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Preliminary communication

Synthesis and characterisation of novel selenium-containing clusters; crystal structures of $[Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu\text{-}CO)_3]$ and $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(Ph_2P(CH_2)_3PPh_2)]$

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Abstract

The compound $[Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu_3\text{-}CO)_3]$ (**1**), has been obtained in good yield by vacuum pyrolysis of $[Ru_3(CO)_{12}]$ with $[Ph_2Se_2]$ at 185°C. Reaction of **1** with 1,3-bis(diphenylphosphino)propane at room temperature affords the novel cluster $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(Ph_2P(CH_2)_3PPh_2)]$ (**2**). The structures of **1** and **2** have been determined by an X-ray diffraction study.

The chemistry of transition-metal Main-Group clusters has developed extensively during the past decade [1]. The introduction of a Main Group element into a transition metal carbonyl cluster often introduces novel reactivity, and frequently stabilises the metal framework with respect to degradation by "clamping" the metal atoms together. In this context the stabilising influence of μ_3-S and μ_4-S ligands has been exploited widely [2], and in the past few years μ_3- and μ_4-Te ligands have also been shown to stabilise triangular and square arrays of metal atoms [3–5]. By comparison, there have been relatively few studies involving the use of selenium as a capping ligand, and until recently [6] all the structurally characterised examples were of osmium carbonyl clusters [7]. The recent upsurge in interest in the use of organoselenium compounds in organic and organometallic chemistry [8] prompted us to investigate the reactivity of the reagent PhSeSePh with ruthenium clusters and to extend some of our earlier work on osmium systems [9]. We now report the preparation and characterisation of the tetraruthenium cluster $[Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu\text{-}CO)_3]$ (**1**) and its subsequent reaction with 1,3-bis(diphenylphosphino)propane to give the triruthenium phosphine-substituted cluster $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(Ph_2P(CH_2)_3PPh_2]$ (**2**).

The vacuum pyrolysis of $[Ru_3(CO)_{12}]$ with PhSeSePh at 185°C affords the cluster $[Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu_3\text{-}CO)_3]$ (**1**) as the only isolable product (40% yield).

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Complex 1 has been characterised by mass and IR spectroscopy * and the crystal structure by X-ray crystallography. ** The molecular structure is shown in Fig. 1 together with selected bond parameters. The molecule lies on a crystallographic two-fold axis which passes through the carbonyl C(21)O(21) and the mid-points of the Ru(1)–Ru(1a) and Ru(2)–Ru(2a) edges. It consists of a trapizoidal array of four ruthenium atoms which is asymmetrically bridged on each side by a μ_4-Se ligand. The three shorter Ru–Ru edges are bridged by carbonyl ligands; the Ru(2)–Ru(2a) edge is symmetrically bridged [Ru(2),Ru(2a)–C(21), 2.07(2) Å; Ru(2)–C(21)–Ru(2a), 84.2(9)°] while the carbonyl along the Ru(1)–Ru(2) edge (and its symmetry equivalent) shows considerable asymmetry [Ru(1)–C(13), 1.92(2) Å; Ru(2)–C(13), 2.52(2) Å; Ru(1)–C(13)–Ru(2), 76.8(6)°] and the bridge may be described as incipient. Each Ru atom is also bonded to two terminal carbonyls which lie on either side of the Ru_4 plane.

Complex 1 is isomorphous and isostructural with the tellurium capped analogues $[Ru_4(\mu_4\text{-}Te)_2(CO)_{11}]$ [4] and $[Fe_2Ru_2(\mu_4\text{-}Te)_2(CO)_{11}]$ [5], and with the iron-sulphur cluster $[Fe_4(\mu_4\text{-}S)_2(CO)_{11}]$ [10]. The bond parameters in 1 follow the same general trends as in the isostructural complexes. The Ru–Se distances in 1 are *ca.* 0.1 Å longer than the Ru–Se distances in $[Ru_4(\mu_3\text{-}Se)(\mu\text{-}C_4H_4)(CO)_{11}]$ [6], consistent with the increase in the coordination number of the Se atoms in 1. The carbonyl bridged Ru–Ru edges in 1 are similar in length to the Ru–Ru carbonyl edge in $[Fe_2Ru_2(\mu_4\text{-}Te)_2(CO)_{11}]$ (2.795(3) Å) [5], and are significantly shorter than the Ru–Ru bond length of 2.854(4) Å in the parent binary carbonyl $[Ru_3(CO)_{12}]$ [11]. The unbridged Ru(1)–Ru(1a) edge length in 1 is similar to that found in $[Ru_3(CO)_{12}]$ [11], whereas, in $[Ru_4(\mu_4\text{-}Te)_2(CO)_{11}]$, presumably with the influence of the larger capping Te atoms, the equivalent Ru-Ru edge that is not bridged by a carbonyl is lengthened to 2.945(1) Å [4].

Complex 1 is a 62 electron system if both μ_4-Se atoms are considered to act as 4-electron donors. This count is consistent with the presence of 7 bonding electron

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* *Spectroscopic data for 1.* IR ν(CO) (CH_2Cl_2): 2061s, 2029s, 1607m cm^{-1}. FAB MS: M^+ (obs) $m/z = 871.2$, (calc.) 870.3. *Spectroscopic data for 2.* IR ν(CO) (CH_2Cl_2): 2050s, 2018s, 1980m, 1649w, 1638w cm^{-1}. FAB MS: M^+ (obs) $m/z = 1070.4$, (calc.) 1069.6. ^{1}H NMR ($CDCl_2$): δ 7.52 (m, 20H, Ph), δ2.81 (m, 6H). ^{31}P NMR (CD_2Cl_2 relative to TMP): δ −92.13 (2P).

** *Crystal data for 1.* $C_{11}O_{11}Ru_4Se_2$, $M = 870.3$, orthorhombic, space group *Pccn*, $a = 6.624(2)$, $b = 16.138(3)$, $c = 18.036(4)$ Å, $V = 1928.1(7)$ Å^3, $Z = 4$, $D_c = 2.998$ Mg/m^3, $F(000) = 1592$, Mo-K_α radiation, $\lambda = 0.71073$ Å, μ(Mo-K_α) = 6.901 mm^{-1}. Dark red block, crystal dimensions: 0.30 × 0.32 × 0.35 mm. 1563 data measured on a Nicolet R3mV four-circle diffractometer ($5.0 \le 2\theta \le 45.0°$), corrected for absorption, 962 unique observed diffractometer data [$F > 4.0\sigma(F)$]. Structure solved by direct methods and Fourier difference techniques, refined by full-matrix least-squares analysis (all atoms anisotropic) to $R = 0.0490$, $wR = 0.0838$. *Crystal data for 2.* $C_{34}H_{26}O_7P_2Ru_3Se_2$, $M = 1069.6$, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.505(5)$, $b = 12.263(6)$, $c = 14.426(9)$ Å, $V = 1858.7(15)$ Å^3, $Z = 2$, $D_c = 1.911$ Mg/m^3, $F(000) = 1032$, Mo-K_α radiation, $\lambda = 0.71073$ Å, μ(Mo-K_α) = 3.292 mm^{-1}. Orange rectangular block, crystal dimensions: 0.10 × 0.20 × 0.32 mm. 5019 data measured on a Nicolet R3mV four-circle diffractometer ($5.0 \le 2\theta \le 45.0°$), corrected for absorption, 3036 unique observed diffractometer data [$F > 4.0\sigma(F)$]. Structure solved by direct methods and Fourier difference techniques, refined by full-matrix least-squares analysis (all non-hydrogen atoms anisotropic) to $R = 0.0579$, $wR = 0.0949$. Hydrogen atoms were placed in idealised positions and were allowed to ride on the relevant carbon (C–H 0.96 Å). The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (UK). Any request should be accompanied by a full literature citation for this communication.

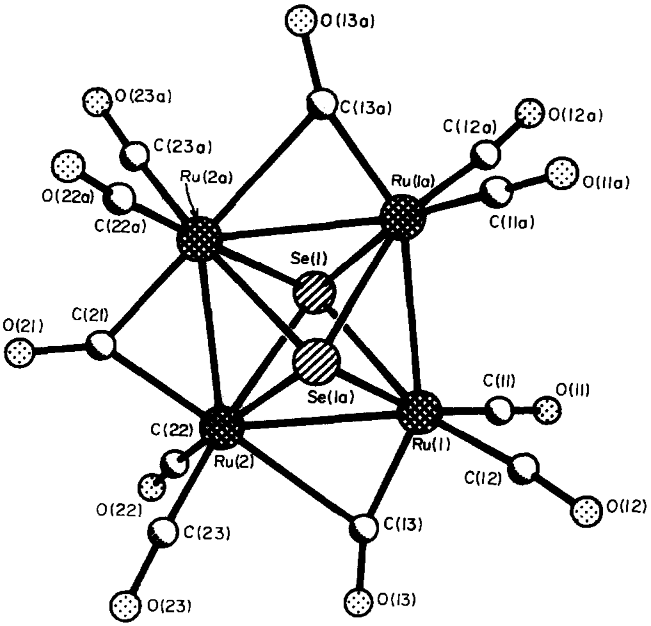

Fig. 1. The molecular structure of 1 showing the atom numbering scheme. Bond distances (Å) and angles (°) are: Ru(1)–Ru(2), 2.796(2); Ru(2)–Ru(2a), 2.778(3); Ru(1)–Ru(1a), 2.845(3); Se(1)–Ru(1), 2.565(2); Se(1)–Ru(2), 2.605(2); Se(1)–Ru(1a), 2.556(2); Se(1)–Ru(2a), 2.610(2); Ru(2)–Ru(1)–Se(1), 58.0(1); Ru(2)–Ru(1)–Ru(1a), 89.3(1); Se(1)–Ru(1)–Ru(1a), 56.1(1); Ru(2)–Ru(1)–Se(1a), 58.2(1); Se(1)–Ru(1)–Se(1a), 80.6(1); Ru(1a)–Ru(1)–Se(1a), 56.4(1); Ru(1)–Ru(2)–Se(1), 56.6(1); Ru(1)–Ru(2)–Ru(2a), 90.7(1); Se(1)–Ru(2)–Ru(2a), 57.9(1); Ru(1)–Ru(2)–Se(1a), 56.3(1); Se(1)–Ru(2)–Se(1a), 78.9(1); Ru(2a)–Ru(2)–Se(1a), 57.7(1); Ru(1)–Se(1)–Ru(2), 65.5(1); Ru(1)–Se(1)–Ru(1a), 67.5(1); Ru(2)–Se(1)–Ru(1a), 100.4(1); Ru(1)–Se(1)–Ru(2a), 100.0(1); Ru(2)–Se(1)–Ru(2a), 64.4(1); Ru(1a)–Se(1)–Ru(2a), 65.5(1).

pairs required by the Polyhedral Skeletal Electron Pair Theory [12] for the *pseudo*-octahedral Ru_4Se_2 core observed.

It is of interest to contrast the formation of 1 with that of $[Os_3(SePh)_2(CO)_{10}]$, which is obtained by the room temperature reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with PhSeSePh [9,13]. When the activated cluster $[Os_3(CO)_{10}(MeCN)_2]$ is used the reaction proceeds under mild conditions, and apparently only the Se–Se bond of PhSeSePh is cleaved in the process. Deeming has shown that three isomers of $[Os_3(SePh)_2(CO)_{10}]$ are formed [13], and these isomers differ in the positions of coordination of the μ-SePh groups, although in the case of one isomer a Se–Se bond may still be present. In the reaction reported in this communication, in which the kinetically more labile carbonyl, $[Ru_3(CO)_{12}]$ (compared with $[Os_3(CO)_{12}]$), was used under forcing pyrolysis conditions Se–Se and Se–C bond rupture has occured and the carbonyl cluster has also fragmented, so that the isolation of the tetraruthenium cluster $[Ru_4(\mu_4\text{-}Se)_2(CO)_{11}]$ (1) from the mixture as the major component suggests that this may be the thermodynamically favoured product. It was therefore of interest to investigate the reactivity of 1 to establish whether the *pseudo*-octahedral core was a stable unit or whether the reaction chemistry would show a change in nuclearity of the product molecules.

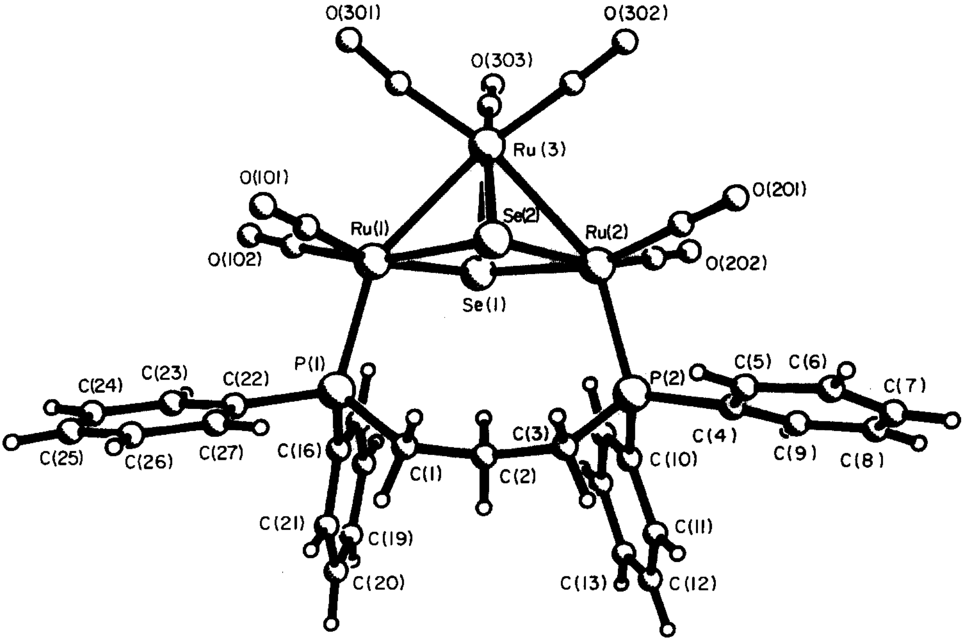

Fig. 2. The molecular structure of 2 showing the atom numbering scheme. Bond distances (Å) and angles (°) are: Ru(1)–Ru(3), 2.836(3); Ru(1)–Se(1), 2.499(3); Ru(1)–Se(2), 2.516(3); Ru(1)–P(1), 2.297(6); Ru(2)–Ru(3), 2.815(3), Ru(2)–Se(1), 2.507(3); Ru(2)–Se(2), 2.520(3); Ru(2)–P(2), 2.320(7); Ru(3)–Se(1), 2.539(3); Ru(3)–Se(2), 2.539(4); Ru(3)–Ru(1)–Se(1), 56.4(1); Ru(3)–Ru(1)–Se(2), 56.3(1); Se(1)–Ru(1)–Se(2), 79.9(1); Ru(3)–Ru(2)–Se(1), 56.6(1); Ru(3)–Ru(2)–Se(2), 56.5(1); Se(1)–Ru(2)–Se(2), 79.7(1); Ru(1)–Ru(3)–Ru(2), 85.8(1); Ru(1)–Ru(3)–Se(1), 55.1(1); Ru(2)–Ru(3)–Se(1), 55.5(1); Ru(1)–Ru(3)–Se(2), 55.5(1); Ru(2)–Ru(3)–Se(2), 55.9(1); Se(1)–Ru(3)–Se(2), 78.7(1); Ru(1)–Se(1)–Ru(2), 100.4(1); Ru(1)–Se(1)–Ru(3), 68.5(1); Ru(2)–Se(1)–Ru(3), 67.8(1); Ru(1)–Se(2)–Ru(2), 99.6(1); Ru(1)–Se(2)–Ru(3), 68.3(1); Ru(2)–Se(2)–Ru(3), 67.6(1).

The room temperature reaction of **1** with the bidentate phosphine, 1,3-bis(diphenylphosphino)propane, in dichloromethane solution, affords the orange triruthenium cluster $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(Ph_2P(CH_2)_3PPh_2]$ (**2**) in 70% yield. The only other product isolated from the reaction was $[Ru_3(CO)_{12}]$, which may be formed by the condensation of "$Ru(CO)_4$" fragments lost from **1** during the formation of **2**. Complex **2** was initially characterised by mass spectrometry, IR spectroscopy and both ^1H and ^{31}P NMR. * The spectroscopic data suggested the presence of only one isomer, and the ^{31}P NMR data indicated that the two phosphorus nuclei are in equivalent environments. The molecular structure of **2** was established by X-ray crystallography ** and is depicted in Fig. 2, which includes some important bond parameters. The three Ru atoms define an isosceles triangle, the long edge of which is sufficiently lengthened (3.846(3) Å) to indicate no direct metal–metal interaction. The two Se atoms μ_3-cap above and below the Ru_3 plane. The bidentate phosphine spans the long Ru(1)–Ru(2) edge, with the two phosphorus atoms occupying equatorial sites on the two metal atoms. The atoms Ru(1) and Ru(2) are also coordinated to two terminal carbonyl ligands, and Ru(3) is coordinated to three.

Complex **2** is a 50 electron system, consistent with the presence of only two "formal" Ru–Ru bonds, and the geometry of the Ru_3Se_2 core is similar to that observed in $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$ [14] and its many Group 8-chalcogenide analogues and their derivatives [2,8]. The Ru–Se distances in **2** are *ca.* 0.06 Å longer than the average value of 2.45 Å for the Ru–(μ_3-Se) distance in $[Ru_4(\mu_3\text{-}Se)(\mu\text{-}C_4H_4)(CO)_{11}]$ [6], while the bonded Ru–Ru distances are similar to the values of 2.814(1) and 2.835(1) Å for two of the edges of the Se-capped triangle in $[Ru_4(\mu_3\text{-}Se)(\mu\text{-}C_4H_4)(CO)_{11}]$ [6]. The Ru–P distances in **2** (average 2.31 Å) lie in the range found for similar bonds in other ruthenium clusters with edges spanned by bidentate phosphine ligands [15].

The results of this study show that the Ru_4Se_2 core observed in **1** may be fragmented by the reaction with a nucleophile under mild conditions. Further investigations of the reactivity of this and other ruthenium-selenium clusters are in progress.

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