

Reaction of $[M_3(CO)_{12}]$ ($M = Ru$ or Os) with the Chalcogenide Elements; X-Ray Crystal and Molecular Structure of $[Os_4(CO)_{12}H_2Se_2]$

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Summary Reaction of $[Os_3(CO)_{12}]$ with X_n ($X = S, Se, or Te$) in *n*-octane under reflux yields $[Os_3(CO)_9H_2X]$, $[Os_3(CO)_9X_2]$, and $[Os_4(CO)_{12}H_2X_2]$, but a CO/H_2 pressure of 35 atm is required to prepare the ruthenium analogues $[Ru_3(CO)_9H_2X]$ and $[Ru_3(CO)_9X_2]$; an X-ray analysis of $[Os_4(CO)_{12}H_2Se_2]$ shows that it has a novel trigonal prismatic Os_4Se_2 core.

ALTHOUGH an extensive chemistry of sulphur, selenium, and tellurium derivatives of the iron carbonyls has been de-

veloped,¹ relatively little is known of the chemistry of the ruthenium and osmium analogues. In this communication we report the synthesis of a series of compounds of general formulae $[M_3(CO)_9H_2X]$ ($M = Ru$ or Os ; $X = S, Se, or Te$), $[M_3(CO)_9X_2]$ ($M = Ru$ or Os ; $X = S, Se, or Te$), and $[Os_4(CO)_{12}H_2X_2]$ ($X = S$ or Se).

Dodecacarbonyltriosmium was treated with X_n ($X = S, Se, or Te$) in *n*-octane under reflux for 15 h. After separation on silica (t.l.c.) three products were identified on the basis of their analytical and spectroscopic data (Table) as

TABLE. Spectroscopic data for $[\text{M}_3(\text{CO})_9\text{X}_2]$, $[\text{M}_3(\text{CO})_9\text{H}_2\text{X}]$, and $[\text{Os}_4(\text{CO})_{12}\text{H}_2\text{X}_2]$.

Compound	$\nu_{\text{CO}}/\text{cm}^{-1}$	$\tau^a/\text{p.p.m.}$	m/e^b
$[\text{Ru}_3(\text{CO})_9\text{S}_2]$	2078, 2057, 2024, 2016	—	628
$[\text{Ru}_3(\text{CO})_9\text{Se}_2]$	2076, 2053, 2019, 2010	—	728
$[\text{Os}_3(\text{CO})_9\text{S}_2]$	2078s, 2058s, 2016s, 2010m	—	892
$[\text{Os}_3(\text{CO})_9\text{Se}_2]$	2075s, 2054s, 2012s, 2008sh	—	992
$[\text{Os}_3(\text{CO})_9\text{Te}_2]$	2067s, 2046s, 2006s, 2002sh	—	1088
$[\text{H}_2\text{Ru}_3(\text{CO})_9\text{S}]$	2118m, 2084s, 2060vs, 2046s, 2016s, 2008s, 1996m, 1991w	28.93	598
$[\text{H}_2\text{Ru}_3(\text{CO})_9\text{Se}]$	2115m, 2082s, 2058s, 2045s, 2015s, 2007s, 1995m, 1989w	30.00	648
$[\text{H}_2\text{Ru}_3(\text{CO})_9\text{Te}]$	2111m, 2078s, 2054vs, 2043s, 2012s, 2006s, 1993m, 1987w	—	696
$[\text{H}_2\text{Os}_4(\text{CO})_{12}\text{S}_2]$	2115w, 2095s, 2078s, 2051s, 2034m, 2022s, 2018m, 2006m, 1993w, 1983w, 1978w	24.25	1170
$[\text{H}_2\text{Os}_4(\text{CO})_{12}\text{Se}_2]$	2111w, 2091s, 2076s, 2049s, 2031m, 2019s, 2017sh, 2004m, 1990w, 1981w, 1975m	24.92	1270

^a Relative to Me_4Si τ 10.00. ^b For ^{192}Os , ^{101}Ru , ^{32}S , ^{82}Se , and ^{130}Te .

$[\text{Os}_3(\text{CO})_9\text{H}_2\text{X}]$, $[\text{Os}_3(\text{CO})_9\text{X}_2]$, and $[\text{Os}_4(\text{CO})_{12}\text{H}_2\text{X}_2]$. Under similar conditions no reaction of X_2 with $[\text{Ru}_3(\text{CO})_{12}]$ was observed. Improved yields of the osmium derivatives were obtained from the reaction of $[\text{Os}_3(\text{CO})_{12}]$ with X_2 under a pressure of CO/H_2 (35 atm; 1:1). Under similar conditions the two ruthenium analogues $[\text{Ru}_3(\text{CO})_9\text{H}_2\text{X}]$ and $[\text{Ru}_3(\text{CO})_9\text{X}_2]$ were also prepared. Under CO pressure, but in the absence of H_2 , the yields of the hydrido-species $[\text{M}_3(\text{CO})_9\text{H}_2\text{X}]$ and $[\text{Os}_4(\text{CO})_{12}\text{H}_2\text{X}_2]$ decreased significantly. The molecular structure of $[\text{Os}_4(\text{CO})_{12}\text{H}_2\text{Se}_2]$ was established by X-ray diffraction. Yellow platelets were obtained by recrystallisation from hexane.

Crystal data: $\text{C}_{12}\text{H}_2\text{O}_{12}\text{Os}_4\text{Se}_2$, $M = 1400.86$, triclinic, $a = 10.004(3)$, $b = 12.764(5)$, $c = 9.711(3)$ Å, $\alpha = 98.14(2)$, $\beta = 113.36(2)$, $\gamma = 100.73(2)^\circ$, $U = 1086.1$ Å³, $Z = 2$, $D_c = 4.28$ g cm⁻³; $\mu(\text{Mo-K}\alpha) = 267.0$ cm⁻¹, space group $P\bar{1}$. 5557 intensities ($2\theta_{\text{max}} = 60.0^\circ$) were recorded on a Philips PW1100 four-circle diffractometer using graphite-monochromated Mo-K α radiation. The data were corrected for absorption and Lorentz polarisation factors, and averaged to give 3286 unique observed intensities [$F > 4\sigma(F)$]. The Os and Se atoms were located by multiresolution Σ_2 sign expansion, and the C and O atoms from a subsequent electron density difference synthesis. The structure was refined by blocked cascade least-squares (Os and Se anisotropic, C and O isotropic). A weighting scheme of the form $w = [\sigma^2(F) + 0.001 F^2]^{-1}$ was employed. The final residuals were $R = 0.035$ and $R = [\Sigma w^{\frac{1}{2}} \Delta / \Sigma w^{\frac{1}{2}} |F_o|] = 0.034$.

The molecular geometry is shown in the Figure which includes some important bond parameters. The four Os and two Se atoms define a distorted trigonal prism. Each Se atom caps a triangular arrangement of Os atoms; two Os–Os distances in each 'Os₃Se' unit are *ca.* 4 Å and hence non-bonding. Three terminal carbonyl ligands are bonded to each Os atom. The two hydride ligands probably edge bridge the two long Os–Os bonds [Os(1)–Os(4) and Os(2)–Os(3)] since the carbonyl ligands bend away from these edges. The *cis* Os–Os–C angles for the two bonds have an average value of 117.4° compared to 86.3° for the Os(1)–Os(2) bond.

If the two Se atoms act as 4-electron donors the molecule is a 66-electron system with 3 more electron pairs than

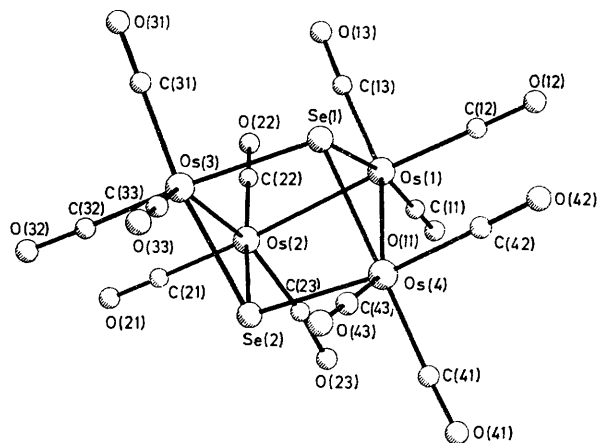


FIGURE. The molecular geometry of $[\text{Os}_4(\text{CO})_{12}\text{H}_2\text{Se}_2]$, including the atom numbering scheme. Bond lengths: Os(1)–Os(2), 2.884(1); Os(1)–Os(4), 2.965(1); Os(2)–Os(3), 2.966(1); Os(1)–Se(1), 2.543(1); Os(3)–Se(1), 2.571(1); Os(4)–Se(1), 2.537(1); Os(2)–Se(2), 2.538(1); Os(3)–Se(2), 2.546(1); and Os(4)–Se(2), 2.576(1) Å; bond angles: Os(2)–Os(1)–Os(4), 86.1(1) and Os(1)–Os(2)–Os(3), 85.7(1)°.

required for the 'electron precise' tetrahedral configuration (*cf.* $[\text{Os}_4(\text{CO})_{12}\text{H}_4]$). The addition of 3 electron pairs causes the breaking of three tetrahedral edges to give the observed cluster geometry.

Trinuclear clusters of iron, ruthenium, and osmium with capping sulphur atoms are known,² and selenium has been found to act as a μ_3 -ligand in the clusters $[\text{FeCo}_2(\text{CO})_9\text{Se}]$ and $[\text{Co}_3(\text{CO})_9\text{Se}]$.³ This is the first structural example of a tetranuclear osmium cluster with two capping chalcogenide ligands. The structure most closely resembles that of $[\text{Fe}_3(\text{CO})_9(\text{Bu}^t\text{NS})\text{S}]$ ⁴ in which one $\text{M}(\text{CO})_3$ unit in the Os cluster has been replaced by the 'Bu^tN' fragment of the η^4 -(Bu^tNS) ligand, and the hydrides removed. The structures of the $[\text{M}(\text{CO})_9\text{X}_2]$ compounds are analogous to that of $[\text{Fe}_3(\text{CO})_9\text{S}_2]$, and those in the $[\text{M}_3(\text{CO})_9\text{H}_2\text{X}]$ series to $[\text{Os}_3(\text{CO})_9\text{H}_2\text{S}]$.²

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† The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-str. 1, D-5300 Bonn 1, West Germany. Any request should be accompanied by the full literature citation for this communication.

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