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Reversible, Electrochemically Controlled Binding of Phosphine to Iron and Cobalt Bis(dithiolene) Complexes

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The homoleptic bis(dithiolene) complexes $[M(S_2C_2R_2)_2]_2$ (M = Fe, Co; R = *p*-anisyl) undergo two successive reductions to form anions that display $[M(S_2C_2R_2)_2]_2^{2-} \leftrightarrow 2[M(S_2C_2R_2)_2]^{1-}$ solution equilibria. The neutral dimers react with Ph_3P to form square pyramidal $[M(Ph_3P)(S_2C_2R_2)_2]^0$. Voltammetric measurements upon $[M(Ph_3P)(S_2C_2R_2)_2]^0$ in CH_2Cl_2 reveal only irreversible features at negative potentials, consistent with Ph_3P dissociation upon reduction. Dissociation and reassociation of Ph_3P from and to $[Fe(Ph_3P)(S_2C_2R_2)_2]^0$ is demonstrated by spectroelectrochemical measurements. These collective observations form the basis for a cycle of reversible, electrochemically controlled binding of Ph_3P to $[M(S_2C_2R_2)_2]_2$ (M = Fe, Co; R = *p*-anisyl). All members of the cycle ($[M(S_2C_2R_2)_2]_2^0$, $[M(S_2C_2R_2)_2]_2^{1-}$, $[M(S_2C_2R_2)_2]_2^{2-}$, $[M(S_2C_2R_2)_2]^{1-}$, $[M(Ph_3P)(S_2C_2R_2)_2]$) for M = Fe, Co have been characterized by crystallography. Square planar $[Fe(S_2C_2R_2)_2]^{1-}$ is the first such iron dithiolene species to be structurally identified and reveals Fe–S bond distances of 2.172(1) and 2.179(1) Å, which are appreciably shorter than those in corresponding square planar dianions.

The rich photo- and electrochemical activity that have long been associated with transition metal dithiolene complexes continue to stimulate a high degree of interest in their applications, which include, to name a select few, their use as conducting or magnetic materials[1] and as sensing devices.[2] Recently, Wang and Stiefel proposed an innovative application for nickel bis(dithiolene) complexes in the selective separation of olefins from hydrocarbon mixtures.[3] Charge-neutral nickel bis(dithiolene) complexes react with olefins to form *S,S*-dialkylated adducts wherein the olefin has added across the adjacent sulfur atoms of two different dithiolene ligands. Wang and Stiefel noted that a one-electron reduction released the olefin and generated a nickel bis(dithiolene) monoanion, thereby forming the basis for a reversible, electrochemically controlled cycle for olefin binding and release. This intriguing observation suggests the idea that other homoleptic metal dithiolene complexes could display analogous possibilities for reversible, electrochemically controlled ligand binding. We report here our findings that both iron and cobalt bis(dithiolene) complexes display such behavior with square pyramidal phosphine adducts.

Using the P_4S_{10}/acyloin method first devised by Schrauzer,[4] the neutral *p*-anisyl-substituted compounds $[M(S_2C_2(C_6H_4\text{-}p\text{-}OCH_3)_2)_2]_2$ (M = Fe (**1a**), Co (**1b**), Figure 1) were synthesized as microcrystalline solids that were readily prepared as diffraction-quality single crystals by vapor diffusion techniques. These neutral dimers readily undergo one-electron reduction by BH_4^- or Cp_2Co to afford the corresponding dimeric monoanions (**2a** and **2b**). A second one-electron reduction reveals the onset of solution equilibria between dimeric dianions (**3a**, **3b**) and monomeric monanions (**4a**, **4b**). The principal difference between the two metals at this stage of reduction is that the cobalt system displays greater access to its monomeric monoanion **4b** in the **3b** ↔ **4b** equilibrium. The neutral dimers **1a** and **1b** are readily cleaved by strong-field σ-donor ligands, such as Ph_3P, to form square pyramidal adducts **5a** and **5b**.

Each of the iron dithiolene complexes (**1a**−**5a**) and cobalt dithiolene complexes (**1b**−**5b**) has been authenticated by X-ray crystallography at 100 K. Figure 1 presents thermal ellipsoid plots at the 50% probability level for the iron compounds **1a**−**5a**; the corresponding cobalt compounds **1b**−**5b** have similar structures, although they crystallized with different unit cells and cell parameters. The use of a constant dithiolene ligand throughout this set of structural studies removes uncertainty about the significance of substituent effects in modulating the dithiolene ligand structural parameters.

Recent structural and spectroscopic work reported by Wieghardt and co-workers with iron complexes bearing the benzene-1,2-dithiolate and 3,5-di-*tert*-butylbenzene-1,2-dithi-

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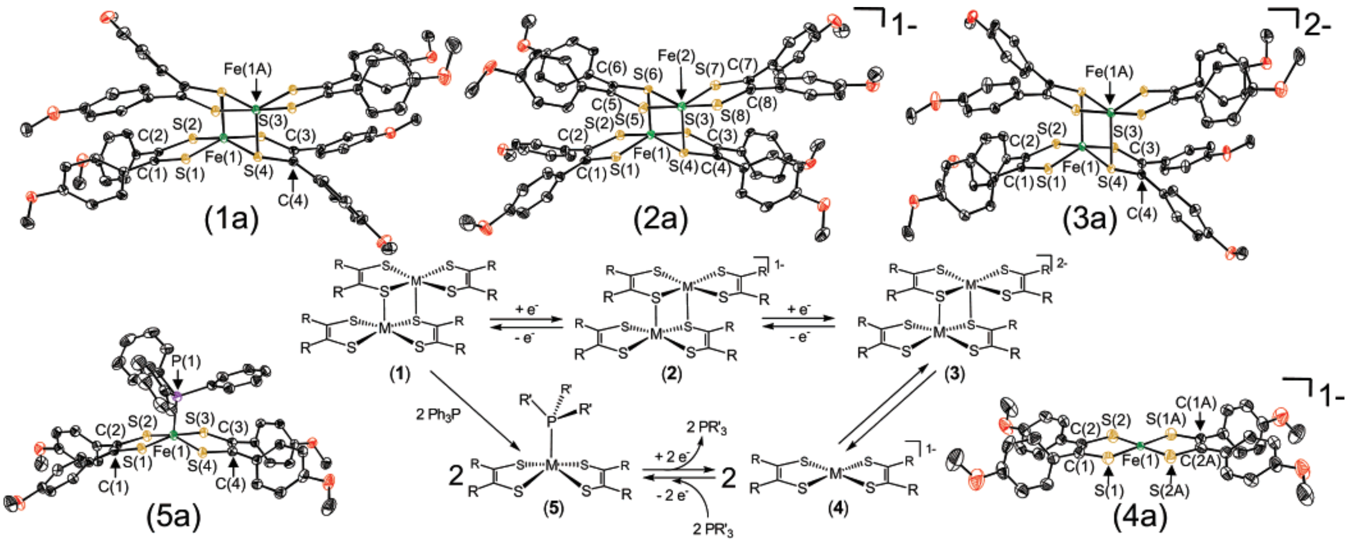

Figure 1. Electrochemical cycle for reversible binding of PR′$_3$ ligand to Fe and CO bis(dithiolene) complexes. R = *p*-anisyl, R′ = Ph, and M = Fe (**1a**−**5a**) or Co (**1b**−**5b**). The 50% probability thermal ellipsoid plots are for the Fe compounds. The Co complexes are homologous to the corresponding Fe compounds.

olate ligands[5] and with the *p*-tolyl- and *p*-*tert*-butylphenyl-substituted ligands[6] has brought considerable clarity to the description of bonding and redox processes in these complexes. One of the salient contributions of their work is the recognition that the redox processes $[Fe(S_2C_2R_2)_2]_2 + e^- \rightarrow [Fe(S_2C_2R_2)_2]_2^{1-}$ and $[Fe(S_2C_2R_2)_2]_2^{1-} + e^- \rightarrow [Fe(S_2C_2R_2)_2]_2^{2-}$ are ligand-based events involving conversion of thienyl radical monoanions $[^{\bullet}S{-}C{=}C{-}S^{-} \leftrightarrow S{=}C{-}C(^{\bullet}){-}S^{-}]$ to fully reduced ene-1,2-dithiolate dianions $(^{-}S{-}C{=}C{-}S^{-})$. The charge-neutral $[Fe(S_2C_2R_2)_2]_2$ compounds are therefore comprised of ferric ions, which are *both* coordinated by one reduced ene-dithiolate dianion *and* one thienyl radical monoanion.

Our structural characterization of **1a**−**5a** and **1b**−**5b** corroborate and add to Wieghardt's interpretation of the electronic structure and redox processes of iron bis(dithiolene) complexes. Compound **1a** is only the second charge-neutral iron bis(dithiolene) dimer to be structurally characterized, and it was found to crystallize on an inversion center from a variety of solvent systems. The C−S and C−C bond lengths of the dithiolene ligands of **1a** clearly reveal a different state of reduction for the terminal chelating ligand in contrast to the ligand involved in the bridging interaction. The S(1)−C(1) (1.708(3) Å) and S(2)−C(2) (1.707(3) Å) bond distances are rather short and imply the participation of the thione resonance structure. These values contrast with the S(3)−C(3) (1.744(3)) and S(4)−C(4) (1.767(3)) bond distances, which are more typical of pure C−S single bonds. Furthermore, the C(1)−C(2) bond length (1.397(4) Å) is somewhat longer than the C(3)−C(4) interatomic distance (1.371(4) Å), which indicates partial single-bond character according to resonance structure (**b**) in Figure 2. Thus, the terminal dithiolene ligand S(1)−C(1)−C(2)−S(2) in **1a** is partially oxidized as a thienyl radical monoanion, while the bridging dithiolene ligand S(3)−C(3)−C(4)−S(4) is a fully reduced ene-1,2-dithiolate. In experimental hindsight, it is plausible that the fully reduced, more electron rich dithiolene would be preferred for bridging interactions between the Lewis acidic Fe(III) centers.

Compound **2a** crystallizes on a general position in $P2_1/c$ with C−S and C−C bond lengths that point toward terminal dithiolene ligand S(7)−C(7)−C(8)−S(8) as the sole dithiolene ligand with thienyl radical monoanion character. The C−S and C−C interatomic distances in **3a** are fully consistent with single and double bonds, respectively, as expected for all dithiolene ligands in a fully reduced state. The C−S and C−C bond lengths within the cobalt dimers **1b**−**3b** are largely similar to those in **1a**−**3a** except that **2b**, possibly because of a static disorder, reveals no clear difference between its two terminal dithiolene ligands.

In the course of efforts to prepare diffraction-quality crystals of dimeric dianion **3a**, the mixed salt [Cp$_2$Co]**2a**·[Cp$_2$Co]**4a** (i.e., $[Cp_2Co][Fe(S_2C_2(C_6H_4\text{-}p\text{-}OCH_3)_2)_2]_2 \cdot [Cp_2Co][Fe(S_2C_2(C_6H_4\text{-}p\text{-}OCH_3)_2)_2]$) was synthesized in which the square planar monoanion **4a** is in the same state of reduction as dimeric **3a**. Despite its formulation as a 1:1 mixture with **2a**, this structural identification is the first for a mononuclear iron bis(dithiolene) monoanion. The existence of **4a** indicates that, with the relatively electron rich *p*-anisyl-substituted dithiolene ligand, the bridging interactions that form dimeric **3a** are weak enough to be disrupted by crystal packing effects. The Fe−S bond lengths in **4a** (2.172(1), 2.179(1) Å) are appreciably shorter than those in its isoelectronic dimer **3a** (2.2110(5), 2.2492(5) Å) and thus provide an insight into the intrinsic Fe(III)−S(thiolate) bond lengths in a square planar field without the strongly perturb-

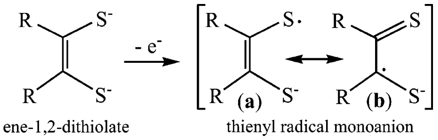

Figure 2. Possible oxidation states of a dithiolene ligand.

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ing effect of additional axial ligation. The Fe−S bond lengths of **4a** are also markedly shorter than those of the square planar dianions $[Fe(S_2C_6H_3(o\text{-}CO_2CH_3))_2]^{2-}$ (2.2055(8)−2.2072(8) Å)[7] and $[Fe(S_2C_6H_4)_2]^{2-}$ (2.2242(3)−2.2263(3) Å).[8] This fact confirms that the reductions that form these latter two species from the corresponding dimeric dianions are metal-based processes (Fe(III) → Fe(II)).

McCleverty has reported voltammetric measurements for **5a** and **5b**, apparently in DMF, and described the existence of one (**5a**) or two (**5b**) reversible reductions, upon scanning to negative potentials.[9] Our own measurements, conducted in CH_2Cl_2 solution display only irreversible waves upon scanning to reducing potentials, which is consistent with the dissociation of axial Ph_3P ligand and hence "destruction" of compounds **5a** and **5b**. A similar behavior was very recently noted by Wieghardt and McCleverty with $[Fe(P(OPh)_3)(S_2C_2Ph_2)_2]$.[10]

To more clearly demonstrate the reversibility of dissociation of Ph_3P from **5a**, a spectroelectrochemical controlled potential coulometry experiment was undertaken. The UV−vis absorption spectrum of **5a** displays a strong, distinctive absorption at 720 nm, which is attributed to an interligand intervalence charge-transfer transition and is completely absent in the reduced homoleptic iron bis(dithiolene) complexes. Using an electrochemical cell fitted with a Pt screen working electrode and with quartz windows for concomitant spectroscopic interrogation, a solution sample of **5a** was poised at a reducing potential of −1.0 V vs Ag/AgCl while the 325−800 nm region of the spectrum was monitored using a diode array light source. Over a period of minutes (Figure 3A), the one-electron reduction of **5a** transformed it into **3a**, as identified by its absorption spectrum. The absence of tight isosbestic points is due to the **3a**−**4a** solution equilibrium. When disappearance of **5a** was complete, bulk electrolytic oxidation of the same sample was then done by switching the working electrode to a +1.0 V potential vs Ag/AgCl. As electrons were removed from **3a** to transiently produce **1a**, reaction of free Ph_3P immediately formed **5a** again (Figure 3B). Over a period of minutes, **5a** was completely restored.

To obtain further insight into the basis for reversible binding of Ph_3P, we undertook BP86 density functional calculations of suitable iron model complexes. The square planar charge-neutral model compound $[Fe(S_2C_2H_2)_2]^0$ has an active state in energetic proximity to the ground state, which is characterized by a LUMO ($2a_g$) of d_{z^2} character. This orbital is favorably oriented for accepting an electron lone pair from an exogenous donor. Reduction of $[Fe(S_2C_2H_2)_2]^0$ results in partial or full occupancy of this orbital, thereby rendering the system unavailable for interactions with electron-pair donor ligands, be they phosphines or other types of σ-donors.

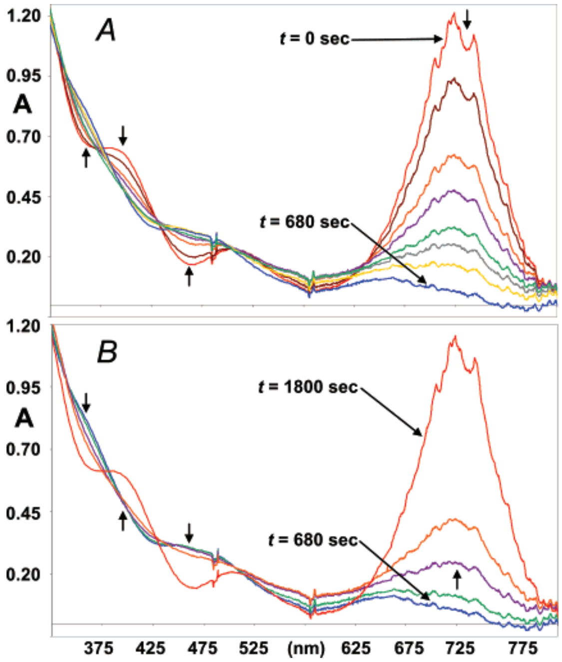

Figure 3. (A) Spectroscopic monitoring of the controlled potential (−1.0 V vs Ag/AgCl) coulometric reduction of **5a** in CH_2Cl_2, which reveals its conversion to **3a**. The absence of clean isobestic points is due to the **3a** ↔ **4a** equilibrium. (B) Re-formation of **5a** from **3a** and $2Ph_3P$ by controlled potential coulometric oxidation at +1.0 V.

The foregoing observations prove the feasibility of a fully reversible, electrochemically controlled cycle for binding and release of Ph_3P to homoleptic iron and cobalt bis(dithiolene) complexes. We are currently exploring the generality of this behavior with other types of Lewis bases, in particular heterocyclic imines and cyclic sulfides, and are studying whether variation of the dithiolene ligand substituent can afford a basis for selectivity for the type of Lewis base adduct.

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Supporting Information Available: X-ray data for **1a**−**5a** and **1b**−**5b** in standard CIF format; thermal ellipsoid plots at the 50% probability level for **1a**−**5a** with complete atom labeling in PDF format; a description of computational details and synthetic procedures in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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