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Cluster growth reactions with selenido–carbonyl clusters. Synthesis and structural characterization of $[M_2Ru_2(\mu_4\text{-}Se)_2(\mu\text{-}CO)_4(CO)_6(PPh_3)_2]$ (M = Mo or W)‡

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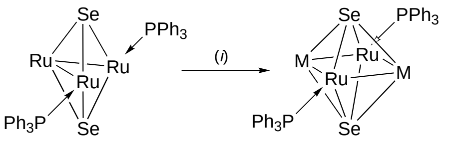
The open-triangular, *nido* cluster $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)_2]$ (50 electrons, seven skeletal electron pairs, s.e.p.s) reacted at room temperature with $[M(CO)_3(MeCN)_3]$ (M = Mo or W) to give unexpectedly the bicapped, square-planar clusters $[M_2Ru_2(\mu_4\text{-}Se)_2(\mu\text{-}CO)_4(CO)_6(PPh_3)_2]$ as unique products; they exhibit an electron-deficient *closo* geometry with 60 electrons and six s.e.p.s.

The chemistry of chalcogenido–carbonyl metal compounds constitutes an active area of research leading to a variety of molecular architectures which span from dinuclear metal species to giant molecular clusters.[1,2] Work by several groups[3] has demonstrated that small chalcogenido clusters, such as dinuclear and trinuclear Group 8 metal complexes, are useful synthons for cluster-growing processes by reaction with suitable transition-metal species. Amongst the possible synthetic routes available to prepare small chalcogenido clusters, that involving the oxidative addition of phosphine chalcogenides to zero-valent metal carbonyl species appears advantageous, if a phosphine-substituted cluster is the target compound.[4,5]

In this regard, we recently found that the reaction of $[Ru_3(CO)_{12}]$ with $SePPh_3$ is quite selective, affording the disubstituted open-triangular cluster $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)_2]$ **1** in high yield.[6] The availability of this complex in workable amounts prompted us to investigate its behaviour in cluster-growing processes by reaction with $[M(CO)_3(MeCN)_3]$ (M = Mo or W). The preliminary results of this study, including the molecular structure of the new bimetallic cluster $[M_2Ru_2(\mu_4\text{-}Se)_2(\mu\text{-}CO)_4(CO)_6(PPh_3)_2]$ (M = Mo **2**; M = W **3**), are the subject of this communication.

Cluster **1**, shown in Scheme 1, is an open-triangular, *nido* cluster with 50 electrons and seven skeletal electron pairs, in accord with the requirements of the 18-electron rule and of the skeletal electron pair (s.e.p.) theory respectively. As a consequence, cluster **1** could be prone to add a zero-s.e.p. fragment, such as $M(CO)_3$ (M = Mo or W), to give the hypothetical *closo* clusters $[MRu_3(\mu_4\text{-}Se)_2(CO)_{10}(PPh_3)_2]$. This would have been expected considering the existence of the analogous monophosphine sulfur derivative $[WRu_3(\mu_4\text{-}S)_2(CO)_{11}(PMe_2Ph)]$, obtained by irradiating a solution of $[Ru_3(\mu_3\text{-}S)_2(CO)_9]$ and $[W(CO)_5(PMe_2Ph)]$.[7]



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M = Mo **2**
M = W **3**

Scheme 1 (*i*) $[M(CO)_3(MeCN)_3]$, CH_2Cl_2, N_2, room temperature

For this purpose, we have treated the labile intermediates $[M(CO)_3(MeCN)_3]$ with complex **1** (1 : 1 molar ratio) in dichloromethane. The reactions, monitored by IR spectroscopy, take place in a few hours, at room temperature, giving the clusters **2** and **3** (Scheme 1, carbonyls omitted) as unique isolable products.§ The IR spectra of **2** and **3** are superimposable, suggesting the same molecular structure for both as confirmed by the

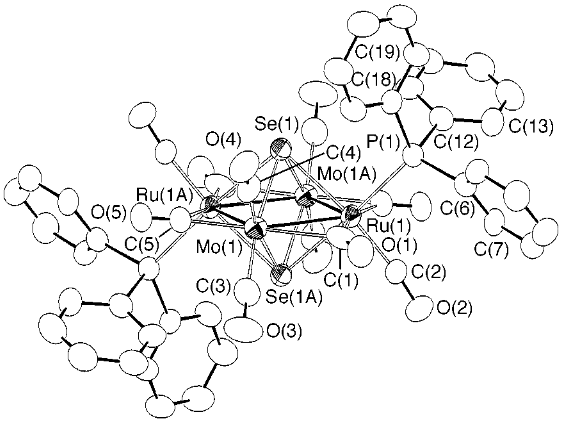

Fig. 1 View of the molecular structure of $[Mo_2Ru_2(\mu_4\text{-}Se)_2(\mu\text{-}CO)_4(CO)_6(PPh_3)_2]$ **2** showing the atom numbering scheme. Selected bond distances (Å) and angles (°) [the values in square brackets refer to cluster **3**]: Mo(1)–Se(1) 2.644(2) [2.595(2)], Mo(1)–Se(1A) 2.646(2) [2.620(2)], Mo(1)–Ru(1) 2.844(2) [2.803(2)], Mo(1)–Ru(1A) 2.860(2) [2.845(2)], Mo(1)–C(1) 2.39(2) [2.44(2)], Mo(1)–C(5) 2.02(1) [2.00(2)], Ru(1)–Se(1) 2.572(2) [2.579(2)], Ru(1)–Se(1A) 2.589(2) [2.598(2)], Ru(1)–P(1) 2.372(3) [2.373(3)], Ru(1)–C(1) 2.02(2) [2.06(2)], Ru(1A)–C(5) 2.50(2) [2.59(3)]; Ru(1)–Mo(1)–Ru(1A) 87.62(4) [89.3(1)], Mo(1)–Ru(1)–Mo(1A) 92.38(4) [90.7(1)]

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‡ Dedicated to Professor Pascual Royo on the occasion of his 60th birthday.

§ The compound $[Ru_3Se_2(CO)_7(PPh_3)_2]$ **1** (200 mg, 0.17 mmol) and $[Mo(CO)_3(MeCN)_3]$ (50 mg, 0.16 mmol) were stirred in dry CH_2Cl_2 (50 cm^3) for 12 h at room temperature under N_2. The resulting dark solution was evaporated to dryness and the residue was dissolved in CH_2Cl_2 (10 cm^3). The brown product (cluster **2**, 55 mg) was separated and purified by TLC on silica, using CH_2Cl_2–light petroleum (b.p. 40–60 °C) (1 : 1) as eluent. Crystals suitable for X-ray analysis were obtained by layering methanol on a dichloromethane solution. IR (CH_2Cl_2), $\nu_{CO}(cm^{-1})$: 2046ms, 2009vs, 1982s, 1910ms, 1840m, 1805m. $^{31}P\text{-}\{^1H\}$ NMR, δ 42.0 (s). The same reaction, under the same conditions, took place between **1** and $[W(CO)_3(MeCN)_3]$, affording cluster **3**; IR (CH_2Cl_2), $\nu_{CO}(cm^{-1})$: 2044m, 2009vs, 1981s, 1893m, 1834m, 1804w. $^{31}P\text{-}\{^1H\}$ NMR, δ 42.8 (s).

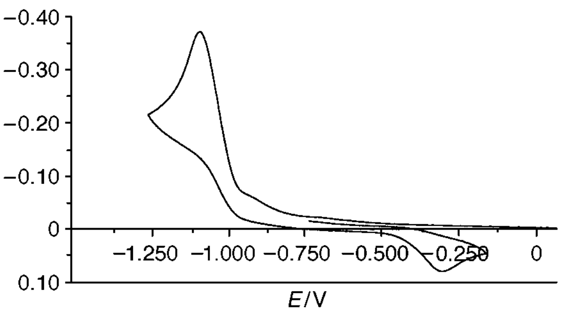

Fig. 2 Cyclic voltammogram at 50 mV s^{-1} of a dichloromethane solution of cluster **2** (10^{-3} M) and $[NBu^n{}_4][PF_6]$ (0.1 M) on a glassy-carbon electrode

X-ray analyses.¶ In fact they are isostructural, and the structure of **2** is shown in Fig. 1. Both of these bimetallic clusters exhibit electron-deficient (60 electrons), planar, centrosymmetrical arrays of two Group 6 metals and two ruthenium atoms, bicapped above and below by two quadruply bridging selenium atoms. As a result, the six atoms of the $M_2Ru_2Se_2$ core from distorted octahedrons, in which four carbonyls asymmetrically bridge the M–Ru edges. The two phosphorus ligands remain attached to the ruthenium atoms.

Apart from the unusual mixed-metal core, clusters **2** and **3** are unique, as they contain only six skeletal electron pairs instead of seven, as observed in all other clusters of this family[3c–e,6–9] and as required by the s.e.p. theory.[10] In particular, $[Mo_2Fe_2S_2(CO)_{12}]^{2-}$ is very similar to **2** and **3**, having the same number of two-electron ligands, but it is dianionic, attaining the predicted electron-pair count.[8] On the contrary, any anionic nature of clusters **2** and **3** should be ruled out, as they are insoluble in polar solvents (water and light alcohols) and their ^1H NMR spectra do not exhibit any other peak (possibly due to hypothetical cations or SeH groups) besides those of the phenyl rings. Furthermore, the final electron density maps for both show a number of residual peaks only around the heavy metals; in the case of **2** the maximum residual peak (1.46 e Å^{-3}) is located at 0.95 Å from Mo(1). The surprising stability of the unsaturated clusters **2** and **3** could be attributed to the presence of two strongly electron-donating phosphine ligands, which could contribute to the increased electron density on the metal atoms.

The electrochemical behaviour has been investigated by recording cyclic voltammograms|| for clusters **2** (Fig. 2), **3** and for the homometallic, seven s.e.p.s cluster $[Ru_4Se_2(CO)_9(PPh_3)_2]$ **4**.[6] Clusters **2** and **3** behave similarly showing reduction peaks at −1080 and −1027 mV respectively both on platinum and glassy-carbon electrodes. On platinum only, after some scans, an adsorption peak appears at *ca.* −830 mV for both mixed-metal clusters and for **4**, which does not show any diffusive reduction peak until −1500 mV, where the solvent reduction takes place. The small, irreversible anodic peaks appearing at *ca.* −300 mV in the voltammograms of **2** and **3** could be diffusion peaks, as suggested by experiments performed on a rotating disc electrode. Moreover the ratio i_{pc}/i_{pa} does not change either by holding the potential at more negative value than E_{pc}, or by increasing the scan rate from 50 to 1000 mV s^{-1}, indicating the presence of oxidizable species which possibly form from the reduction products under steady-state conditions.

¶ Crystal data for complex **2**: $C_{46}H_{30}Mo_2O_{10}P_2Ru_2Se_2$, $M = 1356.58$, triclinic, space group $P\bar{1}$, $a = 10.129(3)$, $b = 11.147(4)$, $c = 11.151(5)$ Å, $\alpha = 95.56(2)$, $\beta = 97.55(2)$, $\gamma = 110.29(3)°$, $U = 1156.8(7)$ Å^3, $Z = 1$, $\mu = 124.61$ cm^{-1}. Intensity data collected at room temperature. 4395 Unique reflections measured and used in refinement. Final *R*1 factor [for 2993 reflections with $I > 2\sigma(I)$] 0.0663. Final *R* factor for all data 0.0965.

Crystal data for complex **3**: $C_{46}H_{30}O_{10}P_2Ru_2Se_2W_2$, $M = 1532.40$, triclinic, space group $P\bar{1}$, $a = 10.102(5)$, $b = 11.156(5)$, $c = 11.205(5)$ Å, $\alpha = 95.86(2)$, $\beta = 97.33(2)$, $\gamma = 110.16(2)°$, $U = 1161.2(9)$ Å^3, $Z = 1$, $\mu = 72.68$ cm^{-1}. Intensity data collected at room temperature. 4087 Unique reflections measured and used in refinement. Final *R*1 factor [for 3412 reflections with $I > 2\sigma(I)$] 0.0783. Final *R* factor for all data 0.0914. CCDC reference number 186/824.

|| Dichloromethane solutions (10^{-3} M) containing $[NBu^n{}_4][PF_6]$ (0.1 M); platinum and glassy carbon were used as working electrodes; the reference was Ag–AgCl–KCl (saturated); scan rate 50 mV s^{-1}.

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