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Syntheses and Crystal Structures of the Ruthenium Carbidocarbonyl Clusters $[Ru_5C(CO)_{11}(\mu\text{-}Br)_2(\eta^3\text{-}C_3H_5)(\mu\text{-}\eta^3\text{-}C_3H_5)]$, $[Ru_5C(CO)_{13}I(\mu\text{-}I)(\mu\text{-}\eta^2\text{-}COMe)]^-$, $[Ru_5C(CO)_{14}(\mu\text{-}Br)_2]$ and $[Ru_6C(CO)_{16}(\mu\text{-}Br)]^-$ with Novel Metal Frameworks†

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The reaction of the octahedral cluster anion $[N(PPh_3)_2][Ru_6C(CO)_{15}(\mu\text{-}\eta^3\text{-}C_3H_5)]$ with allyl bromide at 115 °C afforded the pentanuclear cluster $[Ru_5C(CO)_{11}(\mu\text{-}Br)_2(\eta^3\text{-}C_3H_5)(\mu\text{-}\eta^3\text{-}C_3H_5)]$ containing a square-based pyramidal geometry in which two adjacent apical-to-basal edges are cleaved and replaced by two symmetrically bridging Br atoms. One allyl ligand bridges a Ru–Ru edge of the square base in a $\mu\text{-}\eta^3$ fashion, while the other allyl group co-ordinates to the apical Ru atom as a simple η^3 ligand. The reaction of the octahedral cluster anion $[N(PPh_3)_2][Ru_6C(CO)_{16}(Me)]$ with methyl iodide in CH_2Cl_2 at 150 °C gave the cluster $[N(PPh_3)_2][Ru_5C(CO)_{13}I(\mu\text{-}I)(\mu\text{-}\eta^2\text{-}COMe)]$ displaying a square-based pyramidal geometry in which two opposite apical-to-basal edges are cleaved and bridged by a $\mu\text{-}\eta^2$ acetyl group and an I atom. The complex $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$ reacted with benzyl bromide at 60 °C to give the novel octahedral cluster $[N(PPh_3)_2][Ru_6C(CO)_{16}(\mu\text{-}Br)]$ in which one edge of the metal framework is cleaved and symmetrically bridged by a Br atom. Further reaction with benzyl bromide at 130 °C led to $[Ru_5C(CO)_{14}(\mu\text{-}Br)_2]$, which exhibits the same metal geometry as the iodide with two Br atoms symmetrically bridging two opposite apical-to-basal edges of the square-based pyramidal geometry.

Not only mononuclear alkyl transition-metal species but also surface metal alkyl species are important intermediates in various catalytic processes. However, the number of high-nuclearity cluster complexes containing alkyl or allyl groups is still rather limited.[1] We have reported on the syntheses of alkyl $\{[N(PPh_3)_2][Ru_6C(CO)_{16}Me]$ **1**$\}$, allyl $\{[N(PPh_3)_2][Ru_6C(CO)_{15}(\mu\text{-}\eta^3\text{-}C_3H_5)]$ **2**[2]$\}$ and hydride derivatives $\{[N(PPh_3)_2][Ru_6C(CO)_{15}H]\}$ of hexaruthenium carbidocarbonyl clusters and their catalytic use for hydrogenation of olefins.[3] The clusters **1** and **2** are accessible by treatment of the dianionic cluster $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$ **3**[4] with methyl iodide and allyl bromide, respectively. In these reactions **3** was formally attacked by CH_3^+ and $C_3H_5^+$. As an extension of this work the reactions of **1** and **2** with allyl bromide and methyl iodide have been carried out. In this paper we report on the synthesis and characterization of a new diallyl cluster and a series of clusters displaying novel metal frameworks. The reactions described are summarized in Scheme 1.

Results and Discussion

A CH_2Cl_2 solution of $[N(PPh_3)_2][Ru_6C(CO)_{15}(\mu\text{-}\eta^3\text{-}C_3H_5)]$ **2** and allyl bromide was heated at 115 °C for 1 h in a stainless-steel pressure bottle. Work-up of the resulting solution by silica gel column chromatography (benzene–CH_2Cl_2) afforded air-stable deep red crystals. The ^1H and H–H correlation (COSY) NMR spectra of the product exhibited a complex set of resonances indicating the presence of two different kinds of allyl ligands. The IR spectrum showed only the presence of terminal carbonyl ligands. Hence, the molecular structure was determined by single-crystal X-ray diffraction. The cluster formulated as $[Ru_5C(CO)_{11}(\mu\text{-}Br)_2(\eta^3\text{-}C_3H_5)(\mu\text{-}\eta^3\text{-}C_3H_5)]$ **4** is shown in Fig. 1, and selected interatomic distances and bond angles are listed in Table 1.

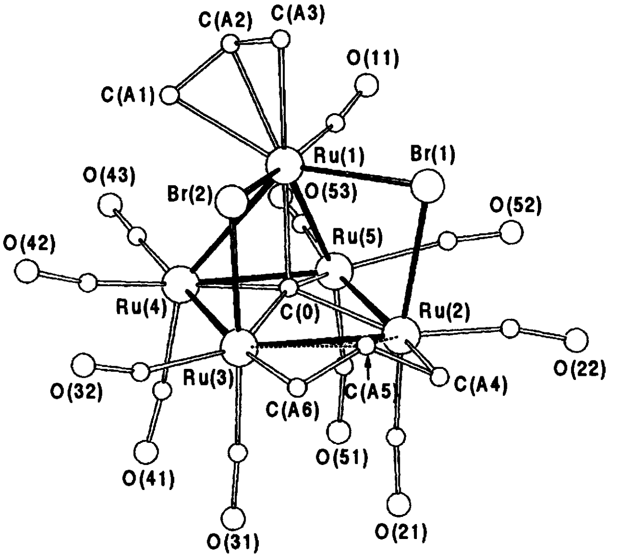

Fig. 1 Molecular structure of $[Ru_5C(CO)_{11}Br_2(C_3H_5)_2]$ **4** with the numbering of the oxygen atoms corresponding to that of the relevant carbonyl carbon atoms. The first digit of each oxygen number is the number of the ruthenium atom to which the carbonyl is attached

From Fig. 1 it can be seen that the octahedral metal framework of the precursor complex **2** has not been retained in **4**. Complex **4** is a pentanuclear carbidocarbonyl cluster and the Ru atoms form an open envelope structure. The metal framework geometry might also be described as a square-based pyramid in which two adjacent apical-basal Ru–Ru bonds are broken [Ru(1) ⋯ Ru(2) 3.485(2) and Ru(1) ⋯ Ru(3) 3.487(2) Å] and replaced by symmetrically bridging Br ligands, corresponding to cleavage of the edges *a* depicted in Scheme 2. The bonding Ru–Ru distances range from 2.778(2) to 2.941(2) Å within the range described for the square-based pyramidal

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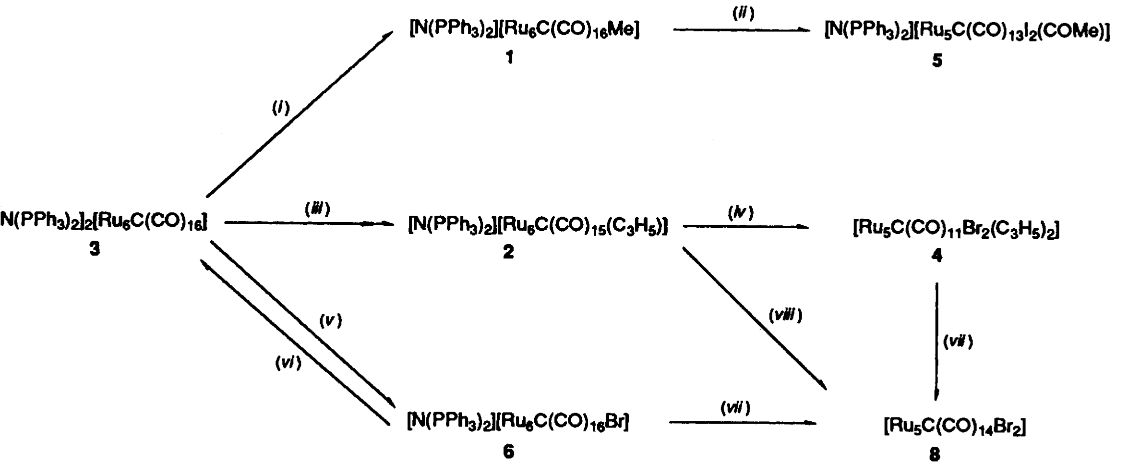
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

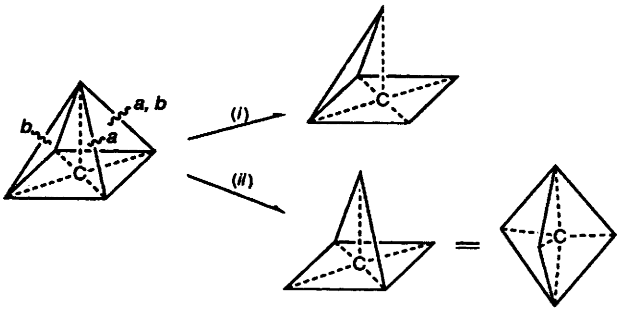


Scheme 1 (*i*) MeI, 130 °C; (*ii*) MeI in CH_2Cl_2, 150 °C; (*iii*) C_3H_5Br, 85 °C; (*iv*) C_3H_5Br, 115 °C; (*v*) Br_2, room temperature or $PhCH_2Br$, 60 °C; (*vi*) MeOH, reflux; (*vii*) $PhCH_2Br$, 130 °C; (*viii*) C_3H_5Br, 130 °C

Table 1 Selected bond lengths (Å) and angles (°) for complex **4**

Ru(1) ··· Ru(2)	3.485(2)	Ru(4)–C(0)	2.02(2)
Ru(1) ··· Ru(3)	3.487(2)	Ru(5)–C(0)	2.04(2)
Ru(1)–Ru(4)	2.856(2)	Ru(1)–C(11)	1.922(15)
Ru(1)–Ru(5)	2.837(2)	Ru(5)–C(11)	2.544(12)
Ru(2)–Ru(3)	2.941(2)	Ru(1)–C(A1)	2.282(19)
Ru(2)–Ru(5)	2.869(2)	Ru(1)–C(A2)	2.266(15)
Ru(3)–Ru(4)	2.891(2)	Ru(1)–C(A3)	2.344(14)
Ru(4)–Ru(5)	2.778(2)	Ru(2)–C(A4)	2.220(16)
Ru(1)–Br(1)	2.627(3)	Ru(2)–C(A5)	2.60(3)
Ru(1)–Br(2)	2.612(3)	Ru(3)–C(A5)	2.57(3)
Ru(2)–Br(1)	2.634(2)	Ru(3)–C(A6)	2.20(2)
Ru(3)–Br(2)	2.630(2)	C(A1)–C(A2)	1.35(2)
Ru(1)–C(0)	2.069(9)	C(A2)–C(A3)	2.36(3)
Ru(2)–C(0)	2.11(2)	C(A4)–C(A5)	1.42(5)
Ru(3)–C(0)	2.10(2)	C(A5)–C(A6)	1.43(5)
Br(1)–Ru(1)–Br(2)	86.16(7)	Ru(2)–C(A4)–C(A5)	88.0(9)
Ru(1)–Br(1)–Ru(2)	82.96(6)	Ru(2)–C(A5)–Ru(3)	69.4(3)
Ru(1)–Br(2)–Ru(3)	83.40(6)	Ru(3)–C(A6)–C(A5)	87.3(11)
C(A1)–Ru(1)–C(A2)	34.5(6)	C(A4)–C(A5)–C(A6)	128.7(12)
C(A1)–Ru(1)–C(A3)	62.4(8)	Ru(1)–C(0)–Ru(2)	122.8(10)
C(A2)–Ru(1)–C(A3)	34.2(7)	Ru(1)–C(0)–Ru(3)	113.7(10)
Ru(1)–C(A1)–C(A2)	72.1(11)	Ru(1)–C(0)–Ru(4)	88.7(7)
Ru(1)–C(A2)–C(A1)	73.4(10)	Ru(1)–C(0)–Ru(5)	87.3(7)
Ru(1)–C(A2)–C(A3)	76.1(9)	Ru(2)–C(0)–Ru(3)	88.6(4)
Ru(1)–C(A3)–C(A2)	69.8(8)	Ru(2)–C(0)–Ru(4)	157.3(5)
C(A1)–C(A2)–C(A3)	124.8(19)	Ru(2)–C(0)–Ru(5)	87.3(12)
Ru(3)–Ru(2)–C(A4)	84.5(4)	Ru(3)–C(0)–Ru(4)	89.3(13)
Ru(3)–Ru(2)–C(A5)	54.8(9)	Ru(3)–C(0)–Ru(5)	158.5(5)
Ru(2)–Ru(3)–C(A5)	55.7(9)	Ru(4)–C(0)–Ru(5)	86.4(4)
Ru(2)–Ru(3)–C(A6)	85.8(6)	Ru(1)–C(11)–Ru(5)	77.5(4)
C(A5)–Ru(3)–C(A6)	33.7(10)	Ru(1)–C(11)–O(11)	161.3(12)
C(A4)–Ru(2)–C(A5)	33.24(9)	Ru(5)–C(11)–O(11)	119.4(11)

cluster $[Ru_5C(CO)_{15}]$ and its derivatives (2.745–2.949 Å).[5] The angles in the square defined by Ru(2)–Ru(3)–Ru(4)–Ru(5) are close to 90° [Ru–Ru–Ru 87.95(5)–91.62(5)°]. The dihedral angle between the least-squares plane Ru(2)–Ru(3)–Ru(4)–Ru(5) and that defined by Ru(1)–Ru(4)–Ru(5) is 71.8(1)°. The carbide carbon atom C(0) displays interactions with all Ru atoms. The average Ru–C(0) distance of 2.07(2) Å is similar to that of $[Ru_5C(CO)_{15}]$ and its derivatives. The position of the carbide carbon in $[Ru_5C(CO)_{15}]$ is 0.11(2) Å below the square-base plane. In contrast, that of **4** is located 0.40(3) Å above; cleavage of the two adjacent apical-basal edges obviously caused the carbide carbon to rise. Several types of metal frameworks in carbide-containing pentanuclear cluster complexes have been described, such as the square-pyramidal and the bridged-butterfly structures.[1a,b] As far as we know, only the pentanuclear carbide cluster $[Os_3Pt_2(\mu-H)_2(\mu_5-C)(CO)_9(\mu-CO)\{P(cyclo-C_6H_{11})_3\}_2]$[6] exhibits an open envelope structure. In complex **4** one carbonyl ligand co-ordinated to the apical Ru(1) atom displays a slight interaction with Ru(5) [Ru(5) ··· C(11) 2.54(1) Å]. Two terminal carbonyl ligands each are bonded to the basal Ru atoms also bound to Br and three to each basal Ru atom without Br.



Scheme 2 Cleavage of metal–metal bonds

One of the two different allyl ligands in complex **4** adopts $\mu-\eta^3$-bonding mode. The peripheral carbon atoms C(A4) and C(A6) are co-ordinated to Ru(2) [2.22(2) Å] and Ru(3) [2.20(2) Å], respectively, and the central carbon atom C(A5) is bound to each ruthenium atom with significantly longer distances [2.60(3) and 2.57(3) Å]. Atom C(A5) is located 0.73(5) Å above the least-squares plane Ru(2)–Ru(3)–Ru(4)–Ru(5), and atoms C(A4) and C(A6) are also 0.14(1) and 0.16(2) Å above the plane, respectively. The dihedral angle between the least-squares plane and the allyl plane C(A4)–C(A5)–C(A6) is 110.5°. The second allyl ligand exhibits a simple η^3-bonding mode. The three Ru(1)–C (allyl) distances are almost equal [mean 2.30(2) Å] and longer than the Ru(2)–C(A4) and Ru(3)–C(A6) separations involving the $\mu-\eta^3$-allyl moiety. On the contrary, the C (allyl)–C (allyl) distances of the η^3-allyl group are shorter than the corresponding separations of the $\mu-\eta^3$-allyl ligand.

Several examples of allyl clusters of high nuclearity have so far been reported: $[N(PPh_3)_2][Ru_6C(CO)_{15}(\mu-\eta^3-C_3H_5)]$ **2**,[2] $[Os_3(CO)_{10}(\mu-\eta^3-C_3H_5)(AuPEt_3)]$,[7] $[Ru_6C(CO)_{14}(SePh)(\mu-\eta^3-C_3H_5)]$,[8] $[PPh_4][Rh_6(CO)_{14}(\mu-\eta^3-C_3H_5)]$,[9] $[NEt_4]_2[Re_7C(CO)_{21}\{Pd(\eta^3-PhC_3H_4\}]$[10] and $[AsPh_4]_2[Re_7C(CO)_{21}\{Pd(\eta^3-C_3H_5\}]$.[11] Compound **4** is the first example of a cluster containing two different types of allyl ligands. Assuming that the allyl groups and the Br ligands behave as three-electron donors complex **4** contains 78 cluster valence electrons, which is four more than in $[Ru_5C(CO)_{15}]$. This corresponds to the absence of two Ru–Ru bonds from the square-pyramidal framework.

When a solution of complex **1** in neat methyl iodide was heated at 180 °C no reaction was observed. Further treatment at 210 °C led to decomposition resulting in a metal mirror. However, heating of a CH_2Cl_2 solution of **1** with methyl iodide at 150 °C gave rise to a new product the ^1H NMR spectrum of which indicated the presence of a $[N(PPh_3)_2]^+$ cation and a methoxy group. In order to elucidate the molecular structure unequivocally a single-crystal X-ray analysis was undertaken. Thus, the product has been established to be $[N(PPh_3)_2][Ru_5C(CO)_{13}I(\mu\text{-}I)(\mu\text{-}\eta^2\text{-}COMe)]$ **5**. The structure of the anionic cluster is shown in Fig. 2, and selected interatomic distances and bond angles are presented in Table 2.

Cluster **5** is a pentanuclear carbide cluster displaying a bridged-butterfly metal framework without hinge bonding. The metal framework may also be viewed as a square-based pyramidal structure in which two opposite apical-to-basal Ru–Ru bonds are cleaved [Ru(1) ··· Ru(2) 3.558(1), Ru(1) ··· Ru(4) 3.425(1) Å] corresponding to the cleavage of the edges *b* in Scheme 2. Most pentanuclear clusters containing a carbide carbon atom adopt a square-based pyramidal or a bridged-butterfly geometry. Only two examples are known of the metal framework geometry of **5**, however: $[Os_5C(CO)_{14}(\mu\text{-}\eta^2\text{-}CO_2Me)(\mu\text{-}I)]$[12] and $[Ru_5C(CO)_{14}(\mu\text{-}Br)_2]$ **8** (see below). In **5** the dihedral angle between the planes defined by Ru(2)–Ru(3)–Ru(5) and Ru(3)–Ru(4)–Ru(5) is 43.27(4)°.

There are two I ligands in complex **5**; one is a spiking and the other one a bridging ligand. The Ru–I distance of the former [2.7359(13) Å] is shorter than those of the latter [2.8149(12) and 2.8869(11) Å]. Two terminal carbonyl groups each co-ordinate to the apical Ru atom and the Ru attached to the spiking I ligand, respectively, and three to each of the other Ru atoms.

Several examples of acyl-substituted metal clusters of high nuclearity have been reported: $[Ru_6C(CO)_{16}(COMe)]^-$,[2] $[Ir_6(CO)_{15}(COEt)]^-$,[13] $[Rh_6(CO)_{15}(COEt)]^-$[14] and $[Ru_5C(CO)_{14}(AuPPh_3)(\mu\text{-}\eta^2\text{-}COMe)]$.[15] The bonding parameters of the acyl group in **5** are closely related to those of the $\mu\text{-}\eta^2$-acetyl ligand in the latter cluster. Assuming that the spiking I ligand serves as a one-electron donor and the bridging I as well as the $\mu\text{-}\eta^2$-COMe group as a three-electron donor, complex **5** contains 78 cluster valence electrons. This is four more than in $[Ru_5C(CO)_{15}]$ corresponding to the absence of two Ru–Ru bonds from the square-pyramidal core.

The reaction of $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$ **3** with benzyl bromide at 60 °C afforded upon appropriate work-up dark brown crystals. The IR spectrum revealed a strong absorption band at 2024 cm^{-1} in the ν(C=O) region suggesting the formation of a monoanionic cluster. The product showed a positive Beilstein test and the FAB mass spectrum indicated the presence of a Br ligand. The ^1H NMR spectrum exhibited no peaks due to benzyl protons. Hence a single-crystal X-ray analysis has been undertaken. The molecular formula was determined as $[N(PPh_3)_2][Ru_6C(CO)_{16}(\mu\text{-}Br)]$ **6**, however due to disorder problems the refinement of the structure failed. In order to obtain suitable single crystals for X-ray analysis the $[N(PPh_3)_2]$ cation was replaced by $[N\{P(C_6H_4Me\text{-}p)_3\}_2]^+$. Starting from $[N\{P(C_6H_4Me\text{-}p)_3\}_2]_2[Ru_6C(CO)_{16}]$ the corresponding cluster $[N\{P(C_6H_4Me\text{-}p)_3\}_2][Ru_6C(CO)_{16}(\mu\text{-}Br)]$ **7** was prepared and successfully characterized by X-ray crystallography. The molecular structure of the cluster anion is shown in Fig. 3, and selected interatomic distances and bond angles are listed in Table 3.

The six ruthenium atoms of complex **7** form a distorted octahedron with one Ru–Ru bond cleaved [Ru(1) ··· Ru(2) 3.448(1) Å] and replaced by a symmetrically bridging Br ligand [Ru(1)–Br 2.729(2) and Ru(2)–Br 2.696(2) Å]. To our knowledge **7** is the first hexanuclear cluster displaying such a distorted structure. Most hexanuclear carbide clusters contain metal frameworks with trigonal-prismatic or regular octahedral geometries.[1a,b] The Ru–Ru bonding distances in **7** range from 2.807(1) to 2.952(1) Å, which is within the range (2.764–3.034 Å) reported[1c] for octahedral hexaruthenium carbide clusters. The two shortest Ru–Ru edges are bridged by carbonyl ligands. The

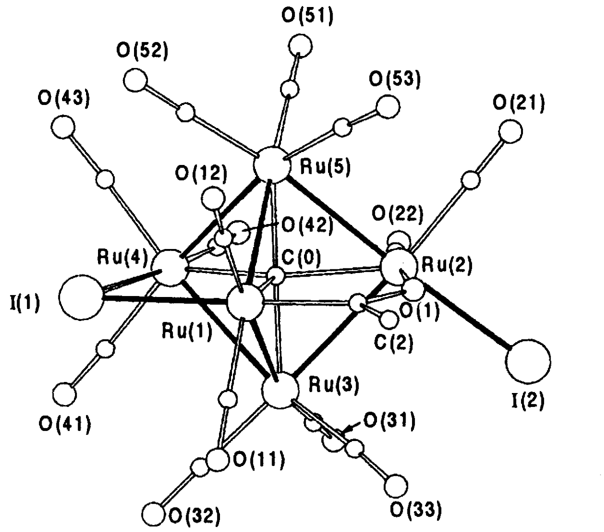


Fig. 2 Molecular structure of $[Ru_5C(CO)_{13}I_2(COMe)]^-$ (anion of **5**) showing the atom numbering scheme

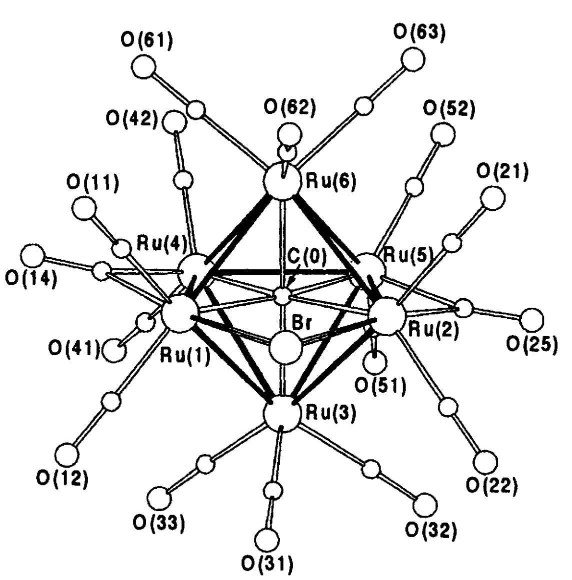


Fig. 3 Molecular structure of $[Ru_6C(CO)_{16}Br]^-$ (anion of **7**) showing the atom numbering scheme

Table 2 Selected bond lengths (Å) and angles (°) for complex **5**

Ru(1) ··· Ru(2)	3.5578(13)	Ru(4)–I(1)	2.8149(12)
Ru(1)–Ru(3)	2.8704(14)	Ru(1)–C(0)	2.146(9)
Ru(1) ··· Ru(4)	3.4248(13)	Ru(2)–C(0)	2.117(8)
Ru(1)–Ru(5)	2.8660(11)	Ru(3)–C(0)	1.981(8)
Ru(2)–Ru(3)	2.9028(11)	Ru(4)–C(0)	2.096(8)
Ru(2)–Ru(5)	2.8607(13)	Ru(5)–C(0)	1.930(8)
Ru(3)–Ru(4)	2.8978(11)	Ru(1)–C(1)	1.990(8)
Ru(4)–Ru(5)	2.8838(12)	Ru(2)–O(1)	2.152(6)
Ru(1)–I(1)	2.8869(11)	O(1)–C(1)	1.278(10)
Ru(2)–I(2)	2.7359(13)	C(1)–C(2)	1.488(12)
Ru(4)–Ru(1)–I(1)	52.13(3)	Ru(2)–C(0)–Ru(4)	139.2(4)
Ru(1)–Ru(4)–I(1)	54.05(3)	Ru(2)–C(0)–Ru(5)	89.9(3)
Ru(1)–I(1)–Ru(4)	73.82(3)	Ru(3)–C(0)–Ru(4)	90.6(3)
I(1)–Ru(1)–C(1)	178.4(3)	Ru(3)–C(0)–Ru(5)	177.0(5)
Ru(1)–C(0)–Ru(2)	113.2(4)	Ru(4)–C(0)–Ru(5)	91.4(3)
Ru(1)–C(0)–Ru(3)	88.0(3)	Ru(2)–O(1)–C(1)	126.0(5)
Ru(1)–C(0)–Ru(4)	107.7(4)	Ru(1)–C(1)–O(1)	120.9(6)
Ru(1)–C(0)–Ru(5)	89.2(4)	Ru(1)–C(1)–C(2)	127.6(6)
Ru(2)–C(0)–Ru(3)	90.2(3)	O(1)–C(1)–C(2)	111.7(7)

Table 3 Selected bond lengths (Å) and angles (°) for complex **7**

Ru(1) ··· Ru(2)	3.4475(12)	Ru(6)–C(0)	1.996(8)
Ru(1)–Ru(3)	2.9234(12)	Ru(1)–Br	2.7290(16)
Ru(1)–Ru(4)	2.8200(14)	Ru(2)–Br	2.6958(18)
Ru(1)–Ru(6)	2.8617(11)	Ru(1)–C(14)	2.121(11)
Ru(2)–Ru(3)	2.8694(12)	Ru(2)–C(25)	2.129(18)
Ru(2)–Ru(5)	2.8066(15)	Ru(4)–C(14)	1.971(12)
Ru(2)–Ru(6)	2.9042(11)	Ru(5)–C(25)	1.978(14)
Ru(3)–Ru(4)	2.9448(11)	O(14)–C(14)	1.177(13)
Ru(3)–Ru(5)	2.9275(12)	O(25)–C(25)	1.158(18)
Ru(4)–Ru(5)	2.8303(13)	P(1)–N	1.584(7)
Ru(4)–Ru(6)	2.9520(12)	P(2)–N	1.586(8)
Ru(5)–Ru(6)	2.9436(13)	C(A4)–C(A7)	1.505(16)
Ru(1)–C(0)	2.101(11)	C(B4)–C(B7)	1.515(19)
Ru(2)–C(0)	2.102(10)	C(C4)–C(C7)	1.524(18)
Ru(3)–C(0)	2.009(8)	C(D4)–C(D7)	1.488(11)
Ru(4)–C(0)	2.137(10)	C(E4)–C(E7)	1.526(20)
Ru(5)–C(0)	2.127(11)	C(F4)–C(F7)	1.518(16)
Ru(2)–Ru(1)–Br	50.12(4)	Ru(4)–C(14)–O(14)	140.5(10)
Ru(1)–Ru(2)–Br	50.97(3)	Ru(2)–C(25)–Ru(5)	86.1(6)
Ru(1)–Br–Ru(2)	78.91(5)	Ru(2)–C(25)–O(25)	133.8(14)
Ru(1)–C(14)–Ru(4)	87.0(4)	Ru(5)–C(25)–O(25)	140.0(15)
Ru(1)–C(14)–O(14)	132.5(10)	P(1)–N–P(2)	138.0(4)

four ruthenium–carbide bonds in the plane defined by Ru(1), Br, Ru(2), Ru(5) and Ru(4) are similar in length [mean 2.117(9) Å] and significantly longer than those perpendicular to the plane [mean 2.003(6) Å]. Hexaruthenium carbidocarbonyl clusters with an intact octahedral metal framework show on the average shorter ruthenium–carbide bond distances.

As is shown in Fig. 3, cluster **7** contains 16 carbonyl ligands. Two are asymmetrically bridging the two shortest Ru–Ru edges with longer separations to the Ru atoms bound to Br. The other 14 are terminal; two are bound to each bromide-bridged Ru atom and three to each of the other Ru atoms. The Ru–C distances and the C–O distances are unremarkable. Cluster **7** has an approximate C_2 axis through the Br and the carbide carbon atom. It is obvious that the carbide carbon plays an important role in keeping an approximate octahedral metal framework even after breaking one of the Ru–Ru bonds by lone-pair electrons of the Br ligand. The bonding parameters of the counter cation $[N\{P(C_6H_4Me\text{-}p)_3\}_2]^+$ are all within the expected range; the average Me–C (phenyl) distance is 1.513(6) Å and the other bonding parameters are essentially equal to the corresponding values in the $[N(PPh_3)_2]^+$ cation. On the premise that the Br ligand behaves as a three-electron donor, **6** and **7** contain 88 cluster valence electrons and thus two electrons more than expected for an intact octahedral metal framework.

Treatment of $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$ **3** with methyl bromoacetate at 85 °C or with Br_2 at room temperature also afforded $[N(PPh_3)_2][Ru_6C(CO)_{16}(\mu\text{-}Br)]$ **6**, and these reactions may be viewed as electrophilic addition of Br^+ to the dianionic cluster **3**. Similar electrophilic addition reactions of I^+ to anionic osmium clusters have been reported to give $[Os_4(CO)_{12}H_3(\mu\text{-}I)]^-$, $[Os_{10}C(CO)_{24}(\mu\text{-}I)]^-$ and $[Os_{10}C(CO)_{24}(\mu\text{-}I)_2]$.[16] When cluster **6** was heated under reflux in methanol for 10 min or chromatographed on alumina, Br^+ was removed and **3** partly reproduced.

A CH_2Cl_2 solution of complex **6** and benzyl bromide was heated at 130 °C for 1 h. Subsequent work-up of the reaction mixture afforded yellow crystals. The IR spectrum of the product revealed a strong absorption band at 2063 cm^{-1} suggesting the formation of a neutral cluster. In the ^1H NMR spectrum no resonances could be detected. In order to establish the molecular structure a single-crystal X-ray analysis has been carried out. The cluster formulated as $[Ru_5C(CO)_{14}(\mu\text{-}Br)_2]$ **8** is depicted in Fig. 4, and selected interatomic distances and bond angles are presented in Table 4.

Table 4 Selected bond lengths (Å) and angles (°) for complex **8**

Ru(1)–Ru(2)	2.8750(18)	Ru(3)–Br	2.5758(21)
Ru(1) ··· Ru(3)	3.4287(19)	Ru(1)–C(0)	2.07(2)
Ru(2)–Ru(3)	2.8941(16)	Ru(2)–C(0)	1.953(1)
Ru(2)–Ru(3′)	2.8730(16)	Ru(3)–C(0)	2.134(7)
Ru(1)–Br	2.5458(15)		
Ru(3)–Ru(1)–Br	48.35(5)	Ru(1)–C(0)–Ru(3)	109.2(6)
Ru(1)–Ru(3)–Br	47.60(4)	Ru(2)–C(0)–Ru(3)	90.0(2)
Ru(1)–Br–Ru(3)	84.05(6)	Ru(2)–C(0)–Ru(2′)	177.7(13)
Br–Ru(1)–Br′	168.63(9)	Ru(2)–C(0)–Ru(3′)	89.2(2)
Ru(1)–C(0)–Ru(2)	91.1(7)	Ru(3)–C(0)–Ru(3′)	141.5(11)

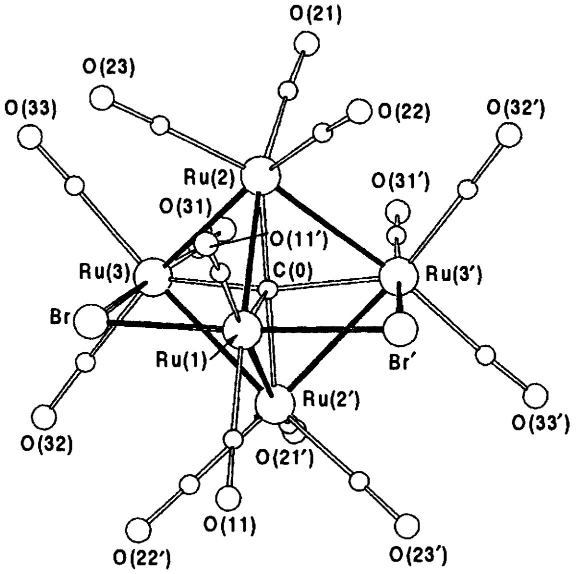


Fig. 4 Molecular structure of $[Ru_5C(CO)_{14}Br_2]$ **8** showing the atom numbering scheme

There is a crystallographic C_2 axis through Ru(1) and the carbide carbon atom C(0). The pentanuclear carbide cluster **8** displays a pseudo-square-pyramidal metal framework in which the two opposite apical-to-basal bonds are replaced with bridging Br ligands [Ru(1) ··· Ru(3) and Ru(1) ··· Ru(3′) 3.429(2) Å]. The dihedral angle between the planes defined by Ru(2)–Ru(2′)–Ru(3) and Ru(2)–Ru(2′)–Ru(3′) is 36.51(6)°. The pentanuclear osmium cluster $[Os_5C(CO)_{15}I_2]$ has a closely related structure, with a spiking and a μ-I ligand.[12] All fourteen carbonyl groups in complex **8** are terminal: two are bound to the apical Ru(1) atom and three to each basal Ru atom. The Ru–C distances and the C–O separations are unremarkable. Cluster **8** contains overall 78 valence electrons on the assumption that both Br ligands behave as three-electron donors.

The carbide cluster **8**, which is thermally stable at 180 °C in CH_2Cl_2, is also accessible by alternative routes: reactions of **1**–**4** with benzyl or allyl bromide under severe conditions (130 °C). However, treatment of **2** or **6** with Br_2 at room temperature affords not **8** but decomposition products. In conclusion, **8** is generally formed in thermal reactions of carbidocarbonyl ruthenium clusters with the less reactive allyl or benzyl bromides as an intermediate to complete decomposition. The carbide carbon atom, which occupies an interstitial site in the cluster, holds the metal atoms together thus preventing complete degradation of the cluster framwork.[17]

Experimental

The complexes $[N(PPh_3)_2][Ru_6C(CO)_{16}Me]$ **1**, $[N(PPh_3)_2][Ru_6C(CO)_{15}(C_3H_5)]$ **2**[2] and $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$ **3**[4] were prepared according to literature methods. Allyl bromide,

Table 5 Crystallographic data

Compound	**4**	**5**	**7**	**8**
Formula	$C_{18}H_{10}Br_2O_{11}Ru_5{\cdot}CH_2Cl_2$	$C_{52}H_{33}I_2NO_{14}P_2Ru_5$	$C_{59}H_{42}BrNO_{16}P_2Ru_6$	$C_{15}Br_2O_{14}Ru_5$
M	1152.36	1716.94	1769.25	1069.31
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group (no.)	$P2_1$(4)	$P\bar{1}$(2)	$P\bar{1}$(2)	*Aba*2(41)
a/Å	13.602(4)	14.224(2)	15.3207(17)	15.346(3)
b/Å	12.021(2)	17.375(3)	19.0025(18)	13.986(3)
c/Å	9.090(3)	12.678(3)	12.1630(15)	11.739(2)
α/°	90	107.42(1)	108.670(9)	90
β/°	102.54(3)	94.59(1)	95.293(9)	90
γ/°	90	74.24(1)	102.091(8)	90
U/Å^3	1451	2877	3231	2504
Z	2	2	2	4
D_c/g cm^{-3}	2.638	1.980	1.819	2.819
Crystal size/mm	0.41 × 0.28 × 0.06	0.35 × 0.30 × 0.16	0.85 × 0.13 × 0.12	0.22 × 0.21 × 0.19
T/°C	−20	21	21	21
F(000)	1932	1640	1720	1968
μ/cm^{-1}	54.65	24.37	20.65	60.82
$2\theta_{max}$/°	55	50	55	60
No. of data measured	3700	11 325	15 402	2050
No. of unique data used	2798 ($F \geqslant 3\sigma$)	6995 ($F \geqslant 3\sigma$)	7911 ($F \geqslant 5\sigma$)	1777 ($F \geqslant 3\sigma$)
No. of parameters	353	686	911	165
Correction made	ψ Scan	No	No	No
Transmission coefficients	0.4786–0.9992			
Final R	0.041	0.044	0.047	0.048
Final R'	0.032 [$w = 1/\sigma(F_o)$]	0.033 [$w = 1/\sigma^2(F_o)$]	0.049 ($w = 1$)	0.043 [$w = 1/\sigma^2(F_o)$]
Goodness of fit	2.46	2.27	3.37	3.98
Maximum Δ/σ	0.635	0.257	0.474	0.512
Δρ/e Å^{-3}	0.91	0.99	1.00	1.96

methyl iodide, benzyl bromide, bromine, and solvents were commercially available and used as received. All the reactions were carried out under argon. The IR and ^{1}H NMR spectra were recorded on JASCO A-202 and JEOL FX-100 and GSX-500 spectrometers.

Preparations.—$[Ru_5C(CO)_{11}(\mu\text{-}Br)_2(\eta^3\text{-}C_3H_5)(\mu\text{-}\eta^3\text{-}C_3H_5)]$ **4**. A CH_2Cl_2 solution (5 cm^3) of complex **2** (500 mg, 0.31 mmol) and allyl bromide (0.5 cm^3, 5.8 mmol) was placed in a stainless-steel pressure vessel equipped with an inner glass tube and heated at 115 °C for 1 h. The solvent was removed from the resulting solution under reduced pressure, and the residue taken up in CH_2Cl_2 and chromatographed on silica gel (3% water, 1.8 cm internal diameter × 50 cm). Elution with hexane–benzene (4 : 1–2 : 1 v/v) separated a reddish brown band. Evaporation of the eluate to dryness afforded **4** as a brown solid (122 mg, 37%). IR(CH_2Cl_2): ν(C=O) 2086s, 2055vs, 2042w, 2011m, 1991w (sh) and 1911m cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 4.97 (1 H, d, J = 7.5, *syn*-H), 4.43 (1 H, d, J = 7.5, *syn*-H), 4.37 (1 H, d, J = 7.5, *syn*-H), 4.09 (1 H, tt, J = 7.5 and 13.7, central H), 3.87 (1 H, d, J = 7.5, *syn*-H), 3.29 (1 H, tt, J = 7.5 and 14.4, central H), 3.03 (1 H, d, J = 13.7, *anti*-H), 2.64 (1 H, d, J = 14.4, *anti*-H), 2.59 (1 H, d, J = 14.4, *anti*-H) and 2.08 (1 H, d, J = 13.7 Hz, *anti*-H) (Found: C, 20.15; H, 0.95. $C_{18}H_{10}Br_2O_{11}Ru_5$ requires C, 20.25; H, 0.95%).

In an analogous manner, reaction of complex **3** (100 mg, 0.047 mmol) with allyl bromide (0.2 cm^3, 2.3 mmol) in CH_2Cl_2 (2 cm^3) at 120 °C for 1 h yielded **4** (10 mg, 20%).

$[N(PPh_3)_2][Ru_5C(CO)_{13}I(\mu\text{-}I)(\mu\text{-}\eta^2\text{-}COMe)]$ **5**. Compound **3** (100 mg, 0.047 mmol) and methyl iodide (0.20 cm^3, 3.2 mmol) were dissolved in CH_2Cl_2 (2 cm^3) and placed in a stainless-steel pressure vessel equipped with an inner glass tube. The solution was heated at 150 °C for 1 h, and subsequently the volatiles were removed under reduced pressure. The residue was worked up by alumina column chromatography (5% water, 1.8 cm internal diameter × 20 cm). A yellow band was eluted with benzene–CH_2Cl_2 (2 : 1–0 : 1 v/v). The eluate was evaporated to dryness, and the residue recrystallized from CH_2Cl_2–methanol (1 : 1) to give yellow crystals of **5** (16 mg, 32%). IR(CH_2Cl_2): ν(C=O) 2082m, 2044s, 2018m, 1998w, 1989w (sh) and 1954w cm^{-1}. ^{1}H NMR [$(CD_3)_2CO$]: δ 7.5–7.9 (30 H, m, Ph) and 1.96 (3 H, s, CH_3) (Found: C, 36.15; H, 1.95; N, 0.75. $C_{52}H_{33}I_2NO_{14}P_2Ru_5$ requires C, 36.40; H, 1.95; N, 0.80%).

Similarly, reaction of complex **1** (200 mg, 0.12 mmol) with methyl iodide (0.2 cm^3, 0.32 mmol) in CH_2Cl_2 (2 cm^3) solution at 150 °C for 1 h gave **5** (83 mg, 64%).

$[N(PPh_3)_2][Ru_6C(CO)_{16}(\mu\text{-}Br)]$ **6**. Compound **3** (200 mg, 0.093 mmol) and neat benzyl bromide (1 cm^3, 8.4 mmol) were placed in a stainless-steel pressure bottle equipped with an inner glass tube, and the mixture was heated at 60 °C for 1 h with magnetic stirring. The resulting solution was worked up by silica gel column chromatography (3% water, 1.5 cm internal diameter × 50 cm). First a red band was eluted with benzene–CH_2Cl_2 (1 : 1 v/v) and then a reddish brown band with benzene–CH_2Cl_2 (1 : 1 to 1 : 2 v/v). The second band was collected and the solvent evaporated to dryness. Recrystallization of the residue from dry CH_2Cl_2–hexane yielded dark brown crystals of **6** (70 mg, 45%). IR(CH_2Cl_2): ν(C=O) 2046m, 2024s, 2014w (sh), 1976w (sh), 1943w (sh) and 1773w cm^{-1}. ^{1}H NMR [$(CD_3)_2CO$]: δ 7.9–7.4 (m, Ph) (Found: C, 37.85; H, 1.80; N, 0.85. $C_{53}H_{30}BrNO_{16}P_2Ru_6$ requires C, 37.80; H, 1.80; N, 0.85%). FAB mass spectrum: *m/z* 1147 ($[Ru_6C(CO)_{16}Br]^-$, 100) and 1067 ($[Ru_6C(CO)_{16}]^-$, 37%).

*Bis(tri-*p*-tolylphosphoranylidene)ammonium chloride* $[N\{P(C_6H_4Me\text{-}p)_3\}_2]Cl$. **CAUTION**: this procedure involves evaporation of liquid chlorine without using a pressure vessel. The reaction should be carried out in a well ventilated fume chamber.

A similar procedure to that described for $[N(PPh_3)_2]Cl$ was employed.[18] Tri-*p*-tolylphosphine (44.7 g, 0.147 mol) and 1,1,2,2-tetrachloroethane (75 cm^3) were placed in a flask (300 cm^3) equipped with a gas-inlet tube and a reflux condenser fitted with a drying tube. After all the tri-*p*-tolylphosphine was dissolved the flask was cooled to −30 °C. Liquid chlorine (4.55 cm^3, 0.1 mol) was collected in a glass trap at −78 °C. To the solution of tri-*p*-tolylphosphine, gaseous chlorine was slowly added by continuous shaking of the glass trap which had been taken out of the cooling bath. Hydroxylamine hydochloride (3.48 g, 0.05 mol) was added, and the mixture refluxed for 20 h. After removal of the solvent the remaining solid was

Table 6 Atomic coordinates (× 10^4) for complex **4**

Atom	*x*	*y*	*z*
Ru(1)	1202.1(7)	938.6(35)	1260.3(10)
Ru(2)	3580.9(8)	−284.4(10)	2115.5(12)
Ru(3)	3582.9(8)	2162.2(10)	2086.2(13)
Ru(4)	2115.1(9)	2094.1(10)	3956.4(13)
Ru(5)	2102.9(8)	−216.8(10)	3935.7(13)
Br(1)	2028.1(12)	−589.8(13)	−147.3(17)
Br(2)	2047.3(13)	2386.0(14)	−216.3(18)
O(11)	−60(8)	−883(11)	1969(14)
O(21)	5390(7)	−327(10)	4607(12)
O(22)	3897(9)	−2772(10)	1943(14)
O(31)	5391(8)	2153(11)	4663(13)
O(32)	3778(9)	4679(9)	1623(14)
O(41)	3781(8)	2413(10)	6765(12)
O(42)	1946(9)	4550(9)	3170(12)
O(43)	415(11)	2158(13)	5724(17)
O(51)	3732(9)	−482(12)	6674(13)
O(52)	1923(11)	−2746(11)	3220(16)
O(53)	478(8)	−394(10)	5757(13)
C(0)	2620(8)	957(28)	2666(11)
C(11)	461(9)	−238(13)	1959(15)
C(21)	4640(11)	−285(13)	3698(20)
C(22)	3661(11)	−1839(14)	1905(20)
C(31)	4702(10)	2129(13)	3648(15)
C(32)	3857(10)	3776(12)	1939(16)
C(41)	3169(9)	2246(12)	5732(12)
C(42)	2096(11)	3592(13)	3520(17)
C(43)	1056(11)	2113(13)	5129(16)
C(51)	3072(13)	−469(15)	5543(20)
C(52)	1938(11)	−1824(13)	3352(19)
C(53)	1078(13)	−340(15)	5071(19)
C(A1)	31(13)	2291(16)	1302(20)
C(A2)	−411(11)	1483(14)	353(20)
C(A3)	−94(10)	1145(29)	−890(17)
C(A4)	4625(11)	−123(12)	559(15)
C(A5)	4197(9)	944(41)	146(13)
C(A6)	4623(13)	2015(18)	545(21)
C(Cl)*	7661(12)	896(49)	3716(17)
Cl(1)*	7611(4)	−254(5)	2592(7)
Cl(2)*	7612(5)	2146(5)	2604(7)

* Solvent molecule.

Table 7 Atomic coordinates (× 10^4) for complex **5**

Atom	*x*	*y*	*z*
Ru(1)	1 299.9(5)	3 337.2(4)	5 277.8(6)
Ru(2)	2 654.1(5)	1 657.9(5)	6 289.3(6)
Ru(3)	574.9(5)	2 462.8(5)	6 490.5(6)
Ru(4)	470.9(5)	1 588.3(5)	4 164.2(6)
Ru(5)	2 434.6(5)	1 723.4(5)	4 052.5(6)
I(1)	−252.4(5)	3 126.7(4)	3 693.0(6)
I(2)	3 005.7(6)	1 762.8(5)	8 474.7(6)
P(1)	5 581.6(17)	3 219.7(14)	11 947.6(19)
P(2)	7 205.3(16)	2 529.6(14)	10 317.2(18)
O(1)	2 889(4)	2 886(3)	6 696(4)
O(11)	−55(5)	4 918(4)	6 712(6)
O(12)	2 176(5)	4 143(4)	3 924(6)
O(21)	4 779(5)	865(4)	5 894(7)
O(22)	2 453(6)	−53(4)	5 982(7)
O(31)	269(5)	1 142(4)	7 471(5)
O(32)	−1 530(5)	3 507(5)	6 632(6)
O(33)	1 065(5)	3 692(4)	8 611(5)
O(41)	−1 680(4)	1 747(4)	4 494(5)
O(42)	1 009(5)	−146(4)	4 377(6)
O(43)	597(5)	814(5)	1 678(5)
O(51)	3 355(5)	−135(4)	3 017(6)
O(52)	2 064(5)	2 189(4)	1 907(5)
O(53)	4 240(5)	2 355(4)	4 543(6)
N	6 446(5)	3 185(4)	11 198(5)
C(0)	1 510(6)	2 059(5)	5 244(7)
C(1)	2 390(6)	3 489(5)	6 339(7)
C(2)	2 726(7)	4 260(5)	6 825(8)
C(11)	470(7)	4 325(5)	6 155(7)
C(12)	1 827(6)	3 839(5)	4 422(7)
C(21)	4 022(7)	1 164(6)	6 043(9)
C(22)	2 503(7)	615(6)	6 070(8)
C(31)	373(6)	1 622(6)	7 105(7)
C(32)	−748(6)	3 110(6)	6 572(7)
C(33)	905(7)	3 197(6)	7 817(8)
C(41)	−875(6)	1 689(5)	4 400(7)
C(42)	847(7)	521(6)	4 348(8)
C(43)	568(7)	1 111(6)	2 619(7)
C(51)	3 022(6)	554(6)	3 385(7)
C(52)	2 187(6)	1 994(6)	2 704(7)
C(53)	3 546(7)	2 092(6)	4 324(7)
C(A1)	4 471(6)	3 922(5)	11 629(6)
C(A2)	3 553(6)	3 871(6)	11 791(8)
C(A3)	2 719(7)	4 434(6)	11 593(8)
C(A4)	2 832(7)	5 051(7)	11 194(8)
C(A5)	3 720(8)	5 130(6)	11 051(9)
C(A6)	4 572(7)	4 563(6)	11 236(8)
C(B1)	5 864(6)	3 639(5)	13 370(6)
C(B2)	5 188(6)	3 779(5)	14 183(7)
C(B3)	5 430(7)	4 058(6)	15 276(7)
C(B4)	6 324(7)	4 203(6)	15 578(7)
C(B5)	6 986(7)	4 082(6)	14 788(7)
C(B6)	6 762(6)	3 802(5)	13 680(7)
C(C1)	5 323(6)	2 229(5)	11 818(6)
C(C2)	5 784(6)	1 771(5)	12 545(7)
C(C3)	5 635(7)	995(5)	12 420(8)
C(C4)	5 021(7)	699(5)	11 606(8)
C(C5)	4 579(7)	1 130(5)	10 875(8)
C(C6)	4 741(6)	1 901(5)	10 986(7)
C(D1)	8 300(6)	2 868(5)	10 456(6)
C(D2)	9 212(6)	2 304(6)	10 127(7)
C(D3)	10 033(6)	2 599(6)	10 213(8)
C(D4)	9 973(7)	3 429(6)	10 600(8)
C(D5)	9 097(7)	3 988(6)	10 907(7)
C(D6)	8 253(6)	3 706(5)	10 836(7)
C(E1)	7 535(6)	1 486(5)	10 462(6)
C(E2)	7 220(6)	844(5)	9 719(7)
C(E3)	7 450(7)	66(5)	9 897(8)
C(E4)	7 977(7)	−57(5)	10 798(9)
C(E5)	8 292(7)	569(6)	11 555(8)
C(E6)	8 073(6)	1 356(5)	11 404(7)
C(F1)	6 768(6)	2 463(5)	8 944(6)
C(F2)	5 788(7)	2 653(6)	8 735(7)
C(F3)	5 426(7)	2 585(6)	7 671(8)
C(F4)	6 063(8)	2 364(7)	6 823(8)
C(F5)	7 032(8)	2 165(7)	7 006(8)
C(F6)	7 390(7)	2 221(7)	8 065(7)

successively washed with hexane and diethyl ether until all tri-*p*-tolylphosphine oxide was removed (monitored by TLC on SiO_2). The resulting solid was recrystallized from boiling water yielding colourless crystals (21.3 g, 66% yield) (Found: C, 72.50; H, 6.45; N, 2.10. $C_{42}H_{42}ClNP_2 \cdot 2H_2O$ requires C, 72.65; H, 6.70; N, 2.00%). M.p. (crystals obtained from tetrahydrofuran–ethyl acetate) 104–105 (glass transition), 234–235 °C (melting). ^1H NMR $[(CD_3)_2CO]$: 7.65–7.31 (24 H, m, C_6H_4) and 2.43 (18 H, s, CH_3).

$[N\{P(C_6H_4Me\text{-}p)_3\}_2][Ru_6C(CO)_{16}(\mu\text{-}Br)]$ **7**. To a CH_2Cl_2 (5 cm^3) solution of $[N\{P(C_6H_4Me\text{-}p)_3\}_2]_2[Ru_6C(CO)_{16}]$ (270 cm^3, 0.117 mmol) a CH_2Cl_2 (5 cm^3) solution of Br_2 (*ca.* 19 mg,

Table 8 Atomic coordinates* for complex 7

Atom	*x*	*y*	*z*
Ru(1)	1 432.4(5)	8 005.3(4)	1 929.9(7)
Ru(2)	3 431.9(5)	7 523.6(5)	1 346.5(7)
Ru(3)	2 962.6(5)	8 097.0(5)	3 639.2(7)
Ru(4)	1 263.4(5)	6 882.4(4)	3 006.2(7)
Ru(5)	2 889.9(6)	6 472.2(5)	2 483.0(8)
Ru(6)	1 611.4(5)	6 521.9(4)	564.8(7)
Br	2 716.4(7)	8 578.9(7)	812.7(11)
P(1)	3 348.3(14)	12 401.3(13)	2 499.5(19)
P(2)	1 561.5(14)	11 963.1(13)	3 394.7(19)
O(11)	−49(5)	7 899(6)	23(8)
O(12)	1 214(7)	9 512(5)	3 559(10)
O(14)	−362(5)	7 462(5)	2 658(7)
O(21)	3 779(6)	6 725(6)	−1 086(8)
O(22)	5 260(6)	8 675(7)	2 143(11)
O(25)	4 772(7)	6 688(8)	2 016(10)
O(31)	3 640(7)	9 750(5)	3 815(9)
O(32)	4 835(6)	8 182(6)	4 840(9)
O(33)	2 235(8)	8 596(7)	5 928(9)
O(41)	869(7)	7 050(5)	5 445(7)
O(42)	105(6)	5 295(5)	2 377(8)
O(51)	3 426(6)	6 461(5)	4 908(7)
O(52)	2 759(12)	4 783(6)	1 622(11)
O(61)	−423(5)	5 821(5)	−14(8)
O(62)	1 493(7)	6 946(5)	−1 642(7)
O(63)	2 109(7)	5 051(5)	−768(8)
N	2 312(4)	11 892(4)	2 578(6)
C(0)	2 278(6)	7 295(5)	2 110(8)
C(11)	526(7)	7 942(7)	750(10)
C(12)	1 313(7)	8 944(6)	2 920(10)
C(14)	390(7)	7 426(6)	2 600(8)
C(21)	3 647(7)	7 040(7)	−183(10)
C(22)	4 570(8)	8 238(8)	1 829(12)
C(25)	4 061(8)	6 807(9)	2 005(12)
C(31)	3 375(8)	9 115(6)	3 723(11)
C(32)	4 114(8)	8 124(7)	4 399(10)
C(33)	2 488(9)	8 371(8)	5 074(11)
C(41)	1 026(8)	7 000(6)	4 536(9)
C(42)	553(8)	5 909(6)	2 611(9)
C(51)	3 233(7)	6 466(6)	3 961(9)
C(52)	2 812(12)	5 437(8)	1 919(11)
C(61)	340(7)	6 080(6)	230(10)
C(62)	1 542(8)	6 787(6)	−813(10)
C(63)	1 921(8)	5 595(6)	−216(10)
C(A1)	3 683(5)	13 272(5)	3 741(7)
C(A2)	4 127(6)	13 252(5)	4 776(8)
C(A3)	4 326(7)	13 891(6)	5 791(9)
C(A4)	4 094(7)	14 555(6)	5 781(10)
C(A5)	3 704(7)	14 588(5)	4 759(10)
C(A6)	3 485(6)	13 947(5)	3 731(8)
C(A7)	4 282(10)	15 234(8)	6 908(13)
C(B1)	3 125(5)	12 650(5)	1 194(7)
C(B2)	2 294(6)	12 448(6)	498(9)
C(B3)	2 200(7)	12 650(7)	−505(9)
C(B4)	2 931(7)	13 049(6)	−825(8)
C(B5)	3 764(7)	13 241(7)	−117(10)
C(B6)	3 864(7)	13 052(7)	877(9)
C(B7)	2 821(10)	13 277(8)	−1 904(10)
C(C1)	4 094(5)	11 848(5)	2 373(7)
C(C2)	3 826(5)	11 073(5)	2 080(8)
C(C3)	4 458(7)	10 641(5)	1 853(9)
C(C4)	5 360(6)	10 984(6)	1 909(9)
C(C5)	5 623(6)	11 761(6)	2 248(10)
C(C6)	4 998(6)	12 211(5)	2 478(9)
C(C7)	6 052(9)	10 514(8)	1 594(11)
C(D1)	493(5)	11 362(5)	2 523(7)
C(D2)	424(6)	10 589(6)	1 968(9)
C(D3)	−352(6)	10 099(5)	1 262(9)
C(D4)	−1 123(6)	10 373(5)	1 050(8)
C(D5)	−1 051(6)	11 139(5)	1 629(8)
C(D6)	−273(6)	11 636(5)	2 343(8)
C(D7)	−1 956(7)	9 848(6)	227(9)
C(E1)	1 777(5)	11 588(5)	4 537(7)
C(E2)	1 109(6)	11 391(6)	5 159(9)
C(E3)	1 265(7)	11 089(7)	6 011(9)
C(E4)	2 125(7)	11 002(6)	6 327(9)
C(E5)	2 789(8)	11 193(6)	5 711(9)
C(E6)	2 622(6)	11 477(6)	4 825(8)
C(E7)	2 292(10)	10 685(8)	7 310(11)
C(F1)	1 435(5)	12 924(5)	4 041(7)
C(F2)	1 229(6)	13 319(5)	3 309(8)
C(F3)	1 182(7)	14 073(6)	3 821(10)
C(F4)	1 336(7)	14 450(6)	5 021(10)
C(F5)	1 538(7)	14 044(6)	5 739(9)
C(F6)	1 587(6)	13 279(5)	5 254(8)
C(F7)	1 301(9)	15 282(7)	5 550(13)
H(A2)	433(5)	1 279(4)	474(7)
H(A3)	459(8)	1 386(7)	638(11)
H(A5)	343(5)	1 496(4)	468(6)
H(A6)	322(5)	1 397(4)	299(6)
H(A71)	382(6)	1 535(5)	717(8)
H(A72)	430(5)	1 562(4)	656(7)
H(A73)	467(5)	1 520(5)	731(7)
H(B2)	184(5)	1 206(5)	56(7)
H(B3)	155(8)	1 245(7)	−120(10)
H(B5)	421(7)	1 371(6)	−25(9)
H(B6)	433(7)	1 330(6)	148(9)
H(B71)	296(5)	1 298(4)	−233(6)
H(B72)	281(5)	1 374(4)	−163(7)
H(C2)	323(5)	1 082(4)	201(7)
H(C3)	428(5)	1 012(4)	168(7)
H(C5)	620(6)	1 208(5)	244(8)
H(C6)	515(6)	1 280(5)	279(8)
H(C71)	620(5)	1 052(4)	233(6)
H(C72)	579(8)	1 006(7)	106(11)
H(D2)	91(6)	1 041(5)	241(9)
H(D3)	−41(5)	946(4)	75(7)
H(D5)	−166(5)	1 139(4)	140(7)
H(D6)	−17(6)	1 217(5)	273(8)
H(D71)	−196(6)	997(5)	−29(8)
H(D72)	−233(8)	966(6)	50(10)
H(E2)	54(6)	1 138(5)	490(8)
H(E3)	82(7)	1 112(6)	655(10)
H(E5)	342(5)	1 109(4)	588(6)
H(E6)	308(8)	1 181(6)	465(10)
H(E71)	269(6)	1 107(5)	800(8)
H(E72)	218(6)	1 025(5)	686(8)
H(F2)	118(6)	1 313(5)	240(8)
H(F3)	114(7)	1 438(6)	343(9)
H(F6)	181(6)	1 302(5)	592(8)
H(F71)	172(8)	1 554(7)	539(10)
H(F72)	129(6)	1 535(5)	630(8)

* Fractional × 10^4 for non-hydrogen atoms and × 10^3 for hydrogen atoms.

0.118 mmol) was slowly added under vigorous stirring until no starting material could be detected by TLC on SiO_2. The solvent was removed under reduced pressure, and the residue worked up by silica gel column chromatography (3% water, 1.5 cm internal diameter × 20 cm). The first, red band eluted with hexane gave a red solid $[Ru_5C(CO)_{15}]$ (12 mg, 11% yield). Elution with benzene–CH_2Cl_2 (1 : 1 v/v) separated a reddish brown band. Evaporation of the solvent followed by recrystallization from CH_2Cl_2–hexane (1 : 1 v/v) afforded dark brown crystals of complex **7** (66.0 mg, 32% yield). IR(CH_2Cl_2): ν(C=O) 2045m, 2020s, 2010w (sh), 1980w (sh), 1950w (sh) and 1777w cm^{-1} (Found: C, 39.75; H, 2.45; N, 0.80. $C_{59}H_{42}BrNO_{16}P_2Ru_6$ requires C, 40.05; H, 2.40; N, 0.80%).

$[Ru_5C(CO)_{14}(\mu\text{-}Br)_2]$ **8**. Compound **6** (111 mg, 0.066 mmol) and benzyl bromide (0.2 cm^3, 1.7 mmol) were dissolved in CH_2Cl_2 (2 cm^3) and placed in a stainless-steel pressure bottle equipped with an inner glass tube and heated at 130 °C for 1 h. Cooling to room temperature afforded orange-yellow crystals of

Table 9 Atomic coordinates (× 10^4) for complex **8**

Atom	*x*	*y*	*z*
Ru(1)*	0(0)	0(0)	3749.0(14)
Ru(2)	1167.0(6)	557.1(7)	5546.2(12)
Ru(3)	514.5(7)	−1325.3(7)	6112.3(12)
Br	694.5(9)	−1643.1(10)	3963.8(14)
O(11)	−1302(7)	−565(8)	1939(10)
O(21)	1895(7)	1126(9)	7873(9)
O(22)	1622(7)	2357(7)	4178(10)
O(23)	2796(7)	−443(8)	4597(13)
O(31)	285(7)	−985(7)	8604(9)
O(32)	−391(7)	−3302(6)	6169(10)
O(33)	2372(7)	−2002(8)	6589(11)
C(0)*	0(0)	0(0)	5513(19)
C(11)	−862(9)	−388(11)	2609(15)
C(21)	1662(10)	889(10)	7012(13)
C(22)	1471(9)	1690(9)	4745(12)
C(23)	2184(10)	−81(15)	4932(16)
C(31)	372(9)	−1122(8)	7645(13)
C(32)	−40(11)	−2546(11)	6159(12)
C(33)	1680(10)	−1740(11)	6394(14)

* Refined with site occupancy factor = 0.5.

8, which were separated, washed with hexane and dried. The reaction mixture was worked up by silica gel column chromatography (1.5 cm internal diameter x 25 cm). A yellow band was eluted with hexane–benzene (1 : 1 v/v), and the elutate was evaporated to dryness. Recrystallization of the residue from benzene–hexane (1 : 1 v/v) yielded yellow crystals of **8** (combined amount 12.0 mg, 17%). IR(CH_2Cl_2): ν(C=O) 2104m, 2081s, 2063vs, 2028s, 2002w, 1995w (sh) and 1978w cm^{-1} (Found: C, 17.20. $C_{15}Br_2O_{14}Ru_5$ requires C, 16.85%).

Reaction of complex **2** with benzyl bromide in CH_2Cl_2 at 130 °C for 1 h afforded **8** in 24% yield. In the same manner **8** was obtained in 9% yield from the reaction of **2** with allyl bromide.

Structure Determinations.—Crystal and data collection. Brown single crystals of complex **4** were obtained by addition of methanol to a CH_2Cl_2 solution of it at −20 °C. A suitable single crystal was fixed with the mother-liquor in a glass capillary under argon. Measurements were carried out at −20 °C because the crystal showed a solid–solid transformation at room temperature. Yellow crystals of **5** were obtained by slow cooling of a CH_2Cl_2–methanol solution down to −20 °C. A single crystal was fixed on the tip of a glass fibre with a cyano acrylate adhesive. Dark brown crystals of **7** were grown by diffusion of hexane into a CH_2Cl_2 solution in a glass tube (internal diameter 8 mm) at ambient temperature. Yellow crystals of **8** were obtained by addition of hexane to a benzene solution at room temperature. The single crystals of **7** and **8** were fixed with Apiezon grease L in glass capillaries under argon.

Intensity data were collected by use of a Rigaku AFC-4 diffractometer for complex **5** and an Enraf-Nonius CAD4 four-circle automated diffractometer for **4**, **7** and **8** with graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å). Crystal data and experimental details are given in Table 5.

Structure analysis and refinement. Survey of the data set for complex **4** and the systematic extinction indicated a monoclinic class with a space group $P2_1$ or $P2_1/m$. The former was confirmed by the successful solution of the structure. Data were corrected for absorption.[19] The analytical form of the scattering factor[20] for the appropriate neutral atom was corrected for both real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion.[21]

The structure was solved by direct methods MULTAN,[22] and all the non-hydrogen atoms were located from subsequent Fourier-difference syntheses. They were refined by the block-diagonal least-squares method[23] with anisotropic thermal parameters for all atoms. The final *R* and *R'* values were 0.041 and 0.032 with the weighting scheme $w = 1/\sigma(F_o)$. Inversion of the entire structure led to marginally higher residuals, indicating that we have defined the correct enantiomeric structure in the polar space group $P2_1$. Cluster **4** crystallized with a molecule of CH_2Cl_2 in the asymmetric crystal unit. Final positional parameters are listed in Table 6.

Data for complex **5** were not corrected for absorption because deviations of F_o for axial reflections at $\chi \approx 90°$ were within ±5%. The structure was solved and refined as for **4**. As refinement proceeded the remaining hydrogen atoms in the methyl group were not located but those in the phenyl groups of the counter cation were located in Fourier maps. These atoms were included as fixed contributions in their idealized positions. The final *R* and *R'* values were 0.044 and 0.033. Final positional parameters are listed in Table 7.

Data for complex **7** were not corrected for absorption because deviations of F_o for axial reflections at $\chi \approx 90°$ were within ±3%. The structure was solved and refined as for **4** except that all the non-hydrogen atoms and 36 hydrogen atoms were located from subsequent Fourier-difference syntheses, and refined with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. The final *R* and *R'* values were 0.047 and 0.049. Final positional parameters are listed in Table 8.

A survey of the data set and the systematic absences for complex **8** indicated the space group *Aba*2 (no. 41) or *Cmca* (no. 64). The former non-centrosymmetric possibility was strongly indicated by the cell volume (consistent with $Z = 4$) and confirmed by the successful solution of the structure. Data were not corrected for absorption. The structure was solved and refined as for **4**. The final *R* and *R'* values were 0.048 and 0.043. Final atomic coordinates are presented in Table 9.

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

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