Synthesis and Chemical Characterization of the New Anions $[Rh_3(\mu_3\text{-}E)_2(CO)_6]^-$ (E = S or Se). Crystal and Molecular Structures of $[PPh_4][Rh_3(\mu_3\text{-}S)_2(CO)_6]$ and $[NMe_4][Rh_3(\mu_3\text{-}Se)_2(CO)_6]$ †

Daniele Galli and Luigi Garlaschelli *
Dipartimento di Chimica Inorganica e Metallorganica, Via G. Venezian 21, 20133—Milano, Italy
Gianfranco Ciani, Alessandro Fumagalli, Secondo Martinengo, and Angelo Sironi *
Centro di Studio per la Sintesi e la Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione, Via G. Venezian 21, 20133—Milano, Italy

Reactions of $[Rh_4(CO)_{12}]$ or $[Rh_6(CO)_{16}]$ in tetrahydrofuran with $[SCN]^-$, $[SeCN]^-$, or with polysulphides give, together with the decanuclear clusters $[Rh_{10}E(CO)_{22}]^{2-}$, the trinuclear anions $[Rh_3(\mu_3\text{-}E)_2(CO)_6]^-$ (E = S or Se). The latter species have been isolated and investigated by *X*-ray analysis. The salt $[PPh_4][Rh_3(\mu_3\text{-}S)_2(CO)_6]$ (1) crystallizes in the orthorhombic space group $Pbc2_1$ (no. 29) with $a = 13.529(2)$, $b = 16.965(2)$, $c = 28.365(6)$ Å, and $Z = 8$; $[NMe_4][Rh_3(\mu_3\text{-}Se)_2(CO)_6]$ (2) crystallizes in the orthorhombic space group $Ccm2_1$ (no. 36) with $a = 14.029(2)$, $b = 10.889(1)$, $c = 12.748(2)$ Å, and $Z = 4$. Both structures were solved by conventional Patterson and Fourier methods and refined on the basis of 3 438 and 1 032 significant independent counter data, respectively, to final conventional *R* values of 0.042 for compound (1) and 0.026 for (2). Both anions consist of a Rh_3 triangle bicapped by triply bridging chalcogenide atoms and each rhodium atom, bearing two terminal CO groups, displays an almost square-planar geometry. The Rh–Rh distances are long [mean values 3.053 and 3.135 Å for compounds (1) and (2), respectively] and suggest very weak, if any, metal–metal interaction. The two anions can therefore be considered as trinuclear rhodium(I) aggregates rather than triangular clusters.

While many trinuclear carbonyl chalcogenides of Group 8 metals are known, no similar compounds of rhodium have, to date, been characterized.

We have already reported [1,2] that both $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ react with $[SCN]^-$ to give a mixture of products from which the bicapped square-antiprismatic $[Rh_{10}S(CO)_{22}]^{2-}$ anion, containing an interstitial sulphur atom, has been isolated and fully characterized. From the same reaction mixture another species was isolated, which, on the basis of preliminary *X*-ray data, was found to be the trinuclear $[Rh_3(\mu_3\text{-}S)_2(CO)_6]^-$ anion.[2]

We report here new high-yield syntheses of this compound, together with the extension of the same reaction scheme to the selenium derivatives, which affords the corresponding $[Rh_3(\mu_3\text{-}Se)_2(CO)_6]^-$ and $[Rh_{10}Se(CO)_{22}]^{2-}$ anions. The complete results of the *X*-ray analyses of $[PPh_4][Rh_3(\mu_3\text{-}S)_2(CO)_6]$ and $[NMe_4][Rh_3(\mu_3\text{-}Se)_2(CO)_6]$ are also reported, and the nature of the bonding between the metal atoms of the two anions is discussed in comparison with structural data of other similar trinuclear species.

Results and Discussion

Preparation of the $[Rh_3(\mu_3\text{-}E)_2(CO)_6]^-$ *Anions* [E = S (1) *or* Se (2)].—Anion (1), as mentioned above, was first isolated as a by-product in the synthesis of the $[Rh_{10}S(CO)_{22}]^{2-}$ cluster.[2] In order to obtain better yields of (1) we attempted different synthetic routes and found that the trinuclear anion can alternatively be obtained by treating neutral or anionic rhodium carbonyl clusters as well as some rhodium(I) derivatives with sulphur or with thiocyanate, sulphide, or polysulphide anions.

Starting from neutral carbonyls, treatment of $[Rh_4(CO)_{12}]$ or $[Rh_6(CO)_{16}]$ with K[SCN] (molar ratio 1 : 4—1 : 6) in refluxing tetrahydrofuran (thf) led to cluster fragmentation, giving a solution from which, after removal of an insoluble by-product (mainly unreacted $[Rh_6(CO)_{16}]$ and a carbonyl species tentatively formulated as $[\{Rh(CO)_2(SCN)\}_2]^3$), the $[Rh_3(\mu_3\text{-}S)_2(CO)_6]^-$ anion can be isolated in up to 70% yields as a salt of bulky cations such as $[N(PPh_3)_2]^+$, $[NMe_3(CH_2Ph)]^+$, and $[PPh_4]^+$. It is worth noting that, in the early stage of the reaction, i.r. spectroscopy indicated the intermediate formation of some anionic species, among which $[Rh_{17}S_2(CO)_{32}]^{3-}$ has been recognized; this is surprising, as this anion was prepared by Vidal *et al.*[4] under forcing conditions. The $[Rh_3(\mu_3\text{-}S)_2(CO)_6]^-$ anion can also be obtained in yields of 60—70% by treating $[Rh_4(CO)_{12}]$ or $[Rh_6(CO)_{16}]$ with an excess of potassium polysulphides, K_2S_x (x = 1—8), in thf at room temperature. The observation that anionic species are obtained as intermediates in the above syntheses prompted us to study the possibility of obtaining compound (1) by treating some rhodium carbonyl cluster anions with sulphur. The results of such reactions depend on both the ratio of sulphur to the cluster anion and the number of metal atoms per negative charge. When the ratio of the negative charge on the anionic cluster to the number of metal atoms is 1 : 3, addition of the stoicheiometric amount of sulphur gives the trinuclear anion in good yields (>70%); *e.g.* equation (i). However, in other cases

$$[Rh_6(CO)_{15}]^{2-} + 4\,S \longrightarrow 2\,[Rh_3(\mu_3\text{-}S)_2(CO)_6]^- + 3\,CO \quad \text{(i)}$$

larger amounts of by-products are formed. For example, starting from $[Rh_5(CO)_{15}]^-$, with a sulphur : cluster anion ratio of 2 : 1, a reaction consistent with equation (ii) is ob-

$$3\,[Rh_5(CO)_{15}]^- + 6\,S \longrightarrow 3\,[Rh_3(\mu_3\text{-}S)_2(CO)_6]^- + [Rh_6(CO)_{16}] + 11\,CO \quad \text{(ii)}$$

---

† Tetraphenylphosphonium bis(μ_3-sulphido)-*cyclo*-tris[dicarbonylrhodate(I)] and tetramethylammonium bis(μ_3-selenido)-*cyclo*-tris-[dicarbonylrhodate(I)].

Supplementary data available (No. SUP 23734, 34 pp.): H-atom co-ordinates for complex (1a), thermal parameters and structure factors for (1a) and (2a). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

served. Careful investigation by i.r. spectroscopy indicates that at the beginning of the reaction both $[Rh_3(\mu_3\text{-}S)_2(CO)_6]^-$ and $[Rh_4(CO)_{12}]$ are formed and only upon completion of the reaction (about 1 d) is there precipitation of $[Rh_6(CO)_{16}]$. The reaction was performed under a carbon monoxide atmosphere to avoid decomposition of $[Rh_5(CO)_{15}]^-$ into $[Rh_{12}(CO)_{30}]^{2-}$.[5] Thus, under a nitrogen atmosphere a different course is observed and after 48 h $[Rh_5(CO)_{15}]^-$ is transformed mainly into $[Rh_{17}S_2(CO)_{32}]^{3-}$ [4] along with some $[Rh_3(\mu_3\text{-}S)_2(CO)_6]^-$. This reaction can be used to obtain the $[Rh_{17}S_2(CO)_{32}]^{3-}$ anion under mild conditions. Similar results were obtained by treating $[Rh_{12}(CO)_{30}]^{2-}$, under a nitrogen atmosphere, with sulphur (molar ratio of carbonyl cluster : sulphur = 1 : 3), but with a large excess of sulphur (molar ratio 1 : 12) only compound (1) and an uncharacterized black by-product, insoluble in all common organic solvents, are formed. This by-product shows broad i.r. bands at 2 060m and 1 750w cm^{-1} (Nujol mull) and is formed in all the reactions involving sulphur or polysulphides. It is interesting that stable cluster anions, such as the above $[Rh_{17}S_2(CO)_{32}]^{3-}$ or the compact cluster $[Rh_{13}H_2(CO)_{24}]^{3-}$ can also be transformed into compound (1). For example, $[Rh_{13}H_2(CO)_{24}]^{3-}$ can be slowly transformed into compound (1) by use of a mixture of S and S^{2-} under a carbon monoxide atmosphere.

A more straightforward synthesis starts from rhodium(I) derivatives, such as $[Rh_2(CO)_4Cl_2]$ and $[Rh(CO)_2Cl_2]^-$, with sulphide anions. In all these cases, halide ligand substitution gives compound (1) as shown in equations (iii) and (iv), respectively.

$$3[Rh_2(CO)_4Cl_2] + 4\,S^{2-} \longrightarrow 2[Rh_3(\mu_3\text{-}S)_2(CO)_6]^- + 6\,Cl^- \quad \text{(iii)}$$

$$3[Rh(CO)_2Cl_2]^- + 2\,S^{2-} \longrightarrow [Rh_3(\mu_3\text{-}S)_2(CO)_6]^- + 6\,Cl^- \quad \text{(iv)}$$

Substitution occurs rapidly, indicating the very high stability of the trinuclear complex.

Crystals of $[PPh_4][Rh_3(\mu_3\text{-}S)_2(CO)_6]$, compound (1a), suitable for *X*-ray investigation, were obtained by slow diffusion of a 1 : 1 mixture of Pr^{i}OH and heptane (30 cm^3) into a thf (10 cm^3) solution of the salt.

In order to verify the possible existence of a series of selenium-containing compounds, analogous to those obtained with sulphur, we have studied the reactivity of $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ towards $[SeCN]^-$ at room temperature or in refluxing thf with molar ratios of the carbonyl cluster to $[SeCN]^-$ ranging from 1 : 1 to 1 : 6. At a molar ratio of $[Rh_6(CO)_{16}]$ to K[SeCN] of 1 : 2 in thf at room temperature a rapid evolution of carbon monoxide is observed and, within 30 min, there is spectroscopic evidence of formation of the $[Rh_6(CO)_{15}(SeCN)]^-$ anion, with ν(CO) bands at 2 095w, 2 075w, 2 040vs, and 1 780s cm^{-1}, very similar to those found [6] for $[Rh_6(CO)_{15}X]^-$ (X = Cl, Br, I, CN, SCN, OCN, CONHPr^i, COMe, or H) derivatives. This anion then reacts further to give mainly $[Rh_{10}Se(CO)_{22}]^{2-}$ (yield 20%) and $[Rh_3(\mu_3\text{-}Se)_2(CO)_6]^-$ (yield 30%). The two products have been separated by fractional crystallization from thf–Pr^{i}OH as $[N(PPh_3)_2]^+$ salts. The formulation of $[Rh_{10}Se(CO)_{22}]^{2-}$ has been inferred by elemental analysis and by the close similarity of its i.r. spectrum [2 000vs and 1 825s cm^{-1} (thf)], in the CO stretching region, with that of the analogous sulphur compound; [2] to date, we have been unable to obtain single crystals of suitable quality for a complete *X*-ray analysis. Better yields (60%) of the $[Rh_{10}Se(CO)_{22}]^{2-}$ derivative, contaminated by compound (2), have been obtained from $[Rh_4(CO)_{12}]$ and $[N(PPh_3)_2][SeCN]$ (molar ratio 1 : 15), in Pr^{i}OH at room temperature. The same kind of mixtures with different percentages of the two anions is obtained from the reaction between $[Rh_4(CO)_{12}]$ and K[SeCN] (molar ratio 1 : 1—1 : 5) in thf. In the last case (molar ratio 1 : 5), after a few minutes, it is also possible to detect by i.r. spectroscopy the formation of some intermediate species such as $[Rh_5(CO)_{15}]^-$ and probably $[Rh_5(CO)_{14}(SeCN)]^{2-}$.[7] The $[Rh_3(\mu_3\text{-}Se)_2(CO)_6]^-$ anion can be obtained, as the only chalcogenide species, on reaction of either $[Rh_4(CO)_{12}]$ or $[Rh_6(CO)_{16}]$ with a large excess of K[SeCN] (molar ratio of carbonyl cluster to K[SeCN] 1 : 6), in refluxing thf, together with some unreacted $[Rh_6(CO)_{16}]$ and a carbonyl species tentatively formulated as $[\{Rh(CO)_2(SeCN)\}_2]$ from the close similarity of its i.r. spectrum, 2 100m, 2 075vs, and 2 020vs cm^{-1} (Nujol mull), with that of $[\{Rh(CO)_2(SCN)\}_2]$.[3]

Crystals of $[NMe_4][Rh_3(\mu_3\text{-}Se)_2(CO)_6]$, compound (2a), suitable for structural investigation were obtained by slow diffusion of heptane (30 cm^3) into a dichloromethane (10 cm^3) solution of the salt.

Chemical Characterization of $[Rh_3(\mu_3\text{-}E)_2(CO)_6]^-$ (E = S *or* Se).—Compounds (1) and (2) are diamagnetic and air stable in the solid state for a few days; they do not decompose upon refluxing in thf, under nitrogen, for several hours. Compound (1) is not effected by an excess of chloride ions and it does not react with a stoicheiometric amount of acid, whereas with a large excess of HCl in dichloromethane evolution of H_2S is observed with formation of the $[Rh(CO)_2Cl_2]^-$ anion. It reacts with $HgCl_2$ to give uncharacterized products. Compounds (1) and (2) do not react with carbon monoxide nor with hydrogen over a long period. This suggests that in the presence of sulphur the poisoning of $[Rh_4(CO)_{12}]$ and some of its neutral substituted derivatives, which are known to play an important role in catalytic hydroformylation,[8] may arise from the formation of sulphur-containing compounds, like $[Rh_3(\mu_3\text{-}S)_2(CO)_6]^-$, as found for the poisoning of cobalt carbonyl clusters.[9]

Spectroscopic Measurements.—The i.r. spectrum of the sulphur derivative (1) in the CO stretching region is shown in Figure 1. Compounds (1) and (2), in thf solution, show very similar ν(CO) bands at 2 040vw, 2 018vs, 1 966vs, and 1 930vw cm^{-1} and at 2 045vw, 2 016vs, 1 962vs, and 1 930vw cm^{-1}, respectively. These spectra are similar to those of the $[Rh(CO)_2Cl_2]^-$ (X = Cl, Br, or I) [3,10] complexes and are in keeping with the presence of two *cis* CO ligands around a rhodium(I) atom having a square-planar co-ordination.

The ^{13}C and $^{13}C\text{-}\{^{103}Rh\}$ n.m.r. data for compounds (1) and (2) are reported in Table 1. The data are entirely consistent with the solid-state structure and in the case of the selenium derivatives no scrambling process between the CO groups was found in the range −95 to +26 °C. The ^{13}C spectrum of both compounds shows only a doublet, due to coupling of the carbonyls with the ^{103}Rh atoms, giving $^1J(^{103}Rh\text{-}^{13}C)$ values as expected for a rhodium(I) derivative.[11] The resonances of the rhodium atoms in compounds (1) and (2) are at rather low frequencies compared with the value of δ −16.7 for $[NBu^t_4][Rh(CO)_2Cl_2]$.[11]

Description of the Structures.—Both structures consist of the packing of discrete anions and cations separated by normal van der Waals contacts. In the case of compound (1a) two independent pairs of ions are present. The bonding parameters within the cations $[PPh_4]^+$ for compound (1a) and $[NMe_4]^+$ for compound (2a) are normal and will not be discussed. A perspective view of the $[Rh_3(\mu_3\text{-}Se)_2(CO)_6]^-$ anion, of idealized D_{3h} symmetry, is shown in Figure 2 and its geometry can be considered as representative also for the sulphur derivative. The bond distances and angles are reported in Table 2 for compound (1a) and in Table 3 for compound (2a). In Table 4

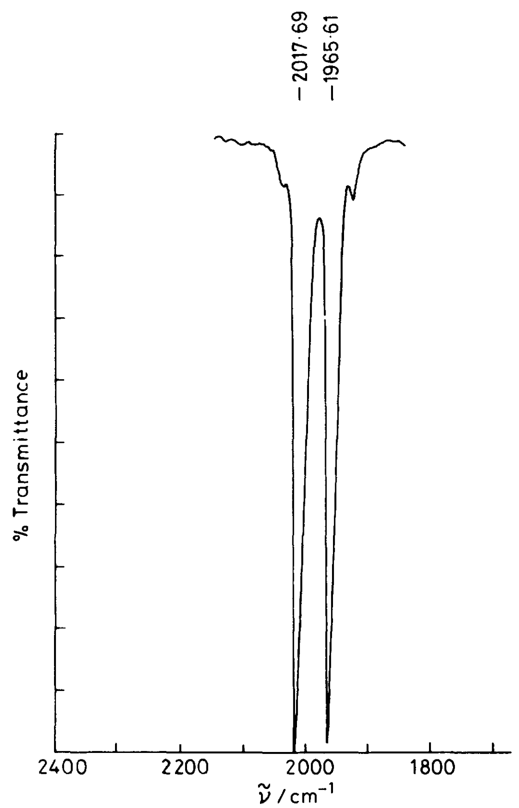

Figure 1. I.r. spectrum of $[N(PPh_3)_2][Rh_3(\mu_3\text{-}S)_2(CO)_6]$ in thf solution

Table 1. N.m.r. data[a] for $[N(PPh_3)_2][Rh_3(\mu_3\text{-}S)_2(CO)_6]$ and $[NMe_4][Rh_3(\mu_3\text{-}Se)_2(CO)_6]$ in thf

Anion	CO	Rh	$^1J(^{103}Rh\text{-}^{13}C)$
$[Rh_3(\mu_3\text{-}S)_2(CO)_6]^-$	183.6	−412.7	70.5 ± 0.5
	—	—	70.6 ± 0.5[b]
$[Rh_3(\mu_3\text{-}Se)_2(CO)_6]^-$	185.7	−428.2	72 ± 0.5
	186.0[b]	−393.7[b]	71.5 ± 0.5[b]

[a] $\delta(^{13}CO)$ in p.p.m. relative to $SiMe_4$; $\delta(^{103}Rh)$, 0 p.p.m. = 3.16 MHz at such a magnetic field that the protons of $SiMe_4$ resonate at exactly 100 MHz. High-frequency shifts are positive; ^1J values are in Hz. Values are at −96 °C unless stated otherwise. [b] At 25 °C.

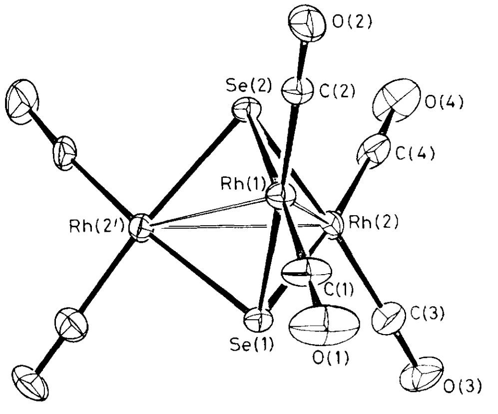

Figure 2. View of the anion of $[NMe_4][Rh_3(\mu_3\text{-}Se)_2(CO)_6]$ (2a). A crystallographic mirror plane passes through atoms Rh(1), Se(1), Se(2)

Table 2. Interatomic distances (Å) and angles (°) within the anion of $[PPh_4][Rh_3(\mu_3\text{-}S)_2(CO)_6]$ (1a), with estimated standard deviations (e.s.d.s) in parentheses

	Molecule A	Molecule B		Molecule A	Molecule B
Rh(1)–Rh(2)	3.007(1)	3.070(1)	Rh(2)–C(3)	1.854(14)	1.821(15)
Rh(1)–Rh(3)	3.021(1)	3.008(1)	Rh(2)–C(4)	1.837(15)	1.845(14)
Rh(2)–Rh(3)	3.121(2)	3.093(1)	Rh(3)–C(5)	1.829(17)	1.843(16)
Rh(1)–S(1)	2.344(4)	2.357(4)	Rh(3)–C(6)	1.835(20)	1.843(15)
Rh(1)–S(2)	2.356(4)	2.347(4)	C(1)–O(1)	1.168(15)	1.168(17)
Rh(2)–S(1)	2.352(4)	2.356(4)	C(2)–O(2)	1.146(16)	1.192(17)
Rh(2)–S(2)	2.347(4)	2.340(4)	C(3)–O(3)	1.151(15)	1.166(15)
Rh(3)–S(1)	2.349(4)	2.354(4)	C(4)–O(4)	1.157(16)	1.131(14)
Rh(3)–S(2)	2.356(4)	2.351(3)	C(5)–O(5)	1.136(17)	1.140(16)
Rh(1)–C(1)	1.833(15)	1.804(18)	C(6)–O(6)	1.167(19)	1.137(14)
Rh(1)–C(2)	1.821(16)	1.782(18)			

	Molecule A	Molecule B		Molecule A	Molecule B
Rh(2)–Rh(1)–Rh(3)	62.36(3)	61.17(3)	S(1)–Rh(2)–C(3)	91.8(4)	93.1(4)
Rh(1)–Rh(2)–Rh(3)	59.05(3)	58.44(3)	S(2)–Rh(2)–C(4)	91.2(5)	92.0(4)
Rh(1)–Rh(3)–Rh(2)	58.59(3)	60.39(3)	S(1)–Rh(3)–C(5)	93.7(5)	91.4(5)
Rh(1)–S(1)–Rh(2)	79.6(1)	81.3(1)	S(2)–Rh(3)–C(6)	92.2(6)	92.6(4)
Rh(1)–S(1)–Rh(3)	80.1(1)	79.4(1)	S(1)–Rh(1)–C(2)	174.1(5)	174.0(5)
Rh(2)–S(1)–Rh(3)	83.2(1)	82.1(1)	S(2)–Rh(1)–C(1)	177.1(4)	176.2(5)
Rh(1)–S(2)–Rh(2)	79.5(1)	81.8(1)	S(1)–Rh(2)–C(4)	173.4(5)	174.6(4)
Rh(1)–S(2)–Rh(3)	79.7(1)	79.6(1)	S(2)–Rh(2)–C(3)	171.5(4)	175.7(4)
Rh(2)–S(2)–Rh(3)	83.1(1)	82.5(1)	S(1)–Rh(3)–C(6)	175.1(6)	174.8(4)
C(1)–Rh(1)–C(2)	91.5(6)	91.6(7)	S(2)–Rh(3)–C(5)	175.9(5)	173.5(5)
C(3)–Rh(2)–C(4)	94.4(6)	92.1(6)	Rh(1)–C(1)–O(1)	174(1)	173(2)
C(5)–Rh(3)–C(6)	91.2(7)	93.3(6)	Rh(1)–C(2)–O(2)	179(1)	176(1)
S(1)–Rh(1)–S(2)	83.0(1)	82.6(1)	Rh(2)–C(3)–O(3)	169(1)	173(1)
S(1)–Rh(2)–S(2)	83.0(1)	82.8(1)	Rh(2)–C(4)–O(4)	178(1)	177(1)
S(1)–Rh(3)–S(2)	82.9(1)	82.6(1)	Rh(3)–C(5)–O(5)	175(1)	176(1)
S(1)–Rh(1)–C(1)	94.2(4)	94.3(5)	Rh(3)–C(6)–O(6)	172(1)	177(1)
S(2)–Rh(1)–C(2)	91.3(5)	91.4(5)			

Table 3. Distances (Å) and angles (°) * within the anion of [NMe$_4$][Rh$_3$(μ_3-Se)$_2$(CO)$_6$] (2a), with e.s.d.s in parentheses

Rh(1)–Rh(2)	3.159(1)	Rh(1)–C(2)	1.866(11)
Rh(2)–Rh(2′)	3.086(1)	Rh(2)–C(3)	1.865(9)
Rh(1)–Se(1)	2.459(1)	Rh(2)–C(4)	1.857(7)
Rh(1)–Se(2)	2.455(1)	C(1)–O(1)	1.165(14)
Rh(2)–Se(1)	2.457(1)	C(2)–O(2)	1.129(13)
Rh(2)–Se(2)	2.460(1)	C(3)–O(3)	1.127(11)
Rh(1)–C(1)	1.839(12)	C(4)–O(4)	1.132(9)
Rh(2)–Rh(1)–Rh(2′)	58.47(2)	Se(2)–Rh(1)–C(2)	91.0(3)
Rh(1)–Rh(2)–Rh(2′)	60.76(1)	Se(1)–Rh(2)–C(3)	88.3(3)
Rh(1)–Se(1)–Rh(2)	79.99(3)	Se(2)–Rh(2)–C(4)	89.1(3)
Rh(2)–Se(1)–Rh(2′)	77.82(3)	Se(1)–Rh(1)–C(2)	176.2(4)
Rh(1)–Se(2)–Rh(2)	79.99(3)	Se(2)–Rh(1)–C(1)	173.8(4)
Rh(2)–Se(2)–Rh(2′)	77.68(4)	Se(1)–Rh(2)–C(4)	173.8(3)
C(1)–Rh(1)–C(2)	95.2(5)	Se(2)–Rh(2)–C(3)	173.4(3)
C(3)–Rh(2)–C(4)	97.4(4)	Rh(1)–C(1)–O(1)	179(1)
Se(1)–Rh(1)–Se(2)	85.18(4)	Rh(1)–C(2)–O(2)	178(1)
Se(1)–Rh(2)–Se(2)	85.11(3)	Rh(2)–C(3)–O(3)	178(1)
Se(1)–Rh(1)–C(1)	88.6(3)	Rh(2)–C(4)–O(4)	175(1)

* Primed atoms are those generated by the crystallographic mirror plane.

Table 4. Comparison of mean bonding parameters (distances in Å, angles in °) within the anions [Rh$_3$(μ_3-E)$_2$(CO)$_6$]$^-$

	E = S	E = Se
Rh···Rh	3.05(2)	3.13(2)
Rh–E	2.351(2)	2.458(1)
Rh–C	1.829(6)	1.858(4)
C–O	1.155(5)	1.135(6)
Rh–E–Rh	81.0(4)	79.2(5)
C–Rh–C	92.4(5)	96.7(7)
E–Rh–E	82.8(1)	85.1(2)
E–Rh–C$_{cis}$	92.4(3)	89.1(4)
E–Rh–C$_{trans}$	174.7(4)	174.1(4)

the mean values of relevant bond parameters in the two anions are compared.

Both anions consist of a triangular moiety of rhodium atoms capped on each side by two triply bridging E atoms (E = S or Se). Neglecting the intermetallic contacts, each rhodium atom displays a square-planar geometry with respect to the two *cis* E atoms and the two terminally bonded CO groups. The values of the metal–metal distances and the ligand stereochemistry in the two compounds raised the problem of whether the compounds should be regarded as aggregates of three square-planar rhodium(I) units, sharing the two E atoms, or as triangular clusters. Analysis of our results and comparison with other related trinuclear species (see below) suggested the first hypothesis as the most probable. Thus the Rh–Rh distances are exceptionally long when compared with corresponding interactions (2.70—2.80 Å) in tetrahedral and in octahedral clusters.[12] Moreover, the values are rather scattered; for instance the two independent anions labelled A and B, in the sulphur derivative, have different Rh–Rh distances one being longer [3.121(2) Å] and two shorter [3.007(1) and 3.021(1) Å] in anion A and two longer [3.070(1) and 3.093(1) Å] and one shorter [3.008(1) Å] in anion B. This implies that in such anions the Rh–Rh interactions are quite weak, being strongly dependent on extramolecular factors such as packing forces. Other evidence in support of the polynuclear nature of these anions is that the Rh–Rh distances increase on passing from the sulphur to the selenium derivative, along with an increase of the Rh–E distances (see Table 4), while the mean values of the Rh–E–Rh bite angles remain quite similar [81.0 and 79.2° for compounds (1) and (2), respectively]. In contrast, in compounds such as [Co$_3$(μ_3-E)(CO)$_9$] (E = S[13] or Se[14]) or [FeCo$_2$(μ_3-E)(CO)$_9$] (E = S[15] or Se[14]) where metal–metal bonds are considered to be present (see below), a change of the chalcogen atom causes minor variations in the M–M bond distances and large variations in the M–E–M angles (see for example Table 5 in ref. 14). The values found for the Rh–E bond distances agree well with the sum of the relevant covalent radii. The main differences between the sulphur and the selenium derivatives are attributable to the size effect of the different chalcogen atoms. For instance, since the Rh–Se bond distances are longer than the Rh–S ones the selenium atom has a lower ' angular ' hindrance than sulphur and the mean value of the Se–Rh–C (*cis*) angles (89.1°) is lower than that of the S–Rh–C (*cis*) angles (92.4°), while the mean value of the angles between carbonyl ligands (C–Rh–C) is larger in the selenium (96.7°) than in the sulphur (92.4°) compound. The mean Rh–C bond distances are moderately longer in the selenium compound as previously found in [MCo$_2$(μ_3-E)(CO)$_9$] (M = Co, E = S;[13] M = Co, E = Se;[14] M = Fe, E = S;[15] and M = Fe, E = Se[14]) for the carbonyl groups transoid to the chalcogenide atom.

Table 5. Some examples of trinuclear μ_3-chalcogenide cluster compounds

Compound	Number of valence electrons	Mean M–M (Å)	Ref.
[FeCo$_2$(μ_3-S)(CO)$_9$]	48	2.554(3)	15
[FeCo$_2$(μ_3-Se)(CO)$_9$]	48	2.577(1)	14
[FeCo$_2$(μ_3-Te)(CO)$_9$]	48	2.598(2)	14
[Co$_3$(μ_3-S)(CO)$_9$]	49	2.637(3)	13
[Co$_3$(μ_3-Se)(CO)$_9$]	49	2.616(1)	14
[Co$_3$(μ_3-S)$_2$(η^5-C$_5$H$_5$)$_3$]	50	2.687(3)	16
[Ni$_3$(μ_3-S)$_2$(η^5-C$_5$H$_5$)$_3$]	53	2.801(5)	17

Comparison of the Metal–Metal Interactions in Trinuclear Species.—Many trinuclear μ_3-chalcogenide metal clusters with different numbers of valence electrons (see Table 5) have been described by Dahl and co-workers,[13–17] the trend in M–M bond distances being interpreted on the basis of the metal–metal antibonding nature of the electron(s) in excess with respect to the 48 valence electrons expected from the effective atomic number rule for a triangular cluster. Also [Fe$_3$(μ_3-As)$_2$(CO)$_9$][18] conforms well to Dahl's scheme, showing metal–metal interactions [mean 2.62(1) Å] which can be considered as normal single bonds. On the other hand, anions (1) and (2) as well as the recently characterized [Ni$_3$(μ_3-E)$_2$(PEt$_3$)$_6$]$^{2+}$ (E = S[19] or Se[20]) [mean M–M bond lengths 2.91(2) and 3.16(2) Å, respectively] and [Ni$_3$(μ_3-S)$_2$(μ-S$_3$N)$_3$]$^-$ [21] (mean M–M 2.904 Å) although containing 48 valence electrons do not conform to the above rationalization. This implies that, in some cases, a formal electron book-keeping is not sufficient to explain the nature of the chemical bond and that the co-ordination geometry of the ligands, *i.e.* the hybridization assumed by a metal atom, is very important in determining the metal–metal bonding abilities of each metal fragment. It is interesting that in all the reported compounds which do not conform to Dahl's scheme the metals show a square-planar co-ordination geometry. Although we exclude the presence of direct Rh–Rh single bonds in anions (1) and (2), distances in the range 3.01—3.16 Å can be taken as indicative of some weak metal–metal interactions.[22]

Experimental

All the solvents were purified and dried by conventional methods and stored under nitrogen. The reactions were carried out under an oxygen-free nitrogen atmosphere using the Schlenk-tube technique. The compounds $[Rh_4(CO)_{12}]$,[23] $[Rh_6(CO)_{16}]$,[23] $[Rh_5(CO)_{15}]^-$,[5] $[\{Rh(CO)_2Cl\}_2]$,[24] $[Rh(CO)_2Cl_2]^-$,[10] and $[Rh_6(CO)_{15}]^{2-}$ [25] were prepared as described in the literature. The salts K[SCN], K[SeCN], and potassium polysulphide, K_2S_x (x = 1—8), were Fluka analytical grade products. The compound $[N(PPh_3)_2]_2S$ was prepared by metathesis in water from $[N(PPh_3)_2]Cl$ and Na_2S; $[N(PPh_3)_2][SeCN]$ was prepared by methathesis in water from $[N(PPh_3)_2]Cl$ and K[SeCN]. The crude product was washed with cold water and recrystallized from dichloromethane and diethyl ether.

Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer and on a Nicolet MX-1FT IR, using calcium fluoride cells previously purged with N_2. Carbon-13 and $^{13}C-\{^{103}Rh\}$ n.m.r. measurements were carried out as described previously [11,26] on thf solutions of $[N(PPh_3)_2][Rh_3(\mu_3\text{-}E)_2(CO)_6]$ (E = S or Se). Carbon-13 carbonyl enrichments (*ca.* 30%) were carried out by direct exchange with ^{13}CO using standard vacuum-line techniques.

Preparation of Sulphur Derivatives.—(a) *From* $[Rh_4(CO)_{12}]$ *and* K[SCN]. To a solution of $[Rh_4(CO)_{12}]$ (0.306 g, 0.41 mmol) in thf (30 cm^3) under nitrogen was added K[SCN] (0.194 g, 2 mmol). The suspension was stirred at room temperature for 30 min and then refluxed for 8 h to give a solution of the potassium salt of the trinuclear anion together with an insoluble by-product. From this solution the product $[Rh_3(\mu_3\text{-}S)_2(CO)_6]^-$ can be isolated as a salt of bulky cations such as $[NMe_4]^+$, $[NEt_4]^+$, $[NMe_3(CH_2Ph)]^+$, $[PPh_4]^+$, and $[N(PPh_3)_2]^+$, by filtration, concentration *in vacuo*, and addition of the concentrated solution to a stirred aqueous solution of the bulky cation. For the larger cations there is immediate precipitation, while for the smaller ones further concentration is necessary to induce precipitation. For example, the above reaction mixture was filtered and the volume of the solution was reduced to 15 cm^3 then added dropwise to an aqueous solution containing $[PPh_4]Cl$ (1.5 g, 75 cm^3 water). The resulting pale yellow precipitate was filtered off, washed with water (5 × 10 cm^3), and dried *in vacuo;* yield 0.34 g, (72%) (Found: C, 40.8; H, 2.1. $C_{30}H_{20}O_6PRh_3S_2$ requires C, 40.9; H, 2.3%). The compound, in the solid state, is stable under nitrogen for a long period; it is soluble in thf, CH_2Cl_2, $CHCl_3$, and EtCN, but insoluble in aliphatic and aromatic hydrocarbons.

(b) *From* $[Rh_6(CO)_{16}]$ *and* K[SCN]. The compound $[Rh_6(CO)_{16}]$ (0.53 g, 0.5 mmol) and K[SCN] (0.5 g, 5.15 mmol) were refluxed in thf (50 cm^3) for 12 h and the product was separated as described in (a); yield 0.446 g (65%) as the benzyltrimethylammonium salt.

(c) *From* $[Rh_4(CO)_{12}]$ *and potassium polysulphide.* The compound $[Rh_4(CO)_{12}]$ (0.48 g, 0.64 mmol) and potassium polysulphide (0.4 g) in thf (30 cm^3) were stirred at room temperature for 16 h and the product was separated as described in (a); yield 0.382 g (65%) as the $[NMe_3(CH_2Ph)]^+$ salt.

(d) *From* $[Rh_6(CO)_{16}]$ *and potassium polysulphide.* The compound $[Rh_6(CO)_{16}]$ (0.41 g, 0.39 mmol) and potassium polysulphide (0.45 g) in thf (25 cm^3) were stirred at room temperature for 18 h and the product was isolated as described in (a); yield 0.334 g (63%) as the $[NMe_3(CH_2Ph)]^+$ salt.

(e) *From* $[N(PPh_3)_2][Rh_5(CO)_{15}]$ *and sulphur.* A solution of sulphur (0.1 mol dm^{-3} in thf, 8 cm^3) was added, dropwise, with stirring to a solution of $[N(PPh_3)_2][Rh_5(CO)_{15}]$ (0.54 g, 0.365 mmol) in thf (7 cm^3) under a carbon monoxide atmosphere {molar ratio, S: $[Rh_5(CO)_{15}]^-$ = 2.2 : 1.0}. The colour of the solution changed from red-violet to brown, and after 18 h a brown precipitate was filtered off. The mother-liquor was evaporated to dryness *in vacuo* and the solid was extracted with acetone (3 × 5 cm^3). The clear brown solution was layered with a mixture of Pr^iOH (25 cm^3) and heptane (45 cm^3) to give, after complete diffusion, crystals of the product; yield 0.25 g (60%).

(f) *From* $Na_2[Rh_{12}(CO)_{30}]$ *and sulphur.* The salt $Na_2[Rh_{12}(CO)_{30}]$ (0.164 g, 0.077 mmol) in thf (10 cm^3 containing 1.5% water) was treated with a thf solution of sulphur (0.1 mol dm^{-3}, 10 cm^3). The solution was stirred at room temperature and after 18 h was filtered. The mother-liquor was treated with $[PPh_4]Br$ (0.5 g) dissolved in water (60 cm^3) containing Pr^iOH (5 cm^3). Upon concentration of this solution *in vacuo* a pale yellow precipitate was formed which was filtered off and vacuum dried. The compound was dissolved in thf (5 cm^3) and layered with heptane (15 cm^3). Upon diffusion of the two solvents, pale yellow crystals of the compound were obtained; yield 0.06 g (22%).

(g) *Reaction of* $[N(PPh_3)_2]_2[Rh_6(CO)_{15}]$ *with sulphur.* A solution of $[N(PPh_3)_2]_2[Rh_6(CO)_{15}]$ (0.08 g, 0.037 mmol) in thf (5 cm^3) was stirred, at room temperature, with sulphur (0.005 g, 0.15 mmol). The colour of the solution changed immediately from green to yellow-brown while a small amount of an insoluble by-product was formed. The i.r. spectrum of the solution indicated formation of the trinuclear species.

(h) *Reaction of* $[\{Rh(CO)_2Cl\}_2]$ *with* $[N(PPh_3)_2]_2S$. A solution of $[\{Rh(CO)_2Cl\}_2]$ (0.16 g, 0.41 mmol) in thf (10 cm^3) was stirred, at room temperature, with $[N(PPh_3)_2]_2S$ (0.62 g, 0.56 mmol). After a few minutes the reaction was complete and compound (1) was precipitated and identified as reported above; yield 0.236 g (80%).

(i) *Reaction of* $[N(PPh_3)_2][Rh(CO)_2Cl_2]$ *with* $[N(PPh_3)_2]_2S$. This reaction was accomplished as reported above using $[N(PPh_3)_2][Rh(CO)_2Cl_2]$ (1.67 g, 2.18 mmol) and $[N(PPh_3)_2]_2S$ (1.6 g, 1.45 mmol); yield of product 0.65 g (83%).

(j) *Reaction of* $[N(PPh_3)_2][Rh_3(\mu_3\text{-}S)_2(CO)_6]$ *with* HCl. The salt $[N(PPh_3)_2][Rh_3(\mu_3\text{-}S)_2(CO)_6]$ (0.312 g, 0.29 mmol) in dichloromethane (15 cm^3) was stirred with aqueous concentrated HCl solution (12 mol dm^{-3}, 0.5 cm^3). Slow evolution of H_2S took place while the i.r. spectrum of the CH_2Cl_2 solution showed that the $[Rh_3(\mu_3\text{-}S)_2(CO)_6]^-$ anion was transformed into $[Rh(CO)_2Cl_2]^-$.

Preparation of the Selenium Derivatives.—(a) *Synthesis of* $[Rh_{10}Se(CO)_{22}]^{2-}$. (i) *From* $[Rh_6(CO)_{16}]$ *and* K[SeCN]. A suspension of $[Rh_6(CO)_{16}]$ (0.752 g, 0.70 mmol) in thf (30 cm^3) was stirred, at room temperature, with K[SeCN] (0.102 g, 0.71 mmol) for 3 h. The brown solution was filtered, concentrated in vacuum to 15 cm^3, and added dropwise to an aqueous alcoholic solution containing $[N(PPh_3)_2]Cl$ (1.5 g, 80 cm^3 water, 10 cm^3 Pr^iOH). The resulting brown precipitate was filtered off, washed with water (3 × 10 cm^3), and vacuum dried. The two products $[N(PPh_3)_2]_2[Rh_{10}Se(CO)_{22}]$ and $[N(PPh_3)_2][Rh_3(\mu_3\text{-}Se)_2(CO)_6]$ can be obtained almost pure by fractional recrystallization from thf–Pr^iOH; yields 0.24 g (20%) for the decanuclear cluster and 0.49 g (30%) for the trinuclear cluster.

(ii) *From* $[Rh_4(CO)_{12}]$ *and* $[N(PPh_3)_2][SeCN]$. To a suspension of $[Rh_4(CO)_{12}]$ (0.805 g, 1.07 mmol) in Pr^iOH (30 cm^3), under a nitrogen atmosphere, was added $[N(PPh_3)_2][SeCN]$ (1.03 g, 1.6 mmol). The mixture was stirred at room temperature for 2 h. The resulting black precipitate was filtered off, washed with Pr^iOH (3 × 10 cm^3), and dried. The crude product was extracted with thf (3 × 20 cm^3) leaving some $[Rh_6(CO)_{16}]$ and an uncharacterized carbonyl species. The thf solution was concentrated *in vacuo* to 20 cm^3 and the product was precipitated by addition of Pr^iOH (75 cm^3). The mother-liquor contained some $[N(PPh_3)_2][Rh_3(\mu_3\text{-}Se)_2(CO)_6]$.

Table 6. Final positional parameters for $[PPh_4][Rh_3(\mu_3-S)_2(CO)_6]$ (1a)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh(1A)	0.661 32(8)	0.260 67(6)	0.000 00	C(121)	0.544 0(9)	0.331 1(7)	0.262 8(4)
Rh(2A)	0.768 09(8)	0.106 05(6)	0.009 53(4)	C(122)	0.447 0(10)	0.344 3(8)	0.274 5(5)
Rh(3A)	0.538 23(9)	0.112 10(6)	0.001 08(5)	C(123)	0.404 7(12)	0.319 0(9)	0.316 3(6)
Rh(1B)	0.037 71(8)	0.499 83(6)	0.243 88(4)	C(124)	0.468 8(13)	0.280 7(10)	0.346 7(6)
Rh(2B)	0.263 13(8)	0.511 86(6)	0.253 87(4)	C(125)	0.560 0(13)	0.265 5(10)	0.337 4(6)
Rh(3B)	0.159 72(8)	0.352 29(6)	0.235 18(4)	C(126)	0.603 5(11)	0.289 0(8)	0.294 3(5)
S(1A)	0.646 7(3)	0.163 1(2)	0.058 1(1)	C(131)	0.618 5(9)	0.478 2(7)	0.221 4(4)
S(2A)	0.664 5(3)	0.151 2(2)	−0.051 1(1)	C(132)	0.668 1(11)	0.518 3(9)	0.186 3(5)
S(1B)	0.146 3(3)	0.441 1(2)	0.298 6(1)	C(133)	0.686 7(11)	0.599 4(8)	0.192 9(5)
S(2B)	0.165 2(3)	0.469 3(2)	0.190 8(1)	C(134)	0.654 5(11)	0.632 8(8)	0.233 8(6)
P(1)	0.594 8(3)	0.374 4(2)	0.211 2(1)	C(135)	0.607 4(11)	0.594 4(9)	0.268 8(5)
P(2)	0.099 0(3)	0.238 0(2)	0.455 0(1)	C(136)	0.586 3(10)	0.513 1(8)	0.262 9(5)
O(1A)	0.663 8(9)	0.390 6(7)	0.071 5(4)	C(141)	0.710 8(9)	0.326 1(6)	0.197 8(4)
O(2A)	0.686 7(9)	0.370 2(7)	−0.080 6(4)	C(142)	0.792 6(10)	0.353 1(8)	0.220 5(5)
O(3A)	0.907 9(9)	0.083 4(6)	0.090 1(4)	C(143)	0.882 1(10)	0.312 2(8)	0.216 2(5)
O(4A)	0.905 9(9)	0.031 6(7)	−0.060 0(4)	C(144)	0.884 6(11)	0.245 2(9)	0.189 1(5)
O(5A)	0.385 1(9)	0.077 3(7)	0.072 8(5)	C(145)	0.800 6(11)	0.218 5(9)	0.166 0(5)
O(6A)	0.418 3(10)	0.058 4(8)	−0.081 6(5)	C(146)	0.712 6(10)	0.259 3(7)	0.170 1(4)
O(1B)	−0.118 7(10)	0.520 7(7)	0.316 1(4)	C(211)	0.010 3(8)	0.227 2(6)	0.409 2(4)
O(2B)	−0.081 9(10)	0.567 2(7)	0.165 7(4)	C(212)	−0.028 2(11)	0.152 8(8)	0.398 9(5)
O(3B)	0.389 2(9)	0.554 4(7)	0.336 2(4)	C(213)	−0.092 3(11)	0.141 6(8)	0.363 0(5)
O(4B)	0.400 5(8)	0.597 5(6)	0.190 0(4)	C(214)	−0.121 6(11)	0.204 7(9)	0.335 2(5)
O(5B)	0.148 0(9)	0.214 0(7)	0.299 8(4)	C(215)	−0.087 8(13)	0.279 4(10)	0.346 3(6)
O(6B)	0.165 5(8)	0.251 8(6)	0.149 1(3)	C(216)	−0.020 3(10)	0.290 0(8)	0.381 2(5)
C(1A)	0.658 9(11)	0.342 4(8)	0.042 3(5)	C(221)	0.051 6(8)	0.190 8(6)	0.507 1(4)
C(2A)	0.677 1(11)	0.328 4(9)	−0.049 2(6)	C(222)	−0.043 8(9)	0.209 6(7)	0.522 0(4)
C(3A)	0.849 2(11)	0.085 6(8)	0.060 8(5)	C(223)	−0.077 8(11)	0.182 6(8)	0.563 9(5)
C(4A)	0.851 6(12)	0.059 8(8)	−0.033 4(5)	C(224)	−0.020 4(11)	0.134 6(9)	0.589 2(5)
C(5A)	0.442 5(12)	0.087 8(9)	0.044 3(6)	C(225)	0.070 1(11)	0.111 5(8)	0.575 3(5)
C(6A)	0.461 0(14)	0.075 2(10)	−0.047 3(6)	C(226)	0.108 6(10)	0.139 6(7)	0.532 6(5)
C(1B)	−0.058 5(13)	0.517 3(10)	0.286 7(6)	C(231)	0.121 2(9)	0.339 9(7)	0.467 2(5)
C(2B)	−0.034 9(13)	0.542 2(10)	0.198 0(6)	C(232)	0.162 9(11)	0.386 5(8)	0.432 1(5)
C(3B)	0.334 7(11)	0.539 6(8)	0.305 6(5)	C(233)	0.182 4(11)	0.466 8(8)	0.441 6(5)
C(4B)	0.346 3(10)	0.566 8(8)	0.214 2(5)	C(234)	0.159 0(12)	0.495 3(9)	0.485 7(5)
C(5B)	0.149 0(11)	0.267 2(9)	0.275 3(5)	C(235)	0.120 0(11)	0.449 6(9)	0.520 4(5)
C(6B)	0.165 8(11)	0.289 9(8)	0.182 1(5)	C(236)	0.101 3(11)	0.370 3(8)	0.511 4(6)
C(111)	0.506 8(9)	0.361 8(7)	0.165 0(4)	C(241)	0.214 4(10)	0.193 4(7)	0.440 2(5)
C(112)	0.468 4(11)	0.288 8(8)	0.155 4(5)	C(242)	0.298 5(10)	0.215 7(8)	0.464 9(5)
C(113)	0.401 8(11)	0.278 6(9)	0.118 7(5)	C(243)	0.387 4(11)	0.178 0(9)	0.458 8(5)
C(114)	0.371 4(11)	0.344 7(10)	0.093 7(6)	C(244)	0.390 5(12)	0.115 1(9)	0.428 6(6)
C(115)	0.405 7(13)	0.417 3(10)	0.102 8(6)	C(245)	0.310 0(12)	0.092 7(9)	0.404 1(6)
C(116)	0.474 2(11)	0.429 0(8)	0.138 8(5)	C(246)	0.221 9(11)	0.131 8(8)	0.409 3(5)

A pure product can be obtained by subsequent recrystallization from thf–Pr^{i}OH; yield 0.723 g (60%) (Found: C, 38.8; H, 2.4; N, 1.2; Rh, 38.5. $C_{94}H_{60}N_2O_{22}P_4Rh_{10}Se$ requires C, 40.3; H, 2.1; N, 1.0, Rh, 36.8%). The compound is soluble and stable for long periods in dry thf, CH_2Cl_2, and EtCN and under a nitrogen atmosphere but it is unstable in damp solvents or in the presence of oxygen.

Salts with other cations can be obtained by treating $[Rh_4(CO)_{12}]$ (0.75 g, 1 mmol) with K[SeCN] (0.74 g 5 mmol) in thf (50 cm^3) at room temperature for 3 h, and treating the resulting potassium salt solution as described for the sulphur derivative.[2] In this way the $[NMe_4]^+$, $[NEt_4]^+$, $[PPh_4]^+$, $[NMe_3(CH_2Ph)]^+$, and $[NBu^t_4]^+$ salts were isolated.

(b) *Synthesis of* $[Rh_3(\mu_3-Se)_2(CO)_6]^-$. This compound was obtained similarly to the analogous sulphur derivative by treating $[Rh_4(CO)_{12}]$ or $[Rh_6(CO)_{16}]$ with K[SeCN] in refluxing thf and treating the resulting solution containing the potassium salt as described in the corresponding section (a). In a typical experiment, reaction of $[Rh_4(CO)_{12}]$ (0.812 g, 1.08 mmol) in refluxing thf (50 cm^3) with K[SeCN] (1 g, 6.9 mmol) for 12 h yielded the $[NMe_3(CH_2Ph)]^+$ salt (0.82 g, 72%). Similarly, refluxing for 12 h a thf (50 cm^3) suspension of $[Rh_6(CO)_{16}]$ (0.945 g, 0.89 mmol) with K[SeCN] (0.76 g, 5.28 mmol) gave 0.945 g (68%) of the $[NMe_3(CH_2Ph)]^+$ salt. The anion has been also isolated as salts of $[NEt_4]^+$, $[PPh_4]^+$, $[AsPh_4]^+$, $[NEt_3(CH_2Ph)]^+$, and $[PPh_3(CH_2Ph)]^+$. These salts are soluble in thf, acetone, and CH_2Cl_2, but insoluble in aliphatic and aromatic hydrocarbons.

X-*Ray Analysis*.—*Crystal data*. $C_{30}H_{20}O_6PRh_3S_2$ (1a), $M = 880.3$, Orthorhombic, space group *Pbc*2$_1$ [non-standard setting of *Pca*2$_1$ (no. 29)], $a = 13.529(2)$, $b = 16.965(2)$, $c = 28.365(6)$ Å, $U = 6\,510.3$ Å^3, $D_m = 1.75(2)$, $Z = 8$, $D_c = 1.80$ g cm^{-3}, $F(000) = 3\,440$, μ(Mo-K_α) = 16.7 cm^{-1}.

$C_{10}H_{12}NO_6Rh_3Se_2$ (2a), $M = 708.8$, Orthorhombic, space group *Ccm*2$_1$ [non-standard setting of *Cmc*2$_1$ (no. 36)], $a = 14.029(2)$, $b = 10.889(1)$, $c = 12.748(2)$ Å, $U = 1\,947.4$ Å^3, $D_m = 2.40(2)$, $Z = 4$, $D_c = 2.42$ g cm^{-3}, $F(000) = 1\,320$, μ(Mo-K_α) = 64.8 cm^{-1}.

Intensity data collection. Well formed prismatic crystals of $[PPh_4][Rh_3(\mu_3-S)_2(CO)_6]$ (pale yellow, 0.14 × 0.20 × 0.22 mm) and of $[NMe_4][Rh_3(\mu_3-Se)_2(CO)_6]$ (yellow, 0.12 × 0.14 × 0.28 mm) were mounted on an Enraf-Nonius CAD-4 automated diffractometer and the setting angles of 25 random intense reflections in the range 2θ 20—26° were used to determine, by least-squares analysis, accurate cell parameters.

In both cases the data collection was made at a constant scan speed of 2.5° min^{-1} using the ω-scan method, with

Table 7. Final positional parameters for [NMe$_4$][Rh$_3$(μ_3-Se)$_2$(CO)$_6$] (2a) *

Atom	*X/a*	*Y/b*	*Z/c*
Rh(1)	−0.137 34(5)	0.000 00	0.000 00
Rh(2)	−0.237 82(3)	−0.141 70(5)	−0.185 84(8)
Se(1)	−0.101 60(6)	0.0000	−0.188 8(1)
Se(2)	−0.305 04(7)	0.0000	−0.055 0(1)
O(1)	0.073 6(7)	0.0000	0.040 3(9)
O(2)	−0.196 8(8)	0.0000	0.225 6(7)
O(3)	−0.134 3(5)	−0.295 3(8)	−0.343 6(7)
O(4)	−0.418 7(5)	−0.284 9(7)	−0.168 7(11)
C(1)	−0.008 4(9)	0.0000	0.025 9(10)
C(2)	−0.173 0(9)	0.0000	0.141 0(10)
C(3)	−0.174 6(6)	−0.237 4(9)	−0.285 2(9)
C(4)	−0.348 6(6)	−0.234 7(7)	−0.178 0(11)
N	−0.388 3(7)	0.000	−0.501(1)
CT(1)	−0.279(1)	0.000	−0.494(2)
CT(2)	−0.421(1)	0.000	−0.613(2)
CT(3)	−0.423(1)	−0.113(2)	−0.452(2)

* CT refers to the carbon atoms of the cation.

graphite-monochromatized Mo-K_α radiation (λ = 0.710 73 Å), and a scan range of (α +0.35 tan θ)° [α = 1.2 and 1.0° for compounds (1a) and (2a), respectively] with a 25% extension at each end for background determination. 7 006 Independent intensities in the range 3 < θ < 26° for complex (1a) and 1 205 in the range 3 < θ < 27° for compound (2a), corresponding to the $+h$, $+k$, $+l$ octant, were collected. The intensities of three standard reflections were measured every 2 h of *X*-ray exposure but no decay was observed for both crystals. For compound (1a), 3 438, and for compound (2a), 1 032 significant independent reflections with $I > 3\sigma(I)$ were derived from the two data sets, taking into account the Lorentz and polarization factors. An absorption correction was applied, using an empirical method based on ψ scans (ψ 0—360 °, every 10°), to reflections with χ values near to 90°; the maximum, minimum, and average relative transmission values were 1.00, 0.91, and 0.97 for compound (1a) and 1.00, 0.84, and 0.93 for (2a).

Structure resolution and refinement. Systematic absences [$0kl$ ($k = 2n + 1$), $h0l$ ($l = 2n + 1$), and derived conditions] suggested that compound (1a) could be assigned either to the centrosymmetric group *Pbcm* (no. 57) or to the non-centrosymmetric group $Pbc2_1$ [non-standard setting of $Pca2_1$ (no. 29)]. Deconvolution of the Patterson map and successful refinements showed that the latter space group was correct.

In an analogous way, compound (2a) was assigned the space group $Ccm2_1$ [non-standard setting of $Cmc2_1$ (no. 36)] among the possible ones (nos. 36, 40, and 63). In both structures the metal atoms were located from Patterson maps. Successive Fourier syntheses gave the positional parameters of all the non-hydrogen atoms, which were refined by full-matrix least-squares methods. The structure of compound (1a) shows the presence of two independent anions and cations in the asymmetric unit, while that of (2a) shows that both anions and cations lie in special positions, on mirror planes. Both compounds crystallize in non-centrosymmetric space groups and therefore we have refined, in both cases, the two possible enantiomers taking into account anomalous scattering effects. The positional parameters reported in Table 6 for compound (1a) and in Table 7 for (2a) correspond to the solutions with lower agreement indices. In compound (1a) the hydrogen atoms of the cations were located in idealized positions (C–H 0.95 Å), after each cycle, but not refined. Weights were assigned according to the formula $w = 1/[\sigma(F_o)]^2$, where the σ values of the reflections were modified by a p factor of 0.03. The final conventional R and R' factors were 0.042 and 0.039 for compound (1a) and 0.026 and 0.030 for (2a). Final difference Fourier maps showed only peaks <0.6 e Å^{-3} near to the metal atoms. All the computations were made on a PDP 11/34 computer using the Enraf-Nonius Structure Determination Package (SDP) and the physical constants tabulated therein.

Acknowledgements

We thank Professor B. T. Heaton, University of Canterbury, for n.m.r. measurements. This work was supported by the Italian National Research Council, C.N.R.

References

1 G. Ciani, L. Garlaschelli, A. Sironi, and S. Martinengo, *J. Chem. Soc., Chem. Commun.*, 1981, 563.
2 L. Garlaschelli, A. Fumagalli, S. Martinengo, B. T. Heaton, D. O. Smith, and L. Strona, *J. Chem. Soc., Dalton Trans.*, 1982, 2265.
3 D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1965, 1900.
4 J. Vidal, R. A. Fiato, L. A. Cosby, and R. L. Pruett, *Inorg. Chem.*, 1978, **17**, 2574.
5 A. Fumagalli, T. K. Koetzle, F. Takusagawa, P. Chini, S. Martinengo, and B. T. Heaton, *J. Am. Chem. Soc.*, 1980, **102**, 1740.
6 P. Chini, S. Martinengo, and G. Giordano, *Gazz. Chim. Ital.*, 1972, **102**, 330.
7 L. Garlaschelli, A. Fumagalli, and S. Martinengo, unpublished work.
8 P. Pino, F. Piacenti, and M. Bianchi, in ' Organic Syntheses *via* Metal Carbonyls,' eds. I. Wender and P. Pino, Wiley, New York, 1977, vol. 2, p. 233; B. Cornils, in ' New Syntheses with Carbon Monoxide,' ed. J. Falbe, Springer, Berlin, 1980, p. 1; P. Chini, S. Martinengo, and L. Garlaschelli, *J. Chem. Soc., Chem. Commun.*, 1972, 709.
9 L. Marko', *Gazz. Chim. Ital.*, 1979, **109**, 274.
10 L. M. Vallarino, *Inorg. Chem.*, 1965, **4**, 161.
11 C. Brown, B. T. Heaton, L. Longhetti, W. T. Povey, and D. O. Smith, *J. Organomet. Chem.*, 1980, **192**, 93.
12 P. Chini, G. Longoni, and V. G. Albano, *Adv. Organomet. Chem.*, 1976, **14**, 285; P. Chini and B. T. Heaton, *Top. Curr. Chem.*, 1977, **71**, 1.
13 C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 1967, **6**, 1229.
14 C. E. Strouse and L. F. Dahl, *J. Am. Chem. Soc.*, 1971, **93**, 6032.
15 D. L. Stevenson, C. H. Wei, and L. F. Dahl, *J. Am. Chem. Soc.*, 1971, **93**, 6027.
16 P. D. Frisch and L. F. Dahl, *J. Am. Chem. Soc.*, 1972, **94**, 5082.
17 H. Vahrenkamp, V. A. Ucthman, and L. F. Dahl, *J. Am. Chem. Soc.*, 1968, **90**, 3272.
18 L. T. J. Dalbaere, L. J. Kruczynski, and D. W. McBride, *J. Chem. Soc., Dalton Trans.*, 1973, 307.
19 C. A. Ghilardi, S. Midollini, and L. Sacconi, *Inorg. Chim. Acta*, 1978, **31**, L431.
20 F. Cecconi, C. A. Ghilardi, and S. Midollini, *Cryst. Struct. Commun.*, 1982, **11**, 25.
21 J. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 705.
22 L. F. Dahl, C. Martell, and D. L. Wampler, *J. Am. Chem. Soc.*, 1961, **83**, 1761; J. G. Norman, jun., and D. J. Gmur, *ibid.*, 1977, **99**, 1446; A. W. Coleman, D. T. Eadie, and S. R. Stobart, *ibid.*, 1982, **104**, 922.
23 S. Martinengo, G. Giordano, and P. Chini, in 'Inorganic Syntheses,' ed. D. H. Bush, Wiley, New York, 1980, vol. 20, p. 209.
24 J. A. McCleverty and G. Wilkinson, in ' Inorganic Syntheses,' ed. H. F. Holtzclaw, jun., McGraw-Hill Book Company, New York, 1966, vol. 8, p. 211.
25 S. Martinengo and P. Chini, *Gazz. Chim. Ital.*, 1972, **102**, 344.
26 G. Longoni, B. T. Heaton, and P. Chini, *J. Chem. Soc., Dalton Trans.*, 1980, 1537.

Received 28*th March* 1983; *Paper* 3/496