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Lewis *vs.* Brønsted-basicities of diiron dithiolates: spectroscopic detection of the "rotated structure" and remarkable effects of ethane- *vs.* propanedithiolate†

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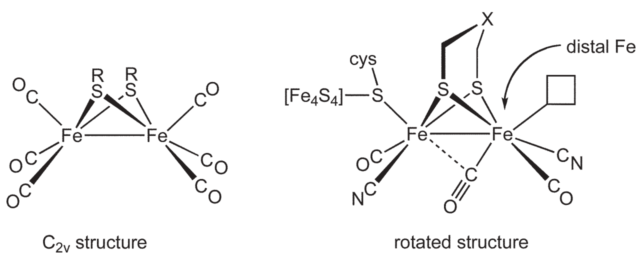
The new complexes $Fe_2(S_2C_nH_{2n})(CO)_2(dppv)_2$ (n = 2, 3; dppv = *cis*-1,2-$C_2H_2(PPh_2)_2$) form adducts with $AlBr_3$ and $B(C_6F_5)_3$, which adopt the "rotated structure" proposed for the active site of the Fe-only hydrogenases—the propanedithiolate is significantly more Lewis basic due to nonbonded interactions between the dithiolate strap and the ligands on Fe.

Hard Lewis acids are known to bind bridging CO ligands in di- and polynuclear metal carbonyl complexes.[1] For example, the affinity of $AlEt_3$ for μ-CO ligands is sufficiently strong that this reagent converts $[CpRu(CO)_2]_2$ into $Cp_2Ru_2(CO)_2(\mu\text{-}COAlEt_3)_2$.[2] In this report we describe an unusual application of Lewis acids to a difficult problem posed in the context of bioorganometallic chemistry.[3]

The active site of Fe-only hydrogenase enzymes can be described as $[Fe_2(SR)_2(\mu\text{-}CO)(CO)_2L_3]^z$, wherein the three diatomic ligands on the distal iron are "rotated" by *ca.* 60°, thereby opening a coordination site *trans* to the Fe–Fe bond (Scheme 1).[4] This vacant site is implicated in binding H_2. Theoretical calculations indicate that such rotated structures are only *ca.* 40 kJ mol^{-1} higher in energy than the conventional C_{2v} isomer.[5] Synthetic modeling efforts have, however, failed to reproduce such rotated structures, despite the preparation of hundreds of compounds of the type $Fe_2(SR)_2(CO)_{6-n}L_n$ (L = CN^-, PR_3, SR_2, CNR).[6] In view of the intensity of the experimental work, it would be reasonable to question the plausibility of the rotated structures. To help resolve this uncertainty, we turned to the use of Lewis acids to generate the rotated structure.



Scheme 1

Initial studies showed that bis- and tris(phosphine) complexes $Fe_2(S_2C_2H_4)(CO)_4(PMe_3)_2$ and $Fe_2(S_2C_2H_4)(CO)_3(dppv)(PMe_3)$[7] do not form adducts with the strong[8] Lewis acid $AlBr_3$. Apparently in such species, the CO sites are insufficiently basic to cleave Al_2Br_6. The electron-rich dianion $[Fe_2(S_2C_2H_4)(CN)_2(CO)_4]^{2-}$ does of course bind Lewis acids, but the nitrogen centres on cyanide are the dominant basic sites,[9] which precludes interactions with CO. In order to conduct our experiments, we required a complex substituted with several donor ligands, the exteriors of which are not basic. We thus undertook the preparation of the complexes $Fe_2(S_2C_nH_{2n})(CO)_2(dppv)_2$ (eqn (1)).

$$\begin{gathered}Fe_2(S_2C_nH_{2n})(CO)_4(dppv) + dppv \rightarrow \\ Fe_2(S_2C_nH_{2n})(CO)_2(dppv)_2 + 2\ CO \\ \mathbf{1}\ddagger\ (n = 2);\ \mathbf{2}\ (n = 3)\end{gathered} \qquad (1)$$

These deep green species, which are unique examples of $Fe_2(SR)_2(CO)_2(PR_3)_4$ derivatives, arise *via* the photochemical reaction of dppv and $Fe_2(S_2C_nH_{2n})(CO)_4(dppv)$.[7] The IR spectra for **1** and **2** are indistinguishable in the ν_{CO} region. The positions of the bands (ν_{CO} = 1888, 1868 cm^{-1}) indicate that these complexes are more electron-rich than $Fe_2(S_2C_2H_4)(CO)_3(dppv)(PMe_3)$ (ν_{CO} = 1943, 1892 cm^{-1}).[7]

The structure of **1** was established crystallographically (Fig. 1). The species is noteworthy because of the presence of four donor ligands on the diiron(I) center. The $Fe_2(S_2C_nH_{2n})(CO)_{6-x}L_x$ framework is similar to less substituted derivatives with respect to Fe–Fe and Fe-ligand distances. Variable temperature ^{31}P NMR spectra confirm that **1** is fluxional in solution: one signal is observed at room temperature (δ 93.2) and an AB quartet at low temperatures (δ 95.8, $J_{P\text{–}P}$ = 21 Hz and 92.2, $J_{P\text{–}P}$ = 22 Hz). The data are consistent with the degenerate interconversion of the enantiomeric C_2-symmetric isomers. Compound **2** is similarly fluxional in solution, but the low temperature spectrum also revealed, in addition to the C_2-symmetric isomer, the presence of 20% of a C_1-isomer wherein one dppv is axial/basal and the other is dibasal (Scheme 2). The appearance of this second isomer is ascribed to a destabilizing interaction between the central CH_2 group of the propanedithiolate and one phenyl group of one dppv ligand (see below).

Addition of Al_2Br_6 to a CH_2Cl_2 solution of **1** at −20 °C induced strong changes in both the IR and ^{31}P NMR spectra. In particular, the ^{31}P NMR spectrum for **1**·$AlBr_3$ sharpened to *four* signals. Following recently described empirical trends,[7] signals at δ 91.1

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† Electronic supplementary information (ESI) available: Details about DFT calculations, atomic coordinates of starting and optimized structures. See DOI: 10.1039/b700754j

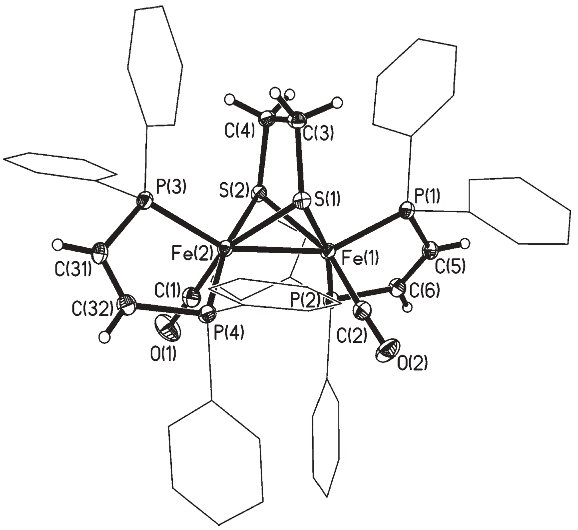
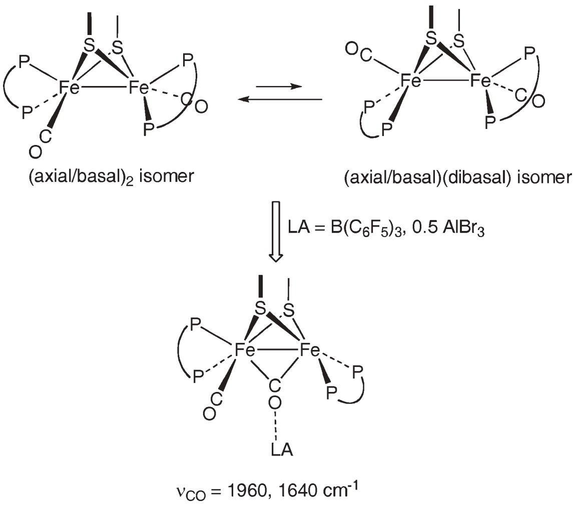


Fig. 1 Structure of $Fe_2(S_2C_2H_4)(CO)_2(dppv)_2$, (**1**), with thermal ellipsoids set at 35%. Phenyl ellipsoids and phenyl hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), and angles (deg): Fe(1)–Fe(2), 2.5678(4); Fe(1)–S(1), 2.2611 (5); Fe(1)–S(2), 2.2485 (5); Fe(1)–P(1), 2.1732 (6); Fe(1)–P(2), 2.2026 (6); Fe(1)–C(2), 1.7357 (19); Fe(2)–P(3), 2.1769 (6); Fe(2)–P(4), 2.1958 (5); Fe(2)–C(1), 1.737 (2); Fe(2)–Fe(1)–P(1), 152.906 (19); Fe(2)–Fe(1)–P(2), 111.874 (18); Fe(2)–Fe(1)–C(2), 104.53 (6); P(1)–Fe(1)–P(2), 87.93 (2); P(1)–Fe(1)–C(2), 92.70 (6); P(2)–Fe(1)–C(2), 91.61 (6).§

and 91.2 ppm are assigned to axial/basal dppv, and those at δ 90.6 and 83.0 ppm, are assigned to dibasal dppv. Completely analogous shifts were observed by ^{31}P NMR spectroscopy for the propanedithiolate **2**·$AlBr_3$. Addition of NEt_3, to these solutions regenerated **1** and **2**, demonstrating that binding of the $AlBr_3$ does not destroy the $Fe_2(SR)_2(CO)_2(dppv)_2$ framework. We analyzed the stoichiometry of the Lewis acid–base reaction by ^{19}F NMR spectroscopy using $B(C_6F_5)_3$ as the Lewis acid.[10] A solution containing two equiv. $B(C_6F_5)_3$ and one equiv. of **1**, showed separate comparably intense signals for the free (δ −129, −145, −162) and complexed (δ −137, −160, −166) Lewis acid. The stoichiometry was also analyzed *via* ^{31}P NMR spectroscopy. A solution containing two equiv. of **2** and half equiv. of Al_2Br_6 showed separate signals in the ^{31}P NMR spectrum for unreacted **2** and **2**·$AlBr_3$. Thus, only one equivalent Lewis acid binds to **1** and **2** and exchange between the bound and free Lewis acid is slow on the NMR time-scale.



Scheme 2

Crucial evidence bearing on the structure of the Lewis acid adduct was provided by IR spectroscopy. The ν_{CO} bands for **1**, at 1888, 1868 cm^{-1}, shifted to 1960 and 1640 cm^{-1} upon complexation to $AlBr_3$. The low energy band is characteristic of the $M_2(\mu\text{-}COAlBr_3)$ group.[1] The 1960 cm^{-1} band for the Fe(dppv)(CO) center is *ca.* 80 cm^{-1} higher energy than the average of the two bands for **1**. This *ca.* 80 cm^{-1} shift is comparable to that produced by protonation or $2e^-$ oxidation of a diiron complex.[11]

Collectively the IR and ^{31}P NMR data are consistent with the stabilization of the rotated structure by the Lewis acid, which "pulls" a terminal CO ligand into the bridging position. Also DFT calculations† indicate that μ-CO isomers are stabilized upon $AlBr_3$ binding (Fig. 2), even though the rotated isomers are not predicted to be the most stable (Table 1). Analogous results are obtained with hybrid functionals (not shown), suggesting that the relative basicity of CO groups in $Fe_2(S_2C_nH_{2n})(dppv)_2(CO)_2$ complexes is not fully satisfactorily predicted by DFT. The computed CO stretching frequencies of the μ-CO **1**·$AlBr_3$ adduct are, however, much closer to experimental values than the corresponding frequencies computed for the un-rotated **1**·$AlBr_3$ isomer (1930, 1632 and 1942, 1694 cm^{-1}, respectively). The possibility that $AlBr_3$ could bind to the axial CO of (axial/basal)(dibasal) isomers was also analysed by DFT calculations. However, the computed ^{31}P NMR spectra for these adducts (not shown) do not fit experimental data.

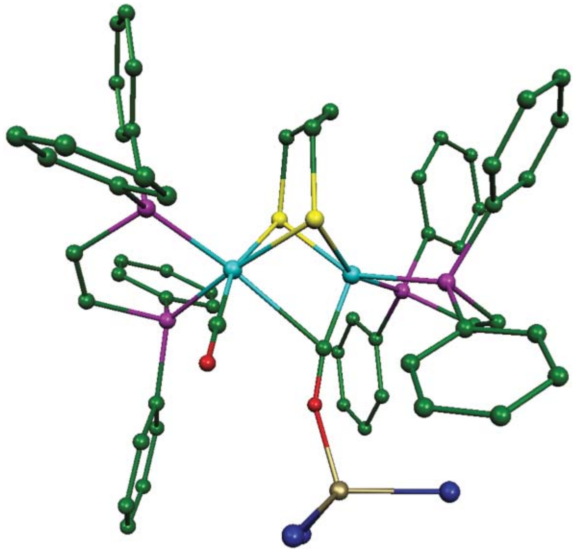


Fig. 2 DFT-optimized structure of $Fe_2(S_2C_2H_4)(\mu\text{-}COAlBr_3)(dppv)_2(CO)$. Selected distances (Å): Atoms are color-coded according to the following scheme: light blue = iron, green = carbon, yellow = sulfur, purple = phosphorus, red = oxygen, grey = aluminium, dark blue = bromine. Selected distances (Å): Fe–Fe, 2.625; Fe^d-μ-C, 1.697; Fe^p-μ-C, 2.604; Fe^d–S, 2.307, 2.316; Fe^p–S, 2.301, 2.340; Fe^p–CO, 1.751; Fe^p–P, 2.241, 2.291; Fe^d–P, 2.213, 2.231.

Table 1 Relative stabilities of $Fe_2(S_2C_nH_{2n})(dppv)_2(CO)_2$ and $Fe_2(S_2C_nH_{2n})(dppv)_2(COAlBr_3)(CO)$ isomers

Compound	Relative stabilities (kJ mol^{-1})
$Fe_2(S_2C_2H_4)(dppv)_2(\mu\text{-}CO)(CO)$	41.4
$Fe_2(S_2C_2H_4)(dppv)_2(CO)_2$	0.0
$Fe_2(S_2C_2H_4)(dppv)_2(\mu\text{-}COAlBr_3)(CO)$	32.0
$Fe_2(S_2C_2H_4)(dppv)_2(COAlBr_3)(CO)$	0.0
$Fe_2(S_2C_3H_6)(dppv)_2(\mu\text{-}CO)(CO)$	32.9
$Fe_2(S_2C_3H_6)(dppv)_2(CO)_2$	0.0
$Fe_2(S_2C_3H_6)(dppv)_2(\mu\text{-}COAlBr_3)(CO)$	24.1
$Fe_2(S_2C_3H_6)(dppv)_2(COAlBr_3)(CO)$	0.0

We found that the propanedithiolate **2** is significantly more Lewis basic than ethanedithiolate **1**. When a solution containing one equiv. each of **1** and **2** was treated with a 0.5 equiv. Al_2Br_6, we observed the *exclusive* formation of **2**·$AlBr_3$. In order to probe the relative thermodynamic preference of Al_2Br_6 for **2** *vs.* **1**, we examined the reaction of *ten* equiv. of **1**, one equiv. **2**, and two equiv. of $AlBr_3$. Even under these biased conditions, **2**·$AlBr_3$ formed quantitatively. Assuming that our detection limit is 5%, this result indicates that the Lewis basicity of **2** is at least 370 × that of **1** at 254 K, corresponding to $\Delta\Delta G \sim 10.9$ kJ mol^{-1} (eqn (2); Scheme 3, LA = Lewis acid).

$$\mathbf{1}\cdot\mathrm{AlBr_3} + \mathbf{2} \xrightleftharpoons{K>162} \mathbf{1} + \mathbf{2}\cdot\mathrm{AlBr_3} \tag{2}$$

IR spectra for **1** and **2** in the ν_{CO} region are indistinguishable. This similarity extends to their apparent Brønsted basicities: treatment of a 1 : 1 solution of **1** and **2** with one equiv. of $H(OEt_2)_2BAr^F{}_4$ resulted in equal amounts of the hydrides **1**H^+ and **2**H^+.

The lack of a difference in Brønsted basicity in **1** and **2**, directly contrasts with their differing Lewis basicities. DFT analysis of the reaction $Fe_2(S_2C_nH_{2n})(dppv)_2(CO)_2 + AlBr_3 \rightarrow Fe_2(S_2C_nH_{2n})(dppv)_2(\mu\text{-}COAlBr_3)(CO)$ shows that the formation of **2**·$AlBr_3$ is favoured (by about 8 kJ mol^{-1}) relative to formation of **1**·$AlBr_3$. This energetic difference arises from the steric clash between the central methylene of the propanedithiolate and the dppv ligand in **2**, an interaction which is partially relieved upon formation of the rotated isomer. In contrast, nonbonding interactions in **1** and **1**·$AlBr_3$ are comparable, thus there is less driving force stabilizing the rotated structure. This finding highlights an unsuspected structural role played by alkanedithiolates in bimetallic complexes.

In summary, using a electron-rich diiron(I) dithiolate, we present a unique case where Lewis acids stabilize a structure for a metal carbonyl that has not been observed experimentally—*except in a protein*. Furthermore, we show how nonbonding ligand–ligand interactions can influence the Lewis basicity of other ligands.

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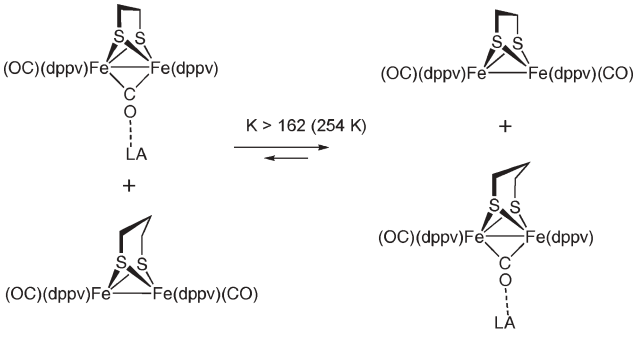

Scheme 3

Notes and references

‡ For **1**: ^1H NMR (CD_2Cl_2): δ 8.1–7.2 (m, 40H, 4.3 (s, 2H), 1.2 ppm (s, 4H). ^{31}P NMR (CD_2Cl_2, 20 °C): δ 93.2 ppm. ^{31}P NMR (CD_2Cl_2, −60 °C): δ 95.8 (J_{P-P} = 21 Hz), 92.2 ppm (J_{P-P} = 22 Hz). IR (CH_2Cl_2): ν_{CO} = 1888, 1868 cm^{-1}. FD-MS: m/z = 1052.2 ([$Fe_2(S_2C_2H_4)(CO)_2(dppv)_2$]). Anal. calcd for $C_{56}H_{48}Fe_2O_2P_4S_2$ (found): C, 63.87 (63.48); H, 4.60 (4.54).

§ $Fe_2(S_2C_2H_4)(CO)_2(dppv)_2$, (**1**), M = 1052.64, monoclinic, a = 10.9417(7), b = 17.3546(10), c = 26.1713(15) Å, β = 97.901(2), U = 4922.5(5) Å^3, T =
193(2) K, space group $P2(1)/n$, Z = 4, μ(Mo-Kα) = 0.847. 21096 reflections 2
were collected, $R1$ ($I > 2\sigma$) = 0.034 and $R1$ = 0.0792 for all data. R_{int} is not reported due to non-merohedral twinning. CCDC 634107. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b700754j

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