

Cyclisation of diacetylenes on $[\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)]$: Structural characterisation of $[(\text{CO})_6\text{Fe}_2\{\mu\text{-SeCC}(\text{H})\text{C}(\text{CH}_3)\text{SeCSe}\}]$

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Abstract. Room temperature reactions of $[\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)]$ with the diacetylenes, $\text{RC}\equiv\text{CC}\equiv\text{CH}$ ($\text{R} = \text{Me}, n\text{-Bu}$) yield the products, $[(\text{CO})_6\text{Fe}_2\{\mu\text{-SeCC}(\text{H})\text{C}(\text{R})\text{SeCSe}\}]$; X-ray analysis of the $\text{R} = \text{Me}$ compound has been carried out and reveals an unusual cyclisation of the diacetylene with incorporation of a selenium atom to form a cyclic C_4Se ligand attached to the $\text{Fe}_2(\text{CO})_6\text{Se}_2$ core.

Keywords. Diacetylene; cyclisation; selenophene; iron carbonyl.

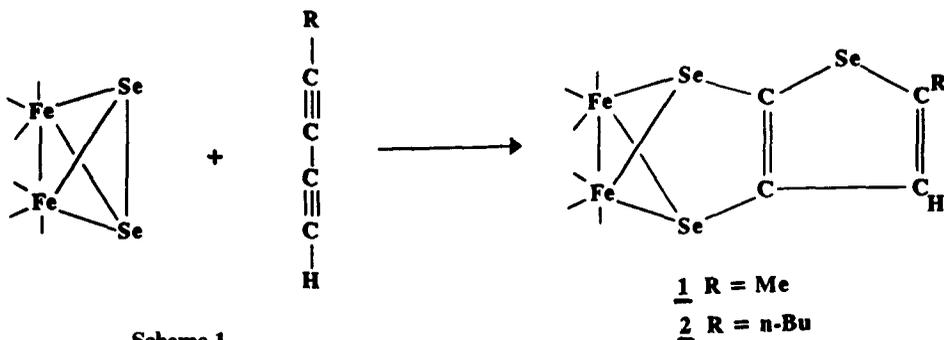
1. Introduction

The synthesis of complexes containing the C_4 ligands has attracted interest in recent times (Adams *et al* 1993a). For instance, 1,4-*bis*(diphenylphosphino)buta-1,3,-diyne ($\text{PPh}_2\text{C}_2\text{C}_2\text{PPh}_2$) has been used for attaching one transition metal–ligand moiety to each end of the linear diacetylenic tertiary phosphine and the addition of $\text{Co}_2(\text{CO})_6$ and $\text{Pt}(\text{PPh}_3)_2$ groups to one of the $\text{C}\equiv\text{C}$ triple bonds (Adams *et al* 1992). This strategy has been extended for the synthesis of several new Ru_3/Os_3 and $\text{M}_3\text{Re}_3(\mu\text{-H})_3$ ($\text{M} = \text{Os}$ or Ru) heterometallic clusters (Adams *et al* 1993b). In previous reports we have described the facile addition of phenylacetylene across the reactive $\text{Se}\text{--}\text{Se}$ bond of $[\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)]$ to form $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SeC}(\text{Ph})=\text{C}(\text{H})\text{Se}\}]$, which readily adds $\text{Pt}(\text{PPh}_3)_2$ group and a $\text{Fe}_2(\text{CO})_6\text{Se}_2$ across its $\text{C}=\text{C}$ bond to yield products in which the acetylenic bond is further reduced (Mathur *et al* 1993). We have now extended this work to the addition of diacetylenes to $[\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)]$. Our motivation for conducting such investigation has been to synthesise a complex in which one $\text{C}\equiv\text{C}$ triple bond is attached to the two Se atoms of $[\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)]$ and the other $\text{C}\equiv\text{C}$ triple bond may interact with transition metal alkynophiles. Here we describe the formation of unusual products obtained from the reactions of $\text{RC}\equiv\text{CC}\equiv\text{CH}$ ($\text{R} = \text{Me}, n\text{-Bu}$) with $[\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)]$.

2. Discussion

When a mixture of equimolar amounts of $[\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)]$ and $\text{RC}\equiv\text{CC}\equiv\text{CH}$ ($\text{R} = \text{Me}$ or $n\text{-Bu}$) was stirred in methanol solvent containing a trace of sodium acetate for 24 hours, an orange compound was isolated in each case and identified as

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$[(\text{CO})_6\text{Fe}_2\{\mu\text{-SeCCH}(\text{R})\text{SeCSe}\}]$, 1 (R = Me, 34%) and 2 (R = *n*-Bu, 37%) (scheme 1)¹. Both compounds were characterised by IR and ¹H NMR spectroscopy. Orange-red crystals of 1 were grown from its hexane solution at -10°C and an X-ray analysis was undertaken². The molecular structure of 1 can be described as consisting of an Fe_2Se_2 butterfly and $\text{CC}(\text{H})\text{C}(\text{CH}_3)\text{SeC}$ cyclic unit attached to the two bridging Se atoms of the Fe_2Se_2 unit (figure 1). The average Se-Fe-Se angle in 1 (82.5°) is significantly larger than in $[\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)]$ (58°) (Campana *et al* 1979), but is comparable to that observed in $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SeC}(\text{Ph})=\text{C}(\text{H})\text{Se}\}]$ (81.4°) (Mathur and Hossain 1993). The Fe-Fe bond distances in 1 ($2.514(3)\text{ \AA}$) and in $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SeC}(\text{Ph})=\text{C}(\text{H})\text{Se}\}]$ ($2.512(1)\text{ \AA}$) are almost identical, as are the average Fe-Se bond distances (2.386 \AA in 1 and 2.3836 \AA in $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SeC}(\text{Ph})=\text{C}(\text{H})\text{Se}\}]$). There is considerable variation in the C-C bond distances in the $\text{CC}(\text{H})\text{C}(\text{CH}_3)\text{SeC}$ unit of 1. The two carbon atoms which are attached to the Se atoms of the Fe_2Se_2 framework, C(7) and C(8) form the shortest bond, $1.336(19)\text{ \AA}$, typical of an olefinic bond order. The remaining two C-C bond distances are longer, C(7)-C(10), $1.42(2)\text{ \AA}$ and C(9)-C(10), $1.41(2)\text{ \AA}$; the former is slightly shorter than the C-C single bond distance of 1.4332 \AA reported for selenophene (Magdesieva and Zefirov 1973), while the latter is somewhat longer than expected for a C=C double bond. The two triply bonded Se atoms form slightly longer bonds to the carbon atoms than does the 2-coordinate Se atom; Se(1)-C(8), $1.92(1)\text{ \AA}$; Se(2)-C(7), $1.93(1)\text{ \AA}$; Se(3)-C(8), $1.85(1)\text{ \AA}$; Se(3)-C(9), $1.89(2)\text{ \AA}$. The C(8)-Se(3)-C(9) angle in 1 is $87.9(6)^\circ$, which compares with the C-Se-C angle of

¹Compound 1: Air-stable orange-red crystals: m.p. $117\text{--}119^\circ\text{C}$. IR [$\nu(\text{CO})/\text{cm}^{-1}$, hexane]: 2071 *m*, 2038 *vs.*, 2000 *s*. NMR [(CDCl_3)]: δ_{H} 6.49(1H), 2.35(3H).

Compound 2: Air-stable red crystals: m.p. $95\text{--}97^\circ\text{C}$. IR [$\nu(\text{CO})/\text{cm}^{-1}$, hexane]: 2071 *m*, 2037 *vs.*, 1999 *s*. NMR [(CDCl_3)]: δ_{H} 6.50(1H), 2.63(2H), 1.53(2H), 1.30(2H), 0.91(3H).

²Crystal data for $\text{C}_{11}\text{H}_4\text{O}_6\text{Fe}_2\text{Se}_3$, $M = 580.69$, triclinic, space group $P\bar{1}$, $a = 7.639(3)$, $b = 10.085(3)$, $c = 11.296(5)\text{ \AA}$, $\alpha = 70.80(3)$, $\beta = 81.83(3)$, $\gamma = 89.53(3)^\circ$, $V = 812.8(6)\text{ \AA}^3$, $Z = 2$, $F(000) = 544$, Mo-K α radiation (graphite monochromated), $\mu = 8.46\text{ mm}^{-1}$, $T = 293\text{ K}$, $D_c = 2.37\text{ g cm}^{-3}$. The structure was solved by direct methods and refined by full matrix least squares methods using NRCVAX programs (Gabe *et al* 1989) to $R = 0.046$ and $R_w = 0.057$ for 1769 ($|F_o| > 3\sigma|F_o|$) reflections from 2810 unique data set collected on CAD4 diffractometer. All nonhydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically but held fixed during refinement. Number of parameters refined was 199. Final ΔF synthesis showed no features above 1.21 e \AA^{-3} . Atomic coordinates, bond lengths and angles, and thermal parameters are available from the authors.

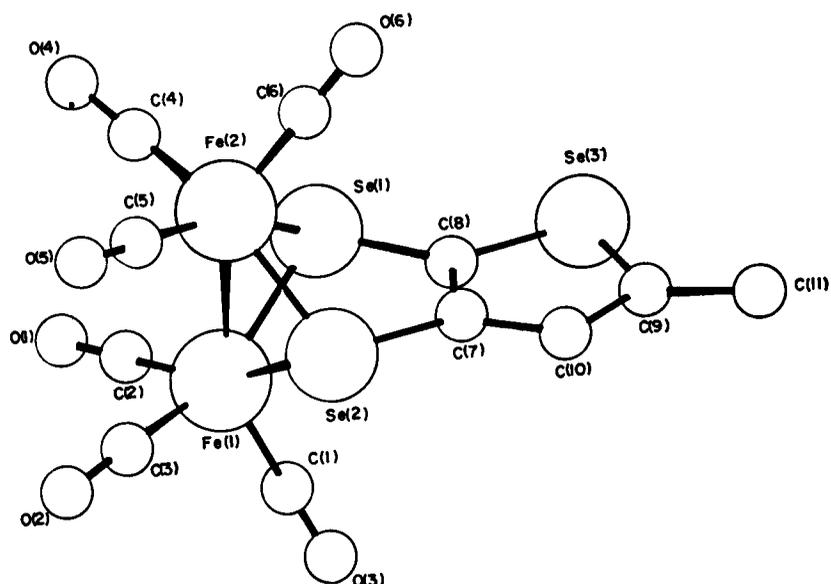


Figure 1. Molecular structure of **1**; selected bond lengths (Å) and angles (°): Fe(1)–Fe(2) 2.514(3), Se(1)–Fe(1) 2.384(2), Se(1)–Fe(2) 2.385(2), Se(2)–Fe(1) 2.388(2), Se(2)–Fe(2) 2.388(2), Se(1)–C(8) 1.92(1), Se(2)–C(7) 1.93(1), Se(3)–C(8) 1.85(1), Se(3)–C(9) 1.89(2), C(7)–C(8) 1.33(2), C(7)–C(10) 1.42(2), C(9)–C(10) 1.41(2), Se(1)–Fe(1)–Se(2) 82.54(7), Fe(1)–Se(1)–Fe(2) 63.63(7), Fe(1)–Se(1)–C(8) 99.6(4), Fe(2)–Se(1)–C(8) 98.2(4), C(8)–Se(3)–C(9) 87.9(6), Se(3)–C(8)–C(7) 112.3(10), Se(3)–C(9)–C(11) 122.3(12), C(10)–C(9)–C(11) 128.3(14), C(7)–C(10)–C(9) 114.0(12), C(8)–C(7)–C(10) 116.6(12).

87.8° observed in selenophene, but is much greater than the smallest C–Se–C angle reported, 81.8° in 1,3,4-selenadiazole (Kendall and Olofson 1970). The remaining four angles of the C₄Se ring of **1** lie in the range 109.3–116.6°.

When [Fe₂(CO)₆(μ-Se₂)] and RC≡CC≡CH were allowed to react in the presence of trace amounts of NaOAc, but in the absence of selenium powder, compounds [(CO)₆Fe₂Se₂{μ-HC=(C≡CR)}] **3** (R = Me) and **4** (R = *n*-Bu) were obtained in yields of 37% and 43% respectively,³ along with trace amounts of **1** and **2**. To test whether compounds **1** and **2** are formed via [(CO)₆Fe₂Se₂{μ-HC=(C≡CR)}], **3** and **4** were separately treated with selenium powder and NaOAc in methanol solvent. The formation of the selenophene derivatives **1** and **2** was not observed in either case after 40 hours of stirring at room temperature, compounds **3** and **4** were recovered intact from the respective reaction solutions. Although intermediates in the reactions yielding the selenophene derivatives have not been identified, an initial reaction of selenium with the carbanionic species formed from the reaction of the free diacetylene and NaOAc

³Compound **3**: Air stable dark red crystals: m.p. 97–99°C. IR[ν(CO)/cm⁻¹, hexane]: 2073 *m*, 2.38 *vs*, 2000 *vs*. NMR(CDCl₃): δ_H 7.2(1H), 1.95(3H).

Compound **4**: Air stable orange crystals: m.p. 127–129°C. IR[ν(CO)/cm⁻¹, hexane]: 2071 *m*, 2.39 *vs*, 2001 *vs*. NMR[CDCl₃]: δ_H 7.18(1H), 2.30(2H), 1.49(2H), 1.49(2H), 1.37(2H), 0.90(3H).

Satisfactory elemental analyses were obtained for **1–4**.

seems to be the first step. This could be followed by the addition across the Se–Se bond of $[\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)]$.

Our initial aim of using the diacetylene as a substrate to carry out cluster growth reactions has not been realised; however, the formation of **1** and **2** suggests that it may be possible to use the Fe_2Se_2 framework of $[\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)]$ to carry out the synthesis of organoselenium and other heterocyclic ligands. Efforts are being made to examine the scope of the reactions of diacetylenes and triacetylenes with $[\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)]$ for new organic ligand syntheses.

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