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Computational Characterization of Redox Non-Innocence in Cobalt-Bis(Diaryldithiolene)-Catalyzed Proton Reduction

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S *Supporting Information*

ABSTRACT: Localized orbital bonding analysis (LOBA) was employed to probe the oxidation state in cobalt-bis(diaryldithiolene)-catalyzed proton reduction in nonaqueous media. LOBA calculations provide both the oxidation state and chemically intuitive views of bonding in cobalt-bis(diaryldithiolene) species and therefore allow characterization of the role of the redox non-innocent dithiolene ligand. LOBA results show that the reduction of the monoanion species $[1Br]^-$ is metal-centered and gives a cobalt(II) ion species, $[1Br]^{2-}$, coordinated to two dianionic ene-1,2-dithiolates. This electronic configuration is in agreement with the solution magnetic moment observed for the analogous salt $[1F]^{2-}$ (μ_{eff} = 2.39 μ_B). Protonation of $[1Br]^{2-}$ yields the cobalt(III)-hydride $[1Br(CoH)]^-$ species in which the Co–H bond is computed to be highly covalent (Löwdin populations close to 0.50 on cobalt and hydrogen atoms). Further reduction of $[1Br(CoH)]^-$ forms a more basic cobalt(II)–H intermediate $[1Br(CoH)]^{2-}$ (S = 0) from which protonation at sulfur gives a S–H bond *syn* to the Co–H bond. Formation of a cobalt-dihydrogen $[1Br(CoH_2)]^-$ intermediate is calculated to occur via a homocoupling (H$^\bullet$ + H$^\bullet$ → H$_2$) step with a free energy of activation of 5.9 kcal/mol in solution (via C-PCM approach).
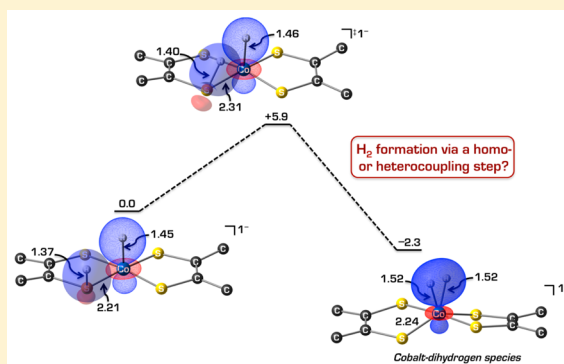
■ INTRODUCTION

The growing interest in renewable energy, coupled with the continuing rise of CO_2 emissions from the burning of fossil fuels, has focused considerable attention on artificial photosynthesis.[1−18] In this context, hydrogen has great potential as an environmentally clean-energy fuel.[19−24] Numerous molecular electrocatalysts based on first-row transition metals for the hydrogen evolution reaction (HER) have been widely studied in organic and aqueous solvents.[25−67] One particular example is the use of cobalt-bis(dithiolene) complexes for the photocatalytic and electrocatalytic reduction of protons.[68−75] These species incorporate redox non-innocent ligands, which act as an electron reservoir during catalysis, and sulfur donor atoms, which may serve as proton relays.[76−84]

Recently, we reported the experimental and computational study of a series of dimeric cobalt-bis(diaryldithiolene) electrocatalysts $[Co(S_2C_2Ar_2)_2]_2$, shown in Figure 1, with various aryl para substituents (X = OMe, F, Cl, and Br) for proton reduction in nonaqueous media (*N,N*-dimethylformamide, DMF).[85] These $[Co(S_2C_2Ar_2)_2]_2$ electrocatalysts, which formally exist as neutral Co–S dimers, have a singlet ground state. Reduction of the dimeric units $[1X]_2$ by one electron to the dimeric anionic species $[1X]_2^-$ (Step A in Figure 2) is reversible. This is followed by a second one-electron reduction, which is irreversible, to afford $[1X]_2^{2-}$ (Step B in Figure 2). As previously reported, this irreversible reduction event is likely

attributed to the chemical conversion of the monomeric anionic species $[1X]^-$ obtained from the dimeric dianionic complex $[1X]_2^{2-}$. The former complexes are further reduced by reversible, one-electron processes to form monomeric dianionic species $[1X]^{2-}$ (Step C in Figure 2; e.g., for X = Br, i_{pc}/i_{pa} = 0.9). The current density associated with this $[1X]^-/[1X]^{2-}$ reduction event is twice that of the preceding one-electron events and is characterized by a peak separation of greater than 60 mV for all derivatives (e.g., for X = Br, ΔEp = 80 mV). This implies that this final reduction process corresponds to the one-electron reduction of two monomeric units (2e$^-$/dimer).

Despite extensive mechanistic studies to understand the electronic structure and bonding of cobalt-bis(dithiolene) species, some debate remains regarding their ground-state properties (spin-state and geometry) as well as the oxidation state of cobalt and dithiolene ligand during catalysis. Scheme 1 illustrates the oxidation state ambiguity that arises with the resting state of the catalyst, $[1X]^-$, due to non-innocence of the dithiolene ligand. Similar and even richer redox questions arise upon reduction, hydride formation, and subsequent reduction and protonation to finally yield the H−H bond. Electronic calculations are a powerful tool not just for computing the
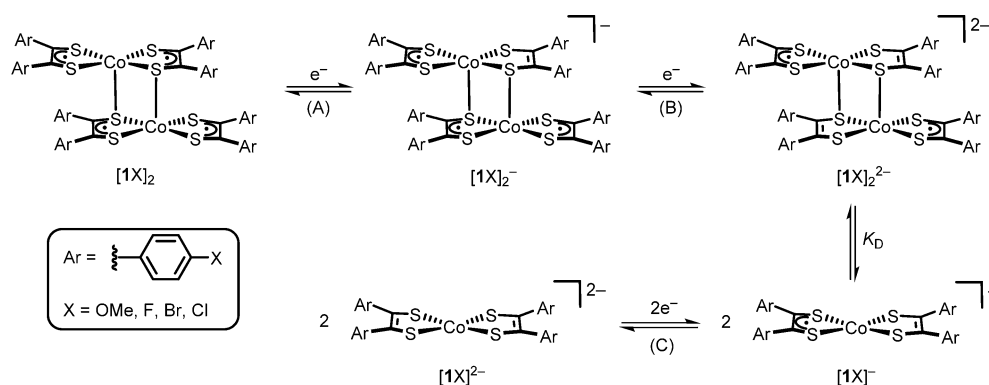
Figure 1. Sequence of reduction events for cobalt-bis(diaryldithiolene) derivatives (X = OMe, F, Cl, and Br). The letters in parentheses correspond to the redox events denoted on the cyclic voltammogram in Figure 2. Note that all cobalt-bis(diaryldithiolene) complexes are arbitrarily depicted in Co(II)-based resonance forms. The figure was reproduced with permission from ref 85. Copyright 2014 American Chemical Society.
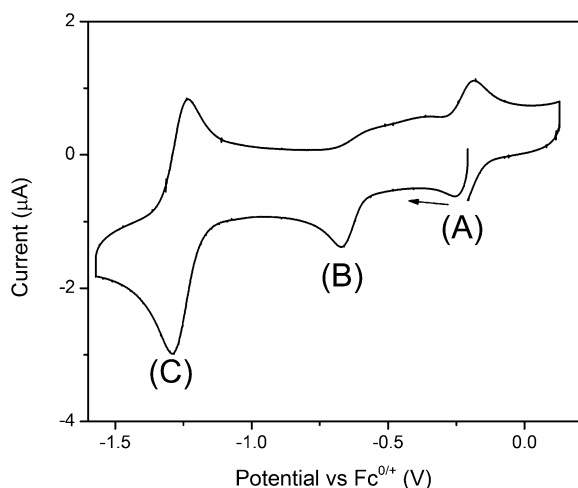

Figure 2. Cyclic voltammogram for $[1Br]_2$ (0.15 mM) in DMF solution with 0.1 M $[NBu_4]PF_6$ as the supporting electrolyte. The labeled redox events correspond to the similarly denoted steps in Figure 1. The figure was reproduced with permission from ref 85. Copyright 2014 American Chemical Society.

Scheme 1. Resonance Structures for the Monoanion Species $[1X]^-$ Due to Non-innocence of the Dithiolene Ligand
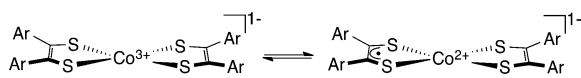
intermediates but also for obtaining a consistent analysis of the charges in bonding at each step in the catalytic cycle.

This report describes the computational characterization of the oxidation states of the redox non-innocence in cobalt-bis(diaryldithiolene) (X = Br) species using the localized orbital bonding analysis (LOBA).[86] LOBA calculations provide both the oxidation state for the transition metal complexes studied as well as chemically intuitive views of bonding. In this case, the Edmiston−Ruedenberg orbitals, which maximize the electrostatic self-interaction of each orbital, were employed in conjunction with the Löwdin population analysis. Only the lowest energy structures calculated at the BP86/BS1 level of theory for the cobalt-bis(diaryldithiolene) (X = Br) species will be discussed. LOBA results showed that all core orbitals are fully localized (Löwdin population >0.99); therefore, only the valence orbitals will be discussed. The oxidation states in cobalt-bis(diaryldithiolene) complexes were determined from

the number of fully localized d-electrons (Löwdin population >0.90) in the α- and β-spaces. However, where LOBA calculations suggest the presence of cobalt-ligand orbitals of a covalent nature (Löwdin population close to 0.50), such bonds are considered to contribute to the oxidation state. In this case, the Löwdin populations in the α- and β-spaces are combined together, which add a full unit to the oxidation number, as is usually the case. Note that a similar approach was employed to calculate the oxidation states of manganese and cobalt catalysts for the oxygen evolution reaction (OER) and the CO_2 reduction reaction (CO2RR), respectively.[86−88]

■ RESULTS AND DISCUSSION

Monoanion Species $[1Br]^-$. As previously mentioned, initial reductive dissociation of the neutral Co−S dimer yields the monomeric anion species $[1Br]^-$. Calculations at the BP86/BS1 level of theory indicate that singlet and triplet states are degenerate ($\Delta G = -2.0$ kcal/mol in favor of the singlet state) and are rigorously square planar (α, which is the dihedral angle between the two ligand CoS_2 planes, is calculated to be 0.0°). In the singlet state, LOBA results show six fully localized d-electrons (Löwdin population >0.90), three in the α-space and three in the β-space (Figure 3). This suggests that the cobalt center is in the +3 oxidation state (d^6). In addition to these six fully localized d-electrons, a set of six localized orbitals corresponding to the donation from sulfur to cobalt (Figure 4) and six lone-pairs on sulfur (Löwdin population >0.80) were
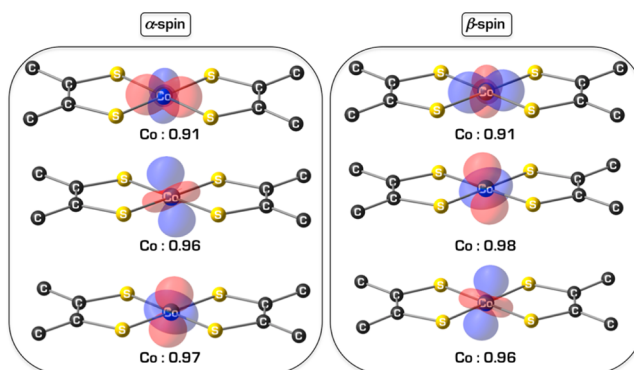

Figure 3. Isosurface (0.07 au) plots of the Edmiston−Ruedenberg localized d-electrons (α- and β-spins) for the square planar monoanion species $[1Br]^-$ (S = 0, $\langle S^2 \rangle$ = 0.3 au). The Löwdin population analyses are provided for cobalt. Aryl groups have been omitted for clarity.
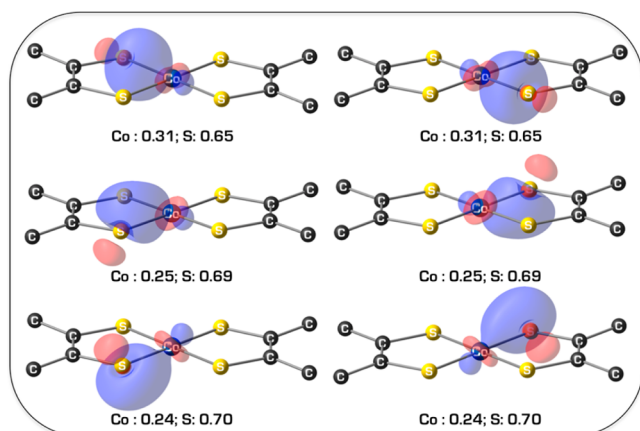
Figure 4. Isosurface (0.07 au) plots of the Edmiston−Ruedenberg localized orbitals (α-spin) corresponding to the donation from sulfur to cobalt for the square planar monoanion species $[1Br]^-$ (S = 0, $\langle S^2 \rangle$ = 0.3 au). The Löwdin population analyses are provided for cobalt and sulfur atoms. Aryl groups have been omitted for clarity.

computed in the α-space (Figure 5). The presence of those six localized orbitals for the donation from sulfur to cobalt is
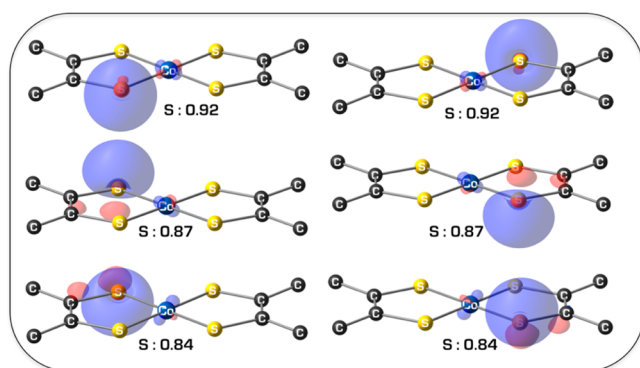

Figure 5. Isosurface (0.07 au) plots of the Edmiston−Ruedenberg localized orbitals (α-spin) for the lone-pairs on the sulfur atoms of the square planar monoanion species $[1Br]^-$ (S = 0, $\langle S^2 \rangle$ = 0.3 au). The Löwdin population analyses are provided for the sulfur atoms. Aryl groups have been omitted for clarity.

required to stabilize the high oxidation state on cobalt (i.e., +3), whereas the $\langle S^2 \rangle$ value of 0.3 au corresponds to the presence of biradical character on the dithiolene ligand. A similar trend is observed in the β-space (Figures S1 and S2). Overall, the monomeric anion species $[1Br]^-$ in the singlet state at the BP86 level of theory is best described as a Co(III) ion center coordinated to two dianionic ene-1,2-dithiolate ligands. The triplet state has also been considered and was computed to be a cobalt(III) center (see Supporting Information). Note, however, that Neese and Wieghardt demonstrated that $\{Co[S_2(3,5-^tBu_2C_6H_2)]_2\}^-$ exhibit both Co^{2+} and Co^{3+} character in the triplet state. In this latter case, the Co $3d_{xy}$ orbital is isoenergetic with the highest π^*-b_{2g} system of the ligand.

Although +3 is clearly the correct assignment of the oxidation state of cobalt in $[1Br]^-$, the ambiguities of redox non-innocence are also clearly evident. If one considers the net donation from the dianionic ene-1,2-dithiolates through the dative interactions in the α- and β-spaces shown in Figures 4 and SI, a total of 3.2 electrons are donated. Combined with the

missing 0.3 electrons from incomplete localization of the d-electrons (Figure 3), one estimates a net charge flow of 2.9 electrons to the Co due to dative interactions. The distinction between formal redox (+3) and effective charge (+0.1) is thus very significant, as should be expected, and illustrates how effectively the high oxidation state is accommodated.

Dianion Species $[1Br]^{2-}$. Reduction of $[1Br]^-$ by one electron gives the dianion species $[1Br]^{2-}$, which is calculated to be nearly square planar (α = 22.2°) and have a doublet ground-state. LOBA calculations suggest that the reduction is metal-centered with the addition of one localized d-electron in the α-space compared to $[1Br]^-$ (Table 1 and Figure 6). This

Table 1. Summary of the Edmiston−Ruedenberg Localized Orbitals for Lowest Energy Structures Computed at the BP86/BS1 for the Cobalt-bis(diaryldithiolene) (X = Br) Species

complex	spin	Co d-electron	S donation to Co	S lone-pair
$[1Br]^-$ (S = 0)	$\alpha-$	3	6	6
	$\beta-$	3	6	6
$[1Br]^{2-}$ (S = 1/2)	$\alpha-$	4	4	8
	$\beta-$	3	4	8
$[1Br(CoH)]^-$ (S = 1/2)	$\alpha-$	3[a]	4	8
	$\beta-$	2[a]	4	8
$[1Br(CoH)]^{2-}$ (S = 0)	$\alpha-$	3[a]	4	8
	$\beta-$	3[a]	4	8
$[1Br(CoH)(SH)]^-$ (S = 0)	$\alpha-$	3[a]	4	7[b]
	$\beta-$	3[a]	4	7[b]
TS (S = 0)	$\alpha-$	3[a]	4	7[b]
	$\beta-$	3[a]	4	7[b]
$[1Br(CoH_2)]^-$ (S = 0)	$\alpha-$	3[c]	4	8
	$\beta-$	3[c]	4	8

[a]One additional localized d-electron for the Co−H bond was computed. [b]One additional localized orbital for the S−H bond was obtained. [c]A localized orbital for the Co−H$_2$ bond was calculated.

total of seven fully localized d-electrons (four in the α-space and three in the β-space) implies an oxidation state of +2 (d^7) on cobalt. Interestingly, in light of our discussion of oxidation state versus effective charge for $[1Br]^-$, our calculations also
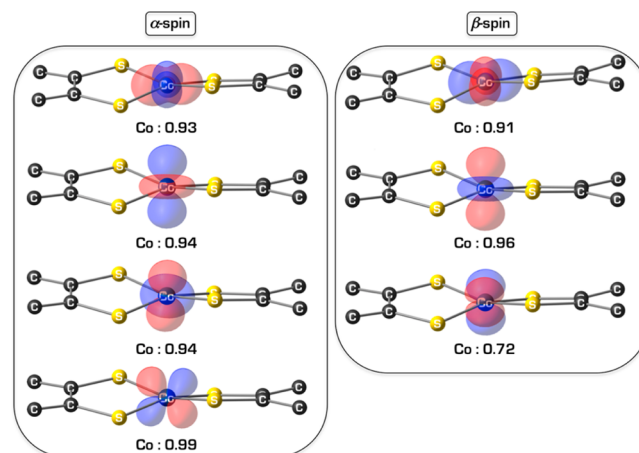

Figure 6. Isosurface (0.07 au) plots of the Edmiston−Ruedenberg localized d-electrons for the nearly square planar dianion species $[1Br]^{2-}$ (S = 1/2, $\langle S^2 \rangle$ = 0.8 au). The Löwdin population analyses are provided for cobalt. Aryl groups have been omitted for clarity.

show a rearrangement of the dithiolate ligand to accommodate the lower oxidation state on the metal center. In this case, a set of four localized orbitals corresponding to donation from S to Co (Figures S7 and S8) and eight lone-pairs on S are computed both in the α- and β-spaces whereas six donor orbitals and six lone-pairs were calculated in $[1Br]^-$, respectively. In addition, the calculated C−S bond of 1.77 Å in $[1Br]^{2-}$ (c.f. 1.75 Å in $[1Br]^-$) supports the view that the ligands are fully reduced to dianionic ene-1,2-dithiolates. Therefore, $[1Br]^{2-}$ is best described as a Co(II) ion coordinated to two dianionic ene-1,2-dithiolates. This electronic configuration is consistent with the solution magnetic moment observed for the analogous salt, $[1F]^{2-}$ (μ_{eff} = 2.39 μ_B), and the square planar coordination geometry confirmed by single X-ray crystallography. Applying the corresponding treatment of charge flow suggests that the effective charge on Co^{2+} in this dianionic complex is roughly −0.4.

Cobalt-Hydride Species [1Br(CoH)]⁻ and [1Br(CoH)]²⁻. After formation of the dianion species $[1Br]^{2-}$, protonation affords the cobalt-hydride species $[1Br(CoH)]^-$ (S = 1/2), which was found to be lower in energy than the formation of an S−H species ($[1Br(SH)]^-$, ΔG = +10.9 kcal/mol). LOBA results on $[1Br(CoH)]^-$ show a total of five fully localized d-electrons (three in the α-space and two in the β-space, Figure S10). In addition to these metal-based d-orbitals, a set of two localized orbitals (one in the α-space and one in the β-space) involving the Co−H bond was computed (Figure 7).

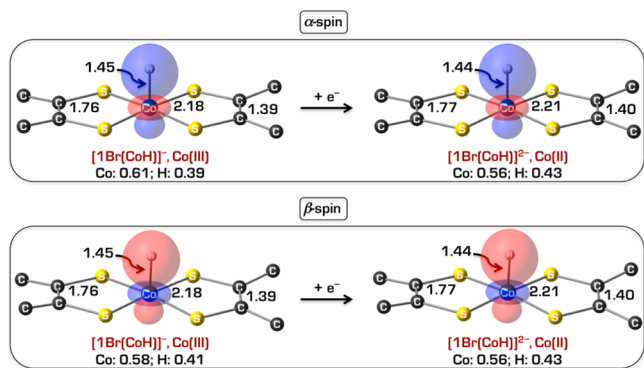**Figure 7.** Isosurface (0.07 au) plots of the Edmiston−Ruedenberg localized orbitals for the cobalt-hydride species $[1Br(CoH)]^-$ (S = 1/2, $\langle S^2 \rangle$ = 0.8 au) and $[1Br(CoH)]^{2-}$ (S = 0, $\langle S^2 \rangle$ = 0.0 au) in the α- and β-spaces. The Löwdin population analyses are provided for cobalt and hydrogen atoms. Key distances are in angstroms, and the aryl groups are omitted for clarity.

Interestingly, the Löwdin population analysis of the d_z^2 orbital for cobalt (0.61 and 0.58 in the α- and β-spaces, respectively) and hydrogen (0.39 and 0.41 in the α- and β-spaces, respectively) implies that the Co−H bond is more covalent than polarized (Löwdin populations close to 0.50). Following this unexpected result in the gas phase, additional LOBA calculations were performed in solution (DMF, via the C-PCM approach). In this case, single-point LOBA calculations were computed on the optimized structures in the gas phase (DMF, SP) as well as on the optimized species in solution (DMF, OPT) using the BP86/BS1 level of theory. As shown in Table 2, the Löwdin populations on cobalt and hydrogen do not significantly change when computed in solution. The cobalt atom becomes slightly more acidic and the basicity of the hydrogen atom increases negligibly from 0.39 in the gas phase

Table 2. Löwdin Population Analyses of the Edmiston−Ruedenberg Localized Orbitals for the Co−H Bond (α- and β-Spaces) in [1Br(CoH)]⁻ and [1Br(CoH)]²⁻ in the Gas Phase and in Solution (DMF, via the C-PCM Approach)

complex	atom	gas phase		DMF (SP)[a]		DMF (OPT)[b]	
		α−	β−	α−	β−	α−	β−
$[1Br(CoH)]^-$	Co	0.61	0.58	0.60	0.57	0.59	0.57
	H	0.39	0.41	0.40	0.42	0.40	0.42
$[1Br(CoH)]^{2-}$	Co	0.56	0.56	0.54	0.54	0.54	0.54
	H	0.43	0.43	0.45	0.45	0.46	0.46

[a]Single-point (SP) LOBA calculations were performed in solution. [b]LOBA calculations were computed on the optimized (OPT) structures in solution.

to 0.40 in DMF. Overall, the Co−H bond remains covalent, which implies that the computed population of the d_z^2 orbital on the cobalt of the Co−H bond (0.61 and 0.58 in the α- and β-spaces, respectively, for a combined total of 1.19) should be considered to determine the oxidation state of the cobalt-bis(diaryldithiolene) species. Therefore, LOBA results show that five d-electrons are fully localized on cobalt (three in the α-space and two in the β-space) to which one additional d-electron for the Co−H bond should be added. This total of six d-electrons for cobalt suggests that the cobalt-hydride species $[1Br(CoH)]^-$ has a Co(III) center coordinated to one dianionic ene-1,2-dithiolate and one monoanionic radical. LOBA calculations also indicate the presence of a set of eight localized orbitals, which involve donation from sulfur to cobalt (four in the α-space and four in the β-space) to stabilize the higher oxidation state of the metal (i.e., Co^{3+}).

After formation of the cobalt(III)-hydride species $[1Br-(CoH)]^-$, three possible pathways for the evolution of H_2 may occur: (1) a dehydrocoupling of two Co(III)−H species to release H_2 and regenerate the monoanion species $[1Br]^-$, (2) protonation of the Co(III)−H bond to directly produce a transient coordinated H_2 complex, and (3) reduction of Co(III)−H to Co(II)−H followed by protonation. Previous studies on derivatives of $[Co(bdt)_2]^-$ support an ECEC mechanism for catalysis (Pathway 3).[68,69] In addition, an EC′ mechanism for proton reduction would likely proceed via double protonation of $[1Br]^{2-}$ followed by subsequent release of H_2. This would be reflected by a growth in catalytic current at the $[1Br]^-/[1Br]^{2-}$ redox wave (Figure S14). However, experimentally, a likely pathway involves initial protonation of $[1Br]^{2-}$ followed by reduction of this protonated species before a second protonation event occurs to liberate H_2. In addition, LOBA results also suggest that the Co−H bond is weakly basic, which further supports the latter pathway.

As expected, reduction of the Co(III)−H species $[1Br-(CoH)]^-$ by one electron is computed to be metal-centered with the addition of one fully localized d-electron in the β-space for a total of six fully localized d-electrons (three in the α-space and three in the β-space). In this case, the cobalt-hydride species $[1Br(CoH)]^{2-}$ becomes slightly more basic (Figure 7). For instance, the Löwdin population analysis varies in the α-space for cobalt from 0.61 to 0.56, whereas the hydrogen atom becomes more hydridic (0.39 in $[1Br(CoH)]^-$, 0.43 in $[1Br(CoH)]^{2-}$). Similar results are observed in the β-space. Again, calculations in solution do not significantly affect the result (Table 2). Overall, as observed in $[1Br(CoH)]^-$, the Co−H bond is covalent (populations close to 0.50). This suggests that the population of the d_z^2 orbital on cobalt (0.56 in
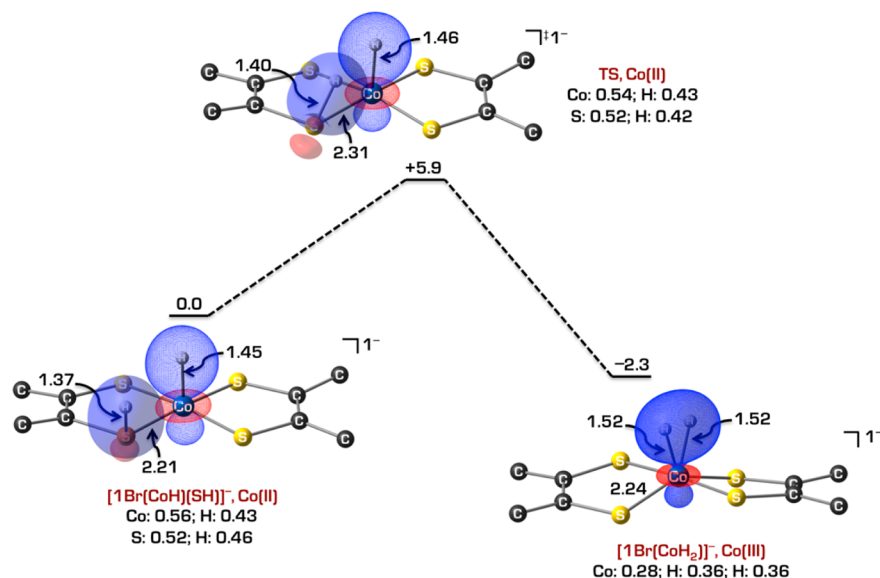
Figure 8. Isosurface (0.07 au) plots of the Edmiston−Ruedenberg localized orbitals for the singlet ground state displaying migration of the hydrogen atom in [**1**Br(CoH)(SH)]⁻ from a sulfur atom to the Co−H Bond. The localized orbitals for the S−H and Co−H bonds are both displayed. Gibbs free energies are in kcal/mol, and the Löwdin population analyses are provided for cobalt, sulfur, and the hydrogen atoms. Aryl groups have been omitted for clarity.
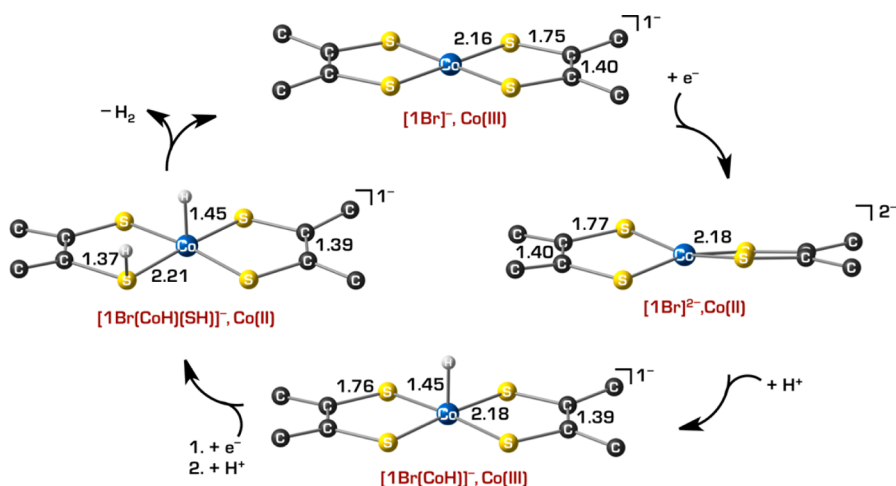

Figure 9. Mechanism of proton reduction catalyzed by cobalt-diaryldithiolenes (X = Br) derived from experimental and computational results. Key distances are in angstroms, and the aryl groups are omitted for clarity. The figure was adapted with permission from ref 85.

the α- and β-spaces for a combined total of 1.12) for the Co−H bond should be considered to determine the oxidation state of the metal center. In this case, there are six fully localized d-electrons (three in the α-space and three in the β-space) and one additional d-electron for the covalent Co−H bond. This confirms that the cobalt center is in the +2 oxidation state (d⁷). Note that the Mulliken spin population of 0.00 on cobalt in [**1**Br(CoH)]²⁻ is normally taken to imply the +3 oxidation state (diamagnetic, d⁶), which is not in agreement with the LOBA results (+2 oxidation state, d⁷). This apparent contradiction arises from presuming that H is hydridic when interpreting spin populations, whereas LOBA shows that there is a shared electron pair bond between cobalt and hydrogen; therefore, one additional d-electron for the covalent Co−H bond should be taken into account in the oxidation state of the cobalt-bis(diaryldithiolene) species.

Second Protonation at Sulfur, [1Br(CoH)(SH)]⁻. After the formation of a Co(II)-hydride species, a second

protonation step is required to release H₂. At this stage, the Co(II)−H complex can react with one proton in solution or undergo a ligand-based protonation at a sulfur atom. We examined this second pathway with protonation of [**1**Br-(CoH)]²⁻ happening at sulfur to form an S−H bond *syn* to the Co−H bond (Figure 8). As expected, despite zero spin density, the oxidation state on cobalt remains +2 (d⁷). As before, LOBA results show the presence of six fully localized d-electrons (three in the α-space and three in the β-space). In addition, the population of the d_{z^2} orbital on cobalt for the Co−H bond (0.56 in the α- and β-spaces) gives one additional d-electron. Interestingly, the S−H bond is also computed to be covalent rather than polarized with a calculated Löwdin population close to 0.50 (i.e., 0.52, Figure 8). We also performed LOBA calculations in solution, and the results are summarized in Table S1. Again, the Löwdin populations obtained in solution are similar to those in the gas phase. For instance, the Löwdin population of the Co−H bond goes on cobalt from 0.56 (in the

gas phase) to 0.55 (in solution), whereas the population on hydrogen does not change.

Cobalt-Dihydrogen Species, $[1Br(CoH_2)]^-$. In $[1Br(CoH)(SH)]^-$, the two hydrogen atoms are in close proximity, which allows the formation of a H—H bond prior to the release of H_2. A transition state, **TS**, from $[1Br(CoH)(SH)]^-$ corresponding to the formation of a cobalt-dihydrogen intermediate, $[1Br(CoH_2)]^-$, was located with a free energy of activation of 5.9 kcal/mol (Figure 8). LOBA calculations show that this **TS** has a cobalt(II) ion center (d^7, six fully localized d-electrons plus one d-electron for the Co—H bond in which the population on cobalt of the d_z^2 orbital is 0.54 in the α- and β-spaces). Moreover, results suggest that the Löwdin population on the hydrogen atoms on cobalt and sulfur remains close to 0.50, which implies that the formation of the cobalt-dihydrogen intermediate $[1Br(CoH_2)]^-$ occurs via a homo-coupling (H$^\bullet$ + H$^\bullet$ → H_2) step. This result contrasts with previous experimental findings for the formation of H_2 using nickel pyridylthiolate and pyrimidinethiolate catalysts.[64,89,90] In this case, a heterocoupling (H$^-$ + H$^+$ → H_2) step involving a ligand-bound proton at nitrogen and a metal-bound hydride is proposed. LOBA calculations in solution confirm that H_2 formation proceeds via a homocoupling mechanism (Table S1). Finally, the cobalt-dihydrogen species, $[1Br(CoH_2)]^-$, has an oxidation state of +3 (six fully localized d-electrons) after formation of the H—H from which H_2 release gives back $[1Br]^-$.

The proposed mechanism, derived from experimental and computational results, of proton reduction catalyzed by cobalt-diaryldithiolenes (X = Br) is shown in Figure 9. The initial monoanion species $[1Br]^-$ is calculated to be a cobalt(III) species. One-electron reduction of $[1Br]^-$ yields a Co(II) ion coordinated to two dianionic 1,2-dithiolates from which protonation at cobalt rather than sulfur forms the cobalt(III)-hydride species $[1Br(CoH)]^-$ (which features a covalent Co—H bond). At this stage, an ECEC mechanism is likely to occur to afford the more basic cobalt(II)—H intermediate $[1Br(CoH)]^{2-}$ (S = 0). In this case, protonation at sulfur gives the syn intermediate $[1Br(CoH)(SH)]^-$ (S = 0) from which formation of a cobalt-dihydrogen species occurs via a homocoupling (H$^\bullet$ + H$^\bullet$ → H_2) mechanism with a free energy of activation of 5.9 kcal/mol in DMF (via the C-PCM approach).

CONCLUSIONS

Density functional theory (DFT) calculations using the localized orbital bonding analysis scheme were employed to characterize the role of the non-innocent ligands in cobalt-diaryldithiolenes (X = Br). LOBA calculations suggest that reduction of the monoanion species $[1Br]^-$ by one electron yields the dianionic $[1Br]^{2-}$ species. This one-electron reduction, which has a doublet ground-state, is calculated to be metal-centered and affords a cobalt(II) ion coordinated to two dianionic ene-1,2-dithiolates. This last point agrees with the solution magnetic moment measured for the analogous salt, $[1F]^{2-}$ (μ_{eff} = 2.39 μ_B).[85] Protonation of $[1Br]^{2-}$ gives the cobalt(III)-hydride species in which the Co—H bond is computed to be covalent rather than polarized. A second metal-based reduction forms the more basic cobalt(II)—H intermediate $[1Br(CoH)]^{2-}$ (S = 0) from which protonation at sulfur gives an S—H bond syn to the Co—H bond. Surprisingly, formation of the cobalt-dihydrogen $[1Br(CoH_2)]^-$ species is calculated to occur via a homocoupling (H$^\bullet$ + H$^\bullet$ → H_2) step

mechanism with a free energy of activation of 5.9 kcal/mol in solution (via the C-PCM approach). The LOBA results reported here provide an additional way of characterizing the role of the non-innocent ligand as well as calculating the oxidation state in cobalt-bis(diaryldithiolene)-catalyzed proton reduction. These new mechanistic insights may allow further development of cobalt-bis(diaryldithiolene) electrocatalysts exhibiting greater activity and can also be applied to other electrocatalysts where non-innocent ligands play an important role.

COMPUTATIONAL DETAILS

Density functional theory (DFT) calculations were performed with the Q-Chem package[91] using the BP86 functional.[92,93] For the geometry optimization, the Wachters+f basis set was used for Co[94,95] and the double-ζ polarized plus diffuse 6-31+G** basis was employed for all other atoms (denoted as BS1).[96,97] Exchange correlation integrals were evaluated with a quadrature grid of 75 radial points and 302 Lebedev angular points. Unrestricted SCF calculations were performed using a matrix element threshold of 10^{-14} Hartrees and a tight convergence criterion of 10^{-8} Hartrees via either the Direct Inversion in the Iterative Subspace (DIIS) algorithm[98,99] or the Geometric Direct Minimization (GDM) algorithm.[100] Stability analyses were performed in addition to analytical frequency calculations on all stationary points to ensure that geometries correspond to local minima (all positive eigenvalues) or transition states (one negative eigenvalue). IRC calculations and subsequent geometry optimizations were used to confirm the minima linked by each transition state. Single-point calculations including solvent-corrected energies have also been computed via the SWIG C-PCM approach[101,102] (DMF, ε = 37.219) using the UFF radii. All energies are corrected for zero-point-vibrational energy, whereas free energies (quoted at 298.15 K and 1 atm) are corrected using the modified harmonic oscillator approximation proposed by Grimme where low-lying vibrational modes are treated by a free-rotor approximation.[103] The localized orbital bonding analysis (LOBA) calculations[86] were performed at the BP86/BS1-optimized geometries using the Def2-SVP basis set for all atoms (denoted BS2).[104] This basis set was used to avoid linear dependencies. The Edmiston–Ruedenberg orbitals, which maximize the electrostatic self-interaction of each orbital, were employed in conjunction with the Löwdin population analysis using the Def2-SVP basis set as auxiliary basis.[104] The thresholds for the LOBA calculated were kept as default (60% for localization and 15% for occupation).

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.5b00968.

> Details of all computed structures and associated energies, plots of the Edmiston–Ruedenberg localized orbitals, and cyclic voltammograms of $[1Br]_2$ (PDF)

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Notes
The authors declare no competing financial interest.

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