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

Received April 8, 2009; E-mail: holland@chem.rochester.edu

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, CH_3).[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 N_2 at room temperature and atmospheric pressure through the bimetallic reductive elimination of H_2.

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 $KHBEt_3$ to toluene solutions of the three-coordinate cobalt(II) complex LCoCl under Ar.[5] Addition of 1 equiv of $KHBEt_3$ to LCoCl gives $[LCo(\mu\text{-}H)]_2$ (**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 $[LFe(\mu\text{-}H)]_2$[6] 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 $LCo(C_6H_{11})$, 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 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-C_2-axis of the β-diketiminate ligand on the same cobalt atom (N−Co−H angles
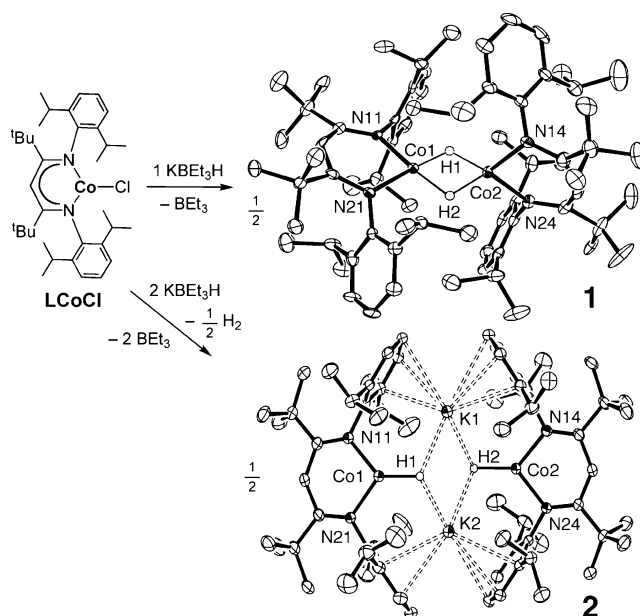

Figure 1. Syntheses and structures (using 50% thermal ellipsoids) of unsaturated cobalt hydride complexes. Carbon-bound hydrogen atoms have been omitted for clarity. The cobalt-bound hydrogen atoms were refined independently for position, with dependent isotropic thermal parameters. Selected bond lengths 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)°.
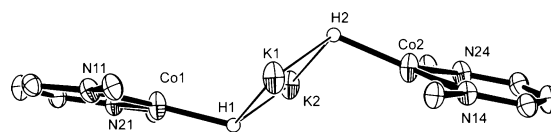

Figure 2. Side view of the core of **2**, showing the relative orientation of the two CoN_2H planes.

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, $\mu_{eff} = 5.6(2)$ μ_B per

dimeric molecule of **2**. Complex **2** is soluble and gives similar ^{1}H 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 ^{1}H NMR spectrum in C$_6$D$_6$ 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$_2$H units are transiently coplanar without dissociation of the molecule into halves.

Scheme 1. Reactions of the Low-Coordinate Cobalt Hydride Complexes with Dinitrogen (R = Isopropyl)
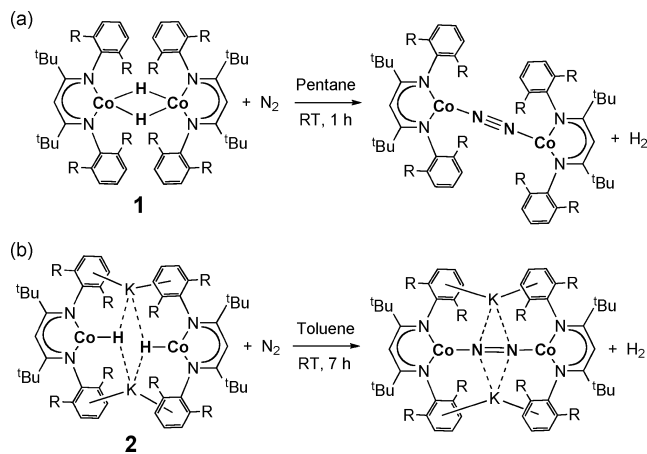
Solutions of **1** and **2** in aromatic and hydrocarbon solvents show no signs of decomposition by ^{1}H NMR when heated to 100 °C for several days *under an Ar atmosphere*. On the other hand, exposure of room-temperature solutions of each compound to an atmosphere of purified N$_2$ in pentane, diethyl ether, or toluene leads to the growth of resonances in the ^{1}H 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 K$_2$[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 K$_2$[LCoNNCoL]. In the latter complex, the N−N distance is 1.22 Å, indicating that the dinitrogen ligand is best described as [N=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 K$_2$[LCo(μ-H)]$_2$ (**2**) and

K$_2$[LCo(μ-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, K$_2$[LCo(μ-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.

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.

References

(1) (a) Cummins, C. C. *Prog. Inorg. Chem.* **1998**, *47*, 685. (b) Alvarez, S. *Coord. Chem. Rev.* **1999**, *193−195*, 13.
(2) Putative three-coordinate complexes [Pt(P^{t}Bu$_3$)$_2$H]$^+$ were not crystallized and probably have a weak fourth ligand. See: (a) Goel, R.; Srivastava, R. C. *J. Organomet. Chem.* **1981**, *204*, C13. (b) Goel, R.; Srivastava, R. C. *Can. J. Chem.* **1983**, *61*, 1352. (c) Butts, M. D.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 11831.
(3) *Recent Advances in Hydride Chemistry*; Peruzzini, M., Poli, R., Eds.; Elsevier Science Ltd.: Amsterdam, 2001.
(4) Holland, P. L. *Acc. Chem. Res.* **2008**, *41*, 905.
(5) (a) Holland, P. L.; Cundari, T. R.; Perez, L. L.; Eckert, N. A.; Lachicotte, R. J. *J. Am. Chem. Soc.* **2002**, *124*, 14416. (b) Ding, K.; Pierpont, A. W.; Brennessel, W. W.; Lukat-Rodgers, G.; Rodgers, K. R.; Cundari, T. R.; Bill, E.; Holland, P. L. *J. Am. Chem. Soc.* **2009**, *131*, 9471.
(6) (a) Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *J. Am. Chem. Soc.* **2003**, *125*, 15752. (b) Yu, Y.; Sadique, A. R.; Smith, J. M.; Dugan, T. R.; Cowley, R. E.; Brennessel, W. W.; Flaschenriem, C. J.; Bill, E.; Cundari, T. R.; Holland, P. L. *J. Am. Chem. Soc.* **2008**, *130*, 6624.
(7) Pfirrmann, S.; Limberg, C.; Ziemer, B. *Dalton Trans.* **2008**, 6689.
(8) The analogous iron hydride complex loses H$_2$ only upon photolysis or the addition of stronger ligands (see ref 6b).
(9) (a) MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385. (b) Gambarotta, S.; Scott, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5298.
(10) (a) Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 11024. (b) Fryzuk, M. D.; Johnson, S. A.; Patrick, B. O.; Albinati, A.; Mason, S. A.; Koetzle, T. F. *J. Am. Chem. Soc.* **2001**, *123*, 3960. (c) Akagi, F.; Matsuo, T.; Kawaguchi, H. *Angew. Chem., Int. Ed.* **2007**, *46*, 8778.
(11) (a) Aresta, M.; Giannoccaro, P.; Rossi, M.; Sacco, A. *Inorg. Chim. Acta* **1971**, *5*, 203. (b) Brintzinger, H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1971**, *93*, 2045. (c) Brintzinger, H.; Marvich, R. H. *J. Am. Chem. Soc.* **1971**, *93*, 2046. (d) de Wolf, J. M.; Blaauw, R.; Meetsma, A.; Teuben, J. H.; Gyepes, R.; Varga, V.; Mach, K.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 4977. (e) Chirik, P. J.; Henling, L. M.; Bercaw, J. E. *Organometallics* **2001**, *20*, 534. (f) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 2241. (g) Hanna, T. E.; Bernskoetter, W. H.; Bouwkamp, M. W.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2007**, *26*, 2431. (h) Avenier, P.; Taoufik, M.; Lesage, A.; Solans-Monfort, X.; Baudouin, A.; de Mallmann, A.; Veyre, L.; Basset, J. M.; Eisenstein, O.; Emsley, L.; Quadrelli, E. A. *Science* **2007**, *317*, 1056. (i) Scott, J.; Vidyaratne, I.; Korobkov, I.; Gambarotta, S.; Budzelaar, P. H. M. *Inorg. Chem.* **2008**, *47*, 896. (j) Pfirrmann, S.; Limberg, C.; Herwig, C.; Stösser, R.; Ziemer, B. *Angew. Chem., Int. Ed.* **2009**, *48*, 3357.
(12) Schrock's catalytic N$_2$ reduction can be initiated by a molybdenum hydride species, indicating that this hydride can somehow form an N$_2$ complex. See: Yandulov, D. V.; Schrock, R. R. *Inorg. Chem.* **2005**, *44*, 1103.
(13) A number of metal−dihydrogen complexes react with N$_2$ to generate N$_2$ complexes. Selected examples: (a) Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1985**, *4*, 1727. (b) Hills, A.; Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J. *J. Organomet. Chem.* **1990**, *391*, C41. (c) Hills, A.; Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; Rowley, A. T. *J. Chem. Soc., Dalton Trans.* **1993**, 3041. (d) Gilbertson, J. D.; Szymczak, N. K.; Tyler, D. R. *J. Am. Chem. Soc.* **2005**, *127*, 10184.
(14) See: Fryzuk, M. D. *Acc. Chem. Res.* **2009**, *42*, 127. The necessity of strong reducing agents has prevented catalysis in some systems that perform stoichiometric N$_2$ reduction cycles. See: Curley, J. J.; Sceats, E. L.; Cummins, C. C. *J. Am. Chem. Soc.* **2006**, *128*, 14036.