

# Evidence for Formation of a Co–H Bond from $(H_2O)_2Co(dmgBF_2)_2$ under $H_2$ : Application to Radical Cyclizations

Gang Li, Arthur Han, Mary E. Pulling, Deven P. Estes, and Jack R. Norton\*

Department of Chemistry, Columbia University, 3000 Broadway, New York, New York 10027, United States

#### **Supporting Information**

**ABSTRACT:** Under H<sub>2</sub>, the radical cyclization of appropriate dienes can be catalyzed by cobaloximes. H• can be abstracted from an intermediate (presumably a cobalt hydride) by trityl radicals (Ar<sub>3</sub>C•) or by TEMPO. The rate-determining step in these reactions is the uptake of H<sub>2</sub>, which is second order in cobalt and first order in hydrogen; the third-order rate constant is 106(3) M<sup>-2</sup>·s<sup>-1</sup>.

Hydrogen atom (H•) transfer (HAT) from transitionmetal hydrides to unsaturated organic molecules is a key step in many reactions, in particular hydrogenation and hydroformylation.<sup>1</sup> Our group has measured the rate constants for HAT from CpCr(CO)<sub>3</sub>H and HV(CO)<sub>4</sub>(P–P) to various olefins<sup>2</sup> and used these reactions to carry out radical cyclizations (eq 1).<sup>2c,3</sup> With CpCr(CO)<sub>3</sub>H, the reaction is



catalytic, as  $CpCr(CO)_3H$  is regenerated from  $CpCr(CO)_3\bullet$ with  $H_2$ ,<sup>4</sup> but HAT is relatively slow. With  $HV(CO)_4(P-P)$ , HAT is faster, but cyclizations can be effected only stoichiometrically because the V–H bond is too weak for  $\bullet V(CO)_4(P-P)$  to cleave  $H_2$ . Both the Cr and V hydrides are air-sensitive and thermally unstable.

The possibility that Co complexes might catalyze the generation of radicals from  $H_2$  was suggested by the 2006 report<sup>5</sup> that the macrocyclic Co<sup>II</sup> complex  $(H_2O)_2$ Co- $(dmgBF_2)_2$  (3a) (dmg = dimethylglyoximato) could initiate the polymerization of acrylates under  $H_2$  gas (eq 2). Such



"cobaloximes" are air- and moisture-stable solids that are widely accepted as models for vitamin  $B_{12}$ . Indeed, van der Donk has shown that vitamin  $B_{12}$  itself can catalyze radical cyclizations with Ti<sup>III</sup> as the stoichiometric reductant,<sup>6</sup> and Carreira has shown that photolysis of cobaloxime complexes generates a catalyst for the cyclization of unsaturated alkyl iodides.<sup>7</sup> A Co<sup>III</sup> hydride is probably formed in all three of these reactions: in eq 2 from  $H_2$ , in the van der Donk chemistry by protonation of the Co<sup>II</sup> vitamin  $B_{12}$  anion, and in the Carreira chemistry from an alkyl–Co<sup>III</sup> intermediate.

Cobaloxime hydrides 4, and the hydrides of similar tetraazamacrocycle complexes, have been proposed as intermediates in the operation of Co catalysts for  $H_2$  evolution. Important recent work in this area has come from Gray,<sup>8</sup> Peters,<sup>8d,9</sup> Eisenberg,<sup>10</sup> Fontecave,<sup>11</sup> Sun,<sup>11b,12</sup> Alberto,<sup>13</sup> Bakac,<sup>14</sup> and Tiede.<sup>15</sup>



Often cobaloxime hydrides are thermodynamically unstable, such as **4b** (L = py).<sup>16</sup> There have been suggestions<sup>17</sup> that hydride **4b** (L = PBu<sub>3</sub>), originally reported to be formed from ClCo(dmgH)<sub>2</sub>(PBu<sub>3</sub>) and NaBH<sub>4</sub>,<sup>18</sup> was mischaracterized and that the original procedure actually gives a Co<sup>II</sup> monomer in equilibrium with its dimer;<sup>17</sup> however, a report of the preparation of the PBu<sub>3</sub> hydride has just appeared,<sup>19</sup> albeit with a <sup>1</sup>H NMR spectrum that differs from that originally reported.<sup>18</sup> The pK<sub>a</sub> of the PBu<sub>3</sub> hydride **4b** was estimated in the original report as 10.5 from "phase-distribution measurements" between MeOH/H<sub>2</sub>O and hexane.<sup>18</sup>

Schrauzer and co-workers reported a reaction between cobaloxime **3b** and  $H_{22}^{20}$  and there were subsequent studies of the kinetics of  $H_2$  uptake by **3b** in the presence of various acceptors, including Schiff bases,<sup>21</sup> the dmgH ligand itself,<sup>22</sup> and styrene.<sup>23</sup> However, no spectroscopic data were reported for the dmgBF<sub>2</sub> hydridocobaloxime **4a** with L =  $H_2O$  until 2010, when Szajna-Fuller and Bakac assigned a peak at 608 nm to **4a** in water.<sup>14</sup> (This peak is close to, but less intense than, the peak at 610 nm assigned to  $[Co^{1}(dmgBF_{2})_{2}]^{-.14}$ )

We therefore set out to trap cobaloxime hydride 4a from the reaction of cobaloxime 3a with H<sub>2</sub>. We began by trying tris(*p*-

Received: June 20, 2012

*tert*-butylphenyl)methyl radical (5), which is monomeric in solution (head-to-tail dimerization is prevented by its *p*-*tert*-butyl substituents<sup>24</sup>) and known to be effective at H• abstraction from transition metals (eq 3).<sup>25</sup> The reactions of

$$\begin{pmatrix} {}^{t}Bu \longrightarrow \\ \end{pmatrix}_{3}C \cdot + M \cdot H \longrightarrow \begin{pmatrix} {}^{t}Bu \longrightarrow \\ \end{pmatrix}_{3}CH + M \cdot$$
(3)  
5 M \cdot H = CpCr(CO)\_{3}H 6  
HMn(CO)\_{6}

**5** are easily monitored by watching the disappearance of its UV-vis signal ( $\lambda_{max} = 526$  nm) or the appearance of the <sup>1</sup>H NMR signal of the product, tris(*p*-tert-butylphenyl)methane (**6**).

Indeed, 5 was converted to 6 in the presence of 3a and  $H_2$  (eq 4). No 6 was observed unless both 3a and  $H_2$  were present.

$$\begin{pmatrix} {}^{\prime}Bu \longrightarrow G^{\bullet} & \xrightarrow{3a} \\ & H_{2}, C_{6}D_{6} \end{pmatrix} ( {}^{\prime}Bu \longrightarrow G^{\bullet} \\ & G \end{pmatrix}$$

$$(4)$$

Cobaloxime 3a *catalyzes* the reaction between trityl radical 5 and  $H_2$ , presumably via cobalt hydride 4a. When eq 4 was monitored by NMR spectroscopy under constant  $H_2$  pressure, the rate of formation of 6 did not change with time (Figure 1); the reaction is thus *zeroth order* in 5.



**Figure 1.** Cobaloxime-mediated formation of **6** from **5** under 2.4 atm  $H_2$  in  $C_6D_6$  at 295 K (eq 4). [**3a**] = 7.60 × 10<sup>-4</sup> M and [**5**]<sub>0</sub> = 1.02 × 10<sup>-2</sup> M.

We confirmed this conclusion by showing that the rate d[6]/dt was independent of the initial concentration of **5** (Figure S17 in the Supporting Information). We then studied reaction 4 at various H<sub>2</sub> pressures and various **3a** concentrations. During a given reaction,  $[H_2]$  remained constant because it was present in substantial excess, and [3a] remained constant because it was regenerated. The reaction proved to be first order in H<sub>2</sub> (Figure 2a) and second order in cobalt (Figure 2b). These results suggest efficient trapping of hydride **4a** by Ar<sub>3</sub>C• **5** and rate-limiting activation of H<sub>2</sub> by **3a**, that is, the rate law in eq 5, which is the same as the rate law reported earlier for catalysis of H<sub>2</sub> uptake by **3b**.<sup>16,22b,d,23</sup>

$$\frac{d[Ar_{3}CH]}{dt} = k[(H_{2}O)_{2}Co(dmgBF_{2})_{2}]^{2}[H_{2}]$$
(5)

This rate law suggests the mechanism in Scheme 1 with large  $k_2$  and small  $k_1$ . From Figure 2a and the value of  $[3a]^2$  we obtain a  $k_1$  value of 108(7)  $M^{-2}s^{-1}$  (Figure S7), and from Figure 2b and the value of  $[H_2]$  we obtain a  $k_1$  value of 104(3)  $M^{-2}s^{-1}$  (Figure S13), implying that  $k_1$  is 106(3)  $M^{-2}s^{-1}$  at 295 K.<sup>26</sup> The first step, eq 6 in Scheme 1, is analogous to those for the activation of  $H_2$  by other metalloradicals, such as



**Figure 2.** (a) Rate d[6]/dt of eq 4 vs  $[H_2]$ . (b) Rate d[6]/dt of eq 4 vs [3a]. All rates were measured at 295 K in  $C_6D_6$ .

Scheme 1. Mechanism of Cobaloxime-Mediated Formation of 6 from 5

$$H_{2} + 2 L_{2}Co^{\parallel} \xrightarrow{k_{1}} 2 LCo^{\parallel} H$$

$$3a \qquad 4a$$

$$LCo^{\parallel} H + ('Bu \longrightarrow)_{3}C \cdot \xrightarrow{k_{2}} L_{2}Co^{\parallel} \cdot + ('Bu \longrightarrow)_{3}CH$$

$$4a \qquad 5 \qquad 3a \qquad 6$$

$$(6)$$

• $Co(CN)_5^{3-}$  (Halpern),<sup>27</sup> •Rh(TMP) (Wayland),<sup>28</sup> • $Cr(CO)_3Cp^*$  (Hoff),<sup>29</sup> • $Cr(CO)_3Cp$  (Franz),<sup>4b</sup> and • $W(CO)_2(NHC)Cp$  (Bullock).<sup>30</sup>

Of course the value of  $k_1$  should be independent of the nature as well as the concentration of the trapping radical. We therefore replaced **5** by 2,2,6,6-tetramethylpiperidine *N*-oxyl (TEMPO, 7), giving eq 8. We examined the rate of eq 8 with

$$\begin{array}{c|c} & & & & & & \\ \hline & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & &$$

 $[3a] = 7.60 \times 10^{-4}$  M and  $P_{H_2} = 3.0$  atm (Figure S16). With [7] = 0.116 M, the rate d[8]/dt was found to be  $1.82(2) \times 10^{-3}$  Mh<sup>-1</sup>, implying a  $k_1$  value of 115(1) M<sup>-2</sup>s<sup>-1</sup>, almost the same as that found with various concentrations of 5 (Figure S18). This result is consistent with the mechanism in Scheme 1.<sup>31</sup>

It seemed likely that the apparent cobalt hydride intermediate 4a would also donate  $H\bullet$  to a cyclization substrate such as 1, so we tried the cobaloximes 3a and 3b under  $H_2$  as catalysts for the cyclization of 1b. With substrate 1b, we saw quantitative cyclization to 2b and 2'b (eq 9), the same result (with the same diastereomer ratio) obtained earlier with the Cr and V hydrides.<sup>3</sup>



We then considered what advantages cobaloximes might offer over our previous catalysts. *If* the reaction of cobaloxime **3a** with H<sub>2</sub> is slower than the reaction of the resulting hydride **4a** with our cyclization substrates, the resting state of our catalyst will be Co<sup>II</sup>, and the concentration of its hydride **4a** will remain low during the cyclization. The increase in  $[M\bullet]/[M-H]$  will change the distribution of byproducts (typically **9** and **10** in Scheme 2) that accompany cyclization. Hydrogenation to

# Scheme 2. How Byproducts Are Formed during Cyclization Reactions



9 requires an additional M–H, while isomerization to 10 requires only M• (here  $Co^{II}$ ). Thus, the cobalt catalyst should give less hydrogenation to 9 and more isomerization to 10.

Indeed, with substrate 1a and cobalt catalyst 3a, *isomerization* to 10a is the prevailing reaction (eq 10). Only traces of the cyclization products 2a and 2'a and the hydrogenation product 9a are observed.



However, with the enone substrate 11,<sup>32</sup> the use of the cobalt catalyst is advantageous. The structure of 11 eliminates isomerization as a possibility. The Cr catalyst results almost exclusively in hydrogenation to give 12, but the Co catalyst *gives substantial cyclization*, albeit to the unhydrogenated product 13 (Scheme 3). Presumably 13 results from removal of H• from the cyclized radical 14 by Co<sup>II</sup> (Scheme 4). The phenyl substituent in 11 directs the cyclization to a five-membered ring<sup>33</sup> instead of the six-membered ring reported for the parent radical.<sup>34</sup> The Co catalyst does give some hydrogenation (the remaining 50% of substrate 11 is converted to 12).

# Scheme 3. Comparison of Cr and Co Catalysts for Cyclization of 11



Scheme 4. Mechanism for the Formation of 12 and 13 from 11



Cobaloxime 3a thus catalyzes the cyclization of 11 without net hydrogen uptake, although the presence of  $H_2$  is required (3a has no effect on 11 in the absence of  $H_2$ ). Our kinetics studies show that 3a and  $H_2$  generate an intermediate (presumably hydride 4a) that can transfer H·. Both of our catalysts for cyclization, CpCr(CO)<sub>3</sub>H and 3a, avoid the need for a heavy atom in the substrate as well as the need for a tin reagent.

# ASSOCIATED CONTENT

### **S** Supporting Information

Synthetic details, spectroscopic data, and kinetic procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

# **Corresponding Author**

jrn11@columbia.edu

### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This work was supported by DOE Grant DE-FG02-97ER14807. We are grateful to Boulder Scientific and OFS Fitel for additional support. A.H. gratefully acknowledges the support of the Herbert Deresiewicz Summer Research Fellowship. M.E.P. thanks Novartis for a graduate fellowship. D.P.E. is supported by the Department of Energy Office of Science Graduate Fellowship Program (DOE SCGF), made possible in part by the American Recovery and Reinvestment Act of 2009 and administered by ORISE-ORAU under Contract DE-AC05-06OR23100. The authors thank John Hartung for helpful discussions.

#### REFERENCES

(1) (a) Brown, T. L. Ann. N.Y. Acad. Sci. 1980, 333, 80. (b) Halpern,
 J. Pure Appl. Chem. 1986, 58, 575. (c) Baird, M. C. Chem. Rev. 1988,
 88, 1217. (d) Tyler, D. R. Prog. Inorg. Chem. 1988, 36, 125.
 (e) Eisenberg, D. C.; Norton, J. R. Isr. J. Chem. 1991, 31, 55.

(2) (a) Tang, L.; Papish, E. T.; Abramo, G. P.; Norton, J. R.; Baik, M.-H.; Friesner, R. A.; Rappé, A. J. Am. Chem. Soc. 2003, 125, 10093.
(b) Choi, J.; Tang, L.; Norton, J. R. J. Am. Chem. Soc. 2007, 129, 234.
(c) Choi, J.; Pulling, M. E.; Smith, D. M.; Norton, J. R. J. Am. Chem. Soc. 2008, 130, 4250.

(3) Smith, D. M.; Pulling, M. E.; Norton, J. R. J. Am. Chem. Soc. 2007, 129, 770.

(4) (a) Fischer, E. O.; Hafner, W.; Stahl, H. O. Z. Anorg. Allg. Chem. 1955, 282, 47. (b) Norton, J. R.; Choi, J.; Spataru, T.; Camaoni, D.; Lee, S.-J.; Franz, J. A. In preparation.

(5) Ittel, S. D.; Gridnev, A. A. Initiation of Polymerization by Hydrogen Atom Donation. U.S. Patent 7,022,792, April 4, 2006.

#### Journal of the American Chemical Society

(6) McGinley, C. M.; Relyea, H. A.; van der Donk, W. A. Synlett 2006, 211.

(7) Weiss, M. E.; Kreis, L. M.; Lauber, A.; Carreira, E. M. Angew. Chem., Int. Ed. 2011, 50, 11125.

(8) (a) Dempsey, J. L.; Brunschwig, B. S.; Winkler, J. R.; Gray, H. B. Acc. Chem. Res. 2009, 42, 1995. (b) Dempsey, J. L.; Winkler, J. R.; Gray, H. B. J. Am. Chem. Soc. 2010, 132, 1060. (c) Dempsey, J. L.; Winkler, J. R.; Gray, H. B. J. Am. Chem. Soc. 2010, 132, 16774. (d) Stubbert, B. D.; Peters, J. C.; Gray, H. B. J. Am. Chem. Soc. 2011, 133, 18070.

(9) (a) Hu, X.; Cossairt, B. M.; Brunschwig, B. S.; Lewis, N. S.; Peters, J. C. Chem. Commun. 2005, 4723. (b) Hu, X. L.; Brunschwig, B. S.; Peters, J. C. J. Am. Chem. Soc. 2007, 129, 8988. (c) Berben, L. A.; Peters, J. C. Chem. Commun. 2010, 46, 398. (d) McCrory, C. C. L.; Uyeda, C.; Peters, J. C. J. Am. Chem. Soc. 2012, 134, 3164.

(10) (a) Du, P.; Schneider, J.; Luo, G.; Brennessel, W. W.; Eisenberg, R. *Inorg. Chem.* **2009**, *48*, 4952. (b) McCormick, T. M.; Han, Z.; Weinberg, D. J.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R. *Inorg. Chem.* **2011**, *50*, 10660.

(11) (a) Artero, V.; Chavarot-Kerlidou, M.; Fontecave, M. Angew. Chem., Int. Ed. 2011, 50, 7238 and references therein. (b) Zhang, P.; Jacques, P.-A.; Chavarot-Kerlidou, M.; Wang, M.; Sun, L.; Fontecave, M.; Artero, V. Inorg. Chem. 2012, 51, 2115.

(12) (a) Zhang, P.; Wang, M.; Dong, J.; Li, X.; Wang, F.; Wu, L.;
Sun, L. J. Phys. Chem. C 2010, 114, 15868. (b) Zhang, P.; Wang, M.;
Li, C.; Li, X.; Dong, J.; Sun, L. Chem. Commun. 2010, 46, 8806.
(c) Dong, J.; Wang, M.; Zhang, P.; Yang, S.; Liu, J.; Li, X.; Sun, L. J.
Phys. Chem. C 2011, 115, 15089. (d) Li, L.; Duan, L.; Wen, F.; Li, C.;
Wang, M.; Hagfeldt, A.; Sun, L. Chem. Commun. 2012, 48, 988.

(13) (a) Probst, B.; Kolano, C.; Hamm, P.; Alberto, R. Inorg. Chem. 2009, 48, 1836. (b) Probst, B.; Rodenberg, A.; Guttentag, M.; Hamm, P.; Alberto, R. Inorg. Chem. 2010, 49, 6453. (c) Probst, B.; Guttentag, M.; Rodenberg, A.; Hamm, P.; Alberto, R. Inorg. Chem. 2011, 50, 3404. (d) Guttentag, M.; Rodenberg, A.; Kopelent, R.; Probst, B.; Buchwalder, C.; Brandstaetter, M.; Hamm, P.; Alberto, R. Eur. J. Inorg. Chem. 2012, 59.

(14) Szajna-Fuller, E.; Bakac, A. Eur. J. Inorg. Chem. 2010, 2488.

(15) Utschig, L. M.; Silver, S. C.; Mulfort, K. L.; Tiede, D. M. J. Am. Chem. Soc. 2011, 133, 16334.

(16) Szeverényi, Z.; Budó-Záhonyi, É.; Simándi, L. I. J. Coord. Chem. 1980, 10, 41.

(17) Sun, Y. A. The Anions of  $C_{60}$  and Its Pyrrolidine Derivatives. B. The Search for Hydridocobaloximes. Ph.D. Thesis, University of Southern California, Los Angeles, CA, 1997 (from the research group of Prof. C. A. Reed).

(18) Schrauzer, G. N.; Holland, R. J. J. Am. Chem. Soc. 1971, 93, 1505.

(19) Bhattacharjee, A.; Chavarot-Kerlidou, M.; Andreiadis, E. S.; Fontecave, M.; Field, M. J.; Artero, V. Inorg. Chem. **2012**, *51*, 7087.

(20) (a) Schrauzer, G. N.; Windgassen, R. J. Chem. Ber. **1966**, 99, 602. (b) Schrauzer, G. N. Ann. N.Y. Acad. Sci. **1969**, 158, 526.

(21) Yamaguchi, T.; Nakayama, M.; Tsumura, T. Chem. Lett. 1972, 1231.

(22) (a) Yamaguchi, T.; Tsumura, T. Chem. Lett. 1973, 409.
(b) Simándi, L. I.; Budó-Záhonyi, É.; Szeverényi, Z. Inorg. Nucl. Chem. Lett. 1976, 12, 237. (c) Yamaguchi, T.; Miyagawa, R. Chem. Lett. 1978, 89. (d) Simándi, L. I.; Budó-Záhonyi, É.; Szeverényi, Z.; Németh, S. J. Chem. Soc., Dalton Trans. 1980, 276.

(23) Simándi, L. I.; Szeverényi, Z.; Budó-Záhonyi, É. Inorg. Nucl. Chem. Lett. 1975, 11, 773.

(24) Colle, T. H.; Lewis, E. S. J. Am. Chem. Soc. **1979**, 101, 1810. (25) (a) Eisenberg, D. C.; Lawrie, C. J. C.; Moody, A. E.; Norton, J.

R. J. Am. Chem. Soc. 1991, 113, 4888. (b) Rodkin, M. A.; Abramo, G. P.; Darula, K. E.; Ramage, D. L.; Santora, B. P.; Norton, J. R. Organometallics 1999, 18, 1106.

(26) The concentration of hydrogen was calculated from its pressure as described in the Supporting Information.

(27) Halpern, J.; Pribanic, M. Inorg. Chem. 1970, 9, 2616.

(28) Wayland, B. B.; Ba, S.; Sherry, A. E. Inorg. Chem. 1992, 31, 148.

(29) Capps, K. B.; Bauer, A.; Kiss, G.; Hoff, C. D. J. Organomet. Chem. 1999, 586, 23.

(30) (a) Roberts, J. A. S.; Franz, J. A.; van der Eide, E. F.; Walter, E. D.; Petersen, J. L.; DuBois, D. L.; Bullock, R. M. *J. Am. Chem. Soc.* **2011**, *133*, 14593. (b) van der Eide, E. F.; Liu, T.; Camaioni, D. M.; Walter, E. D.; Bullock, R. M. *Organometallics* **2012**, *31*, 1775.

(31) A similar "redox switch" process, the metal-catalyzed reduction of trityl *cation* to trityl *radicals* by hydrogen gas, has been reported. See: Hembre, R. T.; McQueen, J. S. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 65.

(32) Such an enone is an attractive substrate because radicals are stabilized by acyl substituents. See: Brocks, J. J.; Beckhaus, H. D.; Beckwith, A. L. J.; Rüchardt, C. J. Org. Chem. **1998**, 63, 1935.

(33) Evidence for the five-membered ring structure is given in the Supporting Information.

(34) (a) Clive, D. L. J.; Cheshire, D. R. J. Chem. Soc., Chem. Commun. 1987, 1520. (b) Porter, N. A.; Chang, V. H. T.; Magnin, D. R.; Wright, B. T. J. Am. Chem. Soc. 1988, 110, 3554. (c) Curran, D. P.; Chang, C. T. J. Org. Chem. 1989, 54, 3140. (d) Broeker, J. L.; Houk, K. N. J. Org. Chem. 1991, 56, 3651.