

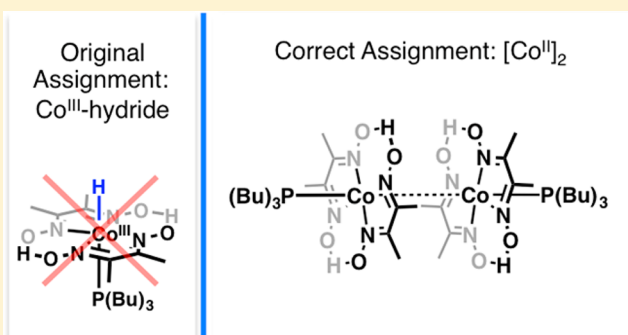
# The Cobalt Hydride that Never Was: Revisiting Schrauzer's "Hydridocobaloxime"

David C. Lacy, Gerri M. Roberts, and Jonas C. Peters\*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

**S** Supporting Information

**ABSTRACT:** Molecular cobalt-dmg (dmg = dimethylglyoxime) complexes are an important class of electrocatalysts used heavily in mechanistic model studies of the hydrogen evolution reaction (HER). Schrauzer's early isolation of a phosphine-stabilized "[H-Co<sup>III</sup>(dmgH)<sub>2</sub>P(*n*Bu)<sub>3</sub>]" complex has long provided circumstantial support for the plausible intermediacy of Co(III)-H species in HER by cobaloximes in solution. Our investigation of this complex has led to a reassignment of its structure as [Co<sup>II</sup>(dmgH)<sub>2</sub>P(*n*Bu)<sub>3</sub>], a complex that contains no hydride ligand and dimerizes to form an unsupported Co–Co bond in the solid state. A paramagnetic *S* = 3/2 impurity that forms during the synthesis of [Co<sup>II</sup>(dmgH)<sub>2</sub>P(*n*Bu)<sub>3</sub>] when exposed to adventitious oxygen has also been characterized. This impurity features a <sup>1</sup>H NMR resonance at –5.06 ppm that was recently but erroneously attributed to the hydride resonance of "[H-Co<sup>III</sup>(dmgH)<sub>2</sub>P(*n*Bu)<sub>3</sub>]". We draw attention to this reassignment because of its relevance to cobaloxime hydrides and HER catalysis and because Schrauzer's "hydridocobaloxime" is often cited as the primary example of a *bona fide* hydride that can be isolated and characterized on this widely studied HER platform.



## INTRODUCTION

Molecular cobalt complexes supported by nitrogen donor ligands have been widely studied as mechanistic model systems for hydrogen evolution catalysis in organic and aqueous solvents.<sup>1</sup> Regardless of the intimate pathway(s) by which H–H bond formation can occur in these various Co systems, a Co(III)-H species is often invoked as a central intermediate in mechanistic studies.<sup>1,2</sup> Cobalt(III) hydrides of these types are especially hard to directly characterize for highly active hydrogen evolution reaction (HER) systems. Comparatively inactive Co(III)-H complexes, for example when stabilized by phosphine ligands, have been reported in several instances,<sup>3</sup> and efforts to study their chemical properties have been the focus of several research endeavors.<sup>4</sup> A particularly significant Co(III)-H species is the putative "[P-Co<sup>III</sup>H]" compound, [H-Co<sup>III</sup>(dmgH)<sub>2</sub>P(*n*Bu)<sub>3</sub>] (dmg<sup>2-</sup> = dimethylglyoxime), originally reported in 1971 by Schrauzer and Holland.<sup>5</sup> Cobaloxime complexes are the most mechanistically well-studied Co HER catalysts, and Schrauzer's hydridocobaloxime, "[P-Co<sup>III</sup>H]", has long provided circumstantial synthetic support for the plausible intermediacy of a Co(III)-H in HER mediated by cobaloximes.<sup>1b,d,e,k,2c,d,3b,4c,6</sup> However, Schrauzer's original characterization data for "[P-Co<sup>III</sup>H]" were unusual in that the <sup>1</sup>H NMR resonance of the Co(III)-H in *n*-hexane was reported at +6 ppm (vs TMS).<sup>5</sup> This downfield chemical shift is atypical of d<sup>6</sup> transition-metal hydrides,<sup>7</sup> and in this context Artero, Fontecave, and co-workers published a DFT study of the proposed "[P-Co<sup>III</sup>H]" hydride complex that predicted a <sup>1</sup>H

NMR Co(III)-H resonance in the more typical upfield region near –5 ppm.<sup>8</sup> This study also described <sup>1</sup>H NMR data in *d*<sub>3</sub>-MeCN showing a resonance at –5.06 ppm for a sample of "[P-Co<sup>III</sup>H]" prepared by the method of Schrauzer. Based on these findings, Artero, Fontecave, and co-workers concluded that the complex "[P-Co<sup>III</sup>H]" was correctly formulated as a Co(III)-H species, as assigned by Schrauzer, but nonetheless warranted reassignment of its <sup>1</sup>H NMR spectrum.

As part of our ongoing interest in mechanistic aspects of Co-glyoxime HER reactivity, we sought to investigate "[P-Co<sup>III</sup>H]" by electrochemical means. Upon investigating this material, several inconsistencies with the isolated compound and its assignment as a Co(III)-H were revealed that led us to question the assignment of "[P-Co<sup>III</sup>H]" as a hydride species. Herein, we provide data that unequivocally show that this putative "[P-Co<sup>III</sup>H]" species does not contain a hydride ligand, but instead exists as a monomer/dimer equilibrium in solution between the Co(II) monomer [P-Co<sup>II</sup>] and the dimer [P-Co<sup>II</sup>]<sub>2</sub>. The <sup>1</sup>H NMR resonance at –5.06 ppm attributed to the Co(III)-H resonance of "[P-Co<sup>III</sup>H]" instead arises from a paramagnetic impurity that we have now isolated and characterized. This result, along with recent work from the Norton laboratory (*vide infra*), removes much of the most compelling experimental evidence for the direct observation of hydridocobaloxime.

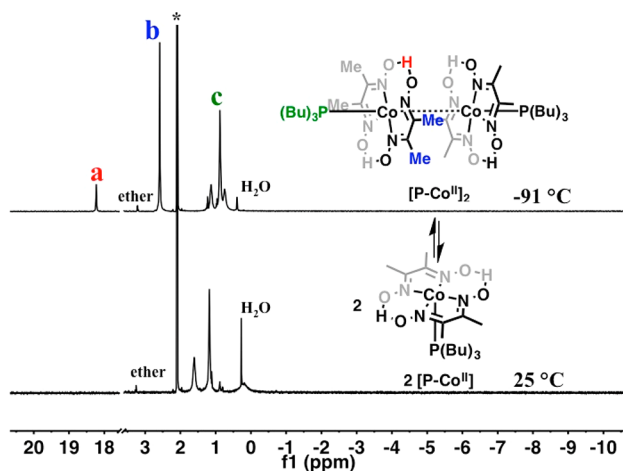
Received: February 18, 2015

Published: March 23, 2015

## RESULTS AND DISCUSSION

**Synthesis of the Putative Hydridocobaloxime.** Our investigation began with the attempted synthesis of the putative “[P-Co<sup>III</sup>H]” complex by following the procedures outlined in the literature.<sup>5,8</sup> The synthesis involves reduction of the [Cl–Co<sup>III</sup>(dmgH)<sub>2</sub>P(*n*Bu)<sub>3</sub>] precursor ([P-Co<sup>III</sup>Cl]) suspended in a 1:1 MeOH:H<sub>2</sub>O (pH 7 phosphate buffer) solution with slow addition of solubilized NaBH<sub>4</sub> in water under an inert atmosphere. The reaction with NaBH<sub>4</sub> is immediate and forms an inky dark-purple solid. As will be described below, the purple product is the neutral Co(II) dimer complex [Co<sup>II</sup>(dmgH)<sub>2</sub>P(*n*Bu)<sub>3</sub>]<sub>2</sub> ([P-Co<sup>II</sup>]<sub>2</sub>) rather than the previously assigned Co(III)-H.

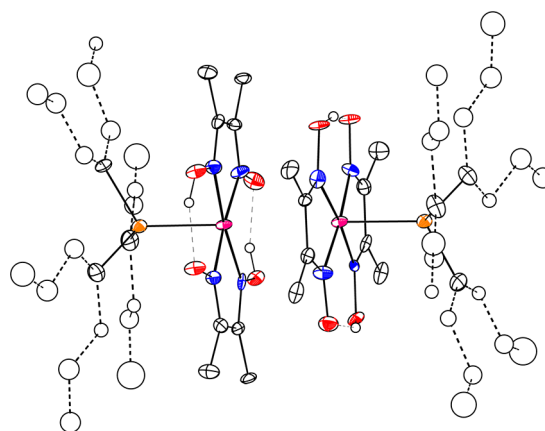
The room-temperature <sup>1</sup>H NMR spectrum of the purple product in *d*<sub>8</sub>-toluene (or *d*<sub>6</sub>-benzene) contains three broad resonances near 1 ppm (the exact position depends on concentration and temperature). In *d*<sub>8</sub>-toluene, these three resonances sharpen upon cooling to –91 °C (27H, P-(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>) along with the appearance of two new resonances at 18.23 ppm (2H, NOH) and at 2.59 ppm (12H, CMe). As seen in Figure 1, the <sup>1</sup>H NMR spectrum of the



**Figure 1.** <sup>1</sup>H NMR spectrum of 3 mM [P-Co<sup>II</sup>]<sub>2</sub> (i.e., the isolated purple compound from NaBH<sub>4</sub> reduction, previously assigned as “[P-Co<sup>III</sup>H]”) collected at –91 °C (top) and 25 °C (bottom) in *d*<sub>8</sub>-toluene (\*). All nonsolvent resonances in the spectrum between 45 to –45 ppm are displayed. See Figure S1 for full variable-temperature data and <sup>31</sup>P NMR at –91 °C.

isolated compound does not contain a resonance upfield of 0 ppm that might be attributed to a hydride resonance. The <sup>31</sup>P NMR spectrum contains no signal at room temperature, suggesting that the product is paramagnetic. However, upon cooling to –91 °C, a weak resonance at –2.4 ppm in the <sup>31</sup>P NMR spectrum begins to appear (Figure S1).

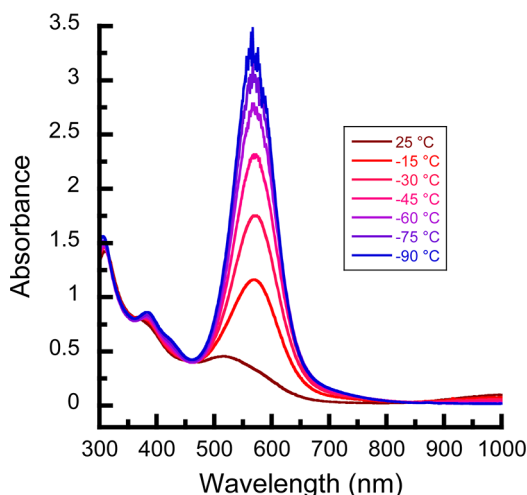
Slow evaporation of a concentrated benzene solution of the dark-purple material afforded nearly black needle crystals from which the solid-state molecular structure was obtained via X-ray diffraction (XRD). The structure contains two Co centers in close proximity, each bound to two [dmgH]<sup>–</sup> ligands and one P(*n*Bu)<sub>3</sub> with an overall molecular formula corresponding to [Co<sup>II</sup>(dmgH)<sub>2</sub>P(*n*Bu)<sub>3</sub>]<sub>2</sub> ([P-Co<sup>II</sup>]<sub>2</sub>) (Figure 2). The structure reveals a Co⋯Co separation of 3.116(2) Å, which is somewhat longer than typical unsupported M–M bonds. For example, the diamagnetic (CO)<sub>5</sub>Mn–Mn(CO)<sub>5</sub>, (CN)<sub>5</sub>Co–Co(CN)<sub>5</sub>, and [(CO)<sub>5</sub>Cr–Cr(CO)<sub>5</sub>]<sup>2–</sup> complexes have metal–metal bond



**Figure 2.** Thermal ellipsoid plot (50% probability) of the molecular structure of [P-Co<sup>II</sup>]<sub>2</sub> with carbon bound H atoms removed for clarity. The butyl groups on the phosphine ligand are heavily disordered across two positions, both of which were not refined anisotropically. Color scheme: blue = nitrogen; red = oxygen; magenta = cobalt; orange = phosphorus; white = carbon.

distances of 2.923, 2.794, and 2.97 Å, respectively.<sup>9</sup> The closely related [Rh<sup>II</sup>(dmgH)<sub>2</sub>PPh<sub>3</sub>]<sub>2</sub> complex has a Rh–Rh bond of 2.936 Å.<sup>10</sup> Interestingly, the rhodoxime dimer was synthesized by reduction of the [Cl–Rh<sup>III</sup>(dmgH)<sub>2</sub>PPh<sub>3</sub>] precursor with NaBH<sub>4</sub> in MeOH/water; these conditions are nearly identical to those used to prepare [P-Co<sup>II</sup>]<sub>2</sub>. A similar dimeric structure to [P-Co<sup>II</sup>]<sub>2</sub> was also obtained for [Co<sup>II</sup>Salen]<sub>2</sub> and contains a much longer unsupported Co⋯Co separation of 3.45 Å<sup>11</sup> and exhibits weak antiferromagnetic coupling as determined by temperature-dependent magnetic susceptibility (*J* ~ –20 cm<sup>–1</sup>).<sup>12</sup> The Co⋯Co separation in [P-Co<sup>II</sup>]<sub>2</sub> is in between these two cases and may represent a weak bond. The temperature-dependent magnetic susceptibility of solid [P-Co<sup>II</sup>]<sub>2</sub> does not exhibit behavior indicative of magnetic coupling and rather appears to reflect a diamagnet (SQUID Figure S2).

The solution-state speciation appears to be consistent with a monomer–dimer equilibrium. For example, the <sup>1</sup>H NMR spectrum of [P-Co<sup>II</sup>]<sub>2</sub> collected at –91 °C is substantially more resolved than the room-temperature spectrum and integrates appropriately to [P-Co<sup>II</sup>]<sub>2</sub> (Figure 1). This is consistent with the appearance of a <sup>31</sup>P NMR resonance observed at low temperature (–91 °C). Similarly, variable-temperature UV–vis spectra display thermochromism with a strong λ<sub>max</sub> at 570 nm (*ε* ~ 25,000 M<sup>–1</sup> cm<sup>–1</sup> at –90 °C, 0.10 mM in toluene) (Figures 3 and S3); this band is presumed to arise from a weak Co–Co σ to σ\* transition.<sup>13</sup> The thermochromism of [P-Co<sup>II</sup>]<sub>2</sub> allows for the thermodynamics of the monomer–dimer equilibrium to be studied.<sup>14</sup> A Van’t Hoff plot (–5 to 30 °C) gives Δ*H*<sup>o</sup> = –5.4 ± 0.2 kcal mol<sup>–1</sup> and Δ*S*<sup>o</sup> = –11.4 ± 0.3 cal mol<sup>–1</sup> K<sup>–1</sup> for the formation of a dimer as the product of two monomeric [P-Co<sup>II</sup>] fragments (Figure S3). A room-temperature EPR spectrum (Figure S4) of a 2 mM toluene solution exhibits a doublet signal and provides additional evidence for the presence of a low-spin [P-Co<sup>II</sup>] species in solution. This signal disappears at 77 K (EPR silent) where the dimer structure is favored. Collectively these data are consistent with a monomer–dimer equilibrium process wherein the monomer is a spin active doublet and the dimer is a diamagnet. While preparing this manuscript we became aware of a PhD thesis (1997) that contains variable-temperature UV–vis and NMR experiments on samples of the purported “[P-Co<sup>III</sup>H]”.<sup>15</sup>



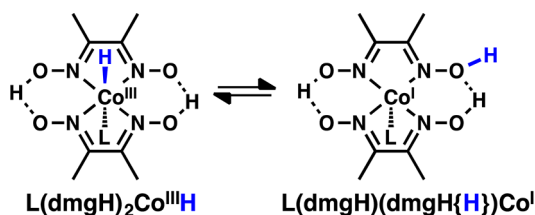
**Figure 3.** Variable-temperature UV–vis spectrum of 100  $\mu\text{M}$   $[\text{P-Co}^{\text{II}}]_2$  in toluene (1 cm cell).

These data led that author to similarly conclude a monomer–dimer equilibrium and an incorrectly assigned “[P-Co<sup>III</sup>H]”.

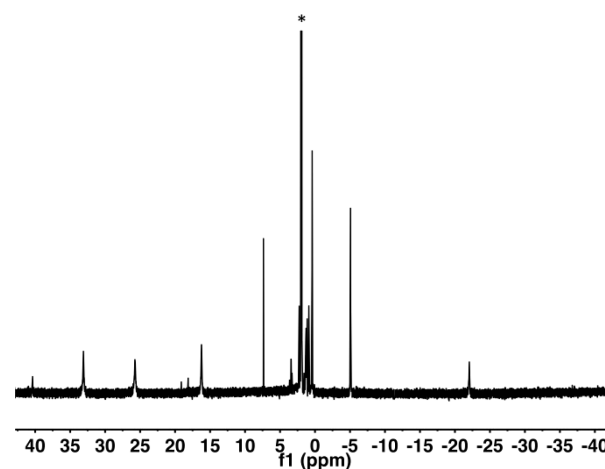
To further substantiate the conclusion that this dark-purple compound is indeed  $[\text{P-Co}^{\text{II}}]_2$ , we pursued alternative synthetic routes to the same species.  $[\text{P-Co}^{\text{II}}]_2$  is the major product when synthesized by treatment of  $[\text{Co}^{\text{II}}(\text{dmgH})_2(\text{H}_2\text{O})_2]$  with 1 equiv of  $\text{P}(n\text{Bu})_3$  in DCM or *n*-pentane (Figure S5).<sup>16</sup> Additionally, treatment of  $[\text{P-Co}^{\text{III}}\text{Cl}]$  with  $\text{Cp}_2\text{Co}$  affords dark-purple solutions with <sup>1</sup>H NMR and UV–vis spectra indicative of the  $[\text{P-Co}^{\text{II}}]_2$  complex (Figure S6).<sup>15</sup> These alternative synthetic routes thus afford the same dark-purple product and further substantiate that  $[\text{P-Co}^{\text{II}}]_2$  is the correct assignment for the spectroscopically observed major product of the  $\text{NaBH}_4$  reductions of  $[\text{P-Co}^{\text{III}}\text{Cl}]$ . It is worth noting that in our hands the powder ATR-IR spectrum of  $[\text{P-Co}^{\text{II}}]_2$  prepared by Schrauzer’s method consistently shows a peak at  $2360\text{ cm}^{-1}$  that arises from  $(n\text{Bu})_3\text{P-BH}_3$ ; Schrauzer had reported an isotopically sensitive peak at  $2240\text{ cm}^{-1}$ ,<sup>5</sup> attributed to a Co–H mode, that may instead have resulted from a borane impurity. More importantly, no peaks in this general region are present in the  $[\text{P-Co}^{\text{II}}]_2$  product obtained by either reduction of  $[\text{P-Co}^{\text{III}}\text{Cl}]$  with  $\text{Cp}_2\text{Co}$  or addition of  $\text{P}(n\text{Bu})_3$  to  $[\text{Co}^{\text{II}}(\text{dmgH})_2(\text{H}_2\text{O})_2]$  (Figure S11).<sup>17</sup>

We note in brief that the addition of  $\text{H}_2$  to a pure sample of  $[\text{P-Co}^{\text{II}}]_2$  in toluene leads to decay of the starting material to a mixture of products over a period of about 24 h but that the <sup>1</sup>H NMR and IR spectra do not indicate the presence of product(s) containing a terminal hydride ligand (Figure S12).<sup>1c,15,18</sup> Whether a tautomeric form (Scheme 1)<sup>8</sup> of the hydride is produced as one of the products remains unclear.

**Scheme 1. Proposed Isomerization of Co(III)-H That Could Form upon Addition of  $\text{H}_2$  to  $[\text{Co}^{\text{II}}]$**

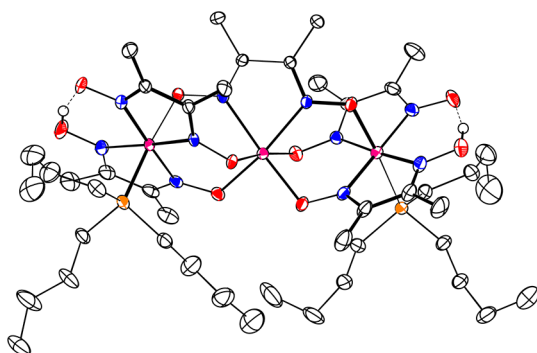


**Identification of the Paramagnetic Impurity.** Independently prepared batches of  $[\text{P-Co}^{\text{II}}]_2$  material in our hands sometimes contained a singlet <sup>1</sup>H NMR resonance at  $-5.06$  ppm in  $d_3$ -MeCN in varying intensities ( $-6.11$  ppm in  $\text{C}_6\text{D}_6$  and  $d_8$ -toluene). This resonance seemed to appear when exclusion of air was not rigorously pursued and is a resonance consistent with that reported by Artero and Fontecave to arise from the putative hydride “[P-Co<sup>III</sup>H]” (Figure S7).<sup>8</sup> The resonance at  $-5.06$  ppm is a singlet, whereas a doublet is anticipated due to <sup>2</sup>J<sub>P,H</sub> coupling from the *trans*-phosphine for a  $\text{R}_3\text{P-Co(III)-H}$  structure. Other examples of Co–H complexes with phosphine ligands contain <sup>1</sup>H resonances with the expected splitting for coordinated phosphines.<sup>3,4</sup> We also noted that the appearance of this downfield  $-5.06$  ppm resonance is always accompanied by other, paramagnetically shifted resonances at  $-22.04$ ,  $0.40$ ,  $16.23$ ,  $25.73$ ,  $33.11$ , and  $40.39$  ppm (Figure 4). The implication is clear; the  $-5.06$  ppm resonance is one of many belonging to a paramagnetic impurity likely generated by adventitious air during the synthesis of  $[\text{P-Co}^{\text{II}}]_2$ .



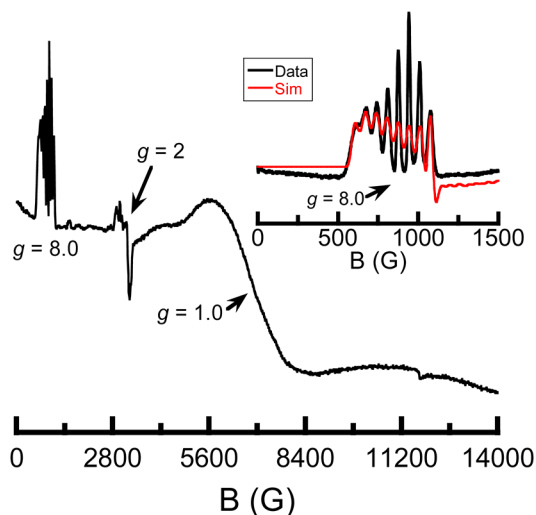
**Figure 4.** <sup>1</sup>H NMR spectrum (45 to  $-45$  ppm) of isolated  $[\text{P}_2\text{Co}_3]$  in  $d_3$ -MeCN (\*) at room temperature.

Extracting the purple dimer  $[\text{P-Co}^{\text{II}}]_2$  with pentane from such crude mixtures containing the aforementioned paramagnet left behind a brown material which, following benzene extraction, afforded the purified paramagnet (see SI). The <sup>1</sup>H NMR spectrum of this purified material in  $d_3$ -MeCN exhibits the same paramagnetically shifted <sup>1</sup>H NMR spectrum as observed in samples from crude  $[\text{P-Co}^{\text{II}}]_2$  material exposed to air, including the resonance at  $-5.06$  ppm (Figure 4). Slow diffusion of *n*-pentane into a dilute benzene solution of this brown material provided crystals suitable for XRD (Figure 5). The molecular structure reveals the trimeric  $[(\text{dmgH})\text{Co}^{\text{III}}\text{P}(n\text{Bu})_3(\text{dmg})]_2(\mu\text{-O}_{\text{dmg}})_2(\mu\text{-O}_{\text{dmgH}})_2[\text{Co}^{\text{II}}\text{dmg}]$  ( $[\text{P}_2\text{Co}_3]$ ) complex with one central Co atom bridging two “edge”  $\{\text{Co}(\text{dmg})(\text{dmgH})\}$  units.<sup>19</sup> The central Co atom is 6-coordinate with four sites occupied by two oxime oxygen atoms each from two adjacent  $\{\text{Co}(\text{dmg})(\text{dmgH})\}$  units. The remaining two sites are occupied by the two nitrogen atoms from a single  $[\text{dmg}]^{2-}$  ligand that span all three Co centers. The edge Co atoms are also 6-coordinate with the axial positions occupied by a phosphorus atom from  $\text{P}(n\text{Bu})_3$  and an oxygen atom from the single bridging  $\text{dmg}^{2-}$  ligand. The <sup>1</sup>H NMR spectrum of these crystals matched the same para-



**Figure 5.** Thermal ellipsoid plot (50% probability) of the molecular structure of  $[\text{P}_2\text{Co}_3]$  with carbon bound H atoms removed for clarity. Also not shown is an uncoordinated  $\text{dmgH}_2$  molecule in close H-bonding contact with an O atom of a coordinated  $[\text{dmgH}]^-$  moiety. Color scheme: blue = nitrogen; red = oxygen; magenta = cobalt; orange = phosphorus; white = carbon.

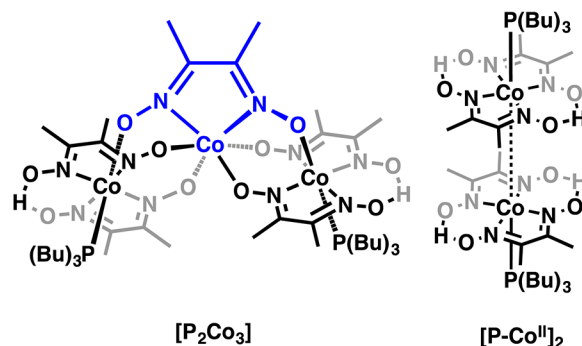
magnetic species obtained from the  $\text{NaBH}_4$  reductions (Figure S8). The trimeric structure appears to remain intact in solution as evidenced from fast atom bombardment mass spectrometry ( $m/z_{\text{found}} = 1153.397$ ;  $m/z_{\text{calcd}} = 1153.400$ ) (Figure S10). The X-band EPR spectrum at 10 K (EPR silent at 77 K) exhibits an unusual signal for an  $S = 3/2$  center ( $\mu_{\text{eff}} = 3.9 \mu_{\text{B}}$ , room temperature in  $\text{C}_6\text{D}_6$ ) with a diagnostic 8-line pattern indicating that the unpaired electrons are interacting with a single Co ion (Figure 6).<sup>20</sup>



**Figure 6.** X-band EPR spectrum of the  $S = 3/2$  trimer  $[\text{P}_2\text{Co}_3]$  in a toluene glass collected at 10 K (see Figure S9 for SQUID data). EPR simulation parameters:  $g_{x,y,z} = 5.717, 2.764, 1.871$ ;  $sg_{x,y,z} = 0.0274, 0.0238, 0.0270$  ( $sg = g$  strain);  $A_x = 544.8 \text{ MHz}$  ( $0.0181 \text{ cm}^{-1}$ );  $D = -11.0 \text{ cm}^{-1}$ ;  $E/D = 0.1875$ ;  $\text{LWmn} = 14.43 \text{ G}$ ;  $\text{Spin} = 1.5$ .<sup>20</sup>

## CONCLUSION

Herein we have described the major products that are obtained from reduction of  $[\text{P-Co}^{\text{III}}\text{Cl}]$  with  $\text{NaBH}_4$  (Figure 7). Previously, the proposed product was thought to be a Co hydride complex with a *trans*-phosphorus ligand. However, the results presented here show that this species is instead the  $\text{Co}^{\text{II}}$  complex  $[\text{Co}^{\text{II}}(\text{dmgH})_2\text{P}(\text{nBu})_3]$ ,  $[\text{P-Co}^{\text{II}}]$ , that crystallizes as a dimer,  $[\text{P-Co}^{\text{II}}]_2$ , and exhibits a monomer–dimer equilibrium in organic solvent. The resonance at  $-5.06 \text{ ppm}$  ascribed



**Figure 7.** Two major isolated products from the reduction of  $[\text{P-Co}^{\text{III}}\text{Cl}]$  with  $\text{NaBH}_4$  in pH 7 water:MeOH (1:1) are  $[\text{P}_2\text{Co}_3]$  and  $[\text{P-Co}^{\text{II}}]_2$  rather than a Co-hydride.

previously to the  $\text{Co}(\text{III})\text{-H}$  resonance is instead one of several paramagnetically shifted resonances arising from a Co trimer (denoted as  $[\text{P}_2\text{Co}_3]$ ) with an  $S = 3/2$  ground state. This trimer can be generated from adventitious oxygen. Therefore, Schrauzer's hydridocobaloxime no longer provides a reliable reference point for a *bona fide*  $\text{Co}(\text{III})\text{-H}$  within the cobaloxime system. We draw attention to this point because this reassignment, along with recent findings from Norton and co-workers that also challenge the reliability of  $\text{Co}(\text{III})\text{-H}$  assignments in cobaloximes,<sup>21</sup> removes key pieces of evidence that have been used to suggest the reactive H atom in HER by these cobaloxime systems is bound to cobalt. While these collective findings do not rule out  $\text{Co}(\text{III})\text{-H}$  as intermediates in HER catalysis, for example they are still plausible if formed by tautomerization of a ligand protonated form (Scheme 1)<sup>8</sup>; caution in invoking them must still be exercised in the absence of compelling experimental evidence. Worth noting in this context, in a recent report Norton and co-workers found that at high pressures (70 atm) of  $\text{H}_2$  a  $[\text{Co}^{\text{II}}\text{L}(\text{dmgBF}_2)_2]$  ( $\text{L} = \text{solvent}$ ) precursor is reduced to a species with a UV-vis spectrum nearly identical to independently generated  $[\text{Co}^{\text{I}}\text{L}(\text{dmgBF}_2)]^-$ . Supported by the reversibility of the reaction and additional NMR data, they postulated that the new compound is a  $\text{Co}(\text{III})\text{-H}$  hydride isomer, whereby the ligand (not cobalt) instead bears the reactive H atom (i.e.,  $[\text{Co}^{\text{I}}\text{L}(\text{dmgHBF}_2)(\text{dmgBF}_2)]^-$ ).<sup>21</sup> Mechanistic studies of cobaloxime mediated HER catalysis will benefit from consideration of ligand-based protonation schemes similar to other HER platforms such as  $\text{NiN}_2\text{P}_2$  and Co-dithiolene HER catalysts.<sup>1g,h,22</sup>

## ASSOCIATED CONTENT

### Supporting Information

Experimental details, spectra, and X-ray crystallographic information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\*jpeters@caltech.edu

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by NSF Center for Chemical Innovation Solar Fuels Grant CHE-1305124. Larry Henling and Dr. Michael K. Takase are thanked for their help with X-ray

crystallography. Sidney E. Creutz is thanked for assistance with SQUID measurements. D.C.L. would like to acknowledge the National Institute of Health (award number F32GM106726). G.M.R. would like to acknowledge the Peter A. Lindstrom, Jr. SURF fellowship.

## REFERENCES

- (1) (a) Hu, X.; Cossairt, B. M.; Brunenschwig, B. S.; Lewis, N. S.; Peters, J. C. *Chem. Commun.* **2005**, 4723. (b) Razavet, M.; Artero, V.; Fontecave, M. *Inorg. Chem.* **2005**, *44*, 4786. (c) Hu, X.; Brunenschwig, B. S.; Peters, J. C. *J. Am. Chem. Soc.* **2007**, *129*, 8988. (d) Carole, B.; Artero, V.; Fontecave, M. *Inorg. Chem.* **2007**, *46*, 1817. (e) Du, P.; Schneider, J.; Luo, G.; Brennessel, W. W.; Eisenberg, R. *Inorg. Chem.* **2009**, *48*, 4952. (f) Bigi, J. P.; Hanna, T. E.; Harman, W. H.; Chang, A.; Chang, C. J. *Chem. Commun.* **2010**, 46, 958. (g) Letko, C. S.; Panetier, J. A.; Head-Gordon, M.; Tilley, T. D. *J. Am. Chem. Soc.* **2014**, *136*, 9364. (h) McNamara, W. R.; Han, Z.; Yin, C.-J.; Brennessel, W. W.; Holland, P. L.; Eisenberg, R. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 15594. (i) McCrory, C. C. L.; Uyeda, C.; Peters, J. C. *J. Am. Chem. Soc.* **2012**, *134*, 3164. (j) Leung, C.-F.; Chen, Y.-Z.; Yu, H.-Q.; Yiu, S.-M.; Ko, C.-C.; Lau, T.-C. *Int. J. Hydrogen Energy* **2011**, *36*, 11640. (k) Szajna-Fuller, E.; Bakac, A. *Eur. J. Inorg. Chem.* **2010**, 2488. (l) Varma, S.; Castillo, C. E.; Stoll, T.; Fortage, J.; Blackman, A. G.; Molton, F.; Deronzier, A.; Collomb, M.-N. *Phys. Chem. Chem. Phys.* **2013**, *15*, 17544. Reviews: (m) Dempsey, J. L.; Brunenschwig, B. S.; Winkler, J. R.; Gray, H. B. *Acc. Chem. Res.* **2009**, *42*, 1995. (n) Thoi, V. S.; Sun, Y.; Long, J. R.; Chang, C. J. *Chem. Soc. Rev.* **2013**, *42*, 2388.
- (2) (a) Muckerman, J. T.; Fujita, E. *Chem. Commun.* **2011**, 47, 12456. (b) Solis, B. H.; Hammes-Schiffer, S. *Inorg. Chem.* **2011**, *50*, 11252. (c) Chao, T. H.; Espenson, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 129. (d) Connolly, P.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 2684.
- (3) (a) Marinescu, S. C.; Winkler, J. R.; Gray, H. B. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 15127. (b) Wiedner, E. S.; Roberts, J. A. S.; Dougherty, W. G.; Kassel, W. S.; DuBois, D. L.; Bullock, R. M. *Inorg. Chem.* **2013**, *52*, 9975. (c) Koelle, U.; Ohst, S. *Inorg. Chem.* **1986**, *25*, 2689. (d) Houlding, V.; Geiger, T.; Kölle, U.; Grätzel, M. *J. Chem. Soc., Chem. Commun.* **1982**, 681.
- (4) (a) Ciancanelli, R.; Noll, B. C.; DuBois, D. L.; Dubois, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 2984. (b) Rahman, A. F. M. M.; Jackson, W. G.; Willis, A. C.; Rae, A. D. *Chem. Commun.* **2003**, 2748. (c) Bhattacharjee, A.; Weiss, A. K. H.; Artero, V.; Field, M. J.; Hofer, T. S. *J. Phys. Chem. B* **2014**, *118*, 5551.
- (5) Schrauzer, G. N.; Holland, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 1505.
- (6) Reviews: (a) Mckone, J. R.; Marinescu, S. C.; Brunenschwig, B. S.; Winkler, J. R.; Gray, H. B. *Chem. Sci.* **2014**, *5*, 865. (b) Eckenhoff, W. T.; McNamara, W. R.; Du, P.; Eisenburg, R. *Biochim. Biophys. Acta* **2013**, *1827*, 958. (c) Artero, V.; Chavarot-Kerlidou, M.; Fontecave, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 7238.
- (7) (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 5th ed.; John Wiley & Sons: Hoboken, NJ, 2009. (b) Hartwig, J. F. *Organotransition Metal Chemistry, From Bonding to Catalysis*; University Science Books: Herndon, VA, 2010. (c) Buckingham, A. D.; Stephens, P. J. *J. Chem. Soc.* **1964**, 2747. (d) Buckingham, A. D.; Stephens, P. F. *J. Chem. Soc.* **1964**, 4583.
- (8) Bhattacharjee, A.; Chavarot-Kerlidou, M.; Andreiadis, E. S.; Fontecave, M.; Field, M. J.; Artero, V. *Inorg. Chem.* **2012**, *51*, 7087.
- (9) Mn–Mn bond in  $\text{Mn}_2(\text{CO})_{10}$ : (a) Dahl, L. F.; Rundle, R. E. *Acta Crystallogr.* **1963**, *16*, 419. Examples of unsupported Co–Co bonds: (b) Peng, S.-M.; Liaw, D.-S.; Wang, Y.; Simon, A. *Angew. Chem., Int. Ed.* **1985**, *24*, 210. (c) Simon, G. L.; Adamson, A. W.; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *94*, 7654. (d) Brown, L. D.; Raymond, K. N.; Goldberg, S. Z. *J. Am. Chem. Soc.* **1972**, *94*, 7664. (e) Cotton, F. A.; Duune, T. G.; Wood, J. S. *Inorg. Chem.* **1964**, *3*, 1495. Cr–Cr bond in  $[\text{Cr}_2(\text{CO})_{10}]^{2-}$  (f) Handy, L. B.; Ruff, J. K.; Dahl, L. F. *J. Am. Chem. Soc.* **1970**, *92*, 7312.
- (10) Caulton, K. G.; Cotton, F. A. *J. Am. Chem. Soc.* **1971**, *93*, 1914.
- (11) Schaefer, W. P.; Marsh, R. E. *Acta Crystallogr.* **1969**, *B25*, 1675.
- (12) Murray, K. S.; Bergen, A. v. d.; Kennedy, B. J.; West, B. O. *Aust. J. Chem.* **1986**, *39*, 1479.
- (13) The 570 nm band in  $[\text{P-Co}^{\text{II}}]_2$  is similar to the strong band at 340 nm in  $\text{Mn}_2(\text{CO})_{10}$ : (a) Rosa, A.; Ricciardi, G.; Baerends, E. J.; Stufkens, D. J. *Inorg. Chem.* **1995**, *34*, 3425. (b) Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 6042. (c) Levenson, R. A.; Gray, H. B.; Ceasar, G. P. *J. Am. Chem. Soc.* **1970**, *92*, 3653.
- (14) For a representative example see McLain, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 643.
- (15) (a) Sun, Y. A. *The Anions of  $\text{C}_{60}$  and Its Pyrrolidine Derivatives and B. The Search for Hydridocobaloximes*. Ph.D. Thesis, University of Southern California, Los Angeles, CA, 1997. Also see: (b) Li, G.; Han, A.; Pulling, M. E.; Estes, D. P.; Norton, J. R. *J. Am. Chem. Soc.* **2012**, *134*, 14662.
- (16) Halpern, J.; Phelan, P. F. *J. Am. Chem. Soc.* **1972**, *94*, 1881.
- (17) The  $(n\text{Bu})_3\text{P-BH}_3$  impurity in  $[\text{P-Co}^{\text{II}}]_2$  from Schrauzer's prep that we reproducibly observe by IR spectroscopy may have also been present, but not assigned, in a spectrum reported by Artero and Fontecave (ref 8, Figure S4) with a broad feature that they attributed to  $\text{CO}_2$ .
- (18) (a) Halpern, J.; Pribanic, M. *Inorg. Chem.* **1970**, *9*, 2616. (b) Wayland, B. B.; Ba, S.; Sherry, A. E. *Inorg. Chem.* **1992**, *31*, 148. Simándi and co-workers have investigated  $\text{H}_2$  oxidation by  $\text{Co}(\text{dmgH})_2$  compounds in detail: (c) Simándi, L. I.; Budó-Záhonyi, É.; Szeverényi, Z.; Németh, S. *J. Chem. Soc., Dalton* **1980**, 276. (d) Simándi, L. I.; Szeverényi, Z.; Budó-Záhonyi, E. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 773. (e) Simándi, L. I.; Budó-Záhonyi, É.; Szeverényi, Z. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 237 (e).
- (19) A similar trimeric  $[\text{P}_2\text{Co}_3]$  structure was obtained by  $\text{NaBH}_4$  reduction of  $[\text{P-Co}^{\text{III}}\text{Br}]$  in MeOH in the presence of certain arsines: Cullen, W. R.; Dolphin, D.; Einstein, F. W. B.; Mihichuk, L. M.; Willis, A. C. *J. Am. Chem. Soc.* **1979**, *101*, 6898.
- (20) Similar EPR spectra have been collected for monomeric, high-spin  $S = 3/2$  Co(II) centers with comparable hyperfine and  $D$  values: Jacobsen, F. E.; Breece, R. M.; Myers, W. K.; Tierney, D. L.; Cohen, S. M. *Inorg. Chem.* **2006**, *45*, 7306.
- (21) Estes, D. P.; Grills, D. G.; Norton, J. R. *J. Am. Chem. Soc.* **2014**, *136*, 17362.
- (22) Helm, M. L.; Stewart, M. P.; Bullock, R. M.; Rakowski DuBois, M.; DuBois, D. L. *Science* **2011**, *333*, 863.