Reactions of $[Ru_5C(CO)_{15}]$ involving Bridging Ligands: Crystal and Molecular Structures † of the Complexes $[Ru_5(H)C(CO)_{14}(SEt)]$, $[Ru_5(H)C(CO)_{13}(PPh_3)(SEt)]$, $[Ru_5(H)C(CO)_{12}(PPh_3)(SEt)]$, and $[Ru_5C(CO)_{13}(PPh_3)\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}I)]$

Alan G. Cowie, Brian F. G. Johnson, Jack Lewis,* J. Nicola Nicholls, Paul R. Raithby, and Maria J. Rosales
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The cluster $[Ru_5C(CO)_{15}]$ reacts with H_2S, H_2Se, and HSR (R = Me or Et) to give $[Ru_5(H)C(CO)_{14}(SH)]$, $[Ru_5(H)C(CO)_{14}(SeH)]$, and $[Ru_5(H)C(CO)_{14}(SR)]$, respectively. The complex $[Ru_5(H)C(CO)_{14}(SEt)]$ crystallises in space group $P2_1/n$ with $a = 15.315(3)$, $b = 16.739(4)$, $c = 10.286(3)$ Å, $\beta = 89.31(2)°$, and $Z = 4$. The structure was solved by a combination of direct methods and Fourier-difference techniques, and refined by blocked-cascade least squares to $R = 0.032$ for 4 134 observed diffractometer data. The Ru_5 metal arrangement is intermediate between a square-based pyramid and a bridged ' butterfly ' with a carbido-carbon at the centre of the cluster. The sulphur atom of the SEt group bridges one edge of the square pyramid where the Ru $\cdots$ Ru separation is 3.410(1) Å. In the reaction of $[Ru_5C(CO)_{15}]$ with HSEt the postulated intermediate $[Ru_5(H)C(CO)_{15}(SEt)]$ was not isolated. The first product was $[Ru_5(H)C(CO)_{14}(SEt)]$ (4). When (4) is heated to 81 °C a further molecule of CO is lost and the complex $[Ru_5(H)C(CO)_{13}(SEt)]$ isolated. A phosphine derivative of this complex was also prepared and characterised crystallographically; $[Ru_5(H)C(CO)_{13}(PPh_3)(SEt)]$ (6) crystallises in space group $P2_1/c$ with $a = 15.892(2)$, $b = 11.474(1)$, $c = 21.387(2)$ Å, $\beta = 92.50(1)°$, and $Z = 4$. The structure was solved and refined using the same techniques as for (4) to $R = 0.036$ for 5 861 reflections. The structure resembles that of (4) with the SEt group bridging a long Ru $\cdots$ Ru edge [3.438(1) Å] but with one of the carbonyl groups on a Ru atom associated with the SEt bridge replaced by a phosphine ligand. An analogous reaction occurs when $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}I)]$ is heated in heptane to give $[Ru_5C(CO)_{13}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}I)]$. This complex also readily takes up phosphine to give $[Ru_5C(CO)_{13}(PPh_3)\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}I)]$ (12), which has been characterised crystallographically, crystallising in space group $P\bar{1}$ with $a = 9.899(3)$, $b = 14.628(6)$, $c = 18.788(7)$ Å, $\alpha = 100.29(3)$, $\beta = 91.31(3)$, $\gamma = 93.69(3)°$, and $Z = 2$. The structure was solved and refined as described above to $R = 0.042$ for 6 075 reflections. The general geometry of the Ru_5C core observed in (6) is retained and the iodine ligand bridges a long Ru $\cdots$ Ru edge [3.526(1) Å], and the $Au(PPh_3)$ group replaces the bridging hydride. Further heating of the cluster (6) results in the loss of a further CO ligand to give $[Ru_5(H)C(CO)_{12}(PPh_3)(SEt)]$ (7) which may exist in two isomeric forms. The structure of one of the isomers shows that Ru–Ru bond formation has occurred and the geometry of the Ru_5C core may be described as a centred, square-based pyramid. The SEt group now bridges a basal Ru–Ru edge [2.698(1) Å] and the phosphine ligand is co-ordinated to a basal Ru atom. The complex (7) crystallises in space group $P\bar{1}$ with $a = 10.162(2)$, $b = 13.807(4)$, $c = 14.660(4)$ Å, $\alpha = 78.20(2)$, $\beta = 74.12(2)$, $\gamma = 87.38(2)°$, and $Z = 2$. This converged to $R = 0.041$ for 4 050 reflections. The adducts $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}X]$ (X = Cl or Br) and their derivatives $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}X]$ react with PPh_3 to eliminate '$Au(PPh_3)X$' and produce $[Ru_5C(CO)_{14}(PPh_3)]$.

There are a number of polynuclear metal carbonyl complexes known containing bridging ligands which formally donate one, three, or five electrons to the cluster. These include one-electron donor groups such as μ-$Au(PR_3)$ and μ-H, as found in the cluster $[Os_4(H)(CO)_{13}\{\mu\text{-}Au(PR_3)\}]$ (R = Ph or Et).[1] Examples of three-electron donor groups are μ-Cl, μ-I, μ-OMe, and μ-SR as found in $[Ru_4(CO)_{13}(\mu\text{-}Cl)]^-$,[2] $[Au_4(\mu\text{-}I)_2(PPh_3)_4]$,[3] $[Os_3(CO)_{10}(\mu\text{-}OMe)_2]$,[4] and $[Os_3(H)(CO)_{10}(\mu\text{-}SEt)]$.[5] In the case of five-electron donor groups examples would be μ_3-I and μ_3-SR as in $[Os_3(H)(CO)_9(\mu_3\text{-}I)]$ [6] and $[Ru_3(H)(CO)_9(\mu_3\text{-}SPr^i)]$.[7] Some complexes may contain both three- and five-electron donor groups, as is found for the cluster $[Fe_3(CO)_9(\mu\text{-}SMe)(\mu_3\text{-}SMe)]$,[8] and a bridging ligand may change from being, for example, a five-electron to a three-electron donor on addition of a two-electron donor molecule. Such behaviour is demonstrated by $[Os_3(H)(CO)_9(\mu_3\text{-}SR)]$ (R = Me or Et).[9]

We have recently reported [10] some reactions of the penta-nuclear carbido-cluster $[Ru_5C(CO)_{15}]$ with ligands able to bridge between two metal centres. The oxidative addition of YX [Y = H or $Au(PPh_3)$; X = Cl, Br, or I] was followed by loss of CO from $[Ru_5(Y)C(CO)_{15}X]$ on heating. The final product involved the formation of a halogen bridge between two ruthenium atoms, to give $[Ru_5(Y)C(CO)_{14}(\mu\text{-}X)]$. We now report a series of reactions for the clusters $[M_5C(CO)_{15}]$ (M = Ru or Os) with H_2S, H_2Se, or HSR (R = Me or Et) and the reactions of the derivatives $[Ru_5(Y)C(CO)_nZ]$ [Y = H or $Au(PPh_3)$; Z = Cl, Br, I, or SEt; n = 13, 14, or 15] with triphenylphosphine, drawing comparisons between the

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† μ_5-Carbido-1,1,1,2,2,2,3,3,3,4,4,4,5,5-tetradecacarbonyl-3,5-μ-ethylthio-1,5-μ-hydrido- and μ_5-carbido-1,1,1,2,2,2,3,3,4,4,4,5,5-tridecacarbonyl-3,5-μ-ethylthio-1,5-μ-hydrido-3-triphenylphosphine-*cyclo*-pentaruthenium(7 *Ru*–*Ru*), μ_5-carbido-1,1,1,2,2,2,3,3,3,4,5,5-dodecacarbonyl-4,5-μ-ethylthio-1,2-μ-hydrido-4-triphenylphosphine-*cyclo*-pentaruthenium(8 *Ru*–*Ru*), and μ_5-carbido-1,1,1,2,2,2,3,3-4,4,4,5,5-tridecacarbonyl-3,5-μ-iodo-3-triphenylphosphine-1,5-μ-triphenylphosphineaurio-*cyclo*-pentaruthenium(7 *Ru*–*Ru*)(2 *Ru*–*Au*), respectively.

Supplementary data available (No. SUP 23683, 146 pp.): structure factors, thermal parameters, H-atom co-ordinates, complete bond parameter data. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Infrared carbonyl stretching frequencies [a]

	$\nu(CO)/cm^{-1}$
(1) $[Ru_5(H)C(CO)_{14}(SH)]$	2 106w, 2 080s, 2 060vs, 2 053m, 2 036m, 2 020m, 2 013m, 2 002w, 1 990w, 1 974w
(2) $[Ru_5(H)C(CO)_{14}Br]$	2 109w, 2 084s, 2 066vs, 2 058m, 2 037m, 2 022m, 2 018m (sh), 2 009w, 1 998w, 1 981vw
(3) $[Ru_5(H)C(CO)_{14}(SeH)]$	2 105w, 2 097w, 2 079s, 2 060vs, 2 052m, 2 035m, 2 019m, 2 012m, 2 001w, 1 991w, 1 974w
(4) $[Ru_5(H)C(CO)_{14}(SEt)]$	2 105w, 2 080s, 2 061s, 2 053m, 2 036m, 2 021m, 2 011m, 2 004w, 1 988w, 1 970w
(5) ' $[Ru_5(H)C(CO)_{13}(SEt)]$ '	2 096w, 2 062s, 2 048vs, 2 041s, 2 027m, 2 010w,br, 1 999w, 1 980w, 1 967vw
(6) $[Ru_5(H)C(CO)_{13}(PPh_3)(SEt)]$	2 090m, 2 050s, 2 030s, 2 018w, 2 002m, 1 991m, 1 979w, 1 960w
(7) $[Ru_5(H)C(CO)_{12}(PPh_3)(SEt)]$	2 081m, 2 050s, 2 036vs, 2 024m, 2 010m, 2 004w, 1 997w, 1 991m, 1 982w, 1 972w, 1 964w, 1 947w
(8) ' $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(SEt)]$ '	2 094m, 2 061s, 2 053s, 2 040m, 2 023w, 2 009m, 1 996w, 1 987w, 1 973w, 1 939w
(9) ' $[Ru_5C(CO)_{13}\{\mu\text{-}Au(PPh_3)\}(SEt)]$ '	2 073w, 2 041s, 2 026m, 2 015m, 2 007m, 1 993w, 1 973vw
(10) $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}I)]$	2 094m, 2 060s, 2 053vs, 2 039s, 2 018w, 2 000m, 1 992m, 1 982w, 1 974w, 1 943w
(11) ' $[Ru_5C(CO)_{13}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}I)]$ '	2 079w, 2 047s, 2 031m, 2 020m, 2 013m, 1 999w, 1 990w
(12) $[Ru_5C(CO)_{13}(PPh_3)\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}I)]$	2 073m, 2 060w, 2 046vs, 2 035m, 2 023s, 2 012w, 1 999m, 1 995 (sh), 1 978m, 1 966w, 1 942w
(13) $[Ru_5(H)C(CO)_{13}(\mu\text{-}I)]$ [b]	2 101w, 2 069s, 2 053vs, 2 046s, 2 034m, 2 021w, 2 016w, 2 006w, 1 987w, 1 976vw
(14) $[Os_5(H)C(CO)_{15}(SH)]$	2 112w, 2 083m, 2 075s, 2 070vs, 2 063m, 2 057 (sh), 2 036m, 2 028m, 2 020w, 2 016w, 2 004w, 1 996w
(15) $[Os_5(H)C(CO)_{14}(SH)]$	2 109w, 2 083s, 2 063vs, 2 057m, 2 031m, 2 015m, 2 005w, 1 983w, 1 964w
(16) ' $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(COMe)]$ '	2 095m, 2 055m, 2 050s, 2 034s, 2 018m, 2 000m, 1 988m

[a] In hexane unless otherwise stated. [b] In nonane.

chemistry and bonding of the sulphur- and halogen-bridged systems.

Results and Discussion

The cluster $[Ru_5C(CO)_{15}]$ reacts quickly in solution, at room temperature, with H_2S, H_2Se, or HSR (R = Me or Et) to give orange solutions of $[Ru_5(H)C(CO)_{14}(SH)]$ (1), $[Ru_5(H)C(CO)_{14}(SeH)]$ (3), or $[Ru_5(H)C(CO)_{14}(SR)]$. These are formulated as such, on the basis of mass spectrometry and carbonyl i.r. spectra. As may be seen from Table 1 the carbonyl i.r. spectra of these species are very similar to those observed for the series $[Ru_5(H)C(CO)_{14}X]$ (X = Cl, Br, or I) although different from the i.r. spectra of the complexes $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}X]$ [10] due to the additional disturbance of the CO polyhedron caused by the bulky $Au(PPh_3)$ group. For this series a bridged-butterfly arrangement of metal atoms was proposed, with the hydride bridging the hinge and the halogen forming a bridge between one ruthenium atom on the hinge and the ruthenium atom bridging the wingtips of the butterfly.

An *X*-ray structural determination was carried out on a single crystal of the cluster $[Ru_5(H)C(CO)_{14}(SEt)]$ (4). The molecular structure is shown in Figure 1, and selected bond parameters are presented in Table 2. The geometry of the cluster is similar to that observed in $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$.[10] The cluster core, which is illustrated in Figure 2, may be described either as a ' bridged-butterfly ' or a distorted square-based pyramid, and is intermediate between the two idealised geometries. A butterfly arrangement is defined by the atoms Ru(1), Ru(2), Ru(3), and Ru(5), and the distances from the ' hinge ' metal atoms, Ru(2) and Ru(5), to the bridging atom, Ru(4) [Ru(2) · · · Ru(4) 4.132(1), Ru(4) · · · Ru(5) 3.410(1) Å], reflect the asymmetry of the bridging arrangement. The Ru(4)–Ru(5) vector is bridged by the sulphur atom of the SEt ligand; the metal–metal distance is too long to make a direct bonding interaction between the two metals likely. However, this vector could be considered to make up the eighth edge of a square pyramid. Although the

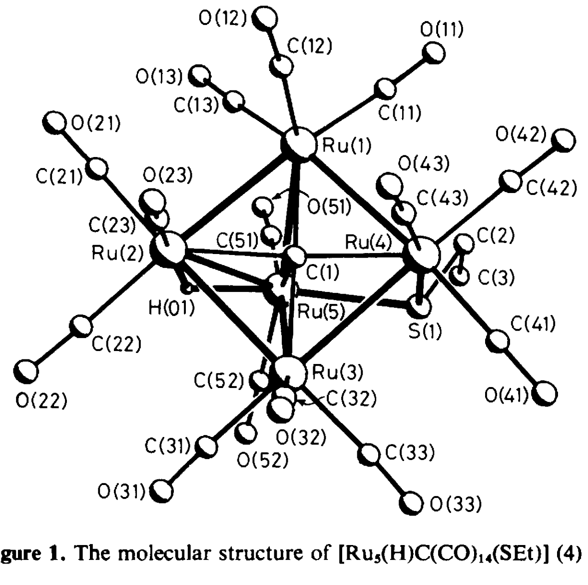


Figure 1. The molecular structure of $[Ru_5(H)C(CO)_{14}(SEt)]$ (4)

Table 2. Selected bond distances (Å) and angles (°) for $[Ru_5(H)C(CO)_{14}(SEt)]$ (4)

Ru(1)–Ru(2)	2.852(1)	Ru(1)–C(1)	1.969(5)
Ru(1)–Ru(4)	2.916(1)	Ru(2)–C(1)	2.075(5)
Ru(1)–Ru(5)	2.851(1)	Ru(3)–C(1)	1.990(5)
Ru(2)–Ru(3)	2.858(1)	Ru(4)–C(1)	2.108(5)
Ru(2)–Ru(5)	2.853(1)	Ru(5)–C(1)	2.049(5)
Ru(3)–Ru(4)	2.902(1)	Ru(4)–S(1)	2.472(1)
Ru(3)–Ru(5)	2.813(1)	Ru(5)–S(1)	2.417(1)
Ru(4) · · · Ru(5)	3.410(1)	S(1)–C(2)	1.831(6)
Ru(2)–H(01)	1.60(8)	C(2)–C(3)	1.482(10)
Ru(5)–H(01)	1.73(8)		
Ru(2)–Ru(1)–Ru(4)	91.5(1)	Ru(2)–Ru(5)–Ru(4)	82.1(1)
Ru(2)–Ru(1)–Ru(5)	60.0(1)	Ru(3)–Ru(5)–Ru(4)	54.6(1)
Ru(4)–Ru(1)–Ru(5)	72.5(1)	Ru(1)–C(1)–Ru(2)	89.6(2)
Ru(1)–Ru(2)–Ru(3)	87.8(1)	Ru(1)–C(1)–Ru(3)	178.4(3)
Ru(1)–Ru(2)–Ru(5)	60.0(1)	Ru(1)–C(1)–Ru(4)	91.3(2)
Ru(3)–Ru(2)–Ru(5)	59.0(1)	Ru(1)–C(1)–Ru(5)	90.4(2)
Ru(2)–Ru(3)–Ru(4)	91.7(1)	Ru(2)–C(1)–Ru(3)	89.3(2)
Ru(2)–Ru(3)–Ru(5)	60.4(1)	Ru(2)–C(1)–Ru(4)	162.2(3)
Ru(4)–Ru(3)–Ru(5)	73.2(1)	Ru(2)–C(1)–Ru(5)	87.5(2)
Ru(1)–Ru(4)–Ru(3)	85.8(1)	Ru(3)–C(1)–Ru(4)	90.1(2)
Ru(1)–Ru(4)–Ru(5)	52.9(1)	Ru(3)–C(1)–Ru(5)	88.3(2)
Ru(3)–Ru(4)–Ru(5)	52.2(1)	Ru(4)–C(1)–Ru(5)	110.2(2)
Ru(1)–Ru(5)–Ru(2)	60.0(1)	Ru(4)–S(1)–Ru(5)	88.4(1)
Ru(1)–Ru(5)–Ru(3)	88.7(1)	Ru(4)–S(1)–C(2)	112.3(2)
Ru(1)–Ru(5)–Ru(4)	54.6(1)	Ru(5)–S(1)–C(2)	111.3(2)
Ru(2)–Ru(5)–Ru(3)	60.6(1)	Ru(2)–H(01)–Ru(5)	118(5)

carbide atom may be considered to occupy an interstitial site in the cluster it is probable that bonding influence of this atom helps to hold the metal framework together while allowing geometrical rearrangements to occur.

The Ru–Ru bond distances within the ' butterfly ' in (4) show some differences from those in $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$.[10] The Ru(hinge)–Ru(wingtip) distances in the latter [mean 2.85(2) Å] are similar to the equivalent distances [mean 2.84(2) Å] in (4), but the Ru–Ru hinge bond which is bridged by the $Au(PPh_3)$ group, at 2.95(1) Å, is *ca.* 0.1 Å longer than the hydride-bridged bond, Ru(2)–Ru(5), in (4). Both the $Au(PPh_3)$ group and the hydride formally donate one electron to the cluster, and there are many examples where both these bridging ligands exert a metal–metal bond lengthening influence.[11] In this case the overall electronic effect appears to reflect a difference between the two ligands, and the electron balance within the metal framework counterbalances the lengthening effect of the symmetrically bridging hydride. In contrast the two ' wingtip '–' bridge ' Ru–Ru bonds [mean 2.91(1) Å] in (4) are longer than those in $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$ where the mean is 2.89(1) Å.[10]

The Ru–C(carbide) distances in (4) follow the same trends as in $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$ with the shorter Ru–C distances involving the ' wingtip ' Ru atoms, and the longest distance involving the bridging metal atom.

The SEt ligand shows slight asymmetry in bridging the Ru(4)–Ru(5) edge, with the shorter distance to the ' hinge ' Ru(5) metal atom. The Ru–S bond lengths are somewhat longer than the mean Ru–S distance of 2.388(4) Å in $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}SCH_2COOH)]$ [12] where the sulphur ligand and the hydride bridge the same Ru–Ru bond of length 2.839(4) Å. Concomitant with this is a much narrower Ru–S–Ru angle of 61.5(3)° in the triruthenium cluster, indicating a flexibility in the bonding ability of the thiol ligand.

The 14 carbonyl ligands are all terminally co-ordinated to the cluster, and the mean Ru–C–O angle is 177(2)°. There are two carbonyl ligands co-ordinated to Ru(5) and three each to each of the remaining four Ru atoms. If the Ru(4)–C(1) interaction is neglected, Ru(4) exhibits a distorted octahedral co-ordination geometry, with the C(43)O(43) ligand *trans* to S(1) while the other two carbonyls are *trans* to metal–metal bonds. However, there is no significant variation in the three Ru–C(carbonyl) bond lengths [mean 1.92(1) Å], which indicates that a sulphur donor group and a Ru atom show similar acceptor properties for the back donation of electron density from the filled metal orbitals. All the other carbonyl groups, except C(23)O(23) which is *trans* to H(01), are *trans* to Ru–Ru bonds, and none of the Ru–C distances shows significant deviations from the average value of 1.91(2) Å. The mean carbonyl C–O distance is 1.14(2) Å.

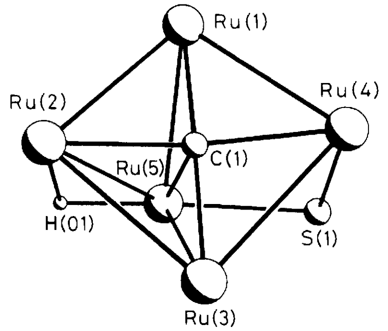


Figure 2. The cluster core of $[Ru_5(H)C(CO)_{14}(SEt)]$ (4)

We propose that, as in the reaction of $[Ru_5C(CO)_{15}]$ with HI, the formation of the complex (4) reflects the ease with which the SR ligand can change from being a one-electron donor to a three-electron donor and results in the initially formed adduct $[Ru_5(H)C(CO)_{15}(SR)]$ (R = H, Me, or Et) or $[Ru_5(H)C(CO)_{15}(SeH)]$ quickly ejecting one molecule of CO and formation of a sulphur or selenium bridge. Under the conditions of the experiment the second step is sufficiently fast that $[Ru_5(H)C(CO)_{14}(SR)]$ or $[Ru_5(H)C(CO)_{14}(SeH)]$ is the first product to be isolated. In the case of the reaction of $[Os_5C(CO)_{15}]$ with H_2S, an intermediate product, formulated on the basis of mass spectrometry and the similarity of its carbonyl i.r. spectrum to that of $[Os_5(H)C(CO)_{15}I]$ as $[Os_5(H)C(CO)_{15}(SH)]$ (14), was isolated. On heating, (14) was found to convert to the new cluster (15), formulated, again on the basis of mass spectrometry and i.r., as $[Os_5(H)C(CO)_{14}(SH)]$.

On heating to 81 °C (4) was found to lose a further molecule of CO to give (5), which from the mass spectrum is $[Ru_5(H)C(CO)_{13}(SEt)]$. Its i.r. spectrum (see Table 1) is very similar to that found for the cluster formed on heating $[Ru_5(H)C(CO)_{14}I]$ to 110 °C for 30 min and formulated as $[Ru_5(H)C(CO)_{13}(\mu\text{-}I)]$ (13).[10] The ^1H n.m.r. spectrum of (5) seemed to indicate the presence of two isomers in solution, however t.l.c. in a variety of solvents only afforded one band in each case. As we were not able to obtain good crystals of (5) a phosphine derivative was synthesized in order to aid characterisation.

The cluster (5) was found to react with triphenylphosphine, in hexane solution, at room temperature, to give a product (6). The mass spectrum and ^1H n.m.r. spectrum of (6) (see Table 3) corresponded to the formulation $[Ru_5(H)C(CO)_{13}(PPh_3)(SEt)]$. An *X*-ray structural determination was carried out on a single crystal of (6).

The molecular structure of $[Ru_5(H)C(CO)_{13}(PPh_3)(SEt)]$ (6) is illustrated in Figure 3 and selected bond parameters are listed in Table 4. The geometry of the cluster core in (6) is similar to that observed in (4), the main difference between these two structures being the replacement of one of the carbonyl groups on the bridging atom of the ' bridged-

Table 3. Proton n.m.r. data [a]

	δ/p.p.m.
(1) $[Ru_5(H)C(CO)_{14}(SH)]$	−3.02 (1 H, s), −25.27 (1 H, s)
(3) $[Ru_5(H)C(CO)_{14}(SeH)]$	−5.86 (1 H, s), −25.09 (1 H, s)
(4) $[Ru_5(H)C(CO)_{14}(SEt)]$	1.88 (2 H, q, *J* = 7 Hz), 1.41 (3 H, t, *J* = 7 Hz), −24.7 (1 H, s)
(5) ' $[Ru_5(H)C(CO)_{13}(SEt)]$ ' [b]	2.59 (2 H, q, *J* = 7.2 Hz), 1.14 (3 H, t, *J* = 7.2 Hz), −22.63 (1 H, s)
(5a) ' $[Ru_5(H)C(CO)_{13}(SEt)]$ ' [b]	1.99 (2 H, q, *J* = 7.2 Hz), 1.05 (3 H, t, *J* = 7.2 Hz), −22.43 (1 H, s)
(6) $[Ru_5(H)C(CO)_{13}(PPh_3)(SEt)]$	7.52 (15 H, m), 1.07 (2 H, q, *J* = 7 Hz), 0.45 (3 H, t, *J* = 7 Hz), −24.67 (1 H, s)
(8) ' $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(SEt)]$ '	7.49 (15 H, m), 2.02 (2 H, q, *J* = 7 Hz), 0.98 (3 H, t, *J* = 7 Hz)
(16) ' $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(COMe)]$ '	7.49 (15 H, m), 2.16 (3 H, s)

[a] In CD_2Cl_2 unless otherwise stated; q = quartet. [b] In C_6D_6.

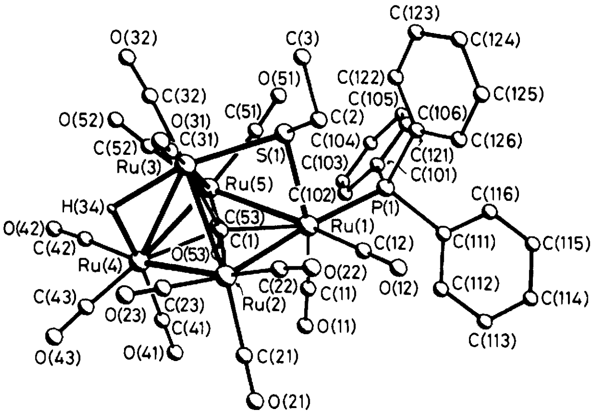


Figure 3. The molecular structure of $[Ru_5(H)C(CO)_{13}(PPh_3)(SEt)]$ (6)

butterfly ' framework by a triphenylphosphine ligand. The asymmetry of the bridging Ru(1) atom to the two ' hinge ' atoms, Ru(3) and Ru(4), observed in (4) is retained, and the Ru(1) · · · Ru(3) and Ru(1) · · · Ru(4) distances are 3.438(1) and 4.109(1) Å, respectively. The SEt group bridges the Ru(1)–Ru(3) edge, and as in (4), it shows a slight asymmetry, the shorter Ru–S distance involving the ' hinge ' atom, Ru(3). The Ru–S distances and Ru–S–Ru angles are similar to those observed in (4). The hydride ligand, H(34), which was located directly, bridges the Ru(3)–Ru(4) bond, but shows an increase in asymmetry over the hydride in (4).

The Ru(hinge)–Ru(wingtip) distances in (6) [mean 2.83(1) Å] are similar in length to the equivalent bonds in (4) [mean 2.84(1) Å], as is the Ru(hinge)–Ru(hinge) [2.864(1) for (6) and 2.853(1) Å for (4)]. The Ru(wingtip)–Ru(bridge) distances in the two structures do show some significant differences. The Ru(1)–Ru(5) bond which is *cis* to the phosphine group in (6) is *ca.* 0.05 Å longer than the Ru(1)–Ru(2) bond in (6) and the average value of 2.91(1) Å for the two bonds in (4). This bond lengthening may be caused by the steric bulk of the phosphine group since a longer metal–metal bond reduces the steric crowding between the phosphine and the carbonyl C(51)O(51) on the adjacent Ru atom. The phosphine group bends away from the Ru(1)–Ru(5) bond with a Ru(5)–Ru(1)–P(1) angle of 107.8(1)°. The two equivalent Ru–Ru–C(carbonyl) angles in (4) are narrower, at 88.0(2) and 94.0(2)°.

The Ru–C(carbide) distances in (6) follow the same trends that have been observed in (4) and in $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)]$,[10] although there is a small increase in all five lengths over those in (4).

Table 4. Selected bond distances (Å) and angles (°) for $[Ru_5(H)C(CO)_{13}(PPh_3)(SEt)]$ (6)

Ru(1)–Ru(2)	2.921(1)	Ru(1)–C(1)	2.086(5)
Ru(1) · · · Ru(3)	3.438(1)	Ru(2)–C(1)	2.011(5)
Ru(1)–Ru(5)	2.972(1)	Ru(3)–C(1)	2.041(5)
Ru(2)–Ru(3)	2.818(1)	Ru(4)–C(1)	2.091(5)
Ru(2)–Ru(4)	2.843(1)	Ru(5)–C(1)	1.979(5)
Ru(3)–Ru(4)	2.864(1)	Ru(1)–S(1)	2.492(1)
Ru(3)–Ru(5)	2.821(1)	Ru(3)–S(1)	2.411(1)
Ru(4)–Ru(5)	2.830(1)	S(1)–C(2)	1.814(6)
Ru(1)–P(1)	2.395(1)	C(2)–C(3)	1.528(8)
Ru(3)–H(34)	2.02(4)		
Ru(4)–H(34)	1.73(5)		

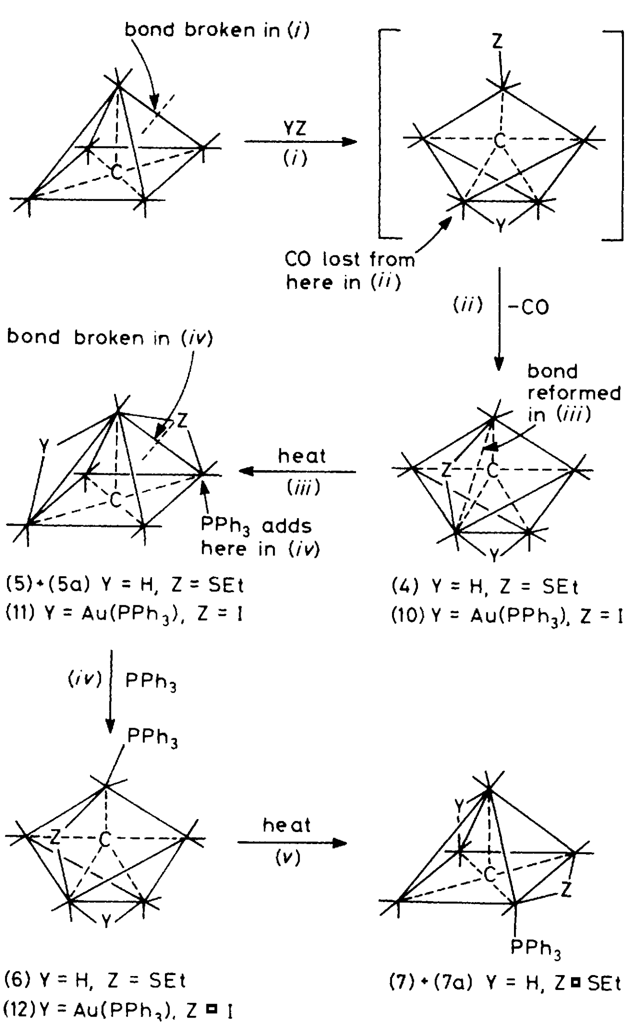
Ru(2)–Ru(1)–Ru(3)	51.8(1)	Ru(1)–Ru(5)–Ru(4)	90.2(1)
Ru(2)–Ru(1)–Ru(5)	85.1(1)	Ru(3)–Ru(5)–Ru(4)	60.9(1)
Ru(3)–Ru(1)–Ru(5)	51.6(1)	Ru(1)–C(1)–Ru(2)	90.9(2)
Ru(1)–Ru(2)–Ru(3)	73.6(1)	Ru(1)–C(1)–Ru(3)	112.8(2)
Ru(1)–Ru(2)–Ru(4)	90.9(1)	Ru(1)–C(1)–Ru(4)	159.3(3)
Ru(3)–Ru(2)–Ru(4)	60.8(1)	Ru(1)–C(1)–Ru(5)	93.9(2)
Ru(1)–Ru(3)–Ru(2)	54.6(1)	Ru(2)–C(1)–Ru(3)	88.1(2)
Ru(1)–Ru(3)–Ru(4)	80.8(1)	Ru(2)–C(1)–Ru(4)	87.7(2)
Ru(1)–Ru(3)–Ru(5)	55.6(1)	Ru(2)–C(1)–Ru(5)	175.0(3)
Ru(2)–Ru(3)–Ru(4)	60.0(1)	Ru(3)–C(1)–Ru(4)	87.8(2)
Ru(2)–Ru(3)–Ru(5)	90.0(1)	Ru(3)–C(1)–Ru(5)	89.1(2)
Ru(4)–Ru(3)–Ru(5)	59.7(1)	Ru(4)–C(1)–Ru(5)	88.1(2)
Ru(2)–Ru(4)–Ru(3)	59.2(1)	Ru(1)–S(1)–Ru(3)	89.0(1)
Ru(2)–Ru(4)–Ru(5)	89.3(1)	Ru(1)–S(1)–C(2)	114.3(2)
Ru(3)–Ru(4)–Ru(5)	59.4(1)	Ru(3)–S(1)–C(2)	111.4(2)
Ru(1)–Ru(5)–Ru(3)	72.8(1)	Ru(3)–H(34)–Ru(4)	99(2)

The Ru(1)–P(1) bond length in $[Ru_5(H)C(CO)_{13}(PPh_3)(SEt)]$ (6) is intermediate in length between the value of 2.380(6) Å in $[Ru_3(CO)_{11}(PPh_3)]$ [13] and that of 2.408(1) Å for the terminal phosphine in $[Ru_3(\mu\text{-}H)_2(CO)_8(PPh_3)(\mu_3\text{-}PPh)]$.[14]

The 13 carbonyl groups are effectively linear with an average Ru–C–O angle of 177(1)°. The average Ru–C and C–O bond lengths for this complex are 1.91(2) and 1.13(3) Å.

On the basis of this result we propose that the structure of (5) comprises a square-based pyramidal array of metal atoms with one hydride and one SEt ligand, possibly bridging opposite apical–basal ruthenium–ruthenium bonds (see Scheme).

In the same way the cluster $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}I)]$ (10) was converted to a new cluster (11) on heating in heptane at reflux for 2.5 h. The cluster (11) readily takes up



Scheme. The reaction of [$Ru_5C(CO)_{15}$] with YZ [Y = H, Z = SEt; Y = $Au(PPh_3)$, Z = I] and, subsequently, with PPh_3

Table 5. Selected bond distances (Å) and angles (°) for [$Ru_5C(CO)_{13}(PPh_3)\{Au(PPh_3)\}(\mu\text{-}I)$] (12)

Au(1)-Ru(1)	2.661(1)	Au(1)-P(1)	2.292(3)
Au(1)-Ru(2)	2.837(1)	Ru(1)-I(1)	2.785(1)
Ru(1)-Ru(2)	2.944(1)	Ru(5)-I(1)	2.818(1)
Ru(1)-Ru(3)	2.840(1)	Ru(5)-P(2)	2.407(3)
Ru(1)-Ru(4)	2.785(1)	Ru(1)-C(1)	2.036(10)
Ru(1) · · · Ru(5)	3.526(1)	Ru(2)-C(1)	2.106(9)
Ru(2)-Ru(3)	2.828(1)	Ru(3)-C(1)	1.977(9)
Ru(2)-Ru(4)	2.838(1)	Ru(4)-C(1)	2.018(10)
Ru(3)-Ru(5)	2.963(1)	Ru(5)-C(1)	2.062(9)
Ru(4)-Ru(5)	2.920(1)		
Ru(1)-Au(1)-Ru(2)	64.7(1)	Ru(1)-Ru(4)-Ru(2)	62.8(1)
Au(1)-Ru(1)-Ru(2)	60.6(1)	Ru(1)-Ru(4)-Ru(5)	75.9(1)
Au(1)-Ru(1)-Ru(3)	100.3(1)	Ru(2)-Ru(4)-Ru(5)	88.9(1)
Au(1)-Ru(1)-Ru(4)	98.7(1)	Ru(3)-Ru(5)-Ru(4)	85.4(1)
Au(1)-Ru(1)-I(1)	171.4(1)	Ru(3)-Ru(5)-I(1)	83.8(1)
Ru(2)-Ru(1)-Ru(3)	58.5(1)	Ru(4)-Ru(5)-I(1)	83.5(1)
Ru(2)-Ru(1)-Ru(4)	59.0(1)	Ru(1)-Au(1)-P(1)	158.0(1)
Ru(2)-Ru(1)-I(1)	127.9(1)	Ru(2)-Au(1)-P(1)	136.6(1)
Ru(3)-Ru(1)-Ru(4)	89.9(1)	Ru(1)-I(1)-Ru(5)	78.0(1)
Ru(3)-Ru(1)-I(1)	86.7(1)	Ru(1)-C(1)-Ru(2)	90.6(4)
Ru(4)-Ru(1)-I(1)	86.1(1)	Ru(1)-C(1)-Ru(3)	90.1(4)
Au(1)-Ru(2)-Ru(1)	54.8(1)	Ru(1)-C(1)-Ru(4)	87.8(4)
Au(1)-Ru(2)-Ru(3)	96.5(1)	Ru(1)-C(1)-Ru(5)	118.7(5)
Au(1)-Ru(2)-Ru(4)	94.1(1)	Ru(2)-C(1)-Ru(3)	87.6(3)
Ru(1)-Ru(2)-Ru(3)	58.9(1)	Ru(2)-C(1)-Ru(4)	86.9(4)
Ru(1)-Ru(2)-Ru(4)	58.2(1)	Ru(2)-C(1)-Ru(5)	150.6(5)
Ru(3)-Ru(2)-Ru(4)	89.5(1)	Ru(3)-C(1)-Ru(4)	174.2(5)
Ru(1)-Ru(3)-Ru(2)	62.6(1)	Ru(3)-C(1)-Ru(5)	94.4(4)
Ru(1)-Ru(3)-Ru(5)	74.8(1)	Ru(4)-C(1)-Ru(5)	91.4(3)
Ru(2)-Ru(3)-Ru(5)	88.2(1)		

PPh_3, at room temperature, to give a new complex (12), for which an *X*-ray structural determination has been carried out.

Due to the close analogy which seems to exist between the reaction sequences involving [$Ru_5C(CO)_{15}$] and HSEt or [$Au(PPh_3)I$], and the structures of the products obtained in each case, we also propose a square-based pyramidal arrangement of metal atoms for the cluster (11) (Scheme). The loss of CO accompanying the transformation of (4) to (5) and (10) to (11) would then simply involve the formation of a metal–metal bond between the two ruthenium atoms bridged by the SR or halogen group. The addition of PPh_3 to (5) and (11) would then require attack of the phosphine at the ruthenium atom in the square base of the pyramid which was involved in the SR or halogen bridge. Indeed, attack at a basal, rather than an apical ruthenium atom has been found to occur in all the examples involving the Ru_5C unit studied to date. Cleavage of the metal–metal bond bridged by the SR or halogen group would then give the structures observed for (6) and (12).

We do not exclude the possibility that the loss of CO from (4) and (10) could have resulted in the formation of five-electron donor (μ_3-SEt and μ_3-I groups) in the structures of (5) and (11) respectively. Subsequent addition of PPh_3 might then be expected to convert the μ_3-SEt (five-electron donor) to a μ-SEt (three-electron donor), as was seen in the case of [$Os_3(H)(CO)_9(SEt)$].[9] However, this would lead to the PPh_3 ligands bonding to a ruthenium atom which is not bound to the μ-SEt group. As clusters (6) and (12) both contain PPh_3 bound to the same atom as the μ-SEt or μ-I bridge it is unlikely that (5) and (11) contain five-electron donor bridging groups, unless drastic rearrangement accompanied the addition of PPh_3, which seems unlikely under such mild conditions.

The molecular geometry of [$Ru_5C(CO)_{13}(PPh_3)\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}I)$] (12) is shown in Figure 4 and selected bond parameters for the complex are presented in Table 5. The cluster geometry is related to that of (4) and (6) except that the bridging hydride is replaced by a bridging $Au(PPh_3)$ group, and the bridging SEt ligand is replaced by a bridging iodine atom which also acts as a three-electron donor.

The Ru_5 framework in (12) is closer to the idealised ' bridged-butterfly ' configuration, with the non-bonded Ru(1) · · · Ru(5) and Ru(2) · · · Ru(5) distances of 3.526(1) and 4.031(1) Å showing less asymmetry than in the previous two structures, This may reflect the ability of iodine to span a longer distance than a SEt group, and in (12) the iodine bridges the Ru(1)-Ru(5) edge. The Ru-I bond lengths show a similar asymmetry to the Ru-S(thiol) distances in (4) and (6) with the shorter distance involving the ' hinge ' Ru(1) bond. The Ru-I bond lengths are somewhat longer than the value of 2.751(2) Å for a related Os-I bond in [$Os_4(\mu\text{-}H)_3(CO)_{12}(\mu\text{-}I)$] [15] where the iodine spans an Os-Os distance of 3.821(1) Å. The corresponding Os-I-Os angle is 88°.

The ' butterfly ' framework in (12) is defined by the atoms Ru(1), Ru(2), Ru(3), and Ru(4), and the Ru(hinge)-Ru(wing-tip) distances [mean 2.83(2) Å] are not significantly different from the values in (4) and (6). The Ru(1)-Ru(2) hinge bond is significantly longer and is similar to the $Au(PPh_3)$ bridged bond [2.95(1) Å] in [$Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Br)$].[10] This suggests that at least in these carbide centred ' bridged-

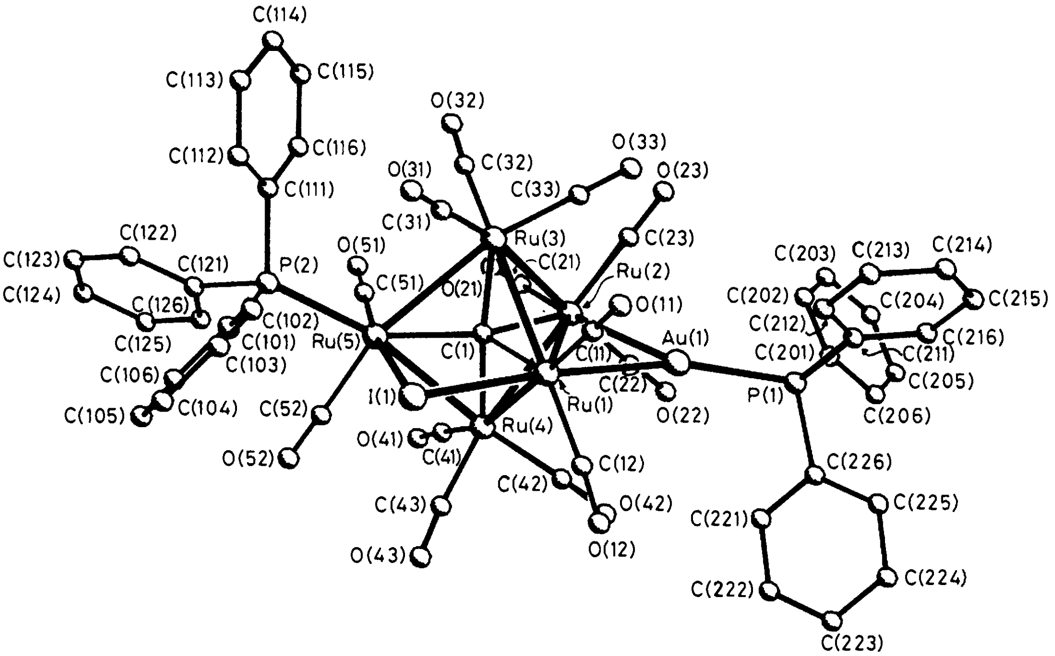


Figure 4. The molecular structure of [Ru$_5$C(CO)$_{13}$(PPh$_3$){μ-Au(PPh$_3$)}(μ-I)] (12)

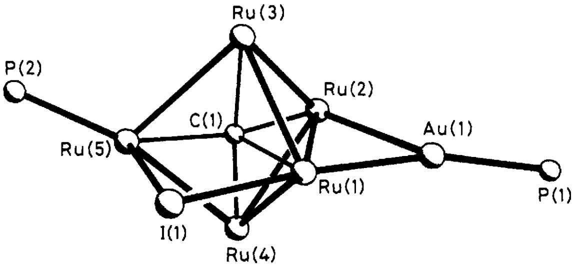


Figure 5. The cluster core of [Ru$_5$C(CO)$_{13}$(PPh$_3$){μ-Au(PPh$_3$)}(μ-I)] (12)

butterfly' systems a hinge-bridging Au(PPh$_3$) group has a greater metal–metal bond lengthening influence than a bridging hydride. The Au–Ru distances in (12) show slightly greater asymmetry than the corresponding values of 2.727(1) and 2.763(1) Å for the bridging Au atom in [Ru$_3$(H)$_2$(μ$_3$-COMe)(CO)$_9${Au(PPh$_3$)}].[16]

The cluster core for (12) is illustrated in Figure 5. The metal–carbide distances follow the same trends as in the other carbide centred clusters.

The phosphine ligand in (12) occupies a similar co-ordination site to that observed in the structure of [Ru$_5$(H)C(CO)$_{13}$(PPh$_3$)(SEt)] (6), and the Ru–P distance is marginally longer than in (6). The Ru(3)–Ru(5) bond which is *cis* to the phosphine again shows a lengthening of *ca.* 0.04 Å compared to the other Ru(wingtip)–Ru(bridge) Ru(4)–Ru(5) bond. As in the case of (6) this is presumably largely steric in origin.

The 13 carbonyl groups are terminally co-ordinated to the cluster. The average Ru–C(carbonyl) and C–O distances are 1.90(3) and 1.14(3) Å, respectively, and the average Ru–C–O angle is 177(3)°.

Further heating (6) results in the loss of a further CO group to give the new cluster (7) and another product (7a) which may be an isomer of (7). The cluster (7) was formulated, on the basis of its mass spectrum, as [Ru$_5$(H)C(CO)$_{12}$(PPh$_3$)(SEt)], and its crystal structure was determined.

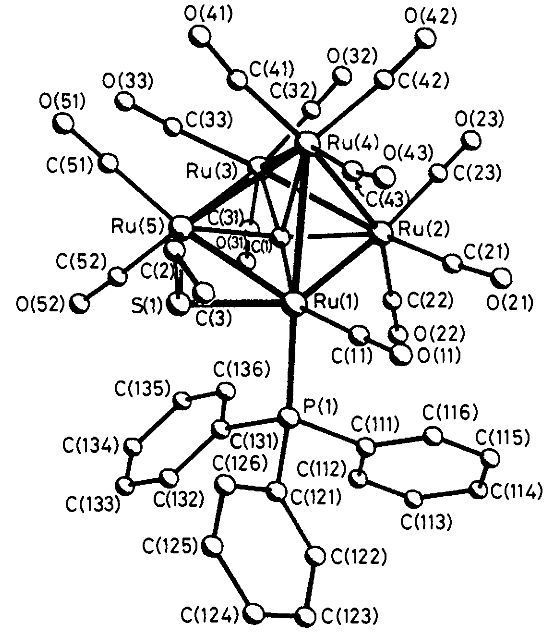


Figure 6. The molecular structure of [Ru$_5$(H)C(CO)$_{12}$(PPh$_3$)(SEt)] (7)

The molecular structure of [Ru$_5$(H)C(CO)$_{12}$(PPh$_3$)(SEt)] (7), which is shown in Figure 6, indicates that an additional Ru–Ru bond has formed; selected bond parameters are listed in Table 6. The five Ru atoms define a square-based pyramid with a carbido-carbon atom lying 0.12 Å below the Ru(1), Ru(2),Ru(3),Ru(5) square base. The SEt group symmetrically bridges the basal Ru(1)–Ru(5) edge, and the phosphine ligand occupies a pseudo-axial site on Ru(1). The hydride was not located directly in the structure determination but potential energy calculations indicate that it bridges the Ru(3)–Ru(4) edge.

Table 6. Selected bond distances (Å) and angles (°) for $[Ru_5(H)C(CO)_{12}(PPh_3)(SEt)]$ (7)

Ru(1)–Ru(2)	2.945(1)	Ru(1)–C(1)	1.993(9)
Ru(1)–Ru(4)	3.024(1)	Ru(2)–C(1)	2.012(6)
Ru(1)–Ru(5)	2.698(1)	Ru(3)–C(1)	2.054(9)
Ru(2)–Ru(3)	2.882(1)	Ru(4)–C(1)	2.197(7)
Ru(2)–Ru(4)	2.791(1)	Ru(5)–C(1)	2.005(6)
Ru(3)–Ru(4)	2.851(1)	Ru(1)–P(1)	2.282(2)
Ru(3)–Ru(5)	2.858(1)	Ru(1)–S(1)	2.317(2)
Ru(4)–Ru(5)	2.899(1)	Ru(5)–S(1)	2.320(3)
C(2)–C(3)	1.477(21)	S(1)–C(2)	1.822(11)

Ru(2)–Ru(1)–Ru(4)	55.7(1)	Ru(1)–Ru(5)–Ru(4)	65.3(1)
Ru(2)–Ru(1)–Ru(5)	90.2(1)	Ru(3)–Ru(5)–Ru(4)	59.4(1)
Ru(4)–Ru(1)–Ru(5)	60.6(1)	Ru(1)–C(1)–Ru(2)	94.7(3)
Ru(1)–Ru(2)–Ru(3)	87.8(1)	Ru(1)–C(1)–Ru(3)	173.5(4)
Ru(1)–Ru(2)–Ru(4)	63.6(1)	Ru(1)–C(1)–Ru(4)	92.3(3)
Ru(3)–Ru(2)–Ru(4)	60.3(1)	Ru(1)–C(1)–Ru(5)	84.9(3)
Ru(2)–Ru(3)–Ru(4)	58.3(1)	Ru(2)–C(1)–Ru(3)	90.3(3)
Ru(2)–Ru(3)–Ru(5)	88.4(1)	Ru(2)–C(1)–Ru(4)	83.0(2)
Ru(4)–Ru(3)–Ru(5)	61.0(1)	Ru(2)–C(1)–Ru(5)	170.1(4)
Ru(1)–Ru(4)–Ru(2)	60.7(1)	Ru(3)–C(1)–Ru(4)	84.2(3)
Ru(1)–Ru(4)–Ru(3)	86.9(1)	Ru(3)–C(1)–Ru(5)	89.5(3)
Ru(1)–Ru(4)–Ru(5)	54.1(1)	Ru(4)–C(1)–Ru(5)	87.1(3)
Ru(2)–Ru(4)–Ru(3)	61.4(1)	Ru(1)–S(1)–Ru(5)	71.2(1)
Ru(2)–Ru(4)–Ru(5)	89.3(1)	Ru(1)–S(1)–C(2)	111.8(3)
Ru(3)–Ru(4)–Ru(5)	59.6(1)	Ru(5)–S(1)–C(2)	110.9(4)
Ru(1)–Ru(5)–Ru(3)	93.3(1)		

The overall geometry of the Ru_5C core is similar to that observed in the parent carbide, $[Ru_5C(CO)_{15}]$, and the phosphine-substituted cluster, $[Ru_5C(CO)_{14}(PPh_3)]$.[17] The Ru–Ru bonds within the square pyramid of (7) show larger variations than in either of the other two square-based pyramidal species. The thiol-bridged Ru(1)–Ru(5) basal bond is *ca.* 0.16 Å, shorter than the average value of 2.86(2) Å for the Ru(basal)–Ru(basal) bonds in $[Ru_5C(CO)_{15}]$ and is also significantly shorter than any of the other three metal–metal bonds in (7). It contrasts the structures of (4) and (6) where the thiol spans a non-bonding Ru–Ru vector. It is also shorter than the Ru–Ru bond length of 2.839(4) Å in $[Ru_3(H)(CO)_{10}(SCH_2COOH)]$ [12] where the edge is also bridged by a hydride, and much shorter than the average distance of 3.03(1) Å for the SEt-bridged Ru–Ru bonds in the hexanuclear cluster $[Ru_6(H)C(CO)_{15}(SEt)_3]$.[18] The Ru–S distances are significantly shorter than the corresponding distances in (4) and (6) and more in keeping with the values of 2.356(7) and 2.331(7) Å observed in $[Ru_6(H)C(CO)_{15}(SEt)_3]$.[18] The Ru–S–Ru angle is *ca.* 10° narrower than the values in (4) and (6).

The other three Ru(basal)–Ru(basal) edges in (7) are similar in length to the values in $[Ru_5C(CO)_{15}]$.[17] The Ru(1)–Ru(2) bond is somewhat longer than the average, but a similar trend was observed for a basal Ru–Ru bond, where one of the metal atoms is co-ordinated to the axial phosphine, in $[Ru_5C(CO)_{14}(PPh_3)]$ and the bond length was 2.940(1) Å. This distortion is presumed to be due to the influence of the phosphine.[17] The Ru–P distance in (7) is *ca.* 0.1 Å shorter than the corresponding distance of 2.377(1) Å in $[Ru_5C(CO)_{14}(PPh_3)]$.[17]

The four Ru(basal)–Ru(apical) bonds in (7) also show significant variations from the average value of 2.86(2) Å in $[Ru_5C(CO)_{15}]$.[17] The bridging hydride exerts an influence on the Ru(3)–Ru(4) bond but the largest Ru–Ru bond is pseudo-*trans* to the phosphine group.

The Ru(basal)–C(carbide) distances [mean 2.02(2) Å] are similar to the values in $[Ru_5C(CO)_{15}]$ [mean 2.02(2) Å] and marginally shorter than the average value of 2.04(2) Å in $[Ru_5C(CO)_{14}(PPh_3)]$.[17]

The carbonyl ligand parameters are not significantly different from those in (4), (6), and (12), the average Ru–C(carbonyl) and C–O bond distances being 1.91(2) and 1.13(3) Å, respectively, and the average Ru–C–O angle is 176(2)°.

The process by which (6) is converted to (7) cannot simply involve metal–metal bond formation on loss of CO, and must involve some rearrangement. On heating (12) to 84 °C, in nonane, for 3 h two products, separable by t.l.c., were obtained. These products remain uncharacterised.

The adducts $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}X]$ (X = Cl or Br) and their derivatives $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}X]$ also react with triphenylphosphine, although instead of a simple addition, elimination of the $[Au(PPh_3)X]$ moiety was also found to occur. The cluster product of the reaction in each case was found to be $[Ru_5C(CO)_{14}(PPh_3)]$. The complex $[Ru_5C(CO)_{15}\{\mu\text{-}Au(PPh_3)\}Br]$ reacted instantaneously with PPh_3 in CH_2Cl_2 at room temperature to give $[Ru_5C(CO)_{14}(PPh_3)]$. The cluster $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}Br]$ was found to react more slowly, but the reaction had proceeded to completion after heating in refluxing hexane for 15 min. The complexes $[Ru_5(H)C(CO)_nX]$ (*n* = 14 or 15; X = Cl or Br) also reacted with PPh_3 to give $[Ru_5C(CO)_{14}(PPh_3)]$ although very much more slowly than their gold analogues.

The clusters (4) and (5) both react with $[Au(PPh_3)Me]$ on stirring for some days in diethyl ether, to give cluster complexes in which the hydride has been replaced by $Au(PPh_3)$. The complex (4) gives a mixture of (8) and (9) as the major and minor products respectively. The complex $[Ru_5C(CO)_{15}]$ also reacts with $[Au(PPh_3)Me]$ to yield (16), formulated as $[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(COMe)]$ on the basis of n.m.r. and the similarity of its carbonyl i.r. spectrum to that of (10). The complex (16) is currently the subject of an *X*-ray crystallographic structure determination.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer using carbon monoxide as calibrant, or on a Perkin-Elmer 983 spectrometer. Proton n.m.r. spectra were obtained on a Varian CFT20 spectrometer with $SiMe_4$ as standard. Mass spectra were recorded on an A.E.I. MS12 spectrometer using tris(perfluoroheptyl)-*s*-triazine as calibrant.

Ruthenium trichloride and chloroauric acid were supplied by Johnson Matthey and Co. Ltd. The complex $[Ru_5C(CO)_{15}]$ was synthesised as described elsewhere.[2] The complex $[Au(PPh_3)Cl]$ was prepared by the reaction of triphenylphosphine with chloroauric acid in acetone; $[Au(PPh_3)I]$ was prepared by passing a stream of HI gas through a stirred solution of $[Au(PPh_3)Cl]$ in dichloromethane for 30 min. The gas H_2Se was prepared as required by the addition of dilute HCl to aluminium selenide, supplied by Fluka. The complex $[Au(PPh_3)Me]$ was prepared by the action of methyllithium on a stirred suspension of $[Au(PPh_3)Cl]$ in diethyl ether. Reactions were performed under nitrogen in reagent grade solvents. Infrared data for all complexes are given in Table 1 and n.m.r. data are given in Table 2.

Preparations.—$[Ru_5(H)C(CO)_{14}(SH)]$ (1). Through a stirred solution of $[Ru_5C(CO)_{15}]$ (20 mg) in CH_2Cl_2 (20 cm^3) was bubbled H_2S gas. After 5 min the colour of the solution had changed from red to orange. The solution was evaporated to dryness, giving the orange solid, (1) (Found: C, 22.5; S, 4.0. Calc. for $C_{15}H_2O_{14}Ru_5S$: C, 19.1; S, 3.6%). Mass spectrum: highest mass 943 *m/e* corresponds to $[Ru_5(H)C(CO)_{14}(SH)]$; lowest mass 517 *m/e* corresponds to Ru_5C (for Ru = 101 mass units).

$[Ru_5C(H)(CO)_{14}(SeH)]$ (3). A stream of H_2Se gas was

Table 7. Molecular structure determination data

Complex	(4)	(6)	(12)	(7)
Molecular formula	$C_{17}H_6O_{14}Ru_5S$	$C_{34}H_{21}O_{13}PRu_5S$	$C_{50}H_{30}AuIO_{13}P_2Ru_5$	$C_{33}H_{21}O_{12}PRu_5S$
M	971.63	1 205.89	1 729.9	1 177.88
Colour	Orange	Red	Orange	Red
Crystal habit	Rectangular block	Plate	Rectangular block	Needle
Crystal dimensions (mm)	0.37 × 0.34 × 0.29	0.39 × 0.15 × 0.02	0.47 × 0.21 × 0.19	0.42 × 0.11 × 0.08
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	15.315(3)	15.892(2)	9.899(3)	10.162(2)
b/Å	16.739(4)	11.474(1)	14.628(6)	13.807(4)
c/Å	10.286(3)	21.387(2)	18.788(7)	14.660(4)
α/°	90.0	90.0	100.29(3)	78.20(2)
β/°	89.31(2)	92.50(1)	91.31(3)	74.12(2)
γ/°	90.0	90.0	93.69(3)	87.38(2)
U/Å^3	2 635.7	3 896.1	2 669.6	1 936.5
D_c/g cm^{-3}	2.448	2.055	2.151	2.019
Z	4	4	2	2
F(000)	1 824	2 320	1 632	1 132
μ(Mo-K_α)/cm^{-1}	28.56	19.80	47.43	19.88
Diffractometer	Syntex $P2_1$	Stoe	Syntex $P2_1$	Syntex $P2_1$
2θ range (°) min.	3.0	5.0	3.0	3.0
max.	50.0	50.0	50.0	50.0
No. reflections measured	4 913	7 682	7 329	4 799
Scan mode	ω/2θ	ω/θ	ω/2θ	ω/2θ
Cell determined from n reflections in	15	72	15	15
2θ range (°)	15 < 2θ < 25	20 < 2θ < 30	15 < 2θ < 25	15 < 2θ < 25
No. of steps in scan	96	24	96	96
Step width (°)	Variable	0.05	Variable	Variable
Minimum scan speed (° min^{-1})	2.5	1.0	2.5	2.5
Maximum scan speed (° min^{-1})	29.3	6.0	29.3	29.3
No. unique observed reflections	4 134	5 861	6 075	4 050
$F > n\sigma(F)$: value of n	3	4	3	3
Method of absorption correction	Empirical; 445 azimuthal scan data	Numerical; 100, 10$\bar{2}$ 011, 01$\bar{1}$	Empirical; 440 azimuthal scan data	Empirical; 393 azimuthal scan data
Transmission factors, min.	0.714	0.491	0.768	0.857
max.	0.950	0.916	1.000	1.000
Weighting scheme, w	$[\sigma^2(F)^{-1}]$	$[\sigma^2(F) + 0.0002\|F\|^2]^{-1}$	$[\sigma^2(F) + 0.0007\|F\|^2]^{-1}$	$[\sigma^2(F) + 0.0005\|F\|^2]^{-1}$
R	0.032	0.036	0.042	0.041
$R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}\|F_o\|$	0.032	0.038	0.043	0.043

Details pertaining to all structures: D_m, not measured; graphite monochromatized Mo–K_α radiation, λ = 0.710 69 Å; method of heavy-atom location, Σ_2 sign expansion; method of light-atom location, Fourier difference; method of refinement, blocked-cascade least squares.

bubbled through a stirred solution of $[Ru_5C(CO)_{15}]$ (20 mg) in CH_2Cl_2 (20 cm^3) for 30 min. A colour change of red to dark orange was observed. Evaporation of the solution to dryness gave the dark orange solid (3).

$[Ru_5(H)C(CO)_{14}(SEt)]$ (4). Addition of one equivalent EtSH to a stirred solution of $[Ru_5C(CO)_{15}]$ (20 mg) in CH_2Cl_2 (30 cm^3) yielded an orange solution after 5 min. The solvent was removed under vacuum and the residue dissolved in hexane and cooled to −20 °C to give crystals of (4) (18.6 mg, 90%) (Found: C, 21.70; H, 1.05. Calc. for $C_{17}H_6O_{14}Ru_5S$: C, 20.9; H, 0.60%). Mass spectrum: highest mass m/e 972, $[Ru_5(H)C(CO)_{14}(SEt)]$; lowest mass m/e 517, Ru_5C.

'$[Ru_5(H)C(CO)_{13}(SEt)]$' (5) *and* (5a). A solution of (4) (15 mg) in cyclohexane (30 cm^3) was heated at reflux for 30 min yielding an orange-red solution of (5) and (5a). The solvent was removed under vacuum and the residue purified by t.l.c. in 50% CH_2Cl_2–hexane giving a mixture of (5) and (5a) as the major product (12 mg, 82%). Mass spectrum: highest mass m/e 944 $[Ru_5(H)C(CO)_{13}(SEt)]$; lowest mass m/e 517, Ru_5C.

$[Ru_5(H)C(CO)_{13}(PPh_3)(SEt)]$ (6). To a stirred solution of (5) and (5a) (10 mg) in hexane (20 cm^3) an excess of PPh_3 was added. After 6 h the solvent was removed under vacuum and the residue purified by t.l.c. in 10% Et_2O–hexane giving (6) (8.5 mg, 66%). Crystals of (6) were obtained by very slow evaporation from a pentane solution at room temperature. Mass spectrum: highest mass m/e 1 178, $[Ru_5(H)C(CO)_{12}(PPh_3)(SEt)]$.

$[Ru_5(H)C(CO)_{12}(PPh_3)(SEt)]$ (7) *and* (7a). A stirred solution of (6) (7 mg) in cyclohexane (20 cm^3) was heated at reflux for 8 h. The solvent was removed under vacuum and the residue purified as for (6). The major product was (7) (5 mg, 71%) with only a trace of (7a). Slow evaporation from a 20% CH_2Cl_2–hexane solution, at room temperature, yielded crystals of (7). Mass spectrum: highest mass m/e 1 178, $[Ru_5(H)C(CO)_{12}(PPh_3)(SEt)]$.

'$[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(SEt)]$' (8) *and* '$[Ru_5C(CO)_{13}\{\mu\text{-}Au(PPh_3)\}(SEt)]$' (9). To a stirred solution of (4) (10 mg) in Et_2O (10 cm^3) one equivalent of $[Au(PPh_3)Me]$ was added. After 60 h the solvent was removed by a fast stream of N_2 and the residue purified by t.l.c. in 50% Et_2O–hexane to give (8) (7 mg, 47%) and (9) (2 mg, 13%) {treatment of (5) with $[Au(PPh_3)Me]$ as for (4) yielded only (9)}. Mass spectrum: highest mass m/e 1 402, $[Ru_5C(CO)_{13}\{\mu\text{-}Au(PPh_3)\}(SEt)]$.

$[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}I)]$ (10). To a stirred solution

Table 8. Atom co-ordinates (× 10^4) for $[Ru_5(H)C(CO)_{14}(SEt)]$ (4)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	3 663(1)	1 119(1)	4 849(1)
Ru(2)	2 967(1)	1 825(1)	2 560(1)
Ru(3)	2 021(1)	2 899(1)	4 213(1)
Ru(4)	3 061(1)	2 457(1)	6 440(1)
Ru(5)	1 820(1)	1 241(1)	4 549(1)
C(1)	2 857(3)	2 015(3)	4 549(5)
S(1)	1 720(1)	1 661(1)	6 794(1)
C(11)	3 957(4)	604(4)	6 443(7)
O(11)	4 176(4)	283(3)	7 374(5)
C(12)	4 851(4)	1 416(4)	4 454(6)
O(12)	5 538(3)	1 600(3)	4 143(5)
C(13)	3 640(5)	103(4)	4 022(6)
O(13)	3 634(4)	−507(3)	3 562(6)
C(21)	3 492(4)	983(4)	1 570(6)
O(21)	3 806(4)	490(3)	967(5)
C(22)	2 352(4)	2 202(4)	1 077(6)
O(22)	2 014(4)	2 429(4)	154(5)
C(23)	3 906(4)	2 561(4)	2 280(6)
O(23)	4 439(4)	3 019(3)	2 149(6)
C(31)	1 163(4)	2 934(3)	2 892(6)
O(31)	614(3)	2 946(3)	2 148(4)
C(32)	2 603(4)	3 908(4)	3 861(6)
O(32)	2 969(4)	4 482(3)	3 644(6)
C(33)	1 151(4)	3 307(4)	5 413(6)
O(33)	606(3)	3 543(3)	6 062(5)
C(41)	2 554(4)	3 347(3)	7 354(6)
O(41)	2 275(3)	3 890(3)	7 894(5)
C(42)	3 621(4)	2 077(3)	7 989(6)
O(42)	3 942(3)	1 876(3)	8 910(4)
C(43)	4 061(4)	3 056(3)	5 866(6)
O(43)	4 651(3)	3 408(3)	5 490(5)
C(51)	1 740(4)	108(4)	4 679(6)
O(51)	1 671(4)	−565(3)	4 709(5)
C(52)	615(4)	1 358(3)	4 165(6)
O(52)	−95(3)	1 430(3)	3 900(6)
H(01)	2 075(52)	1 377(42)	2 923(74)
C(2)	1 892(4)	820(4)	7 902(6)
C(3)	1 069(5)	365(5)	8 080(8)

of $[Ru_5C(CO)_{15}]$ (10 mg) in CH_2Cl_2 (15 cm^3) was added $[Au(PPh_3)I]$ (7 mg). After 1 h a colour change of red to dark orange had occurred, and the i.r. spectrum (see Table 1) indicated the formation of (10).

'$[Ru_5C(CO)_{13}\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}I)]$' (11). A solution of (10) in heptane was heated under conditions of reflux for 2 h, after which time the i.r. spectrum showed reaction to give (11) to be complete. Filtration, to remove a black insoluble metallic powder formed during the reaction by partial decomposition, followed by evaporation of the solution, yielded the brown powder (11).

$[Ru_5C(CO)_{13}(PPh_3)\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}I)]$ (12). To a solution of (11) in heptane was added an excess of triphenylphosphine. After stirring for 20 min the i.r. spectrum showed that no unreacted (11) remained. Evaporation to dryness followed by t.l.c. in 10% ether–hexane, each plate being run twice to improve the separation, yielded traces of $[Ru_5C(CO)_{14}(PPh_3)]$ and $[Ru_5C(CO)_{13}(PPh_3)_2]$ (15%), some material which remained on the baseline (10%), and the orange complex (12). Recrystallisation from CH_2Cl_2–hexane afforded orange crystals of (12) which were used in the *X*-ray experiment.

'$[Ru_5C(CO)_{14}\{\mu\text{-}Au(PPh_3)\}(COMe)]$' (16). To a stirred solution of $[Ru_5C(CO)_{15}]$ (20 mg) in Et_2O (30 cm^3) one equivalent of $[Au(PPh_3)Me]$ was added. After 2 h the solvent was removed under vacuum and the residue purified by t.l.c. in 50% CH_2Cl_2–hexane yielding (16) (19 mg, 64%).

Table 9. Atom co-ordinates (× 10^4) for $[Ru_5(H)C(CO)_{13}(PPh_3)(SEt)]$ (6)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	2 581(1)	914(1)	1 548(1)
Ru(2)	2 385(1)	274(1)	2 856(1)
Ru(3)	1 398(1)	−1 311(1)	2 133(1)
Ru(4)	3 025(1)	−1 995(1)	2 633(1)
Ru(5)	2 743(1)	−1 633(1)	1 332(1)
H(34)	2 003(28)	−2 470(42)	2 707(20)
C(1)	2 576(3)	−625(4)	2 067(2)
S(1)	1 099(1)	230(1)	1 390(1)
C(2)	317(3)	1 232(5)	1 670(3)
C(3)	−569(4)	750(7)	1 537(3)
C(11)	3 755(3)	1 033(5)	1 670(2)
O(11)	4 463(2)	1 056(4)	1 769(2)
C(12)	2 329(3)	2 426(5)	1 853(2)
O(12)	2 207(3)	3 330(3)	2 034(2)
C(21)	3 415(4)	975(5)	3 192(3)
O(21)	4 033(3)	1 371(5)	3 372(2)
C(22)	1 683(4)	1 596(5)	2 997(2)
O(22)	1 284(3)	2 379(4)	3 111(2)
C(23)	1 963(4)	−336(6)	3 608(3)
O(23)	1 690(4)	−658(5)	4 055(2)
C(31)	517(4)	−1 021(5)	2 689(3)
O(31)	−16(3)	−847(4)	3 014(2)
C(32)	797(4)	−2 533(5)	1 702(3)
O(32)	450(3)	−3 290(4)	1 474(2)
C(41)	4 177(5)	−1 561(6)	2 617(3)
O(41)	4 855(4)	−1 316(5)	2 598(3)
C(42)	3 262(5)	−3 591(6)	2 414(3)
O(42)	3 426(4)	−4 517(4)	2 311(2)
C(43)	3 060(6)	−2 285(6)	3 526(3)
O(43)	3 131(5)	−2 462(5)	4 040(2)
C(51)	2 236(3)	−1 272(5)	526(2)
O(51)	1 931(3)	−1 145(4)	45(2)
C(52)	2 446(4)	−3 247(5)	1 198(3)
O(52)	2 236(3)	−4 166(4)	1 096(2)
C(53)	3 876(4)	−1 759(5)	1 062(3)
O(53)	4 550(3)	−1 871(4)	918(3)
P(1)	2 557(1)	1 861(1)	550(1)
C(101)	2 960(2)	1 122(3)	−134(1)
C(102)	3 680(2)	437(3)	−40(1)
C(103)	4 066(2)	−52(3)	−551(1)
C(104)	3 733(2)	143(3)	−1 156(1)
C(105)	3 013(2)	828(3)	−1 250(1)
C(106)	2 627(2)	1 317(3)	−739(1)
C(111)	3 174(2)	3 225(3)	520(1)
C(112)	3 735(2)	3 577(3)	1 003(1)
C(113)	4 211(2)	4 589(3)	939(1)
C(114)	4 125(2)	5 249(3)	393(1)
C(115)	3 563(2)	4 897(3)	−90(1)
C(116)	3 088(2)	3 885(3)	−27(1)
C(121)	1 490(2)	2 320(2)	325(2)
C(122)	938(2)	1 557(2)	7(2)
C(123)	99(2)	1 875(2)	−110(2)
C(124)	−189(2)	2 955(2)	92(2)
C(125)	364(2)	3 717(2)	410(2)
C(126)	1 203(2)	3 399(2)	527(2)

Molecular Structure Determinations.—Single crystals of (4), (6), (7), and (12) were mounted in Lindemann tubes, and cell dimensions and space groups determined *via* Weissenberg (Cu-K_α) photography. The crystals were transferred to four-circle diffractometers upon which intensity data were recorded. Details of crystal parameters, data-collection parameters, and refinement details are summarised in Table 7. In each data collection three reflections were monitored periodically throughout the course of the measurements but showed no significant variations in intensity.

All the data sets were profile fitted [19] and Lorentz polariz-

Table 10. Atom co-ordinates (× 10^4) for $[Ru_5C(CO)_{13}(PPh_3)\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}I)]$ (12)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Au(1)	7 425(1)	5 940(1)	2 859(1)	C(101)	3 701(7)	386(4)	1 634(3)
Ru(1)	6 648(1)	4 169(1)	2 330(1)	C(102)	4 803(7)	162(4)	2 029(3)
Ru(2)	4 583(1)	5 517(1)	2 715(1)	C(103)	5 590(7)	−557(4)	1 729(3)
Ru(3)	4 562(1)	3 856(1)	3 289(1)	C(104)	5 275(7)	−1 052(4)	1 033(3)
Ru(4)	4 686(1)	4 454(1)	1 300(1)	C(105)	4 173(7)	−828(4)	637(3)
Ru(5)	3 566(1)	2 829(1)	1 850(1)	C(106)	3 386(7)	−109(4)	937(3)
I(1)	6 243(1)	2 284(1)	1 734(1)	C(111)	2 276(7)	1 133(4)	2 927(4)
P(1)	8 856(3)	7 258(2)	3 148(2)	C(112)	2 676(7)	376(4)	3 218(4)
P(2)	2 649(3)	1 319(2)	2 011(1)	C(113)	2 334(7)	290(4)	3 920(4)
C(1)	4 586(10)	4 086(6)	2 284(5)	C(114)	1 592(7)	960(4)	4 331(4)
C(11)	7 921(11)	3 992(7)	3 045(6)	C(115)	1 192(7)	1 718(4)	4 040(4)
O(11)	8 711(9)	3 856(7)	3 475(5)	C(116)	1 534(7)	1 804(4)	3 337(4)
C(12)	7 971(10)	4 420(8)	1 663(6)	C(121)	1 002(7)	921(5)	1 549(4)
O(12)	8 728(9)	4 521(7)	1 240(5)	C(122)	427(7)	51(5)	1 627(4)
C(21)	2 709(13)	5 582(7)	2 648(7)	C(123)	−805(7)	−292(5)	1 273(4)
O(21)	1 564(9)	5 604(6)	2 604(6)	C(124)	−1 462(7)	236(5)	840(4)
C(22)	4 950(12)	6 664(8)	2 373(6)	C(125)	−887(7)	1 107(5)	762(4)
O(22)	5 144(11)	7 362(6)	2 186(5)	C(126)	345(7)	1 450(5)	1 116(4)
C(23)	4 732(12)	6 117(8)	3 698(6)	C(201)	8 023(8)	8 355(5)	3 395(4)
O(23)	4 767(10)	6 502(6)	4 286(5)	C(202)	6 888(8)	8 330(5)	3 820(4)
C(31)	4 919(12)	2 674(7)	3 481(6)	C(203)	6 190(8)	9 130(5)	4 020(4)
O(31)	5 201(9)	1 972(5)	3 627(4)	C(204)	6 626(8)	9 955(5)	3 795(4)
C(32)	2 859(13)	3 962(7)	3 772(6)	C(205)	7 760(8)	9 980(5)	3 369(4)
O(32)	1 880(10)	4 077(6)	4 061(5)	C(206)	8 458(8)	9 181(5)	3 170(4)
C(33)	5 697(11)	4 455(7)	4 096(6)	C(211)	10 018(7)	7 259(4)	3 908(4)
O(33)	6 401(8)	4 800(6)	4 582(4)	C(212)	10 202(7)	6 420(4)	4 140(4)
C(41)	3 012(13)	4 708(8)	862(6)	C(213)	11 126(7)	6 393(4)	4 706(4)
O(41)	2 035(11)	4 837(8)	573(6)	C(214)	11 866(7)	7 206(4)	5 041(4)
C(42)	5 716(12)	5 509(9)	1 083(6)	C(215)	11 682(7)	8 045(4)	4 810(4)
O(42)	6 361(10)	6 091(6)	900(4)	C(216)	10 758(7)	8 072(4)	4 244(4)
C(43)	5 410(12)	3 687(8)	493(5)	C(221)	9 283(9)	7 067(6)	1 699(3)
O(43)	5 945(10)	3 267(6)	14(4)	C(222)	10 013(9)	7 110(6)	1 078(3)
C(51)	1 908(11)	3 308(7)	2 036(5)	C(223)	11 346(9)	7 494(6)	1 139(3)
O(51)	887(8)	3 596(5)	2 165(4)	C(224)	11 950(9)	7 837(6)	1 821(3)
C(52)	3 210(11)	2 442(7)	830(6)	C(225)	11 220(9)	7 794(6)	2 442(3)
O(52)	2 940(9)	2 215(6)	246(4)	C(226)	9 887(9)	7 409(6)	2 381(3)

Table 11. Atom co-ordinates (× 10^4) for $[Ru_5(H)C(CO)_{12}(PPh_3)(SEt)]$ (7)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	2 529(1)	7 756(1)	2 476(1)	C(42)	1 129(10)	8 318(7)	5 575(8)
Ru(2)	2 632(1)	6 664(1)	4 403(1)	O(42)	612(8)	8 155(6)	6 385(5)
Ru(3)	4 762(1)	8 017(1)	4 311(1)	C(43)	448(11)	8 667(8)	3 871(7)
Ru(4)	2 090(1)	8 683(1)	4 234(1)	O(43)	−629(8)	8 726(8)	3 761(6)
Ru(5)	4 377(1)	9 078(1)	2 514(1)	C(51)	4 702(10)	10 425(7)	2 449(8)
C(1)	3 634(7)	7 801(5)	3 400(5)	O(51)	4 840(9)	11 253(6)	2 390(7)
P(1)	3 405(2)	6 727(2)	1 426(2)	C(52)	6 109(11)	9 012(7)	1 690(8)
S(1)	3 202(3)	9 204(2)	1 344(2)	O(52)	7 200(8)	8 985(6)	1 207(6)
C(2)	1 891(12)	10 150(7)	1 478(9)	C(111)	3 125(5)	5 400(4)	1 936(4)
C(3)	769(14)	10 027(10)	1 048(9)	C(112)	4 189(5)	4 727(4)	1 779(4)
C(11)	795(9)	7 482(6)	2 348(6)	C(113)	3 943(5)	3 721(4)	2 168(4)
O(11)	−260(6)	7 330(6)	2 277(5)	C(114)	2 632(5)	3 389(4)	2 713(4)
C(21)	900(12)	6 252(7)	4 337(7)	C(115)	1 568(5)	4 063(4)	2 869(4)
O(21)	−165(8)	5 987(6)	4 385(6)	C(116)	1 815(5)	5 068(4)	2 481(4)
C(22)	3 643(10)	5 486(6)	4 143(6)	C(121)	2 781(7)	6 851(3)	341(4)
O(22)	4 256(8)	4 812(5)	4 032(5)	C(122)	2 521(7)	6 012(3)	23(4)
C(23)	2 306(11)	6 196(7)	5 781(7)	C(123)	2 070(7)	6 113(3)	−809(4)
O(23)	2 119(10)	5 899(6)	6 581(5)	C(124)	1 880(7)	7 053(3)	−1 323(4)
C(31)	6 203(9)	7 109(7)	3 948(7)	C(125)	2 140(7)	7 892(3)	−1 005(4)
O(31)	7 037(7)	6 551(5)	3 765(5)	C(126)	2 591(7)	7 791(3)	−173(4)
C(32)	4 597(13)	7 592(9)	5 667(8)	C(131)	5 256(6)	6 814(5)	982(4)
O(32)	4 432(10)	7 358(8)	6 465(6)	C(132)	5 932(6)	7 041(5)	−2(4)
C(33)	5 944(10)	9 164(8)	4 048(9)	C(133)	7 359(6)	7 038(5)	−305(4)
O(33)	6 634(8)	9 811(6)	3 941(7)	C(134)	8 108(6)	6 808(5)	377(4)
C(41)	2 131(10)	10 096(8)	4 055(7)	C(135)	7 432(6)	6 580(5)	1 362(4)
O(41)	2 061(9)	10 919(6)	4 030(6)	C(136)	6 006(6)	6 583(5)	1 664(4)

ation corrections were applied. Where empirical absorption corrections were applied a pseudo-ellipsoid model was used. Neutral-atom scattering factors were employed throughout.[20] The structures were processed using programs written by Professor G. M. Sheldrick.[21] All computations were performed on the University of Cambridge IBM370/165 computer.

During the refinement of (4) all the non-hydrogen atoms except the ethyl carbon atoms were assigned anisotropic thermal parameters, the hydride atom was located directly and refined independently. In the structure of (6) all the non-hydrogen atoms except the phenyl carbons were refined anisotropically, and again the hydride was located directly and refined freely. The same parameters for the non-hydrogen atoms were applied in the structures of (7) and (12) although the hydride was not directly located in (7); the position of the hydride was determined by potential energy calculations.[22] In all the structures the ethyl H atoms were placed in idealized positions (C–H 1.08 Å, H–C–H 109.5°) and constrained to ride on the relevant C atom; the methyl groups were refined as rigid bodies. The phenyl rings were also refined as rigid groups with the H atoms in idealized positions (C–C 1.395 Å, C–C–C 120.0°, C–H 1.08 Å, C–C–H 120.0°). Each type of H atom was assigned a common isotropic thermal parameter.

The final atomic co-ordinates for (4), (6), (7), and (12) are presented in Tables 8—11, respectively.

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References

1 B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1982, 314.
2 R. Steinmetz, A. D. Harley, and G. L. Geoffroy, *Inorg. Chem.*, 1980, **19**, 2985.
3 F. Demartin, M. Manassero, L. Naldini, R. Ruggeri, and M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 1981, 222.
4 M. R. Churchill and H. J. Wasserman, *Inorg. Chem.*, 1980, **19**, 2391.
5 V. F. Allen, R. Mason, and P. B. Hitchcock, *J. Organomet. Chem.*, 1977, **140**, 297.
6 B. F. G. Johnson, J. Lewis, and D. A. Pippard, *J. Chem. Soc., Dalton Trans.*, 1981, 407.
7 D. A. Pippard, Ph.D. Thesis, University of Cambridge, 1978.
8 J. M. Coleman, A. Wojcicki, P. J. Pollick, and L. F. Dahl, *Inorg. Chem.*, 1967, **6**, 1236.
9 B. F. G. Johnson, J. Lewis, and D. A. Pippard, *J. Organomet. Chem.*, 1981, **213**, 249.
10 B. F. G. Johnson, J. Lewis, J. N. Nicholls, J. Puga, and K. H. Whitmire, *J. Chem. Soc., Dalton Trans.*, 1983, 787.
11 B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby, and M. J. Taylor, *Polyhedron*, 1982, **1**, 105; M. R. Churchill, B. G. De Boer, and F. J. Rotella, *Inorg. Chem.*, 1976, **15**, 1843.
12 S. Jeannin, Y. Jeannin, and G. Lavigne, *Inorg. Chem.*, 1978, **17**, 2103.
13 E. J. Forbes, N. Goodhand, D. L. Jones, and T. A. Hamor, *J. Organomet. Chem.*, 1979, **182**, 143.
14 M. J. Mays, P. L. Taylor, and K. Henrick, *Acta Crystallogr., Sect. B*, 1982, **38**, 2261.
15 B. F. G. Johnson, J. Lewis, P. R. Raithby, K. Wong, and K. D. Rouse, *J. Chem. Soc., Dalton Trans.*, 1980, 1248.
16 L. W. Bateman, M. Green, J. A. K. Howard, K. A. Mead, R. M. Mills, J. D. Salter, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1982, 773.
17 B. F. G. Johnson, J. Lewis, J. N. Nicholls, J. Puga, P. R. Raithby, M. J. Rosales, M. McPartlin, and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1983, 277.
18 B. F. G. Johnson, J. Lewis, K. Wong, and M. McPartlin, *J. Organomet. Chem.*, 1980, **185**, C17.
19 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
20 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
21 SHELX, crystal structure solving package, G. M. Sheldrick, University of Cambridge, 1976.
22 A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2509.

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