DALTON

Reactions of heterocyclic organotellurium compounds with triiron dodecacarbonyl: reactions of thiophenes revisited

Karanbir Singh,[a] William R. McWhinnie,[a] Hong Li Chen,[b] Min Sun[b] and Thomas A. Hamor[b]

[a] *Department of Chemical Engineering and Applied Chemistry, Aston University, Aston Triangle, Birmingham B4 7ET, UK*

[b] *School of Chemistry, University of Birmingham, PO Box 363, Birmingham B15 2TT, UK*

The reaction of thiophene and of benzothiophene with [$Fe_3(CO)_{12}$] was greatly accelerated by microwave heating when carried out in the presence of Fe_3O_4. Thus the same yields of products are obtained in 50 min as are achieved in 15–18 h of conventional heating; however no desulfurisation of the benzothiophene ring was observed. By contrast, both tellurophene and, more importantly, dibenzotellurophene undergo detelluration reactions with [$Fe_3(CO)_{12}$], the latter reaction affording a dibenzoferrole $C_{18}H_8Fe_2O_6$, the structure of which has been determined. The reaction of 2-telluraindane with [$Fe_3(CO)_{12}$] gave a complex $C_{19}H_{16}FeO_3$ in which a novel dimer of the detellurated C_8H_8 fragment is co-ordinated to an $Fe(CO)_3$ unit, as determined crystallographically. The released tellurium was isolated as either FeTe or as [$Fe_3Te_2(CO)_9$], depending on the reaction conditions.

In 1960 Stone and co-workers,[1] in a classic contribution, demonstrated that the reaction of thiophene and [$Fe_3(CO)_{12}$] afforded the ferrole $C_4H_4Fe_2(CO)_6$ together with FeS and other minor products. It was known that [$Fe(CO)_5$] would cleave the C–S bonds of alkyl sulfides[2] and Stone and co-workers[3] went on to show that the C–S bonds of vinyl sulfides would cleave in the presence of [$Fe_3(CO)_{12}$]. The initial yields of the ferrole were poor (5% after 15 h),[1] but others demonstrated that more prolonged reaction of thiophene with [$Fe_3(CO)_{12}$] (2 d) increased the yield to 17%.[4] The use of substituted thiophenes gave yields of between 0.7 and 10.7% of the appropriate ferroles.[5]

This chemistry was believed potentially to provide useful mechanistic insight to the initial stages of heterogeneously catalysed hydrodesulfurisation reactions (HDS) of oils and of coal-derived liquids. In particular the laboratories of Rauchfuss[6] and Angelici[7] have been active in the area. Thus, observations by Rauchfuss and co-workers[8] that iron initially enters the thiophene ring to give a thiaferrole may model an important initial step in the heterogeneously catalysed HDS process. Angelici and co-workers[7,9] explored the mode of binding of thiophene derivatives with low-oxidation-state transition-metal centres, arguing that such complexes *may* model the initial interaction of thiophenic moieties with metal sites in the surface of heterogeneous HDS catalysts.

Thiophene is not an ideal molecular model for the bulk of organic sulfur in coal-derived liquids, rather benzothiophene and, more particularly, dibenzothiophene, are superior models.[10] Benzothiophene gives a thiaferrole on reaction with [$Fe_3(CO)_{12}$] which undergoes oxidative demetallation, but no removal of ring sulfur is noted.[8] Dibenzothiophene (dbt) is unreactive under similar conditions but it has been reported to co-ordinate to iron in a monodentate fashion in the complex [$Fe(dbt)(CO)_2(cp)$][BF_4],[11] where cp = η-C_5H_5-. Such co-ordination (through S) has also been observed by Angelici and co-workers[12] in [$M(dbt)Cl_2(\eta\text{-}C_5Me_5)$] (M = Rh or Ir), but when the metal is in oxidation state (I) the co-ordination changes to η^6, *i.e.* [$M(\eta^6\text{-dbt})(\eta\text{-}C_5Me_5)$]. An electron-rich metal centre is believed to be required for metal insertion into the thiophene ring,[13] and Rauchfuss and his group[14] argue that multimetallic reagents are advantageous for sulfur removal.

This paper initially explores the question of the reactivity of materials such as thiophene and benzothiophene with [$Fe_3(CO)_{12}$] under the influence of microwave heating. Since this methodology has been shown to be capable of greatly accelerating the passage to equilibrium of a large number of chemical reactions[15] it was interesting to examine whether, under these conditions, the benzothiophene reaction would proceed to the ferrole stage. Our major purpose, however, was to explore the reactivity of some tellurium heterocyclic compounds with [$Fe_3(CO)_{12}$]. Electronically tellurophenes are similar to thiophenes[16] and may therefore be regarded as thiophene 'models'. The carbon–chalcogen bond strength will be less in the tellurophenes and this may facilitate detelluration reactions, even of dibenzotellurophene, and thereby demonstrate the mechanistic *feasibility* of the dechalcogenation reaction for the more condensed aromatic molecules. Angelici and his group[17,18] have extended their investigations to selenophenes since ^{77}Se NMR spectroscopy allows direct observation of the ligand; a similar advantage based on ^{125}Te NMR spectroscopy is available for tellurophenes: also a new area of organometallic chemistry is accessed.

Experimental and Results

Triiron dodecacarbonyl was obtained from Aldrich and used as received. Tellurophene,[19] dibenzotellurophene[20] and 2-telluraindane[21] were prepared by the indicated literature methods. Thiophene was distilled from CaH_2 prior to use. Pentane was HPLC grade and used as received from Aldrich. All manipulations involving reactions of the tellurium compounds were carried out under an atmosphere of pure argon with the use of Schlenk techniques.

Reactions of triiron dodecacarbonyl with tellurophene

Tellurophene (3.00 g, 17 mmol) and [$Fe_3(CO)_{12}$] (3.02 g, 6 mmol) were refluxed in heptane (100 cm^3) with stirring for 2.5 h. After 45 min the green colour of the iron carbonyl gave way to an intense violet which in turn changed to orange after 1.5 h, following which no further colour change occurred. The cooled solution was filtered to give an orange filtrate and a black solid which adhered to the sides of the flask. The solvent was removed from the filtrate *in vacuo* to give orange flake-like crystals of m.p. 51 °C {0.89 g, 45% based on [$Fe_3(CO)_{12}$]}. The infrared data were consistent with those previously reported[1] for the ferrole **2**, ν(CO) 2078m, 2050m, 2000s, 1967s and 1940s cm^{-1} (Found: C, 37.0; H, 1.40. $C_{10}H_4Fe_2O_6$ requires C, 36.2; H, 1.20%). Electron impact (EI) mass spectrum; *m*/*z* = 332 (M^+), ^{56}Fe. The black solid residue was shown to be FeTe.

The experiment was then repeated exactly as above, but terminated at the point of development of the violet colour. Removal of heptane under vacuum left a deep violet solid which was chromatographed on a 2.0 × 20 cm column of TLC-grade silica thereby giving a small green band preceded by orange and purple bands. Elution with pentane and removal of solvent afforded a dark red powder from the first eluate, orange crystals from the second ($C_{10}H_4O_6Fe_2$), and unreacted $[Fe_3(CO)_{12}]$ from the third. The dark red material was recrystallised from boiling heptane yielding shiny, plate-like crystals, m.p. 41 °C, which were identified as the telluraferrole **1**, yield 1.82 g {66% based on $[Fe_3(CO)_{12}]$} (Found: C, 26.0; H, 0.90. $C_{10}H_4Fe_2O_6Te$ requires C, 26.1; H, 0.90%). Chemical ionisation (CI) mass spectrum: *m*/*z* = 462 (M^+), ^{130}Te and ^{56}Fe. NMR ($CDCl_3$): ^{1}H, δ 9.54 (d, 1 H), 7.32 (q, 1 H), 5.72 (d, 1 H) and 5.22 (q, 1 H); ^{13}C, δ 181.8, 147.8, 88.8, 86.8 and 86.4; ^{125}Te, δ 43.0 [(*J*(Te–H^1) = 93, *J*(Te–H^2) = 19, *J*(Te–H^3) = 5 Hz]. Infrared (KBr, cm^{-1}): ν(CO) 2069m, 2030m, 1981s and 1961m.

With dibenzotellurophene. Dibenzotellurophene (1.93 g, 6.9 mmol) and $[Fe_3(CO)_{12}]$ (1.16 g, 2.3 mmol) dissolved in heptane (100 cm^3) were heated and stirred under reflux for 2.5 h, during which time the solution slowly changed from dark green to orange. After cooling, the solution was filtered giving a brown solid residue and a deep orange filtrate which was evaporated to dryness affording a dark brown solid. The latter solid was chromatographed on a 2.5 × 20 cm column of TLC-grade silica giving a purple band preceded by a small yellow band. Elution with pentane and removal of solvent gave yellow crystals from the first eluate (unreacted dibenzotellurophene) and a red powder from the second, recrystallisation of which from boiling heptane gave violet crystals, yield 0.28 g {28% based on $[Fe_3(CO)_{12}]$}, m.p. 176 °C, identified as a dibenzoferrole **3** (Found: C, 50.2; H, 1.95. $C_{18}H_8Fe_2O_6$ requires C, 50.1; H, 1.85%). CI mass spectrum: *m*/*z* = 432 (M^+), ^{56}Fe. NMR ($CDCl_3$): ^{1}H, δ 7.33 (m, 4 H), 7.25 (m, 2 H) and 7.15 (m, 2 H); ^{13}C, δ 144.1, 128.6, 128.2, 127.9, 127.7 and 119.6. Infrared (KBr, cm^{-1}): ν(CO) 2060m, 2025s, 1992s, 1974s and 1884m. Crystals suitable for X-ray diffraction measurements were grown by cooling a concentrated hexane solution.

With 2-telluraindane. 2-Telluraindane (1.93 g, 8.3 mmol) and $[Fe_3(CO)_{12}]$ (2.8 g, 5.3 mmol) were dissolved in heptane (100 cm^3) and heated, with stirring, under reflux for 3 h during which time the solution changed from green to deep purple. After cooling the solution was filtered affording a black residue and an intense purple solution. The solution was taken to dryness under vacuum leaving a purple solid and a red oil. The mixture was dissolved in pentane (10 cm^3) and chromatographed on a 2.5 × 20 cm column of TLC-grade silica, thereby giving a small orange band preceded by a small yellow and large purple band. Elution with pentane and removal of solvent gave purple crystals from the first eluate and a red-brown solid from the second, m.p. 76 °C; a third component, an unstable yellow oil as yet unidentified, was also eluted. The purple crystals showed infrared absorption only in the carbonyl region, gave no proton NMR resonances and were identified as the previously reported cluster compound $[Fe_3Te_2(CO)_9]$,[8] yield 1.13 g, 40% (based on C_8H_8Te) (Found: C, 16.6; H, 0.10. $C_9Fe_3O_9Te_2$ requires C, 16.0; H, 0.00%). ^{13}C NMR ($CDCl_3$): δ 211.6 and 209.3. EI mass spectrum: *m*/*z* = 680 (M^+), ^{130}Te, ^{56}Fe. Infrared (KBr, cm^{-1}): ν(CO) 2077m, 2052s, 2020s, 1998s, 1976s and 1960s.

The red-brown solid (**4**) was shown to have the molecular formula $C_{19}H_{16}FeO_3$, yield 0.344 g (15.4%) based on C_8H_8Te (Found: C, 65.2; H, 4.80. $C_{19}H_{16}FeO_3$ requires C, 65.5; H, 4.60%). EI mass spectrum: *m*/*z* = 348 (M^+), ^{56}Fe. NMR ($CDCl_3$): ^{1}H, δ 6.98 (m, 4 H), 4.74 (d, 2 H), 4.43 (d, 2 H), 3.67 (m, 2 H) and 3.05 (m, 6 H); ^{13}C, δ 212.1, 155.0, 154.6, 135.6, 128.8–125.8, 102.2 and 40.5–29.8. Infrared (KBr, cm^{-1}): ν(CO) 2043, 1981 and 1950. Crystals suitable for X-ray diffraction were grown by cooling a concentrated hexane solution.

The unstable yellow oil, yield 0.334 g, gave an infrared spectrum showing the presence of both organic fragments and of carbonyl groups: ν(CO) 2051, 1983 and 1962 cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 7.45 (m, 2 H), 7.36 (m, 2 H), 2.44 (d, 2 H) and 0.22 (d, 2 H); ^{13}C, δ 132.0, 128.0, 100.0, 35.5 and 29.3.

The reactions of the tellurium heterocyclic compounds are shown in Scheme 1.

With thiophene and benzothiophene. The reaction was repeated using the conditions reported by Stone and co-workers.[1] and in concurrence with those workers after 15 h of reaction a 5% yield of the ferrole $C_4H_4Fe_2(CO)_6$ was obtained. Following chromatography of the reaction mixture, an additional product, $C_4H_4Fe(CO)_2{\cdot}Fe_2(CO)_6$ [trace, EI mass spectrum *m*/*z* = 444 (M^+), ^{56}Fe] was isolated.

The reaction was then repeated by sealing $[Fe_3(CO)_{12}]$ (1.0 g), thiophene (15 cm^3) and Fe_3O_4 (0.5 g) in a Teflon container and heating the contents in a Sharp Carousel microwave oven for 50 min on a 'high' power setting. Work-up afforded identical products in similar yields. A similar microwave experiment using benzothiophene gave a 49% yield of the benzothiaferrole after 50 min identical to that obtained by Rauchfuss and co-workers[8] after 18 h; however microwave heating was not successful in promoting a desulfurisation reaction.

Physical measurements

Proton, ^{13}C, and ^{125}Te NMR spectra were obtained with a Bruker AC-300 instrument for $CDCl_3$ solutions using $SiMe_4$ (^{1}H, ^{13}C) and Me_2Te (^{125}Te) as standards, infrared spectra with a Bio-Rad FTS-40A spectrometer and EI and CI mass spectra from the EPSRC service at University College, Swansea.

Crystallography

Crystal data. $C_{18}H_8Fe_2O_6$ **3**, M_r = 431.95, triclinic, space group $P\bar{1}$, a = 7.357(2), b = 8.386(8), c = 13.585(3) Å, α = 91.49(4), β = 92.10(10), γ = 102.21(2)°, U = 818 Å^3, Z = 2, D_c = 1.753 g cm^{-3}, $F(000)$ = 432, μ(Mo-Kα) = 1.806 mm^{-1}. $C_{19}H_{16}FeO_3$ **4**, M_r = 348.17, monoclinic, space group $P2_1/c$, a = 19.748(1), b = 6.904(1), c = 12.342(3) Å, β = 107.34(1)°, U = 1606 Å^3, Z = 4, D_c = 1.1440 g cm^{-3}, $F(000)$ = 720, μ(Mo-Kα) = 0.950 mm^{-1}.

Cell dimensions and intensity data were measured with an Enraf-Nonius CAD4 diffractometer operating in the ω–2θ scan mode using Mo-Kα radiation. The angular range for data collection was 2–25° for both compounds. 5733 Reflections for **3** and 5877 for **4** were scanned, of which 2867 (R_{int} = 0.037) and 2818 (0.034) were unique. Three standard reflections were measured every 2 h to check the stability of the system. Small (1%) decay corrections were applied to the data. Both structures were determined by direct methods with SHELXS 86[22] and refined by least squares using anisotropic thermal parameters for Fe, C and O atoms. Hydrogen atoms were placed in calculated positions, riding on their respective bonding atoms.

Structure **3** was refined using the TEXSAN package,[23] the function minimised being $\Sigma w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F_o)$; R,R' 0.048, 0.049 for 2474 reflections with $I > 2.5\sigma(I)$. Residual electron density was within the range +0.9 to −0.9 e Å^{-3}. An empirical absorption correction was applied using DIFABS,[24] transmission factors in the range 0.51–1.00. Structure **4** was refined using SHELXL 93;[25] the function minimised was $\Sigma w(F_o^2 - F_c^2)^2$, $w = 1/[\sigma^2(F_o^2) + 0.004P^2 + 0.13P]$, where $P = \frac{1}{3}F_o^2 + \frac{2}{3}F_c^2$; final R,R' 0.05, 0.127 for all reflections; residual electron density was within the range +0.23 to −0.42 e Å^{-3}. Diagrams were drawn with PLUTO.[26] Atomic coordinates are listed in Tables 3 and 4.

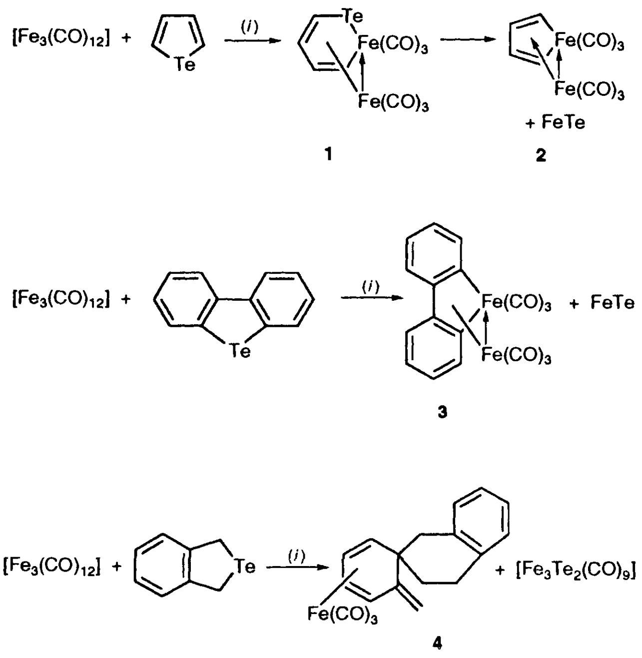
Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Discussion

Coal, like many materials of natural origin, is a difficult substance with which to work. Recently, however, it has been established that microwave heating can be used with benefit in some aspects of coal science. For example derivatisation reactions of coal functional groups have been greatly accelerated leading to the development of new analytical methods.[27] At the outset of this work it was debated that similar acceleration of the desulfurisation reactions of thiophene rings using $[Fe_3(CO)_{12}]$ might be possible and, further, that in the case of benzothiophene the reaction might be driven to the desulfurisation stage. The classic reaction of Stone and co-workers[1] was repeated and found to proceed precisely as reported, although chromatography did reveal a trace of a compound not previously reported (identified by mass spectroscopy), namely $C_4H_4Fe(CO)_2{\cdot}Fe(CO)_6$. When the reaction was repeated in a sealed Teflon container in a microwave oven the yield of the same products obtained after 50 min was identical to that obtained after 15 h of bench reflux. Thiophene does not heat rapidly in a microwave field of 2.45 GHz but the addition of 0.5 g of otherwise inert Fe_3O_4 to the reaction vessel ensured rapid heating.[28] Similar experiments with benzothiophene also produced the same yield of the thiaferrole after 50 min to that obtained by Rauchfuss and co-workers[8] after 18 h, however, no desulfurisation of the benzothiophene was noted.

The use of microwave heating evidently leads to acceleration of previously reported reactions of thiophene derivatives with $[Fe_3(CO)_{12}]$. Since benzothiophene and dibenzothiophene are better models for sulfur in coal and in coal-derived liquids,[10] the failure to observe the desulfurisation of benzothiophene under microwave conditions was disappointing. Attention was directed to reactions of tellurium heterocyclic compounds for reasons stated in the Introduction. All such reactions are summarised in Scheme 1.

Oefele and Dotzauer[29] were, to our knowledge, the first to consider reactions of tellurophene with metal carbonyls. In particular they treated $[Fe_3(CO)_{12}]$ with tellurophene in benzene to obtain black $[Fe_3Te_2(CO)_9]$ and the yellow ferrole $C_4H_4Fe_2(CO)_6$, together with an 18% yield of a third material believed to be $C_4H_4FeTe{\cdot}Fe(CO)_6$. On repeating the reaction under the conditions described in the Experimental section (heptane, 2.5 h) a 45% yield of the ferrole was obtained. Earlier termination of the reaction gave the telluraferrole (found to melt at 41 °C) in 66% yield. The black residue from the 2.5 h reaction was, in our case, FeTe which doubtless arose from $[Fe_3Te_2(CO)_9]$ *via* loss of CO and $Fe(CO)_5$. Encouraged by the good yields from the tellurophene reaction, attention was turned to dibenzotellurophene with no less success; thus the dibenzoferrole, $C_{18}H_8Fe_2O_6$, was obtained in 28% yield. In this case no intermediate was isolated, but extraction of soluble material from the solid residue remaining in the reaction flask gave a black substance giving no IR absorptions above 400 cm^{-1} and shown to contain only Fe and Te (electronic spectroscopy for chemical analysis, ESCA).



Scheme 1 Reactions with iron carbonyl

Table 1 Bond lengths (Å) for complex **3**

Fe(1)–C(17)	1.767(5)	O(4)–C(16)	1.149(5)
Fe(1)–C(18)	1.767(5)	O(5)–C(17)	1.140(6)
Fe(1)–C(16)	1.796(5)	O(6)–C(18)	1.136(6)
Fe(1)–C(6)	2.122(4)	C(1)–C(6)	1.424(7)
Fe(1)–C(8)	2.126(4)	C(1)–C(2)	1.416(6)
Fe(1)–C(1)	2.216(4)	C(1)–C(7)	1.454(6)
Fe(1)–C(7)	2.216(4)	C(2)–C(3)	1.362(7)
Fe(1)–Fe(2)	2.468(1)	C(3)–C(4)	1.398(9)
Fe(2)–C(13)	1.773(5)	C(4)–C(5)	1.361(7)
Fe(2)–C(15)	1.787(5)	C(5)–C(6)	1.431(6)
Fe(2)–C(14)	1.807(4)	C(7)–C(12)	1.418(7)
Fe(2)–C(8)	2.002(4)	C(7)–C(8)	1.409(6)
Fe(2)–C(6)	2.005(4)	C(8)–C(9)	1.448(5)
Fe(2)–C(16)	2.320(5)	C(9)–C(10)	1.358(7)
O(1)–C(13)	1.129(5)	C(10)–C(11)	1.382(7)
O(2)–C(14)	1.139(5)	C(11)–C(12)	1.363(6)
O(3)–C(15)	1.150(5)		

To maintain the theme of reactions of heterocyclic compounds of tellurium with $[Fe_3(CO)_{12}]$, but to model a thioether rather than an aromatic environment, 2-telluraindane was used as a substrate. As detailed in the Experimental section, tellurium was removed from the ring and, in this case, recovered as the cluster compound $[Fe_3Te_2(CO)_9]$ initially reported by Hieber and Gruber.[30] In addition, a 15% yield of a novel complex $C_{19}H_{16}FeO_3$ **4** was obtained which was shown by X-ray crystallography (see below) to contain an organic moiety derived from the unsymmetrical coupling of two C_8H_8 fragments (see Scheme 1). This is in contrast to the formation of a benzocyclobutane following thermochemical extrusion of tellurium.[31] It is to be expected that 2-telluraindane will be a better Lewis base than tellurophene, hence it is possible that the initial stage of the reaction is the monodentate co-ordination of two molecules of the base to the two equivalent iron atoms of $[Fe_3(CO)_{12}]$ thus providing a starting point from which the observed products might plausibly emerge. The retention of an exocyclic double bond is of interest; doubtless the co-ordination of that fragment of the molecule to the iron tricarbonyl unit is responsible for the stabilisation of this form. Indeed, it is possible that in an intermediate stage the C_8H_8 unit is co-ordinated as 1,6-dimethylenecyclohexa-2,4-diene thus facilitating the addition of a similar fragment across one exocyclic double bond.

Structural studies

The structure of the $C_{18}H_8Fe_2O_6$ **3** molecule is shown in Fig. 1; bond lengths are in Table 1. The biphenyl residue is planar to within ±0.018 Å. One of the iron atoms, Fe(1) in our numbering scheme, is displaced by 1.67 Å from the plane and is π bonded to the aromatic bonds C(6)–C(1) and C(7)–C(8). The Fe–C distances involving inner carbon atoms, C(1), and C(7), at 2.216(4) Å are significantly longer than those involving the outer atoms, C(6) and C(8), at 2.122(4) and 2.126(4) Å, respectively. Atom Fe(2) lies close to the biphenyl plane, displacement 0.22 Å, and is σ bonded to C(6) and C(8), forming a metallocyclic ring. The Fe–C bonds at 2.005(4) and 2.002(4) Å are shorter than the π interactions.

The central C(1)–C(7) bond is 1.454(6) Å, some 0.03–0.05 Å shorter than is commonly found in biphenyls, and may indicate some inter-ring electron delocalisation, presumably triggered by the π bonded atom. The Fe(1)–Fe(2) distance is 2.468(1) Å, corresponding to a bonding interaction. The carbonyl group C(16)–O(4) is involved in bonding to both Fe(1) and Fe(2), Fe(1)–C(16) 1.796(5) and Fe(2)–C(16) 2.320(5) Å, forming an unsymmetrical bridge. This Fe_2CO iron carbonyl system is bent, angles Fe(1)–C(16)–O(4) and Fe(2)–C(16)–O(4) 158.4(5) and 129.2(4)°, respectively. The other iron carbonyl groupings have normal dimensions, Fe–C 1.767–1.807, C–O 1.129–1.150 Å, Fe–C–O 177.5–179.0°. The longest Fe–CO bonds, apart from those of the bridging carbonyl group, are those *trans* to the C(6)–Fe(2) and C(8)–Fe(2) σ bonds, indicating a possible weak *trans* influence of these bonds. The C–O bond of the bridging carbonyl group at 1.149(5) Å falls within the range of lengths of the other, non-bridging carbonyl groups. Both iron atoms obey the 18-electron rule.

The central $Fe_2C_4(CO)_6$ residue bears a striking resemblance to the corresponding residue in (hexacarbonylcyclododeca-1,7-diyne)diiron the crystal structure of which has been determined.[32] Here the Fe–Fe separation is 2.462(3) Å and the Fe–CO (bridging) distances are 1.75(2) and 2.32(2) Å with Fe–C–O angles 162(3) and 125(3)°.

The structure of the $C_{19}H_{16}FeO_3$ molecule **4** is shown in Fig. 2. Bond lengths and angles are in Table 2. The iron atom is co-ordinated to three carbonyl groups and to the C(5)–C(6) and C(7)–C(8) double bonds of the organic system. The Fe–CO distances average 1.787(3) Å. The Fe–C(5), –C(6), –C(7) and –C(8) distances are 2.135(2), 2.056(3), 2.042(3) and 2.112(2) Å respectively. These distances may be compared with those found in a selection of 21 structures containing the cyclohexadiene–$Fe(CO)_3$ system extracted from the Cambridge Structural Database.[33] In 18 of these structures the Fe–C(diene) bond lengths follow the pattern observed in our

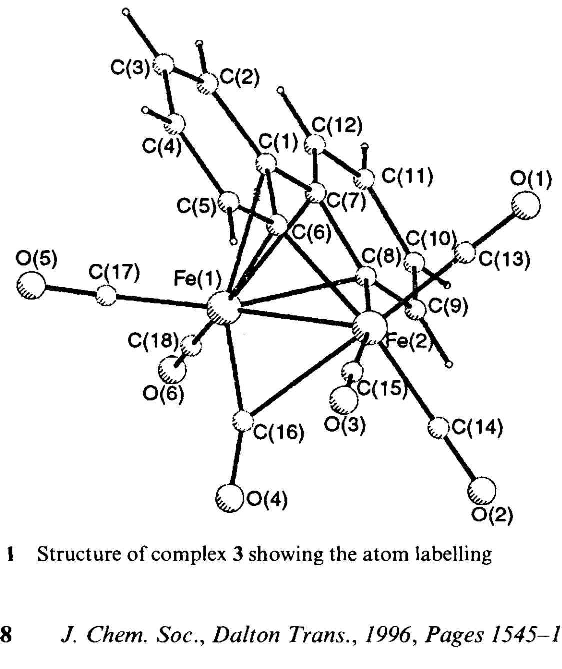


Fig. 1 Structure of complex **3** showing the atom labelling

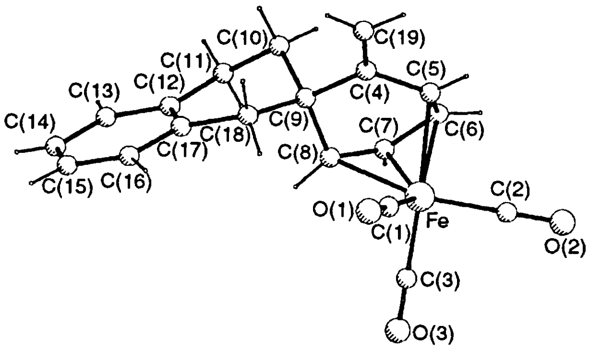


Fig. 2 Structure of complex **4** showing the atom labelling

Table 2 Bond lengths (Å) and selected angles (°) for complex **4**

Fe–C(3)	1.783(3)	C(6)–C(7)	1.397(4)
Fe–C(2)	1.788(3)	C(7)–C(8)	1.404(4)
Fe–C(1)	1.789(3)	C(8)–C(9)	1.529(3)
Fe–C(7)	2.042(3)	C(9)–C(18)	1.518(3)
Fe–C(6)	2.056(3)	C(9)–C(10)	1.554(3)
Fe–C(8)	2.112(2)	C(10)–C(11)	1.523(4)
Fe–C(5)	2.135(2)	C(11)–C(12)	1.496(4)
O(1)–C(1)	1.133(3)	C(12)–C(17)	1.389(4)
O(2)–C(2)	1.134(4)	C(12)–C(13)	1.414(4)
O(3)–C(3)	1.135(3)	C(13)–C(14)	1.365(5)
C(4)–C(19)	1.327(4)	C(14)–C(15)	1.383(5)
C(4)–C(5)	1.459(4)	C(15)–C(16)	1.374(4)
C(4)–C(9)	1.517(3)	C(16)–C(17)	1.389(4)
C(5)–C(6)	1.424(4)	C(17)–C(18)	1.520(4)
O(1)–C(1)–Fe	178.4(2)	C(7)–C(8)–C(9)	118.5(2)
O(2)–C(2)–Fe	179.3(3)	C(4)–C(9)–C(18)	113.1(2)
O(3)–C(3)–Fe	178.4(3)	C(4)–C(9)–C(8)	106.9(2)
C(19)–C(4)–C(5)	120.8(3)	C(18)–C(9)–C(8)	111.7(2)
C(19)–C(4)–C(9)	125.1(3)	C(4)–C(9)–C(10)	109.2(2)
C(5)–C(4)–C(9)	114.1(2)	C(18)–C(9)–C(10)	107.3(2)
C(6)–C(5)–C(4)	122.4(2)	C(8)–C(9)–C(10)	108.7(2)
C(6)–C(7)–C(8)	114.7(2)		

Table 3 Atomic coordinates (× 10^4) for complex **3**

Atom	*x*	*y*	*z*
Fe(1)	1770(1)	7250(1)	2559(1)
Fe(2)	1991(1)	4394(1)	2218(1)
O(1)	5028(2)	2682(2)	2334(1)
O(2)	388(2)	3061(2)	274(1)
O(3)	−660(3)	1917(3)	3225(2)
O(4)	−1881(2)	5439(2)	1886(2)
O(5)	273(4)	8739(4)	4214(2)
O(6)	1466(2)	9883(2)	1259(1)
C(1)	4368(3)	7063(3)	3383(2)
C(2)	5243(3)	7981(3)	4224(2)
C(3)	4701(4)	7514(4)	5139(2)
C(4)	3288(4)	6135(4)	5252(2)
C(5)	2396(3)	5247(3)	4456(2)
C(6)	2910(3)	5663(3)	3474(2)
C(7)	4783(3)	7430(3)	2364(2)
C(8)	3666(2)	6337(3)	1670(2)
C(9)	3990(3)	6646(3)	640(2)
C(10)	5327(3)	7928(3)	381(2)
C(11)	6406(3)	8968(3)	1083(2)
C(12)	6154(3)	8764(3)	2064(2)
C(13)	3852(3)	3354(3)	2282(2)
C(14)	1020(3)	3606(3)	1018(2)
C(15)	357(3)	2913(3)	2836(2)
C(16)	−340(3)	5871(3)	2130(2)
C(17)	850(4)	8179(4)	3552(2)
C(18)	1564(3)	8854(3)	1773(2)

Table 4 Atomic coordinates (× 10^4) for complex **4**

Atom	*x*	*y*	*z*
Fe	1156(1)	1687(1)	1534(1)
O(1)	1789(1)	4653(3)	3221(2)
O(2)	−248(1)	1421(4)	1854(2)
O(3)	628(2)	4070(5)	−495(2)
C(1)	1538(2)	3523(4)	2557(2)
C(2)	295(2)	1523(4)	1723(2)
C(3)	831(2)	3120(5)	285(2)
C(4)	2335(1)	−127(3)	3183(2)
C(5)	1585(1)	−601(4)	2701(2)
C(6)	1294(2)	−1267(4)	1565(2)
C(7)	1578(1)	−417(4)	769(2)
C(8)	2118(1)	942(4)	1219(2)
C(9)	2701(1)	430(3)	2308(2)
C(10)	3120(2)	−1345(4)	2070(3)
C(11)	3427(2)	−946(4)	1098(3)
C(12)	3829(1)	921(4)	1260(2)
C(13)	4324(2)	1263(5)	656(3)
C(14)	4709(2)	2935(5)	794(3)
C(15)	4618(2)	4324(5)	1547(3)
C(16)	4134(1)	4040(4)	2134(2)
C(17)	3737(1)	2349(4)	1996(2)
C(18)	3227(2)	2076(4)	2695(2)
C(19)	2643(2)	−178(5)	4297(2)

structure, with bonds to the inner carbon atoms (mean over all 21 structures 2.05 Å) shorter than those to the outer carbon atoms (mean 2.11 Å). The C–O lengths average 1.134(1) Å and the Fe–C–O angles are all within 1.6° of being linear. As in **3**, here also the iron atom obeys the 18-electron rule.

The bonds C(5)–C(6), C(6)–C(7) and C(7)–C(8) involving the complexed diene moiety are 1.424(4), 1.397(4) and 1.404(4) Å respectively, essentially equal, intermediate between single and double bond distances. It is, nevertheless, of interest that in 17 of the 21 structures cited above the central bond of the diene system is slightly shorter (mean over 21 structures 1.40 Å) than the outer two bonds (mean 1.42 Å), in good agreement with our results, indicating a tendency to bond alternation of the opposite sense to that of the parent free ring system. This effect had been noted[34] previously, but not considered to be significant. Reverse bond alternation is more pronounced in structures where there is a cyclopentadienyl ligand co-ordinated to the iron atom *trans* to the cyclohexadiene.[35] Bonds C(8)–C(9) and C(4)–C(9) are purely single, while C(4)–C(5) (1.459 Å) is slightly shorter than a single bond and C(19)–C(4) (1.327 Å) is very slightly longer than a double bond. Thus the C(19)–C(4) double bond appears to be partly conjugated with the iron–diene system.

The complexed cyclohexadiene-like ring has atoms C(5)–C(8) coplanar to within ± 0.005 Å with C(4) and C(9) displaced on the same side of this plane by 0.725 and 0.974 Å, respectively. The iron atom lies 1.655 Å on the opposite side of this plane. The cyclohexene ring C(9)–C(18) adopts the half-chair conformation. Atoms C(11), C(12), C(17) and C(18) are coplanar to within ± 0.004 Å and C(9), C(10) are located on opposite sides of this plane at distances of 0.35 and 0.44 Å.

Conclusion

Whilst microwave heating is successful in accelerating reactions of thiophene and benzothiophene with $[Fe_3(CO)_{12}]$, it is unable to induce sulfur removal from the thiaferrole formed from benzothiophene. Tellurium is readily removed from tellurophene and, more importantly, from dibenzotellurophene, thus demonstrating the mechanistic feasibility of removal of chalcogen from more condensed systems. Tellurium is also removed from a cyclic telluride, but the major point of interest is an unsymmetrical dimerisation of two organic fragments, which is in contrast to the product of thermal decomposition of the telluride.

References

1 H. D. Kaesz, R. B. King, T. A. Manuel, L. D. Nichols and F. G. A. Stone, *J. Am. Chem. Soc.*, 1960, **82**, 4749.
2 W. Hieber and C. Scharfenberg, *Ber.*, 1940, **73**, 1012.
3 R. B. King, P. M. Triechel and F. G. A. Stone, *J. Am. Chem. Soc.*, 1961, **83**, 3600.
4 G. Dettlof and E. Weiss, *J. Organomet. Chem.*, 1976, **108**, 213.
5 P. Huebener and E. Weiss, *J. Organomet. Chem.*, 1977, **129**, 105.
6 T. B. Rauchfuss, *Prog. Inorg. Chem.*, 1991, **39**, 259.
7 R. J. Angelici, *Coord. Chem. Rev.*, 1990, **105**, 61.
8 A. G. Ogilvy, M. Draganjac, T. B. Rauchfuss and S. R. Wilson, *Organometallics*, 1988, **7**, 1171.
9 J. Chen, L. M. Daniels and R. J. Angelici, *J. Am. Chem. Soc.*, 1991, **113**, 2544.
10 X. D. Hu, L. Zhang, S. M. Cui, Z. H. Wang and J. S. Gao, *Fuel Sci. Technol. Int.*, 1995, **13**, 161.
11 J. D. Goodrich, P. N. Nickias and J. P. Selegue, *Inorg. Chem.*, 1987, **26**, 3424.
12 K. M. Rao, C. L. Day, R. A. Jacobson and R. J. Angelici, *Inorg. Chem.*, 1991, **30**, 5046.
13 S. Harris, *Organometallics*, 1994, **13**, 2628.
14 S. Luo, A. E. Ogilvy, T. B. Rauchfuss, A. L. Rheingold and S. R. Wilson, *Organometallics*, 1991, **10**, 1002.
15 D. M. P. Mingos and D. R. Baghurst, *Chem. Soc. Rev.*, 1991, **20**, 1.
16 F. Fringuelli and A. Taticchi, *J. Chem. Soc., Perkin Trans. 1*, 1972, 199.
17 M.-G. Choi and R. J. Angelici, *J. Am. Chem. Soc.*, 1991, **113**, 565.
18 C. J. White, R. J. Angelici and M.-G. Choi, *Organometallics*, 1995, **14**, 332.
19 W. Lohner and K. Praefke, *Chem. Ber.*, 1978, **111**, 3746.
20 J. D. McCullough, *Inorg. Chem.*, 1975, **9**, 2285.
21 A. Z. Al-Rubai, W. R. McWhinnie, P. Granger and S. Chapelle, *J. Organomet. Chem.*, 1982, **234**, 287.
22 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
23 TEXSAN, Single Crystal Analysis Software, version 1.6, Molecular Structure Corporation, The Woodlands, TX, 1993.
24 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
25 G. M. Sheldrick, University of Göttingen, 1993.
26 W. D. S. Motherwell and W. Clegg, University of Cambridge, 1988.
27 P. Monsef-Mirzai, W. R. McWhinnie, M. C. Perry and P. Burchill, *Fuel*, 1995, **74**, 675.
28 P. Monsef-Mirzai, M. Ravindran, W. R. McWhinnie and P. Burchill, *Fuel*, 1995, **74**, 20.
29 K. Oefele and E. Dotzauer, *J. Organomet. Chem.*, 1972, **42**, C87.
30 W. Hieber and J. J. Gruber, *Z. Anorg. Allg. Chem.*, 1958, **296**, 91.
31 E. Cuthbertson and D. D. MacNichol, *Tetrahedron Lett.*, 1975, 1893.
32 H. B. Chin and R. Bau, *J. Am. Chem. Soc.*, 1973, **95**, 5068.
33 F. H. Allen, J. E. Davies, J. J. Galloy, O. Johnson, O. Kennard, C. F. Macrae, E. M. Mitchell, G. F. Mitchell, J. M. Smith and D. G. Watson, *J. Chem. Inf. Comput. Sci.*, 1991, **31**, 187.
34 F. A. Cotton, V. W. Day, B. A. Frenz, K. I. Hardcastle and J. M. Troup, *J. Am. Chem. Soc.*, 1973, **95**, 4522.
35 M. R. Churchill and R. Mason, *Proc. R. Soc., London, Ser. A*, 1967, **301**, 433.

Received 26*th June* 1995; *Paper* 5/04116C