Improved Syntheses of the Hexanuclear Clusters $[Ru_6(CO)_{18}]^{2-}$, $[HRu_6(CO)_{18}]^-$, and $H_2Ru_6(CO)_{18}$. The *X*-Ray Analysis of $[HRu_6(CO)_{18}]^-$,† a Polynuclear Carbonyl containing an Interstitial Hydrogen Ligand

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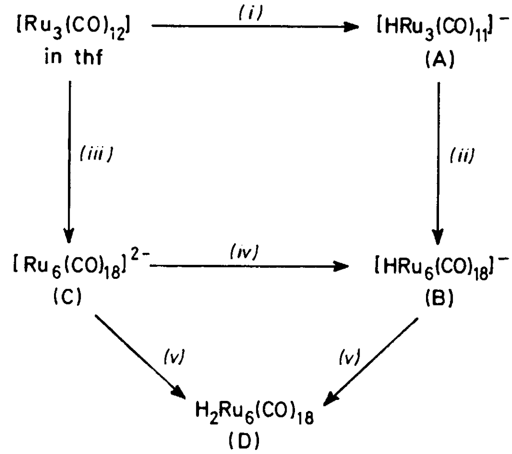
The *X*-ray analyses of two crystalline modifications, (I) and (II), of $[N(PPh_3)_2][HRu_6(CO)_{18}]$ are reported, together with improved synthetic routes to this and the related clusters $[Ru_6(CO)_{18}]^{2-}$ and $H_2Ru_6(CO)_{18}$. Crystals of (I) are triclinic, space group $P\bar{1}$, with a = 18.083(4), b = 19.101(4), c = 19.238(5) Å, α = 117.70(4), β = 78.13(2), γ = 97.05(2)°, and Z = 4. Crystals of (II) are monoclinic, space group $P2_1/n$, with a = 33.82(8), b = 52.55(10), c = 9.832(2) Å, β = 92.66(2)°, and Z = 12. Least-squares refinement using diffractometer data (Mo-K_α) has given an R of 0.068 1 for 9 165 reflections for (I) and an R of 0.23 (Ru only) for 1 485 reflections for (II). The unit cell in (I) contains two independent molecules of $[HRu_6(CO)_{18}]^-$, cluster (1) which is ordered and cluster (2) which is disordered between two sites (2A) and (2B) that are related by a non-crystallographic two-fold axis. The combined evidence of the *X*-ray analyses, ^1H n.m.r. studies, i.r. [ν(CO)] spectra, and variable-temperature ^{13}C n.m.r. is only consistent with the hydrogen ligand lying inside the Ru_6 octahedron.

The monoanion $[HRu_6(CO)_{18}]^-$, which was the first authenticated example of a polynuclear carbonyl compound containing an H atom within the metal polyhedron,[1] is obtained on acidification of $[Ru_6(CO)_{18}]^{2-}$ or $[HRu_3(CO)_{11}]^-$. The dianion was originally prepared in low yield from the reaction of $[Ru_3(CO)_{12}]$ with $[Mn(CO)_5]^-$, but we have since developed more convenient syntheses of this and related compounds [2] which are now reported in detail.

For many years $[HNb_6I_{11}]$ provided the only confirmed example [3] of an H ligand occupying an interstice within a metal polyhedron, although many clusters containing interstitial carbon atoms were known. Recently $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ ($n = 2$ or 3),[4] $[HCo_6(CO)_{15}]^-$,[5] $[HNi_{12}(CO)_{21}]^{3-}$,[6] and $[H_2Ni_{12}(CO)_{21}]^{2-}$ (ref. 6) have also been shown to contain interstitial H atoms; evidence presented for such an H environment in $[HFe_4(CO)_{13}]^-$ (ref. 7) and $[HFeCo_3(CO)_{12}]$ [8] appears to be contradicted by subsequent *X*-ray and neutron-diffraction analyses.[9,10] Therefore, in addition to the three well documented types of bonding for hydrogen attached to polynuclear metal clusters (terminal, edge-bridging, and face-bridging) a fourth class has now been firmly established in which the hydrogen atom is embedded inside the metal polyhedron.

RESULTS AND DISCUSSION

Dodecacarbonyltriruthenium, $[Ru_3(CO)_{12}]$, reacts with $Na[Mn(CO)_5]$ in tetrahydrofuran(thf) at elevated temperatures over a period of 4 h to produce a brown solution. Treatment with concentrated sulphuric acid (slight excess) yields the anions $[HRu_6(CO)_{18}]^-$ and $[H_3Ru_4(CO)_{12}]^-$ as the major products which were separated as their bis(triphenylphosphine)iminium salts. The trihydride $[H_3Ru_4(CO)_{12}]^-$ was not named previously as a product of this reaction, the neutral dihydrides $H_2Ru_4(CO)_{13}$ and $H_4Ru_4(CO)_{12}$ being reported as the major acidification products.[1] Similarly the reaction of $[Ru_3(CO)_{12}]$ with base (K[OH] in methanol,[11] sodium amalgam,[11] or tetrahydroborate),[11,12] which has been extensively studied, was also thought to give $H_2Ru_4(CO)_{13}$ and $H_4Ru_4(CO)_{12}$ as the only hydrido-species. We now find that under slight variation of the conditions, $[Ru_3(CO)_{12}]$ reacts with methanol–K[OH] in thf to produce $[HRu_3(CO)_{11}]^-$ (A) in almost quantitative yield (Scheme). Knight and Mays [13] suggested that the reaction of $[Ru_3(CO)_{12}]$ with $[Mn(CO)_5]^-$ to produce hexaruthenium species involved the intermediate formation of (A), but this anion has only recently been fully characterized.[14]



Scheme (*i*) K[OH]–MeOH; (*ii*) 10% H_2SO_4–thf; (*iii*) $[Ru_3(CO)_{12}]$–thf added to saturated solution of K[OH] in water; (*iv*) acidification in thf by concentrated H_2SO_4; (*v*) acidification in CH_2Cl_2 by concentrated H_2SO_4

This route appears to be confirmed by our observation that careful acidification of (A) with 10% H_2SO_4–thf produces moderate yields of $[HRu_6(CO)_{18}]^-$ (B); rapid addition of acid results in the formation of equal amounts of (B) and $[Ru_3(CO)_{12}]$. The trinuclear dihydride $H_2Ru_3(CO)_{11}$ was not observed under these conditions although the iron and osmium analogues are known to exist.[15,16]

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† Octadecacarbonylhydrogen-*octahedro*-hexaruthenate(1−).

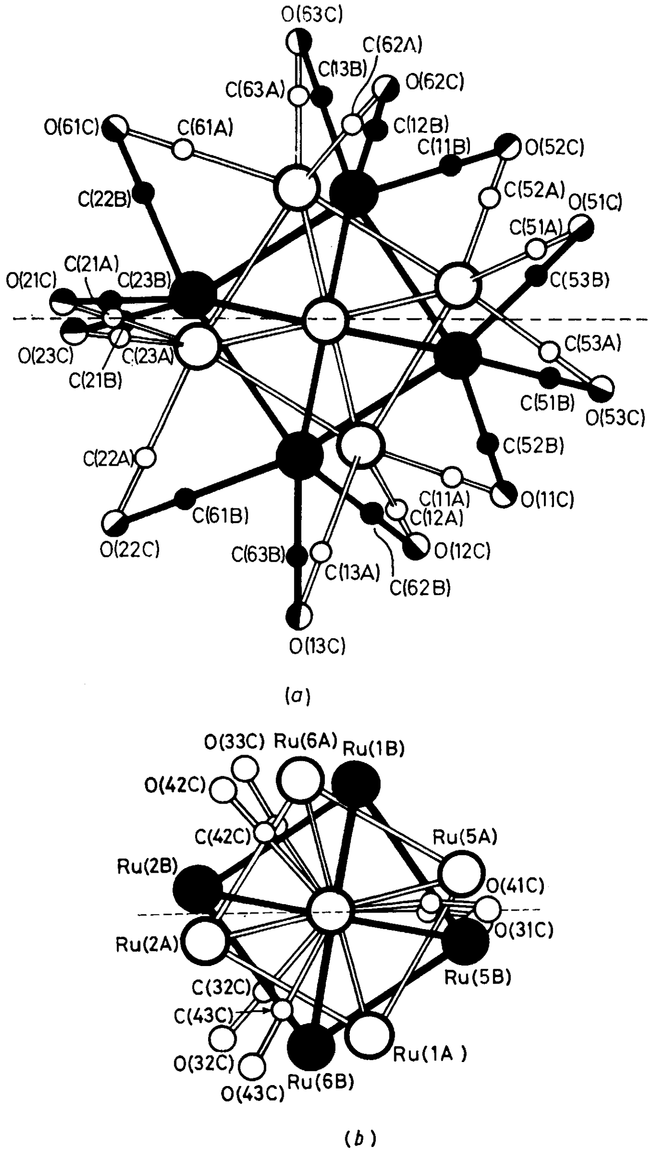
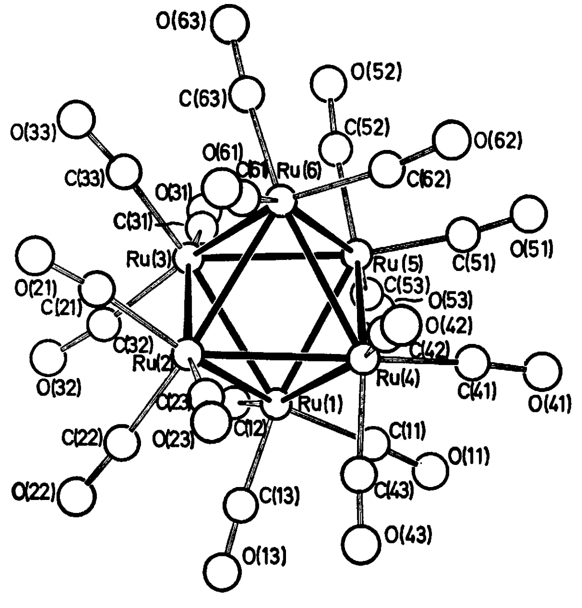


FIGURE 1 (*a*) The disordered cluster (2) of $[HRu_6(CO)_{18}]^-$ (I) viewed down the ordered ruthenium atoms Ru(4C), Ru(3C). The components (2A) and (2B) are related by a pseudo two-fold axis passing through the midpoints of Ru(2A) · · · Ru(2B) and Ru(5A) · · · Ru(5B). All of the oxygen atoms are common to clusters (2A) and (2B) so they have been labelled (C) and numbered to correspond to the carbon atoms of the major component (2A). For clarity the six ordered CO ligands attached to Ru(3C) and Ru(4C) have been omitted. (*b*) The orientation of the six ordered carbonyls in cluster (2) with respect to the metal atoms

The reaction of $[Ru_3(CO)_{12}]$ with K[OH] in aqueous thf is more complex giving a new high yield route to $[Ru_6(CO)_{18}]^{2-}$ (C) together with (A) and (B). The actual product distribution is dependent on the reaction conditions (see Experimental section). Acidification of (C) gives (B) or $H_2Ru_6(CO)_{18}$ (D) depending on the solvent employed, so these ruthenium clusters behave similarly to the $[Os_6(CO)_{18}]^{2-}$, $[HOs_6(CO)_{18}]^-$, $H_2Os_6(CO)_{18}$ series with respect to protonation.[17]

Despite disordering of one of the independent clusters of one crystal modification [(I), see Experimental section] the structure of $[HRu_6(CO)_{18}]^-$ is clearly established and is shown in Figures 1—3. The anion has approximate non-crystallographic D_3 symmetry with three terminal carbonyl ligands per metal atom, and thus the carbonyl distribution has a marked resemblance to that in $[Os_6(CO)_{18}]^{2-}$ [Figure 2(*b*)] which has an overall structure of exact D_3 symmetry.[18] The Ru_6 core has two equivalent parallel faces that are approximately equilateral [mean Ru–Ru, 2.877(13) Å]; these are slightly twisted from O_h symmetry so that the



(*a*) Cluster (1)

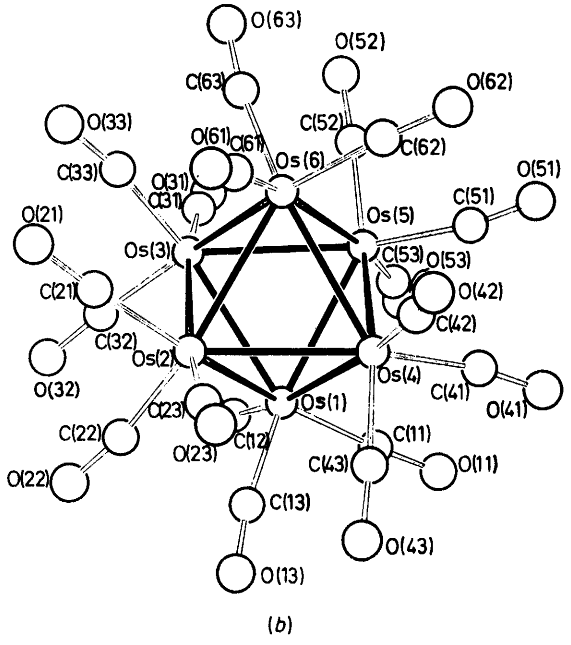
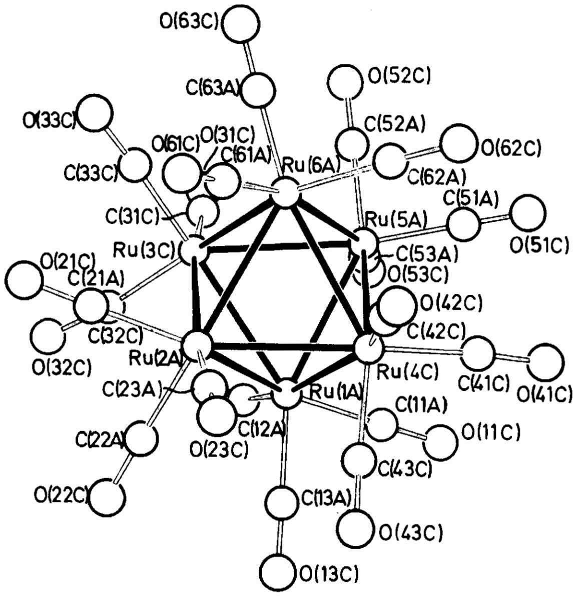
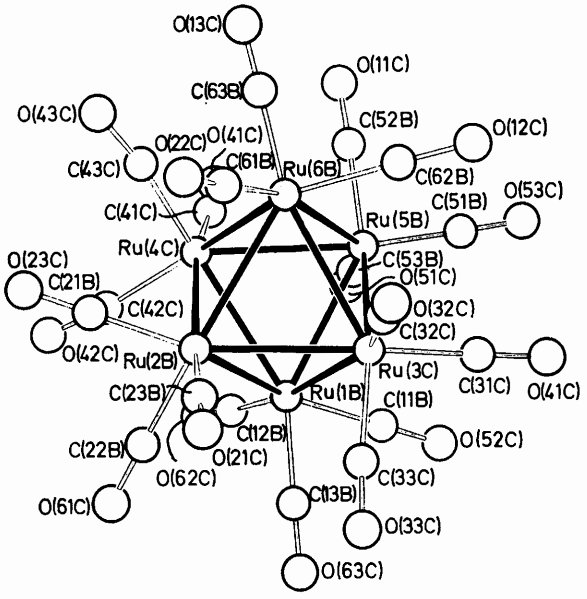


FIGURE 2 Comparison of the geometries of (*a*) $[HRu_6(CO)_{18}]^-$ and (*b*) $[Os_6(CO)_{18}]^{2-}$

remaining bond lengths * are alternately long [mean 2.924(3) Å] and short [mean 2.839(6) Å]. However, the ruthenium octahedron is expanded compared to the metal octahedron in $[Os_6(CO)_{18}]^{2-}$ {and [2] $[Ru_6(CO)_{18}]^{2-}$} in which the medium, long, and short bond lengths are 2.876(2), 2.884(3), and 2.816(3) Å respectively. The insertion of the H atom into $[Co_6(CO)_{15}]^{2-}$ has also been observed to cause a small but appreciable swelling of the Co_6 octahedron.[5] The structure of $[HRu_6(CO)_{18}]^-$ is quite unlike that of $[HOs_6(CO)_{18}]^-$ where the carbonyl ligands on one face are markedly pushed back to accommodate the external H ligand;[18] this confirms the evidence of the solution i.r. spectrum [ν(CO)] which shows just one broad band [Figure 4(*c*)] consistent with the presence of six equivalent $Ru(CO)_3$ groups. The solid-state i.r. spectrum [ν(CO), KBr] shows one main band with shoulders [Figure 4(*d*)] which is again consistent with equivalent $Ru(CO)_3$ groups, the slight asymmetry probably arising from intermolecular interactions in the crystal lattice. These spectra are significantly different from that of $[HOs_6(CO)_{18}]^-$, but closely resemble (in pattern) that of the highly symmetrical $[Os_6(CO)_{18}]^{2-}$ dianion [Figure 4(*b*)]. Thus there is no crystallographic or spectroscopic evidence for an external H atom in $[HRu_6(CO)_{18}]^-$. For comparison, Ru–Ru bond lengths in other octahedral ruthenium clusters are 2.840—3.034 Å for $[Ru_6(CO)_{17}C]$,[19] 2.853—2.956 Å for $[Ru_6(CO)_{14}C(mesitylene)]$,[20] and 2.954(3) and 2.867(5) Å (mean values) for the hydrogen-bridged and normal Ru–Ru bonds in $H_2Ru_6(CO)_{18}$ respectively.[21]



(*a*) Cluster (2A)



(*b*) Cluster (2B)

FIGURE 3 The two components (2A) and (2B) of the disordered cluster in $[HRu_6(CO)_{18}]^-$ (I). See Figure 1 (*a*) for explanation of the labelling scheme

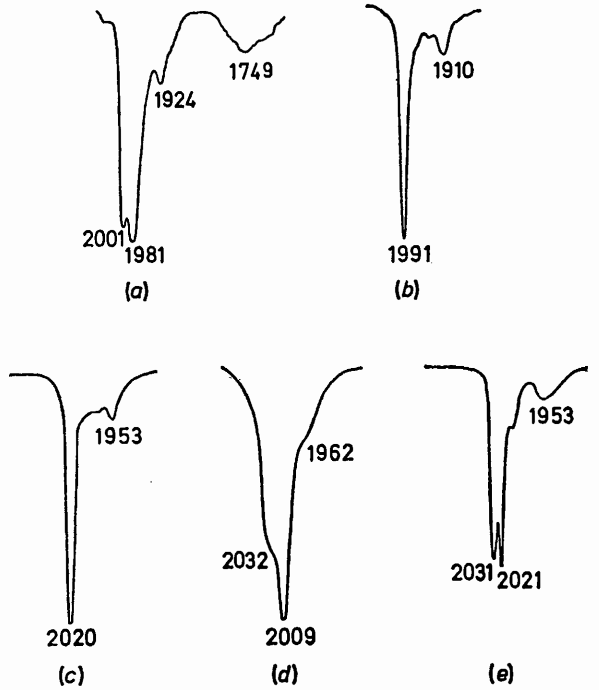


FIGURE 4 Infrared spectra [ν(CO), cm^{-1}] of (*a*) $[Ru_6(CO)_{18}]^{2-}$, (*b*) $[Os_6(CO)_{18}]^{2-}$, (*c*) $[HRu_6(CO)_{18}]^-$, (*d*) $[NMe_4][HRu_6(CO)_{18}]$ solid in KBr, and (*e*) $[HOs_6(CO)_{18}]^-$ {$[N(PPh_3)_2]^+$ salts in CH_2Cl_2 unless otherwise stated, calibrant CO}

TABLE 1

Infrared absorptions in the carbonyl region

	Compound [a]	Maxima (cm^{-1}) [b]
	$[H_3Ru_4(CO)_{12}]^-$	2 034s, 2 029s, 2 014s, 1 994 (s+), 1 969m, br
(A)	$[HRu_3(CO)_{11}]^-$	2 070vw, 2 012s, 1 984s, 1 947m, 1 798vw, 1 725w
(B)	$[HRu_6(CO)_{18}]^-$	2 020s, 1 953vw
(C)	$[Ru_6(CO)_{18}]^{2-}$	2 001s, 1 981 (s+), 1 924w, 1 749w, br
(D)	$H_2Ru_6(CO)_{18}$	2 058s, 2 052s, 2 003w

[a] CH_2Cl_2 as solvent with exception of $[HRu_3(CO)_{11}]^-$ which was run in thf. [b] CO calibrant, central position 2 143 cm^{-1}.

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* These bond lengths refer to the ordered cluster (1), but the same pattern is observed in the disordered cluster (2).

Fourier-transform (F.t.) ^1H spectroscopy {$[N(PPh_3)_2]^+$ salt} over the usual range [22] τ 0—40 failed to show any metal-hydrogen resonances, but an extension of the range to between τ −40 and +100 revealed a singlet at τ −6.43 (CD_2Cl_2, 40 °C, 30-s pulse delay) (Figure 5) together with the expected cation multiplet at τ 2.43; the occurrence of the hydride resonance at such a low-field position indicates a highly unusual environment for the H ligand. The anion $[HCo_6(CO)_{15}]^-$, which has also recently been shown to contain an interstitial H atom,[5] shows a ^1H n.m.r. signal with a similar downfield shift (τ −13.2), whereas the signals of the larger interstitial clusters $[HNi_{12}(CO)_{21}]^{3-}$ (τ 34.0),[6] $[H_2Ni_{12}(CO)_{21}]^{2-}$ (τ 28.0),[6] $[H_2Rh_{13}(CO)_{24}]^{3-}$ (τ 36.7),[4] and $[H_3Rh_{13}(CO)_{24}]^{2-}$ (τ 39.3) [4] are all found at the expected high-field position. The $[NMe_4]^+$ salt of $[HRu_6(CO)_{18}]^-$ shows a similar singlet at τ −6.49 ($[^2H_8]$thf, 40 °C, 30-s pulse delay), so the possibility that the H atom is associated with the $[N(PPh_3)_2]^+$ cation in (I) may be rejected. Furthermore, a variable-temperature ^{13}C (CO) n.m.r. study on $[HRu_6(CO)_{18}]^-$ (^{13}CO, *ca.* 40%) reveals a sharp singlet which remains unchanged over the temperature range 0 to −104 °C, but significantly no ^1H–^{13}C coupling could be detected. This rules out the possibility that the H ligand is located in the vicinity of the carbonyl ligands, as in $H_2Fe_3(CO)_{11}$,[15] which also shows a ^1H n.m.r. signal with a downfield shift. This location for the hydrogen had been suggested for $[HCo_6(CO)_{15}]^-$ before neutron-diffraction analysis showed [5] that, as in $[HRu_6(CO)_{18}]^-$, it was located at the centre of the metal octahedron. In contrast, the related $[HOs_6(CO)_{18}]^-$ shows a characteristic high-field resonance in its ^1H n.m.r. spectrum at τ 21.26 (CD_2Cl_2, 40 °C); [17] ^{13}C n.m.r. studies [17] and single-crystal *X*-ray analysis [18] are consistent with an external face-bridging hydride in this cluster.

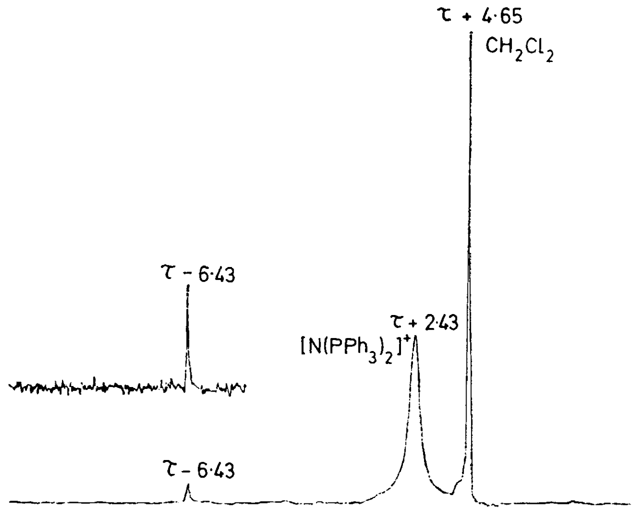

FIGURE 5 F.t. ^1H n.m.r. spectrum of $[N(PPh_3)_2][HRu_6(CO)_{18}]$ in CD_2Cl_2 at 40 °C (CH_2Cl_2 as internal calibrant)

Thus the H ligand in $[HRu_6(CO)_{18}]^-$ occupies a very unusual position as revealed by the ^1H n.m.r. studies, together with the combined evidence of the i.r. [ν(CO)] spectrum, variable-temperature ^{13}C n.m.r., and the *X*-ray analysis that shows it is not outside the metal polyhedron. The only explanation consistent with these facts is that the H atom occupies the centre of the Ru_6 octahedron.* This interstitial position for the hydride ligand explains the stability of $[HRu_6(CO)_{18}]^-$ towards base. Infrared spectroscopy revealed that neither excess of K[OH] in methanol nor excess of KH in thf could deprotonate the cluster, a large excess of base causing decomposition with loss of the carbonyl i.r. spectrum. In contrast, the H atom in $[HCo_6(CO)_{15}]^-$ may quite easily enter and leave the Co_6 octahedron as shown by the protonation of $[Co_6(CO)_{15}]^{2-}$, and the converse reaction of $[HCo_6(CO)_{15}]^-$ observed on simple dissolution in solvents such as water, methanol, or thf.[5] However, the H atom in $[HRu_6(CO)_{18}]^-$ can be made to leave the metal polyhedron by protonation to give $H_2Ru_6(CO)_{18}$ which has two external face-bridging hydride ligands. Although $[HOs_6(CO)_{18}]^-$ may be obtained by the dissociation of $H_2Os_6(CO)_{18}$ in basic solvents,[17] $H_2Ru_6(CO)_{18}$ does not deprotonate to give $[HRu_6(CO)_{18}]^-$, but reacts with K[OH] in methanol under mild conditions to give an unidentified species.

As the six $M(CO)_3$ groups are all equivalent, there is no apparent reason why the metal core in $[Os_6(CO)_{18}]^{2-}$ and $[HRu_6(CO)_{18}]^-$ should distort from regular O_h symmetry. However, exact O_h symmetry for the metal atoms in octahedral clusters is extremely rare; factors such as strongly asymmetric carbonyl bridges, as in $[Co_6(CO)_{14}]^{4-}$,[23] or the presence of an unpaired electron, as in $[Co_6(CO)_{14}C]^-$,[24] are thought to be responsible for the distortion in some clusters although $[Co_6(CO)_{14}]^{4-}$ is geometrically capable of exact overall O_h symmetry.

The structure of the dianion $[Ru_6(CO)_{18}]^{2-}$ is of interest. Since there are no H ligands present it might be expected to have the same metal geometry and carbonyl distribution as $[HRu_6(CO)_{18}]^-$ where the H atom is in the centre of the octahedron. However, the i.r. [ν(CO)] of $[Ru_6(CO)_{18}]^{2-}$ differs considerably from that of $[HRu_6(CO)_{18}]^-$ and $[Os_6(CO)_{18}]^{2-}$; in particular, bridging CO ligands are indicated, implying that it is not isostructural with these anions. This has been confirmed by an *X*-ray analysis of the $[PMePh_3]^+$ salt. Preliminary results show [2] that the metal core is a slightly distorted octahedron with Ru–Ru bond lengths in the range 2.80—2.89 Å, but as well as terminal there are two doubly bridging and two strongly asymmetric triply bridging carbonyl ligands bonded to the cluster.

This work establishes that the complexes $[H_2M_6(CO)_{18}]$, $[HM_6(CO)_{18}]^-$, and $[M_6(CO)_{18}]^{2-}$ (M = Ru or Os) are not isostructural. The preferred structure clearly depends on subtle quantitative factors, and simple electronic arguments [25] cannot be used to predict the structures of metal carbonyl clusters with certainty, especially if one or more hydride ligands are present.[18,26,27]

The versatility of some transition metals in giving

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* *Note added in proof:* We have now confirmed this both by *X*-ray and neutron analyses of the $[AsPh_4]^+$ salt.

polynuclear carbonyl compounds seems to be enhanced if C atoms are inserted into the interstices of the metal polyhedron;[28] the unusual stability of such clusters has been attributed to the presence of additional bonds with the central atom.[24] Significantly, all of the known octahedral ruthenium complexes possess external bridging ligands except for $[HRu_6(CO)_{18}]^-$. The presence of an interstitial atom in this and other octahedral ruthenium complexes [19,20,29] suggests that the role of this atom may be to stabilize an otherwise unfavourable geometry for this metal. In contrast, no octahedral osmium carbonyls have been reported containing interstitial atoms. Recent work has also shown that atoms other than carbon and hydrogen may be successfully incorporated into the interstices of metal polyhedra, for example clusters containing interstitial S and P atoms have been synthesized.[30]

EXPERIMENTAL

All reactions were carried out under an atmosphere of nitrogen. However, the products were stable in air in the solid state although warming to even moderate temperatures (50—60 °C) sometimes initiated decomposition. Solvents were either AnalaR or redistilled, but the exclusion of all water was found to be unnecessary.

Infrared spectra were recorded on a Perkin-Elmer 257 instrument using carbon monoxide gas as calibrant (central position 2 143 cm^{-1}). N.m.r. spectra were obtained on a Varian XL-100 spectrometer.

Preparation of $[Ru_3(CO)_{12}]$.—The salt $RuCl_3 \cdot 3H_2O$ (5 g) in dry methanol (200 cm^3) was pressurised to 50 atm * with CO and heated at 125 °C for 8 h.[31] Orange-red crystals of the required product were filtered from the mother liquor and recrystallized from toluene. Yields were variable but normally between 85 and 95%. It was found to be beneficial to reuse the mother liquor several times, adding a weight of $RuCl_3 \cdot 3H_2O$ equivalent to the weight of $[Ru_3(CO)_{12}]$ removed.

Reaction of $[Ru_3(CO)_{12}]$ *with* $[Mn(CO)_5]^-$.—The compound $[Mn_2(CO)_{10}]$ (195 mg, 0.5 mmol) was reduced to the anion by sodium amalgam in dry thf (30 cm^3) (1 h) and the pale yellow solution added to $[Ru_3(CO)_{12}]$ (639 mg, 1.0 mmol) in dry thf (100 cm^3). The resulting deep red solution was refluxed for 4 h and the then dark brown solution acidified with a small excess of concentrated sulphuric acid (0.25 cm^3) (colour change brown to red). The salt $[N(PPh_3)_2]Cl$ (430 mg, 0.75 mmol) was added to the filtered solution in pure methanol (20 cm^3), and the product obtained by fractional crystallization. Evaporation by nitrogen flow gave first small amounts of a mixture of $H_4Ru_4(CO)_{12}$ and $[Ru_3(CO)_{12}]$. Continued evaporation to remove most of the thf and crystallization from CH_2Cl_2–MeOH then yielded the two major products: $[N(PPh_3)_2][H_3Ru_4(CO)_{12}]$, crystallized first, followed by $[N(PPh_3)_2][HRu_6(CO)_{18}]$. Further smaller amounts of the two anions were recovered and overall yields were $[N(PPh_3)_2][H_3Ru_4(CO)_{12}]$ (394 mg, 41%) and $[N(PPh_3)_2][HRu_6(CO)_{18}]$ (305 mg, 37%). All products were characterized by i.r. spectroscopy, and the two anions crystallized from CH_2Cl_2–MeOH.

Preparation of $[HRu_3(CO)_{11}]^-$.—Potassium hydroxide (11.2 mg, 0.2 mmol) in pure methanol (1 cm^3) was added to a magnetically stirred solution of $[Ru_3(CO)_{12}]$ (63.9 mg, 0.1 mmol) in thf (20 cm^3). The orange-red solution rapidly darkened to deep red and the reaction was complete in 6 h. The anion was characterized by i.r. spectroscopy.

Preparation of $[Ru_6(CO)_{18}]^{2-}$.—The compound $[Ru_3(CO)_{12}]$ (96 mg, 0.15 mmol) in thf (20 cm^3) was added dropwise over 30 min to excess of K[OH] (255 mg, 4.5 mmol) in water (0.1 cm^3) which was stirred under thf (2 cm^3). The resulting deep red-brown solution was stirred for 1.5 h to complete reaction prior to evaporation of the thf by nitrogen flow. The brown residue was taken up in pure methanol, the solution was filtered, and the dianion crystallized by the addition of $[N(PPh_3)_2]Cl$ (103 mg, 0.18 mmol). The product was characterized by microanalysis and i.r. spectroscopy. Yield 80% (Found: C, 49.5; H, 3.05; N, 1.25. Calc. for $C_{90}H_{60}N_2O_{18}P_4Ru_6$: C, 49.4; H, 2.75; N, 1.30%).

Preparation of $[HRu_6(CO)_{18}]^-$.—(*a*) *Acidification of* $[HRu_3(CO)_{11}]^-$. The anion $[HRu_3(CO)_{11}]^-$ was prepared as described above and to the reaction solution was added excess of concentrated H_2SO_4 (0.2 cm^3) in thf (2 cm^3). The salt $[NMe_4]Cl$ (7 mg, 0.06 mmol) in methanol was added. Careful evaporation produced $[Ru_3(CO)_{12}]$ (26 mg, 40% yield) and following complete evaporation and recrystallization from CH_2Cl_2–MeOH, $[NMe_4][HRu_6(CO)_{18}]$ in 50% yield. The monoanion was characterized by microanalysis and i.r. and ^1H n.m.r. spectroscopy (Found: C, 22.05; H, 1.45; N, 0.95. Calc. for $C_{22}H_{13}NO_{18}Ru_6$: C, 22.3; H, 1.10; N, 1.20%).

(*b*) *Acidification of* $[Ru_6(CO)_{18}]^{2-}$. The anion $[Ru_6(CO)_{18}]^{2-}$ was prepared as described above, but prior to isolation a slight excess of concentrated H_2SO_4 was added to the reaction solution until i.r. spectroscopy [ν(CO)] revealed the single-band spectrum of the monoanion. The salt $[N(PPh_3)_2]Cl$ (52 mg, 0.09 mmol) was added in MeOH and, following complete evaporation by nitrogen flow, the product was recrystallized from CH_2Cl_2–MeOH by slow evaporation techniques. The monoanion was characterized as described above, yield 80%.

Preparation of $H_2Ru_6(CO)_{18}$.—Protonation of both $[Ru_6(CO)_{18}]^{2-}$ and $[HRu_6(CO)_{18}]^-$ in non-polar solvents such as CH_2Cl_2 yields $H_2Ru_6(CO)_{18}$. In the case of the dianion the reaction is distinctly two-stage, $[HRu_6(CO)_{18}]^-$ being the product of the first stage. Thus $[N(PPh_3)_2]_2[Ru_6(CO)_{18}]$ (109 mg, 0.05 mmol) was stirred in CH_2Cl_2 (25 cm^3) to give a deep brown solution. Slow addition of excess of concentrated H_2SO_4 (0.5 cm^3) caused the colour to change first to deep red (the monoanion) and finally to purple. The solution was extracted with water, the organic portion dried over $Mg[SO_4]$, and evaporated by nitrogen flow to give $H_2Ru_6(CO)_{18}$, which was recrystallized from CH_2Cl_2 and characterized by i.r. spectroscopy, yield 90%.

Reaction of $[HRu_6(CO)_{18}]^-$ *with Base*.—(*a*) K[OH]. The salt $[N(PPh_3)_2][HRu_6(CO)_{18}]$ was treated with K[OH] in a solution i.r. cell which incorporated a reaction vessel. No reaction was observed in 24 h in either methanol or thf–water solvent systems even though large molar excesses of K[OH] were employed (>10 mol K[OH] per mol of cluster). The anion eventually decomposed when in vast excess of base, with complete loss of the carbonyl i.r. spectrum.

(*b*) KH *in* thf. The salt $[NMe_4][HRu_6(CO)_{18}]$ (47 mg, 0.04 mmol) was dissolved in redistilled dry thf and added to a reaction vessel which was attached to a solution i.r. cell. A thf dispersion of KH suspended in mineral oil [32] (22.7 mg in 0.1 cm^3 oil diluted in 10 cm^3 of thf) was added in small portions *via* a syringe and any reaction followed

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* Throughout this paper: 1 atm = 101 325 Pa.

by i.r. spectroscopy. After 18 h and the addition of KH (0.1 mmol), no reaction had occurred. Subsequent addition of neat KH (0.2 mmol) in mineral oil eventually caused decomposition of the cluster and loss of the carbonyl i.r. spectrum.

X-Ray Crystallographic Determination of $[HRu_6(CO)_{18}]^-$.—Recrystallization by slow diffusion techniques from CH_2Cl_2–cyclohexane gave two crystalline modifications, (I) and (II), of $[N(PPh_3)_2][HRu_6(CO)_{18}]$ which from i.r. spectroscopy appeared to be chemically identical. They pose an unusual crystallographic problem, having different space groups with two and three formula units respectively per equivalent position.

Crystal data. (I). Triclinic, space group $P\bar{1}$, $a = 18.083(4)$, $b = 19.101(4)$, $c = 19.238(5)$ Å, $\alpha = 117.70(4)$, $\beta = 78.13(2)$, $\gamma = 97.05(2)°$, $U = 5\,767$ Å^3, $Z = 4$, $D_c = 1.90$ g cm^{-3}, $F(000) = 3\,196$, θ range 3—25° in one hemisphere, $I/\sigma(I) \geqslant 3.0$, $R = 0.068\,1$ for 9 165 reflections. The primitive cell had a large α angle, so it was converted into a centred cell to avoid correlations during refinement [$C\bar{1}$ cell: $a = 19.248(4)$, $b = 33.912(8)$, $c = 18.081(4)$ Å, $\alpha = 91.23(2)$, $\beta = 101.86(3)$, $\gamma = 92.53(2)°$].

(II). Monoclinic, space group $P2_1/n$, $a = 33.82(8)$, $b = 52.55(10)$, $c = 9.832(2)$ Å, $\beta = 92.66(2)°$, $U = 17\,452$ Å^3, $Z = 12$, $D_c = 1.88$ g cm^{-3}, $F(000) = 9\,588$, θ range 3—

TABLE 2

Fractional atomic co-ordinates (× 10^4) for (I) ($C\bar{1}$ cell)

Atom *	*x*	*y*	*z*
(*a*) Cluster (1)			
Ru(1)	3 947(1)	922(1)	2 787(1)
Ru(2)	4 403(1)	1 750(1)	2 679(1)
Ru(3)	2 940(1)	1 527(1)	2 544(1)
Ru(4)	4 515(1)	1 169(1)	1 531(1)
Ru(5)	2 997(1)	962(1)	1 348(1)
Ru(6)	3 466(1)	1 754(1)	1 202(1)
C(11)	4 130(9)	433(6)	2 410(10)
O(11)	4 258(7)	129(4)	2 212(7)
C(12)	3 318(10)	748(5)	3 388(10)
O(12)	2 966(7)	612(4)	3 775(8)
C(13)	4 725(11)	898(6)	3 556(12)
O(13)	5 204(9)	849(5)	4 043(9)
C(21)	4 109(10)	2 250(6)	2 832(10)
O(21)	3 963(7)	2 558(4)	3 003(8)
C(22)	4 812(10)	1 718(5)	3 687(11)
O(22)	5 086(7)	1 730(4)	4 323(8)
C(23)	5 271(9)	1 914(5)	2 486(10)
O(23)	5 806(7)	2 050(4)	2 384(8)
C(31)	2 092(9)	1 232(5)	2 573(9)
O(31)	1 571(7)	1 067(4)	2 635(7)
C(32)	3 207(10)	1 608(5)	3 581(11)
O(32)	3 313(7)	1 681(4)	4 217(8)
C(33)	2 516(9)	2 007(5)	2 398(9)
O(33)	2 235(7)	2 312(4)	2 381(7)
C(41)	4 482(11)	743(6)	878(12)
O(41)	4 535(8)	473(5)	474(9)
C(42)	4 998(10)	1 487(6)	969(11)
O(42)	5 361(7)	1 678(4)	644(7)
C(43)	5 323(10)	990(6)	2 176(11)
O(43)	5 835(7)	882(4)	2 516(7)
C(51)	2 991(10)	680(6)	470(11)
O(51)	2 913(8)	513(4)	−125(9)
C(52)	2 141(10)	1 184(5)	935(10)
O(52)	1 584(6)	1 292(3)	644(7)
C(53)	2 643(10)	520(6)	1 775(11)
O(53)	2 378(7)	242(4)	1 964(8)
C(61)	4 068(9)	2 193(5)	1 169(10)
O(61)	4 407(7)	2 467(4)	1 071(7)
C(62)	3 491(9)	1 558(5)	253(11)
O(62)	3 468(7)	1 472(4)	−384(8)
C(63)	2 658(10)	2 029(5)	878(10)
O(63)	2 149(7)	2 203(4)	618(8)
(*b*) Cluster (2A)			
Ru(1A)	7 168(1)	3 965(1)	3 096(1)
Ru(2A)	6 954(1)	3 280(1)	4 000(1)
Ru(3C)	5 813(1)	3 790(1)	3 498(1)
Ru(4C)	7 874(1)	3 921(1)	4 614(1)
Ru(5A)	6 707(1)	4 461(1)	4 190(1)
Ru(6A)	6 548(1)	3 802(1)	5 090(1)
C(11A)	7 777	4 391	3 088
O(11C)	8 156(10)	4 658(5)	3 100(11)
C(12A)	6 602	4 063	2 219
O(12C)	6 232(10)	4 132(5)	1 661(11)
C(13A)	7 827	3 772	2 575
O(13C)	8 240(10)	3 645(5)	2 246(11)
C(21A)	6 214	2 894	3 902
O(21C)	5 747(10)	2 654(5)	3 844(10)
C(22A)	7 100	3 005	3 176
O(22C)	7 199(10)	2 838(5)	2 646(11)
C(23A)	7 630	2 998	4 514
O(23C)	8 056(10)	2 818(5)	4 836(11)
C(31C)	5 215(11)	4 163(6)	3 062(12)
O(31C)	4 821(9)	4 379(5)	2 748(9)
O(32C)	5 560(13)	3 453(8)	2 689(15)
O(32C)	5 340(10)	3 209(6)	2 200(12)
C(33C)	5 146(11)	3 559(6)	3 991(12)
O(33C)	4 700(8)	3 420(5)	4 231(9)
C(41C)	8 427(9)	4 388(5)	4 868(10)
O(41C)	8 808(8)	4 665(5)	5 007(9)
C(42C)	8 186(10)	3 696(6)	5 544(11)
O(42C)	8 434(7)	3 548(4)	6 099(8)
C(43C)	8 536(10)	3 680(6)	4 161(11)
O(43C)	8 982(7)	3 513(4)	3 973(8)
C(51A)	7 192	4 856	4 738
O(51C)	7 499(10)	5 109(5)	5 085(11)
C(52A)	5 976	4 614	4 527
O(52C)	5 518(10)	4 703(5)	4 758(11)
C(53A)	6 357	4 796	3 360
O(53C)	6 198(10)	5 010(5)	2 832(10)
C(61A)	6 530	3 316	5 531
O(61C)	6 518(10)	3 018(5)	5 802(11)
C(62A)	7 086	4 117	5 898
O(62C)	7 440(10)	4 323(5)	6 389(11)
C(63A)	5 820	3 826	5 508
O(63C)	5 347(10)	3 848(5)	5 779(11)
(*c*) Cluster (2B)			
Ru(1B)	6 506(2)	4 042(1)	4 954(2)
Ru(2B)	6 779(2)	3 277(1)	4 332(2)
Ru(5B)	6 929(2)	4 425(1)	3 715(2)
Ru(6B)	7 138(2)	3 679(1)	3 063(2)
C(11B)	5 899	4 452	4 837
C(12B)	7 070	4 210	5 847
C(13B)	5 804	3 918	5 456
C(21B)	7 563	2 997	4 642
C(22B)	6 619	3 114	5 239
C(23B)	6 147	2 893	4 030
C(51B)	6 473	4 782	3 177
C(52B)	7 685	4 568	3 327
C(53B)	7 277	4 842	4 555
C(61B)	7 171	3 159	2 815
C(62B)	6 591	3 953	2 207
C(63B)	7 816	3 663	2 562
(*d*) Cations			
P(1)	952(2)	3 320(1)	3 149(2)
P(2)	2 233(2)	3 771(1)	2 930(2)
N(1)	1 717(6)	3 403(4)	2 984(7)
C(111)	989(6)	2 936(3)	3 828(6)
C(112)	429(6)	2 854(3)	4 193(6)
C(113)	458(6)	2 537(3)	4 676(6)
C(114)	1 046(6)	2 302(3)	4 794(6)
C(115)	1 606(6)	2 385(3)	4 429(6)
C(116)	1 577(6)	2 702(3)	3 946(6)
C(121)	556(6)	3 741(2)	3 485(6)
C(122)	804(6)	3 879(2)	4 229(6)
C(123)	579(6)	4 236(2)	4 472(6)
C(124)	107(6)	4 455(2)	3 971(6)
C(125)	−141(6)	4 316(2)	3 227(6)

TABLE 2 (*Continued*)

Atom *	*x*	*y*	*z*
C(126)	84(6)	3 959(2)	2 984(6)
C(131)	358(5)	3 129(3)	2 313(5)
C(132)	−362(5)	3 054(3)	2 305(5)
C(133)	−815(5)	2 896(3)	1 653(5)
C(134)	−548(5)	2 813(3)	1 009(5)
C(135)	173(5)	2 887(3)	1 017(5)
C(136)	625(5)	3 045(3)	1 669(5)
C(211)	1 784(5)	4 213(3)	2 608(6)
C(212)	1 431(5)	4 223(3)	1 854(6)
C(213)	1 053(5)	4 551(3)	1 592(6)
C(214)	1 026(5)	4 869(3)	2 085(6)
C(215)	1 379(5)	4 860(3)	2 840(6)
C(216)	1 757(5)	4 532(3)	3 101(6)
C(221)	2 841(6)	3 882(3)	3 814(5)
C(222)	3 396(6)	4 167(3)	3 867(5)
C(223)	3 824(6)	4 273(3)	4 570(5)
C(224)	3 696(6)	4 094(3)	5 220(5)
C(225)	3 141(6)	3 810(3)	5 167(5)
C(226)	2 713(6)	3 704(3)	4 464(5)
C(231)	2 745(6)	3 647(4)	2 251(6)
C(232)	3 048(6)	3 938(4)	1 865(6)
C(233)	3 445(6)	3 830(4)	1 334(6)
C(234)	3 538(6)	3 432(4)	1 191(6)
C(235)	3 235(6)	3 142(4)	1 577(6)
C(236)	2 838(6)	3 249(4)	2 108(6)
P(3)	8 054(2)	1 309(1)	393(2)
P(4)	9 314(2)	900(1)	1 157(2)
N(2)	8 663(7)	1 000(4)	530(7)
C(311)	7 265(5)	1 061(3)	−144(6)
C(312)	7 323(5)	708(3)	−534(6)
C(313)	6 717(5)	514(3)	−971(6)
C(314)	6 054(5)	673(3)	−1 018(6)
C(315)	5 996(5)	1 026(3)	−628(6)
C(316)	6 601(5)	1 219(3)	−191(6)
C(321)	7 843(6)	1 517(3)	1 234(5)
C(322)	8 173(6)	1 875(3)	1 545(5)
C(323)	8 030(6)	2 028(3)	2 217(5)
C(324)	7 558(6)	1 823(3)	2 580(5)
C(325)	7 229(6)	1 465(3)	2 269(5)
C(326)	7 372(6)	1 312(3)	1 597(5)
C(331)	8 290(6)	1 712(3)	−147(6)
C(332)	8 971(6)	1 750(3)	−298(6)
C(333)	9 159(6)	2 071(3)	−700(6)
C(334)	8 666(6)	2 353(3)	−950(6)
C(335)	7 984(6)	2 315(3)	−799(6)
C(336)	7 796(6)	1 995(3)	−397(6)
C(411)	9 924(5)	662(3)	684(6)
C(412)	10 487(5)	454(3)	1 077(6)
C(413)	10 950(5)	275(3)	688(6)
C(414)	10 850(5)	304(3)	−95(6)
C(415)	10 288(5)	511(3)	−489(6)
C(416)	9 825(5)	691(3)	−99(6)
C(421)	9 779(6)	1 323(3)	1 687(6)
C(422)	9 627(6)	1 449(3)	2 373(6)
C(423)	9 966(6)	1 793(3)	2 741(6)
C(424)	10 456(6)	2 010(3)	2 423(6)
C(425)	10 608(6)	1 884(3)	1 736(6)
C(426)	10 269(6)	1 540(3)	1 368(6)
C(431)	9 045(8)	570(4)	1 814(7)
C(432)	9 489(8)	507(4)	2 511(7)
C(433)	9 248(8)	268(4)	3 034(7)
C(434)	8 563(8)	92(4)	2 860(7)
C(435)	8 119(8)	155(4)	2 164(7)
C(436)	8 360(8)	394(4)	1 641(7)

* Occupancies of atoms labelled (A) in the disordered sites were coupled in the least-squares refinement to a free variable p_A which refined to 0.584 0(11). The occupancy of atoms labelled (B) was set to $1 - p_A$. The rest of the atoms including those labelled (C) [which are common to clusters (2A) and (2B)] are of unit occupancy. Disordered carbon atoms [labelled (A) and (B)] were placed in fixed positions such that $d(\text{M–C})/d(\text{M–O}) = 0.615$ and M–C–O 180°. These positions were recalculated if large shifts were observed for the oxygen atoms.

15° in one quadrant only, $I/\sigma(I) \geqslant 3.0$, $R = 0.23$ (Ru only) for 1 485 reflections.

Data were collected using a Philips PW1100 four-circle diffractometer and graphite-monochromatized Mo-K_α radiation [λ(Mo-K_α) = 0.710 69 Å]. A θ—2θ scan mode was used and weak reflections which gave $I_t - 2(I_t)^{\frac{1}{2}} < I_b$ on the first scan were not further examined. (I_t = the count rate at the top of the reflection peak and I_b = the mean count rate of two preliminary 5-s background measurements on either side of the peak.) Of the remaining reflections, those for which the total intensity recorded in the first scan of the peak (I_i) was <100 were scanned twice to increase their accuracy. A constant scan speed of 0.05° s^{-1} and scan widths of 0.7° (I) and 0.54° (II) were used, with a background measuring time proportional to I_b/I_i. Three standard reflections were measured every 5 h during data collection and showed no significant variations in intensity.

The reflection intensities were calculated from the peak and background measurements using a program written for the PW1100 diffractometer.[33] The variance of the intensity, I, was calculated as the sum of the variance due to counting statistics and $(0.04I)^2$, where the term in I^2 was introduced to allow for other sources of error.[34] I and $\sigma(I)$ were corrected for Lorentz and polarization factors; no absorption corrections were applied (μ = 14.95 cm^{-1}).

TABLE 3

Selected interatomic distances (Å) for (I) [a] with estimated standard deviations in parentheses

(*a*) Metal–metal bonds

	$[HRu_6(CO)_{18}]^-$			
	Cluster (1)	Cluster (2A)	Cluster (2B)	$[Os_6(CO)_{18}]^{2-}$
M(1)–M(2)	2.927(2)	2.931(4)	2.917(5)	2.884(3)
M(3)–M(6)	2.921(2)	2.934(3)	2.951(3)	
M(4)–M(5)	2.924(2)	2.950(3)	2.936(4)	
M(1)–M(4)	2.841(2)	2.812(3)	2.793(3)	2.816(3)
M(2)–M(3)	2.843(2)	2.867(3)	2.928(4)	
M(5)–M(6)	2.832(2)	2.835(4)	2.847(5)	
M(1)–M(3)	2.863(2)	2.890(3)	2.869(4)	2.876(2)
M(1)–M(5)	2.865(2)	2.872(4)	2.856(5)	
M(2)–M(4)	2.878(2)	2.800(3)	2.829(4)	
M(2)–M(6)	2.900(2)	2.870(4)	2.883(5)	
M(3)–M(5)	2.881(2)	2.890(3)	2.838(3)	
M(4)–M(6)	2.876(2)	2.871(3)	2.858(4)	

(*b*) Metal–carbon distances [b]

	Cluster (1)	Cluster (2)
Ru(1)–C(11)	1.856(19)	
Ru(1)–C(12)	1.872(20)	
Ru(1)–C(13)	1.828(19)	
Ru(2)–C(21)	1.843(19)	
Ru(2)–C(22)	1.838(18)	
Ru(2)–C(23)	1.841(19)	
Ru(3)–C(31)	1.886(17)	1.830(21)
Ru(3)–C(32)	1.850(19)	1.808(26)
Ru(3)–C(33)	1.852(17)	1.861(23)
Ru(4)–C(41)	1.838(21)	1.863(17)
Ru(4)–C(42)	1.846(20)	1.858(20)
Ru(4)–C(43)	1.875(18)	1.858(21)
Ru(5)–C(51)	1.833(21)	
Ru(5)–C(52)	1.863(18)	
Ru(5)–C(53)	1.865(20)	
Ru(6)–C(61)	1.853(17)	
Ru(6)–C(62)	1.838(19)	
Ru(6)–C(63)	1.846(18)	
Mean Ru–C	1.850(17) [c]	

TABLE 3 (*Continued*)

(*c*) Carbon–oxygen distances [b]

	Cluster (1)	Cluster (2)
C(11)–O(11)	1.136(24)	
C(12)–O(12)	1.158(25)	
C(13)–O(13)	1.157(24)	
C(21)–O(21)	1.146(24)	
C(22)–O(22)	1.162(22)	
C(23)–O(23)	1.161(23)	
C(31)–O(31)	1.154(21)	1.149(26)
C(32)–O(32)	1.145(24)	1.195(32)
C(33)–O(33)	1.188(22)	1.129(28)
C(41)–O(41)	1.180(27)	1.156(23)
C(42)–O(42)	1.181(25)	1.155(24)
C(43)–O(43)	1.129(22)	1.154(25)
C(51)–O(51)	1.183(26)	
C(52)–O(52)	1.170(21)	
C(53)–O(53)	1.144(25)	
C(61)–O(61)	1.151(21)	
C(62)–O(62)	1.173(24)	
C(63)–O(63)	1.184(23)	
Mean C–O	1.160(18) [c]	

[a] In Figure 3(*b*) cluster (2B) has been rotated about the pseudo-two-fold axis to obtain a view that corresponds to those of clusters (1) and (2A) in Figures 2(*a*) and 3(*a*) respectively. Under this operation Ru(3C) and its associated carbonyl ligands exchange position with Ru(4C) and its carbonyl groups, but in order to allow ease of comparison of their geometries the bond lengths and angles for cluster (2B) have been listed next to those in clusters (1) and (2A) to which they are equivalent. The correct labels for cluster (2B) may be obtained by simply interchanging those involving M(3) and M(4). For the other clusters, the labels given are correct. [b] See footnote to Table 2. [c] Estimated standard deviations of mean bond lengths are calculated from the equation $\sigma = \{[\sum_{1}^{n}(x_i - \bar{x})^2]/(n - 1)\}^{\frac{1}{2}}$ where x_i is the *i*th bond length and $\bar{x}$ is the mean of *n* equivalent bond lengths.

Structure solution and refinement. (*a*) *Triclinic modification* (I). The 12 ruthenium atoms of the asymmetric unit were located by multisolution Σ_2 sign expansion as discrete Ru_6 octahedra. Least-squares refinement of their positional and isotropic thermal parameters gave *R* 0.28. Four of these Ru atoms within one octahedron showed relatively large isotropic thermal parameters, indicative of disorder. Subsequent difference-Fourier syntheses revealed the positions of the two independent $[N(PPh_3)_2]^+$ cations and all the carbonyl ligands associated with cluster 1, but only six carbonyl groups of cluster 2 could be conclusively identified, although all the oxygen atoms appeared to be present.

At this stage a difference-Fourier map in the region of the apparently disordered Ru atoms was computed, these atoms being omitted from the structure-factor calculations. This revealed that each peak, originally assigned as ruthenium sites of full occupancy, could be resolved into two components *ca.* 1 Å apart. Thus the four most intense independent maxima were assigned as Ru(1A), Ru(2A), Ru(5A), and Ru(6A), the remaining four high peaks as Ru(1B), Ru(2B), Ru(5B), and Ru(6B). The isotropic thermal parameter for each of these disordered atoms was initially constrained to be equal to the same free variable; refinement of their population parameters yielded values in the range 0.58—0.60 for the ' A ' set and 0.40—0.42 for the ' B ' set of atoms. Subsequent difference-Fourier syntheses utilizing this model revealed suitable maxima for the missing disordered carbon atoms of the second cluster. The component pairs of these carbon atoms were too close to one another to be refined independently, so they were placed in calculated positions, but their atomic co-ordinates were recalculated after each cycle of refinement if large shifts were observed for the attached oxygen atoms.

Apparently the disorder of the second cluster arises from two different orientations, (2A) and (2B) in the lattice, having occupancies of *ca.* 0.6 and 0.4 respectively. The alternative orientations (2A) and (2B) are approximately

TABLE 4

Selected intramolecular angles (°) for (I) [a] with estimated standard deviations in parentheses

(*a*) Ru–C–O Angles

	Cluster (1)	Cluster (2)
Ru(1)–C(11)–O(11)	176.8(16)	
Ru(1)–C(12)–O(12)	174.0(16)	
Ru(1)–C(13)–O(13)	174.3(18)	
Ru(2)–C(21)–O(21)	173.0(16)	
Ru(2)–C(22)–O(22)	174.4(17)	
Ru(2)–C(23)–O(23)	174.0(16)	
Ru(3)–C(31)–O(31)	175.2(15)	175.2(17)
Ru(3)–C(32)–O(32)	172.9(17)	172.4(24)
Ru(3)–C(33)–O(33)	173.1(15)	173.9(17)
Ru(4)–C(41)–O(41)	173.1(18)	175.3(17)
Ru(4)–C(42)–O(42)	174.1(15)	173.9(18)
Ru(4)–C(43)–O(43)	174.5(19)	171.0(16)
Ru(5)–C(51)–O(51)	172.5(17)	
Ru(5)–C(52)–O(52)	174.1(14)	
Ru(5)–C(53)–O(53)	172.7(15)	
Ru(6)–C(61)–O(61)	172.8(14)	
Ru(6)–C(62)–O(62)	172.2(15)	
Ru(6)–C(63)–O(63)	175.2(17)	
Mean Ru–C–O	173.8(13) [b]	

(*b*) Angles between metal atoms

	Cluster (1)	Cluster (2A)	Cluster (2B)
Ru(2)–Ru(1)–Ru(3)	58.8(1)	59.0(1)	60.8(1)
Ru(2)–Ru(1)–Ru(4)	59.8(1)	58.3(1)	59.3(1)
Ru(2)–Ru(1)–Ru(5)	89.6(1)	89.1(1)	90.2(1)
Ru(3)–Ru(1)–Ru(4)	90.9(1)	90.9(1)	91.7(1)
Ru(3)–Ru(1)–Ru(5)	60.4(1)	60.2(1)	59.4(1)
Ru(4)–Ru(1)–Ru(5)	61.7(1)	62.5(1)	62.6(1)
Ru(1)–Ru(2)–Ru(3)	59.5(1)	59.8(1)	58.8(1)
Ru(1)–Ru(2)–Ru(4)	58.6(1)	58.7(1)	58.2(1)
Ru(1)–Ru(2)–Ru(6)	88.4(1)	89.0(1)	88.4(1)
Ru(3)–Ru(2)–Ru(4)	90.6(1)	91.6(1)	89.8(1)
Ru(3)–Ru(2)–Ru(6)	61.1(1)	61.5(1)	61.0(1)
Ru(4)–Ru(2)–Ru(6)	59.7(1)	60.8(1)	60.0(1)
Ru(1)–Ru(3)–Ru(2)	61.7(1)	61.2(1)	60.4(1)
Ru(1)–Ru(3)–Ru(5)	59.8(1)	59.6(1)	60.1(1)
Ru(1)–Ru(3)–Ru(6)	89.3(1)	88.6(1)	88.0(1)
Ru(2)–Ru(3)–Ru(5)	91.0(1)	90.0(1)	90.3(1)
Ru(2)–Ru(3)–Ru(6)	60.4(1)	59.3(1)	58.7(1)
Ru(5)–Ru(3)–Ru(6)	58.4(1)	58.3(1)	58.9(1)
Ru(1)–Ru(4)–Ru(2)	61.6(1)	63.0(1)	62.5(1)
Ru(1)–Ru(4)–Ru(5)	59.6(1)	59.7(1)	59.7(1)
Ru(1)–Ru(4)–Ru(6)	90.6(1)	91.4(1)	91.4(1)
Ru(2)–Ru(4)–Ru(5)	89.4(1)	90.1(1)	90.3(1)
Ru(2)–Ru(4)–Ru(6)	60.5(1)	60.8(1)	60.9(1)
Ru(5)–Ru(4)–Ru(6)	58.4(1)	58.3(1)	58.9(1)
Ru(1)–Ru(5)–Ru(3)	59.8(1)	60.2(1)	60.5(1)
Ru(1)–Ru(5)–Ru(4)	58.8(1)	57.7(1)	57.6(1)
Ru(1)–Ru(5)–Ru(6)	91.0(1)	90.9(1)	90.3(1)
Ru(3)–Ru(5)–Ru(4)	88.9(1)	88.2(1)	89.5(1)
Ru(3)–Ru(5)–Ru(6)	61.5(1)	61.6(1)	62.5(1)
Ru(4)–Ru(5)–Ru(6)	59.9(1)	59.5(1)	59.2(1)
Ru(2)–Ru(6)–Ru(3)	58.5(1)	59.2(1)	60.2(1)
Ru(2)–Ru(6)–Ru(4)	59.8(1)	58.4(1)	59.0(1)
Ru(2)–Ru(6)–Ru(5)	90.8(1)	91.0(1)	91.0(1)
Ru(3)–Ru(6)–Ru(4)	89.1(1)	88.9(1)	88.8(1)
Ru(3)–Ru(6)–Ru(5)	60.1(1)	60.1(1)	58.6(1)
Ru(4)–Ru(6)–Ru(5)	61.6(1)	62.2(1)	61.9(1)

TABLE 4 (*Continued*)

(*c*) Carbon–metal–metal angles

	Cluster (1)	$[Os_6(CO)_{18}]^{2-}$
C(11)–M(1)–M(2)	137.8(6)	147.5
C(11)–M(1)–M(3)	142.0(5)	141.8
C(11)–M(1)–M(4)	80.6(6)	90.1
C(11)–M(1)–M(5)	83.4(5)	87.5
C(12)–M(1)–M(2)	124.2(6)	122.4
C(12)–M(1)–M(3)	79.4(6)	83.5
C(12)–M(1)–M(4)	162.5(5)	169.3
C(12)–M(1)–M(5)	100.8(5)	108.4
C(13)–M(1)–M(2)	86.2(6)	81.2
C(13)–M(1)–M(3)	127.7(7)	126.3
C(13)–M(1)–M(4)	104.3(7)	99.4
C(13)–M(1)–M(5)	165.3(7)	160.2
C(21)–M(2)–M(1)	140.0(6)	147.5
C(21)–M(2)–M(3)	83.7(6)	90.1
C(21)–M(2)–M(4)	143.5(6)	141.8
C(21)–M(2)–M(6)	86.5(5)	87.5
C(22)–M(2)–M(1)	85.0(6)	81.2
C(22)–M(2)–M(3)	106.0(6)	99.4
C(22)–M(2)–M(4)	124.5(6)	126.3
C(22)–M(2)–M(6)	167.2(6)	160.2
C(23)–M(2)–M(1)	124.1(5)	122.4
C(23)–M(2)–M(3)	164.2(5)	169.3
C(23)–M(2)–M(4)	80.5(5)	83.5
C(23)–M(2)–M(6)	103.1(5)	108.4
C(31)–M(3)–M(1)	100.8(5)	108.4
C(31)–M(3)–M(2)	162.1(5)	169.3
C(31)–M(3)–M(5)	82.4(5)	83.5
C(31)–M(3)–M(6)	127.1(5)	122.4
C(32)–M(3)–M(1)	83.8(6)	87.5
C(32)–M(3)–M(2)	79.9(6)	90.1
C(32)–M(3)–M(5)	142.0(6)	141.8
C(32)–M(3)–M(6)	137.7(6)	147.5
C(33)–M(3)–M(1)	164.0(5)	160.2
C(33)–M(3)–M(2)	102.3(5)	99.4
C(33)–M(3)–M(5)	124.3(5)	126.3
C(33)–M(3)–M(6)	81.9(6)	81.2
C(41)–M(4)–M(1)	108.5(7)	99.4
C(41)–M(4)–M(2)	169.8(7)	160.2
C(41)–M(4)–M(5)	82.9(6)	81.2
C(41)–M(4)–M(6)	119.8(6)	126.3
C(42)–M(4)–M(1)	158.3(6)	169.3
C(42)–M(4)–M(2)	97.6(6)	108.4
C(42)–M(4)–M(5)	130.8(5)	122.4
C(42)–M(4)–M(6)	83.2(6)	83.5
C(43)–M(4)–M(1)	78.4(7)	90.1
C(43)–M(4)–M(2)	88.8(6)	87.5
C(43)–M(4)–M(5)	132.6(6)	147.5
C(43)–M(4)–M(6)	148.8(6)	141.8
C(51)–M(5)–M(1)	128.9(6)	126.3
C(51)–M(5)–M(3)	169.2(6)	160.2
C(51)–M(5)–M(4)	91.3(6)	81.2
C(51)–M(5)–M(6)	109.5(6)	99.4
C(52)–M(5)–M(1)	138.7(6)	141.8
C(52)–M(5)–M(3)	80.7(5)	87.5
C(52)–M(5)–M(4)	137.5(6)	147.5
C(52)–M(5)–M(6)	79.2(5)	90.1
C(53)–M(5)–M(1)	76.6(5)	83.5
C(53)–M(5)–M(3)	97.7(6)	108.4
C(53)–M(5)–M(4)	123.3(6)	122.4
C(53)–M(5)–M(6)	159.2(6)	169.3
C(61)–M(6)–M(2)	78.3(5)	83.5
C(61)–M(6)–M(3)	124.0(5)	122.4
C(61)–M(6)–M(4)	98.8(5)	108.4
C(61)–M(6)–M(5)	160.4(5)	169.3
C(62)–M(6)–M(2)	135.3(5)	141.8
C(62)–M(6)–M(3)	139.9(6)	147.5
C(62)–M(6)–M(4)	78.0(5)	87.5
C(62)–M(6)–M(5)	80.6(6)	90.1
C(63)–M(6)–M(2)	130.0(6)	126.3
C(63)–M(6)–M(3)	89.8(6)	81.2
C(63)–M(6)–M(4)	166.3(5)	160.2
C(63)–M(6)–M(5)	106.2(6)	99.4

TABLE 4 (*Continued*)

(*d*) OC–M–CO Angles

	Cluster (1)	$[Os_6(CO)_{18}]^{2-}$
C(11)–M(1)–C(12)	98.0(8)	89.1
C(11)–M(1)–C(13)	90.2(8)	91.2
C(12)–M(1)–C(13)	93.1(9)	91.3
C(21)–M(2)–C(22)	91.5(8)	91.2
C(21)–M(2)–C(23)	95.7(8)	89.1
C(22)–M(2)–C(23)	89.7(8)	91.3
C(31)–M(3)–C(32)	95.1(8)	89.1
C(31)–M(3)–C(33)	95.2(7)	91.3
C(32)–M(3)–C(33)	93.7(8)	91.2
C(41)–M(4)–C(42)	92.5(9)	91.3
C(41)–M(4)–C(43)	91.4(8)	91.2
C(42)–M(4)–C(43)	96.3(8)	89.1
C(51)–M(5)–C(52)	91.9(8)	91.2
C(51)–M(5)–C(53)	91.2(9)	91.3
C(52)–M(5)–C(53)	99.0(8)	89.1
C(61)–M(6)–C(62)	95.7(8)	89.1
C(61)–M(6)–C(63)	93.2(8)	91.3
C(62)–M(6)–C(63)	94.3(8)	91.2

[a,b] See footnotes *a* and *c* in Table 3.

related by a non-crystallographic two-fold axis which lies in the plane of the disordered atoms, and passes through the midpoints of Ru(2A) · · · Ru(2B) and Ru(5A) · · · Ru(5B) (Figure 1). Under this operation Ru(3C) and its associated carbonyl ligands would exchange position with Ru(4C) and its carbonyl groups, therefore the sites of these atoms are of full occupancy. Significantly, the remaining oxygen atoms also coincide in position for the two orientations, indicating that the packing is effectively determined by these peripheral oxygen atoms and is independent of the arrangement of the internal atoms of the cluster. A similar type of disorder has previously been observed for several other polynuclear carbonyl clusters.[35] Crucially, clusters (1), (2A), and (2B) appear to be stereochemically equivalent [Figures 2(*a*) and 3] within the limits imposed by the crystal disorder.

The structure was further refined with the occupancy (p_A) of orientation (2A) allowed to vary between 0 and 1, and the occupancy of (2B) set to $1 - p_A$. The isotropic temperature factors of the oxygen and carbon atoms of the disordered part of the second cluster were constrained to be equal to two independent free variables. Similarly, the isotropic temperature factors of each pair of disordered Ru atoms were constrained to be equal to a separate free variable. In the final cycles of blocked full-matrix least-squares refinement, the ordered Ru atoms were assigned anisotropic thermal parameters. The phenyl rings of the $[N(PPh_3)_2]^+$ cations were treated as rigid groups (C–C 1.395 Å), no allowance being made for the H atoms in the structure-factor calculations. This resulted in R 0.068 1 and R' 0.068 7 ($= \Sigma||F_o| - |F_c||w^{\frac{1}{2}}/\Sigma|F_o|w^{\frac{1}{2}}$) and weights ($w$) were assigned to reflections as $w = 1/\sigma^2(F_o)$. The final difference-Fourier map showed no maxima greater than 1.7 e Å^{-3} which were in the region of the disordered Ru atoms.

(*b*) *Monoclinic modification* (II). It proved possible to resolve the diffraction data using Mo-K_α radiation in spite of the very long *b* axis of 52.55 Å. This would probably not have been attempted if a preliminary photographic examination of the crystal had been carried out. However, the initial unit-cell dimensions were determined using the PW1100 peak-search routine and a preliminary scan of the *h*0*l* and 0*k*0 data unambiguously indicated the space group $P2_1/n$. Since resolution appeared to be satisfactory, due mainly to the weak diffraction and to the absence of data of the type $0k0$ with $k = 2n + 1$, it was decided to collect a small proportion of low-angle data in order to locate the metal atoms. Multisolution Σ_2 sign expansion showed three separate Ru_6 octahedra in the asymmetric unit, which is consistent with the spectroscopic evidence that the two modifications, (I) and (II), are of the same compound. Least-squares refinement of the Ru atom positions with isotropic thermal parameters gave R 0.23 indicating that the solution for the metal-atom positions was probably correct. No further work was carried out on this modification because of the poor quality of the crystals.

TABLE 5

Selected bond lengths (Å) and angles (°) in the two $[N(PPh_3)_2]^+$ cations * in (I), with estimated standard deviations in parentheses

P(1)–N(1)	1.577(14)	P(1)–N(1)–P(2)	138.1(9)
P(2)–N(1)	1.577(13)	P(3)–N(2)–P(4)	138.8(9)
P(3)–N(2)	1.591(14)		
P(4)–N(2)	1.561(13)		
		N(1)–P(1)–C(111)	109.1(6)
		N(1)–P(1)–C(121)	115.2(6)
		N(1)–P(1)–C(131)	110.1(6)
P(1)–C(111)	1.802(11)	N(1)–P(2)–C(211)	114.2(6)
P(1)–C(121)	1.799(11)	N(1)–P(2)–C(221)	111.8(6)
P(1)–C(131)	1.788(10)	N(1)–P(2)–C(231)	107.5(7)
P(2)–C(211)	1.812(10)	N(2)–P(3)–C(311)	107.9(6)
P(2)–C(221)	1.799(10)	N(2)–P(3)–C(321)	115.1(6)
P(2)–C(231)	1.777(13)	N(2)–P(3)–C(331)	110.7(7)
P(3)–C(311)	1.790(10)	N(2)–P(4)–C(411)	106.5(6)
P(3)–C(321)	1.792(11)	N(2)–P(4)–C(421)	114.6(6)
P(3)–C(331)	1.794(12)	N(2)–P(4)–C(431)	110.6(7)
P(4)–C(411)	1.798(12)		
P(4)–C(421)	1.803(10)		
P(4)–C(431)	1.787(14)		
		C(111)–P(1)–C(121)	108.9(5)
		C(111)–P(1)–C(131)	105.7(5)
		C(121)–P(1)–C(131)	107.4(5)
		C(211)–P(2)–C(221)	108.9(5)
		C(211)–P(2)–C(231)	106.5(6)
		C(221)–P(2)–C(231)	107.6(5)
		C(311)–P(3)–C(321)	107.9(5)
		C(311)–P(3)–C(331)	107.9(5)
		C(321)–P(3)–C(331)	107.0(5)
		C(411)–P(4)–C(421)	108.0(5)
		C(411)–P(4)–C(431)	109.2(6)
		C(421)–P(4)–C(431)	107.7(6)

* The cations are in the usual bent form (R. D. Wilson and R. Bau, *J. Amer. Chem. Soc.*, 1974, **96**, 7601 and refs. therein).

Major computations were made using the 'SHELX' system of programs.[36] Scattering factors were taken from ref. 37 and included both real and imaginary contributions to anomalous scattering.[38] The final atomic co-ordinates for (I) are given in Table 2, selected bond lengths and angles in Tables 3—5. Supplementary Publication No. SUP 22685 (64 pp.) * contains thermal parameters and the observed and calculated structure factors for (I).

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