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# X-ray Absorption Spectroscopy and Theoretical Investigation of the **Reductive Protonation of Cyclopentadienyl Cobalt Compounds**

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S Supporting Information



ABSTRACT: Cobalt(III) hydrides, formed via protonation of basic cobalt(I) centers, have long been recognized as key intermediates in the electrocatalytic reduction of protons to hydrogen. An understanding of the structural and electronic factors that govern their formation is key to developing more efficient and potent catalysts. A combination of Co K-edge X-ray absorption spectroscopy, extended X-ray absorption fine structure, density functional theory (DFT), and time-dependent DFT methods have been used to investigate several cyclopentadienyl (Cp) Co(III)L (L = ligand) species and their two-electron reduced Co(I) analogues. The results reveal that when L is strongly  $\pi$ -accepting, the reduced species demonstrates strong backbonding between the electron-rich Co(I) center and the ligand L, resulting in a weakly basic Co center that does not protonate to form a Co(III)-H. In contrast, a weakly  $\pi$ -accepting or  $\sigma$ -donating ligand system results in an electron-rich Co(I) center, which is readily protonated to form a Co(III)-H. This study reveals the strength of a combined X-ray spectroscopy/ theory method in understanding the role of ligands in tuning the electronic structure and subsequent reactivity of the metal center.

# INTRODUCTION

Catalytic electroreduction is a promising strategy for converting electricity to energy-rich fuels.  $^{1-4}$  Transitionmetal hydrides are key intermediates in many catalytic electroreduction reactions<sup>5-11</sup> and are formed through a series of proton and electron transfer pathways (Figure 1). Proton transfer (PT) and electron transfer (ET) can proceed sequentially along the edges of the scheme presented on the left side of Figure 1 through discrete PT followed by ET or ET followed by PT. A third plausible pathway can proceed along the diagonal of the scheme through synchronous transfer of an electron and a proton, known as a concerted proton-electron transfer (CPET). The key intermediate in many cobalt-based hydrogen evolution (HER) catalysts is a Co(III)-H, which is usually formed through sequential ET and PT. As shown in right side of Figure 1, this Co(III)-H evolves hydrogen through several pathways.<sup>12,13</sup>

The rate, sequence, and timing of multiple proton and electron transfers strongly depends on the nature of the metal and its ligation environment.<sup>9,10,14–16</sup> Several recent reports have used electrochemical techniques, computational modeling, and density functional theory (DFT) to illustrate the presence of Co and Ni hydride intermediates in electrocatalytic

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proton reduction.<sup>9,10,17-19</sup> Recent investigations of the 2phenylazopyridine (azpy) ligated Co cyclopentadienyl (Cp) complex [CpCo(azpy)(CH<sub>3</sub>CN)][ClO<sub>4</sub>]<sub>2</sub>, 1, revealed a facile reversible two-electron reduction from Co(III) to Co(I) at a mild potential of -0.16 V vs Fc/Fc<sup>+</sup> in acetonitrile.<sup>20</sup> Although 1 is a precatalyst for the electrocatalytic reduction of protons, electrocatalytic proton reduction occurs at significantly more negative potential (onset potential of -1.1 V vs Fc/Fc<sup>+</sup> in acetonitrile) than that at which Co(III) is reduced to Co(I).<sup>21</sup> Control studies have indicated that the HER activity is mediated by Co-containing decomposition products deposited on the electrode surface rather than a Co(III)-H intermediate.<sup>21</sup> In contrast, related CpCoL complexes bearing phosphine<sup>22</sup> (such as 7, Figure 2) or pyridyl carbene ligands<sup>2</sup> evolve H<sub>2</sub>, putatively via Co(III)-H intermediates.<sup>22</sup> These studies indicate the important role of the bidentate ligand system in controlling and tuning reactivity at the Co center.

In this study, we perform a combination of electrochemical studies, X-ray absorption spectroscopy (XAS), and DFT calculations to elucidate the geometric and electronic

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Figure 1. Metal hydrides can be formed through sequential or concerted PT and ET events (left). Co(III)-H's are ubiquitous within the proposed mechanisms of Co-mediated electrocatalytic hydrogen evolution (right).







Bis(diphenylphosphino)ethane (dppe) complexes



**Figure 2.** Cyclopentadienyl cobalt complexes bearing 2-phenylazopyridine (azpy), 2,2'-bipyridine (bipy), and 1,2-bis-(diphenylphosphino)ethane (dppe) ligands investigated in this work.

structures of cyclopentadienyl Co complexes 1, 2, and 3 (Figure 2). We investigate the factors that influence the reactivity of reduced Co(I) species toward protonation, with the aim of identifying structural and electronic parameters that favor protonation at the Co center. In order to compare 1 with related ligand systems, we have spectroscopically characterized the 2,2'-bipyridine (bipy) analogues [CpCo(bipy)(CH<sub>3</sub>CN)]- $[ClO_4]_2$  4 and CpCo(bipy) 5 (Figure 2). The diamagnetic Co(III) (low-spin, d<sup>6</sup>) and Co(I) (low-spin, d<sup>8</sup>) ground states of the various CpCoL complexes have been interrogated for local electronic structure elucidation using XAS, and the results combined with theoretical methods to arrive at a spectroscopically calibrated level of DFT. The spectroscopic studies on 1-5 are augmented with theoretical investigations on the 1,2bis(diphenylphosphino)ethane (dppe) analogues 6-8 (Figure 2) to understand salient electronic structure differences between ligand systems that explain reactivity differences.

# RESULTS AND DISCUSSION

**Synthesis of Cyclopentadienyl Co Complexes.** The Co complexes [CpCo(azpy)(CH<sub>3</sub>CN)][ClO<sub>4</sub>]<sub>2</sub> 1,<sup>21</sup> CpCo(azpy)

2,<sup>21</sup> [CpCo(bipy)(CH<sub>3</sub>CN)][ClO<sub>4</sub>]<sub>2</sub> 4,<sup>21</sup> CpCo(bipy) 5,<sup>24</sup> CpCo(dppe) 7,<sup>16</sup> and [CpCo(dppe)(H)][PF<sub>6</sub>] 8<sup>22</sup> were prepared according to literature procedures. The synthesis of [CpCo(dppe)(CH<sub>3</sub>CN)][PF<sub>6</sub>]<sub>2</sub> 6 is detailed in the Experimental section. The synthesis and reactivity of [CpCo-(azpyH)][ClO<sub>4</sub>] 3 is described in detail elsewhere,<sup>26</sup> but is briefly described here. Protonation of 2 with either *N*,*N*dimethylformamidinium triflate ([DMFH][CF<sub>3</sub>SO<sub>3</sub>]) or trifluoromethanesulfonic acid (TfOH) in acetonitrile generates the monocationic azopyridine complex 3, which was isolated in 70% yield.

**Co K-Edge XAS.** The normalized Co K-edge XAS data for **1**, **2**, and **3** are presented in Figure 3 and in Figure S1. The data



Figure 3. Normalized Co K-edge XAS data for 1 (blue, circle), 2 (black, dash), and 3 (red, dot-dash). The reference compounds 4 (black, circle) and 5 (light blue, diamond) are included for comparison. The inset shows the expanded pre-edge region.

for the Co(III) complex  $[CpCo(bipy)(CH_3CN)][ClO_4]_2$  4 and the Co(I) complex CpCo(bipy) 5 are included for comparison purposes. The Co K-edge extended X-ray absorption fine structure (EXAFS) data for 1-5 were evaluated to determine sample integrity and are presented in the Supporting Information (Figures S3-S5, Table S1). The rising edge region, which dominantly represents Co  $1s \rightarrow 4p +$ continuum transitions (~7715-7725 eV),<sup>27</sup> is strongly modulated by the  $Z_{\rm eff}$  (effective nuclear charge) on Co.<sup>28</sup> An increase in  $Z_{\text{eff}}$  results in a greater stabilization of the 1s levels and hence a shift in the rising edge position to higher energies. The rising-edge energy position, measured at first derivative inflection point, occurs at 7719.7 eV for the dicationic complex 4 and 7716.5 eV for the neutral complex 5, indicating a 3.2 eV decrease in rising-edge energy position from Co(III) and Co(I). The rising edges for 1 and 2 occur at

Table 1. Co-L Distances (Å) Obtained from Experimental and Theoretical Methods

			1			2		3		
	Co-N <sub>1</sub>	Co-N <sub>2</sub>	Co-C <sup>a</sup>	Co-(NC)	Co-N <sub>1</sub>	Co-N <sub>2</sub>	Co-C <sup>a</sup>	Co-N <sub>1</sub>	Co-N <sub>2</sub>	Co-C <sup>a</sup>
XRD	1.95	1.93	2.07	1.91	1.82	1.87	2.07	1.82	1.90	2.06
EXAFS	1.93	1.93	2.07	1.93	1.84 (1.81)	1.84 (1.87)	2.06	1.83 (1.80)	1.83 (1.87)	2.05
BP86	1.95	1.95	2.10	1.90	1.83	1.87	2.07	1.82	1.90	2.06
B3LYP	1.98	1.96	2.13	1.93	1.89	1.91	2.15	1.87	1.93	2.12

"The average Co-C(Cp) distance. Individual Co-C(Cp) distances within ±0.02 Å of average.  $N_1$  and  $N_2$  are bonded to Co,  $N_1$  is the azo N, and  $N_2$  is the pyridyl N.

7719.2 and 7716.3 eV, respectively; the 2.9 eV decrease in energy position for **2** relative to **1** is consistent with the formulation of **2** as Co(I) and **1** as Co(III).<sup>21</sup> The rising edge of **3** closely follows that of **2** and **5** (7716.7 eV), which indicates that the cationic complex **3** is most reasonably formulated as a Co(I) complex. This observation is note-worthy, as it implies that protonation of the Co(I) complex **2** at the azopyridine ligand to form **3** occurs without a significant change in the oxidation state of Co.

The inset of Figure 3 shows the expanded Co K-pre-edge region. The pre-edge occurs due to an electric dipoleforbidden, quadrupole-allowed 1s  $\rightarrow$  3d transition, which gains intensity through a mechanism of metal 3d-4p mixing.<sup>28,31–35</sup> The energy position of the pre-edge is mostly affected by ligand-field strength at the Co center.<sup>36</sup> The data show that the pre-edge energy positions for 1 and 4 occur at 7710.2 and 7710.1 eV, respectively, and are at higher energies relative to their Co(I) counterparts 2 (7709.6 eV) and 5 (7709.4 eV), respectively. This blue-shift in pre-edge energy position indicates an increase in ligand field on going from the 5-coordinate Co(I) species to the 6-coordinate Co(III) species. The Co(I) species also have more intense pre-edge positions because their geometries allow greater 3d-4p mixing. Complex 3, which is assigned as a Co(I) complex from the rising-edge energies, has the most intense pre-edge feature at 7709.7 eV. The energy position is very similar to that of 2, implying little change in ligand field. The greater pre-edge intensity in 3 indicates greater 3d-4p mixing relative to 2.

DFT Calculations. To obtain details about the electronic structures of 1, 2, and 3, spin-unrestricted DFT calculations were performed using the ORCA quantum chemical code.<sup>37</sup> A combination of XAS, XRD,<sup>20</sup> and <sup>1</sup>H NMR show that 3 is a low-spin  $(S = 1, 3d^8)$  Co(I) complex, 1 is a low-spin  $(S = 1, 3d^8)$  $3d^6$ ) Co(III) complex, and 2 is a low-spin (S = 1,  $3d^8$ ) Co(I) complex.<sup>21</sup> DFT calculations on high-spin states of each form were significantly higher in energy, consistent with the experimental data. Initial calculations were performed using the hybrid functional B3LYP, which resulted in inaccurate structural parameters as judged by comparison to the EXAFS/ XRD data (Table 1). Choice of a pure functional resulted in significantly improved structural parameters,<sup>21</sup> and therefore BP86 has been applied to all the systems investigated in this study. The close agreement of the structural parameters obtained from DFT calculations (on the low-spin states of 1, 2, and 3) with experiment indicate that a reasonably accurate level of theory has been employed. This level of theory was further used for time-dependent DFT (TD-DFT) (ORCA) calculations to theoretically predict the transitions contributing to the Co K-pre-edge spectra. This method has been successfully applied to transition-metal complexes.<sup>38-41</sup> The results are shown in Figure 4, and a comparison between experimental and calculated results is presented in Figure S6.



Article



**Figure 4.** A comparison of the (A) Co K-pre-edge XAS data and (B) TD-DFT calculated spectra for 1 (blue, circle), 2 (black), and 3 (red, dot-dash) (scaled for comparison). The starred featured in the calculated spectra are transitions from Co 1s level to Co orbitals higher than the 3d level. The calculated spectra have been energy shifted by 197 eV for comparison purposes.

The calculated spectra are in reasonable agreement with the experiment, giving theoretical support to the oxidation state assignments made by the XAS comparative analysis detailed above.

Bonding Changes upon Reduction. The XRD data indicate a dramatic structural change (i.e., shortening of the Co-N bond distance) upon reduction of 1 to  $2^{20}$  which persists when 2 is protonated to form  $3^{26}$ . This ~0.1 Å shortening of the Co-N bond distance occurs despite a twoelectron reduction of 1, assigned as Co(III) from the risingedge XAS data, to 2, assigned as Co(I) from the rising edge XAS data. This shortening is highly unusual because average bond distances usually increase upon reduction.<sup>21</sup> The average Co-C(Cp) distance remains unchanged, indicating that the Co-Cp bonding is not altered significantly upon reduction. Together, the structural data indicate that the Cp and azpy ligands play an innocent and non-innocent role in bonding with Co, respectively. To understand this potential noninnocent role and understand the seemingly inverse trend in Co–N bond distances, the related bipy analogues 4 and 5 were explored using a combination of XRD, EXAFS, and DFT methods (Table S2). Note that the Co K-edge XAS data for 4 and 5 are used in Figure 3 as the bona fide reference Co(III)and Co(I) compounds, respectively. Interestingly, the structural comparison (Table S2) reveals a very similar trend for the bipy complexes: a shortening of Co-N distance upon two-electron reduction. In other words, this "inverse" trend is not limited to the azpy ligand system. It is important to note here that both 1 and 4 have a short Co–N bond with CH<sub>3</sub>CN, which is lost upon reduction to their respective Co(I)analogues. The loss of a ligand is typically associated with

Table 2.	Select DFT	Parameters f	or the	CpCo(	bipy)] <sup>0,1+,2+</sup>	Series	with	No Bound	l Acetonitrile
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	bond distance (Å)			Löewdin charge					Mayer bond orders			
	Co-N <sub>1</sub>	Co-N <sub>2</sub>	Co-C <sup>a</sup>	Co	$N_1$	$N_2$	bipy	Ср	Co-N <sub>av</sub>	Co-C <sup>b</sup>	Co-C <sup>c</sup>	$C-C_{av}^{d}$
[CpCo(bipy)] <sup>0</sup>	1.87	1.87	2.08	0.23	0.20	0.20	-0.40	-0.23	0.87	0.59	2.26	1.13
[CpCo(bipy)] <sup>1+</sup>	1.92	1.93	2.08	0.35	0.23	0.23	0.17	0.03	0.72	0.24	2.25	1.12
[CpCo(bipy)] <sup>2+</sup>	1.92	1.93	2.05	0.48	0.23	0.23	0.52	0.55	0.72	0.22	2.82	1.09

<sup>*a*</sup>The average Co-C(Cp) distance. Individual Co-C(Cp) distances within  $\pm 0.02$  Å of average. <sup>*b*</sup>C of bipy ligand. <sup>*c*</sup>C of Cp. <sup>*d*</sup>Average C-C bond order of the Cp ring.



**Figure 5.** A comparison of the frontier molecular orbitals of molecules in the  $[CpCo(bipy)]^{0,1+,2+}$  series. The Co(I) and Co(III) are S = 0 species, therefore their  $\alpha/\beta$  contribution is shown together for simplicity of depiction. The Co 3d contribution to the valence orbitals is indicated next to the (numbered) orbitals. Contour plots were generated in ChemCraft. The energy levels have been renormalized to the Co 1s orbital. The Co center in each species is 3-coordinate to the Cp ligand.

the shortening of the remaining metal–ligand bonds, which compensate for the loss of bonding interaction. Thus, the loss of the short  $Co-N(CH_3CN)$  interaction in 2 and 5 can potentially contribute to the shortening of the remaining Co–N bonds.

To uncouple the contribution of ligand loss from other bonding factors, DFT calculations were performed on the  $[CpCo(bipy)]^{0,1+,2+}$  series with no acetonitrile bound in any of the redox forms. Select theoretical details are listed in Table 2. Reduction of Co(III) to Co(II) results in an increase in the average Co-C(Cp) bond distance (from 2.05 to 2.08 Å), whereas the Co-N(bipy) distance remains unchanged. Löewdin charge analysis<sup>42,43</sup> shows that the added electron is well distributed over the entire molecule with the biggest change on the Cp and bipy ligands. Mayer bond order analysis<sup>44</sup> shows weakening of the average Co-C(Cp) bond, with a small increase in the Co-C(bipy) interaction.

The calculated orbital contribution to the frontier molecular orbitals is listed in Table S3 and shown in Figure 5. The d<sup>6</sup> Co(III) species has four metal-based holes (two each in  $\alpha$  and  $\beta$ ). Calculations reveal these two as the  $3d_{yz}$  ( $\psi^*_{LUMO}$ ) and  $3d_{x^2-y^2}$  ( $\psi^*_{LUMO+1}$ ) orbitals.  $\psi^*_{LUMO+2}$  is a bipy  $\pi^*$  orbital with weak back-bonding interaction with  $3d_{yz}$  orbital. Upon reduction the  $\alpha \ \psi^*_{LUMO}$  becomes occupied. Comparison of the Co(II)  $\beta \ \psi^*_{LUMO}$  with Co(III)  $\beta \ \psi^*_{LUMO}$  shows an increase in bipy contribution and a decrease in Cp contribution upon reduction (Table S3). In addition, the bipy  $\pi^*$  orbital comes down in energy, becoming the new  $\beta \ \psi^*_{LUMO+1}$ , with a significantly increased Co  $3d_{yz}$  back-bonding interaction.

Together these results indicate that as the Co(III) complex is reduced to the Co(II) complex, the Co-Cp interaction decreases, the Co-bipy interaction increases, and the added electron is delocalized over the molecule. Additionally, the overall decrease in bond order is consistent with reduction and expected weakening of the average Co-ligand bonds. Upon reduction of Co(II) to Co(I), a larger change in bonding occurs: Co-N bonds decrease by ~0.05 Å, while the Co-C(Cp) distances remain unchanged. Thus, a decrease in bond distance occurs upon reduction. Löewdin charge analysis shows that the added electron is distributed over the entire molecule with the majority distributed over the bipy ligand. Mayer bond order analysis shows a significant increase in Co-N(bipy) and Co-C(bipy) bond orders. Upon reduction of Co(II) to Co(I),  $\beta \psi^*_{\text{LUMO}}$  becomes occupied, and the bipy  $\pi^*$ orbital becomes the  $\alpha/\beta \psi^*_{LUMO}$  in the S = 0 Co(I) species with increased back-bonding interaction with Co 3d<sub>yz</sub>. Thus, the reduction of Co(II) to Co(I) is accompanied by a significant increase in Co-bipy interaction aimed at dissipating the added electron from the Co center to the low-lying bipy  $\pi^*$ orbitals. This strengthening of the Co-bipy interaction points to an increase in the overall ligand-field strength in the Co(I) species relative to the Co(II) species, which is at the root of the "inverse" trend mentioned above. Since XAS pre-edges are a measure of the overall ligand field, the Co(II) species is expected to have a pre-edge at lower energy than its reduced Co(I) form.

This prediction of a lower pre-edge feature in the Co(II) species relative to the Co(I) species is borne out in the

		$\psi^*_{LUMO}$		_	$\psi^*_{\text{LUMO+1}}$		${\psi^*}_{ m LUMO+2}$			
	% Co	% Cp	% L <sup>a</sup>	% Co	% Cp	% L	% Co	% Cp	% L	
2	32.1	14.8	52.7	51.5	23.9	24.4	-	_	_	
1	7.1	1.0	90.4	49.3	29.0	21.7	46.5	35.6	11.0	
5	20.7	8.7	70.5	56.1	24.3	19.5	-	_	-	
4	50.8	33.7	7.3	50.0	29.8	20.2	2.1	0.7	97.0	

Table 3. Valence Molecular Orbital Compositions (%)

"L stands for the respective ligands in 2, 1, 5, and 4. All are S = 0 species ( $\alpha = \beta$ ). In each Co(III)/Co(I) pair, the back-bonding orbital contribution is shown in bold.

Table 4.  $\psi^*_{HOMO}$  Composition and Löewdin/Hirshfeld Charges for 2, 5, and 7

	_	$\psi^*_{\rm HOMO}$			Löewdin/Hirshfeld charge						
	% Co	% Cp	% L <sup>a</sup>	Co	$N_1/P_1^b$	$N_2/P_2^b$	N <sub>3</sub> <sup>b</sup>	Cp <sup>c</sup>	$L^{c}$		
2	36.1	15.5	44.2	0.25/-0.01	0.19/-0.07	0.09/-0.11	0.04/-0.16	-0.12/0.08	-0.45/0.27		
5 <sup>d</sup>	36.5	17.0	41.5	0.23/-0.05	0.20/-0.10	0.20/-0.10	_	-0.23/-0.02	-0.40/0.27		
7	49.8	18.2	26.1	-0.20/-0.19	0.76/0.15	0.76/0.15	_	-0.26/-0.07	-1.06/0.00		

<sup>*a*</sup>L stands for the respective ligand in 2, 5, and 7. <sup>*b*</sup>N<sub>1</sub> and N<sub>2</sub> are bonded to Co, N<sub>1</sub> is the azo N, N<sub>2</sub> is the pyridyl N, and N<sub>3</sub> is the azo N which gets protonated in 3. <sup>*c*</sup>The sum of charges on all atoms in the Cp and L is shown. Individual C atom charges are significantly smaller. The most negatively charged atom is shown in bold for each species. <sup>*d*</sup>Löewdin charges for 5 are reproduced from Table 2.

comparison of TD-DFT calculated spectra and Co K-edge XAS data on **5** and the one-electron reduced form of **4** (i.e.,  $[CpCo(bipy)]^{1+}$ , referred to as **4a**) (Figure S7). Although **4a** (the Co(II) species) appears to be stable on the electrochemistry time-scale, our attempts to chemically or electrochemically synthesize it to experimentally test the "inverse" trend were unsuccessful due to its instability in solution. We were only able to produce a mixture of the starting Co(III) complex **4**, the reduced Co(II) species **4a**, and a variety of decomposition products (Figures S15–S18). The Co K-edge XAS data on this mixture (Figure S7) reveal a new low-lying pre-edge feature, which we assign to the Co(II) complex based on agreement with TD-DFT calculations.

The results on  $[CpCo(bipy)]^{0,1+,2+}$  series with no acetonitrile bound reveal that the shortening in the Co–N distance on going from 4 to 5 is not due to the loss of the acetonitrile ligand, but due to increased back-bonding interaction between Co and bipy ligands in the reduced form. This "inverse" trend also occurs for the reduction of 1 to 2 as the Co–azpy backbonding interaction dramatically increases upon reduction (Table 3). Thus, in  $[(Cp)CoL]^0$  (L = azpy, bipy) complexes, the electron-rich Co(I) species is strongly inclined toward charge dissipation by increasing metal–ligand bonding interactions with the non-innocent ligand systems, ultimately leading to the inverse bond distance trend.

Effect of Bonding Changes on Co-H Formation. The XAS data presented here show that the protonation of the neutral Co(I) complex 2 results in the cationic complex 3, a Co(I) species. Thus, the protonation of the N of azopyridine is preferred over the protonation of the Co center (which would result in a Co(III)-H species **3H**). As shown above, the azpy ligand system plays a noninnocent role in bonding and is involved in strong back-bonding interaction with the Co center in the reduced Co(I) form. This back-bonding can also be thought of as increased  $\pi$ -acidity of the ligand, which withdraws electron density from the Co center. DFT calculations on 3 and the hypothetical Co(III)-H hydride species 3H reveal that 3 is 17 kcal/mol more stable than 3H (Table S4).<sup>21</sup> In order to decrease the  $\pi$ -acidity of azpy, modified azo-based ligands were used in theoretical calculations in an attempt to improve the stability of the Co-hydride

form (Figure S9). The results from a select series of ligands are summarized in Table S4. This test reveals that the azo-N will be preferentially protonated even if the azo-containing ligand is modified to decrease the  $\pi$ -acidity of the ligand. Thus, DFT suggests that it is not likely that a Co(III)-hydride complex will form if it is decorated with an azpy derived ligand.

In an effort to extend this theoretical prediction, we attempted to protonate 5 to generate the Co(III)-H. Unlike the azpy complex 2, the bipy complex 5 cannot be protonated at the ligand and can only form a Co(III)-H upon protonation. Attempts to protonate 5 with  $[NH_4][PF_6]$  in acetonitrile led to significant decomposition, and analysis of the resulting <sup>1</sup>H NMR spectrum revealed cyclopentadiene (Figure S14). This suggests that the bipy ligand is also  $\pi$ -acidic and successfully dissipates the charge on the Co center, disfavoring Co(III)-H formation. This behavior can be contrasted with that of the [CpCo(dppe)] (dppe = 1,2bis(diphenylphosphino)ethane) system, which can be reduced from the Co(III) species 6 to the Co(I) species 7 and then successfully protonated to form the isolable Co(III)-hydride species  $8.^{22,16}$  The normalized Co K-edge XAS data for 6, 7,and 8 are provided in Figure S2. The heavier ligand (P-based vs N-based) results in broadening of the spectra for 6-8relative to 1-3. It is clear, however, that the trend observed in the azpy and bipy series is also observed upon two-electron reduction of 6 to 7. Namely, the rising-edge red-shifts upon two-electron reduction by ~3.3 eV from 7718.9 eV in 6 to 7715.6 eV in 7. The pre-edge position of 7 is partially masked by a low-lying rising-edge feature present in all three dppe compounds. Regardless, the pre-edge red-shifts from 7710.3 eV in 6 to 7709.4 eV in 7, which is consistent with the trend observed in the azpy and bipy compounds. As mentioned earlier, protonation of 7 results in the formation of the Co(III)-H species 8. The rising-edge blue-shifts by 1.3 eV upon protonation of 7 to 8. The pre-edge blue-shifts by 1.5 eV from 7 (7709.4 ev) to 8 (7710.9 eV), and its intensity increases. This agrees well with the formation of a short Co(III)-H bond, which significantly increases Co 3d-4p mixing and hence increases the pre-edge intensity. This observation is in stark contrast to the azpy system in which the protonation of 2 to 3 did not significantly change the



**Figure 6.** A comparison of the structural parameters and the  $\psi^*_{HOMO}$  of 7 (left), 5 (center), and 2 (right). The protonation sites are indicated. The blue arrows indicate delocalization over the bipy and azpy ligand systems. The Co center in each species is 3-coordinate to the Cp ligand.

rising-edge and pre-edge energies and only slightly changed the intensity of the pre-edge feature. The Co K-pre-edges of 6, 7, and 8 are well reproduced by TD-DFT calculations (Figure S8), supporting the experimental data and emphasizing the significant spectral difference associated with metal vs ligand based protonations.

To understand the difference in the reactivity of these related yet functionally distinct systems, DFT calculations were performed on 7 and compared with those for 2 and 5. Relevant theoretical parameters are shown in Table 4. This comparison further explains why protonation of 2 preferentially yields 3 rather than 3H. In all three cases (2, 5, and 7), protonation of the reduced Co(I) species would not appear to be precluded by steric constraints.<sup>16</sup> Two important factors lead to facile protonation of the Co center: the charge or electron density at the Co and the availability and nature of frontier molecular orbital involved in accepting the proton. The charge analysis presented in Table 4 reveals that in 7, the Co is relatively electron-rich relative to the Co in 2 or 5. In fact, the Co is the most negatively charged atom in 7, making the proton more likely to be quickly attracted to the Co center. In 2 and 5, the N atoms are more negatively charged than the Co center. In 2, the azo N  $(N_3)$  has the largest negative charge, which results in attraction of the proton to and protonation of the N<sub>3</sub> to result in 3.

Figure 6 shows the structural parameters and the  $\psi^*_{\rm HOMO}$  contour plot of the three Co(I) complexes, while the respective orbital compositions is given in Table 4. Here, the  $\psi^*_{\rm HOMO}$  is under consideration since the two-electron transfer to the proton occurs from this orbital. The Cp contribution to the  $\psi^*_{\rm HOMO}$  remains similar in all three species, making it easier to compare and contrast the effects of the bidentate ligands. The  $\psi^*_{\rm HOMO}$  in 2 and 5 is heavily delocalized onto the azpy and bipy, respectively, such that the total Co character in the  $\psi^*_{\rm HOMO}$  is significantly diminished (~36%) relative to 7 (~53%). This result is consistent with the charge distribution and indicates that the Co center is significantly less basic in 2 and 5 relative to 7.

Thus, the different behavior of 2, 5, and 7 toward protonation can be explained by difference in bonding between Co and azpy, bipy, and dppe, respectively. In all three species, the electron-rich Co(I) attempts to stabilize by charge dissipation onto the ligand. The availability of low-lying  $\pi^*$  orbitals of the bipy and azpy ligand system allows for backbonding and charge dissipation onto the ligands, which results in Co–N bond shortening and a decrease in negative charge and basicity of the Co center. In the azpy ligand, the presence of the electron-rich azo N leads to its protonation and formation of 3. For 5, protonation does not yield a stable

product, resulting in loss of the cyclopentadienyl ligand. For 7, the Co(I) is unable to dissipate its charge to the ligands and remains electron-rich and highly basic; all conditions favorable for the formation of a Co(III)-hydride.

# CONCLUSION

A combination of XAS, EXAFS, and DFT methods was used to investigate the electronic structures of 1, 2, and 3, which were subsequently compared with the electronic structures of 4 and 5. The experimental data demonstrate that 2, 3, and 5 are Co(I) species, while 1 and 4 are Co(III) species. The data also show a dramatic change in the geometry upon reduction of the Co(III) species to their respective two-electron reduced Co(I)counterparts with a *decrease* in bond distance upon reduction. DFT calculations were used to investigate this apparent inverse trend and reveal this to be a result of significant back-bonding interaction between the electron-rich Co(I) center and the valence low-lying  $\pi^*$  orbitals in the azpy/bipy ligand systems, which effectively redistributes the charge onto the ligand and in turn strengthens and shortens the Co-N bond. The results show that this strong back-bonding makes the Co(I) less basic and hence unavailable for protonation. In 2, the availability of an alternate protonation site with a higher negative charge leads to the formation of 3. In contrast, the Co(I) center in 7 only has a strong  $\sigma$ -bonding interaction with dppe ligand system, which keeps the electron density at the Co(I) center and in turn facilitates facile protonation at the basic Co(I)center to form the Co(III)–H. Thus, by evaluating the frontier molecular orbitals obtained from spectroscopically calibrated DFT calculations, it is possible to explain the reactivity of Co(I) complexes toward protonation. Although basicity at the Co(I) center plays an important role in the reactivity differences between 2 and 7, it is not the only metric that matters in the evaluation of hydrogen evolution electrocatalysts. The reduction potential needed to generate the Co(I) species also needs to be evaluated when designing new electrocatalysts. Since DFT can also successfully calculate the reduction potentials of the analogous Co(III) and Co(II) complexes, it is in principle possible to design complexes that can be reduced at mild reductive potentials and protonated to form Co(III)-H. Using an experimentally calibrated DFT method to simultaneously evaluate both the electronic structure of the Co(I) species and redox potentials of the Co(III) and Co(II) species would enable the development of hydrogen evolution electrocatalysts that operate at low overpotentials. Such a guided approach is currently being tested with several ligand systems and is the subject of an ongoing investigation.

# EXPERIMENTAL SECTION

**Materials.** All manipulations were carried out under an inert atmosphere of nitrogen or argon with the use of standard vacuum line, Schlenk, and glovebox techniques. Solvents were dried by standard methods and degassed via three freeze-pump-thaw cycles. Deuterated solvents for NMR were purchased from Cambridge Isotope Laboratories. All reagents were used as received unless otherwise described. The synthesis of  $CpCoI_2(CO)$ ,<sup>45</sup> [CpCo(azpy)-( $CH_3CN$ )][ $ClO_4$ ]<sub>2</sub> 1,<sup>21</sup> CpCo(azpy) 2,<sup>21</sup> [ $CpCo(bipy)(CH_3CN$ )][ $ClO_4$ ]<sub>2</sub> 4,<sup>21</sup> CpCo(bipy) 5,<sup>24</sup> CpCo(dppe) 7,<sup>16</sup> [CpCo(dppe)(H)][ $PF_6$ ] 8,<sup>22</sup> and [DMFH][ $CF_3SO_3$ ]<sup>25</sup> were described previously. Crystallographic data for [ $CpCo(azpy)(CH_3CN$ )][ $ClO_4$ ]<sub>2</sub> 1<sup>21</sup> and similar pentamethylcyclopentadienyl ( $Cp^*$ ) complexes have been previously reported.<sup>46,47</sup>

**Instrumentation.** <sup>1</sup>H and <sup>'13</sup>C NMR spectra were recorded on Varian 300, 400, or 500 MHz spectrometers. All NMR spectra were taken at room temperature unless stated otherwise. Residual solvent proton and carbon peaks were used as reference. Chemical shifts are reported in parts per million ( $\delta$ ). High-resolution mass spectra were obtained by ESI-MS on a Thermo Fisher Exactive Orbitrap mass spectrometer.

**Synthesis.** [*CpCo(azpyH)*][*CF*<sub>3</sub>*SO*<sub>3</sub>] **3.** A solution of [DMFH]-[*CF*<sub>3</sub>*SO*<sub>3</sub>] (22 mg, 0.099 mmol) in benzene (5 mL) was added dropwise to a solution of [*CpCo*(azpy)] **2** (30 mg, 0.098 mmol) in benzene (5 mL) while stirring under N<sub>2</sub>. The solution was stirred at room temperature under N<sub>2</sub> for 30 min. The dark red solid that precipitated from solution was collected via filtration and washed thoroughly with benzene. <sup>1</sup>H NMR (500 MHz, *CD*<sub>3</sub>*CN*)  $\delta$  11.97 (*s*, 1H), 10.22 (d, *J* = 6.4 Hz, 1H), 8.13 (d, *J* = 7.4 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 1H), 7.48–7.42 (m, 3H), 7.36 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 6.98 (td, *J* = 6.5, 1.3 Hz, 1H), 4.84 (s, 5H). The <sup>1</sup>H NMR spectrum is provided in Figure S10.

[CpCo(dppe)(CH<sub>3</sub>CN)][PF<sub>6</sub>]<sub>2</sub> **6**. A solution of CpCoI<sub>2</sub>(CO) (0.4 g, 0.99 mmol) in acetonitrile (10 mL) was added dropwise to a mixture of AgClO<sub>4</sub> (0.61 g, 2.96 mmol) and 1,2-bis(diphenylphosphino)-ethane (0.43 g, 1.08 mmol) in acetonitrile (20 mL) with stirring under N<sub>2</sub>. The color of the solution changed from dark violet to organge-red with precipitation of AgI. This suspension was stirred at room temperature under N<sub>2</sub> for 4 h. After filtration, the filtrate was concentrated down to 3 mL, and roughly 30 mL of pentane was added to precipitate **6** as an orange powder in 70% yield. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN)  $\delta$  7.69 (m, 20H), 5.79 (s, 5H), 3.01 (d, *J* = 16 Hz, 4H), 1.97 (s, 3H). The <sup>1</sup>H NMR spectrum is provided in Figure S11.

**Chemical Studies.** Representative Procedure for the One-Electron Reduction of  $[CpCo(bipy)(CH_3CN)][ClO_4]_2$ .  $[CpCo(bipy)-(CH_3CN)][ClO_4]_2$  4 (5 mg, 0.0096 mmol) was weighed into a sealable NMR tube and dissolved in CD<sub>3</sub>CN (0.8 mL) in an inert atmosphere glovebox. Decamethylferrocene (4.2 mg, 0.013 mmol) was added, and the reaction was stirred at room temperature under N<sub>2</sub> for 10 min. Analysis of the products by <sup>1</sup>H NMR was not very informative due to difficulty locking and shimming the samples, suggesting the presence of paramagnetic, Co(II) species. As shown in Figures S15–S18, the ESI-MS revealed that the  $[CpCo(bipy)]^+$ formed upon reduction rapidly decomposed into a variety of CpCo and Co(bipy) complexes. As a consequence of its instability, a pure sample of  $[CpCo(bipy)]^+$  complex could not be prepared.

Representative Procedure for the Protonation of CpCo(bipy). CpCo(bipy) **5** (6.0 mg, 0.021 mmol) was weighed into a sealable NMR tube and dissolved in CD<sub>3</sub>CN (0.5 mL) in an inert atmosphere glovebox. Upon addition of  $[NH_4][PF_6]$  (3.5 mg, 0.021 mmol), the color of the solution changed from dark purple to pale yellow. To establish the identity of the protonation products, the mixture was analyzed by <sup>1</sup>H NMR. As shown in Figure S14, the appearance of the peaks at  $\delta 6.58$  (m, 2H), 6.48 (m, 2H), 2.99 (m, 2H) is consistent with free cyclopentadiene, indicating that protonation is accompanied by rapid decomposition.<sup>48</sup>

X-ray Crystallography. Single crystals for X-ray analysis were mounted on a Kapton loop using Paratone N hydrocarbon oil or

perfluorinated ether oil. All measurements were made on a Bruker APEX II CCD detector X-ray diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Frames corresponding to an arbitrary sphere of data were collected using  $\omega$ -scans of 0.3° counted for a total of 10 s per frame. Data were integrated using the Bruker SAINT software program<sup>49</sup> to a maximum  $\theta$  value of 28.26°, analyzed for agreement and possible absorption using XPR,<sup>50</sup> and corrected for Lorentz and polarization effects. Absorption corrections were applied using the SADABS program.<sup>49</sup> No decay correction was applied. Structures were solved by direct methods,<sup>49</sup> expanded using Fourier techniques, and refined by fullmatrix least-squares procedures based on  $F^{2.51}$  Hydrogen atoms were included in ideal positions and refined isotropically in riding model with Uiso = 1.5Ueq(X) for methyl groups and Uiso = 1.2Ueq(X) for other atoms, where Ueq(X) are thermal parameters of parent atoms. Non-hydrogen atoms were refined anisotropically. Crystallographic data for 4 and 5 are presented in the Supporting Information. Crystallographic data for 3 has been previously reported.<sup>26</sup> Crystals of 4 suitable for X-ray diffraction were obtained from vapor diffusion of diethyl ether into an acetonitrile solution. Crystals of 5 suitable for Xray diffraction were obtained from the slow evaporation of an acetonitrile solution. The ORTEP for 4 and 5 are shown in Figures S19 and S20, respectively. Crystallographic data for similar pentamethylcyclopentadienyl (Cp\*) complexes have been previously reported.4

X-ray Absorption Spectroscopy. X-ray absorption spectra were measured at the Stanford Synchrotron Radiation Lightsource (SSRL) on the unfocused 20-pole 2 T wiggler side-station beamline 7-3 under standard ring conditions of 3 GeV and ~500 mA. A Si(220) double crystal monochromator was used for energy selection. The no-M0 mirror configuration was used. The monochromator was detuned by 50% to eliminate higher harmonic components in the data. Solid samples were prepared by evenly dispersing the compound in a BN matrix and compacting the mixture into an Al spacer. Solution samples were prepared by dispensing ~2 mM solutions into delrin sample holders with X-ray transparent Kapton windows. During data collection, the samples were maintained at a constant temperature of ~10 K using an Oxford Instruments CF 1208 liquid helium cryostat. A 30-element Ge fluorescence detector from Canberra Industries was employed for fluorescence data measurement on solutions, and ionchambers placed downstream of the cryostat were used to measure transmission data on solid samples.

Co K-edge XAS data were measured on 1-8 as solids; the oneelectron reduction product of 4 was measured in acetonitrile. Solution measurements were performed using soller-slits equipped with Fefilter in front of the Ge detector and using a Co-foil for energy calibration. The first inflection point of the foil spectrum was fixed at 7709.5 eV. The samples were monitored for photoreduction, but no sign of photodamage was observed during the course of data collection. Co K-edge EXAFS data were measured up to  $k = 15 \text{ Å}^{-1}$ . The data presented here are 3-4 scan average spectra for the solid samples and 8 scan average spectra for the solution samples. Data were processed by fitting a second-order polynomial to the pre-edge region and subtracting this from the entire spectrum as background in PySpline.<sup>52</sup> A three-region spline of orders 2, 3, and 3 was used to signals  $\chi(k)$  were calculated by using *FEFF* (macintosh version 7)<sup>53–55</sup> on the crystal structure on the crystal structures of the respective compounds investigated in this study. Theoretical models were fit to the data using EXAFSPAK.<sup>56</sup> The structural parameters varied during the fitting process were the bond distance (R) and bond-variance  $\sigma^2$ , which is related to the Debye-Waller factor resulting from thermal motion and static disorder of the absorbing and scattering atoms. The nonstructural parameter  $\Delta E_0$  (the energy at which k = 0) was also allowed to vary but was restricted to a common value for every component in a given fit. Coordination numbers were systematically varied in the course of the fit but were fixed within a given fit. The Co K-pre-edge data were fit with individual pseudo-Voigt contributions in PeakFit to obtain the total area and the intensity weighted average energy (IWAE) positions.

Theoretical Details. Gradient-corrected (GGA) spin unrestricted DFT calculations were performed using ORCA 3.03.<sup>37</sup> The BP86<sup>57,58</sup> local functional and the following basis sets were employed for the calculations: Ahlrich's all electron triple- $\zeta$  basis set TZVPP<sup>59-61</sup> with three polarization functions on Co, TZVP on all other atoms. B3LYP<sup>57,62</sup> hybrid functional was also employed but resulted in incorrect bond distances. Tight convergence criteria were imposed on all calculations. Calculations were performed in a dielectric continuum using the conductor-like screening model (COSMO)<sup>63</sup> with the dielectric properties of acetonitrile. Starting guess geometries were obtained from the respective crystal structures and modified appropriately where needed. TD-DFT calculations were performed with the electronic structure program ORCA to calculate the energies and intensities of the Co K pre-edges.<sup>39</sup> The tight convergence criterion was imposed on all calculations. The same functional and basis sets were used as the geometry optimizations. The calculated energies and intensities were Gaussian broadened with half-widths of 1.3 eV to account for core-hole lifetime and instrument resolution. The calculated pre-edge energy positions were linearly scaled by 197 eV to match the experimental spectra.<sup>64</sup> This is generally the case with core level TD-DFT calculations since DFT does not describe core potentials accurately, resulting in the core levels being too high in energy relative to the valence levels. The TD-DFT results were compared with experimental data to judge the efficacy of the DFT calculation (see Figure S6). The molecular contour plots were generated in ChemCraft, and the individual atomic orbital contributions to the molecular orbitals were obtained using QMForge.65

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b02475.

Crystallographic data files (CIF format), tabulated X-ray data, and molecular structures obtained from single crystal X-ray diffraction for 4 and 5. <sup>1</sup>H NMR spectrum of 3. <sup>1</sup>H NMR and ESI-MS upon protonation of CpCp(bipy) 5 and reduction of  $[CpCo(bipy)-(CH_3CN)][ClO_4]_2$  4. Additional information detailing the Co K-edge EXAFS analysis and DFT and TD-DFT calculation details on the various complexes investigated in this study (PDF)

#### Accession Codes

CCDC 1866349–1866350 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### **Author Contributions**

R.S., R.M.W, L.J.G., and E.M. designed and performed the research. R.S., L.J.G., and E.M. analyzed the data.

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#### Notes

The authors declare no competing financial interest.

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