The Chemistry of the Selenium-containing Cluster [$Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu\text{-}CO)_3$]: Crystal Structures of [$Ru_3(\mu_3\text{-}Se)_2(CO)_7(Ph_2PC_2PPh_2)$], [$Ru_4(\mu_4\text{-}Se)_2(CO)_{10}(SbPh_3)$] and [$Ru_3(\mu_3\text{-}Se)_2(CO)_9$] *

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The selenium-containing cluster [$Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu\text{-}CO)_3$] **1** may be readily prepared by vacuum pyrolysis of [$Ru_3(CO)_{12}$] with PhSeSePh at 185 °C. The subsequent reaction of **1** with the bidentate phosphine ligand bis(diphenylphosphino)acetylene (dppa) affords the orange triruthenium cluster [$Ru_3(\mu_3\text{-}Se)_2(CO)_7$(dppa)] **2**, in 80% yield. Complex **2** crystallises in the space group $P\bar{1}$ with $a = 12.059(3)$, $b = 12.274(3)$, $c = 13.172(5)$ Å, $\alpha = 66.78(2)$, $\beta = 83.21(3)$, $\gamma = 89.30(2)°$ and $Z = 2$. Treatment of complex **1** with triphenylantimony, $SbPh_3$, yields the antimony-substituted cluster [$Ru_4(\mu_4\text{-}Se)_2(CO)_{10}(SbPh_3)$] **3**, in quantitative yield. Complex **3** crystallises in the space group $P\bar{1}$ with $a = 9.474(4)$, $b = 12.456(3)$, $c = 14.913(5)$ Å, $\alpha = 91.89(2)$, $\beta = 93.88(3)$, $\gamma = 109.99(3)°$ and $Z = 2$. Reaction of cluster **1** with carbon monoxide at room temperature and 70 atm affords the triruthenium selenido-bridged cluster [$Ru_3(\mu_3\text{-}Se)_2(CO)_9$] **4**. Complex **4** crystallises in the space group $P\bar{1}$ with $a = 6.887(3)$, $b = 9.606(7)$, $c = 13.567(9)$ Å, $\alpha = 82.48(6)$, $\beta = 84.91(4)$, $\gamma = 68.85(5)°$ and $Z = 2$.

The chemistry of transition-metal main-group clusters has undergone rapid developments in recent years.[1] Single-atom, main-group element ligands are being increasingly used as bridges between different metal fragments in cluster growth reactions. Such main-group elements often play a key role in stabilising the cluster bonding network, and frequently introduce novel structural and reactivity features.

The triply bridging sulfido ligand has been exploited extensively for the purpose of cluster growth and stabilisation.[2] The larger tellurium atom has also been shown to stabilise triangular and square arrays of metal atoms.[3–5] By comparison, few studies have explored the potential of selenium as a capping ligand, and until recently[6] all the structurally characterised examples were of osmium carbonyl clusters.[7] The current interest in the use of organoselenium compounds in organic and organometallic chemistry[8] prompted us to explore the reactivity of the reagent PhSeSePh with ruthenium clusters. We recently reported[9] the preparation of the tetraruthenium–selenido cluster [$Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu\text{-}CO)_3$] **1**, 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 (dppp). In this paper we describe further aspects of the reactivity of **1** towards the ligands bis(diphenylphosphino)acetylene (dppa), triphenylantimony, $SbPh_3$ and carbon monoxide. The synthesis and crystal structures of [$Ru_3(\mu_3\text{-}Se)_2(CO)_7$(dppa)] **2**, [$Ru_4(\mu_4\text{-}Se)_2(CO)_{10}(SbPh_3)$] **3** and [$Ru_3(\mu_3\text{-}Se)_2(CO)_9$] **4** are presented.

Results and Discussion

Reactions of [$Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu\text{-}CO)_3$] **1** *with Phosphine Ligands.*—The preparation and structural characterisation (Fig. 1) of [$Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu\text{-}CO)_3$] has been reported previously.[9] The availability of the cluster **1** allows the study of its chemistry in more detail. It is soluble in a wide variety of hydrocarbon and chlorinated solvents. Stirring of **1** with the bidentate phosphine dppa in dichloromethane solution at room temperature for 1 h affords the orange triruthenium cluster [$Ru_3(\mu_3\text{-}Se)_2(CO)_7$(dppa)] **2**, in 80% yield. The only other product isolated from the reaction was [$Ru_3(CO)_{12}$] (20% yield) which we believe to be the result of 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 spectroscopy (Table 1). The IR spectrum of **2** shows bands at 2057vs, 2022m, 1998w and 1971 cm^{-1}, indicating only the presence of terminally bonded carbonyls. Mass spectroscopic data suggested the parent ion peak at m/z 1055 and in addition the loss of seven carbonyl groups has been observed. The ^{31}P NMR spectrum showed just one singlet at δ −63.79 and the ^1H NMR spectrum exhibited two multiplets centred at δ 7.52 and 7.71 respectively. This implied the presence of only one isomer, with the phosphorus nuclei in equivalent environments. The structure of **2** has been established by X-ray analysis and is shown in Fig. 2. Selected bond lengths and bond angles for the structure are presented in Table 2. It is interesting that neither the cyclic product [$\{Ru_4Se_2(CO)_9\}_2(dppa)_2$] nor the linked cluster [$\{Ru_4Se_2(CO)_{10}\}_2$(dppa)] were formed, since the reaction of [$Os_3(CO)_{10}(NCMe)_2$] with dppa[10] leads to the formation of [$\{Os_3(CO)_{11}\}_2$(dppa)] and [$\{Os_3(CO)_{10}(dppa)\}_2$] due to the

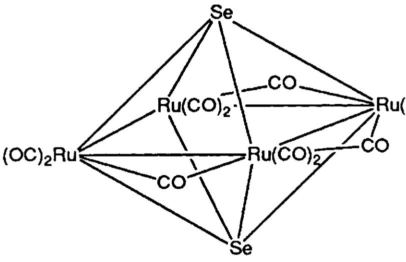

Fig. 1 Representation of the structure of [$Ru_4(\mu_4\text{-}Se)_2(CO)_{11}$] **1**

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: atm = 101 325 Pa.

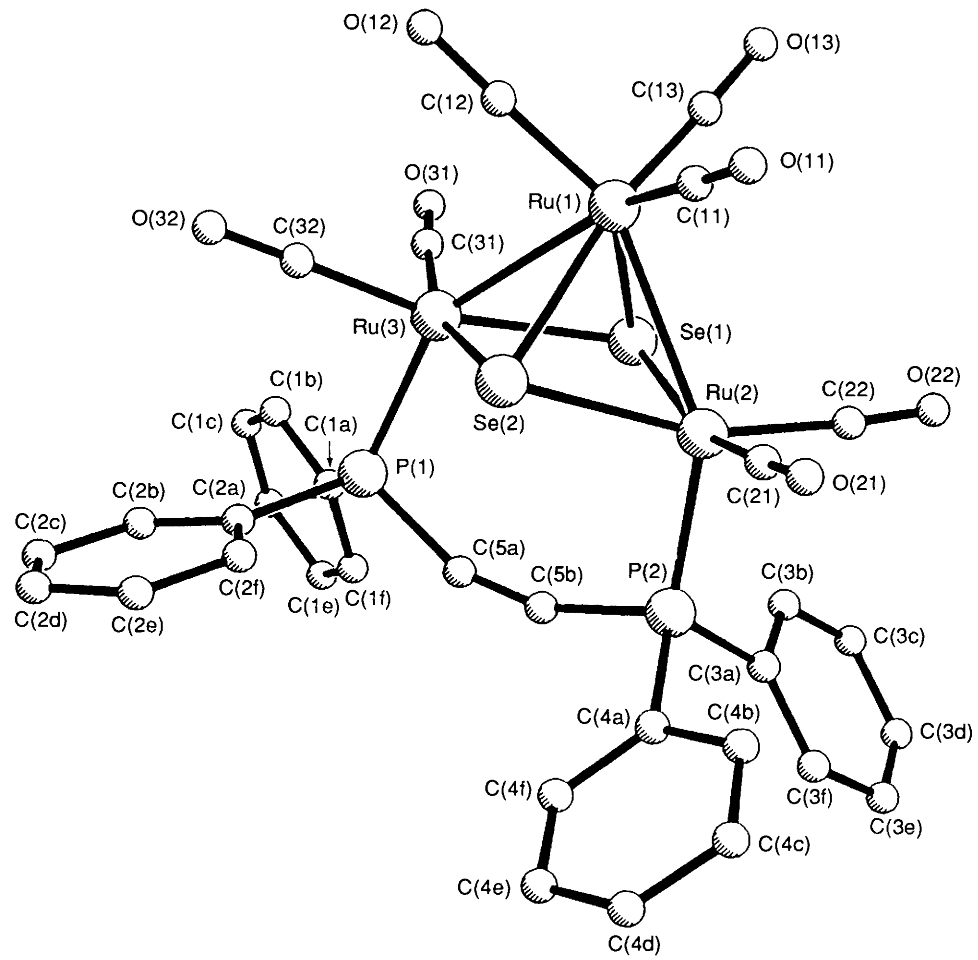


Fig. 2 The molecular structure of $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(dppa)]$ **2**

Table 1 Spectroscopic data for clusters **1**–**4** and **6**

Compound	IR[a] ν(CO/cm^{-1})	MS[b] m/z (calc.)	^{31}P NMR (δ)[c]	^{1}H NMR (δ)[d]
1 $[Ru_4Se_2(CO)_{11}]$	2061s, 2029vs, 1607m	871 (870)	—	—
2 $[Ru_3Se_2(CO)_7(dppa)]$	2057vs, 2022m, 1998w, 1971w	1055 (1051)	−63.79 (s, 2 P)	7.52 (m), 7.71 (m) (20 H)
3 $[Ru_4Se_2(CO)_{10}(SbPh_3)]$	2070m, 2029vs, 2000m, 1822w, 1606m	1196 (1195)	—	7.56 (m) (15 H)
4 $[Ru_3Se_2(CO)_9]$	2077vs, 2053vs, 2020vs	713 (715)	—	—
6 $[Ru_4Se_2(CO)_{10}(PPh_3)]$	2073w, 2037vs, 1998m, 1820w	1102 (1104)	−52.67 (s, 1 P)	7.50 (m) (15 H)

[a] Recorded in CH_2Cl_2. [b] Negative-ion FAB mass spectra: most abundant isotopomer found (simulated). [c] Recorded in CD_2Cl_2 at 295 K, reference $P(OMe)_3$. [d] Recorded in CD_2Cl_2 at 295 K, reference $SiMe_4$.

steric demand of the linear nature of the ligand triple bond. The molecular structure of complex **2** is, in fact, closely related to that of the previously reported cluster $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(dppp)]$.[9] The three ruthenium atoms define an 'isosceles triangle', with no Ru(2)–Ru(3) interaction [Ru(2) ··· Ru(3) 3.745(6) Å]. The two Se atoms μ_3-cap above and below the Ru_3 plane. The bidentate phosphine spans the long Ru(2) ··· Ru(3) edge, with the two phosphorus atoms occupying equatorial sites on the two metal atoms. The atoms Ru(2) and Ru(3) are also co-ordinated to two terminal carbonyl ligands, and Ru(1) is co-ordinated to three. It is of interest that the acetylenic ligand triple bond has been maintained in cluster **2**; the distance C(5a)–C(5b) is 1.183(9) Å. The 'linear' acetylene actually shows a significant degree of bending [P(1)–C(5a)–C(5b) 154.1(7)°, P(2)–C(5b)–C(5a) 158.3(8)°, P(1)–C(5a) 1.758(7) Å, P(2)–C(5b) 1.762(6) Å].

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 $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$ [11] and its many Group 8–chalcogenide analogues and their derivatives. The Ru–Se distances in **2** are *ca.* 0.07 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 found 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 2.29 Å) lie in the range found for other ruthenium clusters with edges spanned by bidentate phosphine ligands.[12] In contrast, the reaction of **1** with monodentate phosphine ligands such as PPh_3 leads to simple substitution to give $[Ru_4Se_2(CO)_{10}(PPh_3)]$ **6**, and the Ru_4Se_2 metal core is preserved.

Reaction with Triphenylantimony, $SbPh_3$.—Room-temperature stirring of **1** with $SbPh_3$ in dichloromethane afforded a red compound $[Ru_4Se_2(CO)_{10}(SbPh_3)]$ **3** as the only product. The IR spectrum shows bands at 2070m, 2029vs, 2000m, 1822w and 1606m cm^{-1}, indicating that **3** contains both terminal and bridging carbonyl groups. The mass spectrum showed the parent ion at m/z 1196, and peaks corresponding to the loss of 10 carbonyl ligands. Proton NMR spectroscopy showed a

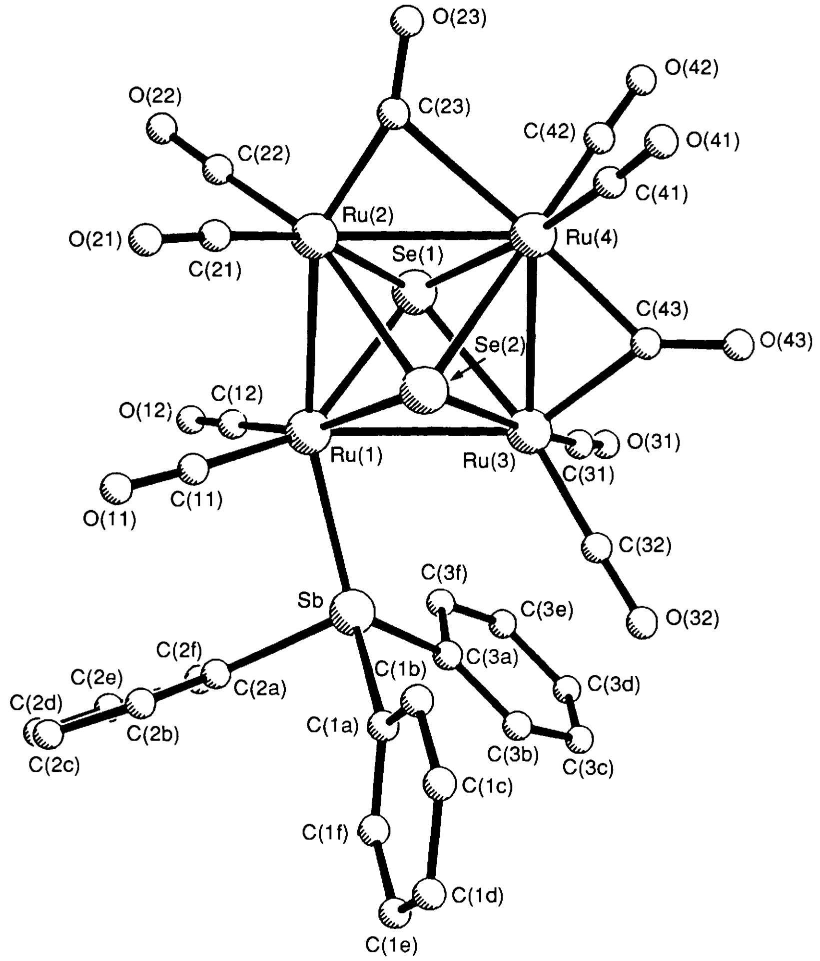


Fig. 3 The molecular structure of $[Ru_4(\mu_4\text{-}Se)_2(CO)_{10}(SbPh_3)]$ **3**

Table 2 Selected bond lengths (Å) and angles (°) for compound **2**

Ru(1)–Ru(2)	2.819(1)	Ru(3)–Se(1)	2.473(1)
Ru(1)–Ru(3)	2.842(1)	Ru(3)–Se(2)	2.512(1)
Ru(1)–Se(1)	2.529(2)	Ru(3)–P(1)	2.275(2)
Ru(1)–Se(2)	2.520(1)	P(1)–C(5a)	1.758(7)
Ru(2)–Se(1)	2.485(1)	P(2)–C(5b)	1.762(6)
Ru(2)–Se(2)	2.517(1)	C(5a)–C(5b)	1.183(9)
Ru(2)–P(2)	2.300(2)		
Ru(1)–Ru(2)–Se(1)	56.5(1)	Ru(2)–Se(2)–Ru(1)	68.1(1)
Ru(1)–Ru(2)–Se(2)	56.0(3)	Ru(3)–Se(1)–Ru(1)	69.2(1)
Ru(1)–Ru(3)–Se(1)	56.3(1)	Ru(3)–Se(2)–Ru(1)	68.8(1)
Ru(1)–Ru(3)–Se(2)	55.7(1)	Ru(3)–P(1)–C(5a)	106.2(3)
Ru(2)–Ru(1)–Ru(3)	83.6(1)	Se(1)–Ru(2)–Se(2)	81.1(1)
Ru(2)–Se(1)–Ru(3)	99.1(1)	Se(1)–Ru(3)–Se(2)	81.4(1)
Ru(2)–Se(2)–Ru(3)	97.2(1)	P(1)–C(5a)–C(5b)	154.1(7)
Ru(2)–P(2)–C(5b)	105.1(3)	P(2)–C(5b)–C(5a)	158.3(8)
Ru(2)–Se(1)–Ru(1)	68.4(1)		

multiplet at δ 7.56 which suggested that substitution of one CO group by $SbPh_3$ had indeed taken place. Dark red air-stable crystals of **3** were obtained by slow evaporation of a dichloromethane–hexane solution, and a single-crystal X-ray analysis was undertaken to establish the molecular structure of **3**, which is illustrated in Fig. 3. Selected bond lengths and bond angles are listed in Table 3.

Table 3 Selected bond lengths (Å) and angles (°) for compound **3**

Ru(1)–Ru(2)	2.778(1)	Ru(3)–Ru(4)	2.779(1)
Ru(1)–Ru(3)	2.898(1)	Ru(3)–Se(1)	2.565(1)
Ru(1)–Se(1)	2.543(1)	Ru(3)–Se(2)	2.587(1)
Ru(1)–Se(2)	2.584(1)	Ru(3)–C(43)	1.999(8)
Ru(1)–Sb	2.579(1)	Ru(4)–Se(1)	2.607(1)
Ru(2)–Ru(4)	2.778(1)	Ru(4)–Se(2)	2.631(1)
Ru(2)–Se(1)	2.557(1)	Ru(4)–C(23)	2.41(1)
Ru(2)–Se(2)	2.589(1)	Ru(4)–C(43)	2.08(1)
Ru(2)–C(23)	1.920(9)		
Ru(1)–Ru(2)–Ru(4)	91.9(1)	Ru(2)–Se(2)–Ru(3)	99.4(1)
Ru(1)–Ru(3)–Ru(4)	89.4(1)	Ru(2)–Ru(4)–Se(1)	56.6(1)
Ru(1)–Se(1)–Ru(2)	66.0(1)	Ru(2)–Ru(4)–Se(2)	57.1(1)
Ru(1)–Se(1)–Ru(3)	69.1(1)	Ru(2)–C(23)–Ru(4)	78.8(3)
Ru(1)–Se(1)–Ru(4)	101.7(1)	Ru(2)–Ru(1)–Sb	160.1(1)
Ru(1)–Se(2)–Ru(2)	65.0(1)	Ru(3)–Se(1)–Ru(4)	65.0(1)
Ru(1)–Se(2)–Ru(3)	68.2(1)	Ru(3)–Se(2)–Ru(4)	64.4(1)
Ru(1)–Se(2)–Ru(4)	100.0(1)	Ru(3)–Ru(4)–Se(1)	56.8(1)
Ru(1)–Ru(2)–Se(1)	56.8(1)	Ru(3)–Ru(4)–Se(2)	57.0(1)
Ru(1)–Ru(2)–Se(2)	57.5(1)	Ru(3)–C(43)–Ru(4)	85.8(3)
Ru(1)–Ru(3)–Se(1)	55.1(1)	Ru(3)–Ru(1)–Sb	77.2(1)
Ru(1)–Ru(3)–Se(2)	55.9(1)	Se(1)–Ru(1)–Se(2)	80.1(1)
Ru(2)–Ru(1)–Ru(3)	88.1(1)	Se(1)–Ru(2)–Se(2)	79.8(1)
Ru(2)–Ru(4)–Ru(3)	90.5(1)	Se(1)–Ru(3)–Se(2)	79.7(1)
Ru(2)–Se(1)–Ru(4)	65.1(1)	Se(1)–Ru(4)–Se(2)	78.1(1)
Ru(2)–Se(1)–Ru(3)	100.9(1)	Se(1)–Ru(1)–Sb	121.2(1)
Ru(2)–Se(2)–Ru(4)	100.0(1)	Se(2)–Ru(1)–Sb	102.6(1)

The distorted octahedral heavy-atom framework of **3** containing the Ru_4 ring is similar to that of the parent cluster $[Ru_4Se_2(CO)_{11}]$ **1**. However, in **3**, only two adjacent Ru–Ru bonds are bridged by CO ligands. The Ru(2)–Ru(4) edge is unsymmetrically bridged [Ru(2)–C(23) 1.920(9), Ru(4)–C(23) 2.41(1) Å, Ru(2)–C(23)–O(23) 156.5(9)°, Ru(4)–C(23)–O(23) 124.4(7)°], while the carbonyl along the Ru(3)–Ru(4) edge is symmetrically bridged within experimental error [Ru(3)–Ru(4)

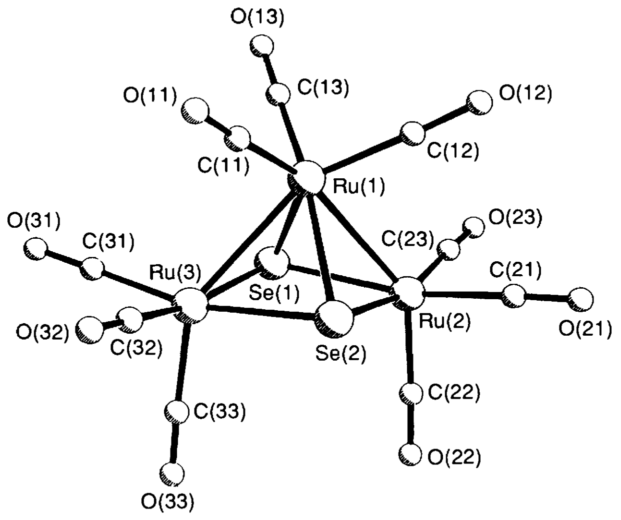
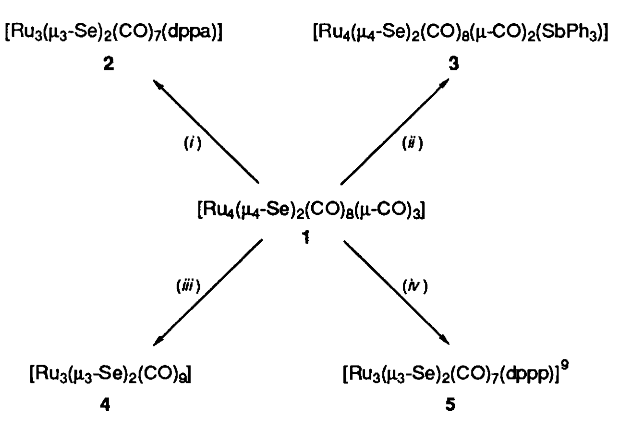


Fig. 4 The molecular structure of $[Ru_3(\mu_3\text{-}Se)_2(CO)_9]$ 4



Scheme 1 Summary of the reactivity of $[Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu\text{-}CO)_3]$ 1: (*i*) +1.0 equivalent dppa in CH_2Cl_2, 25 °C; (*ii*) +2.0 equivalents Me_3NO and 1.5 equivalents $SbPh_3$, CH_2Cl_2, 25 °C; (*iii*) +CO, 70 atm, CH_2Cl_2, 18 h, 25 °C; (*iv*) +1.6 equivalents dppp in CH_2Cl_2, 25 °C

2.779(1) Å]. The Ru–Se distances involving Ru(1), Ru(2) and Ru(3) in 3 (2.543–2.589 Å) are similar to the Ru–Se distances in the parent cluster 1 (2.556–2.610 Å). The metal–selenium distances to Ru(4) (2.607 and 2.631 Å) are longer than all the others (2.543–2.589 Å). In the related sulfur analogue, $[Ru_4(\mu_4\text{-}S)_2(CO)_7(\mu\text{-}CO)_2(PMe_2Ph)_2]$,[13] sulfur also forms longer bonds with the metal atom that is bonded to both bridging carbonyl ligands. Each ruthenium atom in 3 contains two terminally co-ordinated carbonyl ligands. Atom Ru(1), which is not bonded to the bridging carbonyl ligands, also contains the $SbPh_3$ ligand directed out of the Ru_4 plane.

Complex 3 is isomorphous and isostructural with the tellurium-capped analogue $[Ru_4(\mu_4\text{-}Te)_2(CO)_8(\mu_3\text{-}CO)_2(PPh_3)]$.[4] The bond parameters in 3 follow the same general trend as in the isostructural complex. Cluster 3 is a 62-electron system, assuming both μ_4-Se atoms act as four-electron donors, and as such is formally electron deficient by two electrons according to the 18-electron rule. This count is consistent, however, with the presence of 14 cluster-bonding valence electrons required by the Polyhedral Skeletal Electron Pair Theory[14] for the distorted-octahedral metal core geometry observed.

Reaction with Carbon Monoxide.—Reaction of 1 in CH_2Cl_2 in a 100 cm^3 autoclave under a pressure of 70 atm of CO for 12 h afforded an orange residue of 4 in quantitative yield. The IR spectrum of 4 shows three very intense bands at 2077, 2053 and 2020 cm^{-1} in dichloromethane solution, indicating a highly symmetrical metal core framework. The mass spectrum showed the parent ion at *m*/*z* 713, and further peaks corresponding to the loss of nine carbonyl groups were noted. The molecular formula of 4 was therefore proposed to be $[Ru_3Se_2(CO)_9]$; the action of carbon monoxide effectively 'decaps' the substrate carbonyl $[Ru_4Se_2(CO)_{11}]$ 1. This mechanism is similar to that noted in the preparation of the pentanuclear ruthenium carbido cluster $[Ru_5C(CO)_{15}]$ by the direct carbonylation of $[Ru_6C(CO)_{17}]$.[15]

Table 4 Selected bond lengths (Å) and angles (°) for compound 4

Ru(1)–Ru(2)	2.817(2)	Ru(2)–Se(1)	2.477(1)
Ru(1)–Ru(3)	2.826(1)	Ru(2)–Se(2)	2.487(1)
Ru(1)–Se(1)	2.516(2)	Ru(3)–Se(1)	2.473(1)
Ru(1)–Se(2)	2.526(1)	Ru(3)–Se(2)	2.495(1)
Ru(1)–Ru(2)–Se(1)	56.3(1)	Ru(1)–Se(2)–Ru(2)	68.4(1)
Ru(1)–Ru(2)–Se(2)	56.5(1)	Ru(1)–Se(2)–Ru(3)	68.5(1)
Ru(1)–Ru(3)–Se(1)	56.2(1)	Ru(2)–Se(1)–Ru(3)	97.9(1)
Ru(1)–Ru(3)–Se(2)	56.3(1)	Ru(2)–Se(2)–Ru(3)	97.1(1)
Ru(1)–Se(1)–Ru(2)	68.7(1)	Se(1)–Ru(2)–Se(2)	81.9(1)
Ru(1)–Se(1)–Ru(3)	69.0(1)	Se(1)–Ru(3)–Se(2)	81.8(1)

Orange needles of 4 were obtained by slow evaporation of a dichloromethane–hexane solution, and a single-crystal X-ray study was undertaken to establish the molecular geometry.

The crystal structure of 4 is shown in Fig. 4. Selected bond lengths and bond angles are presented in Table 4. The molecule consists of an 'open' cluster of three metal atoms with two metal–metal bonds, Ru(1)–Ru(2) 2.817(2) Å and Ru(1)–Ru(3) 2.826(1) Å, which are slightly shorter than those in $[Ru_3(CO)_{12}]$, average 2.854(4) Å.[16] There are two triply bridging selenido atoms. Each metal atom is bound to three linear terminal carbonyl ligands. The molecule possesses C_s symmetry overall (non-crystallographically imposed) such that the three atoms Se(1), Ru(3), Se(2) and the carbonyl ligand C(13)–O(13) lie in the reflection plane. The Ru–Se distances to the central seven-co-ordinate metal atom Ru(1) [Ru(1)–Se(1) 2.516(2) Å and Ru(1)–Se(2) 2.526(1) Å] are slightly longer than those to the external six-co-ordinate metal atoms Ru(2) and Ru(3) [2.473(1)–2.495(1) Å]. It is of interest that each metal–selenium bonding distance to Se(2) is slightly longer than the corresponding distance to Se(1). This structural feature is also observed in the related osmium–sulfido clusters $[Os_3(\mu_3\text{-}S)_2(CO)_9]$ and $[Os_3(\mu_3\text{-}S)_2(CO)_8(PMe_2Ph)]$.[17] Compound 4 is a 50-electron system, consistent with the presence of only two 'formal' metal–metal bonds. The cluster is isoelectronic and isostructural with the related iron–sulfur and –selenium analogues $[Fe_3(\mu_3\text{-}S)_2(CO)_9]$ and $[Fe_3(\mu_3\text{-}Se)_2(CO)_9]$.[11] A summary of the reactivity of cluster 1, $[Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu_3\text{-}CO)_3]$, is presented in Scheme 1.

Experimental

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk and vacuum-line techniques. The solvents were distilled prior to use under a nitrogen atmosphere, over the appropriate drying agent.

Infrared spectra were recorded as solutions in 0.5 mm CaF_2 cells on a Perkin Elmer 983 spectrometer with carbon monoxide as calibrant. Fast atom bombardment (FAB) mass spectra were obtained on Kratos MS50 or MS890 spectrometers using 3-nitrobenzyl alcohol as matrix and CsI as calibrant. Proton NMR spectra were recorded on a Bruker WM250 spectrometer using CD_2Cl_2 as solvent, ^{31}P spectra on a Bruker AM-400 spectrometer using CD_2Cl_2 as solvent and $P(OMe)_3$ as reference. Routine separation of products was performed by thin-layer chromatography (TLC) using commercially prepared glass plates, pre-coated to 0.25 mm thickness with Merck-Kieselgel $60F_{254}$. Microanalyses were performed

Table 5 Crystal and X-ray structural analysis data for compounds **2**, **3** and **4**

Empirical formula	$C_{33}H_{20}O_7P_2Ru_3Se_2$, **2**	$C_{28}H_{15}O_{10}Ru_4SbSe_2$, **3**	$C_9O_9Ru_3Se_2$, **4**
Molecular weight, M_r	1051.6	1195.4	713.2
a/Å	12.059(3)	9.474(4)	6.887(3)
b/Å	12.274(3)	12.456(3)	9.606(7)
c/Å	13.172(5)	14.913(5)	13.567(9)
α/°	66.78(2)	91.89(2)	82.48(6)
β/°	83.21(3)	93.88(3)	84.91(4)
γ/°	89.30(2)	109.99(3)	68.85(5)
U/Å^3	1777.9	1647.2	828.9
D_c/g cm^{-3}	1.964	2.410	2.857
μ(Mo-Kα)/cm^{-1}	33.9	51.5	70.4
F(000)	1008	1116	652
Crystal size/mm	0.18 × 0.22 × 0.43	0.20 × 0.14 × 0.18	0.12 × 0.14 × 0.22
T/K	298	298	298
2θ range/°	4–46	2–50	4–50
Scan speed/° min^{-1}	1.5–8.2	1.1–8.2	1.1–8.2
Scan range ω/°	0.8 + 0.34 tanθ	0.5 + 0.34 tanθ	0.5 + 0.34 tanθ
Reflections measured	5216	6167	3171
Unique reflections	4938	5783	2905
Observed reflections [$F_o > 3\sigma(F_o)$]	4077	4738	2654
R	0.0410	0.0430	0.0490
R'	0.0510	0.0590	0.0670

Details in common: crystal system, triclinic; space group, $P\bar{1}$; $Z = 2$; $R' = \Sigma w(|F_o| - |F_c|)/\Sigma w|F_o|$ weighting scheme, $w = 4F_o^2/[\sigma^2(F_o^2) + 0.025(F_o^2)^2]$.

Table 6 Atomic coordinates for $[Ru_3Se_2(CO)_7(dppa)]$ **2**

Atom	x	y	z	Atom	x	y	z
Ru(1)	0.335 29(5)	0.329 39(5)	0.262 29(4)	C(2d)	0.524 4(8)	−0.260 7(8)	0.175 5(8)
Ru(2)	0.198 26(5)	0.323 71(4)	0.104 84(4)	C(2e)	0.494 0(10)	−0.153 0(10)	0.113 0(10)
Ru(3)	0.310 09(5)	0.078 30(5)	0.344 29(4)	C(2f)	0.406 0(10)	−0.102 0(10)	0.159 7(9)
Se(1)	0.151 50(6)	0.212 69(6)	0.309 08(5)	C(3a)	−0.046 6(6)	0.215 0(6)	0.047 7(5)
Se(2)	0.374 39(6)	0.210 17(6)	0.144 88(6)	C(3b)	−0.106 5(7)	0.209 5(7)	0.146 0(6)
P(1)	0.024 63(2)	−0.078 3(2)	0.313 3(1)	C(3d)	−0.275 8(8)	0.232 4(8)	0.065 3(7)
P(2)	0.104 8(2)	0.206 2(2)	0.040 7(1)	C(3e)	−0.218 8(8)	0.239 7(8)	−0.032 0(8)
O(11)	0.436 8(5)	0.553 0(5)	0.074 4(5)	C(3f)	−0.101 9(7)	0.230 2(7)	−0.042 2(6)
O(12)	0.054 54(8)	0.264 7(7)	0.372 3(7)	C(4a)	0.152 0(6)	0.207 9(6)	−0.097 4(5)
O(13)	0.240 1(7)	0.459 8(7)	0.403 0(6)	C(4b)	0.162 5(6)	0.316 0(6)	−0.187 9(6)
O(21)	0.305 9(5)	0.501 5(5)	−0.117 7(5)	C(4c)	0.199 4(7)	0.320 4(7)	−0.292 8(7)
O(22)	0.010 1(5)	0.482 2(5)	0.120 3(5)	C(4d)	0.228 3(8)	0.218 4(8)	−0.306 1(7)
O(31)	0.215 0(5)	−0.005 3(5)	0.586 2(5)	C(4e)	0.216 8(8)	0.110 5(8)	−0.216 5(8)
O(32)	0.538 5(6)	−0.023 6(6)	0.380 2(5)	C(4f)	0.178 3(7)	0.105 8(7)	−0.112 4(7)
C(1a)	0.164 3(6)	−0.197 9(6)	0.424 2(5)	C(5a)	0.162 5(6)	−0.018 8(6)	0.204 9(5)
C(1b)	0.199 5(7)	−0.246 6(7)	0.527 8(6)	C(5b)	0.126 8(6)	0.059 4(6)	0.131 2(6)
C(1c)	0.142 4(7)	−0.344 6(7)	0.611 4(7)	C(11)	0.397 4(7)	0.467 8(6)	0.144 4(6)
C(1d)	0.050 7(7)	−0.392 6(7)	0.591 8(7)	C(12)	0.460 4(9)	0.286 0(9)	0.334 6(8)
C(1e)	0.013 1(8)	−0.343 8(7)	0.487 8(7)	C(13)	0.275 4(8)	0.407 7(8)	0.348 7(7)
C(1f)	0.070 0(7)	−0.246 8(6)	0.404 6(6)	C(21)	0.264 1(7)	0.432 1(6)	−0.034 0(6)
C(2a)	0.352 8(6)	−0.154 9(6)	0.259 3(6)	C(22)	0.081 3(6)	0.422 9(6)	0.109 5(6)
C(2b)	0.379 8(9)	−0.267 9(8)	0.319 6(8)	C(31)	0.254 8(7)	0.023 5(6)	0.494 9(6)
C(2c)	0.468 0(10)	−0.318 0(10)	0.274 2(9)	C(32)	0.451 8(7)	0.015 1(7)	0.367 4(6)

by members of the Department of Chemistry, University of Cambridge. Reactions with carbon monoxide were carried out in Roth (100 cm^3) magnetically stirred autoclaves. The compounds PhSeSePh, dppa and $SbPh_3$ were used as obtained from Aldrich.

Preparation of $[Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu\text{-}CO)_3]$ **1**.—A 180 cm^3 Carius tube was filled with a suspension of $[Ru_3(CO)_{12}]$ (210 mg) and PhSeSePh (120 mg) in dichloromethane (20–30 cm^3). The solvent was then removed *in vacuo* at room temperature, and the solid starting material evenly distributed over the interior surface of the tube. After sealing the tube under vacuum, the precursor compounds were pyrolysed at 185 °C for 12 h to yield a red residue. Separation of the reaction mixture by TLC using CH_2Cl_2–hexane (1:1) as eluent afforded a dark red band of $[Ru_4(\mu_4\text{-}Se)_2(CO)_8(\mu\text{-}CO)_3]$ **1** ($R_f = 0.50$). Crystalline product was obtained by slow evaporation of a CH_2Cl_2–hexane solution of **1**, yield 60%.

Reactions of $[Ru_4Se_2(CO)_{11}]$ **1**.—(*a*) *With bis(diphenylphosphino)acetylene* (*dppa*). Addition of 1.0 equivalent of dppa (12 mg, 0.030 mmol) to $[Ru_4Se_2(CO)_{11}]$ **1** (26 mg, 0.030 mmol) in CH_2Cl_2 (50 cm^3) with stirring afforded an orange solution of $[Ru_3Se_2(CO)_7(dppa)]$ **2**. Separation by TLC [eluent CH_2Cl_2–hexane (2:3)] yielded an orange band of **2** ($R_f = 0.75$) and unreacted $[Ru_3(CO)_{12}]$ ($R_f = 0.90$) only. Slow evaporation of a dichloromethane–hexane solution of **2** produced orange crystals suitable for X-ray analysis, yield 80% (Found: C, 37.90; H, 1.95; P, 5.85. Calc. for $C_{33}H_{20}O_7P_2Ru_3Se_2$: C, 37.70; H, 1.90; P, 5.90%).

(*b*) *With triphenylphosphine*. Addition of 2 equivalents of Me_3NO (10 mg, 0.133 mmol) and 1.5 equivalents of PPh_3 (23 mg, 0.088 mmol) to a dichloromethane solution (50 cm^3) of **1** afforded a red solution of $[Ru_4Se_2(CO)_{10}(PPh_3)]$ **6**. Separation by TLC [eluent dichloromethane–hexane (2:3)] yielded one major orange band ($R_f = 0.70$, yield 75%) (Found: C, 30.30; H, 1.40. Calc. for $C_{28}H_{15}O_{10}PRu_4Se_2$: C, 30.45; H, 1.35%).

Table 7 Atomic coordinates for [$Ru_4Se_2(CO)_{10}(SbPh_3)$] **3**

Atom	*x*	*y*	*z*
Sb	0.384 64(5)	0.193 95(4)	0.325 36(3)
Ru(1)	0.225 33(6)	0.266 80(4)	0.211 63(4)
Ru(2)	0.143 90(6)	0.360 55(4)	0.058 39(4)
Ru(3)	0.355 56(6)	0.139 94(4)	0.096 67(4)
Ru(4)	0.267 82(6)	0.238 45(5)	−0.052 06(4)
Se(1)	0.087 74(7)	0.145 74(5)	0.070 51(5)
Se(2)	0.414 19(7)	0.358 58(6)	0.095 08(5)
O(11)	0.293 5(7)	0.490 8(6)	0.318 5(5)
O(12)	−0.053 9(7)	0.156 8(5)	0.307 0(5)
O(21)	0.238 7(8)	0.611 7(6)	0.113 8(6)
O(22)	−0.177 5(8)	0.341 1(6)	0.080 9(5)
O(23)	0.094 4(8)	0.397 0(6)	−0.139 6(5)
O(31)	0.217 4(7)	−0.117 2(5)	0.098 4(4)
O(32)	0.664 3(7)	0.135 0(5)	0.159 3(4)
O(41)	0.455 7(7)	0.368 8(5)	−0.194 2(4)
O(42)	0.081 9(7)	0.079 3(5)	−0.205 1(4)
O(43)	0.467 6(7)	0.096 9(5)	−0.080 3(5)
C(1a)	0.618 6(8)	0.289 3(6)	0.354 9(5)
C(1b)	0.700 5(9)	0.365 1(7)	0.297 2(6)
C(1c)	0.853 0(10)	0.426 1(7)	0.318 9(6)
C(1d)	0.923 0(10)	0.407 5(8)	0.398 0(7)
C(1e)	0.843 0(10)	0.332 4(9)	0.455 6(7)
C(1f)	0.690 0(10)	0.271 1(7)	0.433 9(6)
C(2a)	0.309 1(8)	0.221 3(6)	0.453 8(5)
C(2b)	0.359 0(10)	0.330 3(9)	0.493 2(8)
C(2c)	0.300 0(10)	0.350 0(10)	0.573 6(9)
C(2d)	0.196 0(10)	0.265 6(9)	0.609 9(8)
C(2e)	0.151 0(10)	0.163 0(10)	0.574 5(9)
C(2f)	0.207 0(10)	0.134 4(9)	0.495 6(8)
C(3a)	0.376 3(8)	0.021 5(6)	0.331 3(5)
C(3b)	0.504 0(10)	−0.007 3(8)	0.339 7(7)
C(3c)	0.491 0(10)	−0.123 9(9)	0.333 4(8)
C(3d)	0.354 0(10)	−0.205 7(9)	0.323 8(8)
C(3e)	0.228 0(10)	0.179 8(9)	0.316 5(8)
C(3f)	0.236 0(10)	−0.064 5(8)	0.319 3(7)
C(11)	0.269 6(9)	0.403 3(7)	0.279 5(6)
C(12)	0.052 1(9)	0.199 6(7)	0.271 6(6)
C(21)	0.202 9(9)	0.516 0(7)	0.089 8(6)
C(22)	−0.055 6(9)	0.348 0(7)	0.073 2(6)
C(23)	0.132 7(9)	0.370 4(7)	−0.070 1(6)
C(31)	0.275 8(8)	−0.019 8(6)	0.100 2(5)
C(32)	0.545 4(8)	0.138 5(6)	0.135 9(5)
C(41)	0.387 2(8)	0.319 6(6)	−0.137 7(5)
C(42)	0.150 7(8)	0.141 1(6)	−0.146 4(5)
C(43)	0.398 4(8)	0.134 8(6)	−0.032 6(5)

Table 8 Atomic coordinates for [$Ru_3Se_2(CO)_9$] **4**

Atom	*x*	*y*	*z*
Ru(1)	0.414 94(9)	0.303 92(7)	0.342 76(5)
Ru(2)	0.340 41(9)	0.233 52(7)	0.157 85(5)
Ru(3)	0.288 00(10)	0.598 80(7)	0.244 91(5)
Se(1)	0.561 70(10)	0.383 16(8)	0.177 08(6)
Se(2)	0.081 40(10)	0.431 09(8)	0.251 56(6)
O(11)	0.242 0(10)	0.468 0(10)	0.525 7(7)
O(12)	0.335 0(10)	0.014 8(9)	0.415 4(6)
O(13)	0.858 0(10)	0.178 9(9)	0.413 0(6)
O(21)	0.060 0(10)	0.046 5(8)	0.193 7(6)
O(22)	0.210 0(10)	0.365 9(9)	−0.050 3(6)
O(23)	0.713 0(10)	−0.033 1(9)	0.096 0(7)
O(31)	0.602 0(10)	0.746 2(9)	0.276 2(6)
O(32)	−0.049 0(10)	0.810 1(9)	0.374 2(6)
O(33)	0.160 0(10)	0.776 4(8)	0.046 8(6)
C(11)	0.309 0(10)	0.409 0(10)	0.455 7(8)
C(12)	0.365 0(10)	0.125 0(10)	0.385 5(7)
C(13)	0.692 0(10)	0.226 0(10)	0.385 6(7)
C(21)	0.168 0(10)	0.114 0(10)	0.180 8(7)
C(22)	0.261 0(10)	0.311 0(10)	0.028 0(7)
C(23)	0.574 0(10)	0.068 0(10)	0.121 4(7)
C(31)	0.483 0(10)	0.690 0(10)	0.266 0(7)
C(32)	0.080 0(10)	0.731 0(10)	0.325 5(7)
C(33)	0.204 0(10)	0.713 0(10)	0.123 5(7)

(*c*) *With triphenylantimony*. Addition of 2 equivalents of Me_3NO (10 mg, 0.133 mmol) and 1.5 equivalents of $SbPh_3$ (30 mg, 0.097 mmol) to a dichloromethane solution (50 cm^3) of **1** afforded a brown solution of [$Ru_4Se_2(CO)_{10}(SbPh_3)$] **3**. Separation by TLC [eluent CH_2Cl_2–hexane (2:3)] yielded one major red band (R_f = 0.85). Slow evaporation of a dichloromethane–methanol solution of **3** afforded a crop of dark red single crystals suitable for X-ray analysis, yield 75% (Found: C, 27.95; H, 1.20. Calc. for $C_{28}H_{15}O_{10}Ru_4SbSe_2$: C, 28.15; H, 1.25%).

(*d*) *With carbon monoxide*. The cluster [$Ru_4Se_2(CO)_{11}$] (100 mg) was placed in an autoclave (100 cm^3) with CH_2Cl_2 (50 cm^3). The autoclave was pressurised twice to 30 atm carbon monoxide, then vented to atmospheric pressure, pressurised to 70 atm carbon monoxide and stirred at room temperature for 12 h. It was then cooled, the pressure released, and the orange-yellow solution evaporated to dryness. The orange solid was extracted into dichloromethane and filtered. Slow evaporation of a dichloromethane–hexane solution afforded orange crystals of [$Ru_3Se_2(CO)_9$] **4**, yield 80% (Found: C, 15.20. Calc. for $C_9O_9Ru_3Se_2$: C, 15.15%).

Crystal Structure Analyses of Complexes **2**, **3** *and* **4**.—Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (0.710 73 Å). Three check reflections were monitored periodically throughout data collection and showed no significant variations. All intensity data were corrected for Lorentz polarisation effects and absorption corrections by the Ψ-scan method were also applied for all compounds. Crystal data and a summary of data collection and structure parameters are given in Table 5. Calculations were carried out on a MicroVax II computer using the Structure Determination Package (SDP).[18]

Structures were solved by a combination of direct methods (DIRDIF)[19] and Fourier difference techniques, and refined by full-matrix least-squares analysis. In all complexes, the heavy atoms (Sb, Ru, Se, P) which constitute the core were refined anisotropically. The hydrogen atoms were generated in ideal positions (C–H 0.95 Å). Final atomic coordinates for the three structures are presented in Tables 6–8.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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