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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, NY 14618

Abstract

We report the formation and N₂ reactivity of novel cobalt hydride complexes supported by bulky β-diketiminato ligands (L). Addition of KBHET₃ to LCoCl gives [LCo(μ-H)]₂ (**1**) or K₂[LCoH]₂ (**2**), depending on the amount of borohydride used. Compound **2** is the first example of a crystallographically characterized hydride complex in which a transition metal is three-coordinate. Both **1** and **2** react with N₂ at room temperature to give dinuclear N₂ complexes with loss of H₂.

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 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 introduced the use of the very bulky *bidentate* β-diketiminato ligand L (L = 2,2,6,6-tetramethyl-3,5-bis(2,4-diisopropylphenylimido)hept-4-yl) for enabling the isolation of three-coordinate complexes in which one of the three ligands is small (*e.g.* halide, CH₃).⁴ Here, we report that L can be used 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 come from adding different amounts of KBHET₃ to toluene solutions of the three-coordinate cobalt(II) complex LCoCl under Ar.⁵ Addition of 1 equiv of KBHET₃ to LCoCl gives [LCo(μ-H)]₂ (**1**) in 72% yield. Although we were not able to completely free **1** from impurities (see Supporting Information), several forms of characterization have been possible. The X-ray crystal structure of **1** reveals that it has two hydride ligands (located in the difference Fourier map) that bridge diketiminato-bound cobalt centers. The metal coordination and geometry closely resemble those for the iron(II) complex [LFe(μ-H)]₂⁶ and a dimeric β-diketiminato 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

holland@chem.rochester.edu.

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

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 $\text{LCo}(\text{C}_6\text{H}_{11})$, which results from [1,2]-addition of the cobalt hydride to the C-C double bond.

Reaction of LCoCl with 2 equiv of KHBET_3 under Ar gave compound **2**, with presumed loss of H_2 , in 70% yield. Compound **2** is very unusual. Its X-ray crystal structure reveals two nearly parallel three-coordinate cobalt units related by a pseudo-inversion center. 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-mirror plane of the β -diketiminato ligand on the same cobalt atom (N-Co-H angles 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 -diketiminato ligands. The potassium ions are also close to the hydride ligands (K-H 2.60(2) Å 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 of $\mu_{\text{eff}} = 5.6$ (2) μ_{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 metals 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 -diketiminato resonances are observed in its ^1H NMR spectrum in C_6D_6 from 200-353 K (the hydrides are not observed due to fast relaxation), showing that the β -diketiminato 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.

Solutions of **1** and **2** in aromatic and hydrocarbon solvents show no signs of decomposition by ^1H NMR when heated to 100 °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 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 gave $\text{K}_2[\text{LCoNNCoL}]$ over several hours, 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 N-N distance is 1.22 Å, indicating that the dinitrogen ligand is best described as $[\text{N}=\text{N}]^{2-}$.^{5b} Thus, using this picture, the electrons from the reductive elimination of H_2 end up in the π^* orbital of 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,^{10,11,12,13} 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 H₂ reductive elimination by treating a mixture of the isotopologues K₂[LCo(μ-H)]₂ (**2**) and K₂[LCo(μ-D)]₂ (**2-D**) with N₂ for 2 days. H₂ and D₂ 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 H₂ from **2** is an intramolecular process. The analogous reaction of **1** and **1-D** with N₂ gave a significant amount of HD, probably through the pre-equilibration of isotopologues of **1** through monomer-dimer equilibrium.

In conclusion, we have crystallographically characterized the first three-coordinate transition-metal hydride complex, K₂[LCo(μ-H)]₂ (**2**). The hydride ligands in this species are labile, eliminating as H₂ upon the addition of N₂. It is surprising that **2** readily reacts with N₂ 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 diketiminate ligands.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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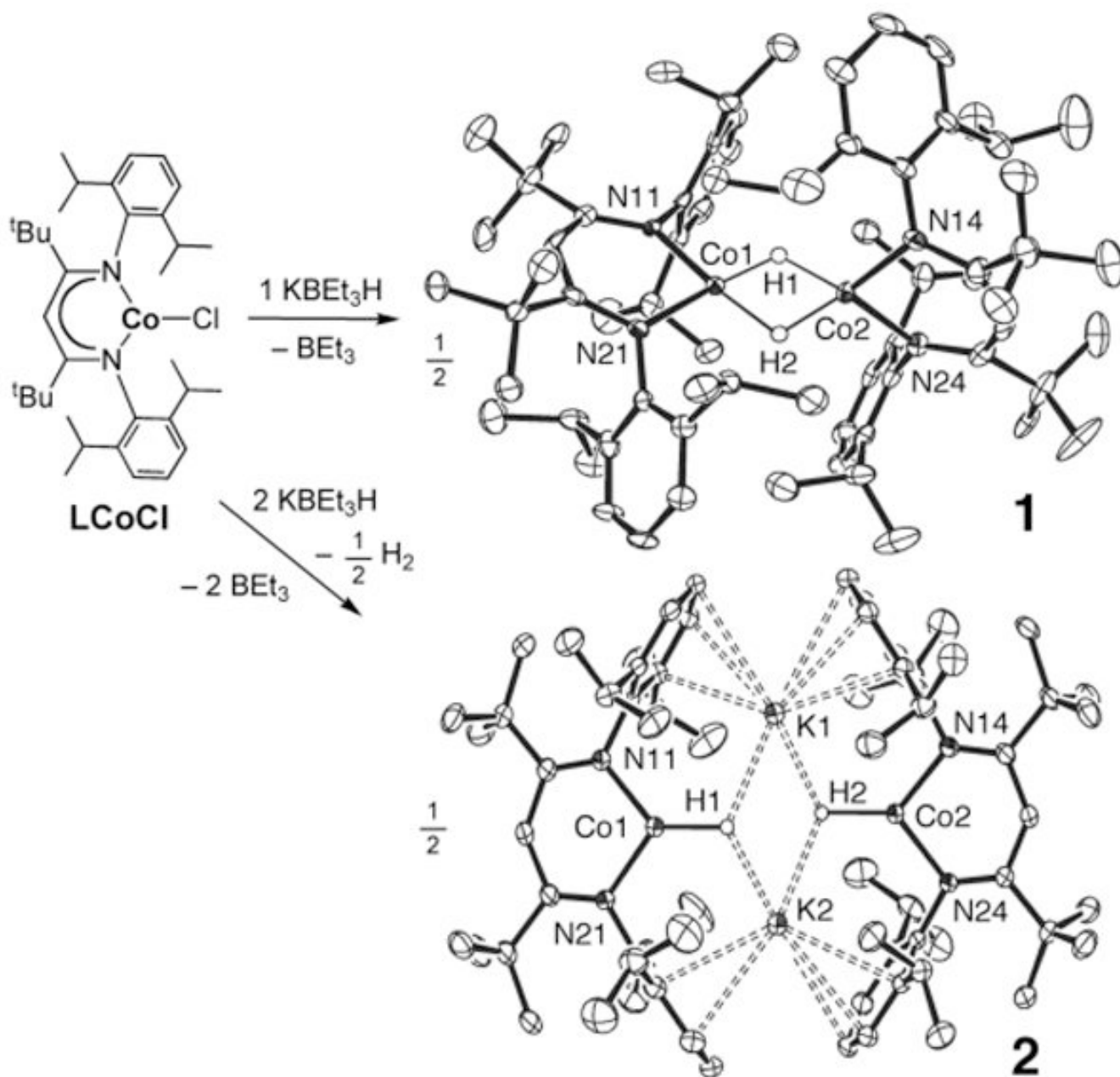


Figure 1.

Formation and structures of unsaturated cobalt hydride complexes, using 50% thermal ellipsoids. Carbon-bound hydrogen atoms are omitted for clarity. All cobalt-bound hydrogens were refined with isotropic thermal parameters. Selected bond lengths and bond angles follow; because compound **1** has three crystallographically independent dimers, ranges are listed here (details are in the Supporting Information). **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)°.

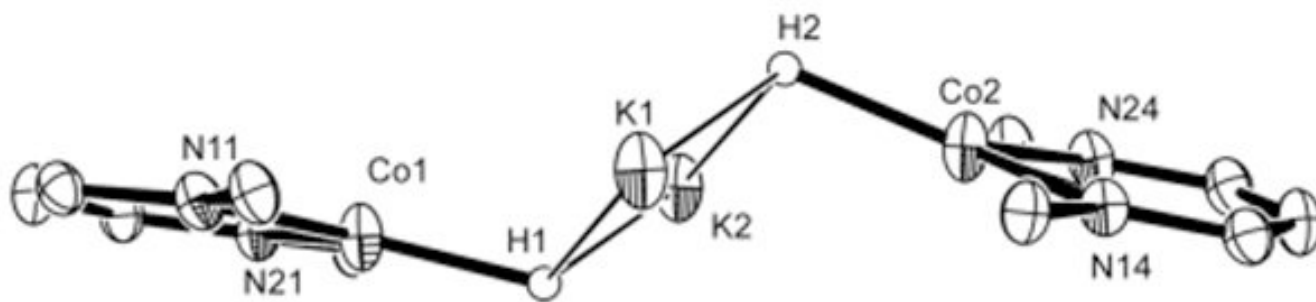
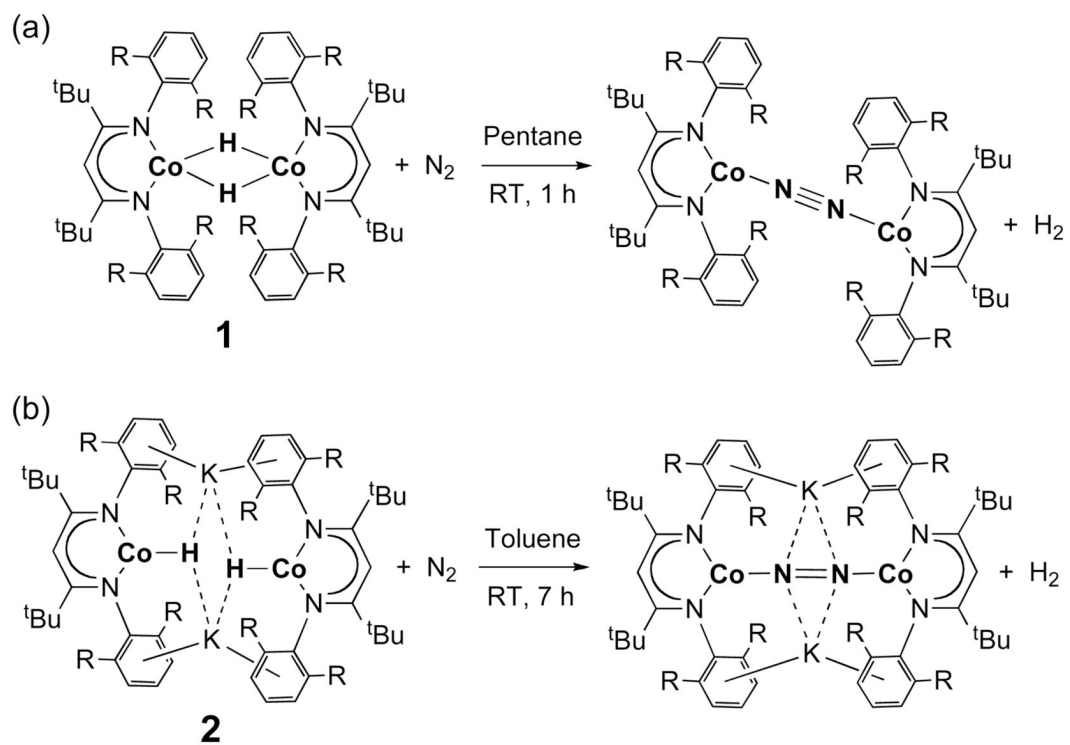


Figure 2.
Side view of the core of **2**, showing the relative orientation of the two CoN₂H planes.

**Scheme 1.**

Reactions of the Low-Coordinate Cobalt Hydride Complexes with Dinitrogen (R = isopropyl)