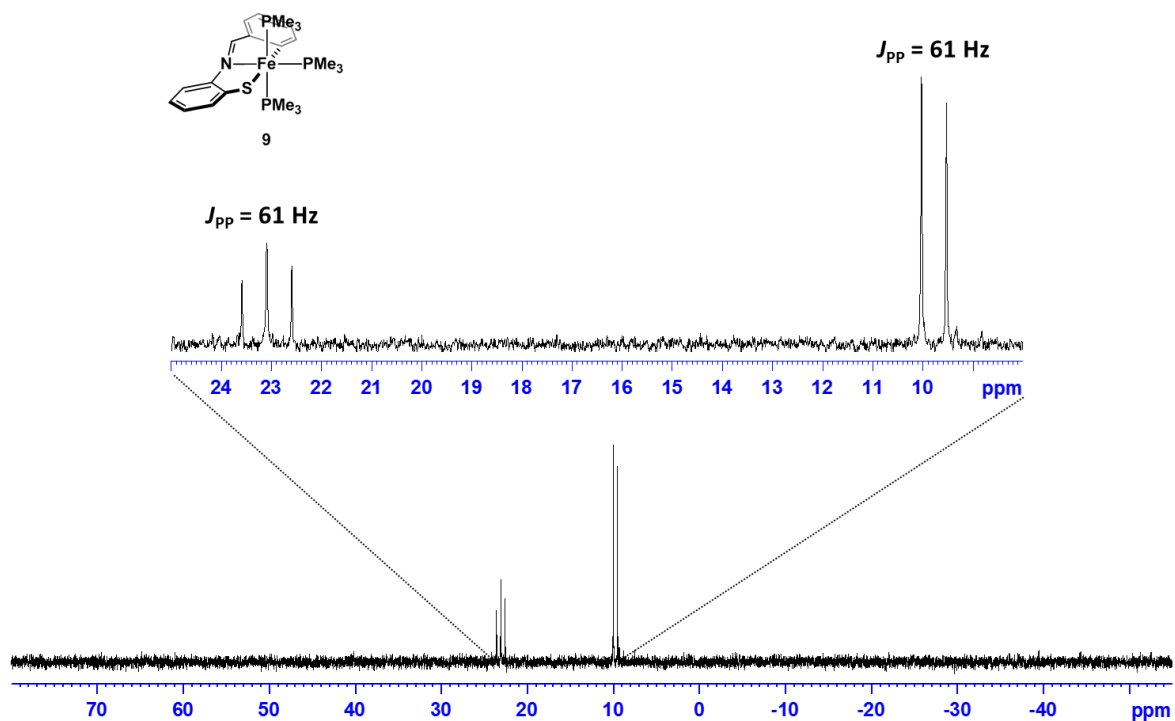
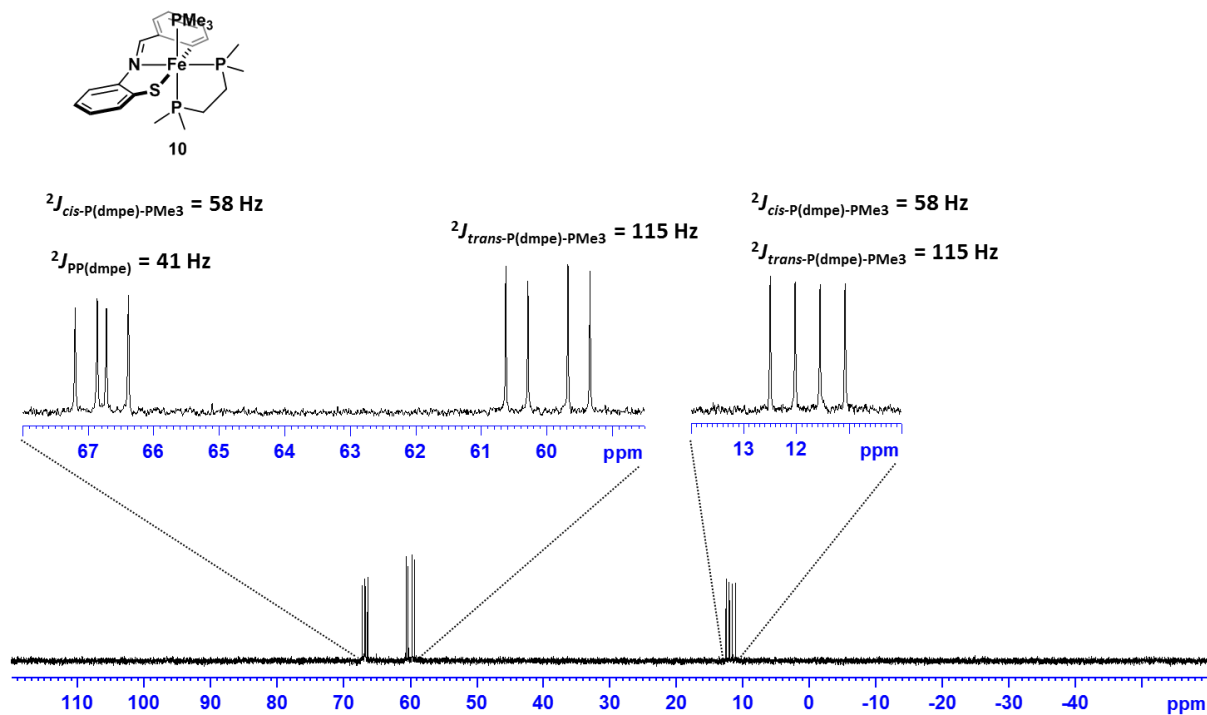
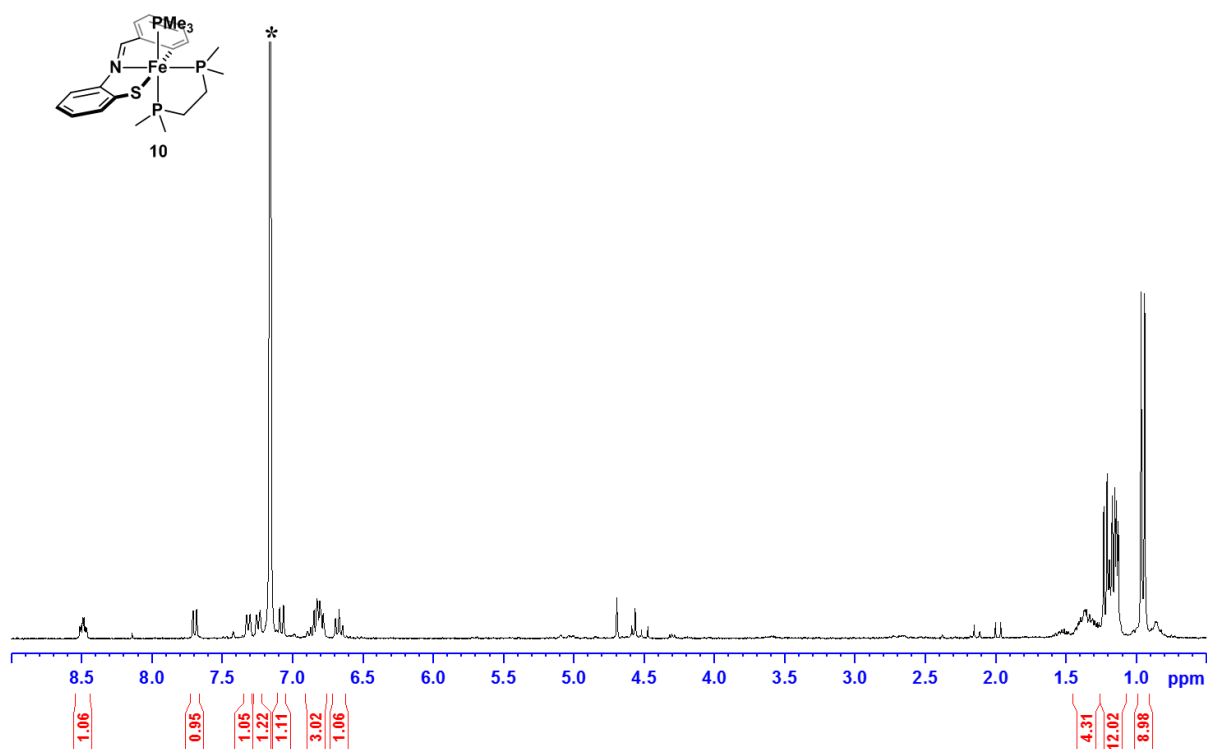


Figure A16. ³¹P {¹H} NMR (121 MHz, C₆D₆) spectrum of [Fe(CNS)(PMe₃)₃] (**9**).



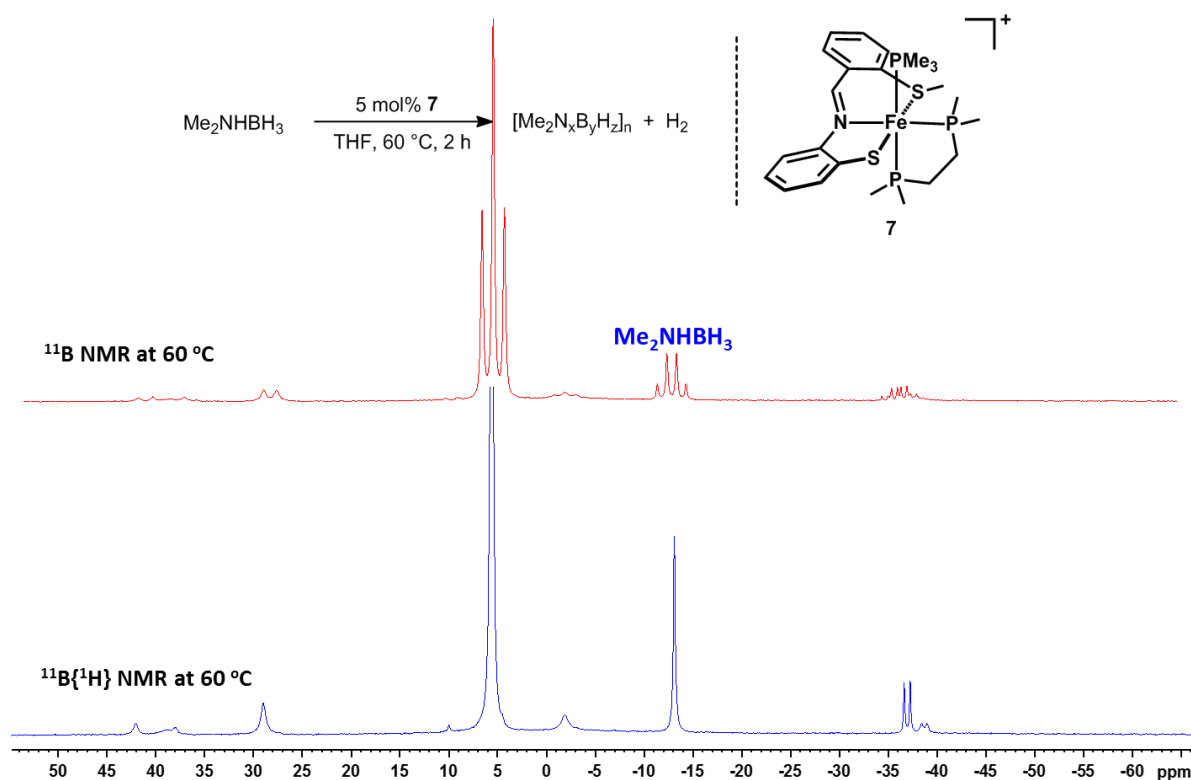


Figure A21. ^{11}B and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of dehydrogenation catalysis of dimethylamine borane (DMAB) using 5 mol% of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{dmpe})(\text{PMe}_3)](\text{OTf})$ (**7**) in THF at 60 $^\circ\text{C}$ for 2 h.

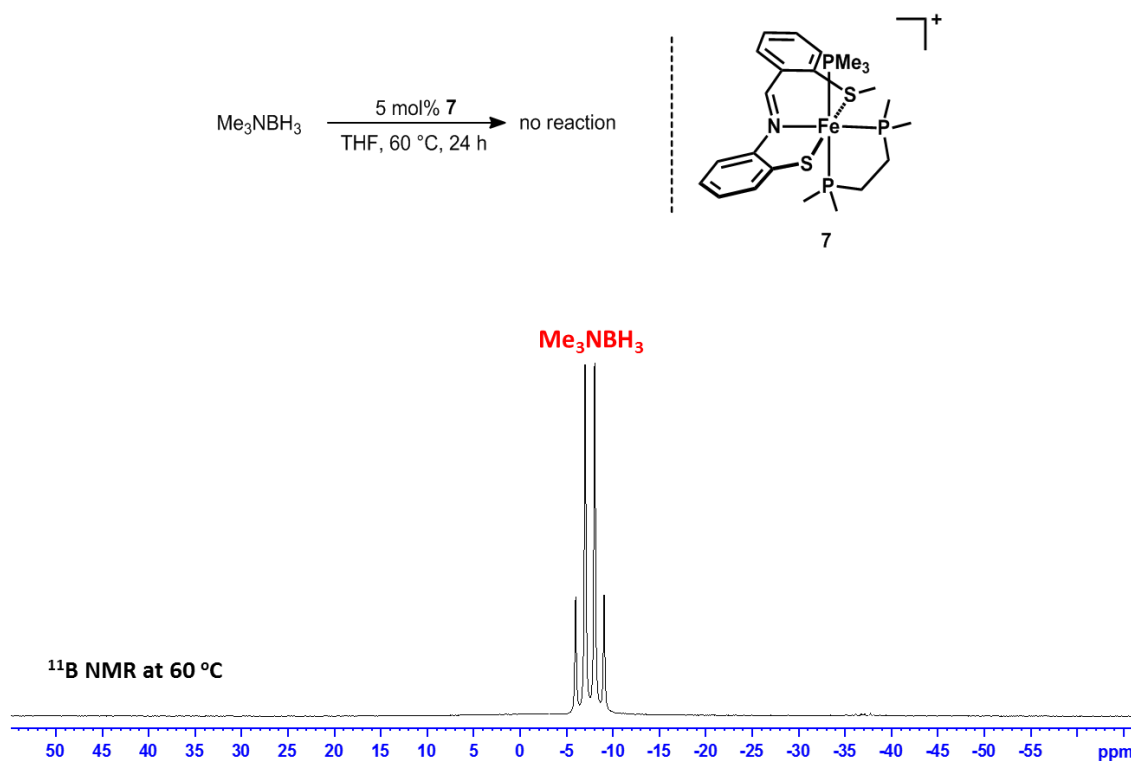


Figure A22. ^{11}B NMR spectrum of dehydrogenation catalysis of trimethylamine borane (TMAB) using 5 mol% of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{dmpe})(\text{PMe}_3)](\text{OTf})$ (**7**) in THF at 60 $^\circ\text{C}$ for 24 h.

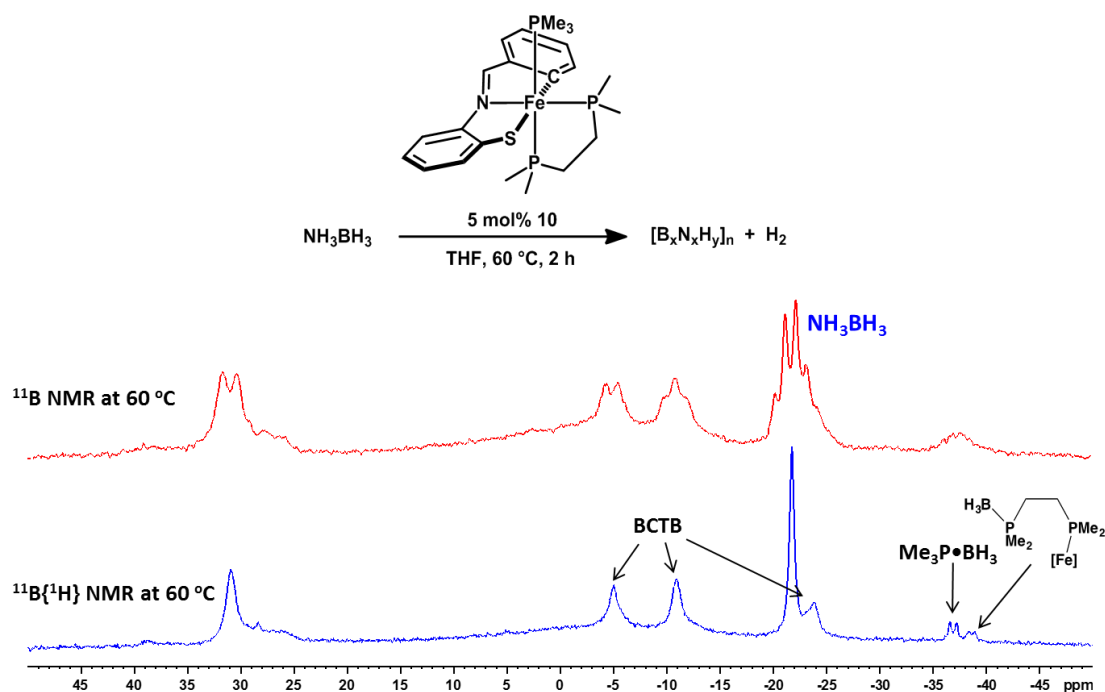


Figure A23. ¹¹B and ¹¹B {¹H} NMR spectra of dehydrogenation catalysis of ammonia borane (AB) using 5 mol% of [Fe(CNS)(dmpe)(PMe₃)] (**10**) in THF at 60 °C for 2 h.

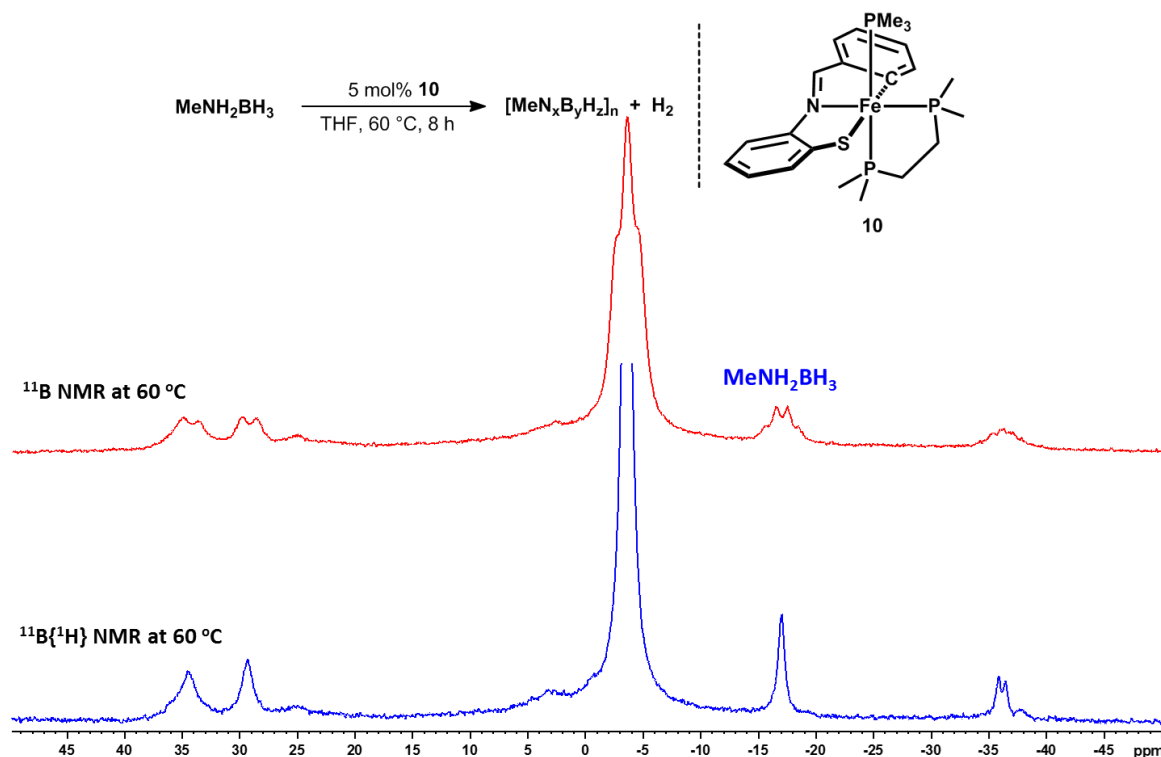


Figure A24. ¹¹B and ¹¹B {¹H} NMR spectra of dehydrogenation catalysis of methylamine borane (MeAB) using 5 mol% of [Fe(CNS)(dmpe)(PMe₃)] (**10**) in THF at 60 °C for 8 h.

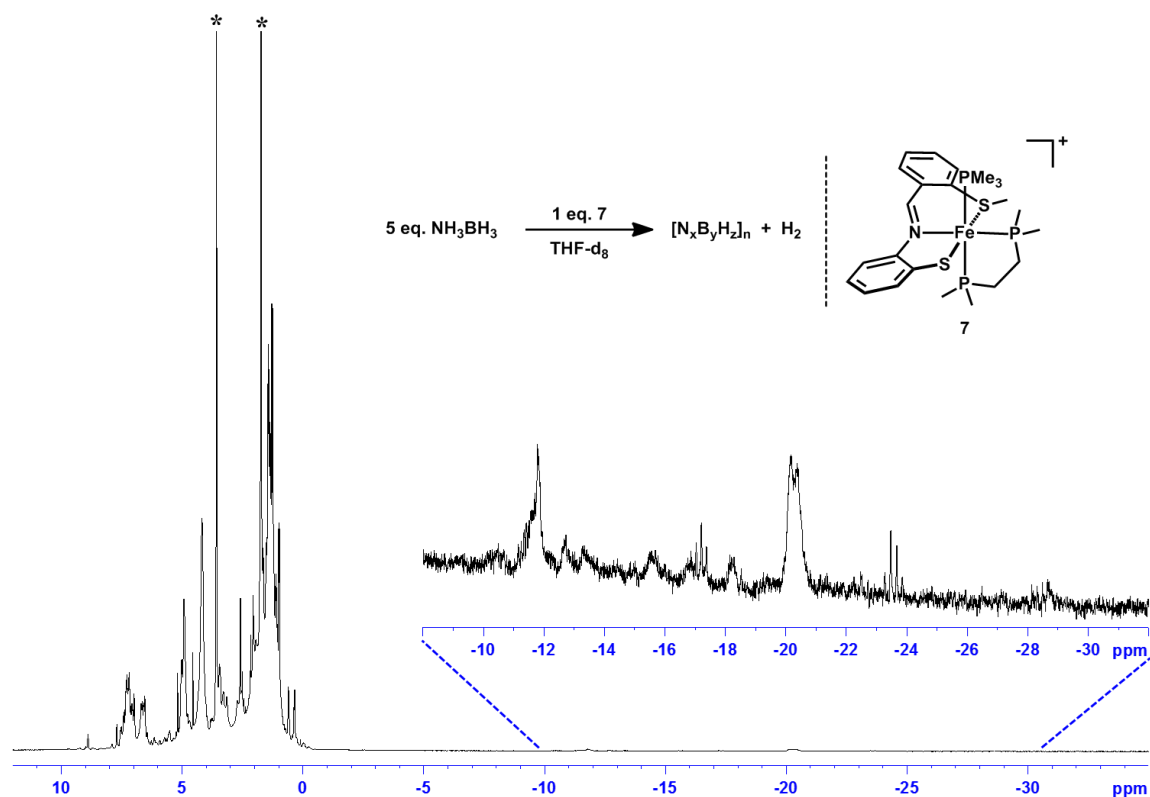


Figure A25. ^1H NMR spectrum (300 MHz, THF-d_8) of dehydrogenation reaction of ammonia borane (AB) using 20 mol% of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{dmpe})(\text{PMe}_3)](\text{OTf})$ (**7**) at -40°C .

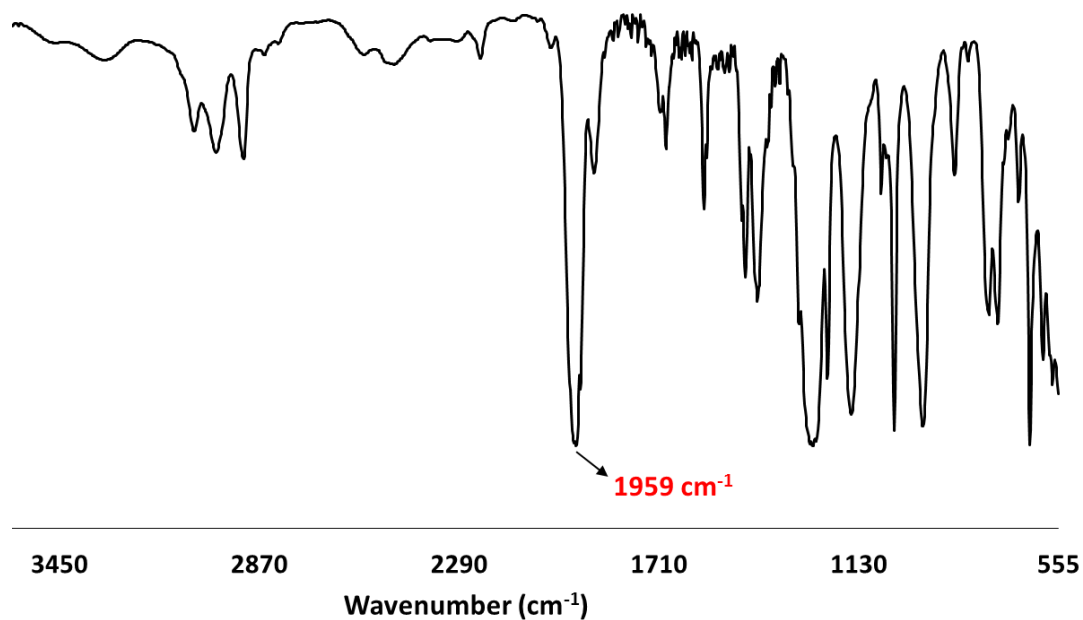


Figure A26. IR spectrum of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_2(\text{CO})](\text{OTf})$ (**3**).

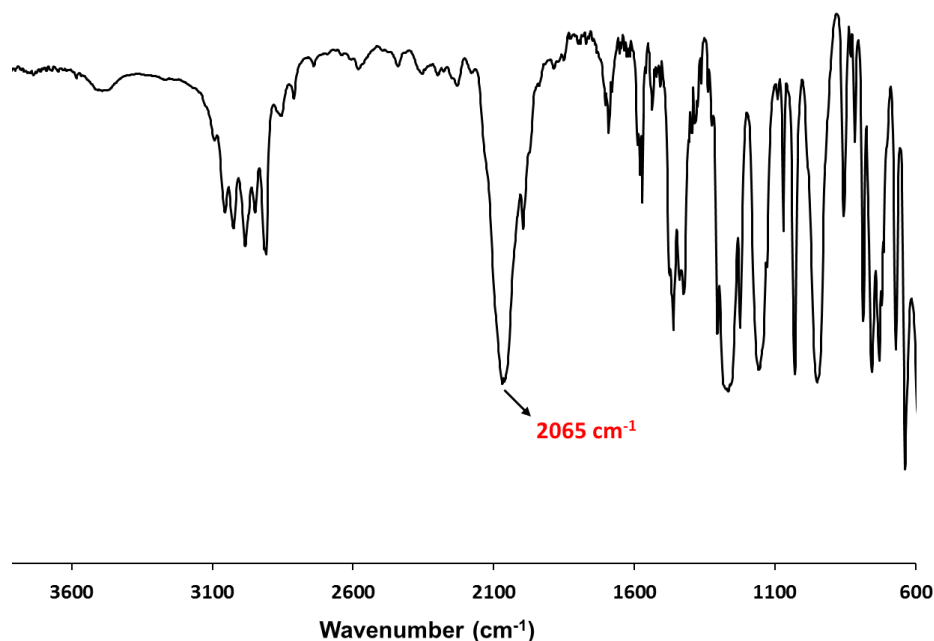


Figure A27. IR spectrum of $[\text{Fe}(\text{S}^{\text{Me}}\text{NS})(\text{PMe}_3)_2(\text{CNxylyl})](\text{OTf})$ (**5**).

Table A1. X-ray diffraction data collection and refinement parameters for complexes **1**, **5**, **7**, and **8**

Parameters	1	5	7	8
Empirical formula	$\text{C}_{24}\text{H}_{39}\text{F}_3\text{FeNO}_3\text{P}_3\text{S}_3$	$\text{C}_{30}\text{H}_{39}\text{F}_3\text{FeN}_2\text{O}_3\text{P}_3\text{S}_3$	$\text{C}_{24}\text{H}_{37}\text{F}_3\text{FeNO}_3\text{P}_3\text{S}_3$	$\text{C}_{23}\text{H}_{36}\text{F}_3\text{FeNO}_3\text{P}_3\text{S}_2$
Formula weight	691.50	746.60	689.48	644.41
Color	purple	dark purple	dark maroon	green
Temperature, K	200(2)	200(2)	200(2)	200(2)
Crystal system	Monoclinic	Trigonal	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P\bar{3}1c$	$C2/c$	$Pbca$
a , Å	14.6938(3)	18.6516(15)	18.497(5)	13.9201(5)
b , Å	14.9817(3)	18.6516(15)	18.910(5)	16.9332(7)
c , Å	15.9700(3)	17.3055(19)	17.827(5)	24.6003(9)
α , °	90	90	90	90
β , °	116.1120(10)	90	99.005(4)	90
γ , °	90	120	90	90
V , Å ³	3156.79(11)	5213.7(10)	6159(3)	5798.6(4)
Z	4	6	8	8
ρ_{cal} , mg/m ³	1.455	1.427	1.487	1.476
μ , mm ⁻¹	0.873	0.756	0.895	0.875
$F(000)$	1440	2328	2864	2680
Crystal size, mm ³	$0.924 \times 0.782 \times 0.592$	$0.598 \times 0.386 \times 0.365$	$0.555 \times 0.353 \times 0.186$	$0.836 \times 0.410 \times 0.114$
Reflections collected/unique	40250/7546	52235/4168	27281/7364	103514/6948
θ range, °	1.966 to 27.925	2.184 to 27.910	1.827 to 27.964	2.067 to 27.932
Index range	-19 $\leq h \leq$ 19, -19 $\leq k \leq$ 19, -20 $\leq l \leq$ 20	-23 $\leq h \leq$ 24, -24 $\leq k \leq$ 19, -22 $\leq l \leq$ 21	-24 $\leq h \leq$ 24, -23 $\leq k \leq$ 24, -23 $\leq l \leq$ 23	-18 $\leq h \leq$ 18, -22 $\leq k \leq$ 22, -29 $\leq l \leq$ 32
R_{int}	0.0261	0.0255	0.0328	0.0468
Completeness to θ	25.242, 100.0 %	25.242, 99.8 %	25.242, 100.0 %	25.242, 100.0 %
Max. and min. transmission	0.7456 and 0.6582	0.7456 and 0.6398	0.746 and 0.633	0.746 and 0.613
Data/restraints/parameters	7546/263/508	4168/37/364	7364/78/398	6948/0/334
Goodness-of-fit on F^2	1.022	1.076	0.960	1.083

Chapter 4:

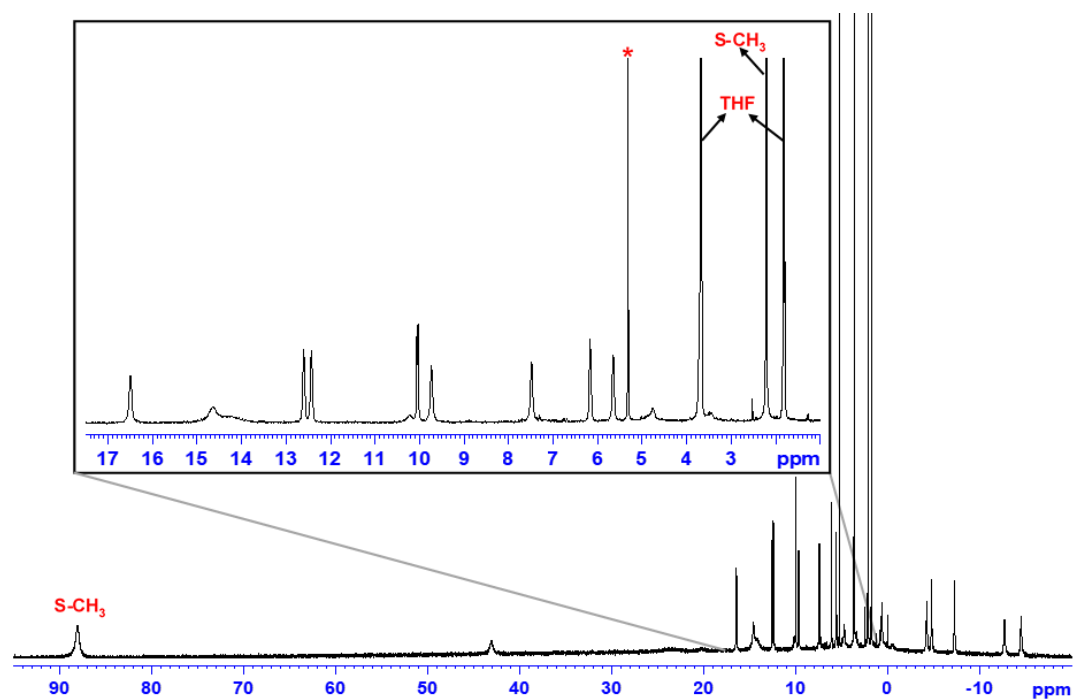


Figure A1. ^1H NMR (300 MHz, CD_2Cl_2) spectrum of $\text{Fe}(\text{N}_2\text{S}_3)$ **1'** [*residual NMR solvent].

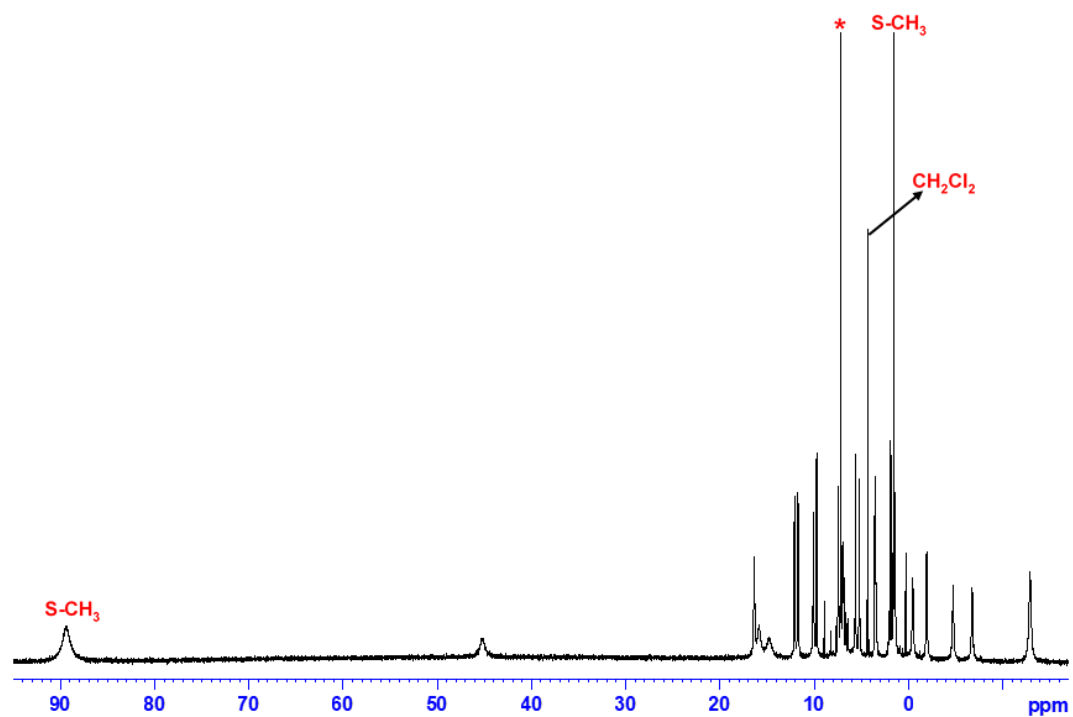


Figure A2. ^1H NMR (300 MHz, C_6D_6) spectrum of $\text{Fe}(\text{N}_2\text{S}_3)$ **1'** [*residual NMR solvent].

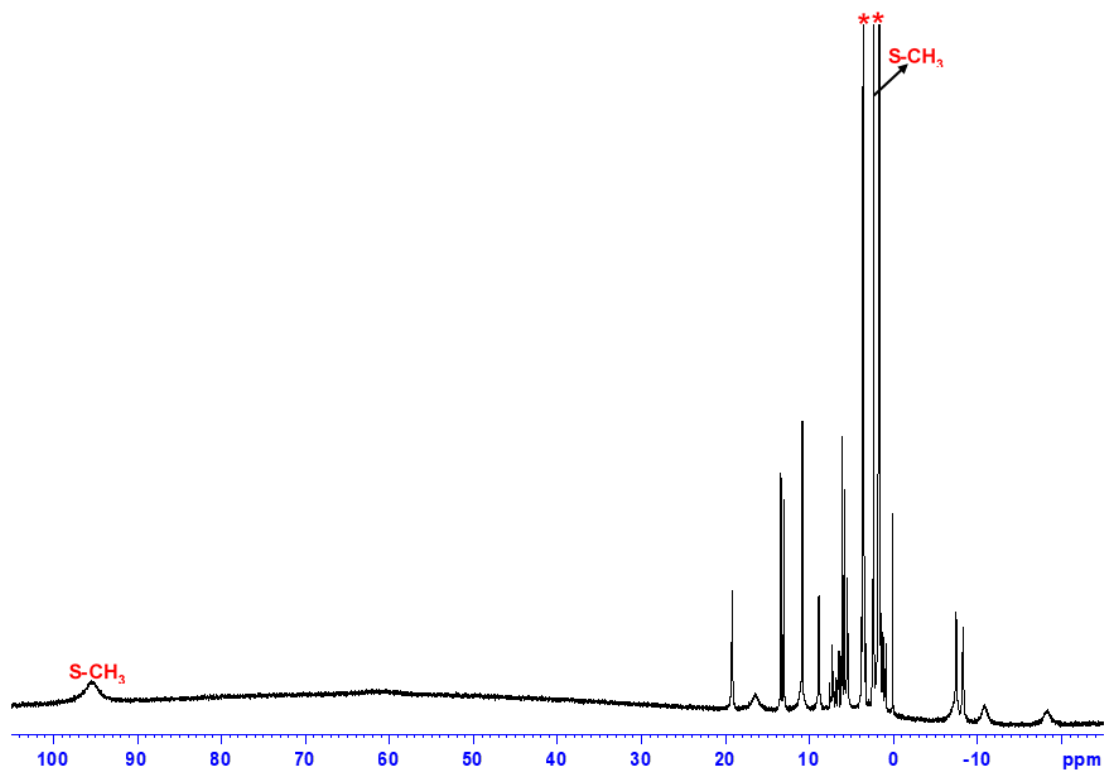


Figure A3. ^1H NMR (300 MHz, $[\text{D}_8]\text{-THF}$) spectrum of $\text{Fe}(\text{N}_2\text{S}_3)$ **1'** [*residual NMR solvent].

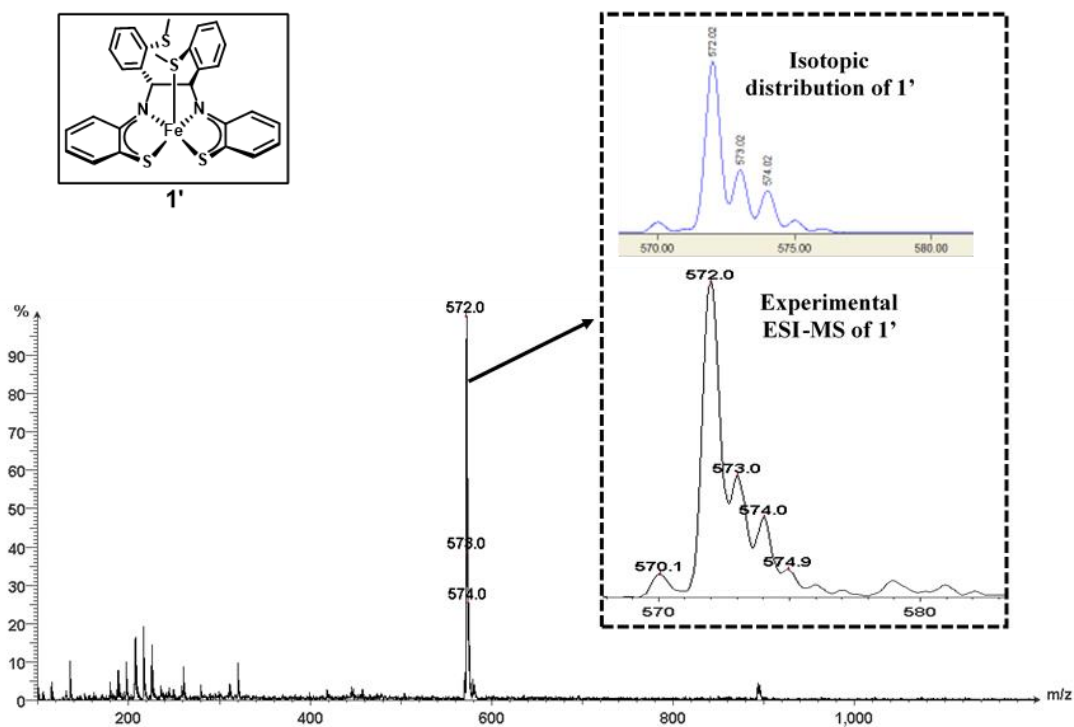


Figure A5. ESI-MS spectrum of $\text{Fe}(\text{N}_2\text{S}_3)$ **1'** (inset: isotopic distribution and experimental peak of $[\text{M}]^+$).

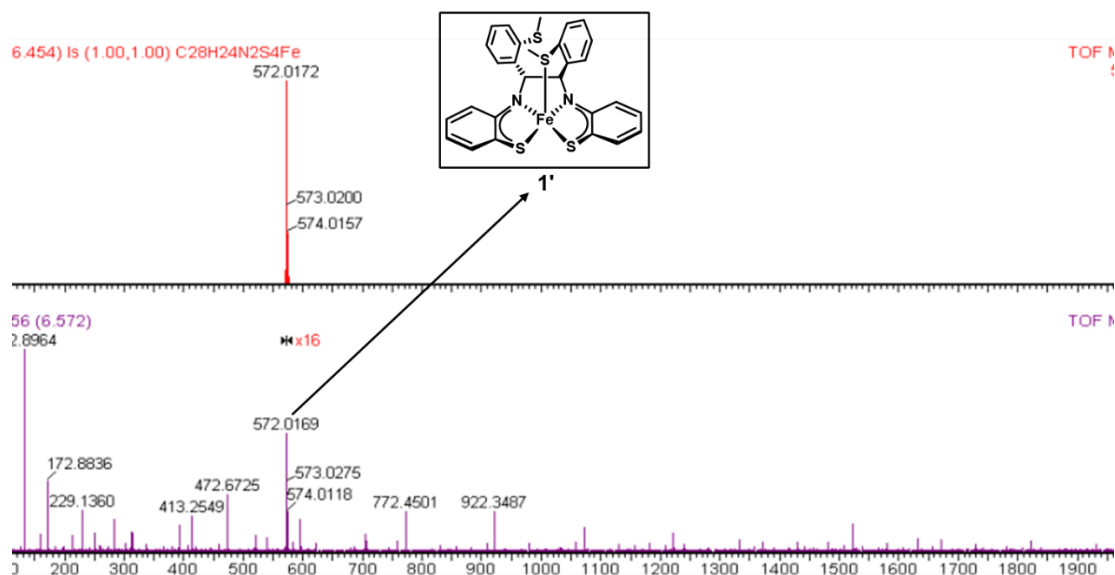


Figure A6. High resolution QTOF-ESI-MS spectrum of Fe(N₂S₃) **1'** (top: isotopic distribution, bottom: experimental).

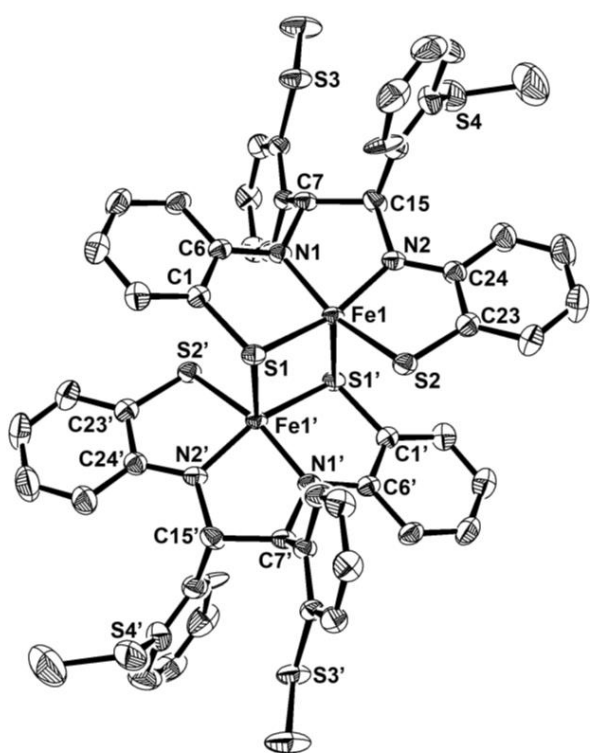


Figure A7. ORTEP diagram of [Fe(N₂S₂)₂] **1**. Thermal ellipsoids are shown at 40% probability. H atoms and acetonitrile molecule are omitted for clarity.

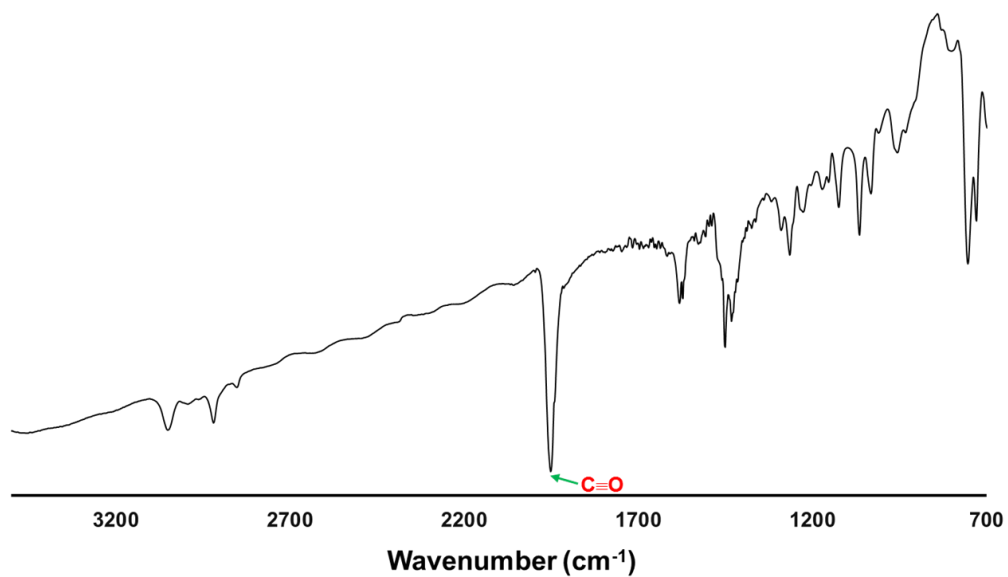


Figure A13. IR (ATR) spectrum of $[\text{Fe}(\kappa^3\text{-SNS})(\kappa^2\text{-SNS})\text{CO}] \mathbf{3}$.

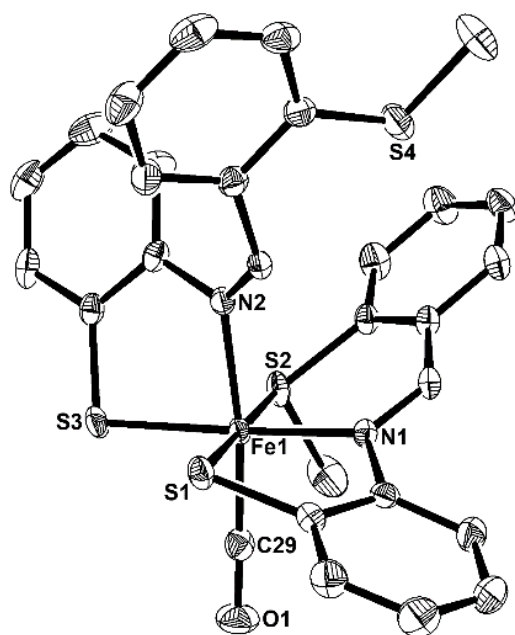


Figure A14. ORTEP diagram of $[\text{Fe}(\kappa^3\text{-SNS})(\kappa^2\text{-SNS})\text{CO}] \mathbf{3}$. Thermal ellipsoids are shown at 40% probability. H atoms and acetonitrile molecule are omitted for clarity.

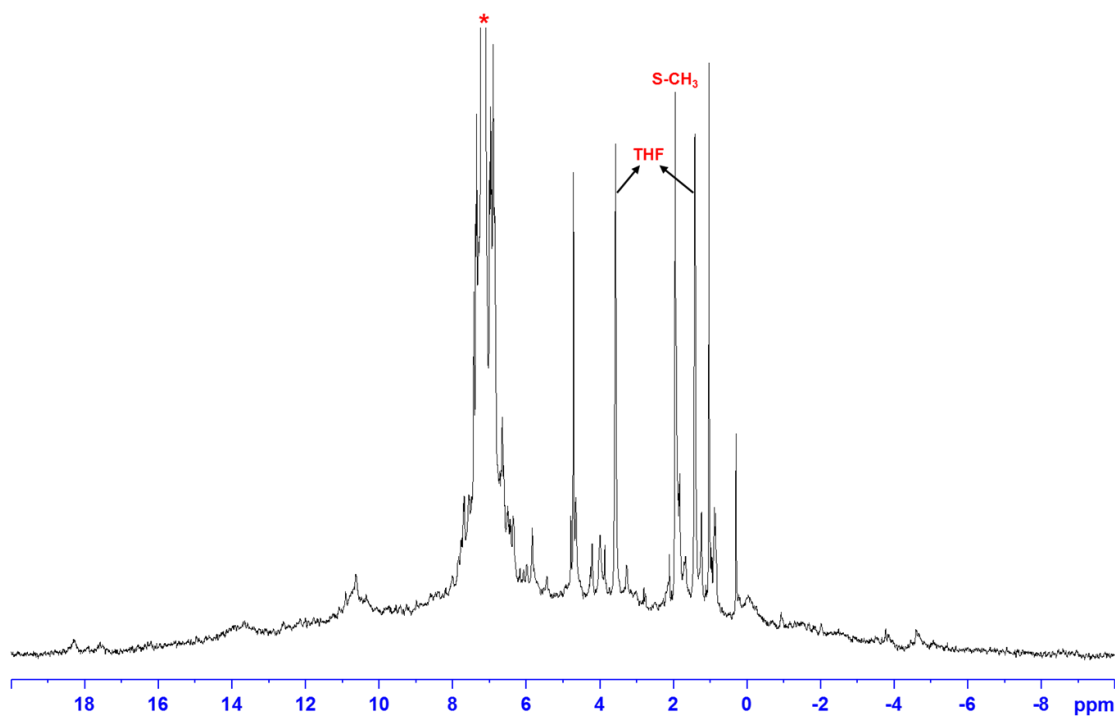


Figure A38. ^1H NMR (300 MHz, C_6D_6) spectrum of working catalyst solution from **1'** [*residual NMR solvent].

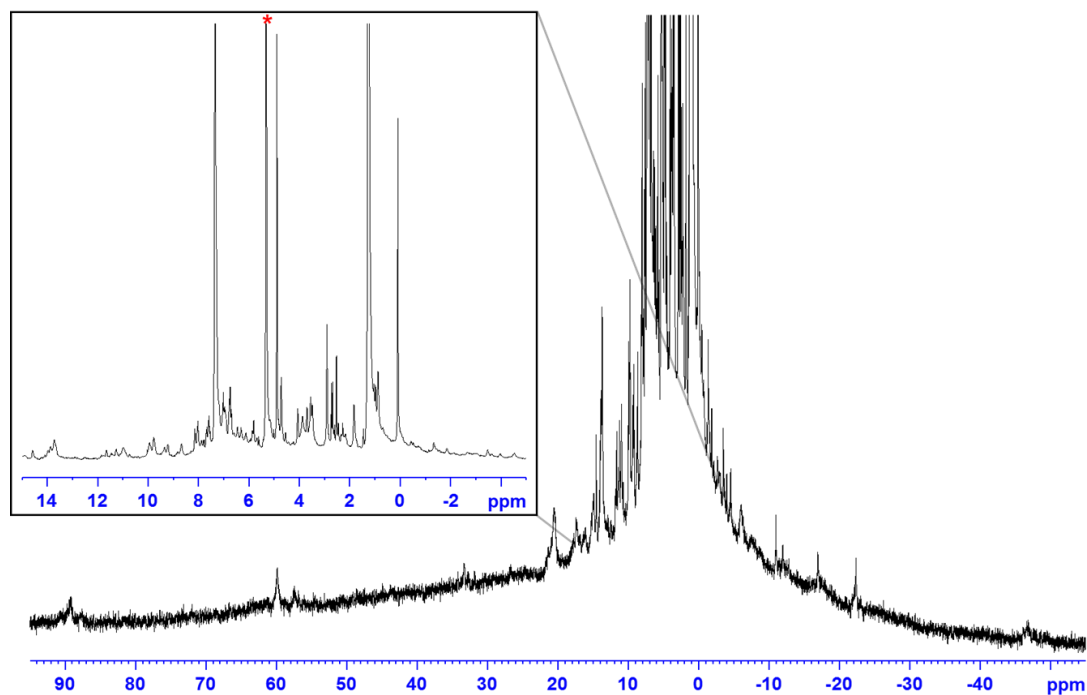


Figure A39. ^1H NMR (300 MHz, CD_2Cl_2) spectrum of working catalyst solution from **2** [*residual NMR solvent].

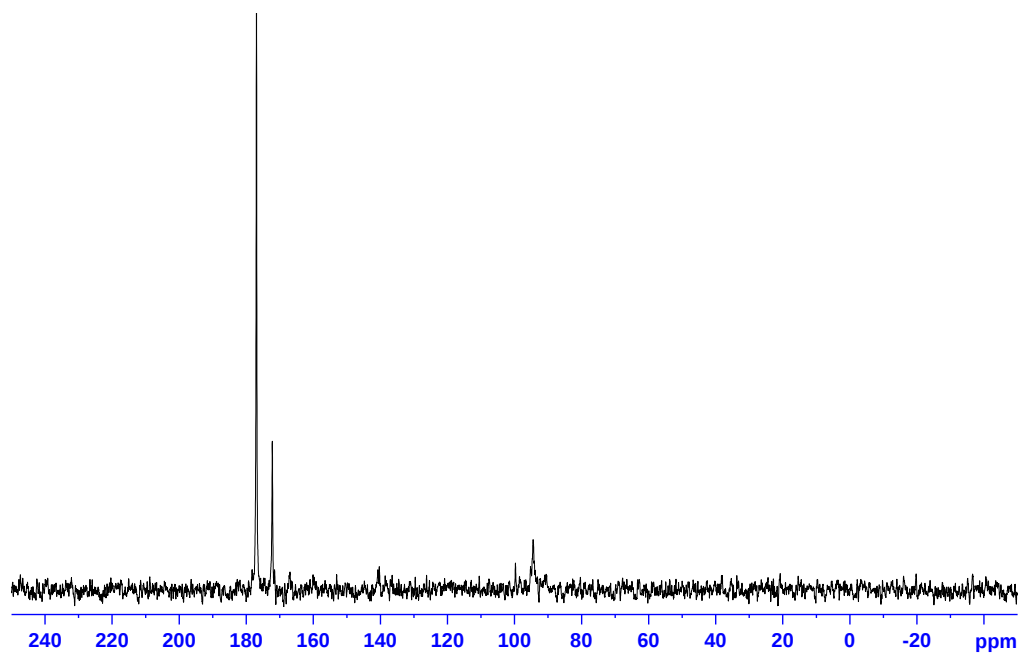


Figure A40. $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2) spectrum of working catalyst solution from **2**. Resonance at 178 ppm is due to free $\text{P}(\text{OMe})_3$.

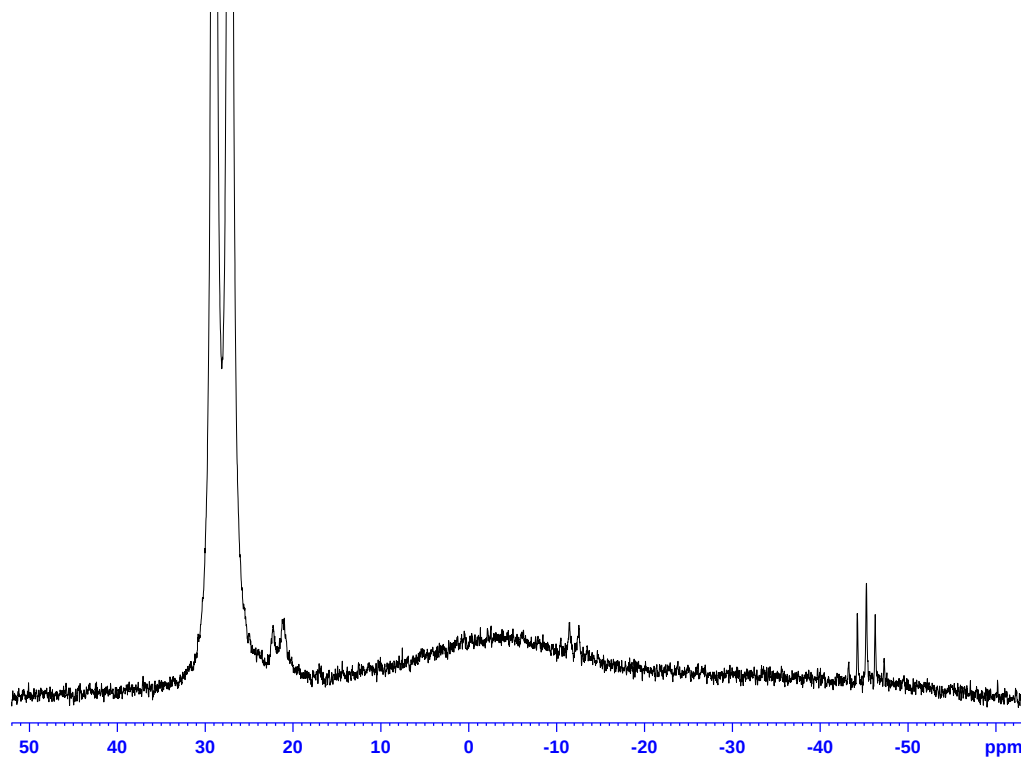


Figure A41. ^{11}B NMR (96 MHz, CD_2Cl_2) spectrum of reaction of complex **2** with HBpin.

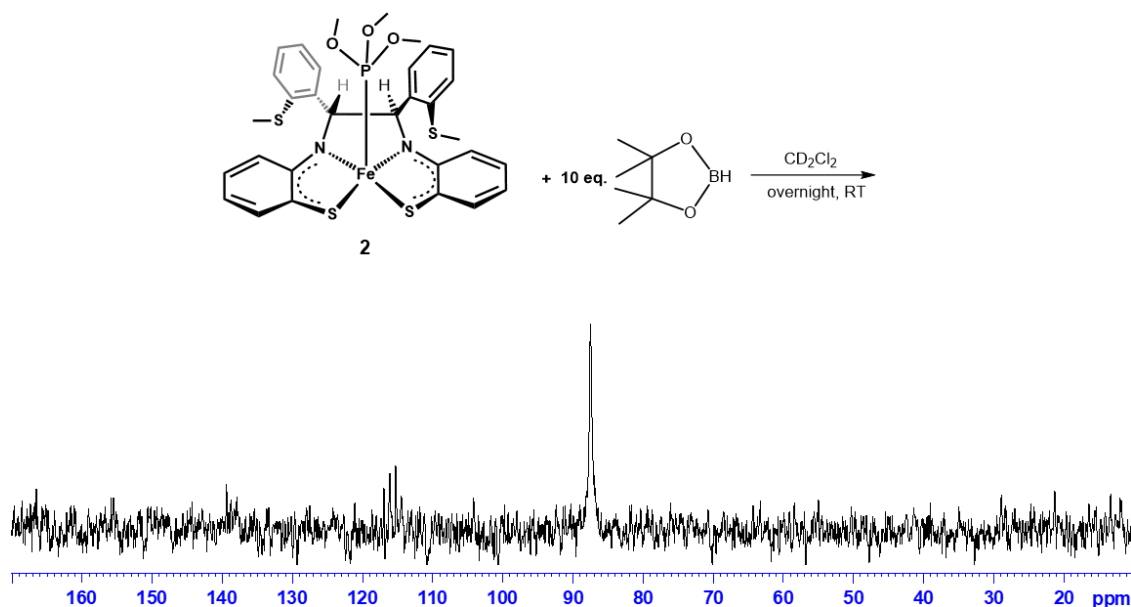


Figure A42. $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2) spectrum of reaction of complex **2** with HBpin.

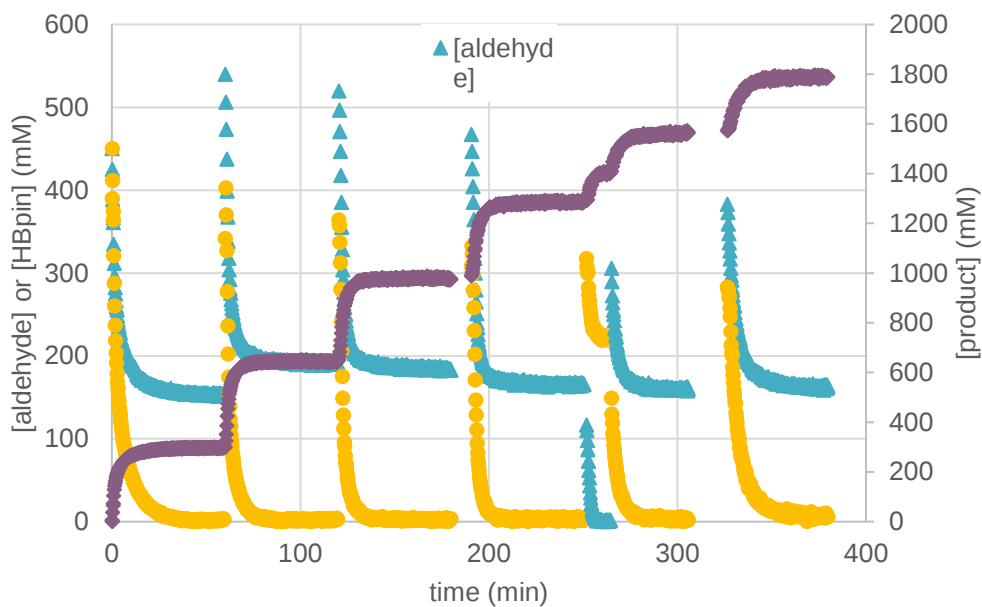


Figure A44. Multiple dosing experiment highlighting catalyst longevity. Concentrations of aldehyde (blue triangles), HBpin (yellow circles), and product (purple diamonds) are shown. Product concentration is plotted on the secondary Y-axis. In cycles 1-4, and 6, HBpin was added ca. 15s after aldehyde. In cycle 5, HBpin addition preceded aldehyde; aldehyde was added ca. 10 minutes later. Each of the cycles in this experiment was run with a 1:1 stoichiometry of aldehyde to HBpin. However, after Cycle 1, aldehyde will remain in excess due to incomplete consumption in this cycle. HBpin is therefore completely consumed in each subsequent cycle, as it is now the limiting reagent. A better metric for comparing catalytic behaviour over multiple cycles is the % conversion data presented in Figure 4.3.

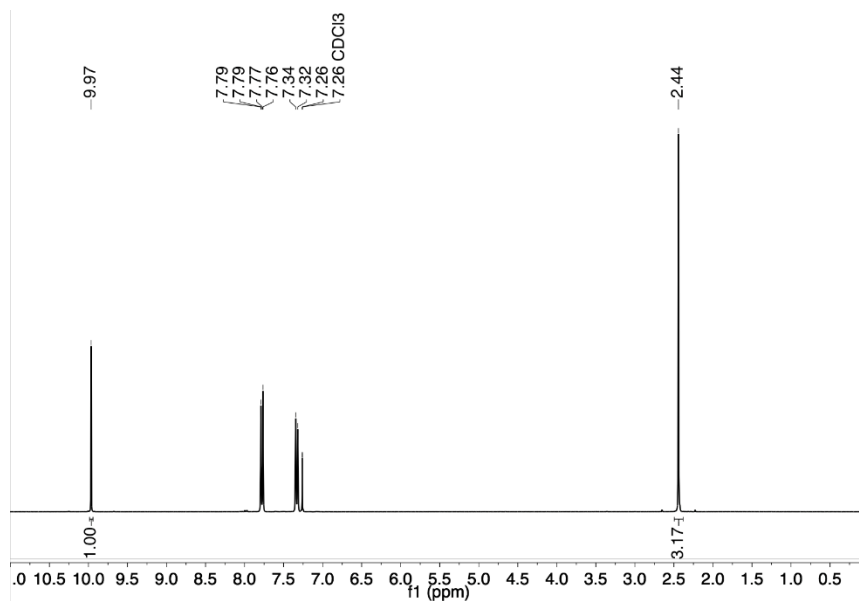


Figure A45. ^1H NMR of crude *p*-methylbenzaldehyde (CDCl_3). Collected using a relaxation delay of 10s, to ensure integration accuracy. Key signals are integrated: 9.97 ppm (aldehyde, CHO), and 2.44 (aldehyde and carboxylic acid, CH_3).

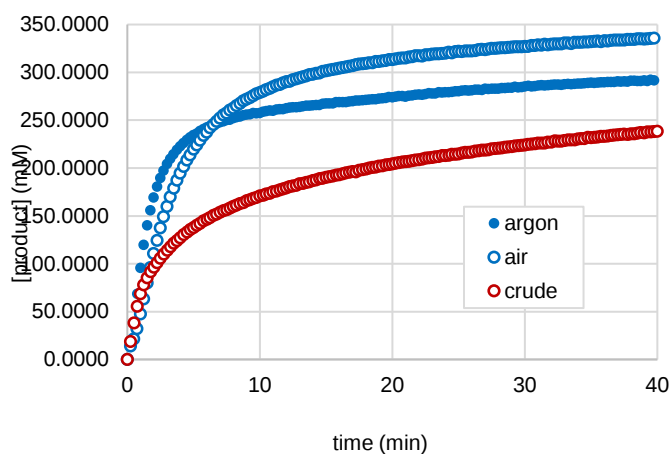


Figure A46. Probing catalyst robustness. Freshly distilled aldehyde under an Argon atmosphere (blue solid), and under a Nitrogen atmosphere (blue hollow); crude aldehyde contaminated with 5% 4-methylbenzoic acid (hollow red). Conditions: $[\text{Fe}] = 0.44 \text{ mM}$, 23°C , C_6H_6 , $[\text{CHO}] = [\text{HBpin}] = 450 \text{ mM}$.

Remaining appendices for Chapter 4 of this thesis can be found in the supporting information of the following published article:

Chapter 4: Das, U. K.; Higman, C. S.; Gabidullin, B.; Hein, J. E.; Baker, R. T. Efficient and Selective Iron-Complex-Catalyzed Hydroboration of Aldehydes. *ACS Catal.* **2018**, 8, 1076-1081.

Chapter 5:

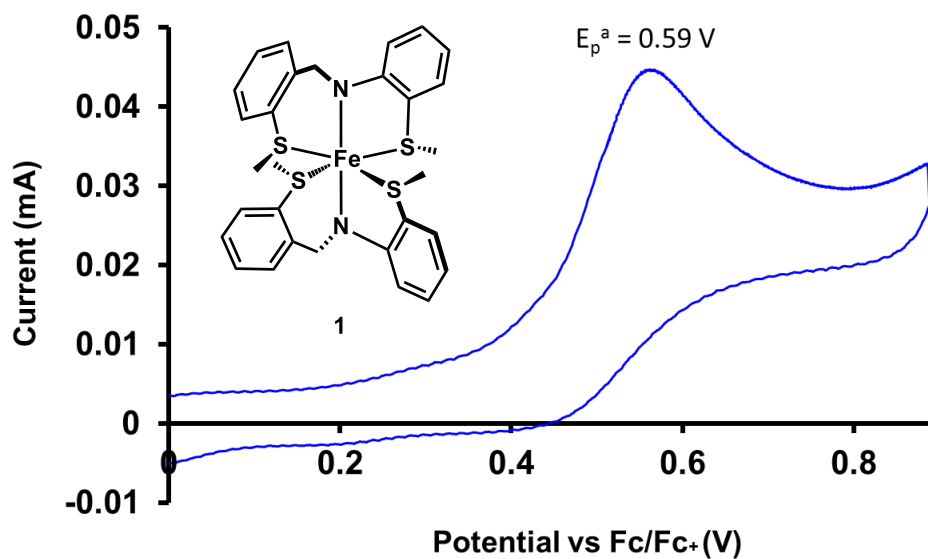


Figure A10. Cyclic voltammogram of $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2]$ (**1**) in CH_2Cl_2 under N_2 atmosphere ([complex] 0.5 mM, at 100 mV scan rate in 0.1 M $n\text{-Bu}_4\text{NPF}_6$).

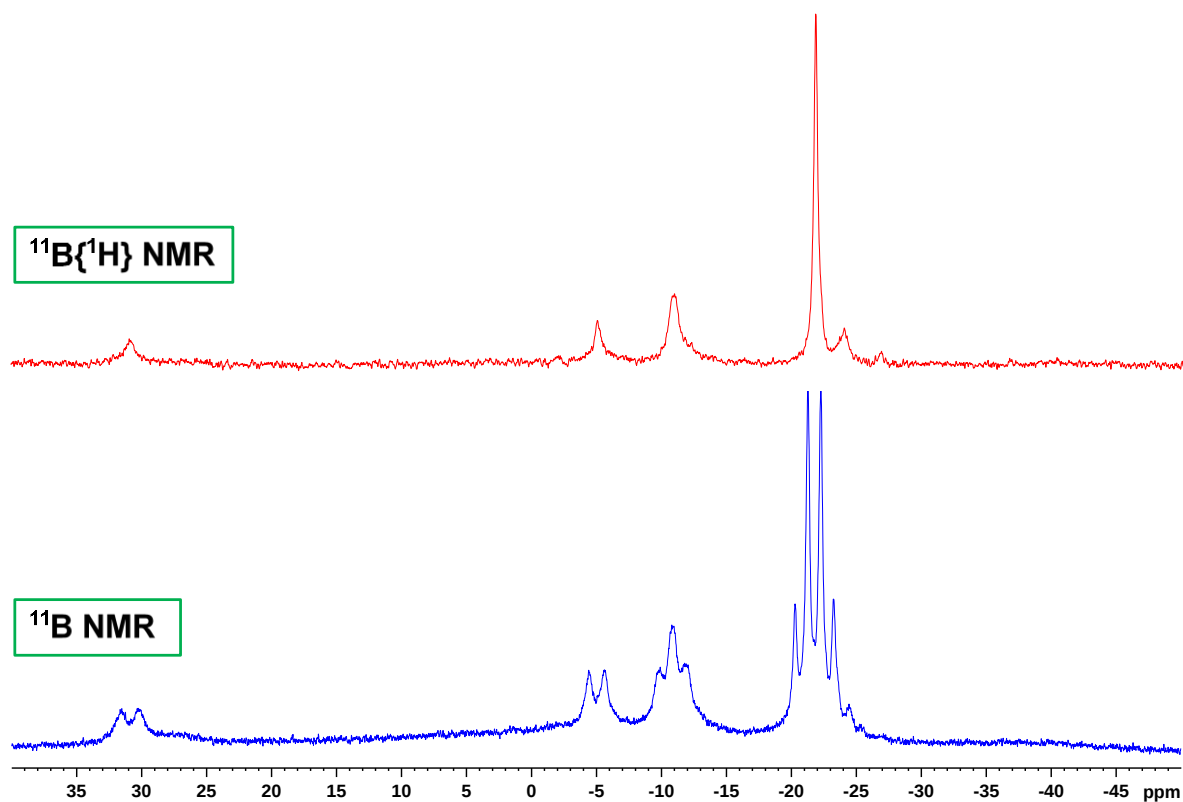


Figure A22. ^{11}B and $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, THF) spectra of dehydrogenation catalysis of AB with **7** (LB = 3 Hz).

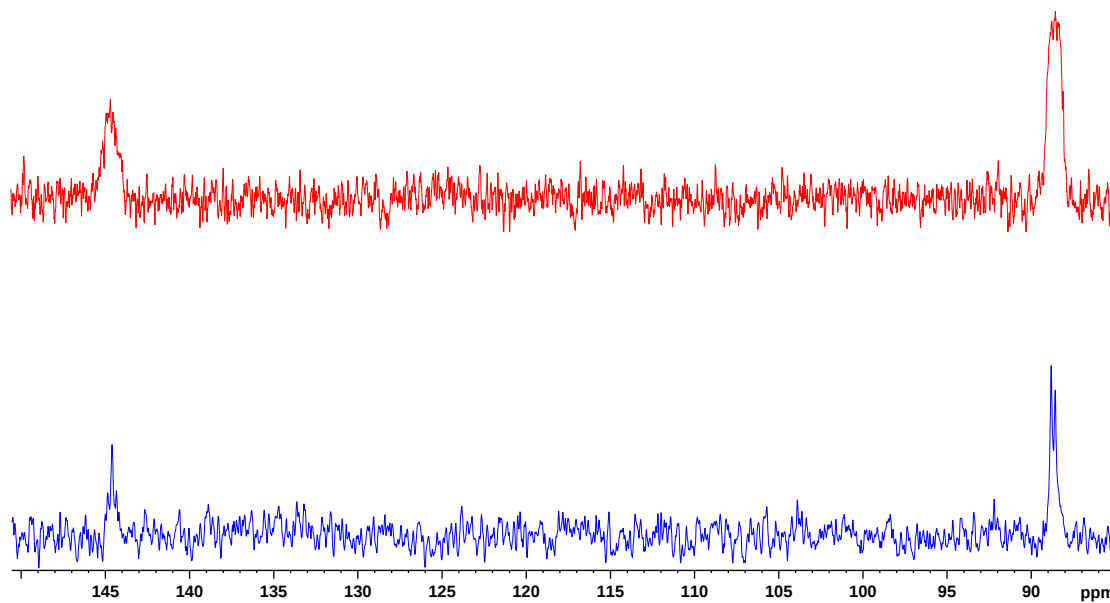


Figure A23. $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, THF) spectra [Gated ^1H decoupling (top spectrum)] of dehydrogenation catalysis of AB with 7 (LB = 10 Hz).

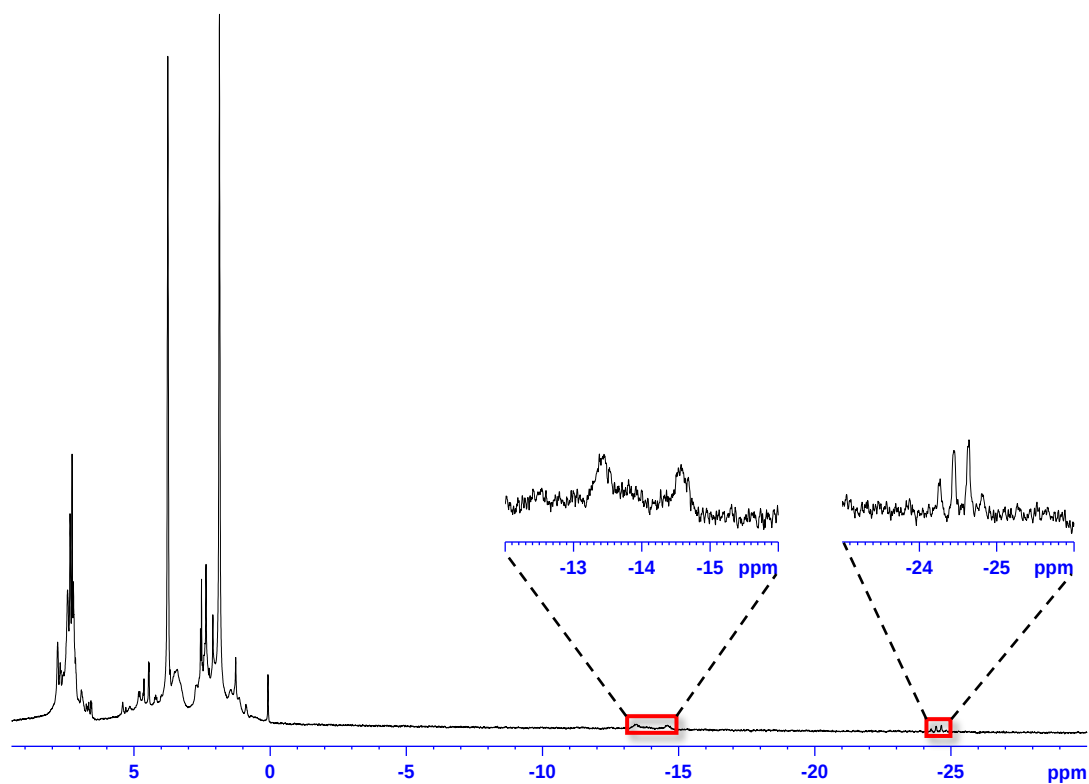


Figure A24. ^1H NMR (300 MHz, CDCl_3) spectrum of dehydrogenation catalysis of AB with 7 (LB = 1 Hz).

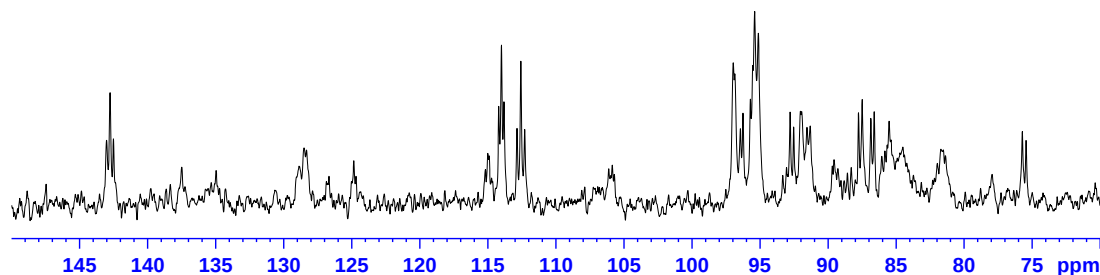


Figure A26. $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, THF) spectrum of dehydrogenation catalysis of DMAB with **7** (LB = 10 Hz).

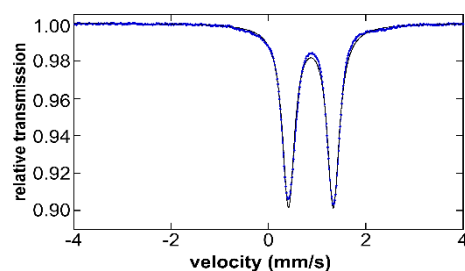


Figure A28. 80 K Mossbauer spectrum of a 3 mM frozen solution of ^{57}Fe -enriched **1** in 1:1 THF/2-MeTHF. The fit to a single major species with $\delta = 0.87$ mm/s and $\Delta E_Q = 0.95$ mm/s gives parameters similar to $[\text{Fe}(\kappa^3\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})_2]$ (**1**) in the solid-state (see **Table 5.1**) though with increased line broadening in solution ($\Gamma = 0.30$ mm/s). It is important to note that the fit is not ideal across the entire spectrum, indicating the likely presence of a second minor species most likely **2** representing < 3 % of total iron.

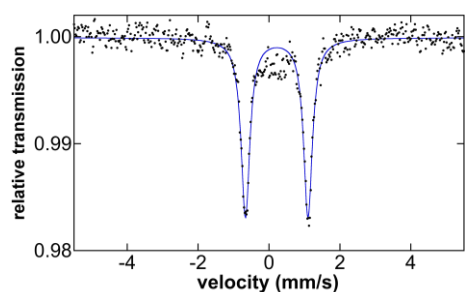


Figure A29. 80 K Mössbauer spectrum of $[\text{Fe}(\kappa^2\text{-S}^{\text{Me}}\text{NS}^{\text{Me}})(\kappa^3\text{-triphos})](\text{NTf}_2)$ (**7**).

Remaining appendices for Chapter 5 of this thesis can be found in the supporting information of the following published article:

Chapter 5: Das, U. K.; Daifuku, S. L.; Iannuzzi, T. E.; Gorelsky, S. I.; Korobkov, I.; Gabidullin, B.; Neidig, M. L.; Baker, R. T. Iron(II) Complexes of a Hemilabile SNS Amido Ligand: Synthesis, Characterization, and Reactivity. *Inorg. Chem.* **2017**, 56, 13766-13776.