Reaction of $CH_2(Ph_2PSe)_2$ with $[Ru_3(CO)_{12}]$. Crystal Structure of $[Ru_4Se_4(CO)_{10}(Ph_2PCH_2PPh_2)]$, a Missing Link in the $[M_4E_4L_{12}]$ Cubane Series (M = Group 8 Metal, E = Chalcogenido Ligand)

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The bis(phosphine selenide) $CH_2(Ph_2PSe)_2$ and $[Ru_3(CO)_{12}]$ (1:1) reacted in toluene to give $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(dppm)]$, $[Ru_4(\mu_4\text{-}Se)_2(CO)_9(dppm)]$ and $[Ru_4(\mu_3\text{-}Se)_4(CO)_{10}(dppm)]$ (dppm = $Ph_2PCH_2PPh_2$), the last of which is the first reported 72-electron Ru–Se cubane-like cage complex.

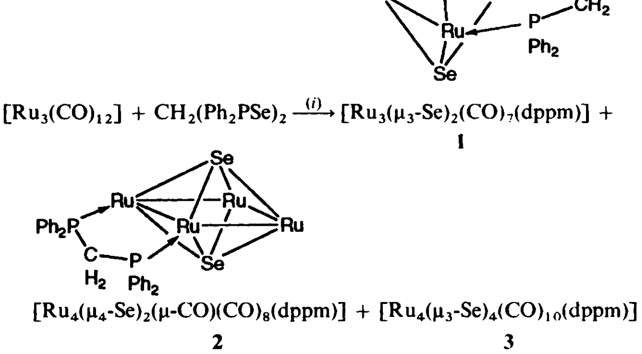
Transition-metal clusters containing main-group elements as bridging ligands, particularly chalcogenido ligands, have important chemical and structural significance, since they can be regarded as discrete molecular models of extended inorganic solids.[1] Furthermore, sulfido, selenido and tellurido ligands are valuable building blocks for cluster growth reactions, spectacular results having recently been obtained for nickel and copper selenides.[2] The entire field of chalcogenide clusters is a rapidly expanding research area after a long period of inactivity due to the lack of suitable starting reagents, particularly for selenium and tellurium.[3] Presently different synthetic routes are available to prepare selenido or tellurido transition-metal clusters,[3,4] among which that involving the oxidative addition of tertiary phosphine calcogenide to zero-valent metal centres appears particularly attractive.[5,6]

A widely studied series of transition-metal (M) chalcogenido (E) complexes is the M_4E_4 cubane-like tetramers, owing to the presence of iron-sulfur cubanes in the active sites of many enzymes.[7] In particular, a limited number of neutral 72-electron $[M_4E_4(CO)_{12-n}L_n]$ (L = two-electron ligand) cubane complexes containing Group 8 metals have been synthesized and structurally characterized (M = Fe, E = S, Se,[8] or Te;[9] M = Os, E = O).[10] For ruthenium only cuboidal 68- or 66-electron Ru_4E_4 complexes have been described.[11,12]

Here we investigate the use of $CH_2(Ph_2PSe)_2$ as an effective precursor for dppm-substituted (dppm = $Ph_2PCH_2PPh_2$) ruthenium selenido clusters. Previously we described the synthesis of some phosphine-substituted selenido carbonyl-iron or -ruthenium clusters by reaction of $SePPh_3$ with the corresponding metal carbonyls.[6] For iron the reaction afforded several di- and tri-nuclear compounds, namely $[Fe_2(\mu\text{-}Se_2)(CO)_{6-n}L_n]$ (n = 1 or 2), $[Fe_3(\mu_3\text{-}Se)_2(CO)_{9-n}L_n]$ (n = 0–2) and $[Fe_3(\mu_3\text{-}Se)(\mu\text{-}CO)(CO)_7L_2]$, whereas for ruthenium the same reaction was found to be quite selective giving the disubstituted trinuclear cluster $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)_2]$ in very high yield, together with minor amounts of $[Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)_2(CO)_7(PPh_3)_2]$.

The reaction of $[Ru_3(CO)_{12}]$ with $CH_2(Ph_2PSe)_2$ (1:1) in refluxing toluene, in the presence of Me_3NO, affords a variety of products, three of which, shown in Scheme 1, could be isolated by preparative TLC.†

The products **1** and **2** were characterized by spectroscopic[13] and elemental analysis data. Their structures (Scheme 1, carbonyls omitted) are proposed on the basis of the known structures of similar compounds.[4a,14,15] Cluster **1** has the well known[4a,15] bicapped open-triangular 50-electron core and is the expected primary product of the oxidative attack of $CH_2(Ph_2PSe)_2$ on the starting carbonyl cluster. Complex **2** also has a known architecture and is formally a substituted derivative of $[Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)_3(CO)_8]$ with a bicapped square-planar 62-electron core.[4a,14] It can be regarded as a secondary product,



$$[Ru_3(CO)_{12}] + CH_2(Ph_2PSe)_2 \xrightarrow{(i)} \underset{\mathbf{1}}{[Ru_3(\mu_3\text{-}Se)_2(CO)_7(dppm)]} +$$

$$\underset{\mathbf{2}}{[Ru_4(\mu_4\text{-}Se)_2(\mu\text{-}CO)(CO)_8(dppm)]} + \underset{\mathbf{3}}{[Ru_4(\mu_3\text{-}Se)_4(CO)_{10}(dppm)]}$$

Scheme 1 (*i*) N_2, Me_3NO, C_6H_5Me, reflux

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† The reagents $[Ru_3(CO)_{12}]$ (105 mg, 0.16 mmol), Me_3NO (13 mg, 0.16 mmol) and $CH_2(Ph_2PSe)$ (90 mg, 0.16 mmol) were refluxed in toluene (90 cm^3) for 1.5 h under N_2. The resulting dark red solution was evaporated to dryness and the residue was dissolved in CH_2Cl_2 (10 cm^3). Three products were separated by TLC on silica, using CH_2Cl_2–light petroleum (b.p. 40–60 °C) (2:1) as eluent mixture: $[Ru_3Se_2(CO)_7(dppm)]$ **1** (20%, red band, R_f 0.9), $[Ru_4Se_2(CO)_9(dppm)]$ **2** and $[Ru_4Se_4(CO)_{10}(dppm)]$ **3** (5 and 14% respectively, brownish yellow band, R_f 0.8). Complexes **2** (light brown) and **3** (light orange) were separated by fractional crystallization by slow diffusion of methanol into a dichloromethane solution, at *ca.* 4 °C. IR (CH_2Cl_2), $\nu_{CO}(cm^{-1})$: **1**, 2066, 2052, 2007, 1956; **2**, 2046, 2013, 1968; **3**, 2091, 2076, 2027, 2003 (sh), 1964.

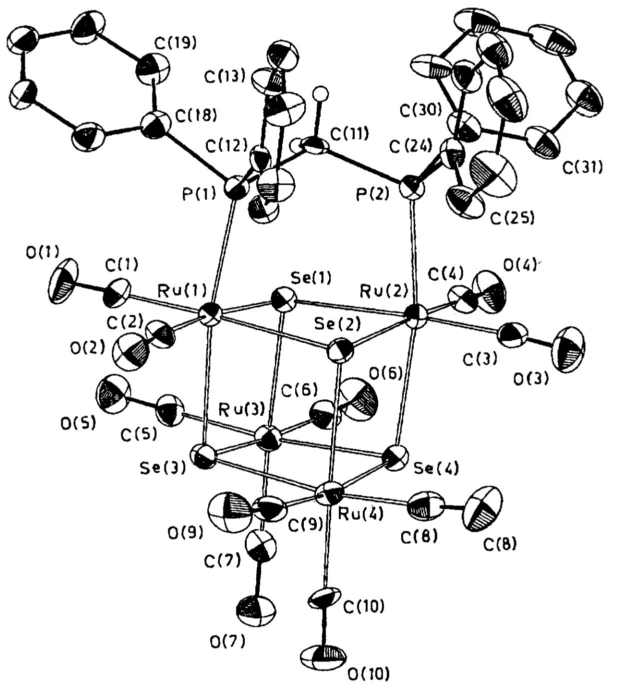

Fig. 1 View of the molecular structure of **3**. Selected bond distances (Å) and angles (°): Ru(1)–Se(1) 2.564(2), Ru(1)–Se(2) 2.557(2), Ru(1)–Se(3) 2.577(1), Ru(1)–P(1) 2.348(3), Ru(2)–Se(1) 2.569(2), Ru(2)–Se(2) 2.570(2), Ru(2)–Se(4) 2.571(1), Ru(2)–P(2) 2.355(3), Ru(3)–Se(1) 2.549(1), Ru(3)–Se(3) 2.560(2), Ru(3)–Se(4) 2.571(2), Ru(4)–Se(2) 2.552(1), Ru(4)–Se(3) 2.567(2), Ru(4)–Se(4) 2.564(2); Se(1)–Ru(1)–Se(3) 83.9(1), Se(1)–Ru(1)–Se(2) 86.1(1), Se(1)–Ru(1)–P(1) 88.7(1), Se(2)–Ru(1)–P(1) 89.4(1), Se(3)–Ru(1)–P(1) 170.5(1), Se(1)–Ru(2)–Se(2) 85.8(1), Se(1)–Ru(2)–Se(4) 83.6(1), Se(1)–Ru(2)–P(2) 88.1(1), Se(2)–Ru(2)–P(2) 91.0(1), Se(4)–Ru(2)–P(2) 170.5(1), Se(1)–Ru(3)–Se(3) 84.5(1), Se(1)–Ru(3)–Se(4) 83.9(1), Se(3)–Ru(3)–Se(4) 85.4(1), Se(2)–Ru(4)–Se(3) 84.5(1), Se(2)–Ru(4)–Se(4) 84.3(1), Se(3)–Ru(4)–Se(4) 85.4(1)

deriving from the addition of a mononuclear metal fragment to cluster **1**, under the adopted pyrolytic conditions.*

The structure of complex **3**, fully elucidated by X-ray analysis,† is shown in Fig. 1; it has a cubane-like, 72-electron M_4E_4 cage core, which is unprecedented for ruthenium and selenium. Also this complex should be regarded as a secondary product, probably formed by the self-assembly of two dinuclear Ru_2Se_2 groups, derived from **1** by loss of a mononuclear metal fragment. The ν(CO) stretching bands in **3** are significantly shifted towards higher frequency values with respect to **1** owing to the higher oxidation state (+2) of the ruthenium atoms. The singlet in the ^{31}P NMR spectrum at δ 9.4 and the triplet in the ^1H NMR spectrum at δ 4.17 indicate, as expected, the equivalence in solution of the two phosphorus and the two methylene hydrogen atoms of the bridging ligand.

The Ru_4Se_4 core has a slightly distorted cubane structure: the inner bond angles Se–Ru–Se and Ru–Se–Ru range from 83.6(1)–86.1(1) and 93.4(1)–96.4(1)°, *i.e.* all angles at Ru are less than 90°, whereas those at Se are all greater than 90°. These angular distortions lead to slight rhombic compressions of the square faces of the cube, which are practically planar, the largest displacement from the corresponding averaged planes being 0.1 Å. Despite the presence of the bridging diphosphine, the overall geometry of **3** is comparable to those of the unsubstituted iron cubanes $[Fe_4E_4(CO)_{12}]$ (E = S or Se).[8] The only reported Ru_4E_4 complexes are the pseudo-cubane, 68-electron clusters $[Ru_4E_4(C_5H_4Me)_4]$ (E = S or Se),[1] the structure of which (determined for E = S) contains two metal–metal bonds, therefore differing substantially from that of **3**.

Each ruthenium atom is in a quasi-octahedral environment, possessing a complete 18-electron count through bonding with three facial selenido ligands and three appropriate two-electron ligands. The average Ru-Se and Ru-P distances [2.564(2) and 2.351(3) Å respectively] are slightly longer than the corresponding distances in the open triangular clusters $[Ru_3(\mu_3\text{-}Se)_2(CO)_{9-n}L_n]$ (n = 0–2).[4a,6,15] The large bite angle [P–C–P 120.5(5)°] of the bridging diphosphine is particularly noteworthy.

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* By refluxing cluster **1** in toluene under N_2 in the presence of Me_3NO for 1 h significant amounts of **2** (19) together with unreacted **1** (46%) and an unidentified product can be obtained. The same pyrolytic decomposition carried out under CO affords the cubane cage **3** (12), unreacted **1** (58) and cluster **2** (23%).

† *Crystal data:* $C_{35}H_{22}O_{10}P_2Ru_4Se_4\cdot CH_2Cl_2$, M = 1469.55, monoclinic, space group $P2_1/n$, a = 19.979(6), b = 10.070(4), c = 22.740(7) Å, β = 104.12(2)°, U = 4437(3) $Å^3$, Z = 4, D_c = 2.200 g cm^{-3}, $F(000)$ = 2784, niobium-filtered Mo-Kα radiation, λ = 0.710 73 Å, μ = 48.62 cm^{-1}.

Intensity data collected on a Siemens AED diffractometer, using the θ–2θ scan technique at room temperature. 7773 Unique reflections measured with θ in the range 3–25°; 4254, having $I > 2\sigma(I)$, used in refinement. Structure solved by Patterson and Fourier methods[16] and refined by full-matrix least-squares procedures, with anisotropic thermal parameters in last cycles of refinement for all non-hydrogen atoms. All hydrogen atoms placed at their geometrically calculated positions in the final ΔF map and isotropically refined, 'riding' on corresponding carbon atoms, R and R' 0.0417 and 0.0420, $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$ (k = 0.9250 and g = 0.00038). Atomic coordinates, thermal parameters and bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, issue 1, pp. xxv–xxx.