

# The reactions of heterocyclic organotellurium and selenium compounds with triiron dodecacarbonyl

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The reaction of 2-telluraphthalide, C<sub>8</sub>H<sub>6</sub>O<sub>2</sub>Te, with [Fe<sub>3</sub>(CO)<sub>12</sub>] gave as the major characterised species compound **1**, [C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>TeFe(CO)<sub>3</sub>]<sub>2</sub>. An iron atom has inserted into the telluracyclic ring, and it is probable that one co-ordinated CO ligand arises from the initially organic carbonyl group. X-Ray single crystal investigations revealed a dimeric structure containing an Fe<sub>2</sub>Te<sub>2</sub> core. The reaction of 2-telluraphthalic anhydride, C<sub>8</sub>H<sub>4</sub>O<sub>2</sub>Te, with [Fe<sub>3</sub>(CO)<sub>12</sub>] gave a known, but unexpected, organic product phthalide, C<sub>8</sub>H<sub>6</sub>O<sub>2</sub>. X-Ray crystallography confirmed its isolation; the main feature of interest is the significant double bond character of C(8)–O(1) at 1.352(4) Å. 2-Selenaphthalic anhydride, C<sub>8</sub>H<sub>4</sub>O<sub>2</sub>Se, gave intractable products on reaction with [Fe<sub>3</sub>(CO)<sub>12</sub>], but 2-selenaphthalide, C<sub>8</sub>H<sub>6</sub>OSe, on reaction with the carbonyl gave a major product **2**, [Fe(CO)<sub>3</sub>{C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SeFe(CO)<sub>3</sub>}] and a minor product **3**, [Fe(CO)<sub>2</sub>{η<sup>6</sup>-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SeFe<sub>2</sub>(CO)<sub>6</sub>}] which is an intermediate in the formation of **2**. Compound **2** was shown by X-ray methods to be very similar to **1** except that the 18 electron rule is satisfied by co-ordination of an Fe(CO)<sub>3</sub> moiety, rather than by dimerisation. Compound **3**, also studied by X-ray crystallography, differs from **2** mainly in the addition of an η<sup>6</sup>-bonded Fe(CO)<sub>2</sub> moiety, but the selenoferrole ring is more distorted. It is proposed that comparative studies of reactions of selenium and tellurium compounds with [Fe<sub>3</sub>(CO)<sub>12</sub>] may assist the development of an understanding of the complex reaction pathways.

## Introduction

In three recent papers it has been shown that heterocyclic compounds containing only tellurium,<sup>1,2</sup> or containing both tellurium and nitrogen,<sup>3</sup> may act as precursors for some interesting new organometallic derivatives of iron<sup>1,3</sup> or rhodium.<sup>2</sup> That several, although not all, of the products obtained involve detelluration of the heterocyclic molecule probably reflects the relatively low carbon–chalcogen bond strengths in the compounds, compared with the sulfur analogues which are generally less reactive under similar conditions.<sup>1,4,5</sup>

Reactions are more likely to proceed to completion with the tellurium containing heterocycles; if, however the corresponding selenium containing materials were to be considered, it is possible that products corresponding to an earlier stage of the reaction sequence may be isolable. Angelici and co-workers<sup>6</sup> have extended their studies of thiophene–transition metal interactions to selenophenes, where, amongst other factors, the ability to measure <sup>77</sup>Se NMR spectra was valuable (similar advantages accrued from our studies of tellurium heterocycles where <sup>125</sup>Te NMR measurements have been valuable<sup>7</sup>). In this brief paper we consider reactions of directly related selenium and tellurium heterocycles with [Fe<sub>3</sub>(CO)<sub>12</sub>].

## Experimental and results

2-Tellura-2,3-dihydroinden-1-one (2-telluraphthalide),<sup>8</sup> 2-tellura-2,3-dihydroindene-1,3-dione (2-telluraphthalic anhydride),<sup>9</sup> 2-selena-2,3-dihydroinden-1-one (2-selenaphthalide)<sup>10</sup> and 2-selena-2,3-dihydroindene-1,3-dione (2-selenaphthalic anhydride)<sup>9</sup> were prepared using literature methods. Triiron dodecacarbonyl [Fe<sub>3</sub>(CO)<sub>12</sub>] was obtained from Aldrich and used as received. All manipulations involving reactions of tellurium and selenium compounds were carried out under an atmos-

phere of pure argon with the use of Schlenk techniques. The TLC was carried out on UV active silica gel plates.

## Reactions of triiron dodecacarbonyl

**With 2-oxo-2,3-dihydrobenzotellurophene.** 2-Telluraphthalide (1 g, 4 mmol) and [Fe<sub>3</sub>(CO)<sub>12</sub>] (2.05 g, 4 mmol) were refluxed, with stirring, in the dark, in toluene (25 cm<sup>3</sup>) for 4.5 h. The reaction mixture was cooled to room temperature and filtered to give a dark red filtrate and a residual black solid which adhered to the sides of the flask. The solvent was removed from the filtrate *in vacuo* to give a red solid. The red solid was recrystallised from hexane to give bright red needles, **1**, which were dried under vacuum. The red crystals decomposed at temperatures greater than 220 °C {0.39 g, 24% based on [Fe<sub>3</sub>(CO)<sub>12</sub>]}. (Found: C, 33.7; H, 1.97. Calc. for C<sub>10</sub>H<sub>6</sub>FeO<sub>3</sub>Te: C, 33.5; H, 1.67%). FTIR (KBr, cm<sup>-1</sup>): ν(CO) 2049, 1980 and 1953. NMR (CDCl<sub>3</sub>): <sup>1</sup>H, δ 7.87, 7.30, 7.06 (C<sub>6</sub>H<sub>4</sub>), 4.30, 4.31, 3.99, 3.97 AB pattern (CH<sub>2</sub>); <sup>13</sup>C, δ 209.4, 205.3, 202.3 (CO), 153.0, 154.4, 147.4, 129.5, 127.3, 124.1 (C<sub>6</sub>H<sub>4</sub>) and 15.6 (CH<sub>2</sub>); <sup>125</sup>Te, δ (decoupled) –729.7, J<sub>TeC</sub> 17.95 Hz, (coupled) –727.9, –728.1, –728.4, –728.6 (AB pattern, J<sub>TeH</sub> 50.27, 21.55 Hz). EI mass spectrum: m/z = 277, [C<sub>7</sub>H<sub>4</sub>FeTe]<sup>+</sup>; 91, [C<sub>7</sub>H<sub>7</sub>]<sup>+</sup>.

Crystals suitable for X-ray diffraction measurements were grown by cooling a concentrated hexane solution.

**With 2-telluraphthalic anhydride.** 2-Telluraphthalic anhydride (0.52 g, 2.0 mmol) and [Fe<sub>3</sub>(CO)<sub>12</sub>] (1 g, 2.0 mmol) were refluxed, with stirring, in the dark, with toluene (25 cm<sup>3</sup>) over 4.5 h. On cooling to room temperature the reaction mixture was filtered to give an orange-red filtrate and a residual black solid which adhered to the side of the flask. The solvent was removed from the filtrate *in vacuo* to give an orange solid. Hot hexane was used to extract the light orange solution, leaving a very

small amount of a dirty white residue. The latter was discarded, and the hexane removed from the light orange solution giving a light brown (tan) product. The light brown solid was recrystallised from hexane to give light brown (tan) needle like crystals of phthalide which were dried under vacuum, mp **2** 70–71 °C (lit., 72–74 °C) {0.11 g, 41% based on  $[\text{Fe}_3(\text{CO})_{12}]$ } (Found: C, 71.4; H, 4.55. Calc. for  $\text{C}_8\text{H}_6\text{O}_2$ : C, 71.6; H, 4.47%). FTIR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1753. NMR ( $\text{CDCl}_3$ ):  $^{13}\text{C}$ ,  $\delta$  170.5, 145.8, 133.3, 128.3, 125.0, 121.4 ( $\text{C}_6\text{H}_4$ ) and 68.9 ( $\text{CH}_2$ ). EI mass spectrum:  $m/z = 134$ ,  $[\text{C}_8\text{H}_6\text{O}_2]^+$ ; 106,  $[\text{C}_7\text{H}_6\text{O}]^+$ .

Crystals suitable for X-ray diffraction measurements were grown by cooling a concentrated acetone solution.

2-Telluraphthalic anhydride (0.52 g, 2.0 mmol) in toluene (25  $\text{cm}^3$ ) was refluxed in the dark for 4.5 h. The work-up of the reaction mixture was carried out as above. Only the starting materials were recovered.

**With 2-selenaphthalide.** 2-Selenaphthalide (0.79 g, 4 mmol) and  $[\text{Fe}_3(\text{CO})_{12}]$  (2.05 g, 4 mmol) were refluxed, with stirring, in the dark, with toluene (25  $\text{cm}^3$ ) over 4.5 h. On cooling to room temperature the reaction mixture was filtered to give a deep red filtrate and a residual black solid which adhered to the sides of the flask. The solvent was removed from the filtrate *in vacuo* to give a deep red oil. This was chromatographed on a column of silica gel (pore diameter *ca.* 6 nm) giving a red band, followed by another smaller red band and finally a pale yellow band. Elution with chloroform–hexane (1:1) and removal of the solvent gave a deep red solid, **2**, from the first eluate, a black solid, **3**, from the second eluate, and pale orange crystals from the third eluate (unchanged 2-selenaphthalide).

The deep red solid, **2**, recrystallised from boiling hexane yielding red crystals; mp 190–192 °C (decomp.) {0.90 g, 50% based on  $[\text{Fe}_3(\text{CO})_{12}]$ } (Found: C, 34.6; H, 1.56. Calc. for  $\text{C}_{13}\text{H}_6\text{Fe}_2\text{O}_6\text{Se}$ : C, 34.7; H, 1.34%). FTIR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  2062, 2021 and 1962. NMR ( $\text{CDCl}_3$ ):  $^1\text{H}$ ,  $\delta$  8.19, 7.35, 6.93 ( $\text{C}_6\text{H}_4$ ), 3.78 ( $\text{CH}_2$ );  $^{13}\text{C}$ ,  $\delta$  209.5 (CO), 159.2, 139.7, 130.5, 127.8, 123.5, 112.4 ( $\text{C}_6\text{H}_4$ ) and 35.5 ( $\text{CH}_2$ ). EI mass spectrum:  $m/z = 450$ ,  $[\text{C}_{13}\text{H}_6\text{O}_6\text{Fe}_2\text{Se}]^+$ ; 394,  $[\text{C}_{11}\text{H}_6\text{O}_4\text{Fe}_2\text{Se}]^+$ .

The black solid, **3**, recrystallised from boiling hexane yielding black crystals, mp 159–160 °C (decomp.) {0.048 g, 2% based on  $[\text{Fe}_3(\text{CO})_{12}]$ } (Found: C, 33.02; H, 1.80. Calc. for  $\text{C}_{15}\text{H}_6\text{Fe}_3\text{O}_8\text{Se}$ : C, 32.13; H, 1.08%). FTIR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  2106, 2061, 2024, 1983 and 1956. NMR ( $\text{CDCl}_3$ ):  $^1\text{H}$ ,  $\delta$  7.22 (br,  $\text{C}_6\text{H}_4$ ), 2.15 (br,  $\text{CH}_2$ );  $^{13}\text{C}$ ,  $\delta$  213.0, 212.0, 211.2, 209.5 (CO), 132.8, 130.2, 128.2, 125.4, 111.7 ( $\text{C}_6\text{H}_4$ ) and 34.7 ( $\text{CH}_2$ ). EI mass spectrum:  $m/z = 562$ ,  $[\text{C}_{15}\text{H}_6\text{O}_8\text{Fe}_3\text{Se}]^+$ ; 506,  $[\text{C}_{13}\text{H}_6\text{O}_6\text{Fe}_3\text{Se}]^+$ ; 450,  $[\text{C}_{13}\text{H}_6\text{O}_6\text{Fe}_2\text{Se}]^+$ ; 422,  $[\text{C}_{12}\text{H}_6\text{O}_5\text{Fe}_2\text{Se}]^+$ .

Crystals suitable for X-ray diffraction measurements were grown by cooling a concentrated chloroform–hexane (1:1) solution for compound **2** and a solution of chloroform for **3**.

**With 2-selenaphthalic anhydride.** 2-Selenaphthalic anhydride (0.49 g, 2.3 mmol) and  $[\text{Fe}_3(\text{CO})_{12}]$  (1.15 g, 2.3 mmol) were refluxed, with stirring, in the dark, with toluene (25  $\text{cm}^3$ ) over 4.5 h. On cooling to room temperature the reaction mixture was filtered to give a deep red filtrate and a residual black solid which adhered to the sides of the flask. The solvent was removed from the filtrate *in vacuo* to give a red solid. This was chromatographed on a column of silica gel (pore diameter *ca.* 6 nm) giving a red band followed by a colourless band. Elution with chloroform–hexane (2:1) and removal of the solvent gave a red solid from the first eluate and pale yellow crystals from the second, which were shown to be unchanged 2-selenaphthalic anhydride. The first component has to date defied attempts to characterise it (Found: C, 27.73; H, 2.40%): FTIR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  2072 and 1958  $\text{cm}^{-1}$ .

### X-Ray crystallography

The crystal structures of compounds **1–3** and phthalide were

determined; crystal parameters and experimental data are listed in Table 1. Cell dimensions and intensity data for all four structures were measured on a Rigaku R-Axis II area detector diffractometer at 293(2) K using graphite-monochromated Mo-K $\alpha$  radiation,  $\lambda = 0.7107$  Å. Conventional absorption corrections were not applied since, on average, each unique reflection intensity is the mean of three intensities measured at different orientations of the crystal, thus minimising absorption effects. The structures were determined<sup>11</sup> by direct methods and refined<sup>12</sup> by least squares on  $F^2$  using anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed in calculated positions, riding on their respective bonding atoms. Diagrams were drawn with ORTEP,<sup>13</sup> thermal ellipsoids are at the 30% probability level. Selected bond lengths and angles are in Table 2.

CCDC reference number 186/1186.

See <http://www.rsc.org/suppdata/dt/1998/3947/> for crystallographic files in .cif format.

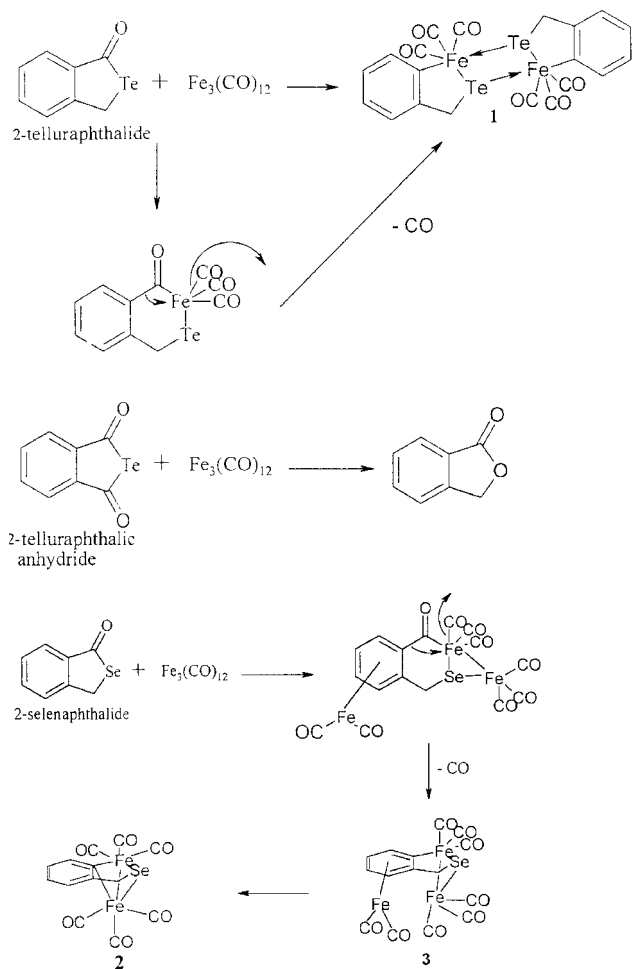
### Physical measurements

Infrared spectra were obtained for KBr discs with a Bio-Rad FTS-40A FTIR spectrometer, proton (300.133),  $^{13}\text{C}$  (75.469),  $^{125}\text{Te}$  (78.580 MHz) NMR spectra with a Bruker AC 300 spectrometer at the indicated frequencies; references used were TMS ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and  $\text{Me}_2\text{Te}$  ( $^{125}\text{Te}$ ). The electron impact (EI) and fast atom bombardment (FAB) mass spectra were obtained *via* the EPSRC mass spectrometry service, University College, Swansea.

### Discussion

The reaction of 2-telluraphthalide with  $[\text{Fe}_3(\text{CO})_{12}]$  gave compound **1** (Scheme 1). It is likely that an initial stage of the reaction involved insertion of iron into the Te–C(O) bond, and that this was followed by what is effectively the reverse of a carbonyl insertion reaction. Thus one of the carbonyl groups on iron is probably of “organic” origin. The monomeric unit (with respect to iron and tellurium) does not satisfy the 18 electron rule, hence dimerisation occurs by co-ordination of tellurium (Lewis base) to the iron in the neighbouring isostructural fragment. The room temperature NMR data ( $^1\text{H}$ ,  $^{13}\text{C}$ ) are entirely consistent with the structure determined by X-ray crystallography (see below).

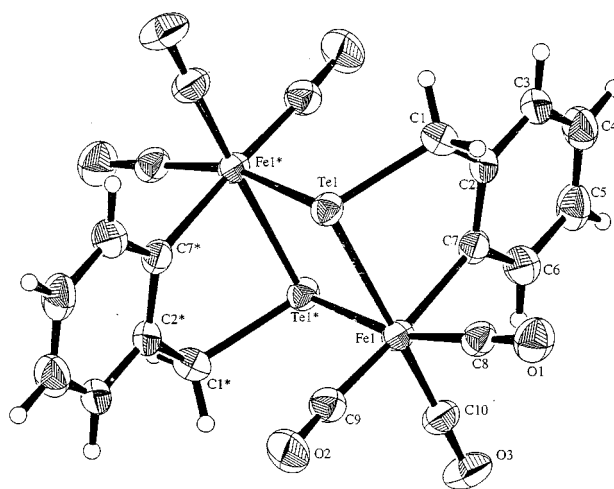
The reaction of  $[\text{Fe}_3(\text{CO})_{12}]$  with 2-telluraphthalic anhydride gives an unexpected product (phthalide), confirmed by X-ray crystallography; it is a case of the mode of origin of the material being of more interest than the actual product. 2-Telluraphthalic anhydride was pure and correctly characterised (mp, FTIR, NMR, C,H,N analysis,<sup>9a</sup> and X-ray crystallographic analysis<sup>9b</sup>), thus the origin of the product cannot be attributed to impurities in the starting materials; the yield would also suggest that this explanation is precluded. In further experiments the 2-telluraphthalic anhydride was recovered unchanged from refluxing toluene; nor did  $[\text{Fe}_3(\text{CO})_{12}]$  react with toluene under the reaction conditions used. This renders it improbable that the carbon skeleton originates from toluene. It is difficult to explain the origin of the product but the postulation of an initial insertion of iron into a Te–C(O) bond is reasonable. It is apparent that removal of Te requires a multimetal centre, hence at least a second iron is expected to be present at this stage of the reaction. Rear attack on one carbonyl by the oxygen of the second carbonyl occurring synchronously with elimination of FeTe is then possible. The resulting carbene may be temporally stabilised by co-ordination to the second iron (a recent example of an iron stabilised carbene has been reported<sup>14</sup>); decomposition by adventitious moisture is possible, although a secondary alcohol may be expected if this were so. Alternatively, proton extraction from the solvent



**Scheme 1** Reaction of organotellurium and organoselenium compounds with triiron dodecacarbonyl.

may occur. Further speculation is not merited at this juncture.

Reaction of 2-selenaphthalide with  $[\text{Fe}_3(\text{CO})_{12}]$  yields compounds **2** and **3**. Their relative yields suggest that **3** (2%) is an intermediate in the formation of **2** (50%). Initial insertion of iron into a Se–C(O) bond, followed by the loss of carbonyl from the iron as shown in Scheme 1 can be postulated, giving product **3**. On prolonged heating of compound **3** the loss of the  $\eta^6$ -bound  $\text{Fe}(\text{CO})_2$  moiety must occur giving **2**. It is of interest that the ring iron atom in **2** satisfies the 18 electron rule by retention of a  $\text{Fe}(\text{CO})_3$  unit, whereas in the related compound **1** loss of this moiety and co-ordination to tellurium of a neighbouring fragment is preferred. The use of the selenium analogue has then given materials which can very reasonably be considered models for intermediate stages of what is doubtless a complex reaction sequence, and to that extent the objectives of the study have been achieved. The room temperature NMR data ( $^1\text{H}$ ,  $^{13}\text{C}$ ) for both **2** and **3** appear too simple to be consistent with the static structures determined by X-ray methods (see below). Thus, for **2**, the  $\text{CH}_2$  protons give a sharp singlet rather than the AB pattern demanded by the static structure; also the  $^{13}\text{C}$  data imply the equivalence of the six carbonyl ligands. A rapid interchange of the two iron atoms rendering the methylene protons equivalent on the NMR timescale is probable. Cooling a  $\text{CDCl}_3$  solution of the complex incrementally to 218 K produces significant broadening of the  $\text{CH}_2$  resonance, but even at this temperature complete resolution into the AB pattern is not observed. It is clear that **3** must also be fluxional in solution at room temperature; only four resonances for the carbonyl ligands are observed and a singlet is again seen for the  $\text{CH}_2$  protons, although in this case the resonance is broad at room temperature and sharpens on heating to 323 K. Under these



**Fig. 1** View of the crystal structure of complex **1**. Starred atoms are related to the corresponding unstarred atoms by an inversion centre.

circumstances, it is surprising that cooling to 233 K, although inducing further broadening of the methylene signal, fails to achieve resolution into the expected AB pattern. The fluxional behaviour of **3** is complex and must certainly involve, at the least, interchange of the two  $\text{Fe}(\text{CO})_3$  groups.

The reaction of the 2-selenaphthalic anhydride with  $[\text{Fe}_3(\text{CO})_{12}]$  afforded only unchanged starting material and an intractable red product (see Experimental section).

Only the starting materials were recovered when the experiments involving the four organo-selenium and -tellurium compounds were repeated with triruthenium dodecacarbonyl  $[\text{Ru}_3(\text{CO})_{12}]$ .

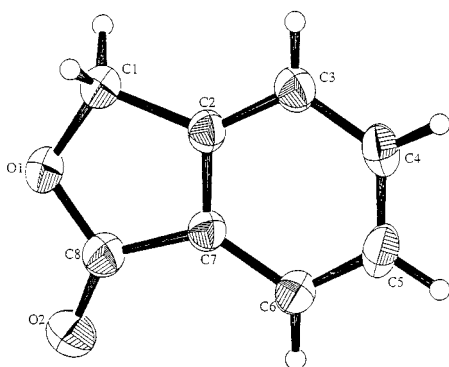
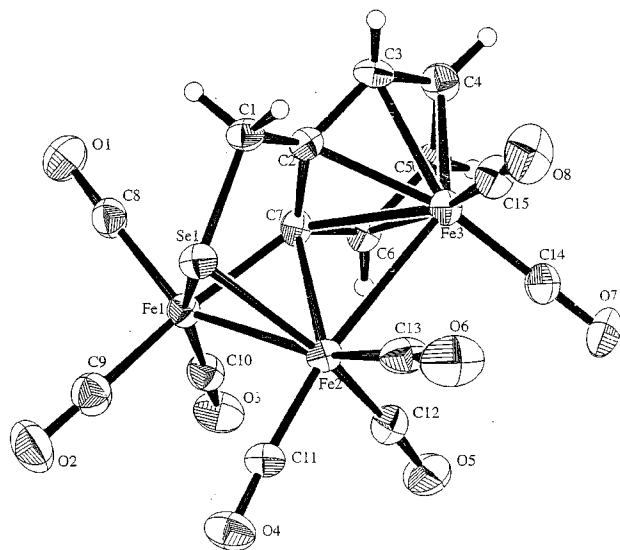
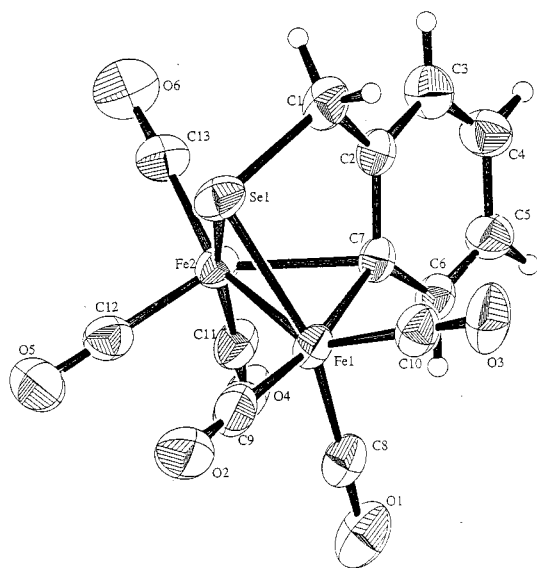
#### X-Ray crystallography

The dimeric complex **1** has crystallographic 1 ( $C_i$ ) symmetry. The central  $\text{Fe}_2\text{Te}_2$  core is approximately square-shaped, with iron–tellurium distances 2.572(1) and 2.575(1) Å, angle at iron 83.22(4)°, angle at tellurium, 96.78(4)° (see Fig. 1 and Table 2). The Fe–Te bond lengths fall near the lower end of the range, 2.54–2.67 Å, found<sup>3,15</sup> in a number of other complexes containing analogous atomic groupings. The co-ordination geometry at iron is approximately octahedral, maximum angular deviation 15.3°, mean deviation 5.5°. The tellurium–carbon bond length,  $\text{Te}(1)\text{--C}(1)$  2.139(9) Å, is slightly shorter than the mean value given<sup>16</sup> for Te–C( $\text{sp}^3$ ) bonds, 2.158 Å, but falls within the range 2.119–2.154 Å found<sup>17</sup> in a number of more recent structure determinations. The eight-atom grouping C(1)–C(7), Fe(1) is coplanar to within 0.03 Å (root mean square, r.m.s. deviation 0.019 Å). The tellurium atom which completes a benzotelluraferrole ring system is, however, displaced by 0.83(1) Å. The plane of the  $\text{Fe}_2\text{Te}_2$  core is oriented at 80.4(1)° to this plane, forming a step to the centrosymmetrically related benzotelluraferrole ring, so that the perpendicular distance between these parallel planes is approximately 3.34 Å.

The non-hydrogen atoms of phthalide are essentially coplanar, r.m.s. atomic deviation 0.014 Å (Fig. 2). The maximum deviation of 0.026(2) Å is that of the carbonyl oxygen atom, O(2), and omitting this atom from the calculations gives a significantly better plane, r.m.s. deviation 0.009 Å, with O(2) displaced by 0.049(5) Å. Noteworthy is the difference in bond lengths between those at the saturated carbon atom, C(1), and those at the trigonally hybridised C(8). Thus, while O(1)–C(1) at 1.455(4) Å approximates to a C–O single bond, the O(1)–C(8) length of 1.352(4) Å indicates significant double bond character, and, also, C(1)–C(2) is significantly longer than C(7)–C(8). The O(2)=C(8) formal double bond, 1.208(4) Å, is similar in length to the corresponding bonds in phthalic anhydride, 1.192(4) Å.<sup>18</sup>

**Table 1** Crystallographic data for compounds 1–3 and phthalide

	1	phthalide	2	3
Formula	C <sub>20</sub> H <sub>12</sub> Fe <sub>2</sub> O <sub>6</sub> Te <sub>2</sub>	C <sub>8</sub> H <sub>6</sub> O <sub>2</sub>	C <sub>13</sub> H <sub>6</sub> Fe <sub>2</sub> O <sub>6</sub> Se	C <sub>15</sub> H <sub>6</sub> Fe <sub>3</sub> O <sub>8</sub> Se
<i>M</i>	715.2	134.1	448.8	560.7
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> /Å	10.863(2)	7.760(2)	9.479(2)	8.264(1)
<i>b</i> /Å	7.245(2)	10.799(3)	15.339(3)	15.591(2)
<i>c</i> /Å	14.380(3)	8.234(3)	10.637(2)	13.628(2)
$\beta$ /°	105.49(2)	112.88(2)	97.73(1)	97.34(1)
<i>U</i> /Å <sup>3</sup>	1090.6(4)	635.7(3)	1532.5(5)	1741.5(4)
<i>Z</i>	2	4	4	4
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	3.985	0.101	4.290	4.597
Reflections collected [ <i>I</i> > $\sigma$ ( <i>I</i> )]	5937	2740	8792	10382
Unique reflections	1888	966	2680	2899
<i>R</i> <sub>int</sub>	0.0583	0.0598	0.0929	0.0478
<i>R</i> , <i>wR</i> 2	0.0579, 0.1060	0.0986, 0.2246	0.0741, 0.1422	0.040, 0.101
Observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	1781	772	2190	2733
<i>R</i> , <i>wR</i> 2	0.0533, 0.1042	0.0739, 0.1944	0.0564, 0.1307	0.037, 0.098

**Fig. 2** View of the crystal structure of phthalide.**Fig. 4** View of the crystal structure of complex 3.**Fig. 3** View of the crystal structure of complex 2.

In the benzoselenoferrole moiety of complex **2**, the two iron atoms appear to be in chemically identical environments (Fig. 3). However, stereochemically they are not identical; Fe(1) lies close [0.18(1) Å] to the plane of the organic residue and may, therefore, be considered to be the iron constituent of the benzoselenoferrole, whereas Fe(2) is displaced by 1.99 Å from this plane and may be considered to be  $\pi$ -bonded to the selenium atom, Fe(1) and C(7). Bond lengths are consistent with this, Fe(1)–C(7) and Fe(1)–Se(1) each being shorter than the corresponding bonds involving Fe(2) (see Table 2). The selenium atom is displaced by 0.72 Å from the organic plane, on the same

side as Fe(2). The crystal structure of the analogous  $\mu$ -[1,2- $\eta$ -selenylcyclohex-1-ene-1-carbaldehydato(2-)- $\mu$ -Se]-bis(tricarbonyliron) has been determined.<sup>19</sup> Here the out-of-plane iron atom is bonded to the selenium atom and both unsaturated carbon atoms of the cyclohexene at distances of 2.353(1), 2.214(8) and 2.132(7) Å, respectively, while the in-plane iron is bonded to selenium at 2.327(1) Å and to the carbonyl carbon atom of the selenoferrole ring at 1.990(8) Å. The Fe–Fe distance of 2.631(2) Å is greater than our distance of 2.482(1) Å which is, however, similar to such distances generally found in Fe<sub>2</sub>(CO)<sub>6</sub> residues.<sup>19</sup> For comparison, in the complex [Cp\*(OC)<sub>2</sub>-Re{ $\mu$ - $\eta^6$ -SeC<sub>4</sub>H<sub>4</sub>Fe(CO)<sub>3</sub>}Fe(CO)<sub>3</sub>] the Fe<sub>2</sub>Se triangle has Fe–Se and Fe–Fe distances 2.357, 2.367 and 2.558 Å,<sup>6a</sup> similar to the values cited above and those measured in complex **3** (see below), although the distinction between the  $\sigma$ - and  $\pi$ -bonded iron atoms is less obvious.

Complex **3** differs from **2** only by the addition of an  $\eta^6$ -bonded Fe(CO)<sub>2</sub> moiety. The selenoferrole ring is more distorted than in **2**, with the “in-plane” iron atom, Fe(1), displaced by 0.407(5) Å from the plane of atoms C(1)–C(7) (Fig. 4). The out-of-plane Fe(2) and the selenium atom are displaced by 2.05 and 0.70 Å, respectively, on the opposite side of the C(1)–C(7) plane, so that the selenoferrole ring [C(1), C(2), C(7), Fe(1), Se(1)] has a half-chair conformation. The Fe–Fe, Fe–Se, Fe–C and Se–C bond distances are similar to those in **2**, apart from Fe(2)–C(7), which is longer by 0.26 Å here, and Fe(1)–Fe(2), which is longer by 0.07 Å. The increase in the Fe(2)–C(7) bond

**Table 2** Selected bond lengths (Å) and angles (°) for compounds **1–3** and phthalide

Compound <b>1</b>			
Te(1)–Fe(1)	2.575(1)	Fe(1)–C(8)	1.767(10)
Te(1)–Fe(1*)	2.572(1)	Fe(1)–C(9)	1.806(10)
Te(1)–C(1)	2.139(9)	Fe(1)–C(10)	1.777(9)
Fe(1)–C(7)	2.062(8)		
Fe(1)–Te(1)–Fe(1*)	96.78(4)	C(7)–Fe(1)–C(8)	84.5(3)
Fe(1)–Te(1)–C(1)	88.9(2)	C(7)–Fe(1)–C(9)	174.9(4)
Fe(1*)–Te(1)–C(1)	106.0(3)	C(7)–Fe(1)–C(10)	92.0(4)
Te(1)–Fe(1)–C(7)	85.6(2)	C(8)–Fe(1)–Te(1*)	164.7(3)
Te(1)–Fe(1)–C(8)	91.6(3)	C(8)–Fe(1)–C(9)	96.3(4)
Te(1)–Fe(1)–C(9)	89.3(3)	C(8)–Fe(1)–C(10)	95.8(4)
Te(1)–Fe(1)–C(10)	172.0(3)	C(9)–Fe(1)–Te(1*)	98.1(3)
Te(1)–Fe(1)–Te(1*)	83.22(4)	C(9)–Fe(1)–C(10)	93.0(4)
C(7)–Fe(1)–Te(1*)	80.7(2)	C(10)–Fe(1)–Te(1*)	88.9(3)
Phthalide			
O(1)–C(1)	1.455(4)	C(1)–C(2)	1.491(5)
O(1)–C(8)	1.352(4)	C(7)–C(8)	1.459(5)
O(2)–C(8)	1.208(4)		
C(1)–O(1)–C(8)	110.7(3)	O(2)–C(8)–O(1)	121.4(4)
O(1)–C(1)–C(2)	104.2(3)	O(2)–C(8)–C(7)	130.5(4)
O(1)–C(8)–C(7)	108.1(3)		
Compound <b>2</b>			
Se(1)–Fe(1)	2.347(1)	Fe(1)–C(9)	1.781(7)
Se(1)–Fe(2)	2.378(1)	Fe(1)–C(10)	1.783(6)
Se(1)–C(1)	1.967(6)	Fe(2)–C(7)	2.194(5)
Fe(1)–Fe(2)	2.482(1)	Fe(2)–C(11)	1.789(5)
Fe(1)–C(7)	2.046(5)	Fe(2)–C(12)	1.757(7)
Fe(1)–C(8)	1.774(6)	Fe(2)–C(13)	1.798(6)
Fe(1)–Se(1)–C(1)	96.3(2)	Se(1)–Fe(1)–Fe(2)	58.93(3)
Fe(2)–Se(1)–C(1)	90.6(2)	C(7)–Fe(2)–Se(1)	78.4(1)
Fe(1)–Se(1)–Fe(2)	63.36(3)	C(7)–Fe(2)–Fe(1)	51.5(1)
Se(1)–Fe(1)–C(7)	82.1(1)	Se(1)–Fe(2)–Fe(1)	57.70(3)
Fe(2)–Fe(1)–C(7)	57.0(1)		
Compound <b>3</b>			
Se(1)–Fe(1)	2.355(1)	Fe(2)–C(13)	1.791(5)
Se(1)–Fe(2)	2.383(1)	Fe(3)–C(2)	2.140(4)
Se(1)–C(1)	1.945(4)	Fe(3)–C(3)	2.122(4)
Fe(1)–Fe(2)	2.551(1)	Fe(3)–C(4)	2.125(4)
Fe(1)–C(7)	2.001(4)	Fe(2)–C(5)	2.129(4)
Fe(1)–C(8)	1.794(5)	Fe(3)–C(6)	2.124(4)
Fe(1)–C(9)	1.811(5)	Fe(3)–C(7)	2.226(4)
Fe(1)–C(10)	1.769(4)	Fe(3)–C(14)	1.765(5)
Fe(2)–C(7)	2.452(4)	Fe(3)–C(15)	1.762(4)
Fe(2)–C(11)	1.757(5)	Fe(3)···Fe(2)	2.836(1)
Fe(2)–C(12)	1.764(4)		
Fe(1)–Se(1)–C(1)	95.2(1)	Se(1)–Fe(1)–Fe(2)	57.96(2)
Fe(2)–Se(1)–C(1)	99.6(1)	C(7)–Fe(2)–Se(1)	72.5(1)
Fe(1)–Se(1)–Fe(2)	65.15(2)	C(7)–Fe(2)–Fe(1)	47.1(1)
Se(1)–Fe(1)–C(7)	81.6(1)	Se(1)–Fe(2)–Fe(1)	56.90(2)
Fe(2)–Fe(1)–C(7)	63.8(1)		

length may be a consequence of the presence of the  $\eta^6$ -bonded Fe(3), which is situated 2.836(1) Å from Fe(2) and 2.226(4) Å from C(7). In a similar situation, an Fe–Fe distance of 2.822 Å has been considered<sup>20</sup> to indicate a metal–metal bond. The Fe(3)–C (phenyl) distances are similar to those measured<sup>20</sup> previously; apart from the Fe(3)–C(7) distance, they are all in the range 2.12–2.14 Å.

In all three iron carbonyl complexes the Fe–C–O moieties are near linear, angular ranges 175.8–178.9° in **1**, 177.7–179.4° in **2** and 175.1–179.6° in **3**. The Fe–CO bond lengths are normal, 1.77–1.81 Å in **1**, 1.76–1.80 Å in **2** and 1.76–1.81 Å in **3**. There is some evidence that Fe–CO bonds in Fe(CO)<sub>2</sub> moieties, mean lengths 1.763(2),<sup>20</sup> 1.736(18)<sup>21</sup> and 1.763(2) Å in **3** are shorter than those in Fe(CO)<sub>3</sub> moieties, mean lengths 1.795(12),<sup>19</sup> 1.791(4),<sup>20</sup> 1.783(12) in **1**, 1.780(6) in **2** and 1.781(9) Å in **3**.

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## References

- 1 K. Singh, W. R. McWhinnie, H. L. Chen, M. Sun and T. A. Hamor, *J. Chem. Soc., Dalton Trans.*, 1996, 1545.
- 2 K. Badyal, W. R. McWhinnie, H. L. Chen and T. A. Hamor, *J. Chem. Soc., Dalton Trans.*, 1997, 1579.
- 3 K. Badyal, W. R. McWhinnie, T. A. Hamor and H. Chen, *Organometallics*, 1997, **16**, 3194.
- 4 T. B. Rauchfuss, *Prog. Inorg. Chem.*, 1991, **39**, 259.
- 5 R. J. Angelici, *Coord. Chem. Rev.*, 1990, **105**, 61.
- 6 (a) M. G. Choi and R. J. Angelici, *J. Am. Chem. Soc.*, 1991, **113**, 5651; (b) C. J. White, T. L. Wang, R. A. Jacobsen and R. J. Angelici, *Organometallics*, 1994, **13**, 4474; (c) C. J. White and R. J. Angelici, *Organometallics*, 1994, **13**, 5132.
- 7 K. Badyal, W. R. McWhinnie, J. Homer and M. C. Perry, *J. Organomet. Chem.*, 1998, in the press.
- 8 L. Engman and M. P. Cava, *J. Org. Chem.*, 1981, **46**, 4194.
- 9 (a) J. Bergman and L. Engman, *Org. Prep. Proced. Int.*, 1978, **10**, 289; (b) Z. Majeed, W. R. McWhinnie, K. Paxton and T. A. Hamer, *J. Organomet. Chem.*, in the press.
- 10 W. H. H. Gunther, *J. Org. Chem.*, 1967, **32**, 3929.
- 11 TEXSAN, Single Crystal Structure Analysis Software, version 1.6, Molecular Structure Corporation, Houston, TX, 1993.
- 12 G. M. Sheldrick, SHELXL 93, Program for Crystal Structure Refinement, University of Göttingen, 1993.
- 13 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- 14 A. Klose, E. Solari, C. Floriani, N. Re, A. Chiesivola and C. Rizzoli, *Chem. Commun.*, 1997, 2297.
- 15 P. Mathur, D. Chakrabarty, M. M. Hossain, R. S. Rashid, V. Rugmini and A. L. Rheingold, *Inorg. Chem.*, 1992, **31**, 1106; G. Gervasio, *J. Organomet. Chem.*, 1992, **441**, 271; L. C. Roof, D. M. Smith, G. W. Drake, W. T. Pennington and J. W. Kolis, *Inorg. Chem.*, 1995, **34**, 337; J. R. Eveland and K. H. Whitmire, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 741.
- 16 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans.*, 1987, S1.
- 17 K. Y. Abid, N. I. Al-Salim, M. Greaves, W. R. McWhinnie, A. A. West and T. A. Hamor, *J. Chem. Soc., Dalton Trans.*, 1989, 1697; H. B. Singh, N. Sudha, A. A. West and T. A. Hamor, *J. Chem. Soc., Dalton Trans.*, 1990, 907.
- 18 R. B. Bates and R. S. Cutler, *Acta Crystallogr., Sect. B*, 1977, **33**, 893.
- 19 R. C. Petterson, K. H. Pannell and A. J. Mayr, *Acta Crystallogr., Sect. B*, 1980, **36**, 2434.
- 20 N. S. Nametkin, V. D. Tyurin, A. I. Nekhaev, Yu. P. Sobolev, M. G. Kondrateva, A. S. Batsanov and Yu. T. Struchkov, *J. Organomet. Chem.*, 1983, **243**, 323.
- 21 J. Chen, J. Yin, Z. Fan and W. Xu, *J. Chem. Soc., Dalton Trans.*, 1988, 2803.