

N=N Bond Cleavage by a Low-Coordinate Iron(II) Hydride Complex

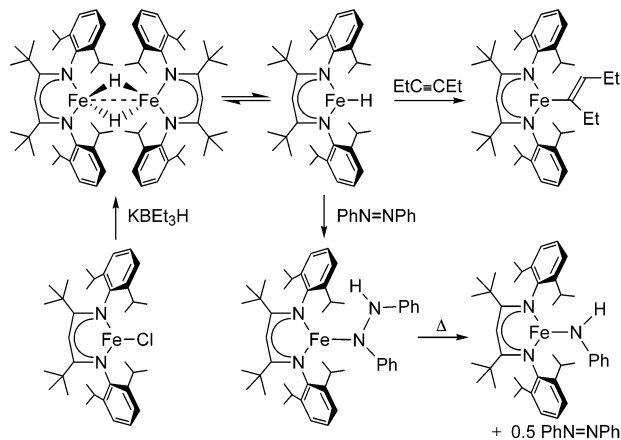
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There is interest in low-coordinate transition-metal complexes¹ because of their characteristically high reactivity, which includes C–H activation, C≡O cleavage, and N≡N cleavage.² The ubiquity of transition-metal hydrides in bond transformations, as well as their broad reactivity patterns,³ suggests that the chemistry of low-coordinate transition-metal hydride complexes would be particularly interesting. Furthermore, biological interest in low-coordinate hydride complexes stems from the proposal that metal hydride species are reactive intermediates in the catalytic cycle of the enzyme nitrogenase.⁴ Here, we report a low-coordinate iron(II) hydride complex and its ability to reduce and cleave multiple bonds.

Scheme 1



Reaction of the three-coordinate complex LFeCl,⁵ where L is the bulky β -diketiminato ligand⁶ in Scheme 1, with KBET_3H led to isolation of dark red crystals in 78% yield. The X-ray crystal structure of the product revealed a dimer in the solid state, with iron atoms bridged by two hydride ligands (Figure 1). The hydrides were located in the Fourier difference map. Steric hindrance within the dimer causes the β -diketiminato rings to twist into a distorted boat conformation, in which the N–Fe–N plane is at an angle of $34.8(8)^\circ$ to the C–C–C plane of the β -diketiminato ligand backbone.

Spectroscopic studies provide evidence for a monomer in equilibrium with the crystallographically characterized dimer. The ^1H NMR spectra of toluene- d_8 solutions of the hydride complex show reversible temperature-dependent behavior. Increasing the temperature leads to an increase in the intensity of a set of signals that have similar paramagnetic shifts as the analogous signals in solutions of three-coordinate iron β -diketiminato complexes LFeX (X = Cl, hydrocarbyl, NHR).^{5,7} Because the chemical shifts in paramagnetic complexes are very sensitive to the electronic and geometric structure at iron, the spectral similarity strongly suggests that the high-temperature spectrum corresponds to a planar three-coordinate hydride complex LFeH.⁸ As these peaks intensify, the

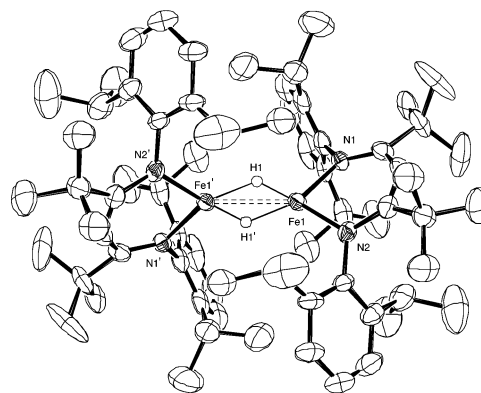


Figure 1. Crystal structure of $[\text{LFeH}]_2$. Thermal ellipsoids shown at 50% probability. In all figures, carbon-bound hydrogen atoms are omitted for clarity. All iron-bound hydrogens were refined with isotropic thermal parameters. Fe1–Fe1' 2.624(2) Å, Fe1–N1 1.990(5) Å, Fe1–N2 2.022(6) Å, N1–Fe1–N2 95.3(2) $^\circ$.

intensity of a complicated series of peaks decreases; these signals are assigned to the dimer $[\text{LFeH}]_2$.⁹

At higher temperature or lower concentration, the color of the solution changes from dark red to orange. The orange color is associated with a visible band at 512 nm, as found in orange three-coordinate β -diketiminato iron alkyl complexes.^{7a} The magnetic moment of toluene solutions increases with temperature and parallels the increase in proportion of the monomer LFeH. The solution magnetic moment at high temperature ($\mu_{\text{eff}} \approx 4.8 \mu_{\text{B}}$) is consistent with monomeric high-spin Fe(II), and the lower magnetic moment at low temperature presumably results from antiferromagnetic coupling in the dimer.¹⁰ In support of the monomer formulation, the molecular weight of a solution at 80 $^\circ\text{C}$ (determined from freezing-point depression of a 1.0% w/w solution of $[\text{LFeH}]_2$ in naphthalene) is 480(80) g/mol (calcd for LFeH = 558 g/mol).

The hydride monomer is trapped with 4-*tert*-butylpyridine to give LFe(H)(4-*t*-Bupy) (Figure 2), a rare example of a four-coordinate transition-metal hydride.¹¹ The hydride ligand was refined to an Fe–H distance of 1.74(2) Å. No agostic interactions are evident (all $\text{Fe}\cdots\text{H}\cdots\text{C}$ contacts are >3.0 Å), and the iron has a trigonal pyramidal geometry with an axial pyridine.

The reactivity of the hydride complex with unsaturated hydrocarbons is typical of metal hydrides and consistent with the presence of a three-coordinate monomer. Reaction of $[\text{LFeH}]_2$ with 3-hexyne in Et_2O at room temperature gives the three-coordinate vinyl complex LFeC(Et)=C(H)Et, characterized by ^1H NMR spectroscopy and X-ray crystallography. The ethyl groups are *cis*, showing that Fe and H add to the same face of the alkyne. The rate of reaction is first-order in $[\text{LFeH}]_2$ and zero-order in [hexyne], with activation parameters $\Delta H^\ddagger = 99(7)$ kJ mol $^{-1}$ and $\Delta S^\ddagger = 32(10)$ J K $^{-1}$ mol $^{-1}$ (277–299 K). The rate of reaction with 2-butyne is similar.¹² These data suggest a mechanism in which rate-determining dimer cleavage is followed by alkyne insertion into the iron-hydride bond of monomeric LFeH.

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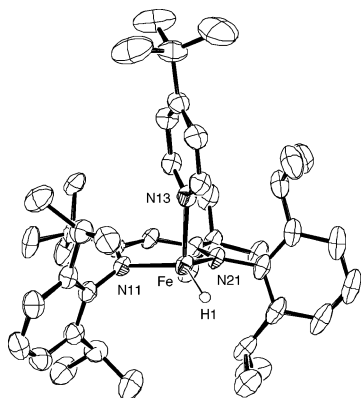


Figure 2. Crystal structure of LFe(H)(4'-Bupy). Thermal ellipsoids shown at 50% probability. Fe–H1 1.74(2) Å, Fe–N11 2.022(1) Å, Fe–N21 2.031(2) Å, Fe–N13 2.124(2) Å, N11–Fe–N21 97.36(6)°, N11–Fe–N13 100.00(6)°, N21–Fe–N13 99.53(6)°, N13–Fe–H1 103.5(6)°.

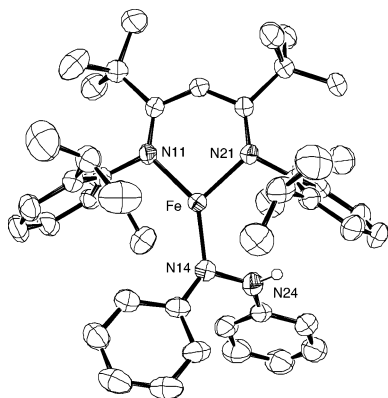


Figure 3. Crystal structure of LFeN(Ph)NHPH. Thermal ellipsoids shown at 50% probability; major disorder component shown. Fe–N11 1.980(2) Å, Fe–N21 2.000(2) Å, Fe–N14 1.932(2) Å, N14–N24 1.423(2) Å, N11–Fe–N21 94.60(7)°, Fe–N14–N24 111.9(1)°.

More interesting is the reaction of $[\text{LFeH}]_2$ with azobenzene, which rapidly inserts into the iron-hydride bond to give the red hydrazido complex LFeN(Ph)NHPH. This complex has trigonal-planar geometry in the solid state (Figure 3). Its solution ^1H NMR spectrum suggests that rotation about the Fe–N(hydrazido) bond is hindered because heating causes the four resonances for the β -diketiminato isopropyl methyl groups to coalesce to two signals. At high temperature, the ^1H NMR spectrum is analogous to those of other three-coordinate β -diketiminato iron complexes.^{5,7}

Extended heating of LFeN(Ph)NHPH (80 °C, 3 h) results in N–N bond rupture, as evidenced by clean formation of the anilidoiron(II) complex LFeNHPH (Scheme 1).¹³ The overall sequence of reactions therefore results in cleavage of the N=N bond of azobenzene by $[\text{LFeH}]_2$. This is a unique transformation for a mononuclear, late transition-metal complex. Most mononuclear examples of N=N bond cleavage are by low-valent early transition-metal complexes, driven by oxidation of the metal.¹⁴ In contrast, the iron atom in each complex in Scheme 1 remains in the +2 oxidation state, and the reducing equivalents come from the hydride ligands.

Preliminary kinetics studies of the decomposition of LFeN(Ph)NHPH show it to be first-order in $[\text{LFeN(Ph)NHPH}]$, with $k_{\text{obs}} = 4.2(3) \times 10^{-4} \text{ s}^{-1}$ at 358 K. While the mechanism of the transformation is still under investigation, the intermediacy of LFeH is unlikely because adding excess 3-hexyne as a trap does not affect the course of the reaction.

In summary, we have prepared three- and four-coordinate iron hydride complexes, whose low coordination number leads to unusual bond cleavage reactivity. Notably, the N=N bond of

azobenzene is cleaved, suggesting that low-coordinate iron hydrides are capable of performing difficult reactions reminiscent of those in the catalytic cycle of nitrogenase.

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Supporting Information Available: Syntheses, characterization, equilibrium, and kinetics data (PDF) and crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) The complexity of the spectra prevents us from ruling out the presence of minor species in the mixture. Assuming a two-component equilibrium tentatively gives $\Delta H^\circ = 72(2) \text{ kJ mol}^{-1}$ and $\Delta S^\circ = 247(4) \text{ J (K}^{-1} \text{ mol}^{-1})$.
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- (12) k_{obs} (288 K, toluene- d_8): 3-hexyne 3.1(3) $\times 10^{-4} \text{ s}^{-1}$; 2-butyne 5.4(1) $\times 10^{-4} \text{ s}^{-1}$.
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