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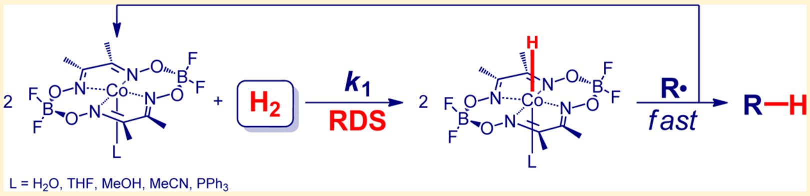
Dihydrogen Activation by Cobaloximes with Various Axial Ligands

Gang Li, Deven P. Estes, Jack R. Norton,* Serge Ruccolo, Aaron Sattler, and Wesley Sattler

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

Ⓢ *Supporting Information*



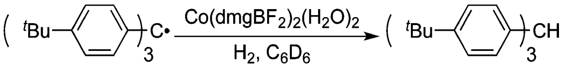
ABSTRACT: We have investigated the effect of axial ligands on the ability of cobaloximes to catalyze the generation of transferable hydrogen atoms from hydrogen gas and have learned that the active catalyst contains one and only one axial ligand. We have, for example, shown that $Co(dmgBF_2)_2$ coordinates only one Ph_3P and that the addition of additional Ph_3P (beyond 1 equiv) to solvated $Co(dmgBF_2)_2$ does not affect its catalytic turnover for H• transfer from H_2.

INTRODUCTION

The use of cobaloximes to catalyze chain transfer in radical polymerizations was suggested by Rempel in 1984,[1] and the effectiveness of these complexes at catalyzing chain transfer under H_2 was shown in a 2006 patent.[2] Cobaloximes and their derivatives have also been shown to be catalysts for the production of hydrogen from protons and electrons, a reaction which is of interest to solar fuels production.[3]

$$2H^+ + 2e^- \xrightarrow{\text{cobaloxime catalysts}} H_2 \qquad (1)$$

We have recently examined cobaloxime/hydrogen reactions in reverse and have found that $Co(dmgBF_2)_2(H_2O)_2$ under H_2 can serve as a source of H•.[4] For example, $Co(dmgBF_2)_2(H_2O)_2$ catalyzes the hydrogenation of the monomeric trityl radical[5] in reaction 2. The rate of reaction 2 is independent of $[Ar_3C\bullet]$



(2)

($Ar = p\text{-}^tBuC_6H_4$), but first-order in H_2 and second-order in cobaloxime, suggesting that the slow step is the activation of H_2 by the cobalt catalyst.

It seems likely that H• transfer arises from a Co(III)−H hydride intermediate; such intermediates appear to be involved in the catalysis of hydrogen evolution. The ability of cobaloximes to catalyze the production of H_2 from protons is substantially affected by the nature of their axial ligands.[6] (The effect of trans ligands L on the reacitivity of ligands X in cobaloximes and related compounds has been reviewed.[7]) We have thus examined the effect of axial ligands on the ability of cobaloximes to catalyze hydrogenations like the one in reaction 2.

EXPERIMENTAL SECTION

All manipulations were performed under an argon atmosphere using standard Schlenk or inert atmosphere box techniques. NMR spectra were taken on either a Bruker 300, 400, or 500 MHz spectrometer. IR spectra were taken with a PerkinElmer Spectrum 2000 FT-IR spectrometer. UV−vis spectra were recorded on a Hewlett-Packard spectrophotometer. X-ray diffraction data were collected on a Bruker Apex II diffractometer. Crystal data, data collection, and refinement parameters are summarized in the Supporting Information. The structures were solved using direct methods and standard difference map techniques and were refined by full matrix least-squares procedures on F^2 with SHELXTL (version 6.1).[8] Benzene and THF were distilled from K/benzophenone ketyl and stored over 3 Å molecular sieves. All other liquids, including benzene-d_6, were dried by distillation from CaH_2 and then deoxygenated by three freeze−pump−thaw cycles and stored under an argon atmosphere.

Materials. $Co(dmgBF_2)_2(H_2O)_2$,[9] $Co(dmgBF_2)_2(MeCN)_2$,[3e] and $Co(dmgBF_2)_2(MeOH)_2$[9] were synthesized by known procedures. Tris(*p-tert*-butylphenyl)methyl radical was prepared by the process described in the literature.[10]

$Co(dmgBF_2)_2(THF)_2$. Diethyl ether (150 mL, O_2 free) was added to a flask containing $Co(OAc)_2\cdot 4H_2O$ (2.0 g, 8 mmol) and $dmgH_2$ (1.9 g, 16 mmol), followed by freshly distilled $BF_3\cdot Et_2O$ (10 mL, an excess). The mixture was stirred for 6 h under argon. The resulting solid was filtered under argon, washed with ice−cold THF (3 × 5 mL, O_2 free), and dried under vacuum. A red solid product was obtained (3.2 g, 4 mmol, 50% yield). IR (ATR): 2968, 2880, 1615 (C═N), 1438, 1385, 1210, 1164, 1092, 1046, 994, 935, 880, 817, 627, 603, 578, 502, 468 cm^{-1}, which includes peaks like those that have been attributed to coordinated THF.[11] UV−vis (C_6H_6, 7.6×10^{-5} M, 1 cm quartz cell): 445 nm [$\varepsilon = 3.3(2) \times 10^3\ M^{-1}\ cm^{-1}$].

Kinetic Measurements. *Caution! Pressure reactions should be handled with care behind a blast shield. Otherwise serious injury may result!* All experiments were performed at 300 MHz. In a typical experiment, a stock solution of trityl radical in C_6D_6 was prepared with an internal standard (hexamethylcyclotrisiloxane), along with a stock solution of cobaloxime in C_6D_6. Appropriate amounts of the two stock solutions were mixed in a thick-walled J-Young tube in the glovebox, and the tube was sealed and removed from the box. After three freeze−pump−thaw cycles to remove the argon from the solution,

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hydrogen gas was added until the desired pressure was reached. The tube was allowed to thaw, and its contents were mixed before it was placed in the probe of the NMR (whose controller was already set to the desired temperature, 295 K). A methanol standard was used for temperature calibration. The H• transfer product, tris(*p-tert*-butylphenyl)methane, was identified by comparing its ^{1}H NMR spectrum with that of an authentic sample.

The integration of the product methine peak relative to that of the internal standard was recorded as a function of time. Sixteen pulses were used for every kinetic point, with 1 s between pulses. The molar concentration of H_2 in benzene was calculated by Henry's law.[12]

■ RESULTS AND DISCUSSION

Structure Discussion. In both solution and solid state, cobaloximes exist as planar macrocyclic complexes with axial ligands L, $Co(dmgBF_2)_2L_n$ (n = 1, 2) (Figure 1). When L is a coordinating solvent molecule, the L = 2 form $Co(dmgBF_2)_2L_2$ dominates and the axial ligands are easily exchanged. $Co(dmgBF_2)_2(MeOH)_2$ and its X-ray structure have been reported,[9] and $Co(dmgBF_2)_2(MeCN)_2$ has been characterized by UV−vis spectroscopy in CH_3CN solution.[3e] We have prepared crystals of the L = THF and the L = CH_3CN adducts and have confirmed by X-ray diffraction that they have the structures below (Figure 2a, 2b), with the two ligands L coordinated axially as in the MeOH complex.

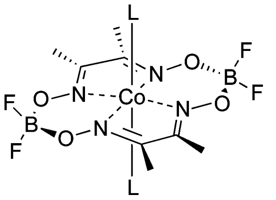


Figure 1. General structure of $Co(dmgBF_2)_2L_2$.

Selected bond distances for the MeOH, THF, and CH_3CN complexes are shown in Table 1.

EPR studies have shown that stronger σ-donor ligands (e.g., Ph_3P, pyridine) form cobaloxime complexes with only a single axial ligand (L = 1).[13] In toluene/CH_2Cl_2 $Co(dmgBF_2)_2(py)_2$ is only formed in the presence of a 10-fold excess of py,[13] although EPR showed that $Co(dmgBF_2)_2(py)_2$ is also formed when a frozen matrix of $Co(dmgBF_2)_2$ is allowed to warm to room temperature.[14]

Table 1. Selected Bond Lengths of $Co(dmgBF_2)_2L_2$

L	M−L (Å)	M−N (Å)	N=C (Å)	C−C (Å)	ref
CH_3CN	2.260	1.878	1.297	1.479	this work
MeOH	2.264	1.877	1.270	1.473	9
THF	2.324	1.890	1.299	1.483	this work

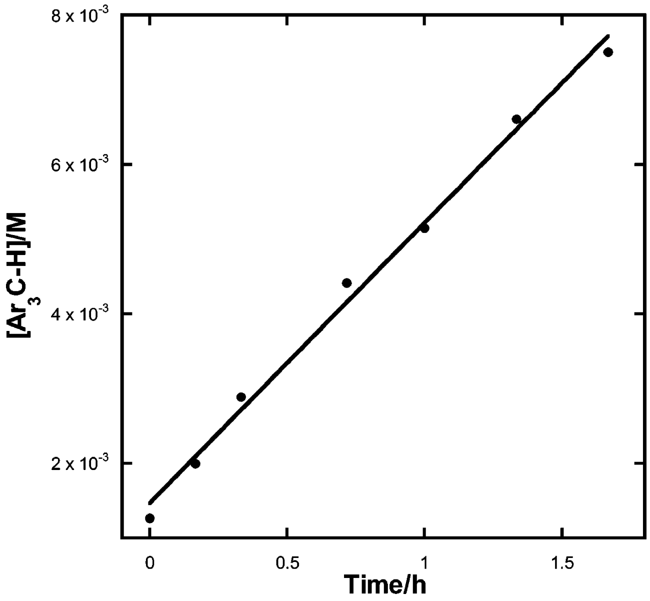
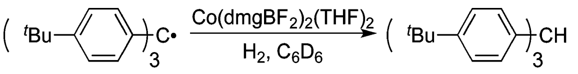


Figure 3. $Co(dmgBF_2)_2(THF)_2$-mediated formation of Ar_3CH from Ar_3C• under 2.4 atm of H_2 in C_6D_6 at 295 K (eq 3): $[Co(dmgBF_2)_2(THF)_2]$ = 3.80 × 10^{-4} M and $[Ar_3C\bullet]_0$ = 1.02 × 10^{-2} M.

Kinetics of Hydrogenation. We have examined the kinetics of the hydrogenation of Ar_3C• radicals in benzene with $Co(dmgBF_2)_2(THF)_2$ as a catalyst (eq 3). The rate is once



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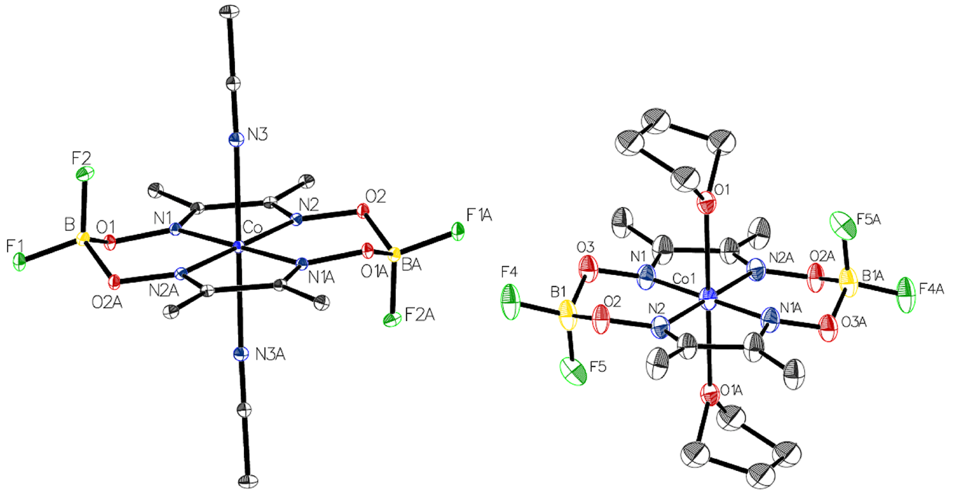


Figure 2. (a, left) Molecular structure of $Co(dmgBF_2)_2(CH_3CN)_2$ (50% ellipsoids, hydrogen atoms omitted for clarity). (b, right) Molecular structure of $Co(dmgBF_2)_2(THF)_2$ (50% ellipsoids; hydrogen atoms are omitted for clarity, the BF_2 groups and the THF ligand are disordered, and only the main contribution to the disorder is shown for clarity).

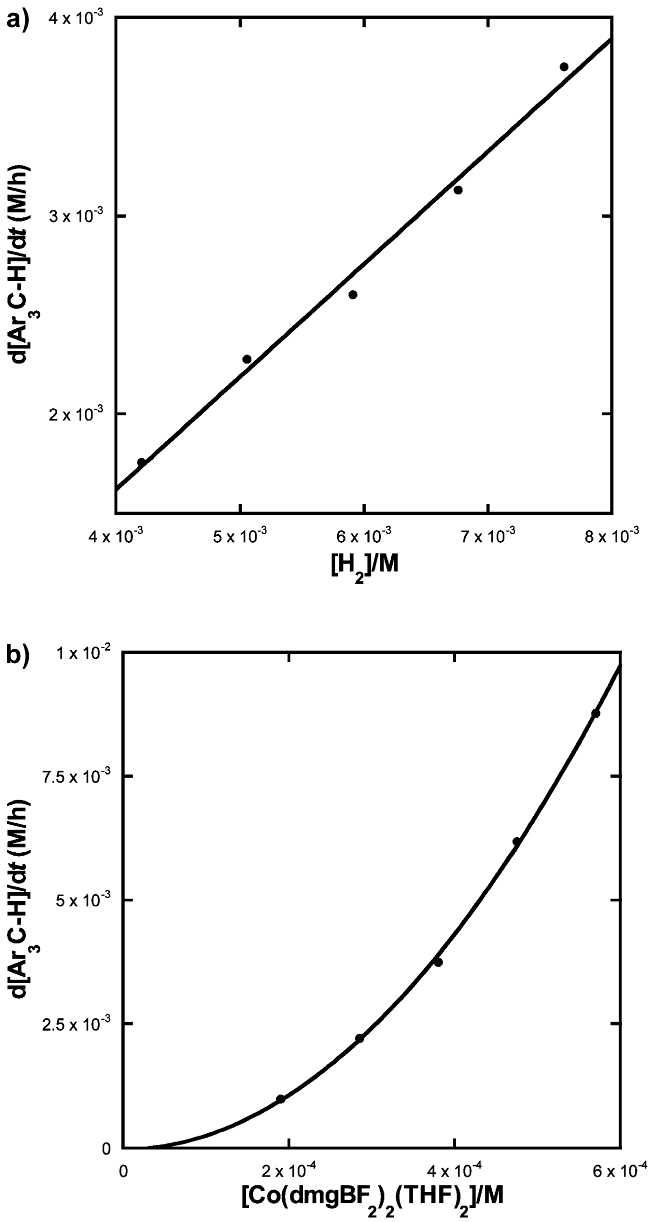


Figure 4. (a) Rate d[Ar_3CH]/dt of the hydrogenation of Ar_3C• vs [H_2]. (b) Rate d[Ar_3CH]/dt of the hydrogenation of Ar_3C• vs [$Co(dmgBF_2)_2(THF)_2$]. All rates were measured at 295 K in C_6D_6.

again independent of [Ar_3C•] (Figure 3), first-order (Figure 4a) in [H_2], and second-order (Figure 4b) in [Co_{Tot}], where [Co_{Tot}] is the concentration of cobaloxime initially added. The rate law is thus the one given in eq 4.

$$\frac{d[Ar_3CH]}{dt} = k[H_2][Co_{Tot}]^2 \tag{4}$$

The data in Figure 4 give a third-order rate constant k (defined in eq 4) of 1.04(6) × 10^3 M^{-2} s^{-1}. Experiments in C_6D_6 with different concentrations of added THF (Figure 5) show that the reaction is inhibited by that ligand, suggesting a dissociative preequilibrium (equilibrium constant K) like that shown in Scheme 1. Subsequent H_2 activation and H• transfer steps, like those found in our previous study of the diaquo complex,[4] complete a plausible mechanism.

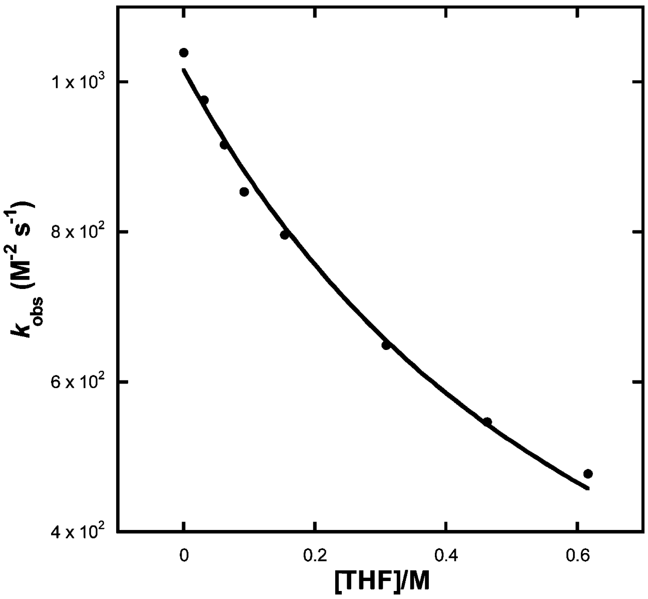
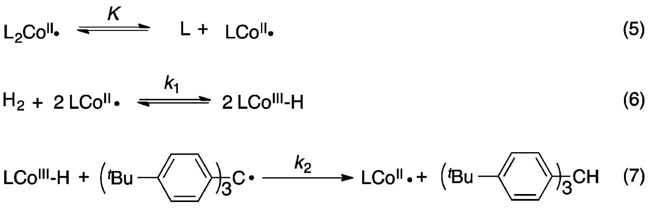


Figure 5. Rate d[Ar_3CH]/dt of eq 3 vs [THF]. All rates were measured at 295 K in C_6D_6.

Scheme 1. Proposed Mechanism for the Hydrogenation Reaction



$$\frac{d[Ar_3CH]}{dt} = k_1\left(\frac{K[Co_{Tot}]}{K + [L]}\right)^2[H_2] \tag{8}$$

The data with added THF fit the rate law in eq 8 if k_1 is 1.02(1) × 10^3 M^{-2} s^{-1} and K is 1.26(6) M. (The amount of THF added far exceeds the amount that arises from dissociation.) The results of similar experiments with MeOH in C_6D_6 fit the same rate law if k_1 is 346(7) M^{-2} s^{-1} and K is 0.128(6) M, respectively (see the Supporting Information). The larger dissociation constant K for L = THF does correlate with the longer M−O distance in the THF adduct. In neither case is there any evidence for dissociation of the second ligand.

It is clear that the nature and concentration of free axial ligand L affect both K and k_1 (see Table 2). It is, unfortunately, impractical to determine these constants for other ligands from the kinetics of trityl hydrogenation. With L = CH_3CN, the rate of the reaction with H_2 is negligible; with L = H_2O the low solubility of water in benzene makes the determination of K impractical.

In order to compare k_1 for THF and MeOH with the rate constant for a stronger σ donor, we examined the catalysis of Ar_3C• hydrogenation by $Co(dmgBF_2)_2(PPh_3)$. We were unable to isolate that complex, but we were able to confirm that only a 1:1 adduct is formed in CH_2Cl_2 solution—the same conclusion reached in toluene/CH_2Cl_2 by the EPR study cited above.[13] The addition of PPh_3 to a solution of $Co(dmgBF_2)_2(H_2O)_2$ changes its UV−vis spectrum (Figure 6), but there are no further changes after 1 equiv of PPh_3 has been added. A Job

Table 2. Equilibrium Constant K and Rate Constants k and k_1 for Dihydrogen Activation by Cobaloximes with Different Axial Ligands and M–L Bond Distances[a]

ligand	THF	MeOH	PPh_3[b]	H_2O	MeCN
k_1(M^{-2} s^{-1})	1.02(1) × 10^3	346(7)	37(5)	–	–
k (M^{-2} s^{-1})[a]	1.04(6) × 10^3	343(7)	37(5)	106(3)	<16[c]
K (M)	1.26(6)	0.128(6)	–	–	–
M–L (Å)	2.324	2.264	–	–	2.260

[a] For each axial ligand, the cobaloxime concentrations used in the measurement of k are given in the Supporting Information. For all axial ligands other than PPh_3 and CH_3CN, the rate and equilibrium constants were measured at 295 K in C_6D_6. [b] These rate constants (k and k_1 do not differ for PPh_3, as there is no coordination of a sixth ligand, vide infra) were extrapolated from measurements between 45 and 60 °C. [c] Conversion is less than 5% after 48 h at either 295 or 323 K.

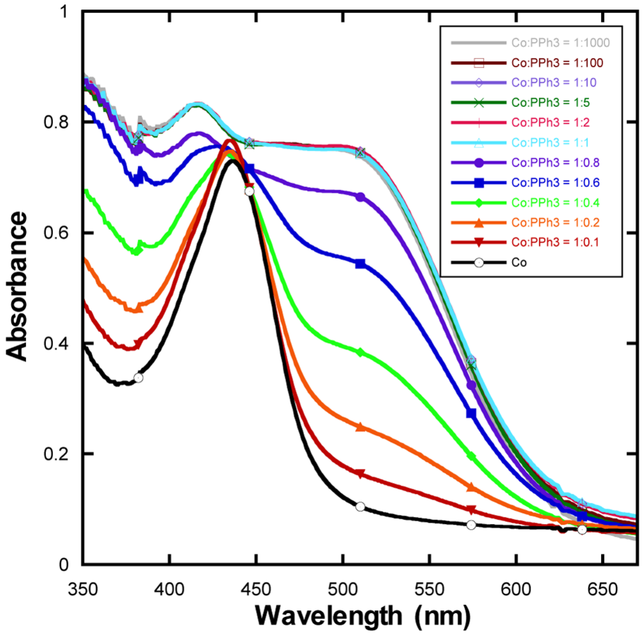


Figure 6. UV–vis study of the Co + PPh_3 system in CH_2Cl_2.

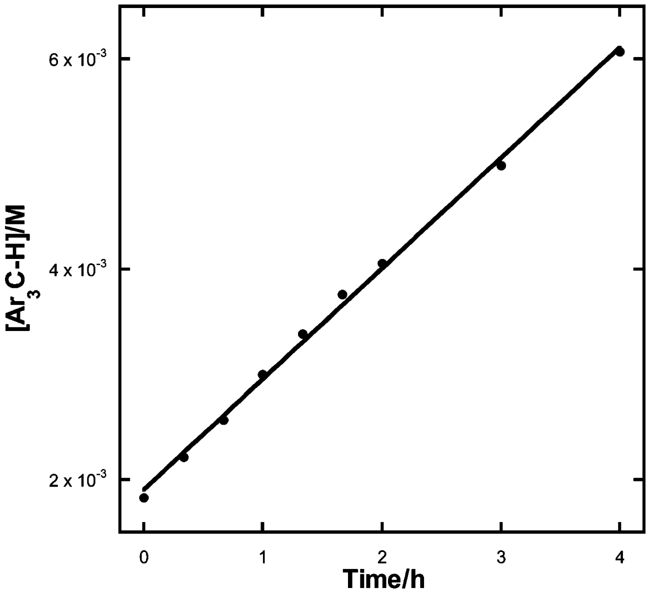


Figure 8. Cobaloxime-mediated formation of Ar_3CH from $Ar_3C\bullet$ under 3 atm of H_2 in C_6D_6 at 323 K (eq 9). $[Co(dmgBF_2)_2(H_2O)_2]$ = 7.60 × 10^{-4} M, $[Ar_3C\bullet]_0$ = 1.02 × 10^{-2} M, $[PPh_3]$ = 5.73 × 10^{-3} M.

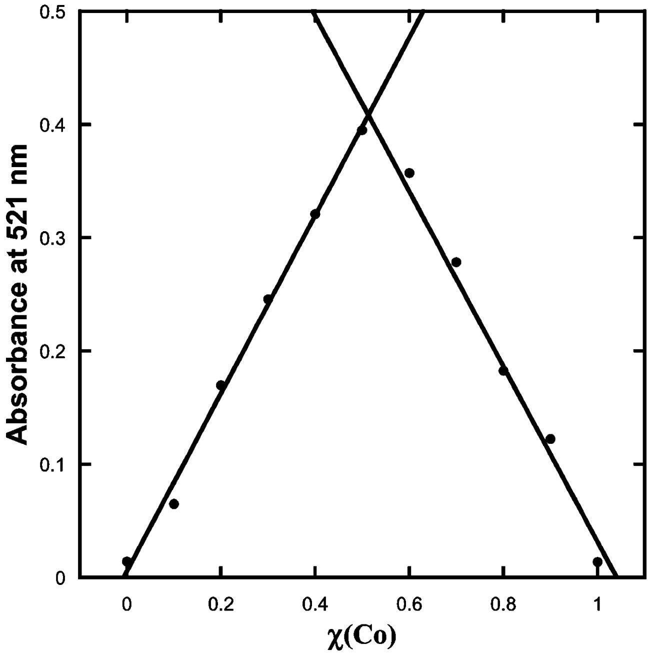


Figure 7. Job plot of the Co + PPh_3 system in CH_2Cl_2.

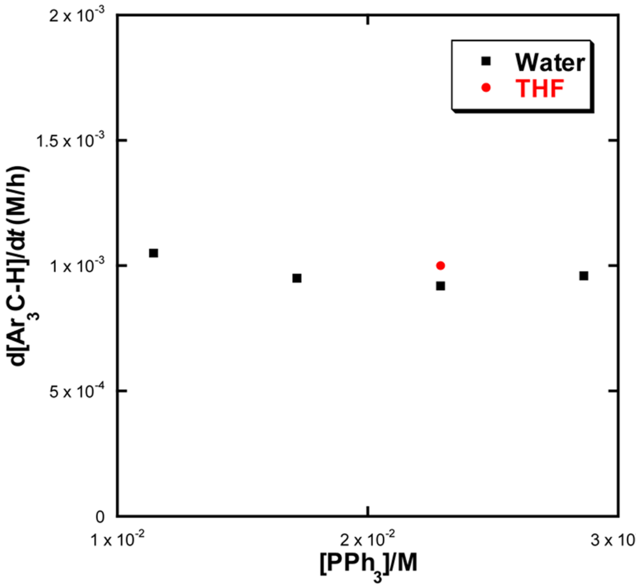
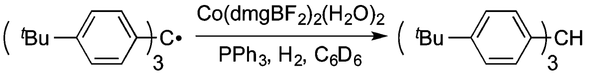


Figure 9. Rate $d[Ar_3CH]/dt$ of eq 9 vs $[PPh_3]$. All rates were measured under 3 atm of H_2 in C_6D_6 at 323 K. The initial concentration of $Co(dmgBF_2)_2(H_2O)_2$ and of $Co(dmgBF_2)_2(THF)_2$ is 3.80 × 10^{-4} M, $[Ar_3C\bullet]_0$ = 1.02 × 10^{-2} M.

plot (Figure 7) of the absorbance at 521 nm confirms the 1:1 stoichiometry.[15]

At 295 K the catalysis of the hydrogenation of Ar_3C• by $Co(dmgBF_2)_2(H_2O)_2/PPh_3$ proved too slow for convenient kinetic measurements, so the reaction was examined at higher temperatures. At 323 K, the reaction (eq 9) was again zero-order in Ar_3C• (Figure 8) but *not* inhibited by Ph_3P (Figure 9). The rate constants between 318 and 333 K gave a $\Delta H^\ddagger$ of 8(1) kcal/mol and a $\Delta S^\ddagger$ of −23(2) cal mol^{-1} K^{-1}, similar to the near-zero $\Delta H^\ddagger$ and negative $\Delta S^\ddagger$ reported for the activation of H_2 by $Co(CN)_5^{3-}$,[16] Rh(II)(TMP),[17] $Cp^*Cr(CO)_3$,[18] and $CpCr(CO)_3$.[19]



(9)

The extrapolation to 295 K of k_1 for $Co(dmgBF_2)_2(PPh_3)$ gives the value in Table 2, showing that k_1(THF) > k_1(MeOH) > $k_1(PPh_3)$. The slowness of $Co(dmgBF_2)_2(PPh_3)$ may be partly the result of its "bowl-shaped" structure, as calculated by Niklas et al.,[13] which will make more difficult a reaction (like eq 6) that is second-order in cobalt. (There appears to be steric hindrance to the approach of P(n-Bu)$_3$ to a five-coordinate alkylcobaloxime.[20])

Overall it is apparent that H_2 is best activated by five-coordinate cobalt, with a single axial ligand: $Co(dmgBF_2)_2$(THF), $Co(dmgBF_2)_2$(MeOH), or $Co(dmgBF_2)_2(PPh_3)$. The H_2/cobaloxime reaction is the reverse of the *bimolecular* mechanism that has been suggested[3a] for the evolution of H_2 from hydrides $HCo(dmgBF_2)_2L$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full preparative, analytical, and crystallographic details. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jrn11@columbia.edu.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Burczyk, A. F.; O'Driscoll, K. F.; Rempel, G. L. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3255.

(2) Ittel, S. D.; Gridnev, A. A. *Initiation of Polymerization by Hydrogen Atom Donation*. U.S. Patent 7022792, April 4, 2006.

(3) (a) Chao, T.-H.; Espenson, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 129. (b) Connolly, P.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 2684. (c) Razavet, M.; Artero, V.; Fontecave, M. *Inorg. Chem.* **2005**, *44*, 4786. (d) Hu, X.; Cossairt, B. M.; Brunschwig, B. S.; Lewis, N. S.; Peters, J. C. *Chem. Commun.* **2005**, 4723. (e) Hu, X. L.; Brunschwig, B. S.; Peters, J. C. *J. Am. Chem. Soc.* **2007**, *129*, 8988. (f) Dempsey, J. L.; Brunschwig, B. S.; Winkler, J. R.; Gray, H. B. *Acc. Chem. Res.* **2009**, *42*, 1995 and references therein. (g) Szajna-Fuller, E.; Bakac, A. *Eur. J. Inorg. Chem.* **2010**, 2488. (h) Dempsey, J. L.; Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **2010**, *132*, 16774 and references therein. (i) Utschig, L. M.; Silver, S. C.; Mulfort, K. L.; Tiede, D. M. *J. Am. Chem. Soc.* **2011**, *133*, 16334. (j) Li, L.; Duan, L.; Wen, F.; Li, C.; Wang, M.; Hagfeldt, A.; Sun, L. *Chem. Commun.* **2012**, *48*, 988 and references therein. (k) Guttentag, M.; Rodenberg, A.; Kopelent, R.; Probst, B.; Buchwalder, C.; Brandstaetter, M.; Hamm, P.; Alberto, R. *Eur. J. Inorg. Chem.* **2012**, *2012*, 59 and references therein. (l) Valdez, C. N.; Dempsey, J. L.; Brunschwig, B. S.; Winkler, J. R.; Gray, H. B. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 15589.

(4) Li, G.; Han, A.; Pulling, M. E.; Estes, D. P.; Norton, J. R. *J. Am. Chem. Soc.* **2012**, *134*, 14662.

(5) Colle, K. S.; Glaspie, P. S.; Lewis, E. S. *J. Chem. Soc., Chem. Commun.* **1975**, 266.

(6) (a) Baffert, C.; Artero, V.; Fontecave, M. *Inorg. Chem.* **2007**, *46*, 1817. (b) Zhang, P.; Wang, M.; Dong, J.; Li, X.; Wang, F.; Wu, L.; Sun, L. *J. Phys. Chem. C* **2010**, *114*, 15868.

(7) De March, M.; Demitri, N.; Geremia, S.; Hickey, N.; Randaccio, L. *J. Inorg. Biochem.* **2012**, *116*, 215.

(8) (a) Sheldrick, G. M. *SHELXTL, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*; University of Gottingen: Gottingen, 1981. (b) Sheldrick, G. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

(9) Bakac, A.; Brynildson, M. E.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 4108.

(10) (a) Colle, T. H.; Lewis, E. S. *J. Am. Chem. Soc.* **1979**, *101*, 1810. (b) Eisenberg, D. C.; Lawrie, C. J. C.; Moody, A. E.; Norton, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 4888.

(11) Allen, E. A.; Johnson, N. P.; Rosevear, D. T.; Wilkinson, W. *J. Chem. Soc. A* **1969**, 788.

(12) (a) Zhou, Z.; Cheng, Z.; Yang, D.; Zhou, X.; Yuan, W. *J. Chem. Eng. Data* **2006**, *51*, 972. (b) Krüger, M. B.; Selle, C.; Heller, D.; Baumann, W. *J. Chem. Eng. Data* **2012**, *57*, 1737.

(13) Niklas, J.; Mardis, K. L.; Rakhimov, R. R.; Mulfort, K. L.; Tiede, D. M.; Poluektov, O. G. *J. Phys. Chem. B* **2012**, *116*, 2943.

(14) Rangel, M.; Leite, A.; Silva, A.; de Castro, B.; Schlindwein, W.; Murphy, L. *J. Organomet. Chem.* **2014**, *760*, 11.

(15) It seems very unlikely that a water or a THF from the original cobaloxime remains coordinated along with one Ph_3P. Note (Figure 7) that the turnover rate is approximately the same whether we begin with $(H_2O)_2$ or $(THF)_2$.

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

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

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

(19) Norton, J. R.; Spataru, T.; Camaoni, D.; Lee, S.-J.; Li, G.; Choi, J.; Franz, J. A. *Organometallics* **2014**, *33*, 2496.

(20) Jensen, F. R.; Kiskis, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 5820.