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A comparison of the reactions of pentacarbonyliron with cyclic thioethers and related dialkyl sulfides

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Abstract

A facile synthesis of the compounds $Fe(CO)_4(ER_2)$, where $ER_2 = SMe_2$, SEt_2, or $SeMe_2$, has been developed. It involves treatment of $Fe(CO)_5$ with trimethylamine N-oxide and the Group 16 compound. With cyclic thioethers, the same synthetic procedure yields dinuclear bis-thiolato complexes of the type $Fe_2(CO)_6\{\mu\text{-}SCH_2CH(R)S\}$, where R = H or Me. The structure of $Fe_2(CO)_6\{\mu\text{-}SCH_2CH(Me)S\}$ has been determined from X-ray diffraction data. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Pentacarbonyliron forms many mono- and di-substitution compounds of the types $Fe(CO)_4L$ and $Fe(CO)_3L_2$, particularly where L is a tertiary phosphine ligand PR_3 [1]. Thermally [2] and photochemically [3] initiated reactions of $Fe(CO)_5$ with tertiary phosphines PR_3 generally give mixtures of $Fe(CO)_4(PR_3)$ and $Fe(CO)_3(PR_3)_2$ which are not easy to separate chromatographically. Related synthetic approaches using $Fe_2(CO)_9$ [4] or $Fe_3(CO)_{12}$ [5] have also been developed, but again mixtures of products are generally formed. Reliable procedures that lead to the conversion of $Fe(CO)_5$ to $Fe(CO)_4(PR_3)$ or $Fe(CO)_3(PR_3)_2$ specifically have been described and include the use of KOH to form the intermediate $K[FeH(CO)_4]$ [6], decarbonylation with trimethylamine N-oxide [7], or addition of small amounts of the electron transfer catalyst $CoCl_2$ [8] to initiate the reactions. Control is achieved because these reactions are accomplished under mild conditions.

The analogous chemistry of $Fe(CO)_4L$ and $Fe(CO)_3L_2$ complexes where L is a Group 16 ligand is not well developed. The tellurium complex $Fe(CO)_4(TePh_2)$ has been prepared from $Fe_3(CO)_{12}$ and $TePh_2$ [9], and some sulfur complexes $Fe(CO)_4L$ where L is a heterocyclic compound such as 1,3-dithiacycloheptene [10] or 1,3-dithiacyclohexane [11] have been formed from $Fe_2(CO)_9$ and the appropriate ligand. An unstable CS_2 complex is also known, and it forms a more stable derivative $Fe(CO)_3(CS_2)(PPh_3)$ [12]. There is a report that photolysis of $Fe(CO)_5$ in the presence of SMe_2 gives $Fe(CO)_4(SMe_2)$ in good yield [13]; this labile complex was used to prepare other complexes $Fe(CO)_4L$. Other complexes of this type have been formed by an indirect route in which $[HFe(CO)_4]^-$ is treated with SRRS to give $[Fe(CO)_4(SR)]^-$ which on further reaction with R′X yields $Fe(CO)_4(SRR')$ [14].

Under some circumstances, iron carbonyls will desulfurise organo-sulfur compounds, especially when the sulfur is the hetero-atom in a ring structure [15]. This observation may be significant in relation to the possible formation of volatile substitution compounds of the type $Fe(CO)_4L$ where L is a strained ring cyclic thioether, and their subsequent use as single source precursors for the chemical vapour deposition of high purity iron sulfide. Iron is an important deep level dopant in InP [16] and its incorporation in other opto-electronic materials such as metal chalcogenides is of interest.

With this in mind, a study was undertaken of the reactions between $Fe(CO)_5$ and selected organo-sulfur compounds under mild conditions. The approach cho-

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sen was to initiate the reactions chemically with trimethylamine N-oxide, which is known to decarbonylate $Fe(CO)_5$ at temperatures as low as −78°C [7]. The approach was applied to selected dialkyl sulfides and cyclic thioethers.

2. Experimental

2.1. General considerations

All experiments were conducted under an atmosphere of dry nitrogen using Schlenk tube techniques. Solid compounds were handled in a polyethylene glove bag or a Miller-Howe dry box and the liquid reagents were manipulated by syringe. Solvents were freshly distilled under nitrogen from appropriate drying agents before use. ^1H- and ^{13}C-NMR spectra were recorded on a Brucker DPX300 spectrometer operating at 300.13 and 75.48 MHz, respectively. The chemical shifts are reported as δ values relative to the solvent peak. Electron-impact mass spectra (EI-MS) were recorded on a VG TRIO-1 GC-MS spectrometer operating at 70 eV. The infrared spectra were recorded on a Perkin–Elmer 1600 series FTIR spectrometer in the range 4000–400 cm^{-1}. Samples were run as Nujol mulls between KBr disks. Microanalyses were performed by Chemical and Micro Analytical Services in Belmont, Victoria. The following reagents were used as received from Aldrich: pentacarbonyliron, ethylene sulfide, propylene sulfide, dimethyl sulfide, diethyl sulfide, and dimethyl selenide. Trimethylamine N-oxide dihydrate was purchased from EGA-Chemie and used as supplied.

2.2. Preparation of $Fe(CO)_4(SMe_2)$ (**1a**)

$Fe(CO)_5$ (0.70 ml, 5.35 mmol) was added slowly to a mixture of $Me_3NO\cdot 2H_2O$ (0.67 g, 5.4 mmol) and dimethyl sulfide (0.80 ml, 10.9 mmol) in acetone (100 ml) cooled to 0°C. Immediate gas evolution was evident, and the colour of the solution changed to brown. The mixture was stirred and heated until the acetone was gently refluxing, and stirring was continued for 1 h. After allowing the reaction mixture to cool, the brown–red solution was concentrated under reduced pressure at 0°C. The orange crystalline product was collected by filtration and sublimed (40–45°C, 0.3 mmHg) to give bright orange crystals of $Fe(CO)_4(SMe_2)$ (0.67 g, 55%); m.p. 33–34°C. NMR (C_6D_6, 298 K): ^1H δ 1.57 (s, CH_3); $^{13}C\{^1H\}$ δ 28.4 (s, CH_3), 214.4 (s, CO). IR (hexane): ν(CO) at 1942 vs, 1951 vs, 1977 s, 2054 s cm^{-1}. MS: 230 ($[M]^+$, 7%), 202 ($[M-CO]^+$, 5%), 174 ($[M-2CO]^+$, 6%), 146 ($[M-3CO]^+$, 13%), 118 ($[M-4CO]^+$, 28%), 62 ($[Me_2S]^+$, 34%), 47 ($[MeS]^+$, 100%). Anal. Found: C, 31.2; H, 2.6; S, 13.8. Calc. for $C_6H_6FeO_4S_2$: C, 31.33; H, 2.63; S, 13.94%.

2.3. Preparation of $Fe(CO)_4(SEt_2)$ (**1b**)

This was prepared in similar manner from $Fe(CO)_5$ (1.40 ml, 10.6 mmol), $Me_3NO\cdot 2H_2O$ (1.18 g, 10.6 mmol) and diethyl sulfide (1.15 ml, 10.60 mmol) in acetone (150 ml). The crude product was a dark red oily residue that was extracted into hexane (2 × 50 ml). Filtration of the extracts, concentration under reduced pressure, and chromatography through a short silica column under nitrogen with hexane as eluent left a clear orange solution. Concentration at 0°C gave $Fe(CO)_4(SEt_2)$ as a red oil (0.94 g, 34%). MS accurate mass. Found: 257.9664. Calc. for $C_8H_{10}FeO_4S$: 258.07. NMR (C_6D_6, 298 K): ^1H δ 0.95 (t, $^3J = 7.36$ Hz, 3H, CH_3), 2.12 (q, $^3J = 7.36$ Hz, 2H, CH_2); $^{13}C\{^1H\}$ δ 11.8 (s, CH_3), 35.1 (s, CH_2), 214.8 (s, CO). IR (hexane): ν(CO) at 1939 vs, 1946 vs, 1972 s, 2052 s cm^{-1}. MS: 258 ($[M]^+$, 9%), 230 ($[M-CO]^+$, 30%), 202 ($[M-2CO]^+$, 18%), 174 ($[M-3CO]^+$, 36%), 146 ($[M-4CO]^+$, 44%).

2.4. Preparation and spectroscopic characterisation of $Fe(CO)_4(SeMe_2)$ (**1c**)

This was prepared in similar manner from $Fe(CO)_5$ (0.26 ml, 2.0 mmol), $Me_3NO\cdot 2H_2O$ (0.23 g, 2.0 mmol) and dimethyl selenide (0.32 ml, 4.0 mmol) in acetone (50 ml). The crude product was a dark red oily residue that was extracted into pentane (10 ml). Filtration of the extracts and concentration under reduced pressure at −5°C gave golden crystals. Two recrystallisations from pentane at −78°C gave $Fe(CO)_4(SeMe_2)$ as golden crystals (0.36 g, 64%). At room temperature (r.t.), the crystals melted to an orange–red oil that slowly discoloured to brown. The product was too unstable for microanalysis. ^1H-NMR (C_6D_6, 298 K): δ 1.26 (s, $2\times CH_3$); a minor peak (ca. 4% relative intensity) was observed for dissociated free ligand at δ 1.61. IR (hexane): ν(CO) at 1947 vs br, 1975 s, 2052 s cm^{-1}. MS: 278 ($[M]^+$, 1%), 250 ($[M-CO]^+$, 2%), 222 ($[M-2CO]^+$, 1%), 194 ($[M-3CO]^+$, 4%), 166 ($[M-4CO]^+$, 6%), 110 ($SeMe_2^+$, 97%), 95 ($SeMe^+$, 100%), 80 (Se^+, 28%), 56 (Fe^+, 15%).

2.5. Preparation of $Fe_2(CO)_6\{\mu\text{-}SCH_2CHMeS\}$ (**2a**)

This was prepared in similar manner from $Fe(CO)_5$ (0.75 ml, 5.35 mmol), $Me_3NO\cdot 2H_2O$ (1.19 g, 10.7 mmol) and propylene sulfide (0.80 ml, 10.2 mmol) in acetone (100 ml). The crude product was isolated as a dark red oily residue that was extracted into hexane (2 × 30 ml). Filtration of the bright orange extracts and removal of solvent from the filtrate left an orange crystalline solid. Sublimation (40–45°C, 0.1 mmHg) gave orange needles of $Fe_2(CO)_6\{\mu\text{-}SCH_2CH(Me)S\}$ (0.65 g, 63%); m.p. 50–51°C. NMR (C_6D_6, 298 K): ^1H

Table 1
Crystal data and details of the structure determination of $Fe_2(CO)_6\{\mu\text{-}SCH_2CH(Me)S\}$ (**2a**)

Crystal data	
Empirical formula	$C_9H_6Fe_2O_6S_2$
Formula weight	385.96
Crystal system	Monoclinic
Space group	$P2_1/m$ (#11)
Lattice type	Primitive
Unit cell dimensions	
a (Å)	6.4251(1)
b (Å)	13.1272(3)
c (Å)	8.1457(2)
β (°)	102.515(1)
V (Å^3)	670.71(2)
Z	2
D_{calc} (g cm^{-3})	1.911
$F(000)$	384.00
μ(Mo–K$_\alpha$) (cm^{-1})	24.86
Crystal size (mm)	0.12 × 0.12 × 0.12
Data collection	
Temperature (°C)	−80
Radiation, λ (Å)	Mo–K$_\alpha$, 0.7169
$2\theta_{max}$ (°)	65.1
Reflections measured	total 11419 unique 2477
Observations ($I > 3.00\sigma(I)$)	1884
Refinement	
N_{ref}, N_{par}	1884, 97
Reflection/parameter ratio	19.42
R, Rw	0.035, 0.049
Goodness of fit indicator	1.67
Weighting scheme	$w = 1/\sigma^2(F_o)$
Max. shift/error in final cycle	0.00
Min. and max. residual density (e Å^{-3})	−0.56, 0.47

Table 2
Bond distances (Å) and selected angles (°) for $Fe_2(CO)_6\{\mu\text{-}SCH_2CHMeS)$ (**2a**)

Fe(1)–Fe(1)	2.5196(7)
Fe(1)–S(1)	2.2417(8)
Fe(1)–S(2)	2.2335(8)
Fe–C	1.792(3)–1.800(3)
S(1)–C(1)	1.829(4)
S(2)–C(5)	1.851(4)
C–O	1.134(3)–1.140(3)
C(1)–C(5)	1.496(6)
C(5)–C(6)	1.360(7)
S(1)···S(2)	2.893(9)
Fe(1)–Fe(1)–S(1)	55.81(1)
Fe(1)–Fe(1)–S(2)	55.66(2)
Fe(1)–Fe(1)–C(2)	99.80(9)
Fe(1)–Fe(1)–C(3)	108.2(1)
Fe(1)–Fe(1)–C(4)	146.33(9)
Fe(1)–S(1)–Fe(1)	68.39(3)
Fe(1)–S(2)–Fe(1)	68.67(3)
C(2)–Fe(1)–C(3)	91.4(1)
C(2)–Fe(1)–C(4)	100.9(1)
C(3)–Fe(1)–C(4)	97.5(1)
Fe(1)–S(1)–C(1)	103.2(1)
Fe(1)–S(2)–C(5)	103.4(1)

δ 0.89 (d, $^3J = 6.70$ Hz, 3H, CH_3), 1.16 (dd, $^2J = 13.0$, $^3J = 5.08$ Hz, 1H, CH), 1.97 (dd, $^2J = 13.0$, $^3J = 7.52$ Hz, 1H, CH), 2.21 (m, 1H, CH); $^{13}C\{^1H\}$ δ 21.8 (s, CH_3), 42.8 (s, CH_2), 48.8 (s, CH), 209.1 (br s, CO). IR (hexane): ν(CO) at 1981 m, 1991 s, 2005 s, 2035 s, 2076 m cm^{-1}. MS: 386 ([M]$^+$, 10%), 358 ([M − CO]$^+$, 13%), 330 ([M − 2CO]$^+$, 13%), 302 ([M − 3CO]$^+$, 13%), 274 ([M − 4CO]$^+$, 13%), 246 ([M − 5CO]$^+$, 30%), 218 ([M−6CO]$^+$, 72%), 176 ([Fe_2S_2]$^+$, 100%), 144 ([Fe_2S]$^+$, 8%), 88 ([FeS]$^+$, 32%), 56 ([Fe]$^+$, 24%). Anal. Found: C, 28.1; H, 1.3; S, 16.85. Calc. for $C_9H_6Fe_2O_6S_2$: C, 28.01; H, 1.57; S, 16.61%.

2.6. Preparation of $Fe_2(CO)_6\{\mu\text{-}SCH_2CH_2S\}$ (*2b*)

Using the same procedure, the complex was prepared from $Fe(CO)_5$ (0.45 ml, 3.4 mmol), $Me_3NO{\cdot}2H_2O$ (0.76 g, 6.9 mmol) and ethylene sulfide (0.30 ml, 5.0 mmol). The crude product was sublimed (60–65°C, 0.1 mmHg) to give bright orange crystals of $Fe_2(CO)_6\{\mu\text{-}SCH_2CH_2S\}$ (0.25 g, 39%); m.p. 75–76°C. NMR (C_6D_6, 298 K): ^1H δ 1.59 (s, 4H, CH_2); $^{13}C\{^1H\}$ δ 36.0 (s, CH_2), 208.7 (s, CO). IR: ν(CO) at 1980 m, 1993 s, 2006 s, 2036 s, 2076 m cm^{-1}. MS: 372 ([M]$^+$, 10%), 344 ([M − CO]$^+$, 5%), 316 ([M − 2CO]$^+$, 9%), 288 ([M − 3CO]$^+$, 7%), 260 ([M − 4CO]$^+$, 12%), 232 ([M − 5CO]$^+$, 20%), 204 ([M − 6CO]$^+$, 18%), 176 ([Fe_2S_2]$^+$, 100%), 144 ([Fe_2S]$^+$, 25%), 88 ([FeS]$^+$, 32%), 56 ([Fe]$^+$, 32%). Anal. Found: C, 25.9; H, 1.0; S, 17.0. Calc. for $C_8H_4Fe_2O_6S_2$: C, 25.83; H, 1.08; S, 17.24%.

2.7. Crystal structure determination, complex *2a*

Single crystals of **2a** were grown from hexane–ether by slow evaporation of solvent. Crystal data and details of the structure determination are provided in Table 1 and Table 2 gives selected bond distances and angles.

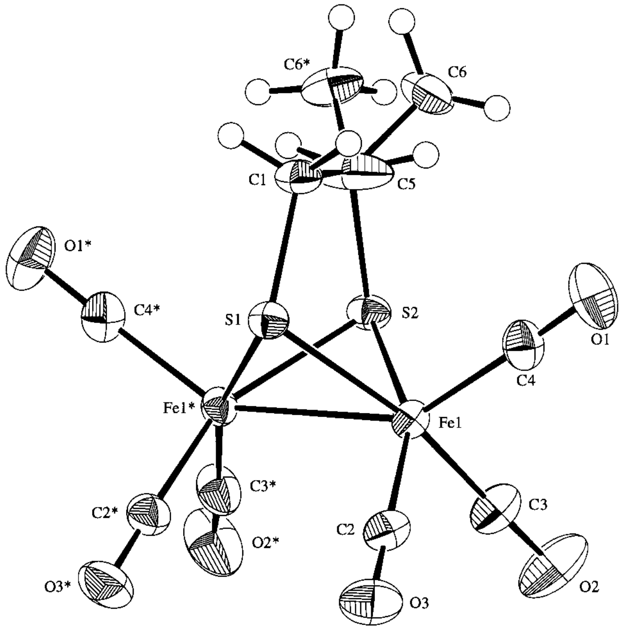

Fig. 1. The molecular structure of **2a**.

3. Results and discussion

Surprisingly, the 'mild condition' approaches to the preparation of $Fe(CO)_4(PR_3)$ and $Fe(CO)_3(PR_3)_2$ seem not to have been extended to the analogous sulfur compound systems. In the present study, it was established that treatment of $Fe(CO)_5$ with hydrated Me_3NO and SR_2 (R = Me, Et) in acetone provides a reliable route to the complexes $Fe(CO)_4(SR_2)$. Immediate reaction was evident at 0°C, but the reaction mixtures were gently heated in refluxing acetone for 1 h to complete the conversion of $Fe(CO)_4(NMe_3)$ to $Fe(CO)_4(SR_2)$. The only complex isolated was $Fe(CO)_4(SR_2)$, even when an excess of SR_2 was used. The complex $Fe(CO)_4(SMe_2)$ (**1a**) was isolated as bright orange crystals in 55% yield after sublimation. This complex was sufficiently stable for microanalysis and complete spectroscopic characterisation (see Section 2). The related product $Fe(CO)_4(SEt_2)$ (**1b**) was obtained as a dark red oil in 34% yield after extraction of the crude product into hexane, and subsequent chromatography on silica. It was more thermally labile than **1a**, and was kept under nitrogen at 0°C. It could be kept for up to 4 days under these conditions and was fully characterised by accurate mass MS and IR and NMR data. These complexes presumably have the molecular stucture (**1**) with L in an axial position. This substitution geometry has been substantiated by X-ray crystallography for $Fe(CO)_4(PPh_3)$ [17] and $Fe(CO)_4$(1,3-dithiane) [11a]; poor quality X-ray diffraction data have also been obtained at low temperature for **1a**, and this supports occupation of an axial site by the sulfur ligand [13]. The observation of four carbonyl stretching frequencies in the IR spectra of the dialkyl sulfide complexes is consistent with a splitting of the *E* mode due to a lowering of the symmetry of the molecule $Fe(CO)_4L$ when PR_3 is changed to SR_2 [18].

A mono-substitution product $Fe(CO)_4(SeMe_2)$ was formed from dimethyl selenide and the $\{Fe(CO)_5 + Me_3NO\}$ system. Although a crystalline product was isolated, NMR evidence established that partial dissociation of the ligand occurred in solution. The MS data showed $SeMe_2$ as the base peak. Nonetheless, the product was isolated in over 60% yield as golden crystals that showed no signs of decomposition when kept in the solid state at −5°C.

There is no evidence for the formation of di-substitution products $Fe(CO)_3(ER_2)_2$ in any of the reactions described above. If such products are formed, they presumably decompose under the reaction conditions. The investigation of reactions where the ratio of $Fe(CO)_5$:Me_3NO:SR_2 was 1:2:2 produced only $Fe(CO)_4(SR_2)$ in good yield. This contrasts with the corresponding reactions with tertiary phosphines where the di-substitution products are formed more readily than the mono-substitution compounds.

These results encouraged us to pursue the synthesis, under similar reaction conditions, of the analogous complexes $Fe(CO)_4L$, where L is a strained ring cyclic thioether. However, the reactions with ethylene sulfide and propylene sulfide both gave dinuclear products of the type (**2**) that contain dithiolate bridging groups. The product **2a** (R = Me) formed from propylene sulfide was isolated in 60 and 40% yield of **2b** (R = H) was obtained from the ethylene sulfide reaction. Formally, the bridging ligands in these complexes are constructed from sulfur that has been extracted from one equivalent of the ligand, and the ring opened form of a second equivalent of the ligand, but the details of the reaction steps have not been established.

The two complexes **2a** and **2b** were characterised from elemental analyses and spectroscopic data (see Section 2). The structure of **2a** was also confirmed by X-ray crystallography, and a drawing of the molecular structure is shown in Fig. 1. The molecule has mirror symmetry, with atoms S1, S2, C1 and C5 in the mirror plane. The methyl carbon C6 is disordered over two sites. There were no unusual geometric features, and the bond parameters (Table 1) were similar to those previously reported for related complexes, including **2b** which was prepared by a very different route outlined below [19]. An interesting feature of the structures in solution is indicated by the observation of just one carbonyl resonance in the ^{13}C-NMR spectra. Presumably, there is a very low barrier to scrambling of the carbonyl groups, as occurs in the related complexes $Fe_2(CO)_6(\mu\text{-}SR)_2$ [20,21].

The complex **2a** is air stable, volatile, and readily purified by sublimation. The base peak in the mass spectrum of this compound is $Fe_2S_2^+$. This combination of properties indicates that the compound has some potential as a single source compound for the chemical vapour deposition of iron sulfide, but this has not yet been further explored.

Other complexes related to **2** have been reported in the literature, but the synthetic approaches are very different. For example, the complex **2b** has been formed from $Fe_3(CO)_{12}$ and ethylene sulfide or ethylene S-oxide [22], and similar reactions occur with $[CpMo(CO)_3]_2$ [23]. Treatment of $Fe_3(CO)_{12}$ with 1,2,5,6-tetrathiacyclooctane also yields **2b** [19]. Some reactions between $[Fe(CO)_3(\mu\text{-}SH)]_2$ and activated alkenes [24] and alkynes [25] also give products that are structurally related to **2**. The reactions described in the present study are clearly the most straightforward approaches to complexes of this type.

4. Conclusion

The $\{Fe(CO)_5 + Me_3NO\}$ system provides easy access specifically to monosubstitution complexes

$Fe(CO)_4(ER_2)$ where ER_2 is a dialkyl sulfide or selenide. These complexes seem to be less thermally inert and less thermally stable than the analogous $TePh_2$ complex [9]. This is consistent with observations reported for related $[CpFe(CO)_2(ER_2)]BF_4$ complexes [26]. Strained ring cyclic thioethers probably form transient complexes of the type $Fe(CO)_4L$ but they rearrange spontaneously to dinuclear products in which dithiolato ligands bridge two $Fe(CO)_3$ units. Because the reactions are done under mild conditions, it is possible to isolate thermally labile products in good yields.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 154811 for compound **2a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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