The Reaction of Cobaloximes with Hydrogen: Products and Thermodynamics

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S *Supporting Information*

ABSTRACT: A cobalt hydride has been proposed as an intermediate in many reactions of the $Co(dmgBF_2)_2L_2$ system, but its observation has proven difficult. We have observed the UV−vis spectra of $Co(dmgBF_2)_2L_2$ (**1**) in CH_3CN under hydrogen pressures of up to 70 atm. A Co(I) compound (**6a**) with an exchangeable proton is eventually formed. We have determined the bond dissociation free energy and pK_a of the new O−H bond in **6a** to be 50.5 kcal/mol and 13.4, respectively, in CH_3CN, matching previous reports.
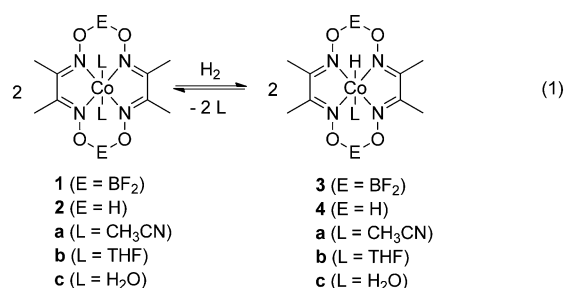
In addition to being functional B_{12} models[1] and catalyzing the production of hydrogen from protons and electricity,[2] cobaloximes catalyze H· transfer from H_2.[3] $Co(dmgBF_2)_2L_2$ (**1**) and $Co(dmgH)_2L_2$ (**2**) (dmg = dimethylglyoximato; L = H_2O, CH_3CN, etc.) can, under H_2, transfer H· to stable radicals such as 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) (Scheme 1)[4] and generate radicals by H· transfer to activated

Scheme 1. Hydrogen Atom Transfer (HAT) from H_2 to Stable Free Radicals (X· = ·CAr_3 or TEMPO) Catalyzed by 1
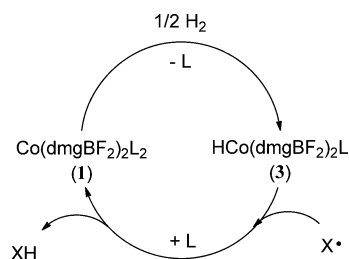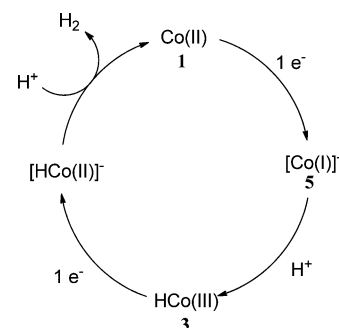
alkenes[4] and alkynes.[5] Cobaloxime **1** can thus generate radicals from α-substituted acrylate esters and catalyze radical cyclohydrogenation reactions.[4] The reaction of **1**, H_2 gas, and TEMPO is independent of [TEMPO], first order in H_2, and second order in **1**, suggesting that its rate-determining step involves one H_2 and 2 equiv of **1** (the forward reaction in eq 1).[4]

When **1** and **2** catalyze the production of H_2 from protons (Scheme 2),[2a,b,6] cobaloxime hydrides **3** and **4** have been proposed as key intermediates, although they have never been directly observed during catalysis. Little is known about their structure, spectroscopy, and reactivity. During the photochemical protonation of $[Co(dmgBF_2)_2(CH_3CN)]^-$ (**5a**), Dempsey and Gray observed an absorbance at 405 nm attributable to **3a**.[6i] However, no other observation of **3** has

$$2 \;\; \underset{\text{1 (E = BF}_2)\;\;\text{2 (E = H)}}{\overset{}{\text{Co}}} \;\; \underset{- 2 L}{\overset{H_2}{\rightleftharpoons}} \;\; 2 \;\; \underset{\text{3 (E = BF}_2)\;\;\text{4 (E = H)}}{\overset{}{\text{Co}}} \qquad (1)$$

1 (E = BF_2)   **3** (E = BF_2)
2 (E = H)   **4** (E = H)
a (L = CH_3CN)   **a** (L = CH_3CN)
b (L = THF)   **b** (L = THF)
c (L = H_2O)   **c** (L = H_2O)

Scheme 2. Electrocatalytic Production of H_2 with 1

been reported. We have therefore attempted to determine the spectroscopic and thermodynamic properties (i.e., the pK_a, the bond dissociation free energy (BDFE), etc.) of the hydride of **1** in various solvents. In this paper, we report the behavior of **1** under relatively high hydrogen pressures (70 atm) and use our findings to assess other observations in the literature about the $1/H_2$ system.

When **1c** is dissolved in CH_3CN, it gives complex **1a**,[6c,7] with λ_{max} at 434 nm (ε = 3240 M^{-1} cm^{-1}). Under H_2 at a pressure of 70 atm at room temperature, its UV−vis spectrum changes slowly (24 h) but smoothly into one with a λ_{max} at 556 nm (7700 M^{-1} cm^{-1}), another at 627 nm (7460 M^{-1} cm^{-1}), and a small peak at 354 nm (Figure 1). The process is reversible: the original spectrum returns slowly (48 h) after release of the gas pressure.

We previously determined that the reaction of **1a** with H_2 is termolecular, with the hydride **3a** as the presumed product.[4] We have now quantified the $1a/H_2$ equilibrium with the Benesi−Hildebrand method, modified for a ternary equilibrium like that in eqs 2−4 (see the Supporting Information (SI) for the
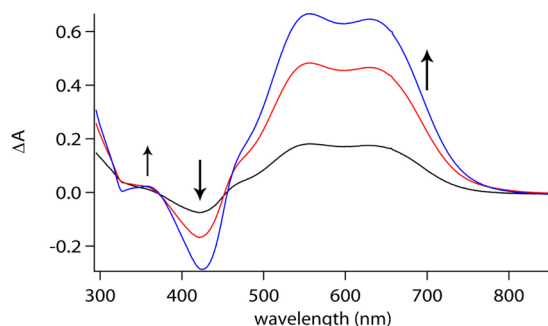
Figure 1. UV−vis difference spectra recorded after 20 min (black), 8 h (red), and 24 h (blue) for complex **1a** in CH_3CN pressurized with H_2 gas at 70 atm at room temperature.
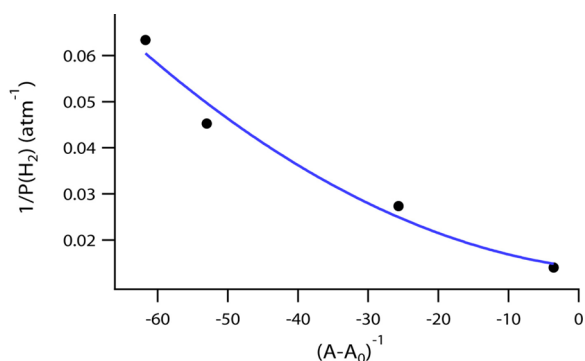

Figure 2. Plot of $P_{H_2}^{-1}$ vs the inverse of the change in absorbance of **1a** at 434 nm, $(A - A_0)^{-1}$, measured in CH_3CN under different H_2 pressures. The blue curve is a fit of the data to eq 4.

derivation).[8] By varying the hydrogen pressure and fitting the absorbance data to eq 4 (Figure 2), we obtain a $\Delta\varepsilon$ of 785 M^{-1} cm^{-1} and an equilibrium constant (K_{eq})[9] of 0.014(7) atm^{-1}. We can use this value of K_{eq} to estimate $\Delta G_{H_2} = 2.5(3)$ kcal/mol for eq 2. Use of the bond dissociation free energy (BDFE) of H_2 (103.6 kcal/mol)[10] with eq 6 gives the free energy change for eq 5 (the free energy of H· donation) as $\Delta G_H = 50.5(3)$ kcal/mol.[10]

From the thermodynamic cycle in eq 7,[10] we can estimate the pK_a of the product as 13.4 in CH_3CN using the ΔG_H from above and the potential of the $Co(I)^-/Co(II)$ couple (-0.93 V vs Fc/ Fc^+).[6d] Artero and Fontecave observed that protonation of **5a** during H_2 evolution occurred with a pK_a of 13.3, in good agreement with our estimate.[6d] This pK_a is consistent with the facts that (a) proton transfer from Et_3NH^+ ($pK_a = 18.8$)[11] to **5b** is slow and unfavorable (still incomplete after 8 s; Figures S11 and S12 in the SI) and (b) catalytic hydrogen evolution in CH_3CN with acids weaker than Et_3NH^+ does not involve protonation of **5a**.
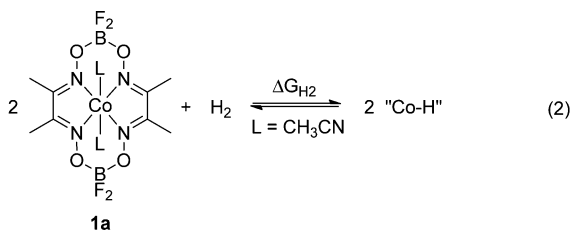
$$K_{eq} = \frac{[\text{"Co-H"}]^2}{[\mathbf{1a}]^2 P_{H_2}} \quad (3)$$

$$\frac{1}{P_{H_2}} = K_{eq}\left[\left(\frac{[\mathbf{1a}]_0 \Delta\varepsilon}{A - A_0}\right)^2 - 2\left(\frac{[\mathbf{1a}]_0 \Delta\varepsilon}{A - A_0}\right) + 1\right] \quad (4)$$
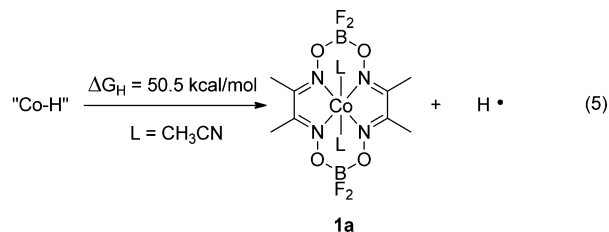
$$\Delta G_H = \frac{1}{2}[\Delta G(\text{H-H}) - \Delta G_{H_2}] \quad (6)$$

$$\text{BDFE} = 1.37 pK_a + 23.06 E_{ox}^\circ + 53.6 \text{ kcal/mol} \quad (7)$$

In order to characterize the product of the reaction shown in eq 2, we monitored the ^1H NMR spectrum of **1a** in CD_3CN under 70 atm H_2. No signal that could be attributed to Co−H was observed as far upfield as -25 ppm (Figure S8). Of course, residual coupling to the ^{59}Co could broaden the hydride signal and make it difficult to observe. We did see a new resonance (Figure 3; the full spectrum is shown in Figure S8) at 2.26 ppm
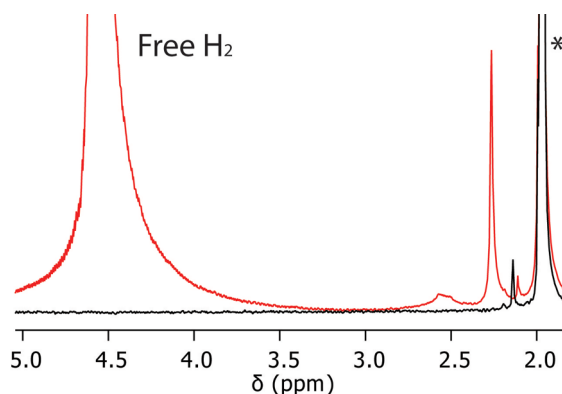

Figure 3. ^1H NMR spectra of a solution of **1a** in CD_3CN under 1 atm argon (black) and 70 atm H_2 (red) at 273 K (* = CHD_2CN).

and a new broad peak at 2.55 ppm.[12] Both peaks disappeared when the pressure was released. In the presence of exchangeable D^+, as in CD_3OD, the 2.55 ppm signal does not appear (Figure S9), suggesting that it belongs to an exchangeable proton. Both **1a** and **2a** catalyze H/D exchange between D_2 and H_2O (^1H NMR in Figure S5, ^2H NMR in Figure S6).

Thus, *the product of the reaction of* **1a** *with* H_2 *may not be the cobalt hydride* **3a**. That hydride was the first species observed by Dempsey and Gray[6i] after protonation of the anion **5a** with a photoacid, a species with a high absorbance at 405 nm. However, as Figure 1 shows, the reaction of **1a** with H_2 gives a species (**6a**) with little absorbance at 405 nm but peaks at 556 and 627 nm, a spectrum similar to that of the electrochemically generated Co(I) anion **5a** (Figure 4).

One possible structure for **6a**, which includes a Co(I) center and an exchangeable proton, is drawn in eq 8. A similar structure has been suggested by Artero and Fontecave for the mischaracterized "HCo(dmgH)$_2$PBu$_3$".[4,13] The fact that no increase in absorbance at 405 nm was observed during the reaction shown in eq 2 in CH_3CN suggests that H_2 activation is rate-determining in the formation of **6a** from **1a** and H_2, a
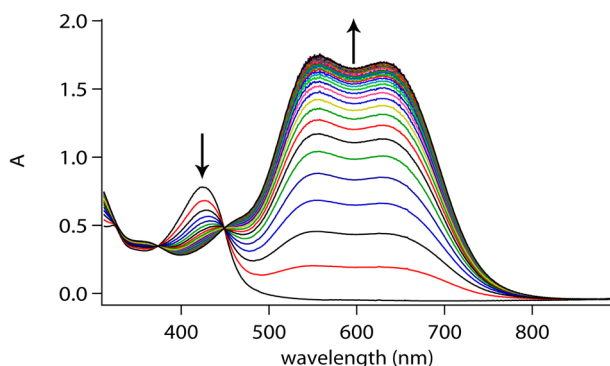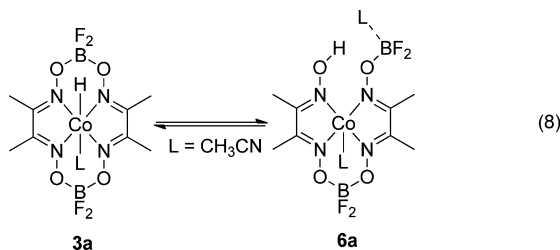
Figure 4. Spectroelectrochemistry of the reduction of **1a** in CH_3CN at an applied potential of -1.0 V vs Ag wire. The solution contained 0.1 M NBu_4BF_4 as an electrolyte.

conclusion supported by measurements of the rate at which **1a** reacts with H_2.[7]

The structure drawn for **6a** would have four inequivalent methyls, although we observed only one peak in the ^1H NMR spectrum that can be so assigned (the one at 2.26 ppm in Figure 3). However, it is possible that the proton causing the inequivalence could undergo proton-coupled electron transfer (PCET) from **6a** to **1a** in solution, causing the methyl groups to exchange with each other on the NMR time scale (Scheme 3).

Scheme 3. Possible Mechanism of PCET between 6a and 1a (Individual Molecules Are Differentiated by Color)
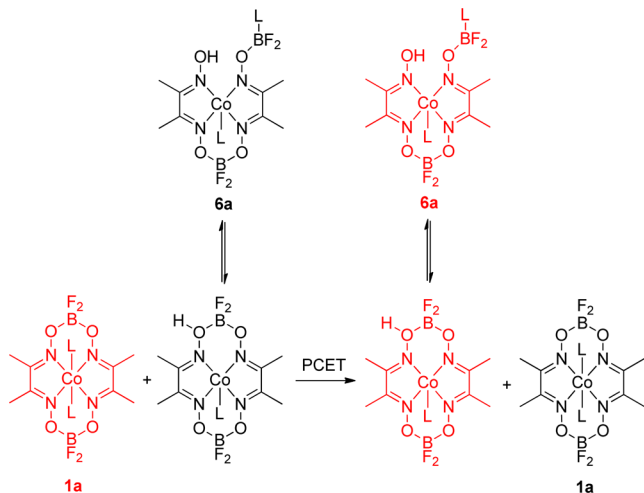
This would produce a spectrum with only one methyl peak. When we lowered the temperature of the pressurized sample (Figure S10), the pressure of H_2 and thus the amount of H_2 dissolved in the solution decreased (see the discussion in the SI and Figure S10b), and the chemical shift of the supposed methyl signal increased. Less dissolved H_2 presumably increases the ratio

of **1a** to **6a** in solution, causing simultaneous broadening and shifting of the methyl resonance while the position and shape of the proton signal at 2.55 ppm remain roughly the same. This behavior was also seen in the ^1H NMR spectra of mixtures of $CpCr(CO)_3H$ and $CpCr(CO)_3\cdot$.[14] Thus, we can tentatively assign the signal at 2.26 ppm as the Me signal of complex **6a** and the signal at 2.55 ppm as the signal of an exchangeable proton on the ligand, possibly an OH.

We also monitored the UV−vis spectrum of a solution of $Co(dmgBF_2)_2(THF)_2$ (**1b**) under 70 atm H_2 in THF (Figure 5).
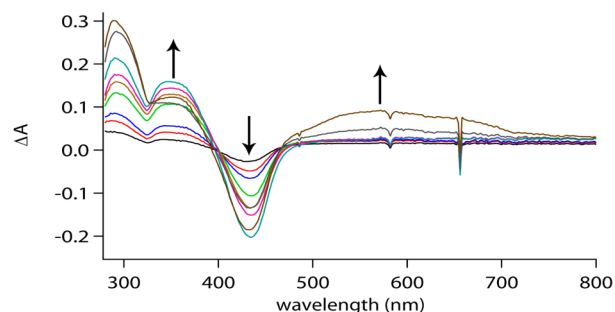

Figure 5. UV−vis difference spectra recorded over 24 h for complex **1b** in THF pressurized with 70 atm H_2 gas at room temperature.

Over the course of 8 h we observed bleaching of the signal at 430 nm in conjunction with the appearance of new peaks at 354 and 305 nm. After 8 h, a third species grew in at 580 nm as the 354 nm absorbance decreased. The absorbance of the intermediate in THF (354 nm) is similar to that observed for Co-$(dmgBF_2)_2(CH_3CN)Me$,[6i] similar to the spectrum calculated for **3a**,[15] and similar to the absorbance observed by Dempsey and Gray,[6i] which they attributed to **3**. The intermediate absorbing at 354 nm in THF is likely the hydride complex **3b**, presumably the initial product of the termolecular reaction with hydrogen.[16] We could not observe a hydride resonance in the ^1H NMR spectra in THF because of the lower solubility of **1b** in that solvent. However, despite the similarities to previous observations, the UV−vis data by itself is not conclusive enough to rule out other species that could have similar absorbances (e.g., $Co(H_2)$-$(dmgBF_2)_2(THF)$). A similar H_2 complex of $CpCr(CO)_3\cdot$ was postulated to be an intermediate in the termolecular activation of H_2 by $[CpCr(CO)_3]_2$, but density functional theory calculations showed that the H_2 was very weakly bound to the metal center.[16] The subsequent absorbance at 580 nm may be due to a tautomerized product similar to **6a**. Changing the axial ligand from CH_3CN to THF may change the pK_a of the hydride (**3a**/**3b**) enough to slow its tautomerization.

A tautomerized product like **6a** could explain some observations in the hydrogen evolution literature that were originally attributed to hydride **3a**. Compound **6** may be the kinetic product of protonation of **5** under certain conditions. Upon rapid mixing of **5c** with acid, Bakac and co-workers observed an intermediate with λ_{max} at 610 nm, similar to that of **5c** but less intense ($10^4\ M^{-1}\ cm^{-1}$).[6f] They attributed this feature to the hydride **3c**, but given the spectrum observed for **3a** by Dempsey and Gray (high absorbance at 405 nm), we question Bakac's assignment and propose that under the conditions of Bakac's experiment the ligand-protonated complex **6c** might be formed instead of **3c** (the spectra are quite similar). Bakac's experiment was done with excess citrate present, which could coordinate to the boron and make the ligand's oxygen available for protonation. The citrate could also catalyze the proton

transfer necessary for the conversion of **6a** to **3a** in the way observed by Bullock and DuBois for $[Ni(P_2N)_2]^{2+}$ complexes.[17]

In summary, in CH_3CN under high pressures of H_2, cobaloxime **1a** is converted to a product **6a** having a Co(I) center and an exchangeable proton, which is possibly a tautomer of the hydride **3a**. In THF, however, the major product under high hydrogen pressures may well be the hydride **3b**. The free energy of H· donation and the pK_a of **6a** are 50.5 kcal/mol and 13.4, respectively. It is possible that the same hydride tautomer is an intermediate in the mechanism of electrocatalytic hydrogen gas production by cobaloximes. It may be the cause of the difficulty in characterizing cobaloxime hydrides in these reactions.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Experimental details, NMR data, UV−vis data, derivation of eq 4, and stopped-flow data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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