Polyhedron Vol. 11, No. 9, pp. 1013–1021, 1992
Printed in Great Britain

0277–5387/92 $5.00+.00

ADDITION OF DISELENIDES RSe_2R TO $[Os_3(CO)_{10}(MeCN)_2]$ TO GIVE ISOMERS OF $[Os_3(\mu\text{-}SeR)_2(CO)_{10}]$

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(*Received* 4 *November* 1991; *accepted* 18 *December* 1991)

Abstract—We have re-examined the oxidative addition reactions of the diselenides RSeSeR (R = Me or Ph) with $[Os_3(CO)_{10}(MeCN)_2]$ and find that the initial products are clusters which we believe should be formulated as $[Os_3(\mu\text{-}RSe_2R)(CO)_{10}]$ [R = Ph (**1a**) and R = Me (**1b**)] with retained Se—Se bonds. Clusters **1** have only been partially characterized because they readily isomerize at room temperature or in contact with silica to the compounds $[Os_3(\mu\text{-}SeR)_2(CO)_{10}]$ [R = Ph (**2a**) or R = Me (**2b**)]. Isomers **2** have the RSe groups bridging different osmium–osmium edges, one of which is metal–metal bonded and the other is not; X-ray structures are reported for R = Me and Ph. The molecular structures of clusters **2a** and **2b** in the crystals differ only in the stereochemistry at one of the selenium atoms. Clusters **2** isomerize on heating to clusters **3** with both SeR bridges on the same osmium–osmium edge. Inversion at selenium is rapid in solution and invertomers of **2a** and **2b** were detected by NMR at low temperatures. Minor by-products of the thermal treatment of clusters **2** include $[Os_2(\mu\text{-}SeR)_2(CO)_6]$ (**4**), $[Os_3(\mu\text{-}Ph)(\mu\text{-}PhCO)(\mu_3\text{-}Se)_2(CO)_8]$ (**5**) and $[Os_3(\mu_3\text{-}Se)_2(CO)_9]$ (**6**).

Lewis *et al.* reported that the reaction of PhSeSePh with $[Os_3(CO)_{11}(MeCN)]$ follows the course shown in Scheme 1 and disulphides were shown to behave similarly.[1] The isomerization of the compound with non-equivalent SePh groups to the one with equivalent groups does not occur at room temperature but only on heating at 125°C and then with associated decomposition and formation of $[Os_3(\mu_3\text{-}Se)_2(CO)_9]$. The barrier to inversion at selenium would need to be very high to account for these observations. Furthermore, we would have expected the two isomers in Scheme 1 to have very similar IR spectra around 2000 cm^{-1}, but, since the reported data are quite different, we considered that the isomers might be structurally more different than indicated in Scheme 1. We have now re-examined this system using MeSeSeMe as well as PhSeSePh and $[Os_3(CO)_{10}(MeCN)_2]$, as well as $[Os_3(CO)_{11}(MeCN)]$, and find that although invertomers do exist, the main feature of the reported slow isomerization is a cluster edge-to-edge shift of SeR groups and that the kinetically controlled product of oxidative addition has the two SeR groups on different edges of the cluster. Inversion at selenium is sufficiently rapid in these systems to give NMR coalescence and is too rapid to account for the slow isomerization. A communication of aspects of this work has appeared.[2]

RESULTS AND DISCUSSION

Oxidative addition of diselenides to triosmium clusters

The cluster $[Os_3(CO)_{10}(MeCN)_2]$, or the monoacetonitrile compound $[Os_3(CO)_{11}(MeCN)]$, react

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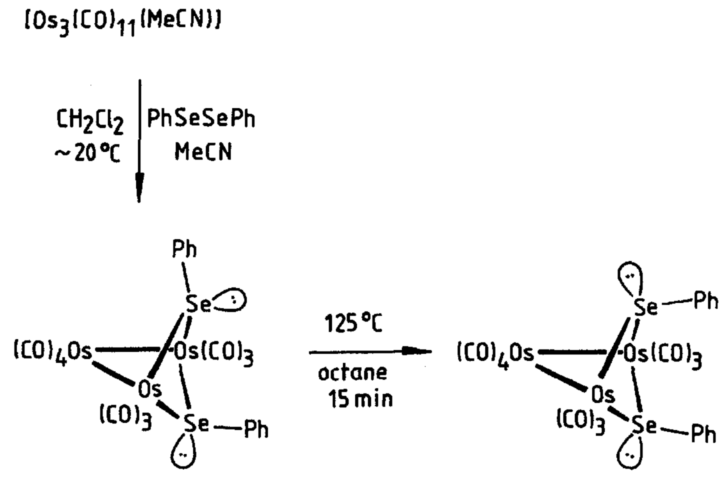


Scheme 1. The originally proposed reaction scheme for the oxidative addition of PhSeSePh to $[Os_3(CO)_{10}(MeCN)_2]$ and the subsequent isomerization.[1] A similar scheme was proposed for the corresponding reactions of disulphides.

with PhSeSePh (6 mol per mol of Os_3) in dichloromethane at room temperature to give, after TLC separation, the clusters $[Os_3(\mu\text{-}PhSe_2Ph)(CO)_{10}]$ (**1a**, 18%) and $[Os_3(\mu\text{-}SePh)_2(CO)_{10}]$ (**2a**, 53%) (yields from the mono-acetonitrile compound). Minor uncharacterized products were also obtained. Cluster **1a** is probably the primary product since it isomerizes in solution at room temperature to **2a**; cluster **2a** was isolated in 80% yield from an acetone solution of **1a** after 4 days at room temperature. This conversion rate is too low to account for the yields of **2a** in the original preparation and the conversion was found to occur more readily when solutions of **1a** are in contact with silica during the TLC work-up, this probably accounts for the good yields of cluster **2a**. It was not possible to obtain **1a** as totally pure because of this easy conversion. Clusters $[Os_3(\mu\text{-}MeSe_2Me)(CO)_{10}]$ (**1b**) and $[Os_3(\mu\text{-}SeMe)_2(CO)_{10}]$ (**2b**) were likewise obtained from the diselenide, MeSeSeMe. Clusters **1** probably contain bridging RSeSeR ligands although we have not yet confirmed this, and the isomerization of **1** to **2** is the oxidative addition step. Bridging RSeSeR ligands have been observed for platinum(IV) complexes but these are stable because they are incapable of oxidative addition.[3]

Characterization of oxidative addition products

IR and ^1H NMR spectroscopic data for compounds **1** and **2** are in Table 1. Both clusters **1b** and **2b** give two Me singlets in the ^1H NMR spectra at room temperature and, since the IR spectra of **1a** and **1b** are very similar and likewise those of **2a** and **2b**, the corresponding compounds are either isostructural or structurally very similar. Each of the four compounds contains non-equivalent SeR groups. Being doubtful about the structure proposed for the initial oxidative addition product from PhSeSePh,[1] we determined the single-crystal X-ray structures of both **2a** and **2b**. Cluster **2a** is the product reported to be formed initially in the reaction of PhSeSePh and, although it does have non-equivalent SePh groups as reported, the structure is not that in Scheme 1. The molecular structure of **2a** is shown in Fig. 1 and selected bond lengths and angles are given in Table 2. We were unable to obtain a good quality single crystal of **2b** and the one selected for structure determination diffracted only weakly and the structure is of poor quality. In spite of this we believe that the molecular shape obtained is reliable. One of the two independent molecules in the unit cell is illustrated in Fig. 2 and selected bond lengths and angles are given in Table 3.

The structures of **2a** and **2b** are very similar except for the configurations at the SeR groups which bridge the open Os···Os edges of the clusters. There are two Os—Os bonds as expected for electron-precise compounds and the SeR groups are found to bridge one closed and one open edge. The SeR group along the closed edge is associated with Os—Os distances of 2.827(1) Å for **2a** and 2.844(3) and 2.840(3) Å for **2b**, which are somewhat shorter than the unbridged edges which are 2.947(1) Å for **2a** and 2.945(3) and 2.962(4) Å for **2b**. The SeR group on the closed edge lies well above the Os_3 plane and the configurations at the corresponding selenium atoms are the same in both compounds. We believe that an inversion at this selenium atom would position the R group rather close to an axial

Table 1. Spectroscopic data for cluster derivatives of PhSeSePh and MeSeSeMe

Compound	$\nu(CO)$[a] (cm^{-1})	^1H NMR[b]
$[Os_3(Se_2Ph_2)(CO)_{10}]$ **1a**	2123w, 2098m, 2044vs, 2010s, 1997sh, 1976sh, 1963w.	7.15–7.73 (m, Ph)[c]
$[Os_3(Se_2Me_2)(CO)_{10}]$ **1b**	2122w, 2094m, 2039vs, 2009s, 2004sh, 1993w, 1975w, 1965sh, 1960w.	2.02 (s, Me), 1.61 (s, Me)
$[Os_3(SePh)_2(CO)_{10}]$ **2a**	2112m, 2065s, 2043s, 2032vs, 2013m, 1991m, 1976m, 1965w, 1958w.	7.66 (m, *ortho*), 7.57 (m, *ortho*), 7.25–7.40 (m, *meta*, *para*)
$[Os_3(SeMe)_2(CO)_{10}]$ **2b**	2109m, 2060s, 2039s, 2029vs, 2013m, 1985s, 1976s, 1958m.	2.65 (s, Me),[d] 2.28 (s, Me)[d]
$[Os_3(SePh)_2(CO)_{10}]$ **3a**	2104m, 2063s, 2056sh, 2019vs, 2000sh, 1988m, 1982sh.	7.49 (m, *ortho*), 7.23 (m, *para*), 7.12 (m, *meta*)
$[Os_3(SeMe)_2(CO)_{10}]$ **3b**	2102m, 2061s, 2053m, 2015vs, 1996w, 1986s, 1978w.	2.60 (s, Me)
$[Os_2(SePh)_2(CO)_6]$ **4a**	2080m, 2050vs, 2000vs, 1989s, 1980m.	7.48 (m, Ph), 7.25 (m, Ph)
$[Os_2(SeMe)_2(CO)_6]$ **4b**	2077m, 2047vs, 1993m,sh, 1988s, 1977w,sh.	2.13 (s, m, Me), 2.12 (s, Me)
$[Os_3(Ph)(PhCO)(Se)_2(CO)_8]$ **5**	2102s, 2080vs, 2027vs, 2022vs, 2018sh, 2006s, 1990m, 1966s.	8.27 (m, *ortho*), 7.62 (m, *ortho*), 7.50 (m, *para*), 7.45 (m, *para*), 7.37 (m, *meta*), 7.24 (m, *meta*)
$[Os_3(Se)_2(CO)_9]$ **6**	2075vs, 2055s, 2032vw, 2014vs.	

[a] Recorded in cyclohexane.

[b] Recorded at 300 MHz at 297 K; compounds **1a**, **3a**, **4a** in CD_3COCD_3; **2a**, **2b**, **3b**, **4b**, **5** in CD_2Cl_2; and **1b** in C_6D_6.

[c] Several multiplets in this range indicate non-equivalent Ph groups and/or the presence of isomers.

[d] At −33°C, major isomer: δ 2.62, 2.30; minor isomer: δ 2.64, 2.10.

Table 2. Selected bond lengths (Å) and angles (°) for the compound $[Os_3(\mu\text{-}SePh)_2(CO)_{10}]$ (**2a**)

Os(1)—Os(3)	2.947(1)	Os(2)—Se(1)	2.531(2)
Os(2)—Os(3)	2.827(1)	Os(3)—Se(1)	2.532(2)
Os(1)···Os(2)	3.988(1)	Se(1)—C(41)	1.92(2)
Os(1)—Se(2)	2.553(2)	Se(2)—C(51)	1.95(2)
Os(2)—Se(2)	2.562(2)		
Os(1)—Os(3)—Os(2)	87.3(1)	Os(2)—Os(3)—Se(1)	56.0(1)
Os(1)—Se(2)—Os(2)	102.5(1)	Os(3)—Os(2)—Se(1)	56.1(1)
Os(2)—Se(1)—Os(3)	67.9(1)	Os(1)—Se(2)—C(51)	107.8(5)
Os(3)—Os(1)—Se(2)	81.8(1)	Os(2)—Se(2)—C(51)	112.0(5)
Os(3)—Os(2)—Se(2)	84.0(1)	Os(2)—Se(1)—C(41)	111.2(5)
Os(1)—Os(3)—Se(1)	91.3(1)	Os(3)—Se(1)—C(41)	107.2(4)

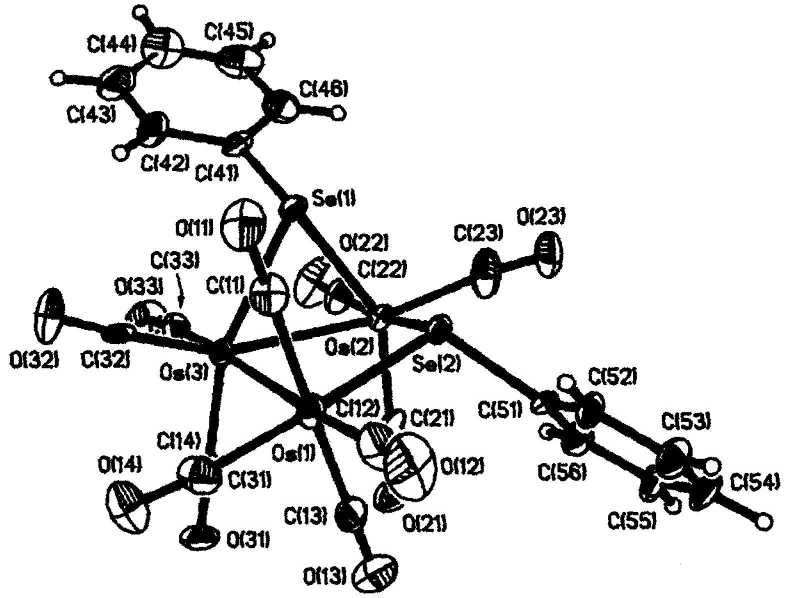


Fig. 1. Molecular structure of the cluster $[Os_3(\mu\text{-SePh})_2(CO)_{10}]$, isomer **2a**.

CO ligand of the $Os(CO)_4$ group so that the alternative configuration generated in this way would be significantly less stable. No evidence for this alternative configuration was obtained. However, there is little to choose between the two alternative configurations at the SeR groups across the open edges of the cluster. Cluster **2a** has the Ph group at Se(2) *exo* to the other SePh group, whereas cluster **2b** has the Me groups at Se(2) and Se(4) *endo* to the other SeMe groups in the molecules. We cannot identify steric reasons why these different configurations should be obtained but in solution isomers with the different configurations are similar in energy (see next paragraph). The different configurations have some minor structural consequences: Se(2) in **2a** is above the Os_3 plane on the side of Se(1) by 0.646 Å, whereas the corresponding selenium atoms in **2b**, Se(2) and Se(4), are only 0.286 and 0.152 Å above the Os_3 plane.

Re-examining the ^1H NMR spectrum of **2b**, it

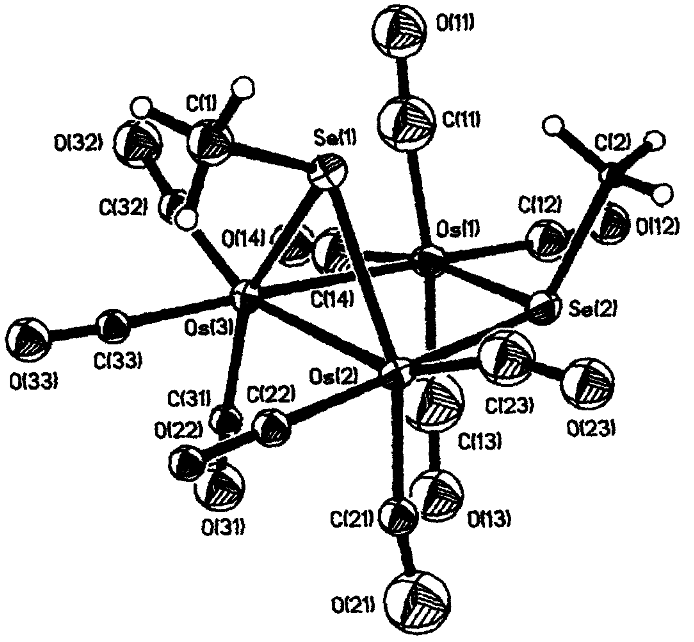


Fig. 2. Molecular structure of one of the two independent molecules in the unit cell of the cluster $[Os_3(\mu\text{-SeMe})_2(CO)_{10}]$, isomer **2b**. The other molecule containing the Os(4)Os(5)Os(6) set of atoms is enantiomeric with this.

Table 3. Selected bond lengths (Å) and angles (°) for the compound $[Os_3(\mu\text{-}SeMe)_2(CO)_{10}]$ (**2b**)

Molecule 1		Molecule 2	
Os(1)—Os(3)	2.945(3)	Os(4)—Os(6)	2.962(3)
Os(2)—Os(3)	2.845(3)	Os(5)—Os(6)	2.840(3)
Os(1)···Os(2)	3.978(3)	Os(4)···Os(5)	4.009(3)
Os(1)—Se(2)	2.562(6)	Os(4)—Se(4)	2.556(6)
Os(2)—Se(2)	2.548(6)	Os(5)—Se(4)	2.557(6)
Os(2)—Se(1)	2.507(8)	Os(5)—Se(3)	2.512(8)
Os(3)—Se(1)	2.534(8)	Os(6)—Se(3)	2.523(8)
Se(1)—C(1)	1.99(5)	Se(3)—C(3)	1.91(7)
Se(2)—C(2)	1.95(6)	Se(4)—C(4)	2.02(8)
Os(1)—Os(3)—Os(2)	86.8(1)	Os(4)—Os(6)—Os(5)	87.4(1)
Os(1)—Se(2)—Os(2)	102.3(2)	Os(4)—Se(4)—Os(5)	103.2(2)
Os(2)—Se(1)—Os(3)	68.7(2)	Os(5)—Se(3)—Os(6)	68.7(2)
Os(3)—Os(1)—Se(2)	83.9(1)	Os(6)—Os(4)—Se(4)	83.3(2)
Os(3)—Os(2)—Se(2)	86.2(2)	Os(6)—Os(5)—Se(4)	85.8(1)
Os(1)—Os(3)—Se(1)	90.4(2)	Os(4)—Os(6)—Se(3)	88.8(2)
Os(2)—Os(3)—Se(1)	55.2(2)	Os(5)—Os(6)—Se(3)	55.5(2)
Os(3)—Os(2)—Se(1)	56.1(2)	Os(6)—Os(5)—Se(3)	55.8(2)
Os(1)—Se(2)—C(2)	111(1)	Os(4)—Se(4)—C(4)	107(2)
Os(2)—Se(2)—C(2)	104(1)	Os(5)—Se(4)—C(4)	109(2)
Os(2)—Se(1)—C(1)	106(2)	Os(5)—Se(3)—C(3)	110(3)
Os(3)—Se(1)—C(1)	111(2)	Os(6)—Se(3)—C(3)	113(3)

was clear that one of the Me signals was broad at room temperature. As the temperature was lowered the spectrum resolved into four singlets corresponding to a major and a minor isomer which are in equilibrium (see Fig. 3). Almost certainly these exchanging isomers have configurations at the SeMe group on the open edge corresponding to the different configurations found for **2a** and **2b**, respectively, in the crystals. Scheme 2 shows the inversion process for **2b** leading to isomer interconversion and NMR coalescence. Inversion at both selenium centres would have given four isomers but only two were obtained, consistent with inversion at one centre only. We have also examined the variable temperature NMR spectra of **2a** to see whether isomerism occurs in that case as well. Two well-resolved multiplets for the *ortho* hydrogen atoms of the different SePh groups are observed at δ 7.66 and 7.57 at 25°C but these broaden at −60°C and separate out at −80°C into different multiplets for a major and a minor isomer. The coalscence temperature is lower for **2a** than for **2b** but we offer the same explanation for the variable temperature ^1H NMR spectra, except that the major and minor isomers almost certainly have reversed configurations.

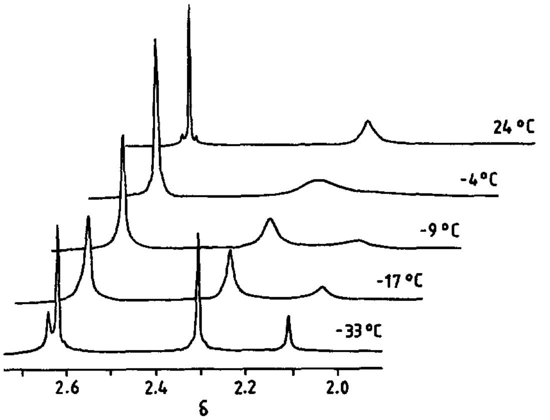
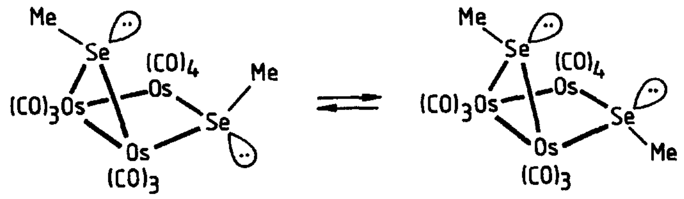


Fig. 3. ^1H NMR spectrum of the cluster $[Os_3(\mu\text{-}SeMe)_2(CO)_{10}]$ (**2b**) recorded in CD_2Cl_2 at 300 MHz.

The mechanism of oxidative addition of halogens (X_2) to triosmium clusters is still not fully resolved, but the reaction appears to occur via ionic intermediates. Thus, intermediates probably of the kind $[Os_3X(CO)_{12}]X$ lead, by coordination of the halide and ring opening, to neutral products $[Os_3X_2(CO)_{12}]$.[4] Subsequent thermal decarbonylation leads to $[Os_3X_2(CO)_{10}]$ with the X ligands bridging the same pair of osmium atoms. We believe that the formation of clusters **1** and **2** occurs in a different way to this. Unfortunately, we have no structural evidence for clusters **1** except that they are not electrolytes and that the SeR groups



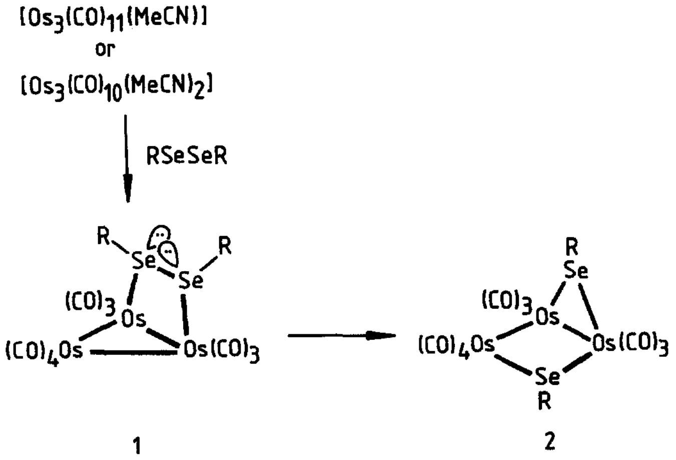
Scheme 2. The rapid isomerization process leading to the ^{1}H NMR spectra shown in Fig. 3.

within each molecule are different, but we believe that the Se—Se bond is still intact. We are still trying to obtain crystals of **1a**, **1b**, or some other suitable related cluster to establish this point crystallographically and to obtain bigger and purer samples to make more detailed NMR studies. At this stage we consider that the mechanism in Scheme 3 is appropriate for the formation of clusters **1** and **2**. Isomers with equivalent SeR groups bridging the same cluster edge are not formed at room temperature in the oxidative addition process.

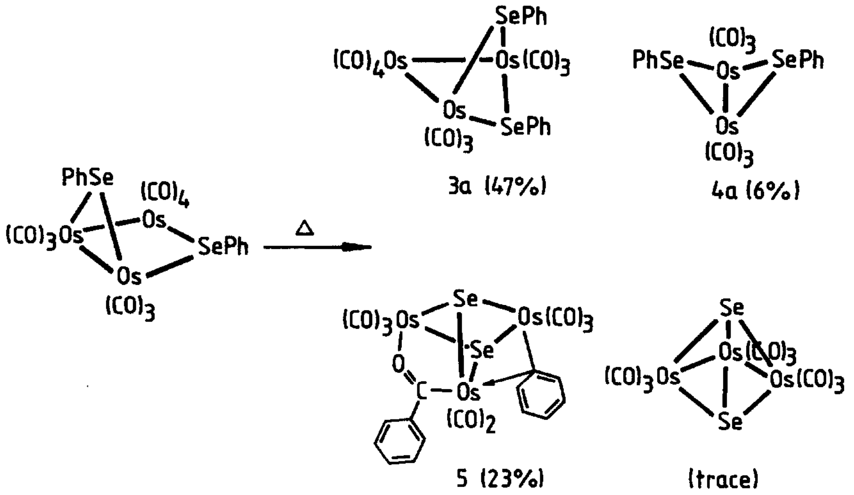
Thermal treatment of clusters 2

Mixtures were obtained from the treatment of clusters **2a** and **2b** in refluxing cyclohexane (Scheme 4). Products $[Os_3(\mu\text{-SeR})_2(CO)_{10}]$ [R = Ph (**3a**) and R = Me (**3b**)], isomeric with **2a** and **2b**, respectively, were the major products (47 and 59% yields, respectively). We did not find very low yields as already reported.[1] Small amounts of the dinuclear products $[Os_2(\mu\text{-SeR})_2(CO)_6]$ [R = Ph (**4a**, 5%) and R = Me (**4b**, 9%)] were formed by extrusion of $Os(CO)_4$ groups from either clusters **2** and **3**. These dinuclear compounds are of a very well-studied class of compounds of the type $[M_2(\mu\text{-ER})_2(CO)_6]$ (M = Fe, Ru, Os; E = O, S, Se)[5] and we did not study these any further. Another product from **2a** was the very interesting compound with the apparent formula $[Os_3(SePh)_2(CO)_9]$, which we showed was the triple oxidative addition product $[Os_3(\mu\text{-Ph})(\mu\text{-PhCO})(\mu_3\text{-Se})_2(CO)_8]$ (**5**) and the crystal structure of which we have described in a communication.[2] This is an osmium(II) compound without any metal–metal bonds. Only when we raised the temperature of the thermolysis (refluxing octane, 125°C) did we obtain traces of the known compound $[Os_3(\mu\text{-Se})_2(CO)_9]$ (**6**).[6]

The main thermolysis products are the isomers **3a** and **3b** which are more stable than the kinetic products **2a** and **2b**. Cluster **3a** is the same compound as reported earlier[1] and we believe that the proposed structure is correct. The IR spectrum around 2000 cm^{-1} is very similar to that of $[Os_3(\mu\text{-OMe})_2(CO)_{10}]$ of known structure.[7] Although the SeR groups in **3a** and **3b** are equivalent in the NMR spectra even down to −70°C and hence the structure in Scheme 4 is preferred, we cannot be sure that this observation is not the result of a very rapid inversion at selenium (see example above) in an isomer or isomers of lower symmetry. However, the overall geometry with SeR groups bridging the same pair of osmium atoms is as clearly established as it could be in the absence of a crystal structure. Thus, the isomerization of **2** to **3** requires



Scheme 3. Speculated mechanism for the formation of clusters **1** and **2** in the reactions of RSeSeR.



Scheme 4. Thermolysis products from $[Os_3(\mu\text{-}SePh)_2(CO)_{10}]$ in refluxing cyclohexane or refluxing octane.

the migration of an SeR group from one cluster edge to another by a slow process of an unknown mechanism.

EXPERIMENTAL

The compounds $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(CO)_{10}(MeCN)_2]$ were prepared as reported.[8] Diphenyl and dimethyl diselenides were used as purchased from Aldrich plc.

Reaction of $[Os_3(CO)_{11}(MeCN)]$ *with* PhSeSePh

A solution of the acetonitrile compound (0.200 g) in dichloromethane (30 cm^3) was stirred with an excess of diphenyldiselenide (0.400 g, 6 mol per mol of Os_3) for 2 h at room temperature under nitrogen. The IR spectrum showed that there was no starting cluster remaining after this time. Removal of the solvent under reduced pressure and separation of the residue by TLC [SiO_2; eluant: light petroleum (b.p. < 40°C)/dichloromethane (v/v 4/1)] gave three yellow bands. These gave $[Os_3(\mu\text{-}PhSe_2Ph)(CO)_{10}]$ (**1a**) (0.035 g, 18%) as a yellow powder, $[Os_3(\mu\text{-}SePh)_2(CO)_{10}]$ (**2a**) (0.105 g, 53%) as yellow crystals, and the third band gave a small amount of unidentified product. Using $[Os_3(CO)_{10}(MeCN)_2]$ in a similar preparation also gave clusters **1a** and **2a** as well as three uncharacterized compounds in small amounts.

Conversion of cluster 1a *to* 2a

A solution of cluster **1a** in acetone which was stirred at room temperature for 4 days gave, after TLC work-up as above, some starting cluster, several very minor uncharacterized compounds and cluster **2a** (80%).

Thermal treatment of compound 2a

The treatment of **2a** in refluxing octane for 15 min was reported to give $[Os_3(\mu\text{-}Se)_2(CO)_9]$ (13%) and $[Os_3(\mu\text{-}SePh)_2(CO)_{10}]$ (**3a**) in only 3% yield.[1] We adopted milder conditions. A solution of compound **2a** (0.060 g) in cyclohexane (60 cm^3) was heated under reflux under nitrogen for 8 h. By this time there were no more changes in the IR spectrum of the reaction solution. Removal of the solvent and TLC work-up as above gave $[Os_2(\mu\text{-}SePh)_2(CO)_6]$ (**4a**) (0.003 g, 6%) as a colourless solid, $[Os_3(\mu\text{-}SePh)_2(CO)_{10}]$ (**3a**) (0.028 g, 47%) as yellow crystals and $[Os_3(\mu\text{-}Ph)(\mu\text{-}PhCO)(\mu_3\text{-}Se)_2(CO)_8]$ (**5**) (0.013 g, 23%) as yellow crystals. Other bands gave traces of uncharacterized materials. Carrying out the reaction in refluxing octane as reported[1] gave in our hands the compounds: **4a** (5%), **3a** (44%), **5** (13%), as well as a trace of $[Os_3(\mu\text{-}Se)_2(CO)_9]$ (**6**).

Reaction of $[Os_3(CO)_{11}(MeCN)]$ *with* $MeSe_2Me$

A solution of the acetonitrile compound (0.100 g) in dichloromethane (30 cm^3) with an excess of dimethyldiselenide (0.040 cm^3, 4 mol per mol of Os_3) was stirred at room temperature under nitrogen, following the reaction by TLC. The solution changed from yellow–orange to deep orange and when the reaction appeared to be complete, the solvent was removed and the residue was separated by TLC [SiO_2; eluant: light petroleum (b.p. < 40°C)/dichloromethane (4 : 1 v/v)]. The lowest band gave the compound $[Os_3(\mu\text{-}MeSe_2Me)(CO)_{10}]$ (**1b**) (0.043 g, 43%) as a yellow solid. The middle band gave $[Os_3(\mu\text{-}SeMe)_2(CO)_{10}]$ (**2b**) (0.017 g, 18%) as yellow–orange crystals, while the top band gave $[Os_3(\mu\text{-}SeMe)_2(CO)_{10}]$ (**3b**) (0.004 g, 4%) as a yellow solid. Similar results were obtained using $[Os_3(CO)_{10}(MeCN)_2]$ as the starting material.

Thermal treatment of cluster **2b**

A solution of **2b** (0.078 g) in cyclohexane (40 cm^3) was heated under reflux under nitrogen for 1 h. Similar TLC work-up using the eluant, light petroleum (b.p. < 40°C)/dichloromethane (9 : 1 v/v), gave four bands, three of which contained enough material to be characterized as cluster **3b** (0.046 g, 59%), cluster **4b** (0.007 g, 9%) and some starting cluster **2b** (0.009 g, 11%).

Single-crystal X-ray structure determinations for clusters **2a** *and* **2b**

General conditions. Details of the crystal data, data collections, structure solutions and refinements are given in Table 4. A good quality single yellow crystal of compound **2a** and a rather poor quality weakly-diffracting crystal of **2b** were fixed to glass fibres and mounted on a goniometer on a Nicolet R3v/m diffractometer operating with Mo-K_α radiation (λ = 0.71073 Å). Unit cells were deter-

Table 4. Crystallographic data for compounds $[Os_3(\mu\text{-}SeR)_2(CO)_{10}]$ where R = Ph (**2a**) and R = Me (**2b**)[a]

	Compound **2a**	Compound **2b**
Formula	$C_{22}H_{10}O_{10}Os_3Se_2$	$C_{12}H_6O_{10}Os_3Se_2$
M (g mol^{-1})	1162.84	1038.70
Colour	Yellow	Yellow
Crystal size (mm^3)	0.20 × 0.30 × 0.04	0.10 × 0.13 × 0.30
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.349(2)	8.425(3)
b (Å)	12.603(2)	9.657(3)
c (Å)	13.418(3)	27.06(1)
α (°)	113.81(2)	91.44(4)
β (°)	98.06(2)	91.83(3)
γ (°)	102.92(1)	114.12(3)
U ($Å^3$)	1361.9(5)	2007(1)
Z	2	4
D_c (g cm^{-3})	2.84	3.44
μ(Mo-K_α) (cm^{-1})	165	226
F(000)	1036	1816
No. orientation reflections; 2θ range	28; $14 \leqslant 2\theta \leqslant 30°$	30; $10 \leqslant 2\theta \leqslant 24°$
Scan mode	ω–2θ	ω
Total data	6614	7406
Unique data	6237	6900
Reflections used	4608	3352
Rejection criterion	$I_o \leqslant 3\sigma(I_o)$	$I_o \leqslant 5\sigma(I_o)$
Parameters refined	334	267
R^b	0.0515	0.0864
$R_w{}^c$	0.0475	0.0887
g	0.00010	0.0010
Max. shift/e.s.d. in final refinement	0.001	0.04
Largest residual peak (e $Å^{-3}$)	3.59	3.76

[a] Data common to both compounds: Mo radiation (λ = 0.71073 Å); Nicolet R3m/v diffractometer, intensity data were collected at 23°C in the range $5 \leqslant 2\theta \leqslant 50$ and were corrected for decay based on intensities of three check reflections, for Lorentz and polarization effects, and for absorption by the azimuthal scan method; direct methods structure solution.

[b] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$.

[c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = [\sigma^2(F_o) + g(F_o{}^2)]^{-1}$.

mined by auto-indexing 28 orientation reflections in the range $14 \leqslant 2\theta \leqslant 30°$ for **2a** and 30 in the range $10 \leqslant 2\theta \leqslant 24°$ for **2b**. Intensity data were measured at 20°C and corrected for Lorentz and polarization effects and for minimal decay using the intensities of three standard reflections measured throughout the data collection. Empirical absorption corrections were applied by the azimuthal scan method.

Compound **2a**. In the refinement all non-hydrogen atoms were treated anisotropically and hydrogen atoms were included in idealized positions and allowed to ride on the corresponding carbon atoms of the phenyl rings (C—H 0.96 Å, $U = 0.08$ Å^2) to give a final $R = 0.0515$ and $R_w = 0.0475$, where $R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ and $w = 1/[\sigma^2(F_o)+0.00010(F_o)^2]$.

Compound **2b**. Only the osmium and the selenium atoms were refined anisotropically and hydrogen atoms were included in the model in idealized positions as above. There are two enantiomerically related and independent molecules in the unit cell. The model gave a final $R = 0.0864$ and $R_w = 0.0887$, where $R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ and $w = 1/[\sigma^2(F_o)+0.0010(F_o)^2]$.

Structures were solved and refined using SHELXTL PLUS[9] on a MicroVax II computer. Atomic coordinates, full tables of bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements—We thank the SERC for a grant for the Nicolet diffractometer and for a research studentship (for D.J.W.).

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