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Rational Synthesis of the Carbonyl(perthiolato)diiron [Fe₂(S₃CPh₂)(CO)₆] and Related Complexes

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Abstract

The photochemical reaction of Fe₂(S₂)(CO)₆ and Ph₂CS affords the perthiolate Fe₂(S₃CPh₂)(CO)₆ (**1**) in good yield. As confirmed crystallographically, **1** contains a previously elusive perthiolate ligand. The related reaction of Fe₂(S₂)(CO)₅-(PPh₃) and Ph₂CS gave Fe₂(S₃CPh₂)(CO)₅(PPh₃). Although Fe₃S₂(CO)₉ and Ph₂CS failed to efficiently give Fe₂(S₂CPh₂)(CO)₆, this compound could be prepared by desulfurization of **1** using PPh₃.

Graphical Abstract

The photoaddition of Ph₂CS to Fe₂(S₂)(CO)₆ gives the rare diiron perthiolate Fe₂(S₃CPh₂)(CO)₆. Desulfurization of the perthiolate gives Fe₂(S₂CPh₂)(CO)₆. These simple reactions provide access to Fe-S-CO compounds that previously were difficult to prepare.

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Keywords

Iron sulfides; Thiones; Photochemistry; Perthiolates; Desulfurization

Introduction

The chemistry of carbonyl(dithiolato)diiron compounds is rich, consisting of both routine and esoteric complexes. Hundreds of compounds are known with the formula $\text{Fe}_2(\text{SR})_2(\text{CO})_6$, and thousands of CO-substituted derivatives of such compounds have been reported. Foundational compounds include $\text{Fe}_2(\text{SR})_2(\text{CO})_6$ with $\text{R} = \text{Me}, \text{Et}, \text{Ph}$, as well as the more recently popularized pdt and adt derivatives.^[1] These complexes have attracted intense attention because of their similarity to the active site of the [FeFe]-hydrogenases, with the hope that synthetic analogues of the enzyme might underpin technologies for producing hydrogen.^[2]

Although the complexes $\text{Fe}_2(\text{SR})_2(\text{CO})_6$ can be produced in excellent yields for many R groups, a handful of related complexes have only been obtained in trace amounts. Some of these “esoteric” compounds are quite simple in composition and could in fact be useful building blocks if they were more readily prepared. Examples of such esoteric but fundamental complexes are shown in Scheme 1; they include $\text{CS}_4\text{Fe}_4(\text{CO})_{12}$, $\text{C}_2\text{S}_4\text{Fe}_4(\text{CO})_{12}$, $\text{CH}_2\text{S}_2\text{Fe}_2(\text{CO})_6$, and $\text{CH}_2\text{S}_3\text{Fe}_2(\text{CO})_6$. The first two are obtained in low (1–2 %) or unspecified yields upon reaction of $\text{Fe}_3(\text{CO})_{12}$ with CS_2 .^[3] The third complex in Scheme 1, $\text{Fe}_2(\text{S}_3\text{CH}_2)(\text{CO})_6$, is a derivative of the thiol-perthiol $\text{H}_2\text{C}(\text{SH})(\text{S}_2\text{H})$, which is unknown and is expected to be labile. The complex was obtained in low yield from the reaction of $\text{Fe}_3(\text{CO})_{12}$, S_8 , and styrene.^[4] It is difficult to envision how this combination of reagents produces the observed perthiolate. This complex is formally an adduct of thioformaldehyde and $\text{Fe}_2(\text{S}_2)(\text{CO})_6$. Since free CH_2S is only stable as a dilute gas, it is not a reasonable reagent.^[5] Only the methanedithiolate can be prepared efficiently, by the reaction of $\text{Fe}_3(\text{CO})_{12}$ and methanedithiol.^[6]

In this paper, we report a new approach to obtaining some of the aforementioned elusive targets. The guiding hypothesis was that stable thioketones (unlike thioformaldehyde), might add to $\text{Fe}_2(\text{S}_2)(\text{CO})_6$. The photoinduced additions of ethylene and CO to $\text{Fe}_2(\text{S}_2)(\text{CO})_6$ afford $\text{Fe}_2(\text{S}_2\text{C}_2\text{H}_4)(\text{CO})_6$ and $\text{Fe}_2(\text{S}_2\text{CO})(\text{CO})_6$, respectively.^[7] The reaction has been extended to other alkenes.^[8] These photoadditions probably proceed via the diferrous sulfide $\text{Fe}_2(\text{S})_2(\text{CO})_6$, an excited state of $\text{Fe}_2(\text{S}_2)(\text{CO})_6$.^[9]

Results and Discussion

We confirmed that $\text{Fe}_2(\text{S}_2)(\text{CO})_6$ does not readily react with Ph_2CS thermally. This nonreactivity was easily checked, because the thione is deep blue. More promising results were obtained upon UV irradiation of a toluene solution of $\text{Fe}_2(\text{S}_2)(\text{CO})_6$ (90 mg) and an equimolar amount of Ph_2CS (50 mg). The reaction was conducted using an LED emitting at 365 nm to give the targeted adduct [Equation (1)].

After ca. 1 h, the red product was obtained in 44 % yield after purification by column chromatography. The new compound **1** exhibited an FT-IR spectrum [2080 (s), 2046 (vs), 2007 (vs) cm^{-1}] that closely ($\pm 5 \text{ cm}^{-1}$) resembled the spectrum for $\text{Fe}_2(\text{S}_2)(\text{CO})_6$. The ^1H and ^{13}C NMR spectra were consistent but not informative, but the EI-MS data showed a progression of peaks for $\text{Fe}_2(\text{S}_3\text{CPh}_2)(\text{CO})_{6-n}$ at $m/z = 513.8 - n(28)$, which are

(1)

assigned to $[\text{M} - n \text{CO}]^+$ for $n = 1-6$. Once isolated, **1** is robust in air and ambient light.

To test the generality of the new reaction, we also investigated the photoaddition of $\text{Fe}_2(\text{S}_2)(\text{CO})_5(\text{PPh}_3)^{[8c]}$ to thiobenzophenone. This reaction proceeded as above to give the adduct $\text{Fe}_2(\text{S}_3\text{CPh}_2)(\text{CO})_5(\text{PPh}_3)$ (**2**) in 45 % isolated yield. The ^{31}P NMR spectrum of the adduct confirmed the presence of a single species with a signal at $\delta(^{31}\text{P}) = 70.6$ ppm, distinct from that of the parent $\text{Fe}_2(\text{S}_2)(\text{CO})_5(\text{PPh}_3)$ [$\delta(^{31}\text{P}) = 60.81$ ppm]. The reaction did not produce SPPH_3 , in contrast to a related reaction below.

The structure of **1** was confirmed crystallographically (Figure 1). The molecule has idealized C_s symmetry but no crystallographically imposed symmetry. The compound adopts the now familiar butterfly structure with six terminal CO ligands. The CS_3 bridge is planar.

The reaction of thiobenzophenone with $\text{Fe}_2(\text{S}_2)(\text{CO})_6$ prompted investigation of its reaction with $\text{Fe}_3\text{S}_2(\text{CO})_9$, the other main Fe-S-CO cluster.^[10] The diphenylmethanedithiolate has been obtained in 5–25 % yield by the reaction of thiobenzophenone with $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$.^[11] These reactions also produce several other products, including $\text{Fe}_3\text{S}_2(\text{CO})_9$. From the perspective of stoichiometry, this triiron cluster is a logical precursor to $\text{Fe}_2(\text{S}_2\text{CPh}_2)(\text{CO})_6$. A reaction between $\text{Fe}_3\text{S}_2(\text{CO})_9$ and excess Ph_2CS could only be induced in refluxing toluene, but the desired **3** was only obtained in ca. 10 % yield [Equation (2)].

This result suggests that **3** is not produced via the Fe_3S_2 cluster. Indeed, the intermediacy of the dithiirane Ph_2CS_2 has been proposed for related reactions.^[11b,11c,12]

A more rational route to **3** involves the desulfurization of the perthiolate **1**. Indeed, treatment of a CH₂Cl₂ solution of **1** with 1 equiv. of PPh₃ at room temperature gave **3** in 85 % isolated yield [Equation (3)].

(3)

The coproduct was SPh₃. The product was identical to that obtained in low yield from Fe₃S₂(CO)₉.

Conclusions

The synthetic chemistry of Fe-S-CO compounds is very old,^[13] and the biological chemistry of related materials is possibly ancient.^[14] Given this rich context, new routes to fundamental derivatives of the Fe-S-CO series are always welcome. The addition of thioketones to Hieber's classic Fe₂S₂(CO)₆^[15] should encourage the development of photoadditions or other hetero-alkenes, hopefully opening new opportunities for this fascinating area.

Experimental Section

General Methods

Spectroscopic instrumentation and methodology have been described.^[16] ¹H NMR (500 MHz) and ¹³C NMR (162 MHz) spectra were referenced to residual solvent relative to TMS. ³¹P{¹H} NMR (202 MHz) spectra were referenced to external 85 % H₃PO₄. Crystallographic data were collected using a Siemens SMART diffractometer equipped with an Mo-K_α source (λ = 0.71073 Å). The preparation of starting reagents are mentioned above, and Ph₂CS was obtained using Lawesson's reagent.^[17] CCDC 1476511 (for **1**), and 1440460 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Fe₂(S₂CPh₂)(CO)₆ (**1**)

A mixture of Fe₂S₂(CO)₆ (90 mg, 0.25 mmol) and Ph₂CS (50 mg, 0.25 mmol) was dissolved in dry toluene (70 mL) in a Pyrex Schlenk tube. The reaction mixture was photolyzed at 365 nm for ca. 1 h. After filtration, the resulting deep-green filtrate was concentrated under vacuum to afford a viscous residue. The residue was chromatographed on silica gel eluting with hexane/CH₂Cl₂ (10:1). The main red band (the second band) was concentrated to give the product, a red solid. Yield 60 mg (44 %). ¹H NMR (500 MHz, CD₂Cl₂): δ = 7.64 (d, *J* = 6.5 Hz, 4 H, Ar*H*), 7.28 (d, *J* = 6.5 Hz, 6 H, Ar*H*) ppm. ¹³C NMR (162 MHz, CD₂Cl₂): δ = 207.5 (FeCO), 143.3 (ArC), 128.57, 128.55, 128.4 (ArCH), 89.8 (S₂CPh₂) ppm. FT-IR (CH₂Cl₂): ν_{CO} = 2080 (vs), 2046 (vs), 2007 (vs) cm⁻¹. EI-MS: *m/z* =

513.8 $[M - CO]^+$, 485.8 $[M - 2 CO]^+$, 457.8 $[M - 3 CO]^+$, 401.9 $[M - 5 CO]^+$, 373.9 $[M - 6 CO]^+$. $C_{19}H_{10}Fe_2O_6S_3$ (541.8): calcd. C 42.09, H 1.86; found C 41.77, H 1.57. The single crystal for X-ray analysis was grown by slow concentration of a concentrated pentane solution.

$Fe_2(S_3CPh_2)(CO)_5(PPh_3)$ (2)

A mixture of $Fe_2S_2(CO)_5(PPh_3)$ (90 mg, 0.15 mmol) and Ph_2CS (30 mg, 0.15 mmol) was dissolved in dry toluene (60 mL) in a Pyrex Schlenk tube. The mixture was irradiated at 365 nm for ca. 1 h. After the solvent had been removed under vacuum, the residue was purified by chromatography on silica gel eluting with hexane/ CH_2Cl_2 (4:1). The intense red band (the third) was concentrated to give the product as a red solid. Yield 50 mg (43 %). 1H NMR (500 MHz, CD_2Cl_2): δ = 7.58–7.44 (br. d, 16 H, ArH), 7.26–7.13 (m, 9 H, ArH) ppm. ^{31}P NMR (202 MHz, CD_2Cl_2): δ = 70.6 (s) ppm. FT-IR (CH_2Cl_2): $\tilde{\nu}_{CO}$ = 2045 (vs), 1991 (vs), 1975 (s), 1934 (m) cm^{-1} .

$Fe_2(S_2CPh_2)(CO)_6$ (3)

Method 1: A mixture of $Fe_2(S_3CPh_2)(CO)_6$ (50 mg, 0.09 mmol) and PPh_3 (27 mg, 0.10 mmol) was dissolved in dry CH_2Cl_2 (10 mL). The reaction solution was stirred at room temperature until the reaction was completed (3 h) as indicated by FT-IR spectroscopy. After the solvent had been removed under vacuum, the residue was purified by chromatography on silica gel eluting with hexane/ CH_2Cl_2 (10:1). The intense red band (the first band) was collected and concentrated to yield the product, an orange-yellow solid. Yield 40 mg (87 %). 1H NMR (500 MHz, CD_2Cl_2): δ = 7.33 (br. s, 8 H, ArH), 7.23 (br. s, 2 H, ArH) ppm. ^{13}C NMR (162 MHz, CD_2Cl_2): δ = 208.7 (FeCO), 150.2 (ArC), 129.0, 128.1, 123.7 (ArCH), 95.1 (S_2CPh_2) ppm. FT-IR (CH_2Cl_2): $\tilde{\nu}_{CO}$ = 2076 (vs), 2039 (vs), 2000 (vs) cm^{-1} . EI-MS: m/z = 510.1 $[M]^+$, 482.1 $[M - CO]^+$, 454.1 $[M - 2 CO]^+$, 426.1 $[M - 3 CO]^+$, 398.1 $[M - 4 CO]^+$, 370.1 $[M - 5 CO]^+$, 342.0 $[M - 6 CO]^+$. **Method 2:** A mixture of $Fe_3S_2(CO)_9$ (97 mg, 0.20 mmol) and Ph_2CS (40 mg, 0.20 mmol) was dissolved in dry toluene (100 mL). The reaction mixture was heated at 90 °C for 2 h and then at reflux for 1.5 h. After the solvent had been removed under vacuum, the residue was purified by chromatography on silica gel, eluting with hexane/ CH_2Cl_2 (10:1). The intensely red band (the first band) was collected and concentrated to yield the product as an orange-yellow solid. Yield 10 mg (10 %).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Structure of $\text{Fe}_2(\text{S}_3\text{CPh}_2)(\text{CO})_6$ (**1**) with thermal ellipsoids drawn at the 50 % probability level. Selected distances [$\text{\AA}$] and angles [$^\circ$]: Fe(1)–Fe(2) 2.5068(6), Fe(1)–S(1) 2.2256(10), Fe(1)–S(3) 2.2427(9), S(1)–S(2) 2.0630(13), S(2)–C(4) 1.847(3), C(4)–S3 1.856(3); S(1)–Fe(1)–S(3) 81.40(3), S(1)–S(2)–C(4) 102.24(11), S(2)–C(4)–S(3) 109.41(16).

Scheme 1.

Simple but elusive compounds of the type $\text{Fe}_2(\text{SR})_2(\text{CO})_6$.