

Three-Coordinate and Four-Coordinate Cobalt Hydride Complexes That React with Dinitrogen

Keying Ding, William W. Brennessel, and Patrick L. Holland*

Department of Chemistry, University of Rochester, Rochester, New York 14618

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Complexes of a transition metal (defined here as a metal with a partially filled d shell) having only three bonds to the metal are interesting because the orbital energies, spin states, and reaction pathways can be different than those in traditional complexes.¹ Isolating three-coordinate complexes invariably depends on the use of extremely bulky supporting ligands, which protect the metal center through steric effects. However, this strategy might seem to be incompatible with three-coordinate hydride complexes, because H[−] is the smallest possible ligand. Accordingly, no three-coordinate hydride complexes are known.² New kinds of hydride complexes are desired because of the many roles for hydrides in organometallic chemistry and catalysis.³

Using iron complexes, we recently utilized the very bulky bidentate β -diketiminate ligand L [L = 2,2,6,6-tetramethyl-3,5-bis(2,4-diisopropylphenylimido)hept-4-yl] to enable the isolation of three-coordinate complexes in which one of the three ligands is small (e.g., halide, CH₃).⁴ Here we report the use of L to stabilize the first crystallographically characterized three-coordinate hydride complex of any transition metal. We also report that this cobalt hydride complex and another related complex react with N₂ at room temperature and atmospheric pressure through the bimetallic reductive elimination of H₂.

Figure 1 shows the syntheses and structures of dimeric cobalt(II) hydride (**1**) and cobalt(I) hydride (**2**) complexes, which are formed by addition of different amounts of KHBET₃ to toluene solutions of the three-coordinate cobalt(II) complex LCoCl under Ar.⁵ Addition of 1 equiv of KHBET₃ to LCoCl gives [LCo(μ -H)]₂ (**1**) in 72% yield. Although we were not able to completely free **1** from impurities (see the Supporting Information), several forms of characterization were possible. The X-ray crystal structure of **1** reveals that it has two hydride ligands (located in the difference Fourier map) that bridge diketiminate-bound cobalt centers. The metal coordination and geometry closely resemble those for the iron(II) complex [LFe(μ -H)]₂⁶ and a dimeric β -diketiminate nickel(II) hydride complex recently reported by Limberg.⁷ The cobalt atoms in **1** are separated by 2.476(5) Å, which is intermediate between the metal–metal distances in the iron [2.624(2) Å] and nickel [2.3939(6) Å] analogues. The presence of the hydride ligands in **1** was confirmed through the reaction of a toluene solution of **1** with 2 equiv of cyclohexene to give the cobalt(II) cyclohexyl product LCo(C₆H₁₁), which results from 1,2-addition of the cobalt hydride to the C=C double bond.

Reaction of LCoCl with 2 equiv of KHBET₃ under Ar gave compound **2**, with presumed loss of H₂, in 70% yield. Compound **2** is very unusual. Its X-ray crystal structure reveals two nearly parallel three-coordinate cobalt units related by a pseudoinversion center (Figure 2). The high quality of the crystallographic data enabled refinement of the positions of the hydrogen atoms, giving Co–H distances of 1.81(3) Å. The cobalt geometry is trigonal-planar, and each H atom lies near the pseudo-C₂-axis of the β -diketiminate ligand on the same cobalt atom (N–Co–H angles

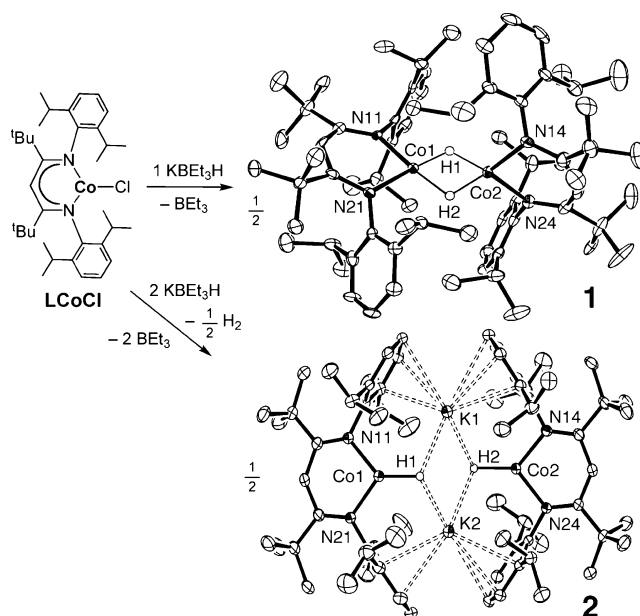


Figure 1. Syntheses and structures (using 50% thermal ellipsoids) of unsaturated cobalt hydride complexes. Carbon-bound hydrogen atoms have been omitted for clarity. The cobalt-bound hydrogen atoms were refined independently for position, with dependent isotropic thermal parameters. Selected bond lengths and bond angles follow; because compound **1** has three crystallographically independent dimers, ranges are listed here (for details, see the Supporting Information). For **1**: Co–Co, 2.472–2.481 Å; Co–N, 1.962–1.993 Å; N–Co–N, 95.4–96.5°. For **2**: Co1–Co2, 5.7386(7) Å; Co1–H1, 1.84(2) Å; Co1–N11, 1.9162(13) Å; Co1–N21, 1.9164(12) Å; N11–Co1–N21, 96.73(6)°; N11–Co1–H1, 128.2(7)°; N21–Co1–H1, 134.1(7)°; Co2–H2, 1.78(2) Å; Co2–N14, 1.9106(13) Å; Co2–N24, 1.9121(13) Å; N14–Co2–N24, 96.59(6)°; N14–Co2–H2, 133.5(7)°; N24–Co2–H2, 129.4(7)°.

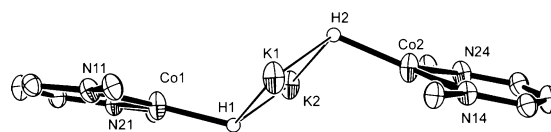


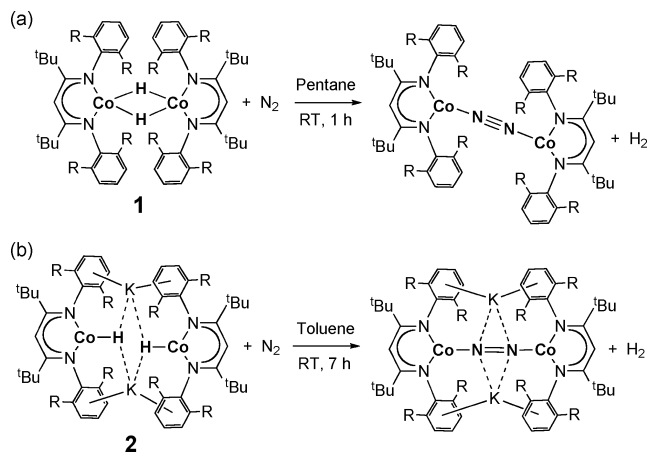
Figure 2. Side view of the core of **2**, showing the relative orientation of the two CoN₂H planes.

ranging from 128 to 134°). The two H atoms are separated by 3.02(3) Å and the two cobalt atoms by 5.7386(7) Å, showing that there is no direct connection between the cobalt-bound atoms. Instead, the halves of the molecule are held together by K⁺ ions that form cation– π interactions with the aryl rings of the β -diketiminate ligands. The potassium ions are also close to the hydride ligands [K–H distances of 2.60(2) and 2.67(2) Å].

The three-coordinate cobalt ions in complex **2** are high-spin cobalt(I), as shown by the paramagnetically shifted ¹H NMR spectrum and the solution magnetic moment, $\mu_{\text{eff}} = 5.6(2) \mu_{\text{B}}$ per

dimeric molecule of **2**. Complex **2** is soluble and gives similar ^1H NMR spectra in cyclohexane, benzene, and THF, suggesting that the alkali metal ions remain bound in solution. The freezing-point depression of a solution of **2** in naphthalene indicated a molecular weight of 1140 ± 200 (3σ), supporting the dimeric formulation in solution. Seven β -diketiminate resonances are observed in its ^1H NMR spectrum in C_6D_6 from 200–353 K (the hydrides are not observed because of fast relaxation), showing that the β -diketiminate ligands of **2** have averaged C_{2v} symmetry in solution. Therefore, there is a low-energy mechanism that enables the molecule to reach an arrangement in which the CoN_2H units are transiently coplanar without dissociation of the molecule into halves.

Scheme 1. Reactions of the Low-Coordinate Cobalt Hydride Complexes with Dinitrogen ($\text{R} = \text{Isopropyl}$)



Solutions of **1** and **2** in aromatic and hydrocarbon solvents show no signs of decomposition by ^1H NMR when heated to $100\text{ }^\circ\text{C}$ for several days *under an Ar atmosphere*. On the other hand, exposure of room-temperature solutions of each compound to an atmosphere of purified N_2 in pentane, diethyl ether, or toluene leads to the growth of resonances in the ^1H NMR spectrum that are characteristic of the analogous bimetallic dinitrogen complexes (Scheme 1). These cobalt dinitrogen complexes have been characterized separately.^{5b} The reaction of **1** with N_2 was complete in less than 1 h, giving an 88% spectroscopic yield of LCoNNCoL . H_2 , the other product of the reaction, was detected by gas chromatography in 80% yield. The reaction of **2** with N_2 over several hours gave $\text{K}_2[\text{LCoNNCoL}]$ in 90% spectroscopic and isolated yield. In the latter reaction, H_2 was detected in 83% yield. The reactions in Scheme 1 occur at roughly the same rate in the dark as in ambient light.⁸

The reactions to produce H_2 are formal reductive eliminations: the dicobalt(II) complex **1** leads to the dicobalt(I) dinitrogen complex LCoNNCoL , and the dicobalt(I) complex **2** gives the formally dicobalt(0) dinitrogen complex $\text{K}_2[\text{LCoNNCoL}]$. In the latter complex, the $\text{N}-\text{N}$ distance is $1.22\text{ \AA}$, indicating that the dinitrogen ligand is best described as $[\text{N}=\text{N}]^{2-}$. Thus, in this picture, the electrons from the reductive elimination of H_2 end up in the π^* orbital of the bound N_2 . This is interesting in the context of N_2 binding and activation.⁹ Although H_2 reductive elimination from metastable hydride complexes has been used previously as a route to dinitrogen complexes,^{10–13} there is only one literature example of N_2 binding directly from a crystallographically verified hydride complex.^{10c} This H_2-N_2 exchange is of interest in the context of catalytic N_2 reduction because the formation of N_2 complexes in this way avoids the use of harsh reducing agents.¹⁴

We explored the mechanism of H_2 reductive elimination by treating a mixture of the isotopologues $\text{K}_2[\text{LCo}(\mu\text{-H})_2]$ (**2**) and

$\text{K}_2[\text{LCo}(\mu\text{-D})_2]$ (**2-D**) with N_2 for 2 days. H_2 and D_2 were present in the headspace, and no HD was detected. This result indicates that (a) **2** does not dissociate in solution at room temperature and (b) the elimination of H_2 from **2** is an intramolecular process. The analogous reaction of **1** and **1-D** with N_2 gave a significant amount of HD, probably through the pre-equilibration of the isotopologues of **1** through monomer–dimer equilibrium.

In conclusion, we have crystallographically characterized the first three-coordinate transition-metal hydride complex, $\text{K}_2[\text{LCo}(\mu\text{-H})_2]$ (**2**). The hydride ligands in this species are labile and are eliminated as H_2 upon the addition of N_2 . It is surprising that **2** readily reacts with N_2 but does not react at room temperature with THF or arenes, suggesting that the approach of additional donors to cobalt is sterically restricted by the potassium-bound β -diketiminate ligands.

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Supporting Information Available: Synthetic, spectroscopic, kinetic, and crystallographic (CIF) data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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