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Electron-Rich, Diiron Bis(monothiolato) Carbonyls: C–S Bond Homolysis in a Mixed Valence Diiron Dithiolate

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Abstract

The synthesis and redox properties are presented for the electron-rich bis(monothiolate)s $\text{Fe}_2(\text{SR})_2(\text{CO})_2(\text{dppv})_2$ for $\text{R} = \text{Me}$ (**[1]**⁰), Ph (**[2]**⁰), CH_2Ph (**[3]**⁰). Whereas related derivatives adopt C_2 -symmetric $\text{Fe}_2(\text{CO})_2\text{P}_4$ cores, **[1]**⁰–**[3]**⁰ have C_s symmetry resulting from the unsymmetrical steric properties of the axial vs equatorial R groups. Complexes **[1]**⁰–**[3]**⁰ undergo $1e^-$ oxidation upon treatment with ferrocenium salts to give the mixed valence cations $[\text{Fe}_2(\text{SR})_2(\text{CO})_2(\text{dppv})_2]^+$. As established crystallographically, **[3]**⁺ adopts a rotated structure,

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Notes

The authors declare no competing financial interest.

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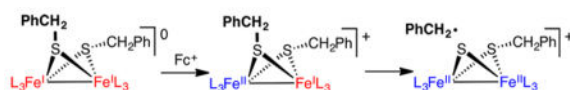
CCDC 1590590–1590593 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Supporting Information

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characteristic of related mixed valence diiron complexes. Unlike $[1]^+$ and $[2]^+$ and many other $[\text{Fe}_2(\text{SR})_2\text{L}_6]^+$ derivatives, $[3]^+$ undergoes C–S bond homolysis, affording the diferrous sulfidothiolate $[\text{Fe}_2(\text{SCH}_2\text{Ph})(\text{S})(\text{CO})_2(\text{dppv})_2]^+$ ($[4]^+$). According to X-ray crystallography, the first coordination spheres of $[3]^+$ and $[4]^+$ are similar, but the Fe–sulfido bonds are short in $[4]^+$. The conversion of $[3]^+$ to $[4]^+$ follows first-order kinetics, with $k = 2.3 \times 10^{-6} \text{ s}^{-1}$ (30 °C). When the conversion is conducted in THF, the organic products are toluene and dibenzyl. In the presence of TEMPO, the conversion of $[3]^+$ to $[4]^+$ is accelerated about 10x, the main organic product being TEMPO-CH₂Ph. DFT calculations predict that the homolysis of a C–S bond is exergonic for $[\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_2(\text{PR}_3)_4]^+$ but endergonic for the neutral complex as well as less substituted cations. The unsaturated character of $[4]^+$ is indicated by its double carbonylation to give $[\text{Fe}_2(\text{SCH}_2\text{Ph})(\text{S})(\text{CO})_4(\text{dppv})_2]^+$ ($[5]^+$), which adopts a bioctahedral structure.

Graphical Abstract



INTRODUCTION

Organometallic radicals have received continuous attention for decades.^{1–3} Within the area of enzymology, a prominent organometallic radical is the H_{ox} resting state in the [FeFe]-hydrogenases. Featuring an $S = 1/2$ Fe(II)Fe(I) center, this state is exceptionally well characterized,⁴ as are low molecular weight synthetic models.⁵ Briefly, one Fe center is pentacoordinate, typically assigned as Fe(I), with a “rotated” geometry, whereas the other Fe center, assigned as Fe(II), is octahedral. The strikingly unsymmetrical structure presents a vacant coordination site adjacent to the amine cofactor substrate activation.

The H_{ox} active site and its models exhibit three kinds of Fe-centered reactions: reduction to Fe(I)Fe(I) derivatives, binding of CO, and activation of dihydrogen in the presence of a second redox agent^{6,7} (Scheme 1). This report describes a new kind of reaction of the H_{ox}-like center: their fragmentation with release of organic radicals.

This report begins with experiments probing the reactivity of bis(*monothiolate*)s $[\text{Fe}_2(\text{SR})_2(\text{CO})_2(\text{dppv})_2]^{+/0}$ (dppv = *cis*-1,2-bis(diphenylphosphino)ethylene). The properties of the related *dithiolate*s have been exhaustively studied,⁵ but the substituted bis(*monothiolate*)s have been rarely described,^{8,9} and mixed valence derivatives have not been characterized.

The radical reactions of iron monothiolates are potentially relevant to the biosynthesis of the [2Fe]_H center (the active site) in the [FeFe]-hydrogenases.^{10–12} The pathway proceeds via a ferrous cysteinylate-cyanide “Complex B” assembled within the multifunctional enzyme HydG. Complex B is transferred to HydF, a scaffold where the enzyme HydE probably operates on cysteinylate to produce the adt cofactor (Scheme 2). Since HydE is a radical-SAM enzyme, radical reactions of diiron *monothiolate*s are implicated.

RESULTS

Preparative Background

The displacement of four CO ligands by a pair of dppv groups has been applied to the preparation of chelating dithiolato complexes, e.g., $\text{Fe}_2[\text{S}_2-(\text{CH}_2)_n](\text{CO})_2(\text{dppv})_2$. In this work, the two dppv were installed for the first time on bis(monothiolate) complexes $\text{Fe}_2(\text{SMe})_2(\text{CO})_2(\text{dppv})_2$ (**[1]**⁰), $\text{Fe}_2(\text{SPh})_2(\text{CO})_2(\text{dppv})_2$ (**[2]**⁰), and $\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_2(\text{dppv})_2$ (**[3]**⁰). For the preparation of alkylthiolato complexes **[1]**⁰ and **[3]**⁰ from the corresponding $\text{Fe}_2(\text{SR})_2(\text{CO})_6$ derivatives, either of two methods proved suitable: one-pot UV-irradiation or a two-pot process that involves isolation of the intermediate $\text{Fe}_2(\text{SR})_2(\text{CO})_4(\text{dppv})$ by a thermal reaction, which is converted to the dicarbonyl in a separate photochemical reaction.

The preparation of **[2]**⁰ proved more complicated as indicated by a recent report.¹³ The intermediate $\text{Fe}_2(\text{SPh})_2(\text{CO})_4(\text{dppv})$ could be efficiently prepared, but its reaction with dppv produced significant amounts of $\text{Fe}(\text{SPh})_2(\text{CO})_2(\text{dppv})$ and $\text{Fe}(\text{CO})_3(\text{dppv})$. Phenylthiolate is a more weakly bridging ligand than alkylthiolates; hence $\text{Fe}_2(\text{SPh})_2(\text{CO})_4(\text{dppv})$ is more susceptible to rupture of the diiron unit. The preparation of $\text{Fe}_2(\text{SPh})_2(\text{CO})_2(\text{dppv})_2$ was achieved by an inefficient photochemical route.

The Fe(I)Fe(I) complexes **[1]**⁰, **[2]**⁰, and **[3]**⁰ are green-brown solids with good solubility in dichloromethane. Solutions appear completely stable at room temperature. The ³¹P NMR spectra, consisting of two signals, remain unchanged over a broad range of temperatures, indicating relatively rigid structures. Two *CH*₂R singlets are also observed in the ¹H NMR spectrum recorded on CD₂Cl₂ (but not C₆D₆) solutions (R = Ph, H). The observation of methylene singlets for **[3]**⁰ is indicative of a plane of symmetry, since alternative geometries would result in diastereotopic signals. The rigidity reflects the high barriers for the axial-equatorial inversion of the μ -SR groups, which are known to be slow to invert on NMR time scales.¹⁴ The unsymmetrical disposition of the thiolate substituents induces the two dppv ligands to adopt a symmetrical arrangement. Thus, **[1]**⁰–**[3]**⁰ have a rigid C_s-symmetric $\text{Fe}_2(\text{SR})_2(\text{CO})_2\text{P}_4$ core as the result of the presence of axial and equatorial thiolates.¹⁴ By contrast, for the complexes $\text{Fe}_2[(\text{SCH}_2)_2\text{X}](\text{CO})_2(\text{dppv})_2$ (X = CH₂, O, NH, nothing), the ³¹P NMR spectra exhibit only a single signal near room temperature. Such compounds adopt a C₂-symmetric $\text{Fe}_2(\text{SR})_2$ core wherein the two dppv ligands undergo a degenerate oscillatory motion (Scheme 3).¹⁵

Stereorigidity was also evident for $\text{Fe}_2(\text{SR})_2(\text{CO})_4(\text{dppv})$, intermediates in the syntheses of **[1]**⁰–**[3]**⁰. Specifically, room temperature NMR spectra of the $\text{Fe}_2(\text{SR})_2(\text{CO})_4(\text{dppv})$ (R = Me, CH₂Ph, Ph) also indicate that the $\text{Fe}(\text{CO})(\text{dppv})$ center is rigid on the NMR time scales. The ³¹P NMR spectra consist of two doublets. The ¹H NMR spectrum of $\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_4(\text{dppv})$ exhibits four equally intense AB quartets, indicative of the diastereotopicity of the methylene protons. By contrast, only singlets are observed for each of these methylene groups in the ¹H NMR spectrum of **[3]**⁰ (Scheme 4).

Crystallographic analysis confirmed the distinctive stereochemistry of **[3]**⁰. The thiolate substituents are indeed axial-equatorial (Figure 1). The two dppv ligands are apical-basal as

is normal, but they are eclipsed, which is rarely observed. Correspondingly the CO ligands are cis-dibasal. The observed isomer appears to be stabilized by avoidance of a steric clash between the equatorial μ -SR group with the arylphosphine ligands.¹⁶

Oxidation of [1]⁰ and [3]⁰ with FcBF₄ afforded [1]BF₄ and [3]BF₄ (Fc⁺ = ferrocenium). Samples of [3]BF₄ were obtained in analytical purity, while [1]⁺ was examined spectroscopically. FT-IR spectra of [1]BF₄ and [3]BF₄ are very similar. The oxidations were accompanied by a color change from red-brown to green. The IR spectrum also changed significantly, including the appearance of a lower energy band near 1904 cm⁻¹ (CH₂Cl₂ solution) assigned to the semibridging CO ligand. This value is typical for Fe(II)Fe(I)/Fe(I)Fe(I) couples for complexes of the type Fe₂(dithiolate)(CO)₂(dppv)₂.⁵

The salt [3]BF₄ was characterized by X-ray crystallography (Figure 2). The geometry of the diiron center is similar to those of related 33e⁻ [Fe₂(SR)₂(CO)_{6-x}L_x]⁺ complexes,¹⁷⁻¹⁹ which are often referred to as “H_{ox} models”.⁵ Thus, one Fe center adopts a “rotated geometry” with an open apical coordination site trans to the Fe–Fe vector. One CO ligand is semibridging (Fe(2)–C–O angle = 171.8(2)°). This ligand gives rise to the ν_{CO} band observed at 1904 cm⁻¹ in the FT-IR spectrum. The dppv on the nonrotated Fe center spans apical-basal sites, retaining the stereochemistry (relative to the axial-equatorial SCH₂Ph groups) seen in [3]⁰. The average C–S distances are relatively unaffected by the oxidation, being 1.855(2) vs 1.847(2) Å for the neutral and cation, respectively.

Conversion of [Fe₂(SCH₂Ph)₂(CO)₂(dppv)₂]⁺ to [Fe₂(SCH₂Ph)(S)(CO)₂(dppv)₂]⁺

When monitored by FT-IR spectroscopy, solutions of [1]BF₄ are stable for days at room temperature. In contrast, C₆D₆ solutions of [3]BF₄ decompose under the same conditions. The principal product is [Fe₂(SCH₂Ph)(S)(CO)₂(dppv)₂]⁺ ([4]⁺, Scheme 5). ESI-MS measurements support the formula. The complex is diamagnetic, judging from its well-resolved ¹H and ³¹P NMR spectra. The ¹H spectrum is simple, consistent with a single isomer. The ³¹P NMR spectrum shows signals at δ 101.7 and 85.6, also consistent with a single isomer. In situ examination of the conversion of [3]⁺ into [4]⁺ by ³¹P NMR spectroscopy revealed that CH₂Cl₂, BF₄⁻, and traces of water interfere with the reaction. These contaminants give [Fe₂(SCH₂Ph)₂(X)(CO)₂(dppv)₂]⁺ (X = OH, Cl, F), as further indicated by ESI-MS analysis (the complex [Fe₂(SCH₂Ph)₂(Cl)(CO)₂(dppv)₂]⁺ was further identified by X-ray crystallography as its BF₄⁻ salt). Complexes of the type [Fe₂(SR)₂(Cl)(CO)_{6-x}(PR₃)_x]⁺ are well-known.²⁰

To minimize side reactions involving counterions and chlorinated solvent, the decomposition of [3]⁺ was examined as its BAr^F₄⁻ salt in THF and in benzene. IR spectra for [3]BF₄ and [3]BAr^F₄ are identical in the ν_{CO} region. The decomposition in dry benzene-*d*₆ gave principally [4]⁺, obtained in 55% yield over the course of 3 days at room temperature. Some insoluble material is observed, pointing to other degradation pathways that parallel the [3]⁺ → [4]⁺ conversion. Solutions of [4]BAr^F₄ are stable in benzene and CH₂Cl₂, so the modest yields are not attributable to the instability of [4]⁺.

The debenzoylation of [3]⁺ appears to follow a radical pathway. Together with [4]⁺, dibenzyl and toluene were observed as coproducts when the reaction was conducted in THF (THF-*h*₈

as well as THF-*d*₈). Using an internal integration standard, the combined yields of dibenzyl and toluene were approximately 60%, which is consistent with the yield of [4]⁺. When conducted in C₆D₆, the reaction is slower and toluene was not observed, only dibenzyl (58% yield). When measured by ³¹P NMR spectroscopy, the appearance of [4]⁺ followed first-order kinetics with a half-life of about 80 h.

Further support for the radical pathway was provided by the finding that the conversion of [3]⁺ to [4]⁺ was accelerated 10× in the presence of 1 equiv of TEMPO. The yield of [4]⁺, evaluated by in situ ¹H NMR analysis vs an internal integration standard, improved to almost 80%. This finding suggests that the diminished yield in the TEMPO-free [3]⁺ → [4]⁺ reaction results from attack of •CH₂Ph on [3]⁺ or on [4]⁺. From the TEMPO-induced reaction, TEMPO-CH₂Ph was isolated in 61% yield.

In control tests, solutions of [1]⁺, [3]⁰, and [4]⁺ were unreactive toward TEMPO over the course of days at room temperature. Qualitatively, the rate of the [3]⁺ + TEMPO reaction is unaffected by excess TEMPO. This finding is consistent with a rate-limiting homolysis reaction, followed by efficient trapping (Scheme 6).

Crystallographic Characterization of [Fe₂(SCH₂Ph)(S)-(CO)₂(dppv)₂]⁺

X-ray crystallographic analysis of [4]BF₄ confirmed the presence of only one benzyl group, which takes an equatorial orientation (Figure 3). In terms of its Fe₂S₂L₆ core, [4]⁺ resembles [3]⁰. The Fe–S distances are disparate: Fe–sulfido distances are 2.1643(7) and 2.1275(7) Å, 0.1 Å shorter than the Fe–SCH₂Ph distances, which are 0.1 Å longer. The Fe–S(R) bond lengths in complexes of the type [Fe₂(SR)₂(CO)_{6-x}L_x]^z are relatively insensitive to oxidation state, as shown by comparison of [3]⁰ and [3]⁺. The short Fe–sulfido distance is attributed to steric effects as well as Fe–S π-bonding. The S–Fe–S angles (85.24, 85.53°) are more open than in [3]⁰ and [3]⁺, which average 80.5° and 78.7°, respectively.

Cyclic Voltammetry of [Fe₂(SR)(S)(CO)₂(dppv)₂]⁺

The cyclic voltammogram of [4]⁺ in CH₂Cl₂ solution exhibits one reversible one-electron reduction wave at -1.1 V (Figure 4). For all couples, the current ratios, *i*_{pc}/*i*_{pa}, were >0.9. When compared to the [3]⁺⁰ couple, this value indicates that S²⁻ stabilizes the oxidized state by 300 mV vs PhCH₂S⁻. The data show that SCH₂Ph substituents are nearly 100 mV less reducing than the analogous SMe complex (Table 1).

DFT Calculations on C–S Homolysis in [Fe₂(SCH₂Ph)₂(CO)_{6-x}(PMe₃)_x]^{0/+}

Method Validation—The pure GGA functional BP86 has been widely adopted when dealing with hydrogenase-inspired Fe₂S₂ compounds, since it has proven to reliably reproduce their structural, spectroscopic, and redox parameters.^{21–26} Further calibration of the method was performed taking into account the reference compound **3**. The potential of the couple [3]⁺⁰ (in CH₂Cl₂) has been estimated at the BP86 level to be -0.800 V. The close match of this value to the experimental value of 0.81 V suggests that the pure functional BP86 can accurately describe the electronic structure of both *S* = 0 and 1/2 spin states of this class of compounds. Moreover, FT-IR ν_{CO} bands of both [3]⁰ and [3]⁺ simulated at the

BP86 level are predicted to be 1895, 1855 cm^{-1} (exp. 1899, 1855 cm^{-1}) and 1950, 1899 cm^{-1} (exp. 1942, 1904 cm^{-1}).

To further validate our choice of functional, since we are dealing with chemical processes involving changes of spin multiplicity, we also tested the performance of a *hybrid* functional (namely, the GGA functional B3LYP). For the $[\mathbf{3}]^{+/0}$ redox potential, the calculated value is -1.231 V, which is far from the experimental value. In addition, to account for the effect of dispersive forces on the homolysis process, we completed the DFT picture by including results obtained at the B97-D/TZVP level. The B97-D functional, which has been developed to *a priori* include noncovalent interaction effects, has provided the best match with experimental data among “dispersion-based” approaches such as BP86-D3/TZVP and M06-L/TZVP schemes (for further details, see the DFT Methods section and the Supporting Information). Fe–Fe and Fe–S(avg) distances for $\mathbf{3}$ (eclipsed geometry structure) are very similar when optimized with BP86 vs B97-D (respectively, Fe–Fe: 2.665 and 2.625 Å and Fe–S(avg): 2.296 and 2.287 Å), although this distance is quite elongated with respect to the crystallographic result.

Results—To systematically clarify the effect of redox potential on the homolysis of the S–C bonds in diiron(I) μ -benzylthiolates, calculations examined the impact of replacing pairs of CO ligands with pairs of PMe_3 ligands. In the parent complex $\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_6$, the C–S bond dissociation free energy (BDFE) is only 27.3 kcal/mol at the BP86/TZVP level, and 29.6 kcal/mol at the B97-D/TZVP one (Figure 5). For comparison, the BDEs for HS– CH_2Ph and HS– CH_3 are 61.7(1.5) and 74.7(1.5) kcal/mol (298 K), respectively.²⁷

The C–S bond in $[\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_{6-x}(\text{PMe}_3)_x]^{0/+}$ is weakened upon replacement of CO ligands by PMe_3 . Each PR_3 -for-CO substitution weakens the C–S bond by about 4–7 kcal/mol, depending on the level of theory. One-electron oxidation of the diiron complexes further weakens the C–S bond. At the BP86 level, the effect of oxidation is predicted to be greatest for the hexacarbonyl (23.7 vs 7.4 kcal/mol) and smallest for the tetraphosphine derivatives $\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_{6-x}(\text{PMe}_3)_x$ (5.2 vs -2.5 kcal/mol) and $\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_2(\text{dppv})_2$ (1.2 vs -8.4 kcal/mol). When dispersion forces are considered (B97-D), the effect of oxidation is predicted to be almost constant upon CO vs P substitutions (about 16–18 kcal/mol). DFT results are qualitatively consistent with experimental observations. Indeed, the overall scenario remains unchanged when switching from BP86 (without dispersion) to B97-D (dispersion including) methods: the C–S bond is weakened by increasing the number of phosphine ligands and upon oxidation, becoming thus very labile for cationic tetra-substituted species, which is experimentally observed to *spontaneously* undergo C–S homolysis. In contrast, the complexes $\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_6$, $\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_4(\text{dppv})$, and $\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_2(\text{dppv})_2$ were thermally stable. Attempts to prepare $\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_2(\text{PMe}_3)_4$ were unsuccessful.

Calculations were also performed to gain mechanistic insight. Information on spin density distribution and SOMO is presented in Tables 2 and 3 for $S = 1/2$ $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$ species $[\mathbf{5}]^0$ and the rotated and unrotated isomers of $[\mathbf{4}]^+$. For $[\mathbf{5}]^0$, the inorganic sulfur carries most of the unpaired electron fraction.

Focusing on the mixed valence species related to $[3]^+$, going from electron-poor to electron-rich derivatives does not affect the spin density distribution, which remains heavily localized on the rotated Fe. In fact, in the more electron-rich complexes, the unpaired electron is even more localized (the rotated Fe). The contribution of the rotated Fe to the SOMO increases when going from $(CO)_6$ to $(CO)_4(PMe_3)_2$, but little effect is observed in going from $(CO)_4(PMe_3)_2$ to $(CO)_2(PMe_3)_4$. We note that a small fraction of the SOMO in $[Fe_2(SCH_2Ph)_2(CO)_2(PMe_3)_4]^+$ is localized on the sulfur of the equatorial thiolate, but the one that does not undergo homolysis (Figure 6).

Carbonylation of $[4]^+$

With 32 valence electrons, $[4]^+$ is highly coordinatively unsaturated. Indeed, in solution, $[4]^+$ binds not 1, but 2 equiv of CO (Scheme 7). The reaction occurs rapidly at room temperature at 1 atm. Previous examples of double carbonylation of metal complexes (without ligand displacement) are invariably associated with insertion of one CO into a metal-carbon bond.²⁸ The dicarbonylation of $[5]^+$ is reversible. When the decarbonylation was monitored by FT-IR spectroscopy, intermediates were not detected. The ^{31}P NMR and IR spectra of $[5]^+$ indicate multiple isomers.

In terms of its structure, $[5]^+$ consists of an edge-shared bioctahedron (Figure 7). The $Fe\cdots Fe$ distance elongates from 2.7453(5) Å in $[4]^+$ to 3.588(3) Å in $[5]^+$. The Fe-S distances, both to the thiolate and especially the sulfide, are strongly affected, elongating to ca. 2.32 Å from 2.26 and 2.14 Å, respectively. Two octahedral Fe(II) centers are bridged by the dithiolate. For one Fe center, the two CO ligands are trans, and for the other center, the CO ligands are cis. Compounds of the type $Fe(pdt)(CO)_2$ (diphosphine) often exist as mixtures of isomers.²⁹

DISCUSSION

Hundreds of bis(*monothiolate*) complexes are known of the type $Fe_2(SR)_2(CO)_6$;³⁰ however, their substituted derivatives $Fe_2(SR)_2(CO)_{6-x}L_x$ have received little attention. These substituted complexes are shown to adopt novel stereochemistry, a consequence of the axial-equatorial disposition of the organic substituents on sulfur. These substituted derivatives oxidize at mild potentials, which led to the discovery that the benzyl derivative $[3]^+$ has a labile C-S bond.

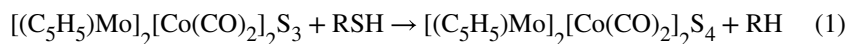
Mechanism and Implications of the Dealkylation of $[3]^+$

The finding that the benzyl derivative $[3]^+$ is more labile than the methyl and phenylthiolates is reasonable in view of the relative bond dissociation energies of the HS-CH₂Ph, HS-CH₃, and HS-Ph bonds, which are 258.2 (6.3), 312.5 (4.2), 367.8 (6.3) kJ/mol.²⁷

Regarding the mechanism of desulfurization, a free-radical pathway is indicated. The evidence includes diagnostic products (dibenzyl, toluene), the accelerating effect of TEMPO, and the nonreactivity of the SMe and SPh derivatives. The pathway for formation of CH₂Ph radicals from $[3]^+$ involves two geometric processes: (i) a small twisting of the “rotated” Fe(dppv)(CO) center to an octahedral geometry observed in $[4]^+$ and (ii) breaking of the C-S bond (Scheme 8). The unrotation of mixed valence Fe(II)Fe(I) dithiolates is nearly barrierless in the few cases that have been investigated.³¹ When monitored by FT-IR

and NMR spectroscopies, the conversion of [3]⁺ into [4]⁺ produced no detected intermediates.

The conversion of [3]⁺ → [4]⁺ is an example of a well-defined desulfurization of a thiolate by a metal complex. In this case, well-defined means that the precursor and products are well characterized and the reaction proceeds in good yields with good stoichiometry. The homolysis of C–S bonds is implicated in hydrodesulfurization (HDS) catalysis. The closest model for HDS of a thiol involves the reaction of an organoMo-Co cluster (eq 1).^{32,33}



For eq 1 and related reactions,^{32–34} the discrete desulfurization step has not been observed. With regard to the conversion [3]⁺ → [4]⁺, our results point to two aspects of complexes and catalysts that facilitate C–S homolysis: (i) the significantly weakened C–S bond in bridging thiolate ligands and (ii) the requirement for redox-active metals that can accommodate the conversion $M_n(\mu-SR) \rightarrow M_n(\mu-S) + R^\bullet$. The qualitative weakening of C–S bonds is implicated for a variety of tri- and tetrametallic complexes.^{32,33,35}

New Members of [Fe₂(SR)_{2-x}(S)_xL₆]²⁺ Series

With [Fe₂(SR)₂(CO)₆]⁰ as the best known members, organometallic 2Fe-2S complexes can be organized according to their oxidation states (Figure 8). The anions [Fe₂(S)_{2-x}(SH)_x(CO)₆]^{(2-x)-} are equivalent to [Fe₂(SR)₂(CO)₆]⁰ with regards to the oxidation state of Fe.^{30,36–38} A mixed valence subset of this family take the form [Fe₂(SR)₂L₆]⁺, manifested in synthetic models for the H_{ox} state of the [FeFe]-hydrogenases.^{17–19} The diferrous members, i.e., [Fe₂(SR)_{2-x}(S)_xL₆]^{(2-x)+}, have not been observed previously but are represented by [4]⁺.

SUMMARY

This report describes the properties of the bis(monothiolate)s [Fe₂(SR)₂(CO)₂(dppv)₂]²⁺, rare complexes of the type [Fe₂(SR)₂(CO)_{6-x}L_x]²⁺. The related chelating dithiolates have been heavily studied.⁵ Studies on the redox properties of bis(monothiolate)s are rare. Similarities obviously exist between the bis(monothiolate)s and the chelating dithiolates: the ν_{CO} band positions in the IR spectra and the $E_{1/2}$ values are comparable. The distinguishing features of the bis-(monothiolate)s arise from the unsymmetrical disposition of the SR groups. The two Fe(CO)(PR₃)₂ centers are related by mirror symmetry. This unsymmetrical steric field rigidifies these [Fe(I)]₂ complexes.

The second advance in this work is the discovery that [Fe₂(SCH₂Ph)₂(CO)₂(dppv)₂]⁺ is prone to homolysis of one C–S bond. According to DFT analysis, the C–S bond in these μ -thiolate complexes is weakened, especially in more electron-rich derivatives. Oxidation of these complexes further weakens the C–S bond. According to our calculations, C–S bond strength follows the order HS-CH₂Ph (61.7 kcal/mol) < Fe₂(SCH₂Ph)₂(CO)₆ <

$\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_2(\text{PMe}_3)_4 < [\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_2(\text{PMe}_3)_4]^+$ or $[\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_2(\text{dppv})_2]^+$, independent of the level of theory.

The third area of discovery involves the product of the C–S homolysis, the 32 e complex $[\text{Fe}_2(\text{SCH}_2\text{Ph})(\text{S})(\text{CO})_2(\text{dppv})_2]^+$. This complex, which is of the type $[\text{Fe}_2(\text{SR})(\text{S})\text{L}_6]^+$, is unprecedented within the otherwise well-studied realm of low-spin 2Fe-2S compounds.³⁰ The unusual character of the new sulfido-thiolate is shown by its unique ability to undergo reversible double decarbonylation.

EXPERIMENTAL SECTION

Materials and Methods

General procedures have been described previously.²¹ Reagents were used as received.³⁹ Literature routes were followed to prepare $\text{Fe}_2(\text{SMe})_2(\text{CO})_6$, $\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_6$,^{40,41} and $\text{Fe}_2(\text{SPh})_2(\text{CO})_6$.⁴² Photochemical reactions were conducted in Pyrex flasks; the light source was an array of 100 W LEDs emitting at 365 nm.

Cyclic voltammograms were recorded using a CH Instruments 760D Electrochemical workstation (Austin, TX). A standard three electrodes configuration was employed using glassy carbon (3 mm diameter) as the working electrode, a Pt wire as a counter electrode, and a “no leak” Ag/AgCl reference electrode (Warner Instruments, Hamden, CN). These reference electrodes have been calibrated after each experiment by adding ferrocene to the solution and recording its half-wave potential.

$\text{Fe}_2(\text{SMe})_2(\text{CO})_2(\text{dppv})_2$ ([1]⁰)—A mixture of 0.10 g (0.27 mmol) of $\text{Fe}_2(\text{SMe})_2(\text{CO})_6$ and 0.106 g (0.27 mmol) of dppv in 10 mL of benzene was heated at reflux for 2 h. The solvent was removed in vacuum; the residue was extracted into 2 mL of CH_2Cl_2 . The product, $\text{Fe}_2(\text{SMe})_2(\text{CO})_4(\text{dppv})$, precipitated as a light-brown solid upon the addition of 20 mL of pentane. Yield: 0.168 g (88%). A mixture of 0.10 g (0.14 mmol) of $\text{Fe}_2(\text{SMe})_2(\text{CO})_4(\text{dppv})$ and 0.055 g (0.14 mmol) of dppv in 90 mL of toluene was irradiated at 365 nm until the conversion was complete (~2 h) as indicated by IR spectroscopy. Solvent was removed under vacuum, and the resulting residue was extracted into 2 mL of CH_2Cl_2 . Upon addition of 30 mL of pentane, the product precipitated as a green-brown solid. Yield: 0.125 g (85%). Anal. Calcd for $\text{C}_{56}\text{H}_{50}\text{Fe}_2\text{O}_2\text{P}_4\text{S}_2 \cdot 1.5\text{CH}_2\text{Cl}_2$: C, 58.15; H, 4.32. Found: C, 58.34; H, 4.42. ¹H NMR (500 MHz, CD_2Cl_2): δ 7.88–6.89, (m, 44H, 8C₆H₅, 2CH=CH), 0.26, 0.86 (s, 6H, 2CH₃). ³¹P NMR (202 MHz, CD_2Cl_2): δ 89.2(d, $J_{\text{p-p}}$ = 20 Hz), 85.6 (d, $J_{\text{p-p}}$ = 20 Hz). IR (CH_2Cl_2): ν_{CO} = 1896, 1861 cm^{-1} .

$\text{Fe}_2(\text{SPh})_2(\text{CO})_2(\text{dppv})_2$ ([2]⁰)—A solution of 0.10 g (0.2 mmol) of $\text{Fe}_2(\text{SPh})_2(\text{CO})_6$ in 10 mL of toluene was treated with a solution of 0.015 g (0.2 mmol) of Me_3NO in 2 mL of CH_3CN . After 15 min, 0.056 g (0.2 mmol) of dppv was added to the mixture, which was then stirred for 2 h. Solvent was removed under vacuum, and the resulting solid residue was extracted into 2 mL of CH_2Cl_2 . Upon addition of 30 mL of pentane to the reaction mixture, the product precipitated as a green-brown solid. Yield: 0.145 g (86%). A solution of 0.10 g (0.12 mmol) of $\text{Fe}_2(\text{SPh})_2(\text{CO})_4(\text{dppv})$ and 0.047 g (0.12 mmol) of dppv in 90 mL of toluene was irradiated at 365 nm until the conversion was complete (~2 h) as indicated by IR

spectroscopy. The solvent was removed under vacuum, and the resulting dark residue was washed with 10 mL of Et₂O to remove other organoiron compounds. The residue was extracted into 2 mL of CH₂Cl₂. Upon dilution of this extract with 30 mL of pentane, the product precipitated as a green-brown solid. Yield: 0.049 g (35%). Anal. Calcd for C₆₆H₅₄Fe₂O₂P₄S₂·CH₂Cl₂: C, 63.68; H, 4.47. Found: C, 63.53; H, 4.32. ¹H NMR (500 MHz, CD₂Cl₂): δ 8.15–6.23, (m, 10C₆H₅, 2CH=CH). ³¹P NMR (202 MHz, CD₂Cl₂): δ 94.0(d, *J*_{p-p} = 20 Hz), 81.3 (d, *J*_{p-p} = 20 Hz). IR (CH₂Cl₂): ν_{CO} = 1900, 1851 cm⁻¹.

Fe₂(SCH₂Ph)₂(CO)₂(dppv)₂ ([3]⁰)—A mixture of 0.10 g (0.19 mmol) of Fe₂(SCH₂Ph)₂(CO)₆ and 0.15 g (0.38 mmol) of dppv in 90 mL of toluene was irradiated at 365 nm until the conversion was complete (~2 h) as indicated by IR spectroscopy. Solvent was removed under vacuum, and the resulting solid residue was extracted into 2 mL of CH₂Cl₂. Addition of 30 mL of pentane precipitated a green-brown solid. Yield: 0.12 g (52%). Syntheses of related Fe₂(SR)₂(CO)₂(dppv)₂ complexes typically proceed in yields near 80%. We verified that Fe₂(SR)₂(CO)₂(dppv)₂ is sensitive to UV irradiation, which may explain the modest yields. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.86–5.97, (m, 54H, C₆H₅, CH=CH), 2.14, 2.23 (s, 4H, 2CH₂). ³¹P NMR (202 MHz, CD₂Cl₂): δ 85.7(d, *J*_{p-p} = 20 Hz), 80.3 (d, *J*_{p-p} = 20 Hz). IR (CH₂Cl₂): ν_{CO} = 1899, 1855 cm⁻¹. Single crystals were grown by slow diffusion of hexane into a CH₂Cl₂ solution.

[Fe₂(SCH₂Ph)₂(CO)₂(dppv)₂]BF₄ ([3]BF₄)—A stirred solution of 75 mg (0.06 mmol) of [3]⁰ in 3 mL of CH₂Cl₂ at -40 °C was treated dropwise with a solution of 17 mg (0.06 mmol) of FcBF₄ in 3 mL of CH₂Cl₂. Within a few min., the solution color changed from green brown to dark green. The solution was concentrated to ~1 mL. A dark-green solid precipitated upon addition of 20 mL of pentane to this solution. Yield: 72 mg (90%). IR (CH₂Cl₂): ν_{CO} = 1942, 1904 cm⁻¹. Anal. Calcd for C₆₈H₅₈Fe₂O₂P₄S₂BF₄·CH₂Cl₂: C, 60.11; H, 4.39. Found: C, 60.48; H, 4.42. Crystals were grown by slow diffusion of hexane into a CH₂Cl₂ solution.

[Fe₂(SCH₂Ph)(S)(CO)₂(dppv)₂]BF₄ ([4]BF₄)—A solution of 26 mg (0.02 mmol) of [3]BF₄ in 3 mL of CH₂Cl₂ was treated with a solution of 3 mg (0.02 mmol) of TEMPO in 1 mL of CH₂Cl₂. After 4 h, the solution changed from dark green to dark red. The solution was concentrated to ~1 mL. A dark-red solid precipitated upon the addition of 20 mL of pentane to this concentrated solution. Yield: 18 mg (75%). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.20–6.87, (m, 49H, C₆H₅, 2CH=CH), 3.67 (s, 2H, CH₂). ³¹P NMR (202 MHz, CD₂Cl₂): δ 101.7 (t, *J*_{p-p} = 20 Hz), 85.6 (t, *J*_{p-p} = 20 Hz). IR (CH₂Cl₂): ν_{CO} = 1958, 1936 cm⁻¹. ESI-MS: *m/z* 1115.2 [M - BF₄]⁺. Crystals were grown by slow diffusion of hexanes into a CH₂Cl₂ solution. *Characterization of TEMPO-CH₂Ph*: Yield: 3 mg (61%). ¹H NMR (500 MHz, CD₂Cl₂): 7.27–7.38 (m, 5H, C₆H₅), 4.81 (s, 2H, Ph-CH₂), 1.42–1.59 (m, 6H, CH₂CH₂CH₂), 1.15, 1.26 (2s, 12H, CH₃).⁴³ HR ESI-MS: *m/z* 248.2003 [M + H] C₁₆H₂₅NO Calcd: 248.2014.

[Fe₂(SCH₂Ph)(S)(CO)₄(dppv)₂]BF₄ ([5]BF₄)—A solution of [4]BF₄ (12 mg, 0.01 mmol) in 1 mL of CH₂Cl₂ was purged with CO. After 1 min, the solution color changed from dark red to bright red, and the IR spectrum indicated a complete conversion. Yield:

~9.5 mg (80%). FT-IR (CH₂Cl₂): $\nu_{\text{CO}} = 2016, 1989, 1945, 1898 \text{ cm}^{-1}$. ¹H NMR (500 MHz, CD₂Cl₂): δ 8.05–6.56, (m, 49H, 9C₆H₅, 2CH=CH); 3.38, 3.35, 3.27, 3.15, 3.13 (m, 2H, CH₂). ³¹P NMR (202 MHz, CD₂Cl₂): δ 88.6, 85.6, 84.9, 75.9, 74.4, 72.3, 71.8, 55.0. Anal. Calcd for C₆₃H₅₁Fe₂O₄P₄S₂BF₄·1.5CH₂Cl₂: C, 56.0 (55.90); H, 4.08 (3.93). Crystals of [5]BF₄ were grown by diffusion of CO-saturated hexane into the CH₂Cl₂ solution at room temperature. Purging a solution of [5]BF₄ with N₂ results in a color change from bright red to dark red and the appearance of IR bands characteristic of [4]⁺.

DFT Methods

Density Functional Theory (DFT) computations have been carried out with the TURBOMOLE 7.2 programs suite,⁴⁴ by using the pure functional BP86^{45,46} and an all-electron valence triple- ζ basis set with polarization functions on all atoms (TZVP).⁴⁷ This level of theory, which has proved to reliably reproduce structures, spectroscopic properties, and reactivity of hydrogenase-mimics,^{21–25} has been further validated by reproducing experimental IR bands and redox potential for the [3]⁺⁰ (vide infra). In addition, computations regarding the S–C bond homolysis process have been also performed with the GGA functional B97-D, developed by Grimme to account for noncovalent interactions.⁴⁸

Alternative approaches, such as Grimme's empirical dispersion corrections (BP86-D3)⁴⁹ and the use of Truhlar's M06-L functional,⁵⁰ have been also tested for the prediction of S–C homolysis energies. Results indicate that, while absolute ΔG values are quite sensitive to the functional choice, the overall picture predicted by the BP86 method is retained, independent of the level of theory. Indeed, S–C homolysis is always predicted to be facilitated upon oxidation and by increasing the number of P-ligands. Only results, however, obtained at the BP86/TZVP and B97-D/TZVP levels are indicative for a process that is spontaneous *only* for Fe^{II}Fe^I tetra-substituted derivatives, in agreement with experiments. Hybrid functionals have not been used to evaluate homolysis ΔG 's, mainly because of their poor performances in reproducing redox potentials which has been verified in the present investigation (see values obtained with the B3LYP^{13–15} functional in the SI).^{45,51,52}

The resolution-of-identity (RI)⁵³ technique has been applied to speed up calculations. Geometry optimizations have been performed by means of energy gradient techniques, and full vibrational analysis has been carried out to further characterize each stationary point. The homolysis products [Fe₂(SCH₂Ph)(S)L₆]⁰ have been treated as unrestricted open-shell doublets ($S = 1/2$), while [Fe₂(SCH₂Ph)(S)-L₆]⁰ as overall unrestricted open-shell singlet ($S = 0$), following the Broken Symmetry (BS) approach.^{54,55} This approximation allows the treatment of antiferromagnetic spin couplings in the framework of the unrestricted formalism, by localizing opposite spins of the mono-determinant wave function in different parts of the molecule. High spin solutions have not been considered since they correspond to high energy structures. Free energy (ΔG) values have been obtained from the electronic KS-SCF energy considering three contributions to the total partition function (Q), $q_{\text{translational}}$, $q_{\text{rotational}}$, $q_{\text{vibrational}}$, assuming that Q can be written as the product of them.⁵⁶ To evaluate enthalpy and entropy contributions, the values for temperature and pressure have been set to 298.15 K and 1 bar, respectively. The scaling factor for the SCF wavenumbers was set either to 0.9914 (default value in the TURBOMOLE).⁴⁴ Solvent was modeled according to the

conductor-like screening model (COSMO)^{57,58} by considering a polarizable continuum medium with $\epsilon = 8.93$ (CH_2Cl_2). Solvent effects have been included in the evaluation of homolysis for $[\mathbf{3}]^0$ and $[\mathbf{3}]^+$, their FT-IR ν_{CO} bands, and the potential of the $[\mathbf{3}]^{+/0}$ couple. The latter has been computed using the equation $\Delta G^\circ_{\text{solv(SCF)}} = -nFE^\circ$, where $\Delta G^\circ_{\text{solv}}$ refers to the free energy difference (respectively) between the optimized reduced and the oxidized structures (including an implicit solvent model), n is the number of electrons involved in the redox process, F is the Faraday constant, and E° is the standard absolute redox potential (which has subsequently been referred to the Fc^+/Fc couple absolute potential, computed at the same level of theory). Both $\Delta E^\circ_{\text{solv}}$ and $\Delta G^\circ_{\text{solv}}$ have been used since it has been shown that the inclusion of entropic correction does not necessarily provide a better match of Fe_2S_2 experimental redox potentials.²⁶ The computed redox potentials for $[\mathbf{3}]^{+/0}$ are $E^\circ(\Delta E^\circ_{\text{solv}}) = -0.800$ V and $E^\circ(\Delta G^\circ_{\text{solv}}) = -0.731$ V for BP86, $E^\circ(\Delta E^\circ_{\text{solv}}) = -0.867$ V and $E^\circ(\Delta G^\circ_{\text{solv}}) = -0.799$ V for B97-D, $E^\circ(\Delta E^\circ_{\text{solv}}) = -1.126$ V and $E^\circ(\Delta G^\circ_{\text{solv}}) = -1.050$ V for M06-L. Computed values at other levels of theory can be found in the Supporting Information.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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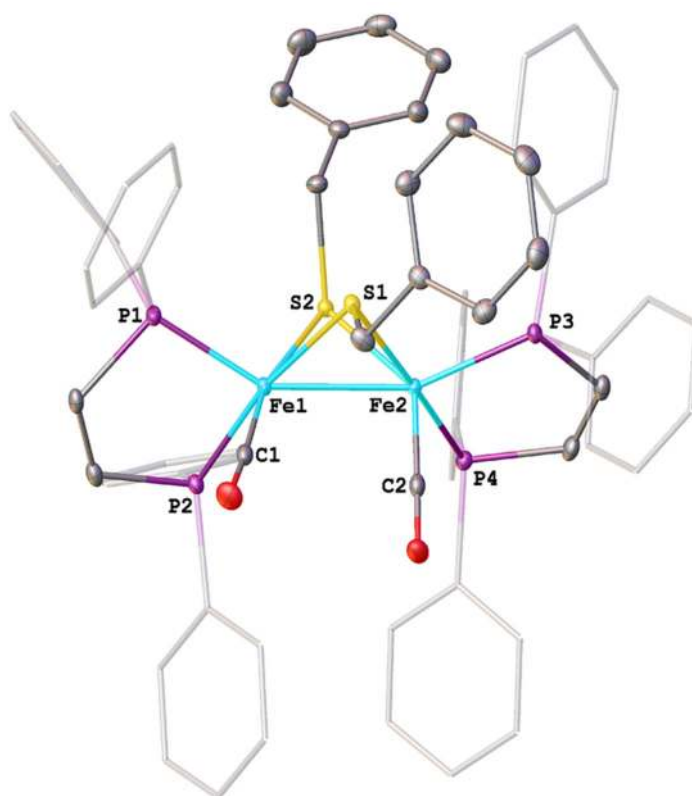


Figure 1. Structure of $\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_2(\text{dppv})_2$ ($[\mathbf{3}]^0$) with 50% probability ellipsoids and hydrogen atoms removed for clarity. Selected bond distances (\AA): Fe1–C1, 1.7500(15), 1.7381(15); Fe–P, 2.1735(4)–2.2144(4); Fe–S, 2.2566(4)–2.2933(4); Fe1–Fe2, 2.5840(3).

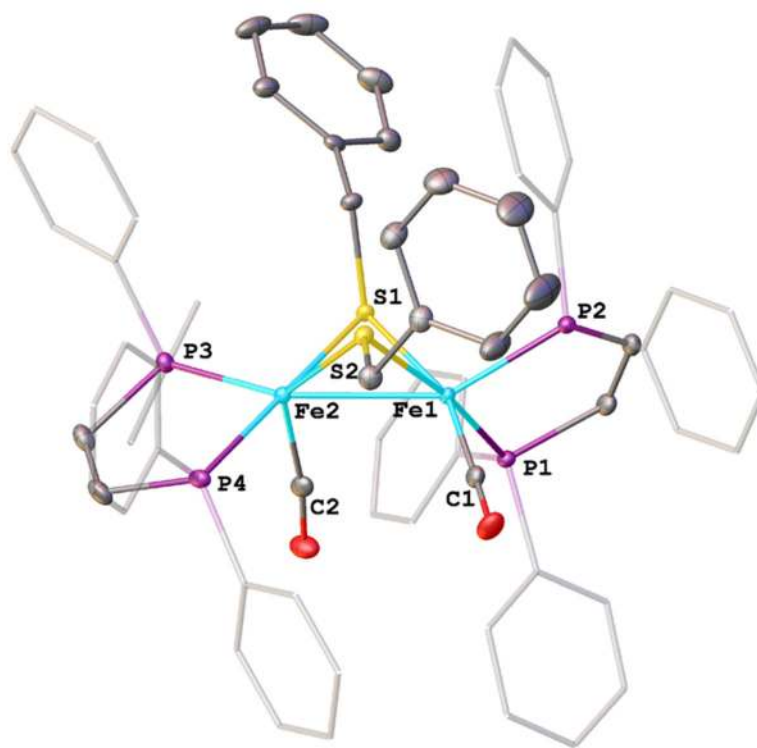


Figure 2. Structure of $[\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_2(\text{dppv})_2]^+$ ($[\mathbf{3}]^+$) with 50% probability ellipsoids and hydrogen atoms removed for clarity. Selected bond distances (\AA): Fe1–C1, 1.752(2); Fe1–P2, 2.2035(6); Fe1–P1, 2.2487(6); Fe1–S2, 2.2504(6); Fe1–S1, 2.2894(5); Fe1–Fe2, 2.6012(4); Fe2–C2, 1.775(2); Fe2–P4, 2.2232(6); Fe2–P3, 2.2263(6); Fe2–S2, 2.2319(5); Fe2–S1, 2.2895(5).

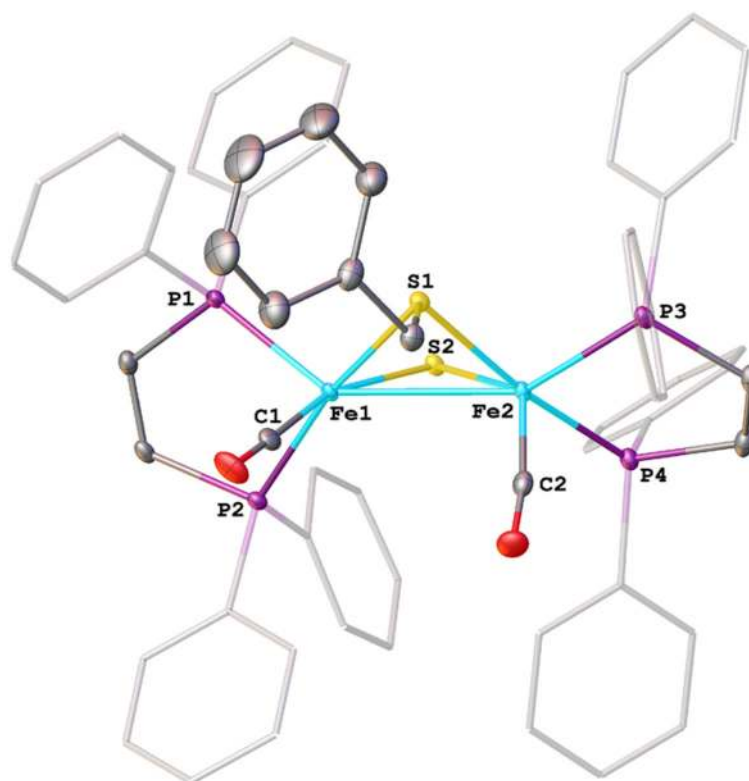


Figure 3. Structure of the cation in the salt $[\text{Fe}_2(\text{SCH}_2\text{Ph})(\text{S})-(\text{CO})_2(\text{dppv})_2]\text{BF}_4$ ($[\mathbf{4}]\text{BF}_4$) with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (\AA): Fe–C, 1.769(3), 1.766(3); Fe1–S2, 2.1643(7); Fe2–S2, 2.1275(7); Fe1–S1, 2.2476(7); Fe2–S1, 2.2707(7); Fe1–P1, 2.1656(7); Fe1–P2, 2.2356(7); Fe2–P3, 2.2078(7); Fe2–P4, 2.2249(7); Fe1–Fe2, 2.7453(5).

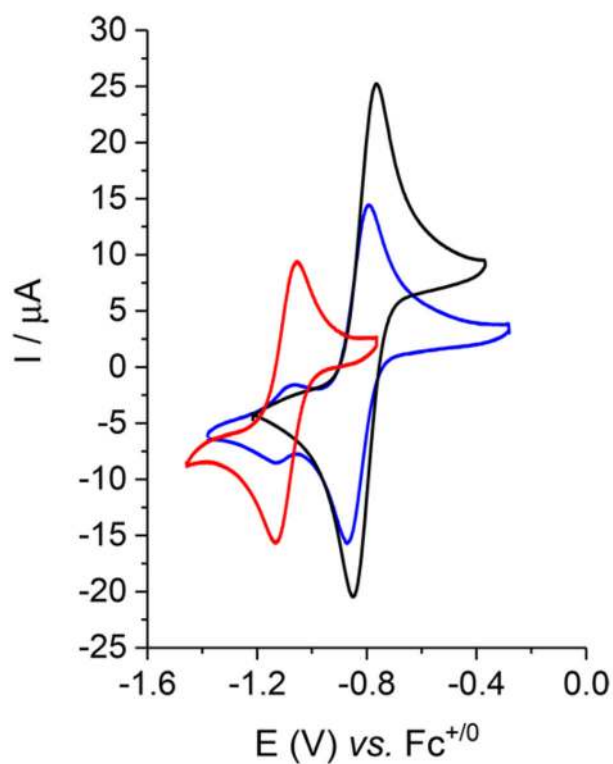


Figure 4. Cyclic voltammograms of 2.7 mM of $[\text{Fe}_2(\text{SBn})_2(\text{CO})_2(\text{dppv})_2]$ ($[\mathbf{3}]^0$, black), $[\mathbf{3}]^+$ (blue), and $[\mathbf{4}]^0$ (red) in CH_2Cl_2 solutions with 0.125 M $[\text{Bu}_4\text{N}]\text{PF}_6$ electrolyte (scan rate = 100 mV/s). The presence of a small amount of $[\mathbf{4}]^+$ is evident in the sample of $[\mathbf{3}]^+$.

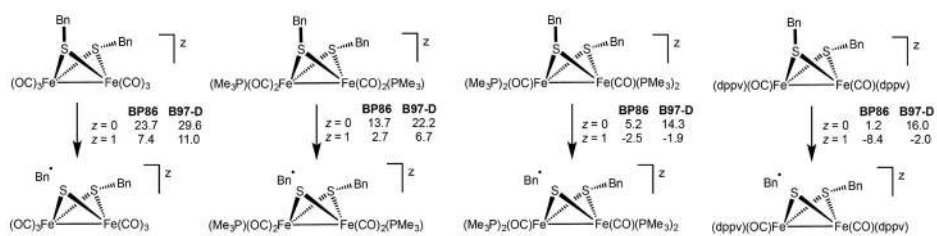


Figure 5.

Relative free energies (kcal/mol at 298 K) associated with the homolytic cleavage of the S–C bond in the series of $[\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_{6-x}(\text{PMe}_3)_x]^{z\pm}$ ($x = 0, 2, 4$) as well as $[\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_2(\text{dppv})_2]^{z\pm}$ (**[3]**^z). Both Fe(I)Fe(I) ($z = 0$) and Fe(II)Fe(I) ($z = 1$) redox states are considered.

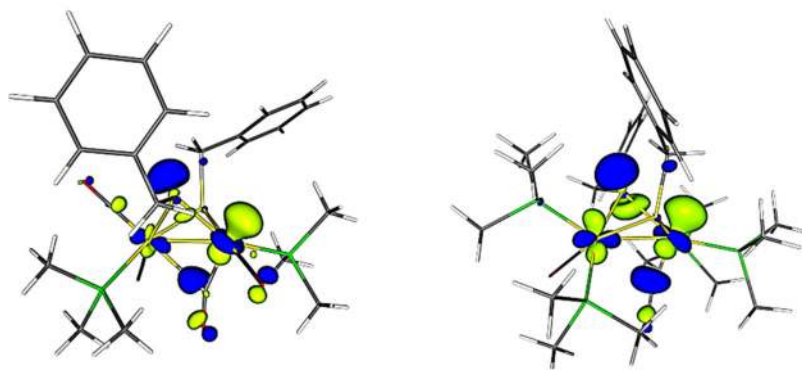


Figure 6. SOMOs for $[\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_4(\text{PMe}_3)_2]^+$ and $[\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_2(\text{PMe}_3)_4]^+$ (BP86/TZVP optimized structures). Isosurface boundary = 0.05 au.

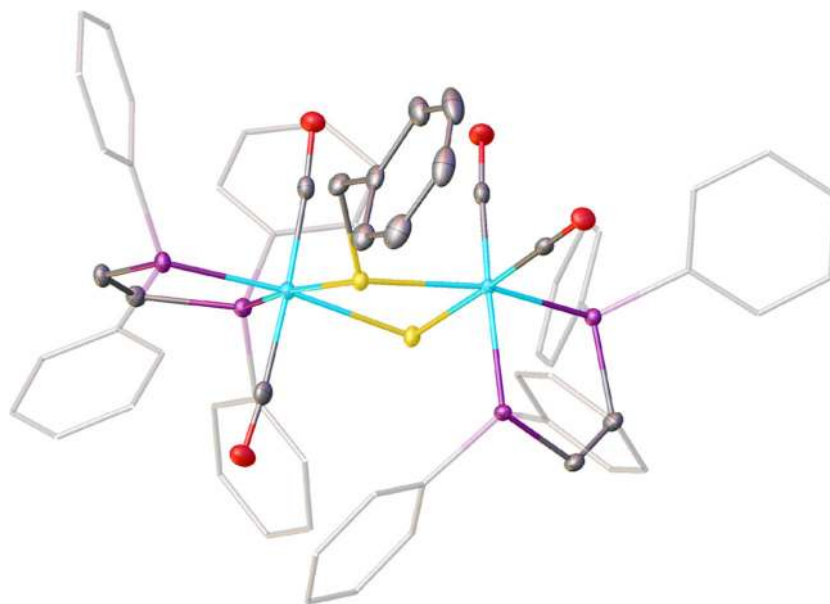


Figure 7. Structure of $[\text{Fe}_2(\text{SBn})(\text{S})(\text{CO})_4(\text{dppv})_2]^+$ ($[\mathbf{5}]^+$) with 50% probability ellipsoids and hydrogen atoms omitted for clarity. Selected bond distances (\AA): Fe1–C27, 1.8125(16); Fe1–C28, 1.8171(16); Fe1–P1, 2.2263(4); Fe1–P2, 2.2521(4); Fe1–S1, 2.3432(4); Fe2–C37, 1.7916(15); Fe2–C36, 1.7985(16); Fe2–P4, 2.2494(4); Fe2–P3, 2.3059(4); Fe2–S1, 2.3336(4); Fe2–S2, 2.3398(4).

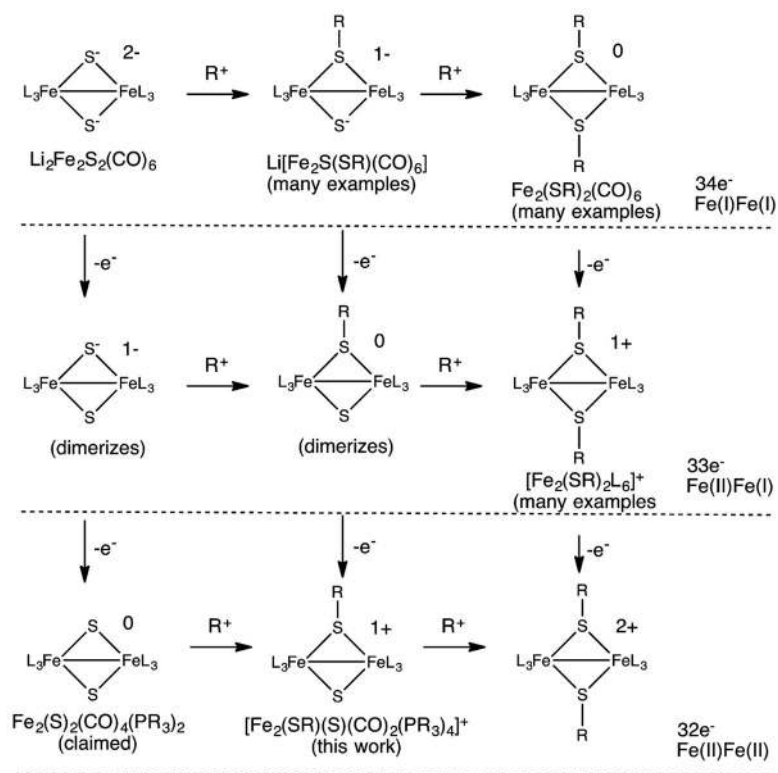
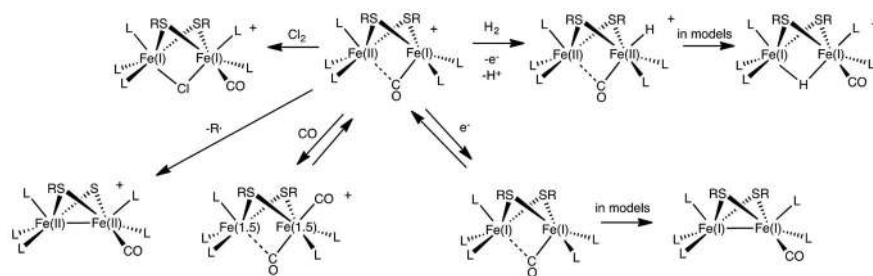
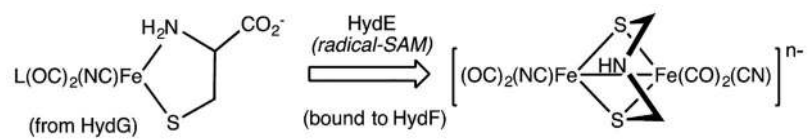
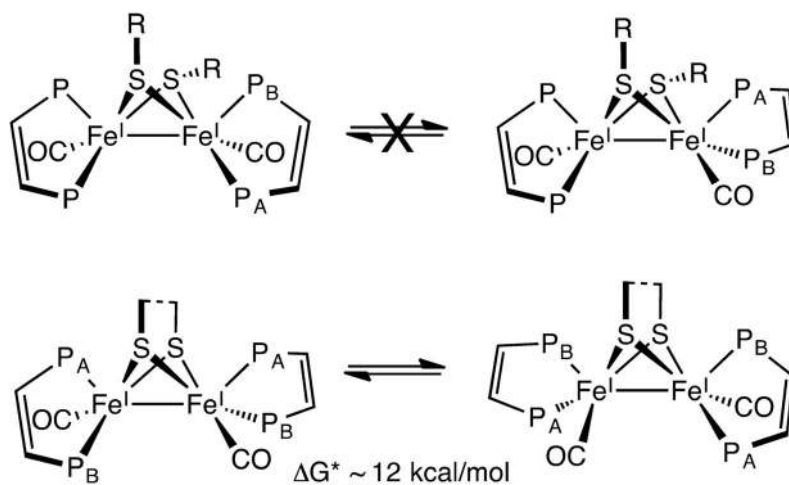


Figure 8. Structure of known and hypothetical $\text{Fe}_2(\text{S})_2\text{L}_6]^z$ complexes in various oxidation states and degrees of alkylation.

**Scheme 1.**Selected Reactions of $[\text{Fe}_2(\text{SR})_2(\text{CO})\text{L}_5]^+$ ($\text{L} = \text{CO}, \text{PR}_3$)

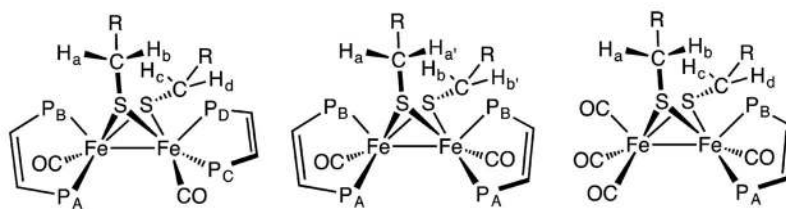


Scheme 2.
Radical Reactions Implicated in the Biosynthesis of the $[2\text{Fe}]_{\text{H}}$ Center

**Scheme 3.**

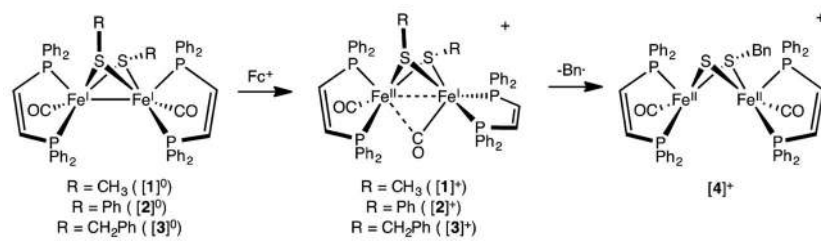
Bis(monothiolates) $\text{Fe}_2(\text{SR})_2(\text{CO})_2(\text{dppv})_2$ Are More Rigid Stereochemically (Top) than the Related Chelating Dithiolates $\text{Fe}_2[(\text{SCH}_2)_2\text{X}](\text{CO})_2(\text{dppv})_2$, Which Undergo Degenerate Racemization^a

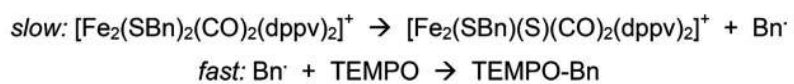
^aPh groups on phosphorus omitted for clarity.

**Scheme 4.**

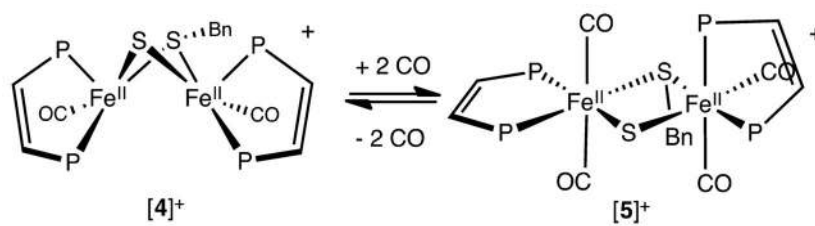
Stereochemistry of Methylene Groups in Two Isomers of $\text{Fe}_2(\text{SCH}_2\text{R})_2(\text{CO})_2(\text{dppv})_2$ (the Isomer on the Left Is Not Observed) and $\text{Fe}_2(\text{SCH}_2\text{R})_2(\text{CO})_4(\text{dppv})^a$

^aPh groups on phosphorus omitted for clarity.

**Scheme 5.**Oxidation of $[1]^0$ – $[3]^0$ and Debenzylation of $[3]^+$



Scheme 6.
Reaction of [3]⁺ with TEMPO

**Scheme 7.**

Double Carbonylation of $[4]^+$. Only the Crystallographically Verified Isomer of $[5]^+$ Is Shown^a

^aPh groups omitted for clarity.

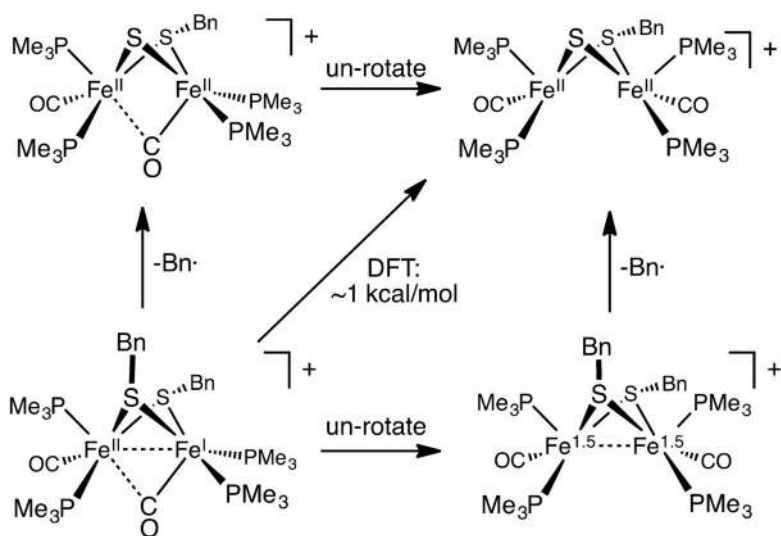
**Scheme 8.**Two Pathways for Debenzylation of $[\text{Fe}_2(\text{SCH}_2\text{Ph})_2(\text{CO})_2(\text{PMe}_3)_4]^+$

Table 1

Reduction Potentials for [4]⁺, [3]⁺, [2]⁺, and [1]⁺ as Well as the Related 1,3-Propanedithiolate (pdt²⁻) Complex

couple	potential, V vs Fc⁺⁰	<i>i</i>_{pa}/<i>i</i>_{pc}
[Fe ₂ (SMe) ₂ (CO) ₂ (dppv) ₂] ⁺⁰	-0.90	1
[Fe ₂ (SPh) ₂ (CO) ₂ (dppv) ₂] ⁺⁰	-0.85	1
[Fe ₂ (SCH ₂ Ph) ₂ (CO) ₂ (dppv) ₂] ⁺⁰	-0.81	1
[Fe ₂ (pdt)(CO) ₂ (dppv) ₂] ⁺⁰	-0.83	1
[Fe ₂ (SCH ₂ Ph)(S)(CO) ₂ (dppv) ₂] ⁺⁰	-1.1	0.95

Spin Densities (at the BP86/TZVP Level) for Selected Atoms in $[\text{Fe}_2(\text{SCH}_2\text{Ph})(\text{S})\text{L}_6]^0$, Rotated- $[\text{Fe}_2(\text{SCH}_2\text{Ph})_2\text{L}_6]^+$, and Unrotated- $[\text{Fe}_2(\text{SCH}_2\text{Ph})_2\text{L}_6]^{\text{+a}}$

Table 2

L_6	$[\text{Fe}_2(\text{SCH}_2\text{Ph})(\text{S})\text{L}_6]^0$			$[\text{Fe}_2(\text{SCH}_2\text{Ph})_2\text{L}_6]^+(\text{rot.})$			$[\text{Fe}_2(\text{SCH}_2\text{Ph})_2\text{L}_6]^+(\text{unrot.})$				
	Fe1	Fe2	S2	Fe1	Fe2	S1	S2	Fe1	Fe2	S1	S2
(CO) ₆	0.26	0.26	0.47	0.14	0.70	0.08	-0.01	0.20	0.53	0.12	-0.01
(CO) ₄ (PMe ₃) ₂	0.34	0.28	0.35	0.12	0.85	0.02	-0.01	0.41	0.42	0.06	-0.01
(CO) ₂ (PMe ₃) ₄	0.40	0.34	0.27	0.09	0.89	0.03	-0.02	0.38	0.54	0.07	-0.01
(CO) ₂ (dppv) ₂	0.53	0.21	0.23	0.09	0.86	0.04	-0.01	0.29	0.50	0.07	-0.01

^aFor $[\text{Fe}_2(\text{SCH}_2\text{Ph})(\text{S})\text{L}_6]^0$, values are shown for the inorganic sulfur. For rotated- $[\text{Fe}_2(\text{SCH}_2\text{Ph})_2\text{L}_6]^+$, Fe2 has the rotated geometry.

Single Atom Contributions to the SOMO (at the BP86/TZVP Level) for Selected Atoms in $[\text{Fe}_2(\text{SCH}_2\text{Ph})(\text{S})\text{L}_6]^0$, Rotated- $[\text{Fe}_2(\text{SCH}_2\text{Ph})_2\text{L}_6]^+$, and Unrotated- $[\text{Fe}_2(\text{SCH}_2\text{Ph})_2\text{L}_6]^{+a}$

Table 3

	$[\text{Fe}_2(\text{SCH}_2\text{Ph})(\text{S})\text{L}_6]^0$			$[\text{Fe}_2(\text{SCH}_2\text{Ph})_2\text{L}_6]^+$ (rot.)			$[\text{Fe}_2(\text{SCH}_2\text{Ph})_2\text{L}_6]^+$ (unrot.)				
	Fe1	Fe2	S2	Fe1	Fe2	S1	S2	Fe1	Fe2	S1	S2
L_6	0.18	0.18	0.47	0.07	0.15	0.06	0.03	0.09	0.17	0.09	0.03
(CO) ₆	0.23	0.21	0.36	0.13	0.45	0.11	0.03	0.24	0.26	0.10	0.03
(CO) ₄ (PMe ₃) ₂	0.26	0.24	0.28	0.23	0.41	0.14	0.01	0.26	0.29	0.08	0.01
(CO) ₂ (PMe ₃) ₄	0.30	0.19	0.27	0.17	0.43	0.12	0.02	0.21	0.25	0.14	0.03

^aFor $[\text{Fe}_2(\text{SCH}_2\text{Ph})(\text{S})\text{L}_6]^0$, values are shown for the inorganic sulfur. For rotated- $[\text{Fe}_2(\text{SCH}_2\text{Ph})_2\text{L}_6]^+$, Fe2 has the rotated geometry.