Triple Oxidative Addition of the Diselenide PhSePh to the Cluster $[Os_3(CO)_{10}(MeCN)_2]$ to give the Osmium(II) Compound $[Os_3(\mu\text{-}Ph)(\mu\text{-}PhCO)(\mu_3\text{-}Se)_2(CO)_8]$

Alejandro J. Arce,[*a] **Pilar Arrojo,**[a] **Antony J. Deeming**[*b] **and Ysaura De Sanctis**[a]

[a] *Chemistry Centre, Instituto Venezolano de Investigaciones Cientificas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela*

[b] *Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK*

The diselenide PhSeSePh reacts with $[Os_3(CO)_{10}(MeCN)_2]$ to give isomers of $[Os_3(CO)_{10}(\mu\text{-}SePh)_2]$ which convert thermally to a compound of apparent formula $[Os_3(CO)_9(SePh)_2]$, which was shown by X-ray diffraction to be the triple oxidative addition product $[Os_3(\mu\text{-}Ph)(\mu\text{-}PhCO)(\mu_3\text{-}Se)_2(CO)_8]$ in which the diselenide has cleaved into four separate ligand fragments as all three osmium(0) atoms are oxidised to osmium(II) atoms by an overall six-electron oxidation.

Oxidative addition of PhSeSePh to $[Os_3(CO)_{10}(MeCN)_2]$ was reported to occur with Se–Se bond cleavage to give one isomer of $[Os_3(CO)_{10}(SePh)_2]$ which converts thermally to another.[1] These isomers were thought to be structurally very similar with both SePh ligands bridging the same Os–Os edge of the cluster as illustrated for compound **3** in Scheme 1 and to be related simply by inversion at the selenium atoms.[1] We have now confirmed that $[Os_3(CO)_{10}(MeCN)_2]$ or $[Os_3(CO)_{11}(MeCN)]$ react at room temperature with PhSeSePh in dichloromethane to give two isomers of $[Os_3(CO)_{10}(SePh)_2]$, **1** (18%) (not reported previously) and **2** (53%) (previously reported as the first isomer formed). Isomer **1** readily converts to **2** on standing in solution at room temperature and we have been unable to characterise it fully. It is possible that **1** retains a Se–Se bond but we have confirmed that this bond is broken in cluster **2** which has been fully characterised spectroscopically† and by X-ray diffraction (structure to be reported elsewhere[2]). Isomer **2** does not have the proposed structure; the SePh ligands bridge different edges of the cluster (Scheme 1).

Isomer **2** converts thermally in refluxing cyclohexane to isomer **3** (47%) as reported previously,[1] traces of $[Os_2(CO)_6(SePh)_2]$ (6%) and other uncharacterised species, together with a compound with the apparent formula $[Os_3(CO)_9(SePh)_2]$, **4** (23%). The ^{1}H NMR spectrum of **4** shows that the two Ph groups are non-equivalent† but their mode of bonding was only established by a single-crystal X-ray structure determination (Fig. 1 shows molecule *A* of the two independent but closely similar molecules *A* and *B* in the unit cell).‡ There are no Os–Os bonds [Os(1) · · · Os(2) 3.449(1), Os(1) · · · Os(3) 3.195(1) and Os(2) · · · Os(3) 3.758(1) Å]; the three Os atoms are linked by two μ_3-Se atoms and by doubly bridging Ph and PhCO ligands. The PhCO ligand is a normal 3e-donating acyl bridge formed by Se–Ph bond cleavage and Ph migration to CO. It is coordinated through the acyl carbon

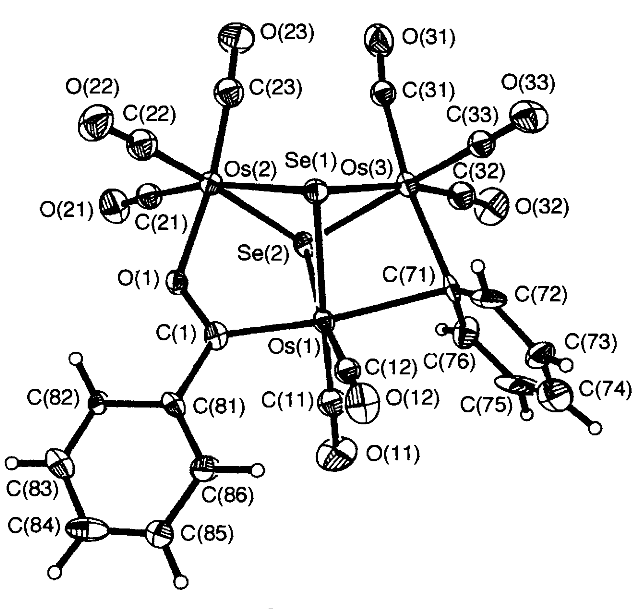
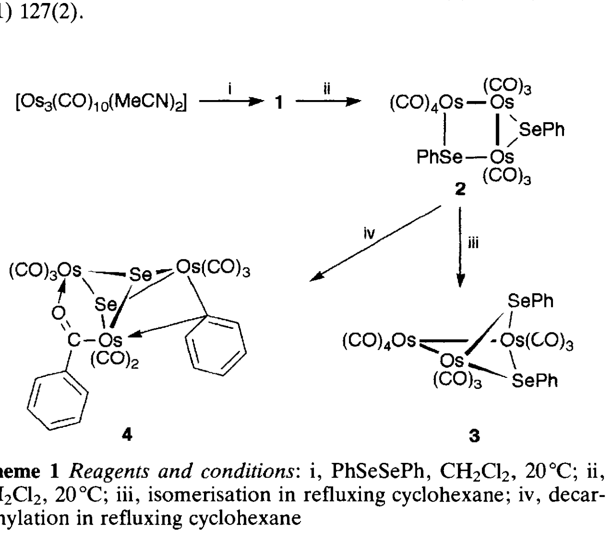


Fig. 1 Molecular structure of $[Os_3(\mu\text{-}Ph)\ (\mu\text{-}PhCO)\ (\mu_3\text{-}Se)_2(CO)_8]$ **4**. Selected bond lengths (Å) and angles (°): Os(1)–Se(1) 2.590(3), Os(2)–Se(1) 2.574(3), Os(3)–Se(1) 2.594(3), Os(1)–Se(2) 2.576(2), Os(2)–Se(2) 2.577(3), Os(3)–Se(2) 2.579(3), Os(3)–C(71) 2.24(2), Os(1)–C(71) 2.51(2), Os(1)–C(1) 2.03(2), Os(2)–O(1) 2.08(1), C(1)–O(1) 1.26(3), Os(1)–C(71)–Os(3) 84.3(8), Os(3)–C(71)–C(72) 121(2), Os(3)–C(71)–C(76) 116(1), Os(1)–C(71)–C(72) 105(2), Os(1)–C(71)–C(76) 101(2), Os(1)–C(1)–O(1) 118(2), Os(2)–O(1)–C(1) 127(2).



Scheme 1 *Reagents and conditions*: i, PhSeSePh, CH_2Cl_2, 20 °C; ii, CH_2Cl_2, 20 °C; iii, isomerisation in refluxing cyclohexane; iv, decarbonylation in refluxing cyclohexane

---

† *Spectroscopic data*: **1**, IR ν(CO)/cm^{-1} (cyclohexane): 2122w, 2098m, 2044vs, 2010s, 1997sh, 1976sh, 1963w; ^{1}H NMR (300 MHz, CD_3COCD_3): δ 7.65m, 7.35m, 7.18m; **2**, IR ν(CO)/cm^{-1} (cyclohexane): 2112m, 2065s, 2043s, 2032vs, 2013m, 2002m, 1991m, 1976m, 1965m, 1958w; ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.66m, 7.33m, 7.26m; **3** IR ν(CO)/cm^{-1} (cyclohexane): 2104m, 2063s, 2056sh, 2019vs, 2000sh, 1988m, 1982sh, ^{1}H NMR (300 MHz, CD_3COCD_3): δ 7.50m, 7.22m, 7.12m; **4**: IR ν(CO)/cm^{-1} (cyclohexane): 2102s, 2080vs, 2027vs, 2022vs, 2018sh, 2006s, 1990m, 1966s, ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.26, 7.61 (*ortho*), 7.50, 7.45 (*para*), 7.37, 7.22 (*meta*).

‡ *Crystal data for* $[Os_3(Ph)(PhCO)(Se)_2(CO)_9]$, **4**: yellow crystal, $C_{21}H_{10}O_9Os_3Se_2$, $M = 1134.83$ g mol^{-1}, size = 0.33 × 0.45 × 0.27 mm^3, triclinic, $P\bar{1}$, $a = 8.808(3)$, $b = 15.346(4)$, $c = 20.108(5)$ Å, $\alpha = 105.23(2)$, $\beta = 99.52(2)$, $\gamma = 102.59(2)°$, $U = 2489(1)$ Å^3, $Z = 4$, $D_c = 3.03$ g cm^{-3}, μ(Mo-Kα) = 180 cm^{-1}, $F(000) = 2016$. Nicolet R3v/m diffractometer, Mo-radiation ($\lambda = 0.70713$ Å), room temperature data corrected empirically for absorption. Direct methods, $R = 0.0513$, $R' = 0.0530$, where $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, after refinement of 5541 data with $I_o > 3\sigma(I_o)$ with $5 \leqslant 2\theta \leqslant 50°$. All non-H atoms except the carbonyl C-atoms were refined anisotropically with H-atoms included in idealised positions (C–H 0.96 Å, $U = 0.08$ Å^3). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

atom C(1) to Os(1) and through the oxygen atom O(1) to Os(2). The Ph group is also bridging and could be regarded as σ-bonded through C(71) to Os(3) and through a long-range π-interaction through C(71) to Os(1). Although the Os(1)–C(71) distance is very long compared with Os(3)–C(71) [2.51(2) compared with 2.24(2) Å], atom C(71) occupies a normal octahedral coordination site at Os(1) and the Ph group should be considered a 3e-donor. The metal atoms are all octahedral diamagnetic d^6 osmium(II) atoms. Overall the triple oxidative addition of PhSeSePh into four units has led to a six-electron oxidation of three osmium(0) to three osmium(II) atoms. The compound is electron-precise without any requirement for metal–metal bonds. In total the Ph and PhCO groups and the two Se atoms donate 14 electrons counting these as radicals (20 electrons counting them as anions). We do not believe that such extensive fragmentation in an oxidative addition reaction has been reported previously. Whereas Se–C and S–C bond cleavage at transition metal centres is common, the incorporation of the organo fragments from the cleavage into the metal oxidative addition product is exceptional.

We thank the SERC for a grant towards the diffractometer.

Received, 18th July 1991; Com. 1/03662I

References

1 P. V. Broadhurst, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1982, 1881.

2 A. J. Arce, P. Arroja, A. J. Deeming, Y. De Sanctis and D. West, manuscript in preparation.