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A Mercurial Route to a Cobalt Dihydrogen Complex**

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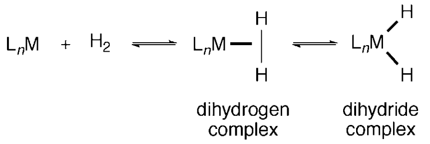
cobalt · dihydrogen · hydride ligands · mercury ·
NMR spectroscopy

The report[1] by Kubas and co-workers in 1984 of a metal complex with dihydrogen as a ligand heralded the advent of a new era in organometallic and inorganic chemistry. Hydrogenations are a cornerstone of homogeneous catalysis,[2] so reactions of metal complexes with H_2 had been studied for decades, but the idea that H_2 could bind to the metal as a ligand, without complete cleavage of the H–H bond to make a dihydride, was a surprising concept.

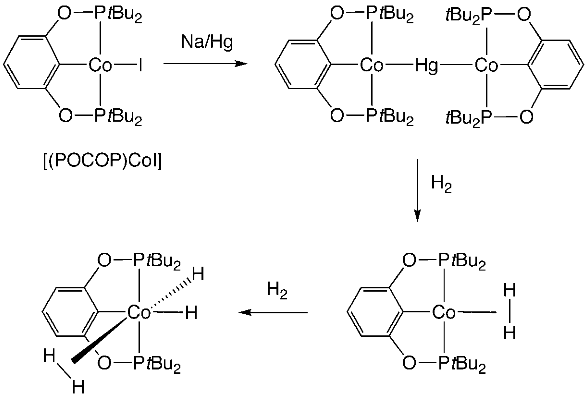
Traditional ligands use lone pairs of electrons in their bonding, but in dihydrogen complexes, the bonding to the metal comes from donation of electron density from the nonpolar H–H σ bond to d orbitals on the metal. Back-bonding from filled metal d orbitals to the σ* orbital on H_2 also contributes to the bonding; in cases where this back-bonding is large, cleavage of the H–H bond can occur, thus leading to a dihydride with two M–H bonds, and no remaining H–H bond (Scheme 1). The discovery that H_2 could be bound to a metal led to detailed studies by many groups that revealed structural, spectroscopic, and reactivity characteristics of dihydrogen complexes.[3] Hundreds of complexes with H_2 ligands have been reported, and as a result of these studies, the formation of a complex with an H_2 ligand is no longer a surprise.



Scheme 1. Formation of a dihydrogen complex and its equilibrium with a dihydride.

Despite the evolution of H_2 from a novel ligand to a more commonly encountered ligand in the last 25 years, the distribution of dihydrogen complexes across the periodic table has not been egalitarian. Second- and third-row metals such as tungsten, rhenium, ruthenium, and osmium have dominated the population of dihydrogen complexes. A substantial number of cationic $Fe(H_2)$ complexes has been prepared.[4] Other first-row metals, in contrast, have had significantly fewer dihydrogen complexes reported. $[Cr(CO)_5(H_2)]$[5] is only stable under high pressure of H_2 or at low temperatures. Kubas and co-workers prepared $[Cr(CO)_3(P\mathit{i}Pr_3)_2(H_2)]$, which readily dissociates H_2 in solution.[6] Manganese dihydrogen complexes [Mn(diphosphine)(CO)(H_2)] are known but lose H_2 readily.[7] Some nickel complexes react readily with dihydrogen, in the electrocatalytic oxidation of H_2,[8] for example, but only recently have Caulton and co-workers reported a dihydrogen complex of nickel.[9] It is not surprising that H_2 ligands of first-row metals remain rare compared to second- and third-row congeners. The bond dissociation energies of first-row transition-metal hydrides (M–H bonds) tend to be significantly lower than those for second- and third-row metals, and this trend is similarly apparent in the relative scarcity of $M(H_2)$ complexes from the first-row metals.

Heinekey et al. discovered a fascinating route for preparation of a cobalt dihydrogen complex (Scheme 2).[10] Dihydrogen ligands on cobalt are very rare, though a few examples are known. Brookhart and co-workers reported the cationic complex $[Cp^*Co(PMe_3)(H)(\eta^2\text{-}H_2)]^+$ ($Cp^* = C_5Me_5$), which has a hydride ligand that exchanges with the H_2 ligand.[11] $[Co(CO)_2(NO)(H_2)]$ was characterized by IR spectroscopy at −104 °C in liquid xenon under 10 bar H_2 pressure, but it decomposed when the pressure was released.[12]



Scheme 2. Synthesis of a Co-Hg-Co complex and its reactions with H_2.

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Even the starting complex [(POCOP)CoI] (Scheme 2) has some unusual features. The paramagnetic Co^{II} iodide, with one unpaired electron, is an unusual example of a 15-electron complex. In many cases metal halide complexes that are coordinatively and electronically unsaturated form dimers in which two halides bridge two metal atoms, but such behavior is not observed in the case of [(POCOP)CoI], as the crystal structure shows it to be monomeric. The bulky *tert*-butyl groups on the two P donors may provide steric protection that disfavors formation of a $Co(\mu\text{-}I)_2Co$ structure. Reduction of [(POCOP)CoI] with Na/Hg gave a surprising result (Scheme 2). Similar to [(POCOP)CoI], the paramagnetic product exhibited broad resonances in the ^1H NMR spectrum outside of the normal diamagnetic chemical shift region. Single-crystal X-ray diffraction showed that the product, isolated in 68 % yield, had two {Co(POCOP)} units bonded to mercury! Although mercury was used in the Na/Hg amalgam, it was not intended to be involved in the product formation, yet the Co-Hg-Co product formed by surreptitious involvement of the mercury. Complexes of this type, [L_nCo-Hg-CoL_n], have been reported; for example, the Co-Hg-Co bonding in [$(CO)_4$Co-Hg-Co$(CO)_4$] was confirmed by crystallography.[13]

Addition of H_2 gas to a solution of [Hg{Co(POCOP)}$_2$] at −78 °C led to the appearance of a singlet at $\delta = -11.6$ ppm in the ^1H NMR spectrum. A T_1 value of 30 ms was found at −53 °C; the low value suggests that the complex has an H_2 ligand rather than two terminal Co−H ligands. While low T_1 values are associated with H_2 ligands, a more definitive assignment of H_2 ligands can be obtained by NMR spectroscopy studies of corresponding complexes with an HD ligand. The ^1H NMR spectrum of [(POCOP)Co(HD)] exhibited a 1:1:1 triplet, owing to coupling of the D (spin = 1) to H, thus confirming the assignment as a dihydrogen complex. The magnitude of the coupling constant correlates with the length of the H−H bond,[14] with the J_{HD} value of 28 Hz suggesting a H−H distance of 0.95 Å in the H_2 ligand. The Hg atom serves as a convenient way to protect the highly reactive {Co(POCOP)} fragment. This preparative route to a dihydrogen complex is unusual; many dihydrogen complexes have been prepared by H_2 binding to a vacant coordination site, but the vacant site is normally created by dissociation of a weak solvent or agostic interaction, not by rupture of a metal–metal bond. The dihydrogen complex [(POCOP)Co(H_2)] is a 16-electron complex, whereas most H_2 complexes are electronically saturated 18-electron complexes.

At higher pressures of H_2 (5 bar), a new resonance is detected in the ^1H NMR spectrum at $\delta = -9.3$ ppm that integrates to 4 H. The new complex was stable only at temperatures below −53 °C. Use of HD rather than H_2 led to resonances in the NMR spectra for the isotopologues [Co]H_3D, [Co]H_2D_2, and [Co]HD_3 slightly upfield of the resonances for the [Co]H_4 complex. It is clear that a second H_2 molecule has added to [(POCOP)Co(H_2)], but is the product [(POCOP)Co$(H_2)_2$], with two dihydrogen ligands, [(POCOP)Co$(H)_4$], with four terminal Co−H bonds, or [(POCOP)Co(H_2)$(H)_2$], with one H_2 ligand and two Co−H bonds? The T_1(minimum) value of 25 ms measured at −93 °C is so small that the tetrahydride complex [(POCOP)Co$(H)_4$] is ruled out, since terminal hydrides would lead to a much larger value of T_1. Moreover, a tetrahydride complex would have a formal oxidation state of Co^V, which is uncommon in organometallic complexes. The NMR spectroscopy data do not definitively distinguish between [(POCOP)Co$(H_2)_2$] and [(POCOP)Co(H_2)$(H)_2$], but DFT calculations found the minimum energy for [*cis*-(POCOP)Co(H_2)$(H)_2$] with the two Co−H bonds cis to each other, as shown in Scheme 2. An isomer with the Co−H bonds trans to each other was calculated to be 1.6 kcal mol^{-1} higher energy, and the bis(dihydrogen) complex [(POCOP)Co$(H_2)_2$] was calculated to be 4.8 kcal mol^{-1} higher than [*cis*-(POCOP)Co(H_2)$(H)_2$]. The transition state for loss of H_2 was found at 12.7 kcal mol^{-1} above the energy of [*cis*-(POCOP)Co(H_2)$(H)_2$] and 17.8 kcal mol^{-1} above the energy of [*trans*-(POCOP)Co(H_2)$(H)_2$].

Several novel features emerge from the new results of Heinekey et al. The involvement of mercury was unexpected, yet it provided an excellent route to the formation of novel H_2 complexes of cobalt. Will the protection of a highly reactive organometallic fragment by mercury be more generally applicable to other systems? The low stability of the cobalt dihydrogen complex means high reactivity, which will be useful if that reactivity can be harnessed in catalytic reactions. The related third-row iridium dihydride complex [(POCOP)Ir$(H)_2$][15] catalyzes the release of H_2 from alkanes and from amine borane (NH_3BH_3). There is a broad interest[16] in finding catalysts based on earth-abundant, inexpensive metals to replace the use of precious metals like iridium in catalysis. The discovery of this new cobalt chemistry offers hope that further development of this chemistry will lead to new uses of cobalt complexes in catalytic reactions.

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[1] G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini, H. J. Wasserman, *J. Am. Chem. Soc.* **1984**, *106*, 451 – 452.

[2] J. G. de Vries, C. J. Elsevier, *Handbook of Homogeneous Hydrogenations*, Wiley-VCH, Weinheim, **2007**.

[3] a) G. J. Kubas, *Metal Dihydrogen and σ-Bond Complexes: Structure, Theory, and Reactivity*, Kluwer Academic/Plenum Publishers, New York, **2001**; b) D. M. Heinekey, W. J. Oldham, Jr., *Chem. Rev.* **1993**, *93*, 913 – 926; c) R. H. Crabtree, *Angew. Chem.* **1993**, *105*, 828 – 845; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 789 – 805; d) G. J. Kubas, *Chem. Rev.* **2007**, *107*, 4152 – 4205.

[4] R. H. Morris, *Coord. Chem. Rev.* **2008**, *252*, 2381 – 2394.

[5] a) R. K. Upmacis, G. E. Gadd, M. Poliakoff, M. B. Simpson, J. J. Turner, R. Whyman, A. F. Simpson, *J. Chem. Soc. Chem. Commun.* **1985**, 27 – 30; b) S. L. Matthews, V. Pons, D. M. Heinekey, *J. Am. Chem. Soc.* **2005**, *127*, 850 – 851.

[6] G. J. Kubas, J. E. Nelson, J. C. Bryan, J. Eckert, L. Wisniewski, K. Zilm, *Inorg. Chem.* **1994**, *33*, 2954 – 2960.

[7] a) W. A. King, X.-L. Luo, B. L. Scott, G. J. Kubas, K. W. Zilm, *J. Am. Chem. Soc.* **1996**, *118*, 6782 – 6783; b) W. A. King, B. L. Scott, J. Eckert, G. J. Kubas, *Inorg. Chem.* **1999**, *38*, 1069 – 1084; c) K. D. Welch, W. G. Dougherty, W. S. Kassel, D. L. DuBois, R. M. Bullock, *Organometallics* **2010**, *29*, 4532 – 4540.

[8] a) J. Y. Yang, R. M. Bullock, W. J. Shaw, B. Twamley, K. Fraze, M. Rakowski DuBois, D. L. DuBois, *J. Am. Chem. Soc.* **2009**, *131*, 5935 – 5945; b) M. Rakowski DuBois, D. L. DuBois in

Catalysis Without Precious Metals (Ed.: R. M. Bullock), Wiley-VCH, Weinheim, **2010**, Chap. 7, pp. 165–180.

[9] T. He, N. P. Tsvetkov, J. G. Andino, X. Gao, B. C. Fullmer, K. G. Caulton, *J. Am. Chem. Soc.* **2010**, *132*, 910–911.

[10] T. J. Hebden, A. J. St. John, D. G. Gusev, W. Kaminsky, K. I. Goldberg, D. M. Heinekey, *Angew. Chem.* **2011**, *123*, 1913–1916; *Angew. Chem. Int. Ed.* **2011**, *50*, 1873–1876.

[11] M. D. Doherty, B. Grant, P. S. White, M. Brookhart, *Organometallics* **2007**, *26*, 5950–5960.

[12] G. E. Gadd, R. K. Upmacis, M. Poliakoff, J. J. Turner, *J. Am. Chem. Soc.* **1986**, *108*, 2547–2552.

[13] G. M. Sheldrick, R. N. F. Simpson, *J. Chem. Soc. A* **1968**, 1005–1009.

[14] R. Gelabert, M. Moreno, J. M. Lluch, A. Lledos, V. Pons, D. M. Heinekey, *J. Am. Chem. Soc.* **2004**, *126*, 8813–8822.

[15] a) I. Göttker-Schnetmann, P. White, M. Brookhart, *J. Am. Chem. Soc.* **2004**, *126*, 1804–1811; b) K. Zhu, P. D. Achord, X. Zhang, K. Krogh-Jespersen, A. S. Goldman, *J. Am. Chem. Soc.* **2004**, *126*, 13044–13053; c) M. C. Denney, V. Pons, T. J. Hebden, D. M. Heinekey, K. I. Goldberg, *J. Am. Chem. Soc.* **2006**, *128*, 12048–12049.

[16] *Catalysis Without Precious Metals* (Ed.: R. M. Bullock), Wiley-VCH, Weinheim, **2010**.