New Routes to Low-Coordinate Iron Hydride Complexes: The Binuclear Oxidative Addition of H_2

Thomas R. Dugan and **Patrick L. Holland**
Department of Chemistry, University of Rochester, Rochester, NY 14627

Abstract

The oxidative addition and reductive elimination reactions of H_2 on unsaturated transition-metal complexes are crucial in utilizing this important molecule. Both biological and man-made iron catalysts use iron to perform H_2 transformations, and highly unsaturated iron complexes in unusual geometries (tetrahedral and trigonal planar) are anticipated to give unusual or novel reactions. In this paper, two new synthetic routes to the low-coordinate iron hydride complex $[L^{tBu}Fe(\mu\text{-}H)]_2$ are reported. Et_3SiH was used as the hydride source in one route by taking advantage of the silaphilicity of the fluoride ligand in three-coordinate $L^{tBu}FeF$. The other synthetic method proceeded through the binuclear oxidative addition of H_2 or D_2 to a putative Fe(I) intermediate. Deuteration was verified through reduction of an alkyne and release of the deuterated alkene product. Mössbauer spectra of $[L^{tBu}Fe(\mu\text{-}H)]_2$ indicate that the samples are pure, and that the iron(II) centers are high-spin.

Keywords

Iron; hydride; dihydrogen; oxidative addition; deuteration

Introduction

The oxidative addition of H_2 to transition metal complexes to form hydride complexes is now a well known reaction.[1] It has been studied in detail in part due to chemists' desire to understand the mechanism of homogeneous catalytic transformations of H_2 such as hydrogenation.[2] The interaction of H_2 with transition metal complexes during oxidative addition is usually thought to proceed through a dihydrogen complex, followed by scission of the H-H bond to give a dihydride complex.[3-7]

The standard organometallic description of the first part of this reaction is that the σ orbital of H_2 interacts with an empty d orbital (Figure 1a). [1,8] This model has been supported by the spectroscopic and crystallographic characterization of hundreds of dihydrogen complexes, which typically have diamagnetic transition metal sites from strong-field ligands. [6] The subsequent H_2 cleavage formally oxidizes the metal by two electrons (Figure 1b).

The Holland research group has focused its organometallic chemistry efforts on complexes that have a high-spin electronic configuration.[9] We use bulky β-diketiminate ligands that are weak-field π-donors to enforce a low coordination number. High-spin complexes like these

with 5 or more *d* electrons have *no empty d orbitals*, so the model above does not apply unless a spin-state change or other electronic reorganization can occur.

Recent computational and experimental work has been instrumental in demonstrating the importance of spin-state changes in organometallic chemistry. [10] [11] [12] [13] [14] [15] [16] One of our goals with β-diketiminate complexes is to discover new reactions that do not fit the usual organometallic mold and that may involve spin-state changes or use singly-occupied orbitals as acceptors (2-center/3-electron interactions). For example, alkyl complexes $L^RFeCH_2CH_2R$ ($L^R = L^{Me}$ or L^{tBu}, Figure 2) readily undergo β-hydride elimination upon mild heating.[17] As shown in Scheme 1, the transient hydride complex is trapped by the addition of another alkene. The β-hydride elimination mechanism was confirmed by the use of isotope labeling, activation parameters, and an H/D kinetic isotope effect (KIE) of 2.2.[17] Therefore, a pathway exists for high-spin complexes to undergo β-hydride elimination in the absence of *completely* empty d orbitals. Based on these ideas, we have also been interested to find examples of oxidative addition and reductive elimination, especially involving the fundamentally interesting molecule H_2.

In previous work, we isolated a dimeric hydride complex, $[L^{tBu}Fe(\mu-H)]_2$, from the reaction of $L^{tBu}FeCl$ with $KBEt_3H$ (Scheme 2a). [18] This was the first iron hydride complex with a coordination number less than five, and the only other one known is its close analogue $[L^{Me}Fe(\mu-H)]_2$.[19] $[L^{tBu}Fe(\mu-H)]_2$ is curious because the hydride bridges hold the two iron (II) ions exceptionally close to one another (2.624(2) Å). [18] Despite the dimeric structure in the solid state, in solution the great steric interference between the diketiminate ligands on the two iron atoms leads the molecule to partially dissociate into monomers $L^{tBu}FeH$, which were observed by ^1H NMR spectroscopy. [18] Both the monomer and dimer show ^1H NMR spectra with broadened resonances over a large chemical shift range, which are characteristic of paramagnetic molecules. Therefore, the available data suggested a high-spin electronic configuration for the iron(II) centers in $[L^{tBu}Fe(\mu-H)]_2$, but were not definitive because an excited electronic state might be accessed at room temperature.

The reactivity of the dimeric hydride complex, $[L^{tBu}Fe(\mu-H)]_2$, has been examined with a range of substrates in solution.[18-21] The most relevant reaction to this work is the addition of strong field ligands such as CO to the hydride complex, which resulted in reductive elimination of H_2 to form Fe(I) products (Scheme 3). [19] This observation shows that the reductive elimination of H_2 from $[L^{tBu}Fe(\mu-H)]_2$ is facile in the presence of strong field ligands. However, photolysis was required to eliminate H_2 in the presence of weaker ligands. For example, photolysis of the hydride complex under N_2 atmosphere resulted in loss of H_2 and formation of the dinitrogen complex, $L^{tBu}FeNNFeL^{tBu}$. [19] The intermediate species in this process are unknown, but it is conceivable that a highly unsaturated "$L^{tBu}Fe$" species is formed; then this iron(I) intermediate would be trapped by N_2. The prospect of trapping this species with H_2 inspired us to evaluate the oxidative addition of H_2 to highly unsaturated iron(I) species in the absence of N_2.

The hydride complex also reacts with boranes R_3B to give $L^{tBu}Fe(\mu-H)_2BR_2$ and $L^{tBu}FeR$ (Scheme 2b). [21] While the mechanistic study of this reaction was interesting, [21] the reactivity of $[L^{tBu}Fe(\mu-H)]_2$ towards boranes posed a practical problem. The synthesis of $[L^{tBu}Fe(\mu-H)]_2$ utilized $KBEt_3H$ as the hydride source, giving BEt_3 as a byproduct. The desired hydride complex was the kinetic product of the reaction (formed within 15 minutes), but $[L^{tBu}Fe(\mu-H)]_2$ immediately began to react with the BEt_3 byproduct to give the thermodynamic product $L^{tBu}Fe(\mu-H)_2BR_2$ over several hours. Therefore, our samples of crude $[L^{tBu}Fe(\mu-H)]_2$ were invariably contaminated with the dihydridoborate complex, and the separation of the two complexes by crystallization was laborious. [19] Therefore, another motivation for the studies below was the development of a new synthetic route to $[L^{tBu}Fe(\mu-H)]_2$. Since $[L^{tBu}Fe$

$(\mu\text{-H})]_2$ demonstrated the ability to reductively eliminate H_2, we decided to explore the microscopic reverse, oxidative addition of H_2 to Fe(I), as a possible synthetic route. Here we report two new independent syntheses of $[L^{tBu}Fe(\mu\text{-H})]_2$ and provide further characterization of the complex using Mössbauer spectroscopy.

Results and Discussion

Synthesis of $[L^{tBu}Fe(\mu\text{-H})]_2$ from a Silane

We have previously shown that $L^{tBu}FeF$ undergoes reactions with silylated substrates, eliminating Et_3SiF and leaving the formerly silicon-bound group on iron.[22] This methodology was used to generate $[L^{tBu}Fe(\mu\text{-H})]_2$ from $L^{tBu}FeF$ using Et_3SiH as a hydride source (Scheme 4). A slurry of pink $L^{tBu}FeF$ in toluene was treated with 10 molar equivalents of Et_3SiH and was heated overnight at 100 °C to produce a red-brown solution. Removal of the volatile components and crystallization from a saturated Et_2O solution at -45 °C yielded $[L^{tBu}Fe(\mu\text{-H})]_2$ in 83% yield. The identity of the product as the desired hydride complex was established through ^1H NMR spectroscopy in C_6D_6, which was compared to the literature spectrum.[18]

The synthesis of $[L^{tBu}Fe(\mu\text{-H})]_2$ via Et_3SiH as a hydride source utilizes the formation of the strong Si-F bond as a thermodynamic driving force for the reaction. This method was inspired by Roesky, who used Et_3SiH as hydride source to generate a β–diketiminate zinc-hydride dimer from the corresponding zinc fluoride complex.[23] However, a stoichiometric amount of Et_3SiH was used in the zinc system while an excess was needed for the Fe system. Repeated attempts to generate $[L^{tBu}Fe(\mu\text{-H})]_2$ using only 2 equivalents of Et_3SiH resulted in incomplete conversion, as evidenced by a small amount of $L^{tBu}FeF$ remaining in the ^1H NMR spectrum. The use of excess Et_3SiH is not a problem as it is easily removed during the workup.

Synthesis from Dihydrogen

In another method, $[L^{tBu}Fe(\mu\text{-H})]_2$ can be synthesized directly from $L^{tBu}FeCl$ using H_2 as the hydride source (Scheme 5). Reduction of $L^{tBu}FeCl$ in Et_2O with potassium graphite (KC_8) under argon gave a dark green mixture. The mixture was degassed and placed under an atmosphere of purified H_2, and the mixture turned red-brown. (The reaction is complete within 5 min of addition, as shown by a small-scale experiment in a J. Young NMR tube in C_6D_6.) After 18 h, H_2 was removed, and the mixture was filtered through Celite to yield a red-brown solution. The red-brown solution was identified as $[L^{tBu}Fe(\mu\text{-H})]_2$ by ^1H NMR spectroscopy in C_6D_6.[18] Crystalline $[L^{tBu}Fe(\mu\text{-H})]_2$ was obtained in 58% yield by cooling a saturated Et_2O solution to -45 °C. $[L^{tBu}Fe(\mu\text{-D})]_2$ was obtained in 62% yield through the same reaction conditions by substituting D_2 for H_2. Characterization of $[L^{tBu}Fe(\mu\text{-D})]_2$ by ^1H NMR spectroscopy in C_6D_6 revealed that the deuteride and the hydride complexes have identical ^1H NMR spectra. The hydrides are not visible by ^1H NMR spectroscopy, probably due to the proximity to the paramagnetic Fe atoms. Therefore, a different method was required to quantify the amount of deuteration in $[L^{tBu}Fe(\mu\text{-D})]_2$.

We took advantage of the high-yield reaction of $[L^{tBu}Fe(\mu\text{-H})]_2$ with 3-hexyne to form the three-coordinate Fe vinyl complex, $L^{tBu}FeC(Et)=CHEt$.[18] Subsequently, a sample of $L^{tBu}FeC(Et)=CHEt$ was quenched with H_2O, and the volatile components were separated and examined by GC-MS. As expected, the parent ion of 3-hexene (m/z 84) was observed. The experiment was repeated with $[L^{tBu}Fe(\mu\text{-D})]_2$ to give $L^{tBu}FeC(Et)=CDEt$, leading to 3-hexene-d_1. The same analysis as above gave a mass spectrum with the parent ion at m/z 85 and a small peak at m/z 84. The relative intensities of the peaks showed that the sample of $[L^{tBu}Fe(\mu\text{-D})]_2$ was 89% deuterated.

The absence of N_2 is crucial for the success of the reaction of $L^{tBu}FeCl$ with KC_8 and H_2 to give $[L^{tBu}Fe(\mu\text{-}H)]_2$. If any N_2 was present, the previously characterized dinitrogen complex, $L^{tBu}FeNNFeL^{tBu}$, was isolated. [24] Morris and co-workers have documented the parallels between H_2 and N_2 binding to unsaturated metal complexes. [25-27] They found that the fragments that bind N_2 to give a M-N_2 complex with an N-N stretching frequency below 2060 cm^{-1} did not form a stable H_2 complex; rather, they oxidatively add H_2 to give a dihydride species. A few complexes that deviate from the trend have been reported.[28-32] In the system examined here, the parallel is that two "$L^{tBu}Fe$" fragments can either cooperatively bind N_2 in $L^{tBu}FeNNFeL^{tBu}$ or cooperatively add H_2 to give $[L^{tBu}Fe(\mu\text{-}H)]_2$. The N-N stretching frequency in $L^{tBu}FeNNFeL^{tBu}$ is 1778 cm^{-1},[24] so the observation of H_2 oxidative addition fits the established trend. We note that Mössbauer spectroscopy and DFT computations on $L^{tBu}FeNNFeL^{tBu}$ show that the N_2 ligand is reduced by two electrons (N_2^{2-}).[33] Therefore, the iron(I) $L^{tBu}Fe$ fragment gives exceptionally strong backbonding, and it is reasonable that the same bimetallic system oxidatively adds H_2 and binds N_2.

There are several possible mechanisms through which $[L^{tBu}Fe(\mu\text{-}H)]_2$ might be formed (Scheme 6). In each mechanism, we assume that $L^{tBu}FeCl$ is first reduced by KC_8 to yield KCl and "$L^{tBu}Fe$" (see below). In Scheme 6a, the $L^{tBu}Fe$ fragment binds H_2 to form $L^{tBu}Fe(H_2)$, and subsequently attracts another $L^{tBu}Fe$ fragment to give $[L^{tBu}Fe(\mu\text{-}H)]_2$. The π–backbonding from two Fe(I) centers results in homolytic cleavage of the H-H bond. However, it is possible that H_2 is reduced by one or two electrons in the mononuclear intermediate. A one electron reduction of H_2 would form a Fe(II) intermediate, $L^{tBu}Fe(H_2)$, with an H_2^- ligand (Scheme 6b). Though the radical anion H_2^- is unprecedented as a ligand, previous studies on alkyne and N_2 binding to the $L^{tBu}Fe$ fragment gave evidence for transfer of a single electron from the metal to the π-acceptor ligand. [33] [34] Alternatively, oxidative addition of H_2 to the $L^{tBu}Fe$ fragment would give the iron(III) intermediate $L^{tBu}FeH_2$ (Scheme 6c). Either mononuclear complex could interact with an additional $L^{tBu}Fe$ fragment to give $[L^{tBu}Fe(\mu\text{-}H)]_2$. Finally, the reaction of two $L^{tBu}Fe$ species simultaneously with H_2 is possible (Scheme 6d). This reaction would be topologically similar to the homolytic cleavage of H_2 and alkanes by rhodium porphyrins, which has been demonstrated to be termolecular [35-37]. The monomeric hydride complexes would then dimerize to give $[L^{tBu}Fe(\mu\text{-}H)]_2$.

It is most likely that reaction with H_2 with $L^{tBu}FeCl$ does not precede reduction, as $L^{tBu}FeCl$ showed no reactivity with H_2 in the absence of a reducing agent. Reduction of a red solution of $L^{tBu}FeCl$ with KC_8 in the absence of N_2 or H_2 produced a dark green mixture, for which the ^1H NMR spectrum in C_6D_6 changed to have many peaks over the course of 3 h, accompanied by a pronounced color change from dark green to brown. These observations suggest the formation of a reactive intermediate, which unfortunately we have not been able to isolate or further characterize in Et_2O, toluene, or pentane.

In order to test the reactivity of H_2 toward a more stable high-spin Fe(I) complex with a very labile KCl ligand, we treated the iron(I) species $L^{tBu}Fe(\mu\text{-}Cl)K(18\text{-}crown\text{-}6)$[24] with H_2. Surprisingly, $L^{tBu}Fe(\mu\text{-}Cl)K(18\text{-}crown\text{-}6)$ did not react with H_2 over 2 d at room temperature in C_6D_6, as judged by ^1H NMR spectroscopy. In addition, this isolable Fe(I) complex was not very reactive with N_2 as only partial conversion to $L^{tBu}FeNNFeL^{tBu}$ was observed after 3 d. The low reactivity of $L^{tBu}Fe(\mu\text{-}Cl)K(18\text{-}crown\text{-}6)$ provides insight into the pathway of hydride formation: we surmise that the incoming H_2 molecule must have access to the site occupied by the chloride ligand in $L^{tBu}Fe(\mu\text{-}Cl)K(18\text{-}crown\text{-}6)$, and that coordination of the (18-crown-6)KCl ligand is strong enough to inhibit the formation of essential $L^{tBu}Fe(H_2)$ or $L^{tBu}Fe(N_2)$ intermediates.

To our knowledge, the reaction reported here is the first example of binuclear oxidative addition of H_2 to give a bridging diiron-hydride complex. There are a few other examples of binuclear

oxidative addition of H_2 to give a four-coordinate metal with two bridging hydride ligands. Bach and coworkers synthesized $[(dtbpe)Ni(\mu-H)]_2$ by the reduction of $(dtbpe)NiCl_2$ with excess Mg under a H_2 atmosphere.[38] $[(dtbpe)Ni(\mu-H)]_2$ was also prepared independently from a Ni(0) complex by treating (dtbpe)Ni-benzene with H_2.[38] Schwartz and Andersen isolated a series of $[P_2PtH]_2$ complexes, where P_2 is a chelating phosphine ligand,[39]by treating P_2PtCl_2 complexes with sodium amalgam under an atmosphere of H_2. However, ^1H NMR experiments show that these $[P_2PtH]_2$ complexes have terminal hydride ligands unlike $[(dtbpe)Ni(\mu-H)]_2$, which has bridging hydride ligands. These systems, like ours, utilize a reducing agent to open a coordination site for H_2 and to reduce the metal to a low oxidation state that is more amenable to oxidative addition. Note that there are other complexes that utilize H_2 as a hydride source for the synthesis of four-coordinate dinuclear bis(μ-hydride) complexes; however, these hydride complexes are generated via the hydrogenolysis of alkyl, aryl, or allyl metal complexes.[40-47]

Characterization

The stretching frequency, ν_{Fe-H}, of the Fe-H bond in $[L^{tBu}Fe(\mu-H)]_2$ could not be assigned in previous reports due to the lack of a deuterated isotopomer. [18,19] The isolation of $[L^{tBu}Fe(\mu-D)]_2$ led to the examination of the IR spectra of $[L^{tBu}Fe(\mu-H)]_2$ and $[L^{tBu}Fe(\mu-D)]_2$ for a band that shifts between the two isotopomers. However, these complexes have identical IR spectra, and the spectra are featureless in the hydride stretch region between 1700 cm^{-1} and 2300 cm^{-1}. The reason for the apparently low oscillator strength of the Fe-H stretching modes is not clear. We note that the hydride formulation is not in question, based on the X-ray crystal structure, [18] the insertion reactivity, [19] and the reaction with ligands to form H_2. [19]

The purity and electronic structure of solid $[L^{tBu}Fe(\mu-H)]_2$ was evaluated using Mössbauer spectroscopy. The zero-field Mössbauer spectrum of solid $[L^{tBu}Fe(\mu-H)]_2$ at 80 K is shown in Figure 3. The spectrum exhibits one quadrupole doublet with $\delta = 0.59$ mm/s and $\Delta E_Q = 1.58$ mm/s. The isomer shift is very close to the range (0.62-0.86 mm/s) observed in other high-spin Fe(II) diketiminate complexes.[33,34,48-52] High-spin, tetrahedral iron(II) sites in iron-sulfide clusters have similar parameters ($\delta = 0.6-0.7$ mm/s and $\Delta E_Q = 2-3$ mm/s).[53,54] Low-spin octahedral iron sites have very different isomer shifts and quadrupole splittings: $\delta = 0.3-0.45$ mm/s and $\Delta E_Q < 1.5$ mm/s.[54] The intermediate-spin ($S = 1$) iron(II) hydride complex $[Fe(dppe)_2H]^+$ has been characterized by Mössbauer spectroscopy, giving $\delta = 0.23$ mm/s and $\Delta E_Q = 1.53$ mm/s.[55] The much higher isomer shift in $[L^{tBu}Fe(\mu-H)]_2$ (0.59 mm/s) strongly supports the assignment of the spin state at iron as high-spin ($S = 2$), and is consistent with the paramagnetically shifted ^1H NMR spectrum.

Concluding Remarks

Two new synthetic routes to $[L^{tBu}Fe(\mu-H)]_2$ were developed. In one, $[L^{tBu}Fe(\mu-H)]_2$ was synthesized from $L^{tBu}FeF$ using Et_3SiH as a hydride source, utilizing the formation of the strong Si-F bond as the driving force for the reaction. $[L^{tBu}Fe(\mu-H)]_2$ was also synthesized via the binuclear oxidative addition of H_2 to a low-coordinate Fe(I) intermediate. This reaction results in the homolytic binuclear cleavage of the H-H bond. These new syntheses were adapted to enable the isolation of the first low-coordinate iron deuteride complex, $[L^{tBu}Fe(\mu-D)]_2$.

These results show a new example of a high-spin complex that undergoes an organometallic reaction that is typically viewed through "2-electron" mechanisms. The oxidative addition of H_2 is facile, and complements a number of recently reported ligand-induced reductive elimination reactions. [19] Continued research will address the mechanisms of these reactions.

Experimental

General Considerations

All manipulations were performed under a nitrogen atmosphere (or argon atmosphere where specified) by Schlenk techniques or in an M. Braun glovebox maintained at or below 1 ppm of O_2 and H_2O. NMR data were recorded on a Bruker Avance 500 spectrometer (500 MHz). All peaks in the NMR spectra are referenced to residual protiated solvents (benzene δ 7.16 ppm; toluene δ 2.08 ppm; cyclohexane δ 1.38 ppm). Infrared spectra (450-4000 cm^{-1}) were recorded on KBr pellet samples in a Shimadzu FTIR spectrophotometer (FTIR-8400S) using 32 scans at 2 cm^{-1} resolution. GC-MS was performed using a Shimadzu QP2010 system with electron impact ionization. Pentane, hexane, tetrahydrofuran (THF), diethyl ether, and toluene were purified by passage through activated alumina and "deoxygenizer" columns from Glass Contour Co. (Laguna Beach, CA). Deuterated solvents were first dried over CaH_2, then over Na/benzophenone, and then vacuum transferred into a storage container. Before use, an aliquot of each solvent was tested with a drop of sodium benzophenone ketyl in THF solution. Glassware was dried at 150 °C overnight, and Celite was dried overnight at 200 °C under vacuum. Ultra-high purity H_2 was purchased from Air Products and was dried by passage through a column of activated alumina. D_2 was purchased from Sigma-Aldrich and was dried by passage through a column of activated alumina. Et_3SiH was stored under N_2 over 4 Å molecular sieves. L^{tBu}FeCl,[56] L^{tBu}FeCH$_3$[48] and L^{tBu}FeF[22] were prepared by published procedures.

Synthesis of [L^{tBu}Fe(μ-H)]$_2$ from Et$_3$SiH

L^{tBu}FeF (400 mg, 0.694 mmol) was added to a flask with a Teflon pin closure. Toluene (40 mL) was added to the flask to produce a pink slurry. Et_3SiH (1.10 mL, 6.89 mmol, 9.9 equiv) was added to the flask via syringe. The flask was sealed, and the mixture was heated and stirred at 100 °C overnight. The solution changed color from pink to red-brown over the course of the reaction (~14 h). The solution was cooled to room temperature and the volatile components were removed under reduced pressure to yield a red-brown residue. The residue was dissolved in Et_2O (70 mL) and was filtered through Celite. This solution was concentrated to 35 mL and was cooled to -45 °C to yield 243 mg of red-brown crystalline product. The mother liquor was concentrated to 5 mL and was cooled to -45 °C to produce a second crop of crystals (79 mg). The total yield was 322 mg (83%). ^{1}H NMR (500 MHz, C_6D_6): 118, 70, 42, 24, 22, 20, 15, 12, 10, 6, 3, 1, -2, -3, -5, -8, -11, -12, -15, -16, -17, -23, -27, -28, -32, -38, -52, -58, -111, -115, -124 ppm. The complexity of the spectrum is attributed to hindered rotations and partial dissociation into monomeric L^{tBu}FeH, as discussed previously. [18] IR (KBr pellet): 3057 (w), 3020 (w), 2962 (s), 2939 (s), 2869 (s), 1579 (w), 1539(m), 1485(s), 1475 (s), 1433 (s), 1385 (s), 1362 (s), 1312 (s), 1273 (m), 1253(m), 1215 (m), 1201 (m), 1184 (m), 1155 (w), 1120 (m), 1099 (m), 1072 (w), 1055 (w), 1022 (w), 935 (w), 887 (w), 843 (w), 800 (w), 779 (s), 756 (m), 711 (m), 667 (w) cm^{-1}.

Synthesis of [L^{tBu}Fe(μ-H)]$_2$ from H$_2$

In an N_2-filled glove box, L^{tBu}FeCl (334 mg, 0.563 mmol, 1 equiv) was added to a flask with a Teflon pin closure and was dissolved in Et_2O (40 mL) to produce a bright red solution. The flask was sealed, and the solution was degassed. In an argon-filled glove box, KC_8 (86.5 mg, 0.640 mmol, 1.08 equiv) was added to the solution which resulted in an immediate color change from red to dark green. The flask was sealed, and the mixture was degassed again. The dark green mixture was stirred for 1 h. The mixture was frozen, and purified H_2 (1 bar) was added to the frozen reaction mixture. H_2 was removed after stirring overnight, and the mixture was filtered through Celite to yield a red brown solution. This solution was concentrated to 12 mL and cooled to -45 °C to yield 149 mg of red-brown crystalline product. The mother liquor was concentrated to 2 mL and was cooled to -45 °C to produce a second crop of crystals (32 mg).

The total yield was 181 mg (58%). Synthesis of $[L^{tBu}Fe(\mu\text{-}D)]_2$ from D_2 used the same method, and gave a yield of 62%.

Mössbauer spectroscopy

Mössbauer data were recorded on a spectrometer with alternating constant acceleration. The minimum experimental line width was 0.24 mm/s (full width at half-height). The sample temperature was maintained constant in an Oxford Instruments Variox cryostat. The γ-ray source was ca. 0.6 GBq ^{57}Co/Rh. Isomer shifts are quoted relative to iron metal at 300 K. The zero-field spectra were simulated by using Lorentzian doublets.

Acknowledgments

References

1. Crabtree, RH. The Organometallic Chemistry of the Transition Metals. Wiley; Hoboken, NJ: 2005.

2. Cotton, FA.; Wilkinson, G.; Murillo, CA.; Bochmann, M. Advanced Inorganic Chemistry. Wiley; New York, NY: 1999.

3. Deutsch PP, Eisenberg R. Chem Rev 1988;88:1147–1161.

4. Crabtree RH. Acc Chem Res 1990;23:95–101.

5. Heinekey DM, Oldham WJ Jr. Chem Rev 1993;93:913–926.

6. Kubas, GJ. Metal Dihydrogen and σ-Bond Complexes: Structure, Theory and Reactivity. Kluwer Academic / Plenum Publishers; New York, NY: 2001.

7. McGrady GS, Guilera G. Chem Soc Rev 2003;32:383–392. [PubMed: 14671793]

8. Morris, RH. Non-Classical Hydrogen Bonding Along the Pathway to the Heterolytic Splitting of Dihydrogen. In: Peruzzini, M.; Poli, R., editors. Recent Advances in Hydride Chemistry. Elsevier; New York: 2001. p. 1-38.

9. Holland PL. Acc Chem Res 2008;41:905–914. [PubMed: 18646779]

10. Harvey JN, Poli R, Smith KM. Coord Chem Rev 2003;238-239:347–361.

11. Poli R, Harvey JN. Chem Soc Rev 2003;32:1–8. [PubMed: 12596540]

12. Veige AS, Slaughter LM, Lobkovsky EB, Wolczanski PT, Matsunaga N, Decker SA, Cundari TR. Inorg Chem 2003;42:6204–6224. [PubMed: 14514296]

13. Poli R. J Organomet Chem 2004;689:4291–4304.

14. Carreon-Macedo J-L, Harvey JN. J Am Chem Soc 2004;126:5789–5797. [PubMed: 15125671]

15. Harvey JN. Phys Chem Chem Phys 2007;9:541.

16. Besora M, Carreon-Macedo J-L, Cowan AJ, George MW, Harvey JN, Portius P, Ronayne KL, Sun X-Z, Towrie M. J Am Chem Soc 2009;131:3583–3592. [PubMed: 19236096]

17. Vela J, Vaddadi S, Cundari TR, Smith JM, Gregory EA, Lachicotte RJ, Flaschenriem CJ, Holland PL. Organometallics 2004;23:5226–5239.

18. Smith JM, Lachicotte RJ, Holland PL. J Am Chem Soc 2003;125:15752–15753. [PubMed: 14677959]

19. Yu Y, Sadique AR, Smith JM, Dugan TR, Cowley RE, Brennessel WW, Flaschenriem CJ, Bill E, Cundari TR, Holland PL. J Am Chem Soc 2008;130:6624–6638. [PubMed: 18444648]

20. Sadique AR, Gregory EA, Brennessel WW, Holland PL. J Am Chem Soc 2007;129:8112–8121. [PubMed: 17564444]

21. Yu Y, Brennessel WW, Holland PL. Organometallics 2007;26:3217–3226. [PubMed: 18725998]

22. Vela J, Smith JM, Yu Y, Ketterer NA, Flaschenriem CJ, Lachicotte RJ, Holland PL. J Am Chem Soc 2005;127:7857–7870. [PubMed: 15913376]

23. Hao H, Cui C, Roesky HW, Bai G, Schmidt H-G, Noltemeyer M. Chem Commun 2001:1118–1119.

24. Smith JM, Sadique AR, Cundari TR, Rodgers KR, Lukat-Rodgers G, Lachicotte RJ, Flaschenriem CJ, Vela J, Holland PL. J Am Chem Soc 2006;128:756–769. [PubMed: 16417365]

25. Morris RH, Earl KA, Luck RL, Lazarowych NJ, Sella A. Inorg Chem 1987;26:2674–2683.

26. Jessop PG, Morris RH. Coordination Chemistry Reviews 1992;121:155–284.

27. Morris RH. Inorg Chem 1992;31:1471–1478.

28. Earl KA, Jia G, Maltby PA, Morris RH. J Am Chem Soc 1991;113:3027–3039.

29. Leal AJ, Tenorio MJ, Puerta MC, Valerga P. Organometallics 1995;14:3839–3847.

30. King WA, Luo X-L, Scott BL, Kubas GJ, Zilm KW. J Am Chem Soc 1996;118:6782–6783.

31. Reid SM, Neuner B, Schrock RR, Davis WM. Organometallics 1998;17:4077–4089.

32. Seino H, Arita C, Nonokawa D, Nakamura G, Harada Y, Mizobe Y, Hidai M. Organometallics 1999;18:4165–4173.

33. Stoian SA, Vela J, Smith JM, Sadique AR, Holland PL, Münck E, Bominaar EL. J Am Chem Soc 2006;128:10181–10192. [PubMed: 16881648]

34. Stoian SA, Yu Y, Smith JM, Holland PL, Bominaar EL, Münck E. Inorg Chem 2005;44:4915–4922. [PubMed: 15998018]

35. Sherry AE, Wayland BB. Journal of the American Chemical Society 1990;112:1259–1261.

36. Wayland BB, Ba S, Sherry AE. Journal of the American Chemical Society 1991;113:5305–5311.

37. Wayland BB, Ba S, Sherry AE. Inorganic Chemistry 1992;31:148–150.

38. Bach I, Goddard R, Kopiske C, Seevogel K, Pörschke K-R. Organometallics 1999;18:10–20.

39. Schwartz DJ, Andersen RA. J Am Chem Soc 1995;117:4014–4025.

40. Brown RK, Williams JM, Fredrich MF, Day VW, Sivak AJ, Muetterties EL. Proc Natl Acad Sci USA 1979;76:2099–2102. [PubMed: 16592645]

41. Teller RG, Williams JM, Koetzle TF, Burch RR, Gavin RM, Muetterties EL. Inorg Chem 1981;20:1806–1811.

42. Fryzuk MD. Can J Chem 1983;61:1347–1351.

43. Fryzuk MD, Jones T, Einstein FWB. Organometallics 1984;3:185–191.

44. Goeden GV, Huffman JC, Caulton KG. Inorg Chem 1986;25:2484–2485.

45. Bennett BL, Roddick DM. Inorg Chem 1996;35:4703–4707.

46. MacAdams LA, Buffone GP, Incarvito CD, Golen JA, Rheingold AL, Theopold KH. Chem Commun 2003:1164–1165.

47. Monillas WH, Yap GPA, Theopold KH. Angew Chem Int Ed Engl 2007;46:6692–6694. [PubMed: 17668893]

48. Andres H, Bominaar EL, Smith JM, Eckert NA, Holland PL, Münck E. J Am Chem Soc 2002;124:3012–3025. [PubMed: 11902893]

49. Holland PL, Cundari TR, Perez LL, Eckert NA, Lachicotte RJ. J Am Chem Soc 2002;124:14416–14424. [PubMed: 12452717]

50. Vela J, Stoian S, Flaschenriem CJ, Münck E, Holland PL. J Am Chem Soc 2004;126:4522–4523. [PubMed: 15070362]

51. Eckert NA, Stoian S, Smith JM, Bominaar EL, Münck E, Holland PL. J Am Chem Soc 2005;127:9344–9345. [PubMed: 15984842]

52. Cowley RE, Elhaik J, Eckert NA, Brennessel WW, Bill E, Holland PL. J Am Chem Soc 2008;130:6074–6075. [PubMed: 18419120]

53. Beinert H, Holm RH, Münck E. Science 1997;277:653–659. [PubMed: 9235882]

54. Münck E. Physical Methods in Bioinorganic Chemistry 2000:287–319.

55. Franke O, Wiesler BE, Lehnert N, Peters G, Burger P, Tuczek F. Z Anorg Allg Chem 2006;632:1247–1256.

56. Smith JM, Lachicotte RJ, Holland PL. Chem Commun 2001:1542–1543.
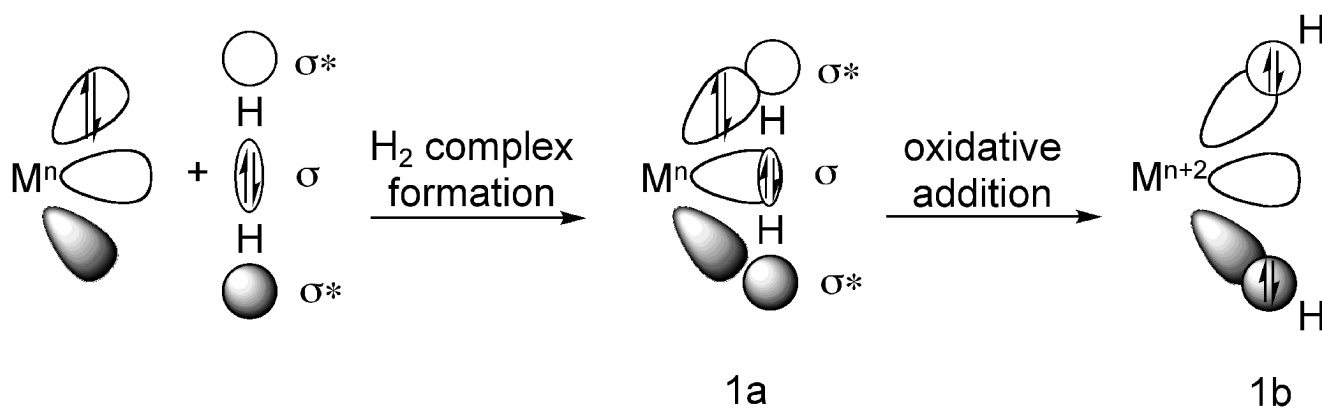
Figure 1.
Interaction of dihydrogen orbitals with metal d orbitals. In the standard model, an empty d orbital lobe forms a σ interaction with the H-H bonding orbital, and two lobes of a filled d orbital donate into the empty σ* orbital of H_2.
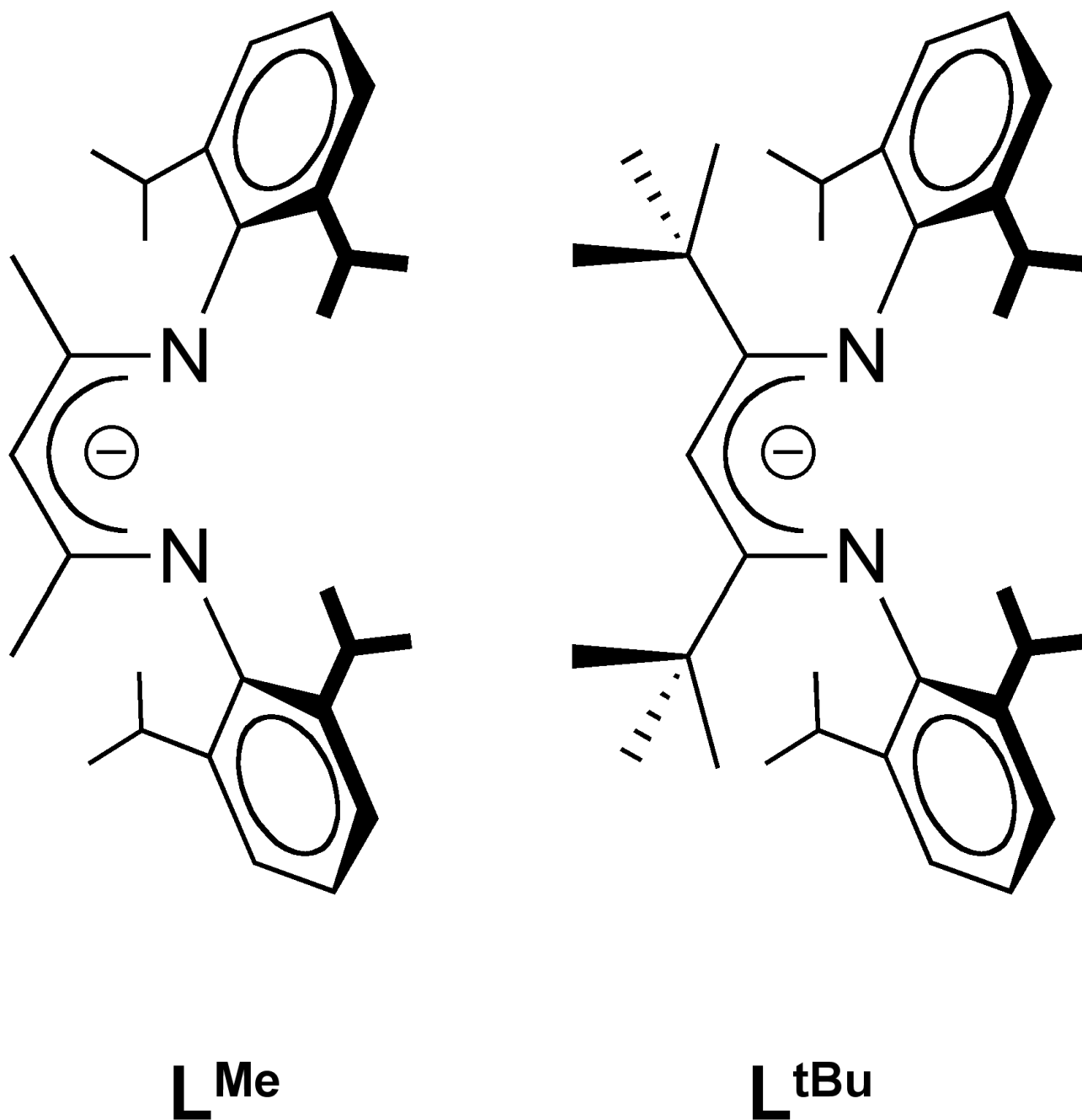
Figure 2.
β-diketimate ligands L^R, where R indicates the substituent on the 2 and 4 positions of the C_3N_2 backbone.
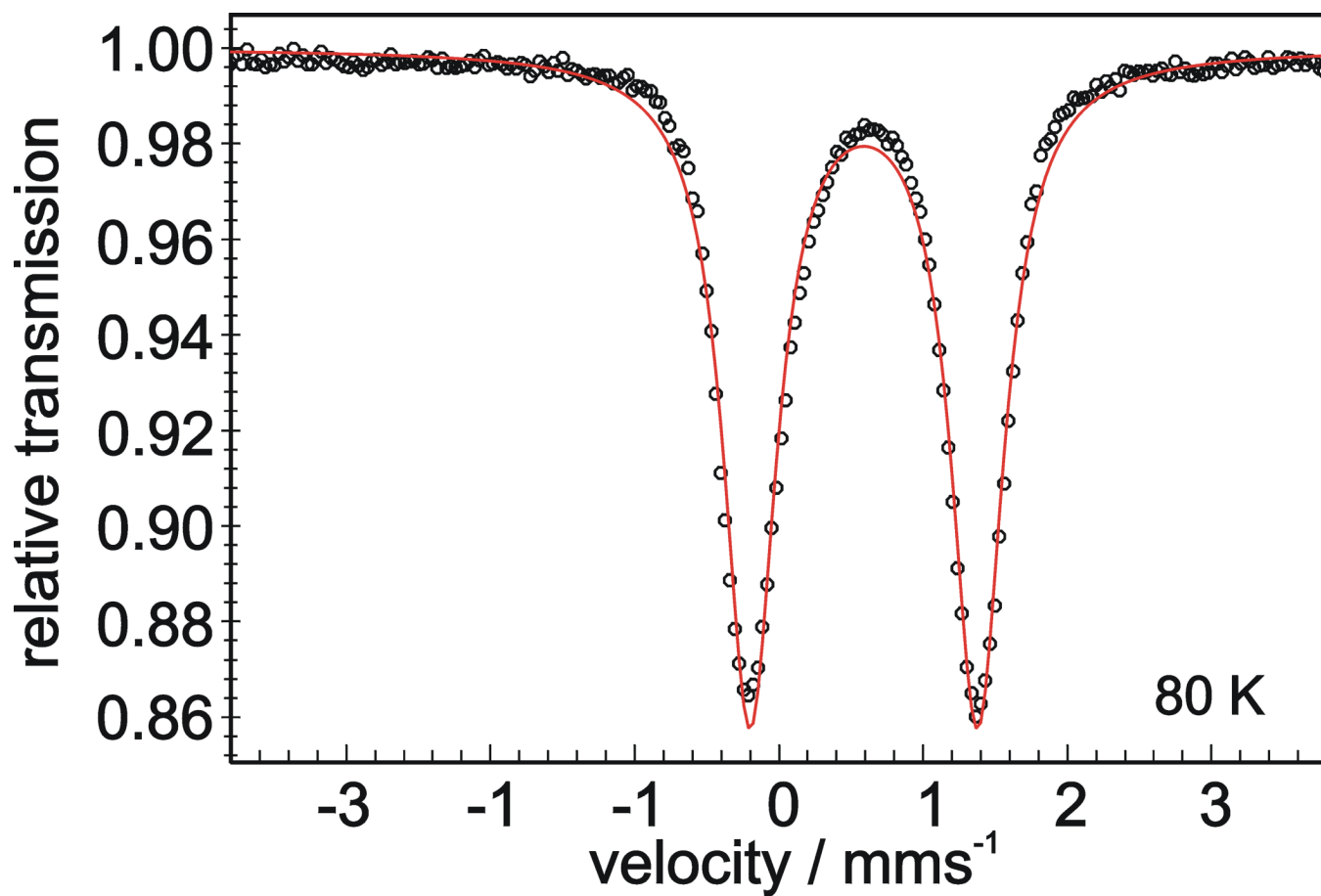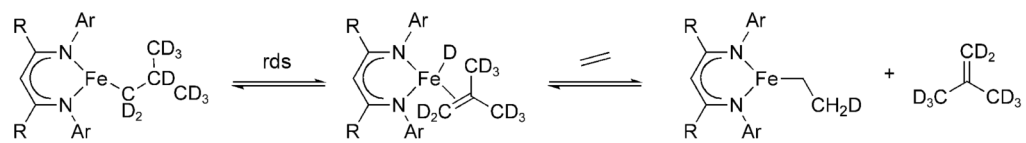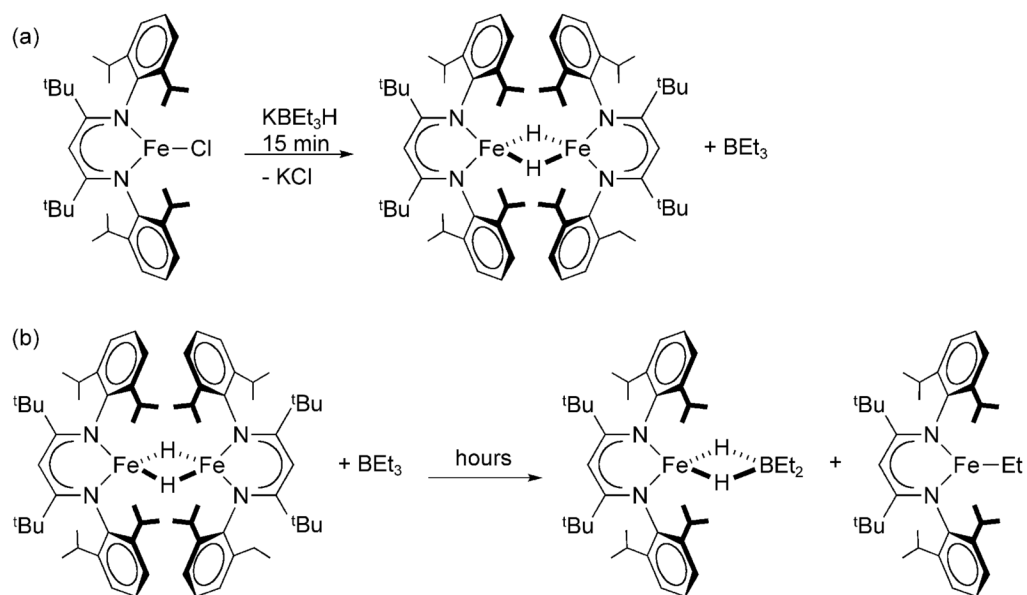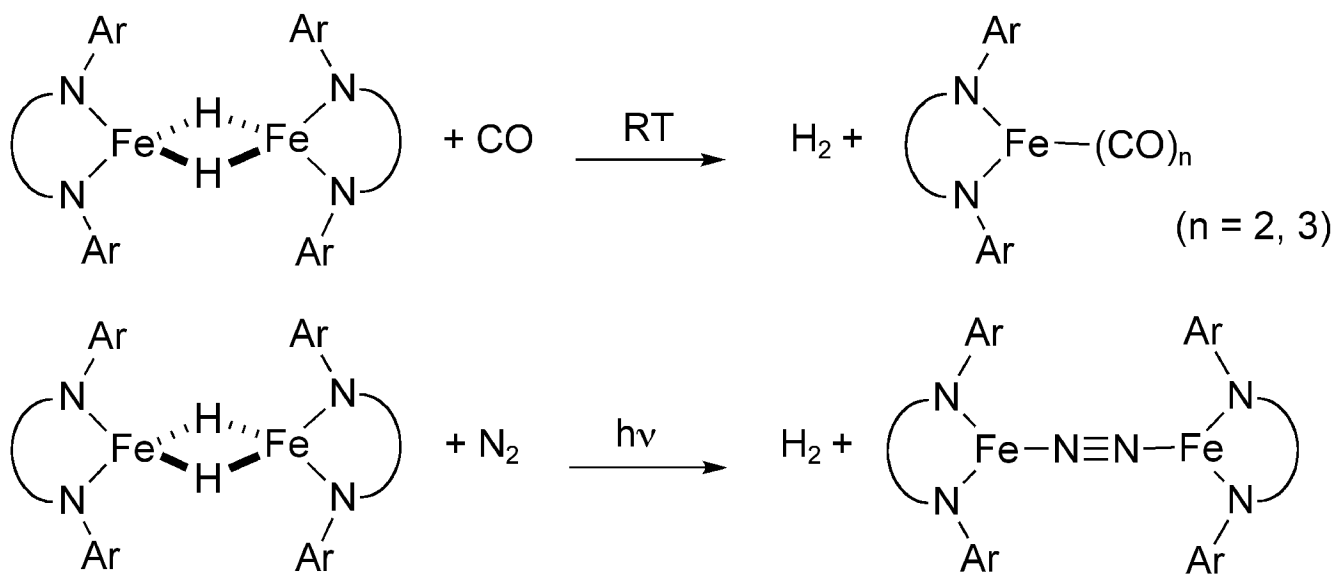
Figure 3.
Mössbauer spectrum of solid $[L^{tBu}Fe(\mu\text{-}H)]_2$ at 80 K. The black circles are the data, and the red line represents a simulated spectrum using the parameters given in the text.
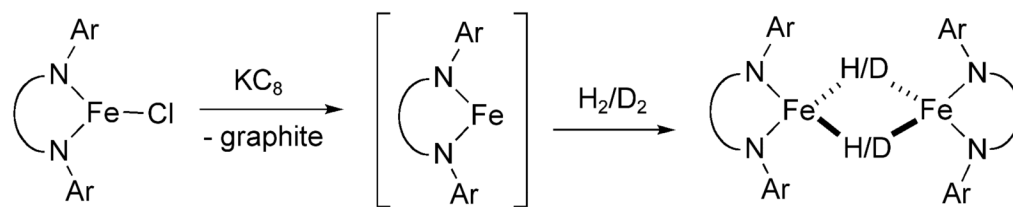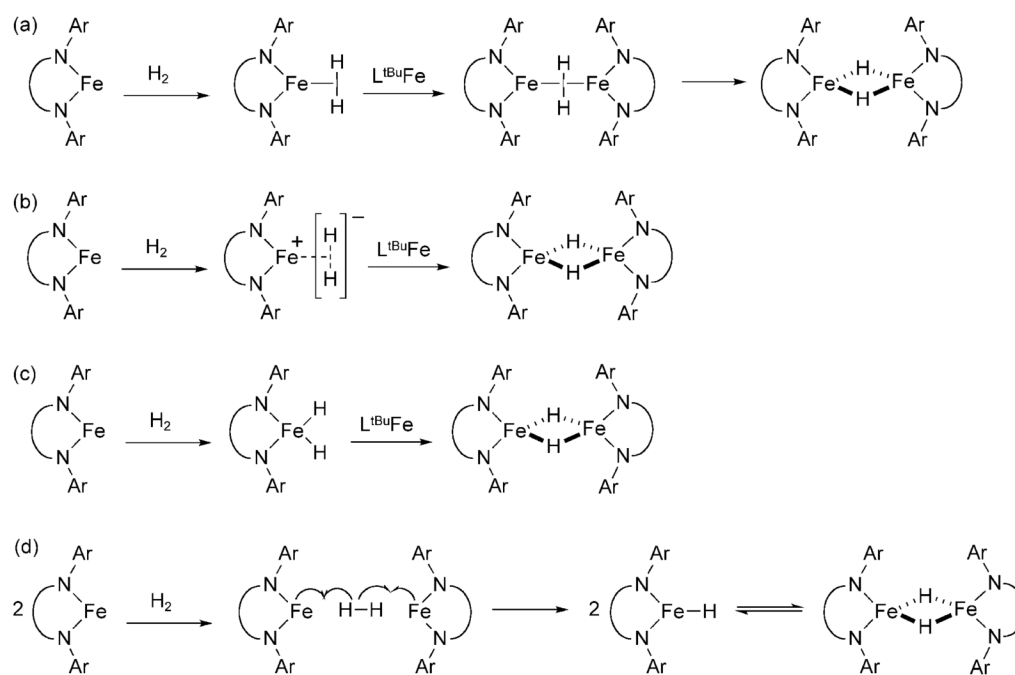
Scheme 1.

(a)

(b)
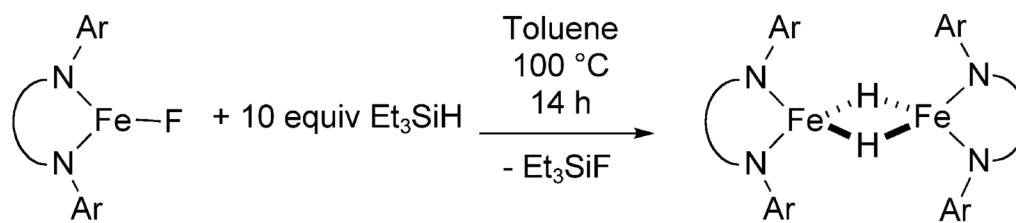
Scheme 2.

Scheme 3.

Scheme 4.

Scheme 5.

Scheme 6.
Possible mechanisms for addition of H_2 to the putative "$L^{tBu}Fe$" fragment. The diketiminate ligand is simplified in these pictures for clarity.