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Preliminary Communication

Synthesis of novel selenium-containing osmium carbonyl clusters: X-ray structures of $[Os_5(\mu\text{-}H)(CO)_{15}(\mu_3\text{-}SePh)]$ and $[Os_6(\mu\text{-}H)(CO)_{18}(\mu\text{-}SeH)]$

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Abstract

The neutral osmium-selenido clusters $[Os_5(\mu\text{-}H)(CO)_{15}(\mu_3\text{-}SePh)]$ (**2**) and $[Os_6(\mu\text{-}H)(CO)_{18}(\mu_3\text{-}SeH)]$ (**5**) have been isolated in good yield by reaction of PhSeCl with $[Os_5H(CO)_{15}]^-$ and $[Os_6H(CO)_{18}]^-$ respectively. The structures of **2** and **5** have been established by single crystal X-ray analysis.

The stabilising influence of main-group elements, *e.g.* phosphorus, sulphur and tellurium on transition metal carbonyl clusters have been widely exploited during the past decade [1]. By comparison, relatively few studies have explored the potential of selenium as a capping ligand, and until recently [2] all the structurally characterised examples were of osmium carbonyl clusters [3]. The current interest in the use of organoselenium compounds in organic and organometallic chemistry [4] prompted us to explore the reactivity of selenium reagents with ruthenium carbonyl clusters and to extend our earlier work on osmium systems [5]. We recently reported [6] the preparation of the tetraruthenium selenido cluster $Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu\text{-}CO)_3$ from the pyrolysis of $Ru_3(CO)_{12}$ with PhSeSePh at 185°C in a sealed tube, and its subsequent reaction with the bidentate phosphine ligand 1,3-bis(diphenylphosphino)propane to afford $Ru_3(\mu_3\text{-}Se)_2(CO)_7(Ph_2P(CH_2)_3PPh_2$. Very recently, Dahl [7] has shown the reagent PhSeCl to be an effective agent for selenylation and cluster growth in nickel carbonyl systems. In this communication we describe the reactivity of phenylselenylchloride towards the penta- and hexanuclear osmium carbonyl monoanions $[Os_5H(CO)_{15}]^-$ and $[Os_6H(CO)_{18}]^-$. The syntheses and X-ray crystal structures of $Os_5(\mu\text{-}H)(CO)_{15}(\mu_3\text{-}SePh)$ (**2**) and $[Os_6(\mu\text{-}H)(CO)_{18}(\mu\text{-}SeH)]$ (**5**) are presented.

The $[Os_5H(CO)_{15}]^-$ anion can be readily prepared by the action of excess isopropylamine on $Os_6(CO)_{18}$, and isolated as the $[(Ph_3P)_2N]^+$ salt [8]. The room temperature reaction of $[(Ph_3P)_2N][Os_5H(CO)_{15}]$ **1** with PhSeCl, in dichloromethane solution, affords the red selenido-substituted penta-osmium cluster $Os_5(\mu\text{-}H)(CO)_{15}(\mu_3\text{-}SePh)$ **2** in quantitative yield. Complex **2** was initially characterised by mass spectrometry, IR spectroscopy and ^1H NMR *. The molecular structure of **2** was established by X-ray crystallography ** and is depicted in Fig. 1 which includes some important bond parameters. The metal core framework of **2** is unusual; the cluster framework can be viewed as being derived from the trigonal bipyramidal geometry of the parent monoanion [9] where the Os(1)–Os(5) and Os(2)–Os(5) "bonds" have been broken (Os(1)–Os(5), 3.982 Å; Os(2)–Os(5) 4.080 Å) to accommodate the μ_3-capping Se atom. Alternatively, Os(1), Os(2), Os(3) and Os(4) can be considered to form a butterfly where the Os(1)–Os(2) and Os(3)–Os(4) edges are bridged by the bonded Se and Os(5) atoms respectively (Se–Os(5), 2.487(3) Å).

The Os–Os bond lengths in **2** are *ca.* 0.07 Å longer than the Os–Os distances in $[Os_5H(CO)_{15}]^-$ metal framework [8], consistent with the incorporation of the Se atom into the metal core. Each Os atom is coordinated to three terminal carbonyl ligands. Although the hydride ligand was not located directly in the X-ray analysis of $Os_5(\mu\text{-}H)(CO)_{15}(\mu_3\text{-}SePh)$, its site was deduced from the significant lengthening of the Os(3)–

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* *Spectroscopic data for 2*: IR ν(CO) (CH_2Cl_2): 2071vs, 2039w, 2024s cm^{-1}. FAB MS: M^+(obs) $m/z = 1535$, (calc.) 1527. ^1H NMR (CD_2Cl_2): δ 7.55 (m, 5H, Ph), δ −13.10 (s, 1H). *Spectroscopic data for 5*: IR ν(CO) (CH_2Cl_2): 2305m, 2132m, 2089m, 2065vs, 2032s cm−1. FAB MS: M^+ (obs) $m/z = 1726$, (calc.) 1724. ^1H NMR (CD_2Cl_2): δ 7.28 (s, 1H), δ −19.62 (s, 1H).

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Os(5) bond (Os(3)–Os(5), 2.993(1) Å) and confirmed by potential energy minimisation calculations [10].

Complex **2** is a 76 electron system if the Se–Ph unit is considered to act as a 5-electron donor. This is consistent with the electron count of 72 electrons required for a basic trigonal bipyramidal core (9 metal–metal bonds) with 2 bonds broken by the addition of 4 electrons.

Treatment of $Os_6(CO)_{18}$ (**3**) with sodium borohydride (1 mol) in THF leads smoothly to the formation of $[Os_6H(CO)_{18}]^-$ (**4**) [11]. Immediate addition of PhSeCl to a solution of **4** in THF affords the neutral cluster $Os_6(\mu\text{-H})(CO)_{18}(\mu\text{-SeH})$ (**5**) as the major product (70% yield). Cluster **5** has been characterised by mass and IR spectroscopy * and the crystal structure established by single crystal X-ray analysis **. The structure is shown in Fig. 2 together with selected bond parameters. Complex **5** has a metal-core consisting of a trigonal bipyramidal arrangement of five osmium atoms with the sixth, Os(5), bonded to an equatorial atom, Os(1) in a "spike" arrangement. The most unusual feature of the structure is the presence of the bridging Se–H group (IR: 2305 cm^{-1}) across the "spike" bond Os(1)–Os(5) (Os(1)–Os(5): 2.900(4) Å). The phenyl

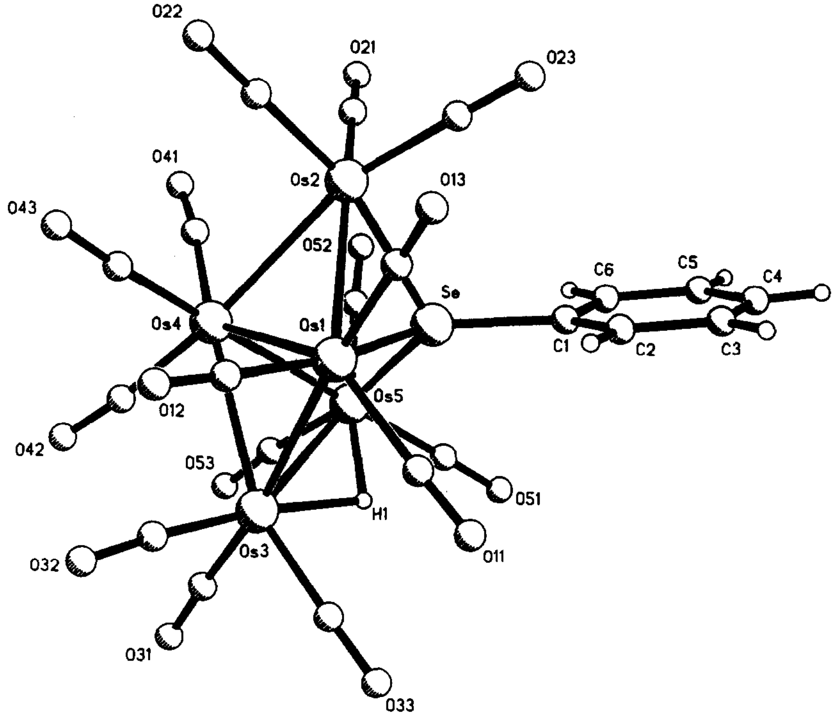

Fig. 1. The molecular structure of **2** showing the atom numbering scheme. Bond distances (Å) and angles(°) are: Os(1)–Os(2), 2.852(1); Os(1)–Os(3), 2.912(1); Os(1)–Os(4),, 2.865(1); Os(2)–Os(4), 2.887(1); Os(3)–Os(4), 2.809(1); Os(3)–Os(5), 2.993(1); Os(4)–Os(5), 2.917(1); Os(1)–Se, 2.481(2); Os(2)–Se, 2.463(2); Os(5)–Se, 2.487(2); Se–C(1), 1.930(2); Os(1)–Os(2)–Os(4), 59.9(1); Os(1)–Os(2)–Se, 55.1(1); Os(1)–Os(3)–Os(4), 60.1(1); Os(1)–Os(3)–Os(5), 83.5(1); Os(1)–Os(4)–Os(2), 59.5(1); Os(1)–Os(4)–Os(3), 61.2(1); Os(1)–Se–Os(2), 70.5(2); Os(1)–Se–C(1), 120.2(4); Os(2)–Os(1)–Os(3), 113.8(1); Os(2)–Os(4)–Os(3), 116.0(1), Os(2)–Os(4)–Os(5), 89.4(1); Os(2)–Se–C(1), 117.0(1); Os(3)–Os(4)–Os(5), 63.0(1); Os(3)–Os(5)–Os(4), 56.8(1); Os(3)–Os(1)–Se, 84.9(1); Os(3)–Os(5)–Se, 83.1(1); Os(4)–Os(2)–Se, 72.5(1); Os(5)–Se–C(1), 122.2(5).

** *Crystal data for 2*: $C_{21}H_6O_{15}SeOs_5$, $M = 1528.2$, monoclinic, space group $P2_1/c$, $a = 15.058(4)$, $b = 10.051(2)$, $c = 18.859(5)$ Å, $\beta = 101.45(2)°$, $V = 2797.3(1)$ Å^3, $Z = 4$, $D_c = 3.626$ g cm^{-3}, $F(000) = 2664$, Mo Kα radiation, $\lambda = 0.71073$ Å, μ(Mo Kα) = 240.24 cm^{-1}. Dark red block, crystal dimensions: 0.25 × 0.28 × 0.32 mm. 4311 data measured on an Enraf-Nonius CAD4 diffractometer ($4.0 < 2\theta < 46.0°$), corrected for absorption, 2959 unique observed diffractometer data [$F > 3\sigma(F)$]. Structure solved by direct methods (MULTAN) and Fourier difference techniques, refined by full-matrix least squares analysis (all non-hydrogen atoms anisotropic) to $R = 0.0380$, $wR = 0.0480$. Hydrogen atoms were placed in idealised positions and were allowed to ride on the relevant carbon (C–H 0.96 Å).

Crystal data for 5: $C_{18}H_2O_{18}Os_6Se$, $M = 1724.3$, orthorhombic, space group $Pbcn$, $a = 23.350(2)$, $b = 16.746(5)$, $c = 18.516(7)$ Å, $V = 7239(7)$ Å^3, $Z = 8$, $D_c = 3.164$ Mg m^{-3}, $F(000) = 5936$, Mo Kα radiation, $\lambda = 0.71073$ Å, μ(Mo Kα) = 220.48 cm^{-1}. Red prism, crystal dimensions: 0.14 × 0.28 × 0.18 mm. 4737 data measured on Nicolet R3m/V four-circle diffractometer ($7.0 < 2\theta < 45.0°$), corrected for absorption, 1690 unique observed diffractometer data [$F > 6.0\sigma(F)$]. Structure solved by direct methods and Fourier difference techniques, refined by full-matrix least squares analysis (Os, Se atoms anisotropic) to $R = 0.0661$, $wR = 0.0794$. The atomic coordinates for this work are available on request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ (UK). Any request should be accompanied by a full literature citation for this communication.

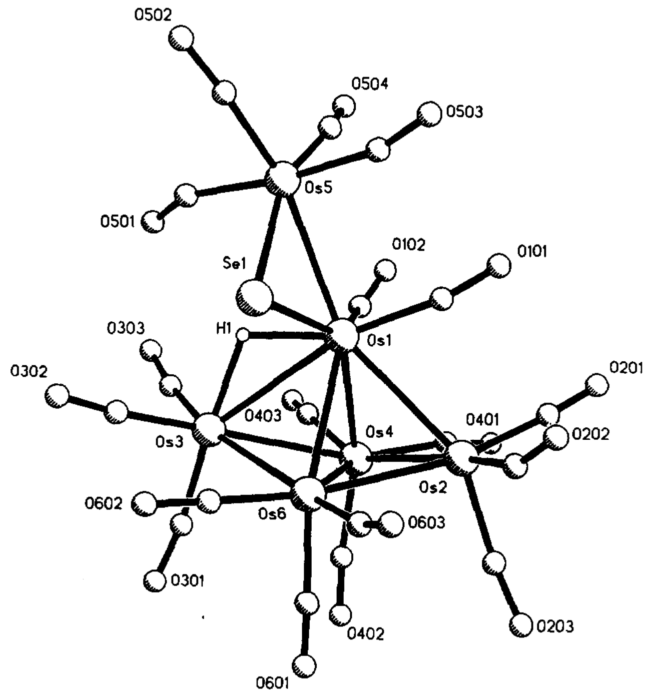

Fig. 2. The molecular structure of **5** showing the atom numbering scheme. Bond distances (Å) and angles (°) are: Os(1)-Os(2), 2.958(4); Os(1)-Os(3), 3.072(6); Os(1)-Os(4), 2.848(5); Os(1)-Os(5), 2.900(4); Os(1)-Os(6), 2.874(4); Os(1)-Se(1), 2.496(7); Os(2)-Os(4), 2.766(6); Os(2)-Os(6), 2.729(5); Os(3)-Os(4), 2.788(4); Os(3)-Os(6), 2.783(5); Os(4)-Os(6), 2.767(4); Os(5)-Se(1), 2.520(7); Os(1)-Os(2)-Os(4), 49.6(1); Os(1)-Os(2)-Os(6), 60.6(1); Os(1)-Os(3)-Os(4), 57.9(1); Os(1)-Os(3)-Os(6), 58.6(1); Os(1)-Os(4)-Os(2), 63.6(1); Os(1)-Os(4)-Os(3), 66.0(1); Os(1)-Os(4)-Os(6), 61.5(1); Os(1)-Os(5)-Se(1), 54.3(2); Os(1)-Os(6)-Os(2), 63.7(1); Os(1)-Os(6)-Os(3), 65.8(1); Os(1)-Os(6)-Os(4), 60.6(1); Os(1)-Se(1)-Os(5), 70.6(2); Os(2)-Os(1)-Os(3), 100.8(1); Os(2)-Os(1)-Os(5), 150.2(2); Os(2)-Os(1)-Se(1), 118.7(2); Os(2)-Os(4)-Os(6), 59.1(1); Os(2)-Os(6)-Os(4), 60.4(1); Os(3)-Os(1)-Os(5), 107.5(1); Os(3)-Os(1)-Se(1), 87.0(2); Os(3)-Os(4)-Os(6), 60.1(1); Os(3)-Os(6)-Os(4), 60.3(1); Os(4)-Os(1)-Os(5), 150.5(2); Os(4)-Os(1)-Se(1), 136.4(2); Os(5)-Os(1)-Os(6), 137.6(1); Os(6)-Os(1)-Se(1), 83.4(2).

group is presumably lost as benzene during the reduction of the neutral octahedral cluster $Os_6(CO)_{18}$ **3** to $[Os_6H(CO)_{18}]^-$ **4** due to the presence of excess $NaBH_4$. The second hydrogen ligand was located by use of the HYDX program [10] in an edge-bridging mode across the Os(1)-Os(3) edge (Os(1)-Os(3), 3.072(6) Å).

This unusual metal core arrangement has been observed only once previously in the molecule $Os_6(CO)_{17}(Py)_2$ [12], prepared by the action of excess pyridine (py) on $Os_6(CO)_{18}$. This molecule also exhibits a ligand bridge across the "spike" bond in the form of an unusual metal-carbonyl $\{\mu_3\text{-(CO)}\}$ linkage. The Os-Os bond lengths in **5** are *ca.* 0.03 Å longer than in the structural analogue $Os_6(CO)_{17}(py)_2$. The Os-Os distance in the "spike" bond in **5** (Os(1)-Os(5), 2.900(4) Å) is very slightly longer than that in $Os_6(CO)_{17}(py_2)$ (Os(1)-Os(6), 2.881 Å). The atoms Os(2), Os(3), Os(4) and Os(6) in **5** are each coordinated to three terminal carbonyl ligands; Os(1) and Os(5) are bonded to two and four terminal CO ligands respectively. The donation of all 3 electrons from the '$Os(CO)_4(\mu\text{-SeH})$' unit to the 69-electron '$Os_5(\mu\text{-H})(CO)_{14}$' trigonal bipyramidal metal core brings the total electron count for cluster **5** to 72. This count is consistent with the observed metal core geometry according to the Polyhedral Skeletal Electron Pair Theory [13].

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