

# The Reaction of Cobaloximes with Hydrogen: Products and Thermodynamics

Deven P. Estes<sup>†</sup>, David C. Grills<sup>‡</sup>, Jack R. Norton<sup>†\*</sup>

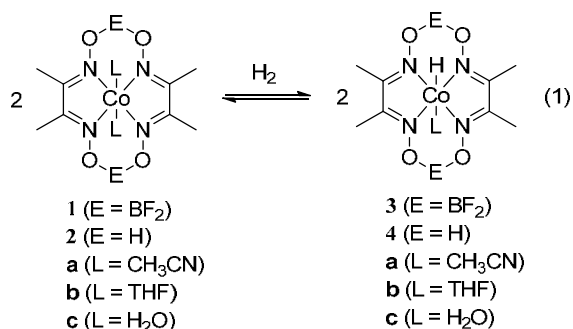
<sup>†</sup>Department of Chemistry, Columbia University, 3000 Broadway, New York, NY, 10027

<sup>‡</sup>Chemistry Department, Brookhaven National Laboratory, P.O. Box 5000, Upton, NY 11973-5000

## Supporting Information Placeholder

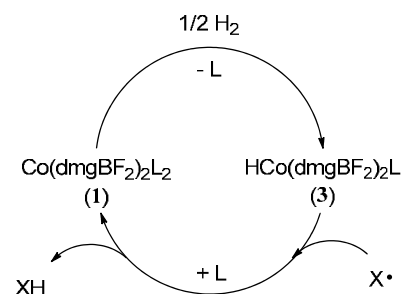
**ABSTRACT:** A cobalt hydride has been proposed as an intermediate in many reactions of the  $\text{Co}(\text{dmgBF}_2)_2\text{L}_2$  system, but its observation has proven difficult. We have observed the UV-vis spectra of  $\text{Co}(\text{dmgBF}_2)_2\text{L}_2$  (**1**) in  $\text{CH}_3\text{CN}$  under hydrogen pressures up to 70 atm. A  $\text{Co}(\text{I})$  compound (**6**), with an exchangeable proton, is eventually formed. We have determined the bond dissociation free energy and  $\text{p}K_{\text{a}}$  of the new O–H bond in **6** to be 50.5 kcal/mol and 13.4, respectively, in  $\text{CH}_3\text{CN}$ , matching previous reports.

In addition to being functional  $\text{B}_{12}$  models<sup>1</sup> and catalyzing the production of hydrogen from protons and electricity,<sup>2</sup> cobaloximes catalyze  $\text{H}\cdot$  transfer from  $\text{H}_2$ .<sup>3</sup>  $\text{Co}(\text{dmgBF}_2)_2\text{L}_2$  (**1**) and  $\text{Co}(\text{dmgH})_2\text{L}_2$  (**2**) (dmg = dimethylglyoximate; L =  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{CN}$ , etc.) can, under  $\text{H}_2$ , transfer  $\text{H}\cdot$  to stable radicals such as TEMPO (Scheme 1)<sup>4</sup> and generate radicals by  $\text{H}\cdot$  transfer to activated alkenes<sup>4</sup> and alkynes.<sup>5</sup> The cobaloxime **1** can thus generate radicals from  $\alpha$ -substituted acrylate esters, and catalyze radical cyclohydrogenation reactions.<sup>4</sup> The reaction of **1**,  $\text{H}_2$  gas, and TEMPO is independent of  $[\text{TEMPO}]$ , first order in  $\text{H}_2$ , and second order in **1**, suggesting that its rate-determining step involves an  $\text{H}_2$  and two equiv of **1** (the forward reaction of eq 1).<sup>4</sup>



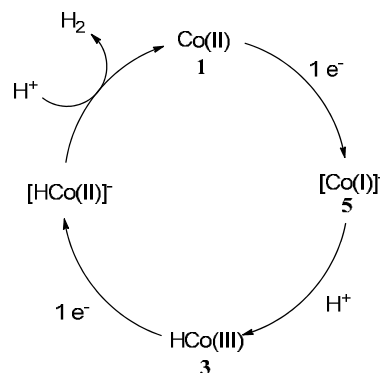
When **1** and **2** catalyze the production of  $\text{H}_2$  from protons (Scheme 2),<sup>2a, b, 6</sup> cobaloxime hydrides **3** have been proposed as key intermediates, although they have never been directly observed. Little is known about their structure, spectroscopy, and reactivity.

**Scheme 1.** Hydrogen atom transfer (HAT) from  $\text{H}_2$  to stable free radicals ( $\text{X}\cdot = \cdot\text{CAR}_3$  or TEMPO) catalyzed by **1**

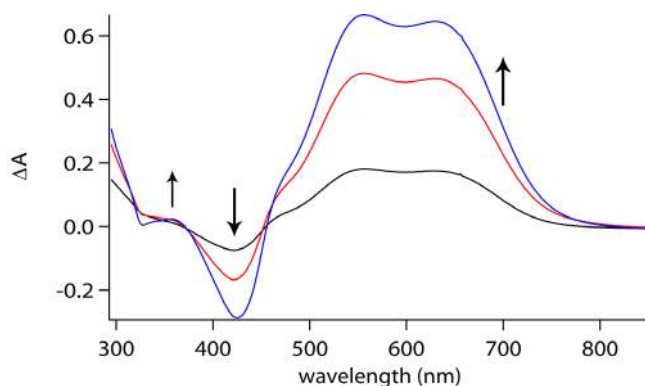


We have therefore attempted to determine the spectroscopic and thermodynamic properties (i.e. the  $\text{p}K_{\text{a}}$ , the bond dissociation free energy (BDFE), etc.) of the hydrides of **1** in various solvents. In this paper, we report the behavior of **1** under relatively high hydrogen pressures (70 atm) and use our findings to assess other observations in the literature about the  $1/\text{H}_2$  system.

**Scheme 2.** Electrocatalytic production of  $\text{H}_2$  with **1**

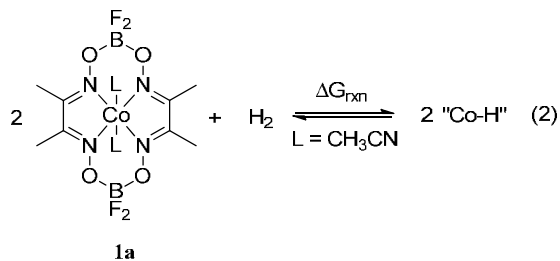


When **1c** is dissolved in  $\text{CH}_3\text{CN}$  it gives complex **1a**,<sup>6c, 7</sup> with  $\lambda_{\text{max}}$  at 434 nm ( $3240 \text{ M}^{-1}\text{cm}^{-1}$ ). Under 70 atm of  $\text{H}_2$  at room temperature its UV-vis spectrum changes slowly (24 h) but smoothly (Figure 1) into one with a  $\lambda_{\text{max}}$  at 556 nm ( $7700 \text{ M}^{-1}\text{cm}^{-1}$ ), another at 627 nm ( $7460 \text{ M}^{-1}\text{cm}^{-1}$ ), and a small peak at 354 nm. The process is reversible; the original spectrum returns slowly (48 h) after release of the gas pressure.



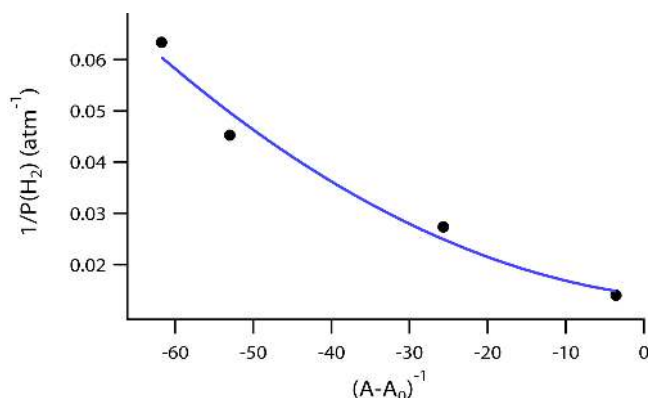
**Figure 1.** UV/vis difference spectra recorded over the course of 24 h for complex **1a** in CH<sub>3</sub>CN, pressurized with 70 atm of H<sub>2</sub> gas at room temperature.

We previously determined that the reaction of **1a** with H<sub>2</sub> is termolecular, with the hydride **3a** as the presumed product.<sup>4</sup> We have now quantified the **1a**/H<sub>2</sub> equilibrium with the Benesi–Hildebrand method, modified for a ternary equilibrium like that in eqs 2–4 (see the Supporting Information for derivation).<sup>8</sup> By varying the hydrogen pressure and fitting the absorbance data to eq 4 (Figure 2) we obtain a  $\Delta\epsilon$  of 785 M<sup>-1</sup> cm<sup>-1</sup> and an equilibrium constant ( $K_{eq}$ )<sup>9</sup> of 0.014(7) atm<sup>-1</sup>.



$$K_{eq}(\text{atm}^{-1}) = \frac{[\text{Co-H}]^2}{[\mathbf{1a}]^2 P_{H_2}} \quad (3)$$

We can use this value of  $K_{eq}$  to estimate a  $\Delta G_{rxn} = 2.5(3)$  kcal/mol for eq 2. Use of the bond dissociation free energy (BDFE) of H<sub>2</sub> (103.6 kcal/mol)<sup>10</sup> with eq 6 gives the free energy change of eq 5,  $\Delta G_H = 50.5(3)$  kcal/mol.<sup>10</sup>

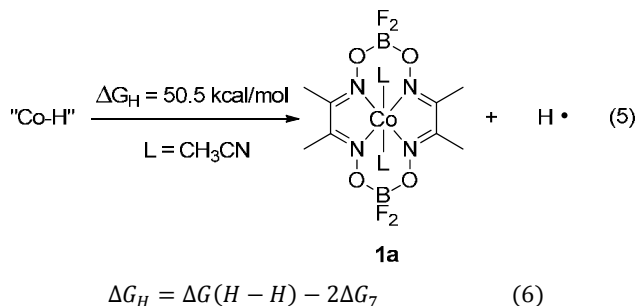


**Figure 2.** Plot of  $P_{H_2}^{-1}$  vs the inverse of the change in absorbance of **1a** at 434 nm  $(A-A_0)^{-1}$ , measured in CH<sub>3</sub>CN under different H<sub>2</sub> pressures. The blue curve is a fit of the data to eq 4.

From the thermodynamic cycle in eq 7<sup>10</sup> we can estimate the  $pK_a$  of the product as 13.4 in CH<sub>3</sub>CN using the  $\Delta G_H$  from above and the potential of the Co(I)–/Co(II) couple ( $-0.93$  V vs Fc/Fc<sup>+</sup>).<sup>6d</sup> Artero and Fontecave observed that the protona-

tion of **5a** during H<sub>2</sub> evolution occurred with a  $pK_a$  of 13.3, in good agreement with our estimate.<sup>6d</sup> This  $pK_a$  is consistent with the facts that (a) proton transfer from HNEt<sub>3</sub><sup>+</sup> ( $pK_a = 18.8$ )<sup>11</sup> to **5b** is slow and unfavorable (still incomplete after 8 s, Figures S11 and S12), and (b) catalysis of hydrogen evolution by **1a** does not occur with acids weaker than HNEt<sub>3</sub><sup>+</sup>.

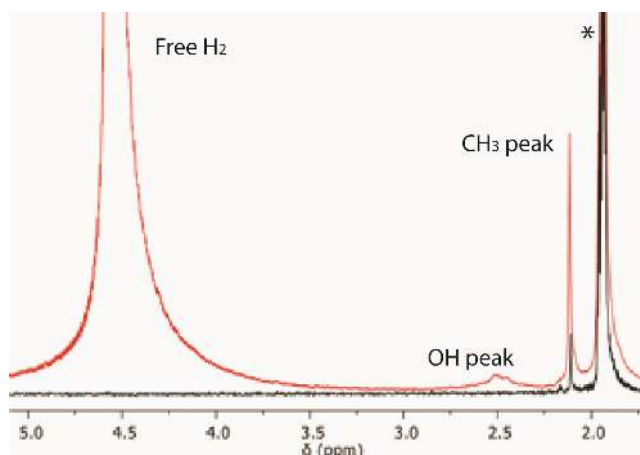
$$\frac{1}{P_{H_2}} = K_{eq} \left( \frac{[\mathbf{1a}]_0^2 \Delta\epsilon^2 \left( \frac{1}{A-A_0} \right)^2}{-2[\mathbf{1a}]_0 \Delta\epsilon \left( \frac{1}{A-A_0} \right) + 1} \right) \quad (4)$$



$$BDFE = 1.37pK_a + 23.06E_{ox}^0 + 53.6 \frac{\text{kcal}}{\text{mol}} \quad (7)$$

In order to characterize the product of reaction 2, we monitored the <sup>1</sup>H NMR spectrum of **1a** in CD<sub>3</sub>CN under 70 atm of H<sub>2</sub>. No signal that could be attributed to Co–H was observed, as far upfield as  $\delta = -25$  ppm (see Figure S8). Of course, residual coupling to the <sup>59</sup>Co could broaden the hydride signal and make it difficult to observe. We did see a new resonance (see Figure 3, the full spectrum is in Figure S8) at  $\delta$  2.06 ppm and a new broad peak at  $\delta$  2.50 ppm.<sup>12</sup> The peak at  $\delta$  2.50 ppm disappeared when the pressure was released. In the presence of exchangeable D<sup>+</sup>, as in CD<sub>3</sub>OD, the  $\delta$  2.50 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<sub>2</sub> and H<sub>2</sub>O (<sup>1</sup>H NMR in Figure S5, <sup>2</sup>H NMR in Figure S6).

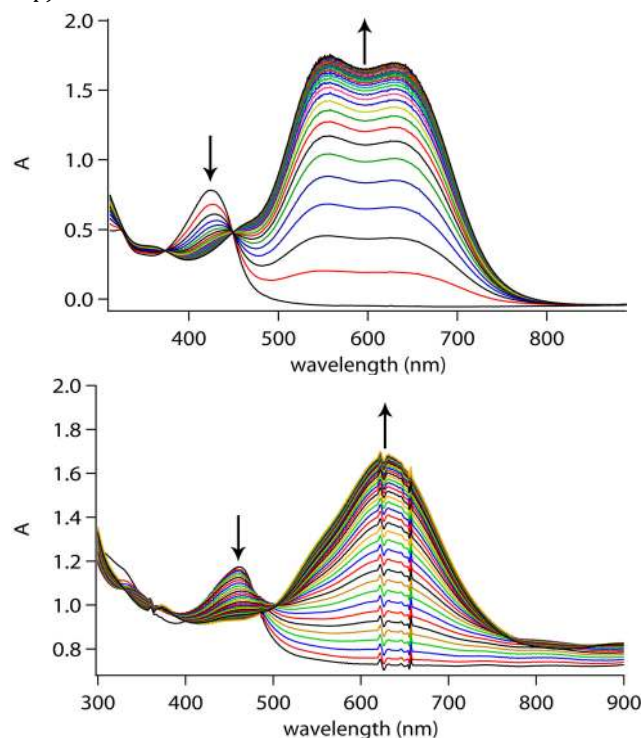
6i



**Figure 3.** <sup>1</sup>H NMR spectra of **1a** in CD<sub>3</sub>CN under 1 atm of argon (black) and 70 atm of H<sub>2</sub> (red) (\*CHD<sub>2</sub>CN)

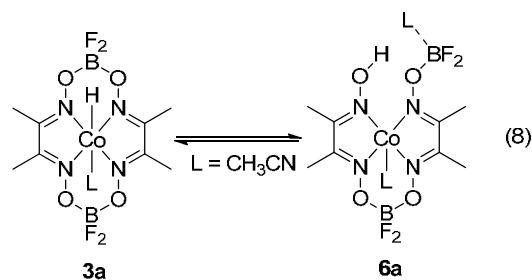
Thus *the product of the reaction of 1a with H<sub>2</sub> may not be the cobalt hydride 3a*. That hydride is probably the first species observed by Dempsey and Gray after protonation of the anion **5a** with a photoacid<sup>6i</sup> — a species with a high absorb-

ance at 405 nm. However, as Figure 1 shows, the reaction of **1a** with H<sub>2</sub> 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, top).



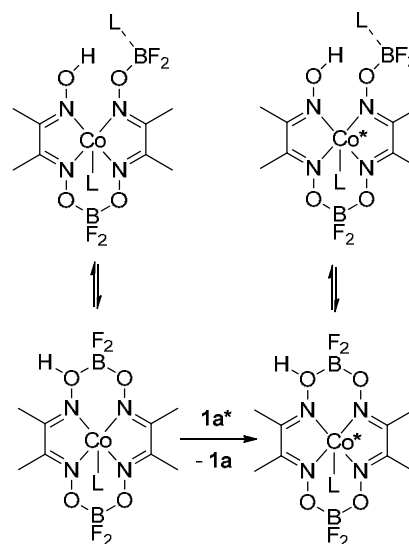
**Figure 4.** Spectroelectrochemistry of the reduction of **1a** in CH<sub>3</sub>CN (top) and **1b** in THF (bottom) at an applied potential of -1.0 V vs Ag wire. Solutions contain 0.1 M NBu<sub>4</sub>BF<sub>4</sub> as an electrolyte.

One possible structure for **6a** — which includes a Co(I) and an exchangeable proton — is drawn in eq 8 below. A similar structure has been suggested by Artero and Fontecave for the mischaracterized “HCo(dmgH)<sub>2</sub>PBu<sub>3</sub>”.<sup>4,13</sup> The fact that no hydride resonance is observed during reaction 2 in CH<sub>3</sub>CN suggests that H<sub>2</sub> activation is rate determining in the formation of **6a** from **1a** and H<sub>2</sub>, a conclusion supported by measurements of the rate at which **1a** reacts with H<sub>2</sub>.<sup>7</sup>



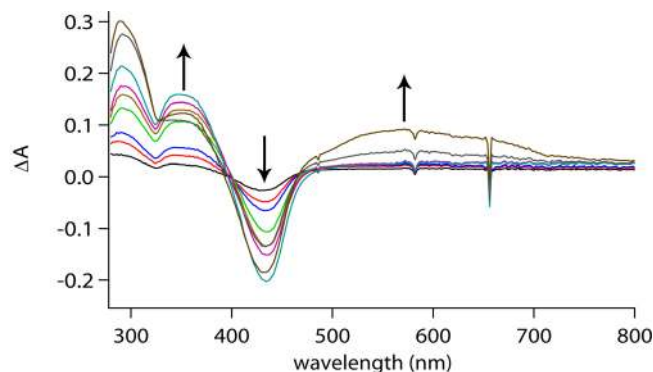
The structure drawn for **6a** would have four inequivalent methyls, although we observe only one peak (the one at  $\delta$  2.06 ppm) in the <sup>1</sup>H NMR that can be so assigned. However, it is possible that the proton causing the inequivalence could undergo a proton-coupled electron transfer (PCET) from **6a** to **1a** in solution, causing the methyl groups to exchange with each other on the NMR time scale (Scheme 3). This would produce a spectrum with only one methyl peak. When we lower the temperature of the pressurized sample (Figure S10), the pressure of H<sub>2</sub>, and thus the amount of H<sub>2</sub> dissolved in the solution, decreases (as indicated by the intensity of the

free H<sub>2</sub> peak in the NMR), and the chemical shift of the supposed methyl signal at 2.06 ppm increases. This 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 at 2.5 ppm remains the same.



**Scheme 3.** Possible mechanism of PCET between **6a** and **1a**.

We also monitored the UV-vis spectrum of a solution of Co(dmgBF<sub>2</sub>)<sub>2</sub>(THF)<sub>2</sub> (**1b**) under 70 atm H<sub>2</sub> in THF (Figure 5). 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.



**Figure 5.** UV-vis difference spectra recorded over the course of 24 h for complex **1b** in THF pressurized with 70 atm of H<sub>2</sub> gas at room temperature.

The absorbance of the intermediate in THF (354 nm) is similar to that observed for Co(dmgBF<sub>2</sub>)<sub>2</sub>(CH<sub>3</sub>CN)Me,<sup>6i</sup> similar to the spectrum calculated for **3a**,<sup>14</sup> and similar to the absorbance observed by Dempsey and Gray which they attributed to **3**.<sup>6i</sup> We believe that in THF the intermediate at 354 nm is the hydride complex **3b** — presumably the initial product of the termolecular reaction with hydrogen.<sup>15</sup> We have not been able to look for a hydride resonance in the NMR spectra in THF because of the low solubility of **1b** in that solvent. The subsequent 580 nm absorbance may be due to a tautomerized product, similar to **6a**. This 580 nm peak is shifted relative to the 630 nm peak seen for the Co(I) anion **5b** (Figure 4, bottom). This could be the result of different populations of the open and closed forms of **6b** shown in Scheme 3. Changing the

axial ligand from CH<sub>3</sub>CN to THF may change the p*K*<sub>a</sub> of the hydride (**3**) enough to slow down 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**. Upon rapid mixing of **5c** with acid, Bakac and co-workers observed an intermediate with λ<sub>max</sub> at 610 nm, similar to that of **5c** but less intense (10<sup>4</sup> M<sup>-1</sup>cm<sup>-1</sup>).<sup>6f</sup> They attributed this feature to the hydride **3c**, but given the spectrum observed for the hydride **3a** by Dempsey and Gray (high absorbance at 405 nm), we question this assignment, and propose that the Bakac spectrum may be due to the ligand-protonated complex **6c** (the spectra are quite similar). However, during the photochemical protonation of **5a**, Gray and coworkers observed direct protonation of the metal.<sup>6i</sup> 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 Bullock and DuBois observe for [Ni(P<sub>2</sub>N)<sub>2</sub>]<sup>2+</sup> complexes.<sup>16</sup>

In summary, in CH<sub>3</sub>CN under large pressures of H<sub>2</sub>, 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**. This difference in reactivity is most likely due to the hydride **3b** being less acidic than **3a**. The free energy of H• donation and the p*K*<sub>a</sub> of **6a** are 50.5 kcal/mol and 13.4, respectively. However, the assignment of the position of the proton on the ligand cannot conclusively be determined from the data presented.

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 detail, NMR data, UV-vis data, derivation of eq 6, stopped flow data.

## AUTHOR INFORMATION

### Corresponding Author

\*3000 Broadway MC 3102, New York, NY 10027,  
(212)854-7649, jrn11@columbia.edu

The authors declare no competing financial interests.

## ACKNOWLEDGMENT

Support for this work was provided by the Department of Energy (DE-FG02-97ER14807). We also thank Boulder Scientific and OFS Fitel for support. D.E. was 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, administered by ORISE-ORAU under contract no. DE-AC05-06OR23100. The work at BNL was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences, under contract # DE-AC02-98CH10886. We would like to thank Etsuko Fujita and Andreja Bakac for helpful discussions.

## REFERENCES

- (a) Schrauzer, G. N.; Sibert, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 1022; (b) Schrauzer, G. N. *Inorg. Synth.* **1968**, *11*, 61.
- (a) Razavet, M.; Artero, V.; Fontecave, M. *Inorg. Chem.* **2005**, *44*, 4786; (b) Hu, X.; Cossairt, B. M.; Brunschwig, B. S.; Lewis, N. S.; Peters, J. C. *Chem. Commun.* **2005**, 4723; (c) Chao, T.-H.; Espenson, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 129.
- (a) Simándi, L. I.; Szeverényi, Z.; Budó-Záhonyi, É. *Inorg. Nucl. Chem. Letters* **1975**, *11*, 773; (b) Simándi, L. I.; Budó-Záhonyi, É.; Szeverényi, Z. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 237; (c) Simándi, L. I.; Budó-Záhonyi, É.; Szeverényi, Z.; Németh, S. *J. Chem. Soc., Dalton Trans.* **1980**, 276.
- Li, G.; Han, A.; Pulling, M. E.; Estes, D. P.; Norton, J. R. *J. Am. Chem. Soc.* **2012**, *134*, 14662.
- Estes, D. P.; Norton, J. R.; Jockusch, S.; Sattler, W. *J. Am. Chem. Soc.* **2012**, *134*, 15512.
- (a) Du, P.; Knowles, K.; Eisenberg, R. *J. Am. Chem. Soc.* **2008**, *130*, 12576; (b) Du, P.; Schneider, J.; Luo, G.; Brennessel, W. W.; Eisenberg, R. *Inorg. Chem.* **2009**, *48*, 4952; (c) Hu, X. L.; Brunschwig, B. S.; Peters, J. C. *J. Am. Chem. Soc.* **2007**, *129*, 8988; (d) Baffert, C.; Artero, V.; Fontecave, M. *Inorg. Chem.* **2007**, *46*, 1817; (e) Fihri, A.; Artero, V.; Razavet, M.; Baffert, C.; Leibl, W.; Fontecave, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 564; (f) Szajna-Fuller, E.; Bakac, A. *Eur. J. Inorg. Chem.* **2010**, 2488; (g) Dempsey, J. L.; Brunschwig, B. S.; Winkler, J. R.; Gray, H. B. *Acc. Chem. Res.* **2009**, *42*, 1995, and references therein; (h) Dempsey, J. L.; Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **2010**, *132*, 1060; (i) Dempsey, J. L.; Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **2010**, *132*, 16774, and references therein.
- Li, G.; Estes, D. P.; Norton, J. R.; Ruccolo, S.; Sattler, A.; Sattler, W. *Inorg. Chem.* **2014**, *ASAP*.
- Drago, R. S., *Physical Methods for Chemists, 2nd Ed.* Saunders College Publishing: 1992.
- Purwanto; Deshpande, R. M.; Chaudhari, R. V.; Delmas, H. *J. Chem. Eng. Data* **1996**, *41*, 1414. We calculated *K*<sub>eq</sub> using a standard state of

1M in H<sub>2</sub>. The Henry's law constant for H<sub>2</sub> in acetonitrile is 284.1 atm M<sup>-1</sup>.

10. Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287.

11. Kaljurand, I.; Kutt, A.; Soovali, L.; Rodima, T.; Maemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2005**, *70*, 1019.

12. The extremely large absorbance of H<sub>2</sub> in the NMR spectrum causes truncation errors in the FID of these spectra. This produces a "rippling" effect radiating from the edges of the H<sub>2</sub> peak. This causes large errors in the integral of the broad peak at 2.50 ppm and thus the ratio of the peak at 2.5 ppm to that at 2.06 ppm, with observed ratios being between 1:4 and 1:15. The spectrum with the least H<sub>2</sub> (at 243 K) had the least truncation error and with the integral of the peak at 2.50 ppm being 0.82.

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

14. Muckerman, J. T.; Fujita, E. *Chem. Commun.* **2011**, *47*, 12456.

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

16. Helm, M. L.; Stewart, M. P.; Bullock, R. M.; DuBois, M. R.; DuBois, D. L. *Science* **2011**, *333*, 863.

