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Extrusion of selenium and tellurium atoms from selenophene and tellurophene by reaction with trinuclear iron, ruthenium, and osmium clusters: crystal structures of $[Os_6(\mu\text{-}H)(\mu_3\text{-}Se)(\mu_4\text{-}C_4H_3)(CO)_{20}]$ and of $[Ru_4(\mu_3\text{-}Se)\mu\text{-}C_4H_4)(CO)_{11}]$

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Abstract

The trinuclear carbonyl clusters $[Fe_3(CO)_{12}]$, $[Ru_3(CO)_{12}]$, $[Os_3(CO)_{11}(MeCN)]$, and $[Os_3(CO)_{10}(MeCN)_2]$ react with selenophene and tellurophene (*cyclo*-C_4H_4X, X = Se or Te) under mild conditions to give compounds containing the open-chain ligands CHCHCHCHX or the fragments X, C_4H_4, C_4H_3, or H as bridging ligands. The following compounds were isolated and characterised: $[Os_3(CO)_{10}(C_4H_4X)]$, **1** where X = Se (X-ray structure reported previously) and **8** where X = Te, $[Os_6H(Se)(C_4H_3)(CO)_{20}]$, **2**, $[Os_2(CO)_6(C_4H_4Se)]$, **3**, $[Ru_2(CO)_6(C_4H_4)]$, **4**, $[Ru_4(Se)(CO)_{11}(C_4H_4)]$, **5**, $[Fe_2(CO)_6(C_4H_4)]$, **6**, and $[Fe_2(CO)_6(C_4H_4Se)]$, **7**. The clusters **2** and **5** were shown by single-crystal X-ray diffraction methods to have had both Se–C bonds broken to give μ_3-Se ligands in each case. Compound **2** contains an interesting μ_4-C_4H_3 ligand linking two Os_3 units through a μ-alkylidyne bridge, a σ-Os–C bond, and an η^3-allyl component. Compound **5** has a μ-C_4H_4 ligand of a type previously found to be formed by alkyne coupling. The other compounds were characterised spectroscopically.

Introduction

The group 16 heterocycles, furan, thiophene, selenophene, and tellurophene, are a series of closely related compounds, *cyclo*-C_4H_4X (X = O, S, Se, or Te), which may be compared in their reactivity towards transition-metal compounds. When considering the chemistry of a group of elements, the first row compound is usually very different from the heavier analogues. However, we find that, in the reactions of C_4H_4X with triosmium clusters, a discontinuity in chemistry occurs between thiophene and selenophene. Himmelreich and Müller have shown that furan reacts with $[Os_3(CO)_{10}(MeCN)_2]$ by metallation at the 2-position to give the 2-furyl

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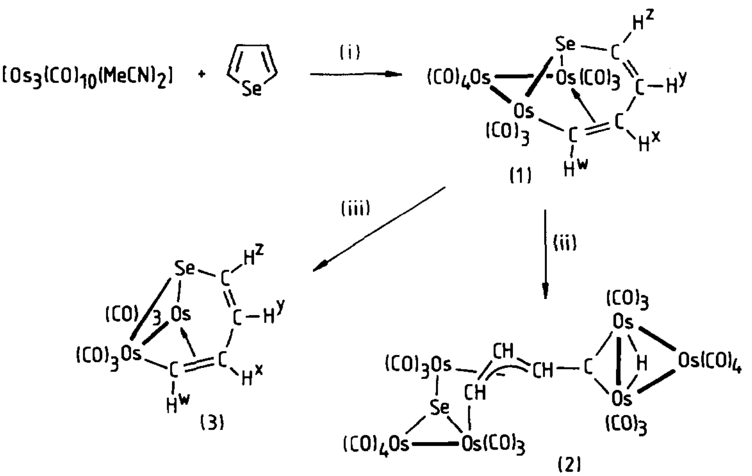
cluster $[Os_3H(\mu\text{-}2\text{-}C_4H_3O)(CO)_{10}]$ in which the furyl ligand forms a μ,η^2-vinyl type bridge and acts as a three-electron donor [1]. We have shown that thiophene behaves in a totally analogous way but the heavier congeners, selenophene [2] and tellurophene [3], give stoichiometrically equivalent but non-hydridic compounds $[Os_3(CO)_{10}(C_4H_4X)]$ (X = Se or Te) in which a C–X rather than a C–H bond has been broken [4]. Following an earlier communication of some of this work [4], we report here in full our results on the reactions of selenophene and tellurophene with trinuclear iron, ruthenium and osmium carbonyl clusters, which in all cases lead to the breaking of C–X rather than C–H bonds. In some products open-chain CHCHCHCHX ligands are present whereas in others both C–X bonds have been broken to give μ_3-X ligands and C_4H_4 or C_4H_3 fragments as bridging ligands.

There has been little previous work on the chemistry of these heterocycles with transition metals. Curiously, whereas thiophene in the compound $[Re(\eta\text{-}C_5Me_5)(CO)_2(C_4H_4S)]$ is η^1-S-bonded, selenophene in the corresponding compound is η^2-coordinated through the carbon atoms at the 2- and 3-positions [5]. We have not been able to synthesise simple C_4H_4X cluster compounds to compare with these but obtained only oxidative addition products. Our results show that there has been C–H cleavage in thiophene and Se–C cleavage of selenophene.

Results and discussion

Selenophene reacts with $[Os_3(CO)_{10}(MeCN)_2]$ in refluxing cyclohexane to give the 1 : 1 product $[Os_3(CO)_{10}(C_4H_4Se)]$, **1** (35% yield) and another compound with the 2 : 1 stoichiometry $[\{Os_3(CO)_{10}\}_2(C_4H_4Se)]$, **2** (20% yield). Compound **1** and its X-ray structure have been described in a communication [4]. The compound contains a doubly-bridging ring-opened selenophene ligand as shown in Scheme 1. The C_4H_4Se ligand is a 6-electron donor coordinated through a μ-Se (3 electron donor) atom and a μ,η^2-vinyl (3 electron donor) group. The complex was further characterised by IR and ^1H NMR data (Table 1). Although spin–spin coupling



Scheme 1. (i) Refluxing cyclohexane; (ii) $[Os_3(CO)_{10}(MeCN)_2]$, refluxing cyclohexane; (iii) refluxing octane.

Table 1

IR and ^1H NMR data for the new complexes

Compound	$\nu(CO)$ [a] (cm^{-1})	^1H NMR [b]	
$[Os_3(CO)_{10}(C_4H_4Se)]$ (1)	2100w, 2063vs, 2051m, 2014vs, 2009s, 1996w, 1988w, 1976w.	7.10 (dd, H^y) 6.54 (d, H^w) 6.30 (dd, H^z) 5.65 (ddd, H^x)	J_{yz} 7.3 J_{xy} 4.4 J_{wx} 10.2 J_{xz} 0.6
$[Os_6H(Se)(C_4H_3)(CO)_{20}]$ (2)	2112vw, 2103w, 2090m, 2077sh, 2062sh, 2060vs, 2038m, 2024s, 2013sm, 2002m, 1995m, 1988w, 1981mw.	10.2 (dd, H^x) 8.4 (d, H^z) 7.0 (dd, H^y) −16.7 (d, OsH^w)	J_{xy} 13.4 J_{yz} 13.4 J_{xw} 0.6
$[Os_2(CO)_6(C_4H_4Se)]$ (3)	2088m, 2060s, 2012vs, 2002vs, 1988s.	9.2 (d, H^w) 6.8 (dd, H^y) 6.0 (dd, H^x) 5.3 (d, H^z)	J_{wx} 10.4 J_{xy} 5.6 J_{yz} 6.4
$[Ru_2(CO)_6(C_4H_4)]$ (4)	2090w, 2075vs, 2055vs, 2029m, 2017vs, 1998w, 1934m, 1897w.	7.0 (m, $H^xH^{x'}$) [c] 5.4 (m, $H^yH^{y'}$)	J_{xy} 7.6 $J_{xy'}$ 3.0 $J_{yy'}$ 5.0 $J_{xx'}$ 0.5
$[Ru_4(Se)(C_4H_4)(CO)_{11}]$ (5)	2097m, 2094sh, 2076s, 2073sh, 2050vs, 2047sh, 2038m, 2033m, 2010s, 2003ms, 1988m, 1931w, 1899w.	7.15 (m, $H^xH^{x'}$) [c] 6.15 (m, $H^yH^{y'}$)	J_{xx} 8.0 $J_{xy'}$ 3.0 $J_{yy'}$ 5.0 $J_{xx'}$ 0
$[Fe_2(CO)_6(C_4H_4)]$ (6)	2077w, 2040s, 2004s, 1996m, 1962w.	6.8 (m, $H^xH^{x'}$) [c] 6.2 (m, $H^yH^{y'}$)	J_{xy} 7.4 $J_{xy'}$ 4.2 $J_{yy'}$ 3.0 $J_{xx'}$ 0
$[Fe_2(CO)_6(C_4H_4Se)]$ (7)	2075s, 2042vs, 2035sh, 2005vs, 1991s.	9.2 (d, H^w) 6.6 (dd, H^y) 5.6 (d, H^x) 5.1 (dd, H^z)	J_{wx} 9.1 J_{xy} 6.6 J_{yz} 5.4
$[Os_3(CO)_{10}(C_4H_4Te)]$ (8)	2098w, 2059vs, 2049m, 2014s, 2005s, 1995m, 1988m, 1976w.	7.2 (dd, H^y) 6.4 (d, H^w) 6.3 (dd, H^z) 5.6 (ddd, H^x)	J_{yz} 8.1 J_{xy} 4.6 J_{wx} 11.2 J_{xz} 0.5

[a] Recorded in cyclohexane. [b] Recorded in $CDCl_3$ at 300 MHz at room temperature. [c] XX′YY′ spectrum.

within the CHCHCHCH chain was easily analysed, we could not be entirely sure which end was bonded to selenium. The assignments in Table 1 having CH^z bonded to Se as in Scheme 1 are based on our expectations of what the chemical shifts ought to be, but possibly the order of assignments *w* to *z* should be reversed.

One carbon–carbon double bond in **1** remains uncoordinated so that the ligand has the potential for donating more electrons without the remaining Se–C bond being broken. Thermal treatment of **1** in refluxing octane (125 °C) did not give any simple decarbonylation products containing a more extensively coordinated C_4H_4Se ligand nor did it give cleavage of the Se–C bond, but rather thermolysis led to the loss of a $Os(CO)_4$ group. Presumably it is the Os unit not bonded to C_4H_4Se that is displaced to give the product, $[Os_2(CO)_6(C_4H_4Se)]$, **3**. We have characterised **3** by IR and ^1H NMR spectra. The IR spectrum is simple (five carbonyl absorptions

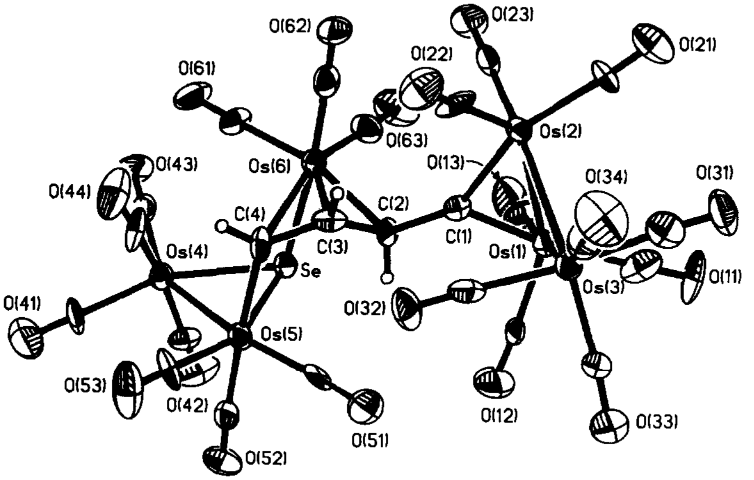


Fig. 1. Molecular structure of the cluster $[Os_6(\mu\text{-}H)(\mu_3\text{-}Se)(\mu_4\text{-}C_4H_3)(CO)_{20}]$. Only the labels of the oxygen atoms of the CO ligands are shown; the carbon atoms are labelled correspondingly.

around 2000 cm^{-1}) consistent with the dinuclear formula, although the ^1H NMR spectrum is significantly different from that of **1** in the values of the chemical shifts although the coupling constants do not differ by more than 1 Hz (Table 1). Formation of a Os–Os bond is required for coordinative saturation and the consequential shortening of the distance from 3.378(1) Å in **1** has a distinct affect on the ligand coordination. It may be that this shortening causes the other carbon–carbon double bond to be coordinated instead. However, we prefer the structure for **3** shown in Scheme 1, although we do not have a crystal structure do establish the correct structure.

Product **2** from the initial reaction (Scheme 1) is an interesting compound. Its complex IR spectrum around 2000 cm^{-1} led us at first to doubt its purity and it was only by a crystal structure determination that we were able to formulate it correctly as $[Os_6(\mu\text{-}H)(\mu_3\text{-}Se)(\mu_4\text{-}C_4H_3)(CO)_{20}]$. Interpretation of its spectra was only possible after we had established the X-ray structure shown in Fig. 1. Selected bond lengths and angles are in Table 2. Two Os_3 units are discernable. Three Os atoms are linked by a μ_3-Se atom and two of these are further co-ordinated to the organic ligand through the σ-Os(5)–C(4) bond and through an η^3-allyl bond from C(2)C(3)C(4) to Os(6). This Os_3 unit is a 52-electron system and as such the presence of only one Os–Os bond, that between Os(4) and Os(5), is required in the Os(4)Os(5)Os(6) unit. The other metal–metal distances in this group [Os(4)–Os(6) 4.169(1) and Os(5)–Os(6) 3.754(1) Å] are far too long for these atoms to be considered bonded. The C_4H_3 ligand provides the only link between the two Os_3 components. The other Os_3 cluster is of a type familiar from known compounds in the literature. It is an alkylidyne cluster of known type $[Os_3(\mu\text{-}H)(\mu\text{-}CR)(CO)_{10}]$, structures of which are known for R = H [6], Ph [7], and CH_2CHMe_2 [8]. The CR ligand is a 3-electron donor and some multiple Os–C bonding in the Os(1)–C(1)–Os(2) bridge is implied. The distances Os(1)–C(1) [2.04(2) Å] and Os(2)–C(1) [2.05(2) å] are the shortest Os–C distances in the molecule except for those for the strongly π-bonding CO ligands. The dihedral angle between the Os(1)Os(2)C(1) and

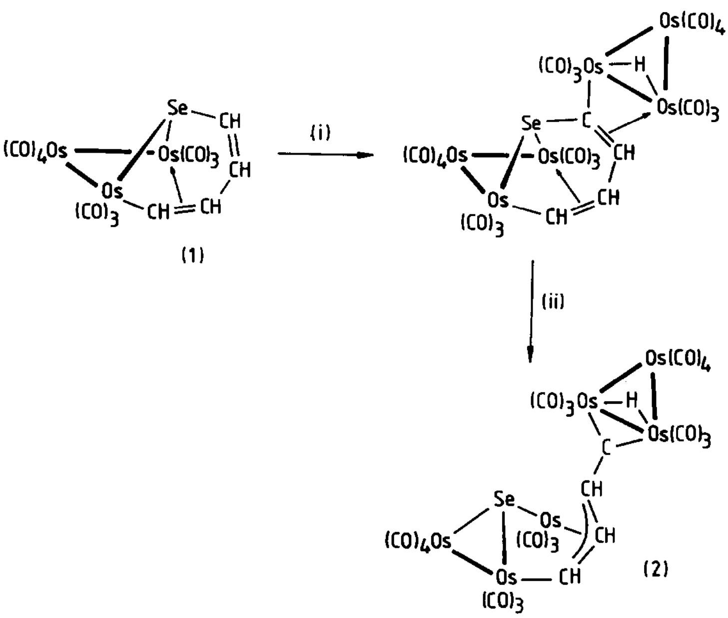
Table 2

Selected bond lengths (Å) and angles (°) for the cluster $[Os_6H(Se)(C_4H_3)(CO)_{20}]$, **2**

Os(1)–Os(2)	2.823(1)	Os(1)–C(1)	2.04(2)
Os(1)–Os(3)	2.873(1)	Os(2)–C(1)	2.05(2)
Os(2)–Os(3)	2.839(1)	Os(5)–C(4)	2.17(2)
Os(4)–Os(5)	2.858(1)	Os(6)–C(2)	2.25(2)
Os(4)···Os(6)	4.169(1)	Os(6)–C(3)	2.22(1)
Os(5)···Os(6)	3.754(1)	Os(6)–C(4)	2.44(2)
Os(4)–Se	2.564(2)	C(1)–C(2)	1.42(2)
Os(5)–Se	2.509(2)	C(2)–C(3)	1.44(3)
Os(6)–Se	2.572(2)	C(3)–C(4)	1.43(3)
Os(3)···C(1)	3.00(2)		
Os(1)–Os(2)–Os(3)	61.0(1)	Os(1)–C(1)–C(2)	129(1)
Os(1)–Os(3)–Os(2)	59.2(1)	Os(2)–C(1)–C(2)	144(1)
Os(2)–Os(1)–Os(3)	59.8(1)	Os(5)–C(4)–C(3)	124(1)
Os(4)–Se–Os(5)	68.6(1)	Os(6)–C(2)–C(3)	70.2(9)
Os(4)–Se–Os(6)	108.5(1)	Os(6)–C(3)–C(2)	72.3(8)
Os(5)–Se–Os(6)	95.3(1)	Os(6)–C(3)–C(4)	80.8(9)
Os(4)–Os(5)–Se	56.6(1)	Os(6)–C(4)–C(3)	63.9(8)
Os(5)–Os(4)–Se	54.8(1)	C(1)–C(2)–C(3)	125(1)
Os(1)–C(1)–Os(2)	87.5(6)	C(2)–C(3)–C(4)	122(1)
Os(5)–C(4)–Os(6)	108.9(7)		

the Os(1)Os(2)Os(3) planes is 95.1° in compound 2, compared with 69.7° for R = H, 78.2° for R = Ph, and 82.1° for $R = CH_2CHMe_2$. In the compound with R = H, the CH group tilts most strongly towards the $Os(CO)_4$ group so that the Os–C distance is 2.353(10) Å, while for $R = CH_2CHMe_2$ the distance is 2.640(26) Å and for R = Ph the distance is 2.586(10) Å. In compound **2** the Os(3)–C(1) distance is 3.00(2) Å, very much longer than for the other μ-CR examples given above. This distance is expected to be longer when π-bonding between the C atom and the R group is possible; in the compound with R = H, this kind of stabilization is not possible and as a consequence there is a bonding interaction between the alkylidyne carbon and the osmium atom of the $Os(CO)_4$ group. Such interactions are not apparent in the structure of **2**. The C–C distances along the C_4 chain are similar, in the range 1.42(2) to 1.44(2) Å, implying π-delocalization over all four carbon atoms. The η^3-allyl ligand is essentially normal [Os(6)–C(2), 2.25(2); Os(6)–C(4), 2.22(1); Os(6)–C(4), 2.44(2) Å].

We do not have any clear evidence for the chemical route to cluster **2** but the reaction of cluster **1** with $[Os_3(CO)_{10}(MeCN)_2]$ in refluxing cyclohexane for 1 h does yield some of cluster **2** (13%) as well as some of the dinuclear compound **3** (6%). The route given in Scheme 1 is consistent with this. Scheme 2 shows a possible mechanism. Oxidative addition of alkenes at $[Os_3(CO)_{10}(MeCN)_2]$ with C–H cleavage to give vinyl clusters is known to be possible. Reaction at the free carbon–carbon double bond of compound **1** would give the di-μ-vinyl intermediate shown which could isomerise with concerted Se–C and Os–Os bond cleavages and Os–Se bond formation to give cluster **2**. The C_4H_3 ligand is a 7-electron donor so that the original C_4H_4Se molecule is donating 12 electrons overall through its separate components (C_4H_3, Se, and H) in cluster **2**.



Scheme 2. (i) $[Os_3(CO)_{10}(MeCN)_2]$, cyclohexane; (ii) isomerization.

Reaction of $[Ru_3(CO)_{12}]$ with selenophene in dry refluxing THF gave two products. The dinuclear compound $[Ru_2(CO)_6(\mu\text{-}C_4H_4)]$, **4** does not contain selenium but is clearly derived from selenophene by loss of an Se atom. One could regard it as being derived from selenophene by substitution of Se by $Ru(CO)_3$ to give $Ru(C_4H_4)(CO)_3$ which is then π-complexes to another $Ru(CO)_3$ unit. Compound **4** is of a known type commonly formed by reaction of alkynes with $[Ru_3(CO)_{12}]$ but the mechanism of formation in this case and the fate of the Se atom are unknown. The ^1H NMR spectrum is of the XX'YY' type as expected. The second product **5** also gives a similar ^1H NMR spectrum indicating that there is a C_4H_4 ligand coordinated in the same sort of way. The stoichiometry of this compound, $[Ru_4(\mu_3\text{-}Se)(\mu\text{-}C_4H_4)(CO)_{11}]$, was suggested by spectroscopic data and was confirmed by a single-crystal X-ray structure determination (Fig. 2). Selected bond lengths and angles are in Table 3. The cluster contains a Se-capped triangle of ruthenium atoms and there is a spiked ruthenium atom supporting the bridging C_4H_4 ligand. In this case the selenium atom has been extruded from the heterocycle but remains in the cluster. The compound is a 64-electron cluster and is expected therefore to have four metal–metal bonds as observed. There are three terminal CO ligands at each of three Ru atoms whereas the central Ru atom only carries two CO ligands. These show some degree of semi-bridging to Ru(1) and Ru(2). Recently the cluster $[Os_4(\mu_3\text{-}S)\{\mu\text{-}C_4Me_2(NMe_2)_2\}(CO)_{11}]$ formed from the alkyne MeC_2NMe_2 and $[Os_4(S)(CO)_{12}]$ has been shown to have a very similar structure [9]. Almost certainly the cluster **5** is formed by the oxidative addition of the selenophene ring to a metal atom, as with osmium, followed by subsequent transfer of Se to a μ_3 position as the other C–Se bond is broken.

The reaction of selenophene with $[Fe_3(CO)_{12}]$ gives only two dinuclear compounds: $[Fe_2(CO)_6(\mu\text{-}C_4H_4)]$, **6**, directly analogous to compound **4**, and $[Fe_2(CO)_6\text{-}$

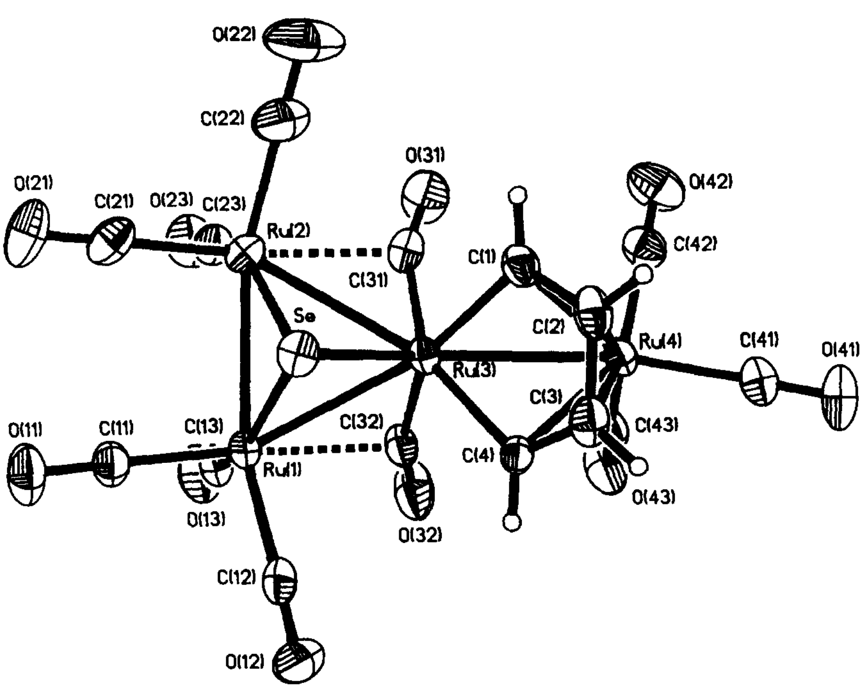
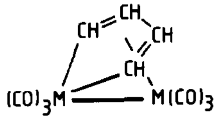


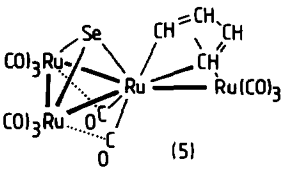
Fig. 2. Molecular structure of the cluster [Ru$_4$(μ_3-Se)(μ-C$_4$H$_4$)(CO)$_{11}$], 5.

Table 3

Selected bond lengths (Å) and angles (°) for the cluster [Ru$_4$(Se)(C$_4$H$_4$)(CO)$_{11}$], 5

Ru(1)–Ru(2)	2.737(1)	Ru(4)–C(1)	2.235(6)
Ru(1)–Ru(3)	2.814(1)	Ru(4)–C(2)	2.220(6)
Ru(2)–Ru(3)	2.835(1)	Ru(4)–C(3)	2.221(6)
Ru(3)–Ru(4)	2.736(1)	Ru(4)–C(4)	2.254(6)
Ru(1)–Se	2.458(1)	Ru(3)–C(31)	1.939(7)
Ru(2)–Se	2.458(1)	Ru(3)–C(32)	1.941(6)
Ru(3)–Se	2.435(1)	Ru(2) ··· C(31)	2.491(6)
Ru(3)–C(1)	2.053(6)	Ru(1) ··· C(32)	2.518(6)
Ru(3)–C(4)	2.038(6)		
Ru(1)–Ru(2)–Ru(3)	60.6(1)	Ru(3)–Ru(2)–Se	54.2(1)
Ru(1)–Ru(3)–Ru(2)	58.0(1)	Ru(4)–Ru(3)–Se	135.0(1)
Ru(2)–Ru(1)–Ru(3)	61.4(1)	Ru(3)–C(1)–Ru(4)	79.2(2)
Ru(1)–Ru(3)–Ru(4)	151.2(1)	Ru(3)–C(4)–Ru(4)	79.0(2)
Ru(2)–Ru(3)–Ru(4)	150.3(1)	Ru(3)–C(1)–C(2)	116.9(5)
Ru(1)–Se–Ru(2	67.7(1)	Ru(3)–C(4)–C(3)	116.8(5)
Ru(1)–Se–Ru(3)	70.2(1)	C(1)–C(2)–C(3)	113.1(5)
Ru(2)–Se–Ru(3)	70.8(1)	C(2)–C(3)–C(4)	115.0(6)
Ru(1)–Ru(2)–Se	56.2(1)	Ru(3)–C(32)–O(32)	160.6(6)
Ru(1)–Ru(3)–Se	55.3(1)	Ru(3)–C(31)–O(31)	157.9(5)
Ru(2)–Ru(1)–Se	56.2(1)	Ru(1)–C(32)–O(32)	122.1(5)
Ru(2)–Ru(3)–Se	55.0(1)	Ru(2)–C(31)–O(31)	122.9(5)
Ru(3)–Ru(1)–Se	54.5(1)		


(4) (M = Ru)
(6) (M = Fe)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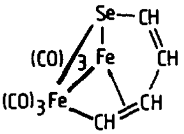
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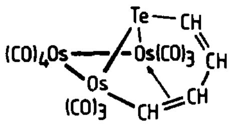
(8)

$(C_4H_4Se)]$, 7, related to compound 3. We do not understand why no Fe compound related to the ruthenium compound 5 nor a Ru compound related to the osmium and iron compounds 3 and 7 were isolated. We have looked for the tri-iron cluster analogous to the osmium cluster 1 that might have been the precurser of 7 as in the osmium case, but could find no compound of the kind.

Reactions of trinuclear clusters with tellurophene are believed to follow similar pathways to those with selenophene, although the reactions are more difficult to control and the same full range of products is not accessible. Nonetheless the few isolated products indicate that the same sort of chemistry as for selenophene is occurring, that is, metal atom insertion into Te–C bond. With $[Os_3(CO)_{10}(MeCN)_2]$ the only product isolated was $[Os_3(CO)_{10}(C_4H_4Te)]$, **8** which is spectroscopically (IR and NMR) very similar to cluster **1** and was characterised accordingly. With $[Ru_3(CO)_{10}(MeCN)_2]$, only $[Ru_2(CO)_6(C_4H_4)]$, **4** was obtained. Although no Te-containing product was isolated, it seems likely that a stepwise breaking of Te–C bonds had occurred to give the isolated metallacyclopentadiene complex **4**. The cluster $[Fe_3(CO)_{12}]$ also gave a dinuclear compound, $[Fe_2(CO)_6(C_4H_4)]$, **6** but again no Te-containing species was isolated. These results seem to indicate the difficulty of synthesising or isolating complexes with μ_3-Te as none was isolated from our work.

Experimental

The starting clusters $[M_3(CO)_{10}(MeCN)_2]$ (M = Ru [10] or Os [11]) were prepared as previously described. $[Fe_3(CO)_{12}]$, from Strem Chemicals Inc., was purified by column chromatography (SiO_2, petroleum ether, b.p. 40–60 °C, as eluant). Selenophene [2] and tellurophene [3] were synthesised by published methods and distilled prior to use. IR spectra (cyclohexane solutions) were recorded on a Nicolet 5DXC FTIR spectrometer and ^1H NMR spectra on a Bruker AM-300 spectrometer.

Syntheses

(a) Osmium with selenophene

Reaction of selenophene with triosmium clusters. A solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.250 g) and freshly distilled C_4H_4Se (1.0 cm^3) in cyclohexane (40 cm^3)

was refluxed under nitrogen for 20 min. Removal of the solvent under reduced pressure and TLC separation [SiO_2; eluant, petroleum ether (b.p. 40–60 °C)] gave four main bands. The fastest band gave the cluster [$Os_3(CO)_{10}(SeC_4H_4)$], **1** as yellow crystals (0.092 g, 35%) from cyclohexane (Found: C, 17.15; H, 0.4. $C_{14}H_4O_{10}Os_3Se$ calc.: C, 17.15; H, 0.4%). The second band gave [$Os_6(\mu\text{-}H)(\mu_3\text{-}Se)(\mu_5\text{-}C_4H_3)(CO)_{20}$], **2** as orange crystals (0.050 g, 20%), while the other two bands gave only traces of uncharacterisable material. Crystals of **2** suitable for X-ray structure determination were obtained by slow evaporation of a cyclohexane solution containing some methanol.

Thermolysis of compound 1. A solution of compound **1** (0.050 g) in n-octane (50 cm^3) was heated under reflux under nitrogen for 30 min. Removal of the solvent under reduced pressure and TLC separation as above gave three pale yellow bands yielding [$Os_2(CO)_6(C_4H_4Se)$], **3** (0.007 g, 20%), [$Os_3(CO)_{12}$] (0.010 g), and another uncharacterised cluster (0.010 g).

Reaction of 1 with [$Os_3(CO)_{10}(MeCN)_2$]. A solution of equimolar amounts of **1** and the bis-acetonitrile compound in cyclohexane was refluxed under nitrogen for 1 h. Work-up as above gave cluster **2** (13%), small amounts of the dinuclear compound **3** (6%), starting material **1**, and traces of other uncharacterised materials.

(b) Ruthenium with selenophene

A solution of [$Ru_3(CO)_{12}$] (0.200 g) and C_4H_4Se (1.0 cm^3) in dried THF (50 cm^3) was refluxed under nitrogen for 3.5 h. Removal of the solvent under reduced pressure and TLC separation [SiO_2; eluant, petroleum ether (b.p. 40–60 °C)] gave four bands of which only two contained sufficient material for characterisation. The two characterised compounds were the dinuclear compound [$Ru_2(CO)_6(\mu\text{-}C_4H_4)$], **4** as a yellow solid (0.045 g, 20%) and the tetranuclear cluster [$Ru_4(\mu_3\text{-}Se)(\mu\text{-}C_4H_4)(CO)_{11}$], **5** (0.060 g, 30%). Compound **5** was not obtained totally free from hydrocarbon impurity (Found: C, 23.5; H, 0.9. $C_{15}H_4O_{11}Ru_4Se$ calc.: C, 21.35; H, 0.5%) but a few crystals suitable for X-ray structure determination were obtained by slow evaporation of a cyclohexane solution.

(c) Iron with selenophene

A solution of [$Fe_3(CO)_{12}$] (0.220 g) and C_4H_4Se (1.0 cm^3) in cyclohexane (50 cm^3) was heated under reflux for 2.5 h under nitrogen. The brown residue after removal of the solvent was separated by TLC [SiO_2; eluant, pentane] to give [$Fe_2(CO)_6(C_4H_4Se)$], **7** as a yellow solid (0.075 g, 34%) [$Fe_2(CO)_6(C_4H_4)$], **6** (0.065 g, 29%) as orange needles, and some unreacted [$Fe_3(CO)_{12}$].

(d) Osmium with tellurophene

C_4H_4Te (0.5 cm^3) was added to a solution of [$Os_3(CO)_{10}(MeCN)_2$] (0.050 g) in dichloromethane (40 cm^3) at room temperature. After about 1 min the colour of the reaction mixture had changed from orange-yellow to deep orange-red. The solution was stirred for 30 min and TLC work-up gave only one orange band which was characterised as [$Os_3(CO)_{10}(C_4H_4Te)$], **8** as orange crystals (0.020 g, 38%).

(e) Ruthenium with tellurophene

When [$Ru_3(CO)_{10}(MeCN)_2$] (0.075 g) was added as a solid to a solution of C_4H_4Te (0.5 cm^3) in dichloromethane (20 cm^3), there was an immediate colour change to orange-red. The mixture was stirred at room temperature for 10 min. Removal of the solvent and TLC of the residue [SiO_2; eluant: pentane] gave one main product [$Ru_2(CO)_6(C_4H_4)$], **4** as an orange-yellow solid (0.030 g, 40%).

(f) Iron with tellurophene

C_4H_4Te (1.0 cm^3) was added to a refluxing solution of [$Fe_3(CO)_{12}$] (0.200 g) in cyclohexane (50 cm^3) and the reaction monitored by the IR spectrum until nearly all of the starting iron compound had been consumed. Removal of the solvent under reduced pressure and TLC [SiO_2; eluant: petroleum ether (b.p. 40–60 °C)] gave one main product characterised as [$Fe_2(CO)_6(C_4H_4)$], **6** as a yellow solid (0.050 g, 25%) and some unreacted iron starting material.

Table 4

Crystallographic data for compounds **2** and **5** [a]

Compound	**2**	**5**
Formula	$C_{24.5}H_6O_{20.5}Os_6Se$	$C_{15}H_4O_{11}Ru_4Se$
M, g mol^{-1}	1848.46	843.43
Colour	orange	yellow
Size, mm^3	0.06 × 0.18 × 0.40	0.15 × 0.20 × 0.30
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a, Å	9.095(1)	8.315(1)
b, Å	14.496(3)	14.012(3)
c, Å	14.600(5)	18.560(3)
α, ^{3}	76.18(2)	
β, °	86.68(2)	100.83(1)
γ, °	83.97(1)	
U, $Å^3$	1857.5(8)	2123.9(6)
Z	2	4
D_c, g cm^{-3}	3.30	2.64
μ(Mo-K_α), cm^{-1}	215.1	43.4
$F(000)$	1614	1568
No. of orientation reflections; 2θ range	30; 7 to 28	30; 11 to 28
Total no. data	6964	5435
No. unique data	6518	5218
No. data used in refinement	5301	4195
No. parameters in refinement	468	280
g in weighting scheme	0.00162	0.00050
R	0.0504	0.0388
R_w	0.0528	0.0379
Max. shift /e.s.d. in final least-squares refinement	0.004	0.002
Max. height in final difference Fourier/e$Å^{-3}$	3.3	0.70

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[a] Both structures: Nicolet R3v/m, Mo-K_α radiation, temp. 22 °C, $\lambda = 0.71073$ Å, scan mode ω–2θ, 2θ range: $5 \leqslant 2\theta \leqslant 50°$, data corrected for Lorentz and polarization effects and for absorption by the azimuthal scan method, rejection criterion: $F_o < 3\sigma(F_o)$, structure solution: direct methods, weight w in weighting scheme: $1/[\sigma^2(F) + gF^2]$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 5

Fractional atomic co-ordinates ($\times 10^4$) for the cluster $[Os_6H(Se)(C_4H_3)(CO)_{20}]\cdot CH_3OH$, **2**

	x	*y*	*z*
Os(1)	3101(1)	3367(1)	179(1)
Os(2)	321(1)	2659(1)	199(1)
Os(3)	2660(1)	1454(1)	1196(1)
Os(4)	4316(1)	3187(1)	−5222(1)
Os(5)	4974(1)	1906(1)	−3447(1)
Os(6)	1476(1)	3324(1)	−2902(1)
Se	4079(2)	3634(1)	−3620(1)
C(1)	2122(16)	2750(9)	−713(11)
C(2)	2676(18)	2565(11)	−1590(11)
C(3)	2148(17)	1880(10)	−2029(13)
C(4)	2706(21)	1751(12)	−2929(12)
C(11)	3697(24)	3763(13)	1308(20)
O(11)	4004(24)	4014(12)	1937(12)
C(12)	5039(20)	2995(14)	−160(14)
O(12)	6197(17)	2794(12)	−422(14)
C(13)	3013(21)	4617(12)	−582(16)
O(13)	2989(24)	5362(11)	−1055(12)
C(21)	−954(23)	2567(15)	1371(15)
O(21)	−1653(18)	2545(14)	1994(14)
C(22)	−557(20)	1638(13)	−162(17)
O(22)	−1036(17)	1052(10)	−318(12)
C(23)	−860(20)	3707(11)	−567(12)
O(23)	−1551(17)	4318(10)	−1032(11)
C(31)	2089(24)	2084(13)	2207(18)
O(31)	1801(20)	2436(12)	2825(11)
C(32)	3051(19)	848(12)	140(15)
O(32)	3296(18)	418(9)	−432(10)
C(33)	4671(21)	1139(14)	1591(14)
O(33)	5850(18)	928(12)	1796(13)
C(34)	1593(26)	412(16)	1825(17)
O(34)	926(20)	−209(11)	2215(14)
C(41)	5072(27)	2505(14)	−6157(14)
O(41)	5504(22)	2153(13)	−6712(14)
C(42)	6179(19)	3778(12)	−5333(13)
O(42)	7205(17)	4124(11)	−5408(13)
C(43)	3204(22)	4283(14)	−6014(14)
O(43)	2511(19)	4886(11)	−6470(12)
C(44)	2803(26)	2311(13)	−4969(14)
O(44)	1826(21)	1865(13)	−4946(12)
C(51)	5546(19)	1442(12)	−2186(13)
O(51)	5984(16)	1190(9)	−1451(11)
C(52)	6995(23)	2101(13)	−3880(14)
O(52)	8209(16)	2174(10)	−4071(12)
C(53)	5146(25)	668(13)	−3771(15)
O(53)	5228(25)	−29(11)	−3944(12)
C(61)	744(20)	3683(13)	−4154(13)
O(61)	277(16)	3958(13)	−4870(11)
C(62)	−486(22)	2999(12)	−2439(13)
O(62)	−1652(14)	2841(11)	−2205(11)
C(63)	1123(21)	4612(13)	−2736(16)
O(63)	859(20)	5336(11)	−2614(15)
O(1S)	8840(42)	582(23)	4294(28)
C(1S)	9947(58)	243(33)	4357(38)

Table 6

Fractional atomic co-ordinates ($\times 10^4$) for the cluster $[Ru_4(Se)(C_4H_4)(CO)_{11}]$, **5**

	x	y	z
Ru(1)	488(1)	6997(1)	4212(1)
Ru(2)	−1329(1)	7712(1)	5175(1)
Ru(3)	−2024(1)	8308(1)	3689(1)
Ru(4)	−3969(1)	9261(1)	2565(1)
Se	467(1)	8689(1)	4560(1)
C(1)	−2860(8)	9684(4)	3712(3)
C(2)	−2358(8)	10332(4)	3224(3)
C(3)	−1479(8)	9894(5)	2726(4)
C(4)	−1275(7)	8913(5)	2809(3)
C(11)	2292(8)	6659(5)	4934(3)
O(11)	3397(7)	6445(4)	5363(3)
C(12)	1748(8)	7042(4)	3436(3)
O(12)	2508(7)	7063(4)	2996(3)
C(13)	−305(8)	5722(5)	4125(3)
O(13)	−787(7)	4957(4)	4076(3)
C(21)	259(9)	7432(5)	6002(3)
O(21)	1203(8)	7252(5)	6504(3)
C(22)	−2490(12)	8641(6)	5645(4)
O(22)	−3197(11)	9182(5)	5913(4)
C(23)	−2443(8)	6549(5)	5295(3)
O(23)	−3013(7)	5837(4)	5395(3)
C(31)	−3778(8)	7937(5)	4187(3)
O(31)	−5080(6)	7860(5)	4284(3)
C(32)	−1983(8)	7088(4)	3197(4)
O(32)	−2296(8)	6501(4)	2773(3)
C(41)	−4732(9)	10085(5)	1736(4)
O(41)	−5161(7)	10555(4)	1249(3)
C(42)	−6085(8)	9268(5)	2827(4)
O(42)	−7312(7)	9269(4)	2991(4)
C(43)	−4482(8)	8125(5)	2010(4)
O(43)	−4784(7)	7445(4)	1680(3)

*Crystal structure determinations of **2** and **5***

A crystal of each compound was mounted on a glass fibre and attached to a goniometer on a Nicolet R3v/m four-circle diffractometer. Essential details of the crystal data, intensity data collections, structure solutions and refinements are given in Table 4. Only details particular to each determination are given below.

$[Os_6(\mu\text{-}H)(\mu\text{-}Se)(\mu_4\text{-}C_4H_3)(CO)_{20}]\cdot 0.5CH_3OH$, **2**

The orange crystal used was obtained from a cyclohexane solution containing a little methanol and appeared to contain 0.5 mol of CH_3OH per Os_6 cluster. The structure was solved by direct methods in the space group $P\bar{1}$ and was refined by alternating cycles of full-matrix least-squares and by difference Fourier synthesis. All non-H atoms were refined anisotropically and the H-atoms bonded to C(2) to C(4) were included in idealised positions (C–H = 0.96 Å and $U = 0.08$ Å^2). In the later stages of the refinement peaks between the clusters and well separated from them were observed and these were best refined as CH_3OH molecules with occupancies of 0.5; only the C and O atoms were included and these were refined isotropically. This solvent molecule was poorly defined and there were several weak peaks around these atoms in the difference map indicating possible disorder of the solvent molecule. Removal of this solvent molecule from the model altogether made very little difference to the quality of the refinement and the molecular parameters of the cluster were not significantly changed in doing so. We do not believe this difficulty has any bearing on the quality of the structure. Fractional atomic co-ordinates are given in Table 5.

[$Ru_4(Se)(C_4H_4)(CO)_{11}$], 5

A yellow crystal was obtained by evaporation of a cyclohexane solution. The structure was solved by direct methods in space group $P2_1/c$ and was refined by alternating cycles of full-matrix least-squares and by difference Fourier synthesis. All non-H atoms were refined anisotropically and the H-atoms were observed in the later stages of the refinement and included in the final model in idealised positions (C–H 0.96 Å and $U = 0.08$ Å^2) but their positions were not allowed to refine. Fractional atomic co-ordinates are given in Table 6.

All calculation were carried out using a MicroVax II computer running SHELXTL-PLUS [12].

Tables of H-atom coordinates, thermal parameters, full lists of bond lengths and angles and lists of structure factors are available from the authors.

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