DALTON

Cluster build-up using the $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$ cation; synthesis and structural characterisation of some cyclopentadienyl-substituted hexa- and hepta-nuclear ruthenium carbido clusters†

Jack Lewis, Catherine A. Morewood, Paul R. Raithby* and M. Carmen Ramirez de Arellano

Department of Chemistry, Lensfield Road, Cambridge UK, CB2 1EW

The reaction of the dianion $[Ru_5C(CO)_{14}]^{2-}$ with 2 equivalents of $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$ afforded two new clusters, the hexanuclear anion $[Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_5)]^-$ **1** and the neutral heptanuclear cluster $[Ru_7C(CO)_{14}(\eta^5\text{-}C_5H_5)_2]$ **2** in high yields. In a similar reaction the hexanuclear dianion $[Ru_6C(CO)_{16}]^{2-}$ may be 'capped' by $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$ to afford good yields of both the heptanuclear monoanion $[Ru_7C(CO)_{16}(\eta^5\text{-}C_5H_5)]^-$ **3** and the neutral cluster **2**. The clusters **1**, **2** and **3** have been fully characterised by both spectroscopic and crystallographic methods. The crystal structures show that the metal framework of all three clusters is based on a central Ru_6C octahedral core. In **1** one of the core atoms is co-ordinated to an $\eta^5\text{-}C_5H_5$ ligand, while in **2** an additional $Ru(\eta^5\text{-}C_5H_5)$ group caps one triangular face of the octahedron to give a capped octahedral framework. In **3** the single $\eta^5\text{-}C_5H_5$ ligand is co-ordinated to the capping Ru atom in the capped octahedral framework.

The first mononuclear organometallic compound with a π-bound cyclopentadienyl group as a ligand was ferrocene, which was characterised and the bonding rationalised independently by Wilkinson and Fischer in 1952.[1] Since then the $\eta^5\text{-}C_5H_5$ ligand (Cp) has been shown to be extremely useful and versatile, exhibiting a wide range of bonding characteristics, and many thousands of organometallic complexes containing this group are now known.[2] More recently it has been incorporated into platinum-group metal cluster complexes, as opposed to mononuclear species, *via* several different synthetic routes,[3,4] and pentamethyl-[5] and phenyl-substituted[6] cyclopentadienyl ligands have been used extensively in ruthenium and osmium cluster chemistry.

Our initial interest in the cyclopentadienyl ligand was aimed at a comparison with six-membered arene ring systems bonded to clusters[7] with respect to their structure and isomerism. The arene complexes obtained can be prepared by one of three main synthetic routes, (*i*) where the co-ordination mode and level of unsaturation of the organic ligand is modified once it has been co-ordinated to the cluster,[8] (*ii*) where there is ligand exchange between co-ordinated carbonyl ligands and an unco-ordinated arene group,[9] and (*iii*) where a cationic organometallic fragment containing the organic group is coupled to a carbonyl cluster anion.[10] For this third method of synthesis the dicationic species '$M(\eta^6\text{-}C_6H_{6-n}R_n)^{2+}$' (M = Ru or Os, R = H or Me)[11] have been used extensively. However, ionic coupling of dicationic species with anions appears to be limited to certain systems, since fragmentation, recombination or electron transfer can predominate, depending on the relative stability of the parent cluster and the anion. For example, the reaction of $[M(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ (M = Ru or Os) with the dianion $[Os_3(CO)_{11}]^{2-}$ results in the regeneration of $[Os_3(CO)_{12}]$ by redox exchange instead of the anticipated tetranuclear arene-substituted cluster.[12] Ionic coupling of the same cation with $[Os_6(CO)_{18}]^{2-}$ does not proceed, but regenerates $[Os_6(CO)_{18}]$, and $[Os_{10}C(CO)_{24}]^{2-}$ does not react at all with dicationic capping fragments, presumably because of the delocalisation of the negative throughout the metal framework of the high-nuclearity cluster.

Monocationic capping species, such as that generated by the cation $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$, would overcome some of the difficulties described for dicationic species. Since the cap is monocationic, electron transfer must occur in two separately defined steps, and consequently there is less redox activity and electron transfer at the expense of ionic coupling is suppressed. Also, the reaction of a dianion with monocationic species opens up the possibility of increasing the nuclearity of the resultant neutral cluster by two metal units, instead of one. We have recently reported the synthesis of the novel mixed-metal cluster $[Os_5Ru_2(CO)_{15}(\eta^5\text{-}C_5H_5)_2]$ by the capping of $[Os_5(CO)_{15}]^{2-}$ with $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$,[13] and now describe an extension of this work to include the use of the cation $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$ in capping reactions on the $[Ru_5C(CO)_{14}]^{2-}$ and $[Ru_6C(CO)_{16}]^{2-}$ anions.

Results and Discussion

The room-temperature reaction of the cluster dianion $[Ru_5C(CO)_{14}]^{2-}$, as its $[N(PPh_3)_2]^+$ salt, with 2 molar equivalents of the preformed mononuclear 'capping' fragment, $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$, in dichloromethane, affords an anionic and a neutral product, each in *ca.* 40% yield (Scheme 1). After separation by TLC, these two products were characterised as the monoanion, $[Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_5)]^-$ **1**, as its $[N(PPh_3)_2]^+$ salt, and the neutral heptaruthenium cluster $[Ru_7C(CO)_{14}(\eta^5\text{-}C_5H_5)_2]$ **2** by spectroscopic techniques (Table 1). The IR spectrum of the two complexes showed the presence of both terminal and bridging carbonyl ligands as in the dianion $[Ru_6C(CO)_{16}]^{2-}$.[14] In the positive-ion FAB mass spectrum the molecular ion peak was observed for **1**, but not in the spectrum of **2**, however there was a strong peak at *m/z* 1075, which corresponds to loss of a '$Ru(C_5H_5)$' unit from the cluster (as confirmed by the X-ray crystallographic study). In the room-temperature ^1H NMR spectrum of **1** the singlet at δ 4.44 may be assigned to the protons of the η^5-co-ordinated cyclopentadienyl ring, while the multiplet between δ 7.2 and 7.8 results from the protons on the $[(N(PPh_3)_2]^+$ counter ion. The position of the cyclopentadienyl proton signal is in the same region as that found for the two equivalent cyclopentadienyl rings (δ 4.99) in the octahedral cluster $[Ru_6C(CO)_{12}(\eta^5\text{-}C_5H_5)_2]$,[4] but shows a slight shift to lower chemical shift. The ^1H NMR spectrum of **2** shows two singlets at δ 5.22 and 4.66 with a 1:1 integral ratio, which arise from the presence of two inequivalent cyclopentadienyl ligands on the cluster; these ligands are not fluxional at room temperature. The former signal is at higher shift than that

† Dedicated to Professor Sir Geoffery Wilkinson in commemoration of his outstanding contribution to Inorganic Chemistry.

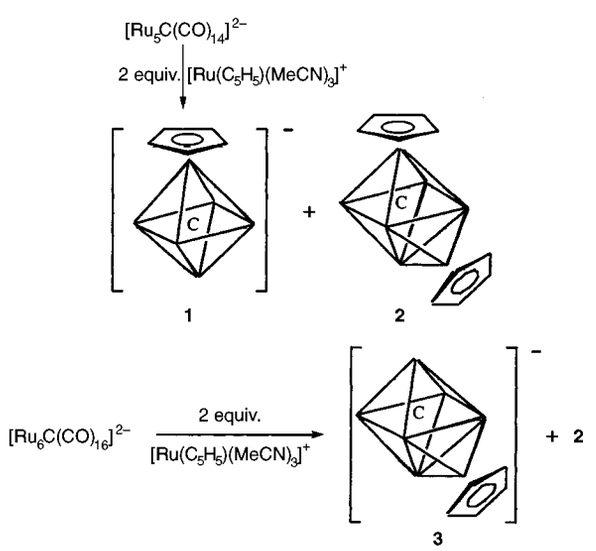
Table 1 Spectroscopic data for complexes **1**, **2** and **3**

Compound	IR [a], $\tilde{\nu}_{CO}$/cm^{-1}	Mass spectrum,[b] *m*/*z* (calc.)	^{1}H NMR,[c] δ
1	2050m, 2001vs, 1828w	1076 (1075)	7.2–7.8 (m, 30 H), 4.44 (s, 5 H)
2	2061m, 2021s, 1823w	1075 (1241)	5.22 (s, 5 H), 4.66 (s, 5 H)
3	2048w, 2002s, 1931m (br), 1827w, 1738w (br)	1235 (1232)	7.2–7.8 (m, 30 H), 5.20 (s, 5 H)

[a] s = Strong, m = medium, w = weak and br = broad. Spectrum run in dichloromethane. [b] Positive-ion FAB based on ^{101}Ru. [c] Spectrum run in $CDCl_3$.

Table 2 Selected bond lengths (Å) and angles (°) for $[Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_5)]^-$ **1**

Ru(1)–Ru(2)	2.877(2)	Ru(1)–Ru(3)	2.854(2)
Ru(1)–Ru(4)	2.878(2)	Ru(1)–Ru(5)	2.951(2)
Ru(1)–C(1)	2.058(13)	Ru(1)–C(12)	1.883(19)
Ru(2)–Ru(3)	2.872(2)	Ru(2)–Ru(5)	2.869(2)
Ru(2)–Ru(6)	2.875(2)	Ru(2)–C(1)	1.955(14)
Ru(2)–C(21)	2.165(18)	Ru(2)–C(22)	2.111(17)
Ru(2)–C(23)	2.163(18)	Ru(2)–C(24)	2.147(21)
Ru(2)–C(25)	2.197(22)	Ru(3)–Ru(4)	2.887(2)
Ru(3)–Ru(6)	2.934(2)	Ru(3)–C(1)	2.061(14)
Ru(3)–C(33)	1.904(20)	Ru(4)–Ru(5)	2.881(2)
Ru(4)–Ru(6)	2.850(2)	Ru(4)–C(1)	2.071(14)
Ru(5)–Ru(6)	2.859(2)	Ru(5)–C(1)	2.050(14)
Ru(5)–C(12)	2.78(2)	Ru(5)–C(62)	2.126(16)
Ru(6)–C(1)	2.034(13)	Ru(6)–C(33)	2.94(2)
Ru(6)–C(62)	2.049(16)	Ru(2)–Cp (centroid)	1.841
C(1)–Ru(2)–Cp (centroid)	171.8	Ru(1)–C(12)–O(12)	166(2)
Ru(5)–C(12)–O(12)	118(2)	Ru(1)–C(12)–Ru(5)	75.9(6)
Ru(3)–C(33)–O(33)	171(2)	Ru(6)–C(33)–O(33)	118(2)
Ru(3)–C(33)–Ru(6)	71(2)	Ru(5)–C(62)–O(62)	135.0(13)
Ru(6)–C(62)–O(62)	138.6(13)	Ru(5)–C(62)–Ru(6)	86.4(6)



Scheme 1 Syntheses of $[Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_5)]^-$ **1**, $[Ru_7C(CO)_{14}(\eta^5\text{-}C_5H_5)_2]$ **2** and $[Ru_7C(CO)_{16}(\eta^5\text{-}C_5H_5)]^-$ **3**

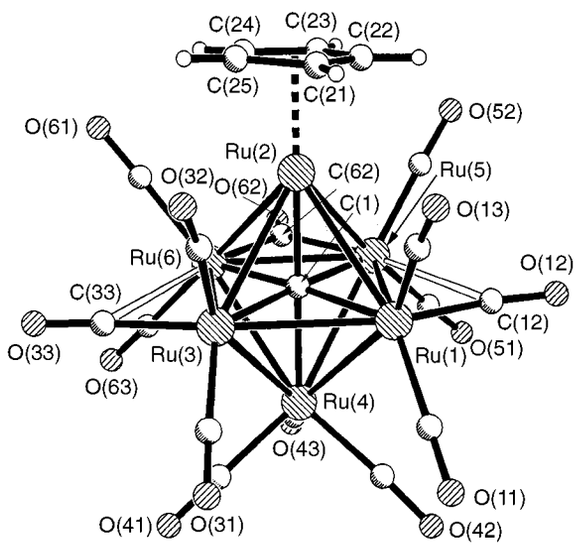


Fig. 1 Molecular structure of the anion $[Ru_6C(CO)_{14}(\eta^5\text{–}C_5H_5)]^-$ **1** showing the atom numbering scheme

observed for $[Ru_6C(CO)_{12}(\eta^5\text{-}C_5H_5)_2]$,[4] but is similar to the value of δ 5.12 observed for the two rings in the square-based pyramidal cluster $[Ru_5C(CO)_{10}(\eta^5\text{-}C_5H_5)_2]$,[4] and to that observed (δ 5.19) for the two equivalent rings in the bicapped trigonal-bipyramidal cluster $[Os_5Ru_2(CO)_{15}(\eta^5\text{-}C_5H_5)_2]$.[13] The latter signal is at a similar position to that observed for **1**.

In order to confirm the spectroscopic characterisations and establish the positions of the '$Ru(\eta^5\text{-}C_5H_5)$' caps single-crystal X-ray analyses were carried out on compounds **1** and **2**. The structure of the anion $[Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_5)]^-$ **1** is shown in Fig. 1 while selected bond parameters are listed in Table 2. The molecular structure of $[Ru_7C(CO)_{14}(\eta^5\text{-}C_5H_5)_2]$ **2** is illustrated in Fig. 2 and selected bond parameters are presented in Table 3.

The crystal structure of compound **1** shows well separated cation and anion units with no contacts less than the sum of the appropriate van der Waals radii. The structure of the anion consists of a carbide-centred octahedral Ru_6 core with the $\eta^5\text{-}C_5H_5$ ligand bound to one of the Ru atoms, Ru(2). In terms of the synthesis, the '$Ru(\eta^5\text{-}C_5H_5)$ cap' has clipped on to the carbide-centred square face of the square-based pyramidal $[Ru_5C(CO)_{15}]^{2-}$ dianion,[15] and the remaining anionic charge is delocalised over the octahedral core. The electron count of 86e$^-$ is consistent with the observed octahedral metal framework. The planar cyclopentadienyl ring is slightly tilted with respect to the Ru(1)Ru(3)Ru(5)Ru(6) plane, and makes an angle of 8.6° with it. The carbido carbon atom, C(1), is slightly offset with respect to the centre of the octahedral cavity, lying closest to Ru(2), the metal co-ordinated to the cyclopentadienyl ligand. A similar shortening of the Ru–C (carbide) distance has been observed in all of the η^6-monoarene complexes based on Ru_6C

Table 3 Selected bond lengths (Å) and angles (°) for $[Ru_7C(CO)_{14}(\eta^5\text{–}C_5H_5)_2]$ **2**

Ru(1)–Ru(2)	2.788(1)	Ru(1)–Ru(3)	2.878(1)
Ru(1)–Ru(4)	2.824(1)	Ru(1)–Ru(5)	2.984(1)
Ru(1)–C(1)	2.076(7)	Ru(1)–C(13)	2.185(10)
Ru(1)–C(43)	2.243(10)	Ru(2)–Ru(3)	2.888(1)
Ru(2)–Ru(5)	2.885(1)	Ru(2)–Ru(6)	3.056(1)
Ru(2)–C(1)	2.046(7)	Ru(2)–C(13)	1.978(10)
Ru(3)–Ru(4)	2.869(1)	Ru(3)–Ru(6)	2.836(1)
Ru(3)–C(1)	1.924(7)	Ru(3)–C(31)	2.169(9)
Ru(3)–C(32)	2.194(10)	Ru(3)–C(33)	2.178(9)
Ru(3)–C(34)	2.180(9)	Ru(3)–C(35)	2.162(9)
Ru(4)–Ru(5)	2.826(1)	Ru(4)–Ru(6)	2.963(1)
Ru(4)–Ru(7)	2.717(1)	Ru(4)–C(1)	2.048(7)
Ru(4)–C(42)	1.936(9)	Ru(4)–C(43)	2.013(9)
Ru(5)–Ru(6)	2.829(1)	Ru(5)–Ru(7)	2.774(1)
Ru(5)–C(1)	2.087(7)	Ru(5)–C(52)	2.107(9)
Ru(6)–Ru(7)	2.926(1)	Ru(6)–C(1)	2.065(7)
Ru(7)–C(42)	2.382(9)	Ru(7)–C(52)	2.018(9)
Ru(7)–C(71)	2.178(9)	Ru(7)–C(72)	2.197(10)
Ru(7)–C(73)	2.209(10)	Ru(7)–C(74)	2.188(9)
Ru(7)–C(75)	2.183(9)	Ru(3)–Cp (centroid 3)	1.829
Ru(7)–Cp (centroid 7)	1.840		
C(1)–Ru(3)–Cp (centroid 3)	177.8	Ru(1)–C(13)–O(13)	132.3(9)
Ru(2)–C(13)–O(13)	143.6(9)	Ru(1)–C(13)–Ru(2)	83.9(4)
Ru(4)–C(42)–O(42)	156.0(10)	Ru(7)–C(42)–O(42)	126.4(8)
Ru(4)–C(42)–Ru(7)	77.2(4)	Ru(4)–C(43)–O(43)	145.6(9)
Ru(1)–C(43)–O(43)	131.3(9)	Ru(1)–C(43)–Ru(4)	82.9(3)
Ru(5)–C(52)–O(52)	135.0(8)	Ru(7)–C(52)–O(52)	140.5(8)
Ru(5)–C(52)–Ru(7)	84.5(4)		

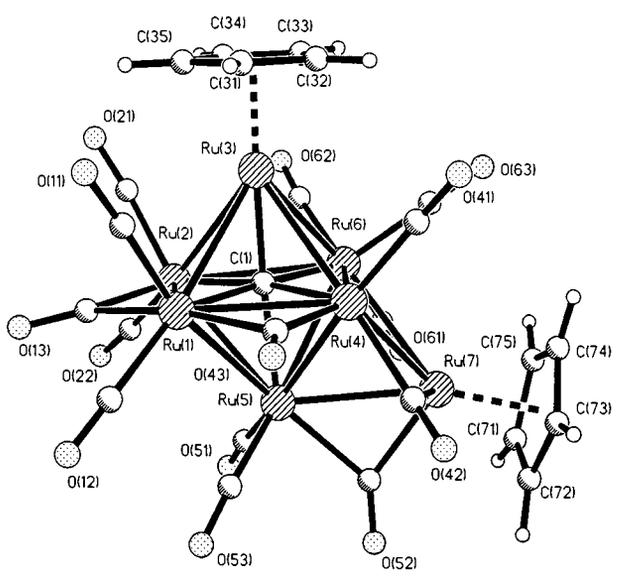


Fig. 2 Molecular structure of $[Ru_7C(CO)_{14}(\eta^5\text{-}C_5H_5)_2]$ **2** showing the atom numbering scheme

core units.[16] This has been described as a compensatory effect to balance the electron density on the metal atom bearing the arene; formal substitution of three carbonyl groups in $[Ru_6C(CO)_{16}]^{2-}$ [average Ru–C (carbide) 2.05 Å][14,17] for the better σ-donating and poorer π-accepting arene ligand increases the electron density on the metal atom, and the carbido carbon atom relieves this disparity by moving in towards the metal atom.[18] The distribution of the carbonyl ligands in **1** is similar to that in the $[Ru_6C(CO)_{16}]^{2-}$ anion[14,17] except for the cyclopentadienyl-bound Ru atom. Eleven of the carbonyl groups are terminal and essentially linear. Of the remaining three, all of which lie close to the Ru(1)Ru(3)Ru(5)Ru(6) plane, the carbonyl C(62)O(62) symmetrically bridges the Ru(5)–Ru(6) edge, and C(12)O(12) and C(33)O(33) form 'incipient' asymmetric bridges across the Ru(1)–Ru(5) and Ru(3)–Ru(6) edges, respectively, with the shorter Ru–C distances associated with Ru(1) and Ru(3), the metal atoms not involved in the symmetric bridge. A similar carbonyl pattern is also observed in the polymorphs of the neutral binary carbonyl $[Ru_6C(CO)_{17}]$.[19] Within the metal octahedron the Ru–Ru distances can be divided up into groups; the four involving the Ru atom [Ru(2)] bound to the η^5-cyclopentadienyl ring average 2.873 Å, which is almost identical to the four involving the tricarbonyl bound Ru(4) atom (average 2.874 Å). The two 'incipiently' bridged equatorial edges are the longest in the framework (average 2.943 Å), and the symmetrically bridged equatorial edge, Ru(5)–Ru(6), and the unbridged edge, Ru(1)–Ru(3), are almost equal, average 2.857 Å. These distances can be compared to the average non-bridged distance of 2.90 Å and the average bridged distance of 2.85 Å in the $[Ru_6C(CO)_{16}]^{2-}$ anion.[17]

The crystal structure of $[Ru_7C(CO)_{14}(\eta^5\text{-}C_5H_5)_2]$ **2** shows that the molecules are packed such that the cyclopentadienyl groups in one molecule are at van der Waals contact distances to carbonyl groups in other molecules, and there are no intermolecular cyclopentadienyl–cyclopentadienyl interactions. The core structure of each molecule of **2** retains the carbido-centred octahedral Ru_6 unit observed in **1**, with an $\eta^5\text{-}C_5H_5$ ligand bound to ruthenium atom Ru(3). However, in **2**, a second '$Ru(\eta^5\text{-}C_5H_5)$' caps one of the triangular faces of the octahedron, Ru(4)Ru(5)Ru(6), to give the capped octahedral framework consistent with the electron count of $98e^-$ for the cluster. In terms of the synthesis, the structure may be viewed as the second capping '$Ru(\eta^5\text{-}C_5H_5)^+$' fragment clipping on to a face of the preformed anion **1**. While isomers are possible, all the spectroscopic and crystallographic evidence supports the existence of only one isomeric product. In **2** the planar ring C(31)–C(35) makes an angle of 2.3° with the equatorial metal plane Ru(1)Ru(2)Ru(4)Ru(6) while the other planar ring C(71)–C(75) makes an angle of 17.7° with the Ru(4)Ru(5)Ru(6) plane. As in **1**, the carbido carbon atom, C(1), is offset from the centre of the octahedral cavity, and is significantly closer to the cyclopentadienyl-bound Ru(3) atom. The Ru(7) atom caps the Ru(4)Ru(5)Ru(6) face in an asymmetric manner, with relatively short distances to Ru(4) and Ru(5) (average 2.75 Å) and a relatively long distance to Ru(6). While all three metal atoms,

Ru(4), Ru(5) and Ru(6), are eight-co-ordinate, the short Ru(4)–Ru(7) and Ru(5)–Ru(7) contacts are spanned by asymmetrically bridging carbonyl ligands while the Ru(6)–Ru(7) edge is unbridged and Ru(6) has three terminal carbonyl ligands bonded to it. Bridging carbonyls have been found to be associated with '$M(\eta^6\text{-}C_6H_6)$' (M = Ru or Os) face-capping units in $[Os_5Ru(CO)_{15}(\eta^6\text{-}C_6H_6)]$[20] and $[Os_6(CO)_{15}(\eta^6\text{-}C_6H_5Me)]$,[11] and are thought to accept excess of electron density from the relatively 'electron rich' metal. A similar explanation is appropriate in the case of **2**. With the presence of the '$Ru(\eta^5\text{-}C_5H_5)$' capping group there is a redistribution of the carbonyl ligands attached to the Ru_6 octahedral core, compared to the arrangement in **1**. Ten of these carbonyl groups are terminal, and two are involved in the bridges to Ru(7). The remaining two lie close to the Ru(1)Ru(2)Ru(4)Ru(6) equatorial plane of the octahedron, and asymmetrically bridge the Ru(1)–Ru(2) and Ru(1)–Ru(4) edges. The Ru–Ru distances in the octahedron also span a greater range than in **1**. The four apical–equatorial distances involving the cyclopentadienyl-substituted Ru(3) atom average 2.868 Å, similar to the value found for **1**, however the four apical–equatorial distances involving Ru(5) range from 2.984(1) to 2.826(1) Å; the longest distance involves the Ru(1)–Ru(5) edge, where the Ru(1) atom is co-ordinated to both bridging carbonyl ligands, and the two shortest distances, average 2.828 Å, are capped by Ru(7). The four equatorial–equatorial distances also show considerable variation. The longest edge is the unbridged Ru(2)–Ru(6) bond, and the Ru(4)–Ru(6) edge which is capped by Ru(7) is also relatively long compared to the two capped apical–equatorial edges. The two carbonyl-bridged equatorial edges are not equivalent.

In order to study the capping reactions of $[Ru_6C(CO)_{16}]^{2-}$ this dianion was prepared by the reduction of $[Ru_6C(CO)_{17}]$ with potassium–benzophenone, in tetrahydrofuran (thf). The dianion was isolated as its $[N(PPh_3)_2]^+$ salt by the addition of a methanolic solution of $[N(PPh_3)_2]Cl$. This method differs from the reduction described in the literature[14] and offers a simpler, high-yield route to the anion. Using the dianion $[Ru_6C(CO)_{16}]^{2-}$ in the reaction with $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$ under the same conditions as described for $[Ru_5C(CO)_{14}]^{2-}$, two products were isolated (Scheme 1), and characterised spectroscopically (Table 1), after purification by TLC. The high-yield product, obtained in *ca.* 60% yield, was characterised as the new monoanionic, heptanuclear cluster $[Ru_7C(CO)_{16}(\eta^5\text{-}C_5H_5)]^-$ **3**, while the neutral cluster $[Ru_7C(CO)_{14}(\eta^5\text{-}C_5H_5)_2]$ **2** was isolated in *ca.* 10% yield.

The IR spectrum of compound **3** exhibited carbonyl resonances in the regions for terminal and edge bridging carbonyl ligands, and the weak band at 1738 cm^{-1} was indicative of the presence of a μ_3-face-capping carbonyl ligand. The positive-ion FAB mass spectrum exhibited a molecular ion peak consistent with the formulation of **3**. In the ^1H NMR spectrum, at room temperature, as well as signals corresponding to the $[N(PPh_3)_2]^+$ cation, the signal at δ 5.20 could be assigned to a metal-bound $\eta^5\text{-}C_5H_5$ ligand. The position of the signal suggests that the cyclopentadienyl ring is co-ordinated to a ruthenium atom in a face-capping position, by comparison with the spectrum for **2** and with other capped clusters.[4,13]

In order to establish the structure of the anion, and in particular to locate the position of the cyclopentadienyl ring, a single-crystal structure determination of the $[N(PPh_3)_2]^+$ salt of $[Ru_7C(CO)_{16}(\eta^5\text{-}C_5H_5)]^-$ **3** was undertaken. The structure of the anion is illustrated in Fig. 3, and selected bond parameters are listed in Table 4. Although the quality of the crystals obtained for **3** was poor it was possible to resolve the crystal structure which showed that the cations and anion in the lattice were separated by normal van der Waals distances, and that there was one quarter of a disordered molecule of dichloromethane in the asymmetric unit.

The structure of the anion **3** consists of a carbido-centred, capped octahedral metal core, with the 'Ru($\eta^5\text{-}C_5H_5$)' unit in the face-capping position. In terms of the synthesis, the 'Ru($\eta^5\text{-}C_5H_5$)' cap has clipped on to one face of the $[Ru_6C(CO)_{16}]^{2-}$ octahedral core, and the remaining negative charge has been delocalised over the metal framework. The electron count of 98e^- for the cluster is consistent with the observed core geometry. The planar cyclopentadienyl ring makes an angle of 8.4° with the Ru(1)Ru(2)Ru(4) capped octahedral face. Unlike the carbido carbon atom in the structures **1** and **2**, the C(1) atom in **3** shows only a slight distortion away from the centre of the Ru_6 octahedron towards Ru(4), the Ru atom of the octahedron associated with the capping group, and the average Ru–C (carbide) distance is 2.05 Å, similar to that found in $[Ru_6C(CO)_{16}]^{2-}$.[13,16] The capping Ru(7) atom forms asymmetric contacts with the three face-capped Ru atoms. As found in **2**, the longest edge, Ru(2)–Ru(7), is unbridged, and the Ru(4)–Ru(7) edge, which is intermediate in length, is associated with

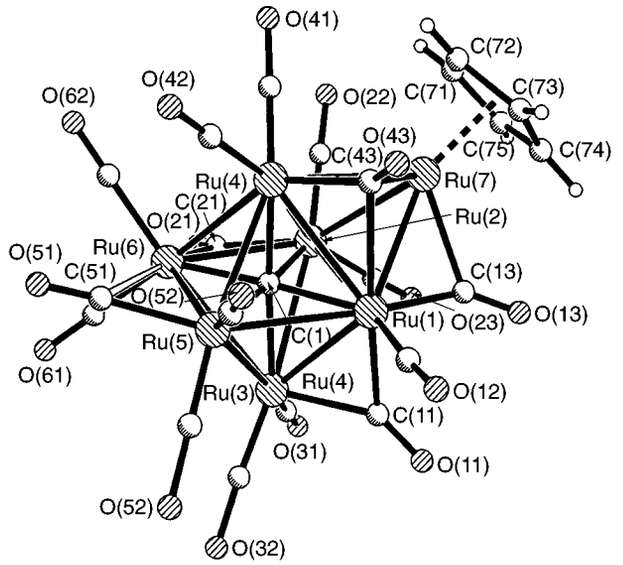


Fig. 3 Molecular structure of the anion $[Ru_7C(CO)_{16}(\eta^5\text{-}C_5H_5)]^-$ **3** showing the atom numbering scheme

Table 4 Selected bond lengths (Å) and angles (°) for $[Ru_7C(CO)_{16}(\eta^5\text{–}C_5H_5)]^-$ **3**

Ru(1)–Ru(2)	2.942(3)	Ru(1)–Ru(3)	2.778(3)
Ru(1)–Ru(4)	2.859(3)	Ru(1)–Ru(5)	2.913(3)
Ru(1)–Ru(7)	2.660(4)	Ru(1)–C(1)	2.02(2)
Ru(1)–C(11)	2.08(3)	Ru(1)–C(43)	2.52(4)
Ru(2)–Ru(3)	2.938(4)	Ru(2)–Ru(4)	2.848(3)
Ru(2)–Ru(6)	2.828(3)	Ru(2)–Ru(7)	2.926(4)
Ru(2)–C(1)	2.02(3)	Ru(2)–C(21)	2.13(3)
Ru(3)–Ru(5)	2.934(3)	Ru(3)–Ru(6)	3.007(3)
Ru(3)–C(1)	2.10(2)	Ru(3)–C(11)	2.05(3)
Ru(4)–Ru(5)	2.865(4)	Ru(4)–Ru(6)	2.909(4)
Ru(4)–Ru(7)	2.817(3)	Ru(4)–C(1)	1.99(2)
Ru(4)–C(43)	2.05(3)	Ru(5)–Ru(6)	2.883(4)
Ru(5)–C(1)	2.08(3)	Ru(5)–C(51)	1.98(4)
Ru(6)–C(1)	2.06(2)	Ru(6)–C(21)	2.14(3)
Ru(6)–C(51)	2.70(3)	Ru(7)–C(13)	2.21(3)
Ru(7)–C(43)	2.17(3)	Ru(7)–C(71)	2.17(4)
Ru(7)–C(72)	2.10(4)	Ru(7)–C(73)	2.16(5)
Ru(7)–C(74)	2.17(5)	Ru(7)–C(75)	2.22(5)
Ru(7)–Cp (centroid)	1.825		
Ru(1)–C(11)–O(11)	137(3)	Ru(3)–C(11)–O(11)	139(3)
Ru(1)–C(11)–Ru(3)	84.5(11)	Ru(1)–C(13)–O(13)	151(3)
Ru(7)–C(13)–O(13)	129(3)	Ru(1)–C(13)–Ru(7)	79.2(14)
Ru(2)–C(21)–O(21)	141(3)	Ru(6)–C(21)–O(21)	136(3)
Ru(2)–C(21)–Ru(6)	83.1(11)	Ru(1)–C(43)–O(43)	129(2)
Ru(4)–C(43)–O(43)	141(3)	Ru(7)–C(43)–O(43)	130(3)
Ru(1)–C(43)–Ru(4)	76.7(12)	Ru(1)–C(43)–Ru(7)	68.6(10)
Ru(4)–C(43)–Ru(7)	83.7(12)	Ru(5)–C(51)–O(51)	162(3)
Ru(6)–C(51)–O(51)	123(3)	Ru(5)–C(51)–Ru(6)	74.3(14)

the asymmetrical face-capping carbonyl, C(43)O(43). The shortest edge, Ru(1)–Ru(7), is spanned by both the edge-bridging carbonyl C(13)O(13) and the face-capping carbonyl C(43)O(43). As was discussed for the structure of **2**, the presence of an η^5-C_5H_5 ligand or an η^6-C_6H_6 ligand co-ordinated to a face-capping metal atom is always concomitant with the presence of one or more bridging carbonyl groups bound to the capping atom in order to delocalise the excess of electron density on the 'electron rich' metal. There are few examples of μ_3-face-capping carbonyl ligands co-ordinated to ruthenium or osmium clusters,[21] but their presence has been established in electron-rich, cyclopentadienyl-substituted clusters[22] where their high π-acceptor ability is required. In this case the carbonyl C(43)O(43) forms a highly asymmetric cap with a relatively long interaction to Ru(1) [2.52(4) Å]. Apart from the presence of the face-capping carbonyl and the absence of a co-ordinated cyclopentadienyl ligand attached to the Ru_6 octahedron, the carbonyl distribution in **3** is related to that in **2**. Of the sixteen carbonyls, two are associated with the capping Ru(7), as described above, eleven others are terminal, and two of the remaining three, C(21)O(21) and C(51)O(51), lie close to the Ru(1)Ru(2)Ru(5)Ru(6) equatorial plane of the octahedron. The C(21)O(21) ligand spans the Ru(2)-Ru(6) edge in a symmetric manner, while the C(51)O(51) ligand forms a very asymmetric 'incipient' bridge, spanning the Ru(5)-Ru(6) edge, with the short carbon contact to Ru(5). Various degrees of 'incipient' carbonyl bridge bonding have been observed in the polymorphs of $[Ru_6C(CO)_{17}]$.[19] The last carbonyl, C(11)O(11), symmetrically bridges the equatorial–apical Ru(1)-Ru(3) edge of the octahedron, a feature not observed in the structures of **1** and **2**. The Ru–Ru distances in the octahedral core of **3** show a greater variation in values than those in **2**. Three of the four equatorial–apical distances involving the tricarbonyl-substituted Ru(3) atom (average 2.960 Å) are considerably longer than the equivalent distances to the cyclopentadienyl-substituted Ru(3) in **2**; the fourth distance, Ru(1)–Ru(3), which is bridged by a carbonyl ligand is significantly shorter. The four equatorial–apical distances involving Ru(4), which is attached to the Ru(7) capping atom, range from 2.848(3) to 2.909(4) Å, with the two shorter distances associated with the capping Ru(7) atom, as seen in **2**. Within the equatorial plane of the octahedron, the long Ru(1)–Ru(2) edge is associated with the presence of the cap, and the shorter edges are again bridged by carbonyl ligands. The differences between the Ru–Ru edge lengths between the heptanuclear clusters **2** and **3** reflect the different electronic demands of the carbonyl and cyclopentadienyl ligands and the requirement for the delocalisation of the negative charge in the anion **3**.

The presence of a small amount of compound **2** in the reaction between $[Ru_6C(CO)_{16}]^{2-}$ and $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$ shows that it cannot be considered simply as an ionic coupling reaction. It is apparent that addition of the second mononuclear fragment does not increase the nuclearity of the cluster by one but, instead, the cyclopentadienyl group is transferred to the cluster to form **2**. Such migration of an arene ligand from a mononuclear species onto a cluster has previously been observed in the synthesis of $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)]$,[9] and of a cyclopentadienyl ligand in the formation of $[Ru_6C(\mu_3\text{-}CH)(\mu\text{-}PPh_2)_2(CO)_{10}(\eta^5\text{-}C_5H_5)]$.[23] Thus, the neutral, octanuclear cluster '$Ru_8C(CO)_{16}(\eta^5\text{-}C_5H_5)_2$' is not formed from the reaction, and it may be that the negative charge on **3** is sufficiently delocalised to prevent the ionic coupling reaction from occurring, and the ligand-replacement reaction takes precedence.

Experimental

All the reactions were performed under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques. Technical grade solvents were purified by distillation over the appropriate drying agents and under an inert nitrogen atmosphere prior to use. Routine separation of products was performed by thin-layer chromatography (TLC), using commercially prepared glass plates, precoated to 0.25 mm thickness with Merck Kieselgel 60 F_{254}, as supplied by Merck, or using laboratory-prepared glass plates coated to 1 mm thickness with Merck Kieselgel 60 F_{254}. The complexes $[(N(PPh_3)_2]_2[Ru_5C(CO)_{14}]$[15] and $[Ru(C_5H_5)(MeCN)_3]PF_6$[24] were prepared by literature procedures. The FAB mass spectra were recorded using a Kratos model MS 902 instrument, IR spectra on a Perkin-Elmer 1710 FT-IR spectrometer, using 0.5 mm NaCl or CaF_2 cells, and ^{1}H NMR spectra on a Bruker WH 250 MHz spectrometer.

Reaction of $[N(PPh_3)_2]_2[Ru_5C(CO)_{14}]$ with $[Ru(C_5H_5)(MeCN)_3]PF_6$

2 Molar equivalents of the salt $[Ru(C_5H_5)(MeCN)_3]PF_6$ (50 mg, 11.1×10^{-5} mol), were added to a solution of the salt $[N(PPh_3)_2]_2[Ru_5C(CO)_{14}]$ (100 mg, 5.0×10^{-5} mol) in dichloromethane (25 cm^3). The solution went dark brown immediately after the addition and was stirred for 30 min before the solvent was removed *in vacuo*. The resultant residue was separated by TLC using CH_2Cl_2–hexane (70:30) as eluent, to yield two products, $[N(PPh_3)_2][Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_5)]$ **1** (39 mg, 2.4×10^{-5} mol) and $[Ru_7C(CO)_{14}(\eta^5\text{-}C_5H_5)_2]$ **2** (24 mg, 1.9×10^{-5} mol) in similar yield (*ca.* 40%) {Found for **1**: C, 40.70; H, 2.07. Calc. for $[N(PPh_3)_2][Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_5)]$: C, 41.66; H, 2.17. Found for **2**: C, 23.88; H, 0.78. Calc. for $[Ru_7C(CO)_{14}(\eta^5\text{-}C_5H_5)_2]$: C, 24.17; H, 0.81%}.

Alternative preparation of $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$

To $[Ru_6C(CO)_{17}]$ (120 mg, 11.0×10^{-5} mol) in thf (30 cm^3), a solution of K^+–Ph_2CO in thf (30 cm^3) was added dropwise, until the blue colour from the K^+–Ph_2CO persisted for 30 s and the solution changed from red to orange-brown. The salt $[N(PPh_3)_2]Cl$ (76 mg, 13.0 x 10^{-5} mol) was added to stabilise the anion formed and after stirring for 10 min the solution was taken to dryness. The resulting orange oil containing $[Ru_6C(CO)_{16}]^{2-}$ had an analogous IR spectrum to that of $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$ prepared *via* the literature method,[14] and was used without further purification.

Reaction of $[N(PPh_3)_2]_2[Ru_5C(CO)_{14}]$ with $[Ru(C_5H_5)(MeCN)_3]PF_6$

2 Molar equivalents of $[Ru(C_5H_5)(MeCN)_3]PF_6$ (105 mg, 24.2×10^{-5} mol) was added to a solution of $[(N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$ {prepared from 120 mg of $[Ru_6C(CO)_{17}]$}. The solution went dark brown immediately and was stirred for 30 min. The solid obtained after removing the solvent was chromatographed by TLC, eluting with CH_2Cl_2–hexane (70:30). Two products were isolated, the neutral complex $[Ru_7C(CO)_{14}(\eta^5\text{-}C_5H_5)_2]$ **2** (12% yield, 16 mg, 1.3×10^{-5} mol) and the salt, $[N(PPh_3)_2][Ru_7C(CO)_{16}(\eta^5\text{-}C_5H_5)]$ **3** (60% yield, 81 mg, 6.6×10^{-5} mol) {Found for **3**: C, 39.79; H, 1.82. Calc. for $[N(PPh_3)_2][Ru_7C(CO)_{16}(\eta^5\text{-}C_5H_5)]$: C, 39.32; H, 1.97%}.

Crystallography

Suitable single crystals for compounds **1**–**3** were mounted on glass fibres with epoxy resin, and data were recorded at room temperature on a Siemens R3mV diffractometer, using graphite-monochromated Mo-Kα radiation, and an ω–2θ scan procedure. Data were corrected for absorption using a semiempirical method based on ψ scans. Details of crystal data, data collection and structure refinement are summarised in Table 5. The structures were solved by direct methods[25] (Ru atom positions) and by subsequent Fourier-difference syntheses, and refined by full-matrix least squares[26] on F^2, with all non-hydrogen atoms assigned anisotropic displacement parameters. The cyclopentadienyl H atoms were placed in idealised

Table 5 Crystallographic data * for compounds **1**, **2** and **3**

	1	**2**	**3**
Molecular formula	$C_{56}H_{35}NO_{14}P_2Ru_6$	$C_{25}H_{10}O_{14}Ru_7$	$C_{58}H_{35}NO_{16}P_2Ru_7 \cdot 0.25\ CH_2Cl_2$
M	1614.21	1241.82	1792.53
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	9.606(4)	9.380(2)	10.196(6)
b/Å	25.520(10)	18.018(4)	16.126(7)
c/Å	22.866(8)	17.895(4)	19.488(12)
α/°	—	—	91.23(4)
β/°	94.89(3)	97.70(3)	92.12(5)
γ/°	—	—	102.29(4)
U/Å^3	5585(4)	2997.1(11)	3127(3)
Z	4	4	2
D_c/mg m^{-3}	1.920	2.752	1.904
Crystal size/mm	0.13 × 0.14 × 0.16	0.32 × 0.42 × 0.45	0.28 × 0.36 × 0.38
Crystal habit	Orange block	Red block	Red block
F(000)	3136	2320	1733
μ/mm^{-1}	1.705	3.500	1.782
Maximum, minimum relative transmission	0.371, 0.317	0.43, 0.31	0.366, 0.240
Data collection range/°	$2.51 < \theta < 23.55$	$3.57 < \theta < 25.05$	$2.59 < \theta < 22.55$
h,k,l Index ranges	−2 to 10, 0–28, −25 to 25	0–11, 0–21, −21 to 21	0–10, −17 to 16, −21 to 21
Reflections measured	9182	5821	9013
Independent reflections (R_{int})	8305 (0.0194)	5297 (0.0342)	8189 (0.0322)
Parameters, restraints	712, 8	415, 0	754, 1
$wR2$ (all data)	0.139	0.305	0.579
x,y	0.0346, 9.20	0.0520, 21.47	0.1733, 134.57
$R1$ [$I > 2\sigma(I)$]	0.0685	0.0380	0.123
Observed reflections	4006	4300	5659
Goodness of fit on F^2 (all data)	1.069	1.110	1.107
Maximum shift/σ	0.017	0.008	0.113
Peak, hole in final difference map/e Å^{-3}	0.614, −0.604	0.895, −1.133	3.741, −2.073

* Data in common: $\lambda = 0.710\ 73$ Å; $T = 293(2)$ K; $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}$; goodness-of-fit = $[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$ where n is the number of reflections and p the number of parameters.

positions and allowed to ride on the relevant carbon atom; H atoms were refined with common isotropic displacement parameters. The quality of the data obtained for compound **3** was poor as the crystal was weakly diffracting, the displacement parameters for many of the atoms in the $[N(PPh_3)_2]^+$ cation were high, consistent with the presence of disorder, and a quarter of a disordered dichloromethane molecule was located in the asymmetric unit; these atoms were refined with partial occupancies and the two C–Cl distances were constrained to be equal. The poor quality of the data is reflected in the relatively high final R factor. For each structure, in the final cycles of refinement, a weighting scheme of the form $w = 1/[\sigma^2(F_o)^2 + (xP)^2 + yP]$ where $P = (F_o^2 + 2F_c^2)/3$ was introduced, and this resulted in a relatively flat analysis of variance.

CCDC reference number 186/588.

Acknowledgements

We gratefully acknowledge the financial support of the Cambridge Overseas Trust, the Overseas Research Scheme and ICI plc (to C. A. M.), and the European Union for a Human Capital and Mobility Grant (to M. C. R. de A.). We thank Johnson Matthey plc for a generous loan of ruthenium salts.

References

1 G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, *J. Am. Chem. Soc.*, 1952, **74**, 2125; E. O. Fischer and W. Pfabl, *Z. Naturforsch., Teil B*, 1952, **7**, 377.
2 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 5th edn., 1988.
3 See, for example, M. S. Paquette and L. F. Dahl, *J. Am. Chem. Soc.*, 1980, **102**, 6621; M. A. Gallop, B. F. G. Johnson, J. Lewis and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1986, 706; H. Wadepohl, T. Borchert and H. Pritzkow, *J. Chem. Soc., Chem. Commun.*, 1995, 1447.
4 A. J. Blake, P. J. Dyson, R. C. Gash, B. F. G. Johnson and P. Trickey, *J. Chem. Soc., Dalton Trans.*, 1994, 1105.
5 See, for example, P. J. Bailey, A. J. Blake, P. J. Dyson, B. F. G. Johnson, J. Lewis and E. Parisini, *J. Organomet. Chem.*, 1993, **452**, 175; J. R. Galsworthy, C. E. Housecroft, D. M. Matthews, R. Ostrander and A. L. Rheingold, *J. Chem. Soc., Dalton Trans.*, 1994, 69; T. Adatia, H. Curtis, B. F. G. Johnson, J. Lewis, M. McPartlin and J. Morris, *J. Chem. Soc., Dalton Trans.*, 1994, 243; 1109; J. R. Galsworthy, C. E. Housecroft, A. J. Edwards and P. R. Raithby, *J. Chem. Soc.*, Dalton Trans., 1995, 2935; J. E. Davies, S. Nahar, P. R. Raithby and G. P. Shields, *J. Chem. Soc.*, Dalton Trans., 1997, 13.
6 A. J. Blake, J. L. Haggitt, B. F. G. Johnson and S. Parsons, *J. Chem. Soc., Dalton Trans.*, 1997, 991.
7 H. Wadepohl, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 247; D. Braga, P. J. Dyson, F. Grepioni and B. F. G. Johnson, *Chem. Rev.*, 1994, **94**, 1585.
8 A. J. Blake, P. J. Dyson, B. F. G. Johnson, C. M. Martin, J. G. M. Mairn, E. Parisini and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1993, 981; A. J. Edwards, M. A. Gallop, B. F. G. Johnson, J. U. Köhler, J. Lewis and P. R. Raithby, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1093.
9 M. P. Goméz-Sal, B. F. G. Johnson, J. Lewis, P. R. Raithby and A. H. Wright, *J. Chem. Soc., Chem. Commun.*, 1985, 1682.
10 J. Lewis, C.-K. Li, P. R. Raithby and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1993, 999.
11 J. Lewis, C.-K. Li, M. C. Ramirez de Arellano, P. R. Raithby and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1993, 1359; J. Lewis, C.-K. Li, C. A. Morewood, M. C. Ramirez de Arellano, P. R. Raithby and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1994, 2159.
12 M. A. Gallop, Ph.D. Thesis, University of Cambridge, 1987.
13 J. Lewis, C. A. Morewood, P. R. Raithby and M. C. Ramirez de Arellano, *J. Chem. Soc., Dalton Trans.*, 1996, 4509.
14 B. F. G. Johnson, J. Lewis, M. McPartlin, W. J. H. Nelson, S. W. Sankey and K. Wong, *J. Organomet. Chem.*, 1993, **452**, 175.
15 B. F. G. Johnson, J. Lewis, J. N. Nicholls, M. McPartlin, W. J. H. Nelson, J. Puga, P. R. Raithby, M. J. Rosales, M. Schröder and M. Vargas, *J. Chem. Soc., Dalton Trans.*, 1983, 2447.
16 D. Braga, F. Grepioni, B. F. G. Johnson, H. Chen and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1991, 2559; L. J. Farrugia, *Acta Crystallogr., Sect. C*, 1988, **44**, 997.
17 G. B. Ansell and J. S. Bradley, *Acta Crystallogr., Sect. B*, 1980, **36**, 726.

18 P. J. Dyson, B. F. G. Johnson, J. Lewis, M. Martinelli, D. Braga and F. Grepioni, *J. Am. Chem. Soc.*, 1993, **115**, 9062; P. J. Bailey, D. Braga, P. J. Dyson, F. Grepioni, B. F. G. Johnson, J. Lewis, P. R. Raithby, P. Sabatino and D. Stalke, *J. Chem. Soc., Dalton Trans.*, 1993, 985.
19 D. Braga, F. Grepioni, P. J. Dyson, B. F. G. Johnson, P. Frediani, M. Bianchi and F. Piacenti, *J. Chem. Soc., Dalton Trans.*, 1992, 2565.
20 R. K. Henderson, P. A. Jackson, B. F. G. Johnson, J. Lewis and P. R. Raithby, *Inorg. Chim. Acta*, 1992, **198–200**, 393.
21 R. J. Goudsmit, B. F. G. Johnson, J. Lewis, P. R. Raithby and K. H. Whitmire, *J. Chem. Soc., Chem. Commun.*, 1983, 246.
22 R. Buntem, J. Lewis, C. A. Morewood, P. R. Raithby and M. C. Ramirez de Arellano, unpublished work.
23 C. J. Adams, M. I. Bruce, B. W. Skelton and A. H. White, *J. Cluster. Sci.*, 1994, **3**, 419.
24 T. P. Gill and K. R. Mann, *Organometallics*, 1982, **1**, 485.
25 SHELXTL PLUS, PC Release 4.0, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1990.
26 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.

Received 25*th April* 1997; *Paper* 7/02837G