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Stereochemistry of electrophilic attack at $34e^-$ dimetallic complexes: the case of diiron dithiolato carbonyls + $MeS^+\dagger$

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Abstract

Experimental and computational experiments show that the electrophile MeS^+ attacks a single Fe center in $Fe_2(\text{propanedithiolate})(CO)_4(PMe_3)_2$ followed by isomerization of this terminal thiolato complex to the corresponding μ -SMe derivative.

The addition of electrophiles to compounds containing metal–metal bonds is a process of fundamental interest.¹ The specific case of protonation is directly relevant to the mechanism for the formation of H_2 by the two major hydrogenase enzymes, the [FeFe]- and [NiFe]-hydrogenases.² The protonation of diiron(i) dithiolates has been intensely scrutinized since the discovery that many compounds of the type $Fe_2(SR)_2(CO)_4(\text{chelate})$ protonate at a single Fe center, followed by isomerization of the initial terminal hydride to a bridging position.³ The terminal protonation pathway applies to a number of unsymmetrically^{3–5} and even some symmetrically substituted diiron dithiolates.⁶ Protonation of the very simple models of the type $Fe_2(SR)_2(CO)_4(PMe_3)_2$ however affords μ -hydrido derivatives, with no experimental evidence for terminal hydride intermediates (Scheme 1).^{4,7}

In contrast to the extensive work on protonation, the stereochemical course for the addition of other electrophiles to diiron(i) dithiolates has not been reported. The question is broad because $34e^-$ compounds of the type $M_2(\mu-E)_2L_n$ ($E = S, P, \text{halide}$) are numerous⁸ and susceptible to attack by a variety of electrophiles, including halogens,⁹ $HgCl^+$, NO^+ ,¹⁰ and alkynes.¹¹

Of the various electrophilic reactions of $Fe_2(SR)_2(CO)_6L_n$, those installing thiolate ligands are of interest because, in addition to the two bridging thiolates, Fe^{proximal} of the H-cluster in the [FeFe]-hydrogenases is bound to a third thiolate that is linked to a $4Fe-4S$ cluster (Scheme 1).² This terminal thiolate occupies an apical position, a site of the previously demonstrated protonations.^{3–5}

The addition of MeS^+ , provided by salts of $Me_3S_2^+$, to diiron dithiolato carbonyls has been investigated previously. $Fe_2(SMe)_2(CO)_4(PMe_3)_2$ and $[Me_3S_2]BF_4$ react to give the red bioctahedral derivative $[Fe_2(\mu-SMe)_3(CO)_4(PMe_3)_2]BF_4$.¹² The analogous derivative

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$[\text{Fe}_2(\text{pdt})(\mu\text{-SMe})(\text{CO})_4(\text{PMe}_3)_2]^+$ ($[\mathbf{1}(\mu\text{-SMe})]^+$) is also known.¹³ Our reexamination of the reaction of $\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{PMe}_3)_2$ ($\mathbf{1}$) and $[\text{Me}_3\text{S}_2]\text{BF}_4$ using *in situ*-IR spectroscopy suggested the presence of an intermediate, but the interpretation of the results was hindered by the poor solubility of $[\text{Me}_3\text{S}_2]\text{BF}_4$. We therefore repeated these experiments using the more lipophilic salt $[\text{Me}_3\text{S}_2]\text{BAr}^{\text{F}}_4$ ($\text{BAr}^{\text{F}}_4^- = \text{B}(\text{C}_6\text{H}_3\text{-3,5-(CF}_3)_2)_4^-$), which was prepared by ion exchange from $[\text{Me}_3\text{S}_2]\text{BF}_4$ and KBar^{F}_4 . $[\text{Me}_3\text{S}_2]\text{BAr}^{\text{F}}_4$ is highly soluble in CH_2Cl_2 even at -78°C .

Treatment of $\mathbf{1}$ with $[\text{Me}_3\text{S}_2]\text{BAr}^{\text{F}}_4$ afforded a dark green product, not the red color of $[\mathbf{1}(\mu\text{-SMe})]^+$.¹³ Furthermore the reaction was quantitative, whereas previous work resulted in incomplete conversions. The IR spectrum of the product features a strong band at 1895 cm^{-1} in the region assigned to $\nu_{\mu\text{-CO}}$ for other diferrous dithiolates. For comparison, the $\nu_{\mu\text{-CO}}$ band for two terminal hydrides of the formula $[\text{HFe}_2(\text{SR})_2(\mu\text{-CO})(\text{CO})(\text{PR}_3)_4]^+$ occurs at 1874 and 1905 cm^{-1} .^{6,14} ^{31}P NMR spectroscopy confirmed that the kinetically favored species is unsymmetrical with two weakly coupled phosphine ligands, consistent with a terminal thiolato ligand. ^1H NMR spectroscopy confirmed the presence of inequivalent PMe_3 ligands as well as a $\text{Fe-SC}H_3$ resonance that is weakly coupled to a single phosphorus center. This complex was isolated as an analytically pure green powder.

Crystallographic analysis confirmed that the new complex is a terminal thiolate, *i.e.*, $[\mathbf{1}(t\text{-SMe})]\text{BAr}^{\text{F}}_4$. The MeS ligand is *trans* to a bridging carbonyl ligand, which is unsymmetrically bound ($\text{Fe}(1)\text{-}\mu\text{-CO} = 2.305(5)$ vs. $\text{Fe}(2)\text{-}\mu\text{-CO} = 1.818(5)\text{ \AA}$). The shorter distance for $\text{Fe}(2)\text{-}\mu\text{-CO}$ is consistent with the stabilizing influence of the donor MeS attached to the same Fe center. The phosphine ligands in $[\mathbf{1}(t\text{-SMe})]^+$ are *trans*-dibasal, an arrangement that contrasts with the *cis* dibasal arrangement in the thermodynamic product $[\mathbf{1}(\mu\text{-SMe})]^+$.¹³ The Fe-Fe distance in $[\mathbf{1}(t\text{-SMe})]^+$ of $2.5629(10)\text{ \AA}$ is far shorter than the $\sim 3.109\text{ \AA}$ distance reported for $[\mathbf{1}(\mu\text{-SMe})]^+$.¹³ The conversion of $[\mathbf{1}(t\text{-SMe})]^+$ into $[\mathbf{1}(\mu\text{-SMe})]^+$ is a rare example of the isomerization of a 34 to a $36e^-$ dimer.

The isomerization of $[\mathbf{1}(t\text{-SMe})]^+$ to $[\mathbf{1}(\mu\text{-SMe})]^+$ was monitored by NMR spectroscopy (eqn (1)). Conversion proceeds *via* a first-order process with $t_{1/2}$ of $\sim 27\text{ min}$ ($k = 4.30 \times 10^{-4}\text{ s}^{-1}$, 25°C). Analysis of the temperature dependence of the rate constant from 14 to 34°C revealed that the reaction proceeds with $\Delta H^\ddagger$ of $25(2)\text{ kcal mol}^{-1}\text{ K}^{-1}$ and $\Delta S^\ddagger$ of $1.1(1)\text{ kcal K}^{-1}$. The small value of the entropy of activation is consistent with an intramolecular process.

(1)

We analyzed the isomerization computationally. As a starting point, our DFT protocol accurately reproduced the key structural parameters of $[\mathbf{1}(t\text{-SMe})]^+$ (see caption in Fig. 1). The intimate mechanism for the terminal-to-bridge isomerization of related hydrides have been determined computationally.¹⁵ The mechanism involves a combination of Ray-Dutt and Bailar twists of the pseudo-octahedral Fe centers. Ray-Dutt and Bailar twists entail the movement of four or three ligands, respectively, to form trigonal prismatic transition states.

DFT analysis reveals that isomerization of $[\mathbf{1}(\textit{t}\text{-SMe})]^+$ is subject to a much higher barrier than for the corresponding hydride, consistent with experiment.

The elevated barrier for isomerization of the SMe complex *vs.* the corresponding hydride is explicable in terms of both electronic and steric factors. To achieve the proposed trigonal-prismatic transition state *via* a Ray–Dutt mechanism, isomerization requires the scission of the longer of the two Fe– μ -CO bonds (Fig. 2). The asymmetry of the Fe– μ -CO-Fe subunit is calculated to be greater for $[\mathbf{1}(\textit{t}\text{-H})]^+$ ($d_{\text{Fe}-\mu\text{-CO}}=1.814, 2.382 \text{ \AA}$) than in $[\mathbf{1}(\textit{t}\text{-SMe})]^+$ ($d_{\text{Fe}-\mu\text{-CO}} = 1.819, 2.306 \text{ \AA}$). The greater asymmetry in the hydride suggests that scission of this CO bridge would be easier than in the analogous *t*-SMe derivative. In terms of steric effects, we note that interligand repulsions are more severe in non-octahedral-transition states, which may also influence the barriers.¹⁶ Thus, steric factors would elevate the barrier for the MeS derivative *vs.* that for the hydride.¹⁷

Overall, the energy profile confirms that the conversion of $[\mathbf{1}(\textit{t}\text{-SMe})]^+$ to $[\mathbf{1}(\mu\text{-SMe})]^+$ is highly exothermic, even more than the conversion of $[\mathbf{1}(\textit{t}\text{-H})]^+$ to $[\mathbf{1}(\mu\text{-H})]^+$, with ΔH of -6.5 and $-14.7 \text{ kcal mol}^{-1}$, respectively. Both theory and experiment¹³ indicate that the stable isomer of $[\mathbf{1}(\mu\text{-SMe})]^+$ features a *cis*-dibasal arrangement of the PMe_3 ligands, which is favored over the transoid isomer by $3.7 \text{ kcal mol}^{-1}$. The isomerization of the cisoid isomer of $[\mathbf{1}(\mu\text{-H})]^+$ is proposed to occur *via* a Bailar twist.

To summarize, experimental and computational results show that electrophilic attack at a representative $34e^-$ diiron(i) dithiolate initiates at a single metal followed by isomerization.¹⁸ We suggest that this stereochemistry will apply to other electrophiles and other $34e^-$ dimetal centers. Finally, we note that $[\mathbf{1}(\textit{t}\text{-SMe})]^+$ resembles the CO-inhibited state of the diiron active site in the [FeFe]-hydrogenase with respect to the relative stereochemistry of the σ -donors, π -donors, and π -acceptor ligands.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1.

Structure of the cation in $[1(\textit{\textit{t}}\text{-SMe)]BAr^F_4}$ with thermal ellipsoids set at 35% probability. Hydrogen atoms have been omitted for clarity. Key bond distances ($\text{\AA}$) and angles ($^\circ$) with results from the DFT-calculated structure in brackets: Fe(1)–Fe(2): 2.5629(10) [2.594], Fe(1)–C(6): 2.305(5) [2.288], Fe(2)–C(6): 1.818(5) [1.812], Fe(2)–S(3): 2.3124(14) [2.345], Fe(1)–Fe(2)–C(6): 60.71(17) [59.5], Fe(2)–Fe(1)–C(6): 43.46(13) [43.0], C(6)–Fe(2)–S(3): 163.86(17) [164.2], S(1)–Fe(2)–S(3): 93.28(5) [93.9], Fe(2)–S(3)–C(11): 110.6(2) [111.6].

Fig. 2. Calculated energies (kcal mol⁻¹) for the isomerization of $[\text{XFe}_2(\text{pdt})(\text{CO})_4(\text{PMe}_3)_2]^+$ for X = H (red) and SMe (black).

Scheme 1. Stereochemistry of electrophilic attack at diiron(I) dithiolates. Inset: active site of [FeFe]-hydrogenase.