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Syntheses and structures of methyl-, acetyl- and allyl-ruthenium carbidocarbonyl clusters

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Abstract

Reaction of the dianionic ruthenium carbidocarbonyl cluster $[PPN]_2[Ru_6C(CO)_{16}]$ (PPN = $(PPh_3)_2N$) (**1**) with methyl iodide at 120 °C proceeds with retention of the octahedral metal framework and gives the methyl cluster $[PPN][Ru_6C(CO)_{16}(CH_3)]$ (**3**). Treatment of **3** with CO (50 atm) at room temperature gives the acetyl cluster $[PPN][Ru_6C(CO)_{16}(COCH_3)]$ (**6**). Reaction of **1** with allyl bromide at 85 °C gives the allyl cluster $[PPN][Ru_6C(CO)_{15}(C_3H_5)]$ (**7**) in which the allyl ligand coordinates to one of the edges of the metal octahedron in μ,η^3-manner. The structures of these clusters were unequivocally determined by X-ray diffraction. **3**: monoclinic, space group $P2_1/n$, a 18.785(4), b 17.762(5), c 17.085(4) Å, β 94.42(2)°, $Z = 4$; $R = 0.059$, $R_w = 0.050$ for 5937 unique observed reflections. **6**: monoclinic, $P2_1/n$ (isomorphous with **3**), a 18.965(5), b 17.646(7), c 17.366(5) Å, β 94.79(3)°, $Z = 4$; $R = 0.069$, $R_w = 0.040$ for 7156 unique observed reflections. **7**: monoclinic, $P2_1/a$, a 19.343(3), b 19.099(3), c 15.802(3) Å, β 98.50(2)°, $Z = 4$; $R = 0.054$, $R_w = 0.031$ for 6304 unique observed reflections.

Introduction

Metal carbonyls belong to an important class of organometallic compounds. Mono- and di-nuclear metal carbonyls have been often employed as useful reagents for organic synthesis and as important homogeneous catalysts for industrial use. In order to elucidate the reaction mechanisms and to improve their functions, many investigations on synthesis, structure, and reactivity of organic derivatives of metal carbonyls have been made.

Polynuclear metal carbonyl clusters have also drawn much attention as a possible new source of homogeneous catalysts exhibiting high selectivity, because they can induce reactivity into a ligand through multicenter bonding that differs significantly from that produced by mononuclear coordination. However little so far is known about such specific cluster catalysts [1]. Inability of metal clusters to act as specific

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catalysts may be attributed to facile degradation of the metal cluster framework under reaction conditions which results from the inherent weakness of metal–metal bonds. To overcome this problem and to achieve homogeneous metal cluster catalysis, we believe, that it is necessary to study systematically the synthesis, structure and reactivity of organic derivatives of stable metal clusters. There is a rather extensive chemistry of trinuclear ruthenium and osmium carbonyl clusters which has been done along this line [2–6]. However, such studies of high nuclearity metal carbonyl clusters are rare [7].

There are only few examples of alkyl derivatives of high-nuclearity metal clusters. Alkyl derivatives of hexanuclear molybdenum and tungsten clusters were prepared by the alkylation of the corresponding chloro complexes with trialkylaluminum [8,9]. A methyl derivative of a mixed-metal cluster was also prepared through a capping reaction of a heptarhenium cluster by a mononuclear methyl platinum complex, recently [10].

We are interested in the use of clusters having encapsulated elements in the cavity of metal polyhedra for the synthesis of alkyl derivatives of high-nuclearity metal clusters, because the interstitial elements are expected to support weak metal–metal bonds from the inside of the metal skeleton without disturbing the coordination of organic ligands and thus make it possible to study reactions on the cluster "surface". The dianion, $[Ru_6C(CO)_{16}]^{2-}$, has been known since 1980 [11,12] and can be prepared in a high yield starting from readily accessible $Ru_3(CO)_{12}$ and sodium [13].

We have examined the reaction of the dianion $[Ru_6C(CO)_{16}]^{2-}$ with carbon electrophiles in order to obtain organic derivatives, because the reaction of a metal complex anion with carbon electrophiles has been known as one of the general methods for the preparation of metal–carbon bonds in the field of the chemistry of mononuclear metal complexes [14]. We wish to report here the syntheses and the structures of methyl, acetyl, and allyl derivatives of hexanuclear ruthenium carbidocarbonyls.

Results and discussion

Synthesis of a methylruthenium carbidocarbonyl cluster

The reaction of $[PPN]_2[Ru_6C(CO)_{16}]$ (**1**) ($PPN = (Ph_3P)_2N$) with neat methyl iodide at 120 °C for 1 h followed by chromatography on alumina afforded air-stable deep-red crystals. The IR spectrum of the product showed a strong absorption at 2011 cm^{-1} in the $\nu(C{=}O)$ region. This may imply that the product is monoanionic, because the frequency shows an intermediate value between those of dianion $[Et_4N]_2[Ru_6C(CO)_{16}]$ (1978 cm^{-1}) [13] and neutral complex $Ru_6C(CO)_{17}$ (**2**) (2064 and 2049 cm^{-1}) [15]. The ^1H NMR spectrum of the product showed a singlet at δ 1.01 attributable to the methyl protons. On the bases of these spectroscopic data and the elemental analysis, the complex was considered to be the methyl hexaruthenium carbidocarbonyl cluster $[PPN][Ru_6C(CO)_{16}(CH_3)]$ (**3**).

In order to elucidate the exact molecular structure of **3** the single-crystal X-ray analysis was undertaken. The structure is shown in Fig. 1. The selected interatomic distances and angles are presented in Tables 1 and 2, respectively.

The metal framework geometry of **1** is maintained in **3**. The metal–metal distances in **3** range from 2.854(2) to 2.999(2) Å, and a carbonyl bridged Ru(2)–Ru(3)

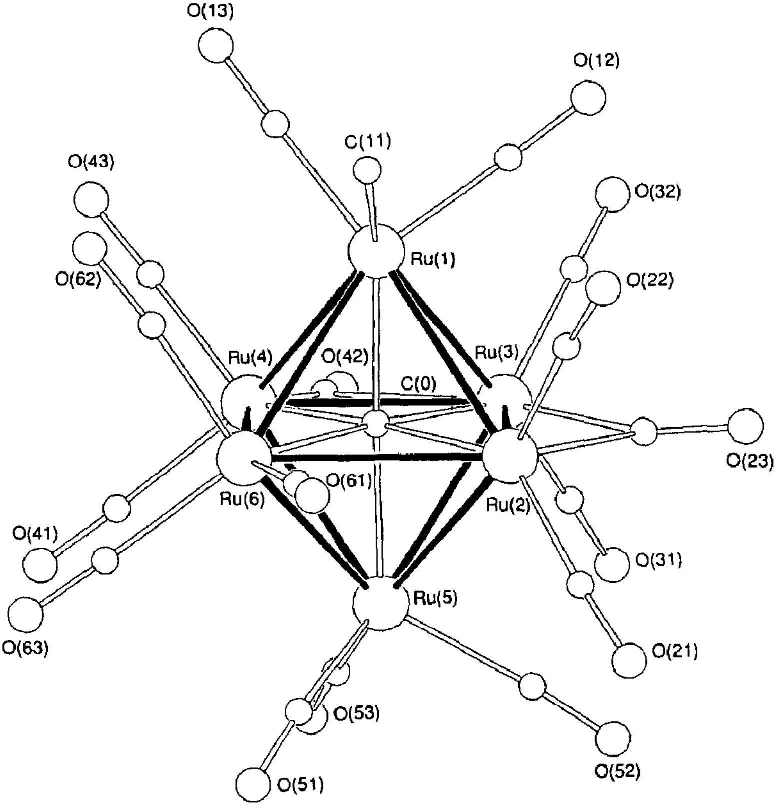

Fig. 1. The molecular structure of $[Ru_6C(CO)_{16}(CH_3)]^-$ (anion of 3) with the numbering of the oxygen atoms corresponding to that of the relevant carbonyl carbon atoms. The first digit of each oxygen number is the number of the ruthenium atom to which the carbonyl is attached.

edge is 2.859(2) Å, which is the second shortest metal–metal bond length in this cluster. The average unbridged metal–metal distance is 2.903 Å, which is similar to those of **2** (2.907 Å) [16], $[Me_4N]_2[Ru_6C(CO)_{16}]$ (**4**) (2.90(10) Å) [17], and

Table 1

Selected interatomic distances (Å) and esd values for $[PPN][Ru_6C(CO)_{16}(CH_3)]$ (3)

Ru(1)–Ru(2)	2.899(2)	Ru(3)–C(0)	2.081(12)
Ru(1)–Ru(3)	2.971(2)	Ru(4)–C(0)	2.060(13)
Ru(1)–Ru(4)	2.968(2)	Ru(5)–C(0)	2.102(12)
Ru(1)–Ru(6)	2.916(2)	Ru(6)–C(0)	2.027(12)
Ru(2)–Ru(3)	2.859(2)	Ru(1)–C(11)	2.194(12)
Ru(2)–Ru(5)	2.859(2)	Ru(2)–C(23)	2.052(13)
Ru(2)–Ru(6)	2.999(2)	Ru(3)–C(23)	2.160(13)
Ru(3)–Ru(4)	2.879(2)	Ru(3)–C(42)	2.646(16)
Ru(3)–Ru(5)	2.860(2)	Ru(4)–C(42)	1.930(13)
Ru(4)–Ru(5)	2.891(2)	Ru(6)–C(61)	1.842(16)
Ru(4)–Ru(6)	2.854(2)	O(23)–C(23)	1.153(16)
Ru(5)–Ru(6)	2.883(2)	O(42)–C(42)	1.128(17)
Ru(1)–C(0)	2.016(12)	O(61)–C(61)	1.150(19)
Ru(2)–C(0)	2.039(13)		

Table 2

Selected interatomic angles (deg) and esd values for [PPN][$Ru_6C(CO)_{16}(CH_3)$] (**3**)

C(0)–Ru(1)–C(11)	128.5(5)	C(0)–Ru(4)–C(43)	130.5(6)
C(0)–Ru(1)–C(12)	122.3(7)	C(41)–Ru(4)–C(42)	103.1(5)
C(0)–Ru(1)–C(13)	134.0(6)	C(41)–Ru(4)–C(43)	89.2(6)
C(11)–Ru(1)–C(12)	84.6(6)	C(42)–Ru(4)–C(43)	92.0(7)
C(11)–Ru(1)–C(13)	80.8(6)	C(0)–Ru(5)–C(51)	118.4(6)
C(12)–Ru(1)–C(13)	91.1(7)	C(0)–Ru(5)–C(52)	119.2(5)
C(0)–Ru(2)–C(21)	139.5(5)	C(0)–Ru(5)–C(53)	126.0(5)
C(0)–Ru(2)–C(22)	124.8(5)	C(51)–Ru(5)–C(52)	96.3(6)
C(0)–Ru(2)–C(23)	95.5(5)	C(51)–Ru(5)–C(53)	98.0(6)
C(21)–Ru(2)–C(22)	91.5(6)	C(52)–Ru(5)–C(53)	92.3(6)
C(21)–Ru(2)–C(23)	97.1(6)	C(0)–Ru(6)–C(61)	113.5(6)
C(22)–Ru(2)–C(23)	96.9(6)	C(0)–Ru(6)–C(62)	111.9(6)
C(0)–Ru(3)–C(23)	91.1(5)	C(0)–Ru(6)–C(63)	138.9(5)
C(0)–Ru(3)–C(31)	133.9(5)	C(61)–Ru(6)–C(62)	97.6(7)
C(0)–Ru(3)–C(32)	135.1(6)	C(61)–Ru(6)–C(63)	95.8(7)
C(0)–Ru(3)–C(42)	86.1(4)	C(62)–Ru(6)–C(63)	90.8(7)
C(23)–Ru(3)–C(31)	93.4(6)	Ru(2)–C(23)–Ru(3)	85.5(5)
C(23)–Ru(3)–C(32)	97.7(5)	Ru(2)–C(23)–O(23)	139.9(11)
C(23)–Ru(3)–C(42)	172.9(5)	Ru(3)–C(23)–O(23)	134.4(11)
C(31)–Ru(3)–C(32)	89.6(6)	Ru(3)–C(42)–Ru(4)	76.2(5)
C(31)–Ru(3)–C(42)	83.8(6)	Ru(3)–C(42)–O(42)	121.4(10)
C(32)–Ru(3)–C(42)	88.8(5)	Ru(4)–C(42)–O(42)	162.4(13)
C(0)–Ru(4)–C(41)	125.9(5)	Ru(6)–C(61)–O(61)	169.1(14)
C(0)–Ru(4)–C(42)	109.3(6)		

[Ph_4As]$_2$[$Ru_6C(CO)_{16}$] (**5**) (2.89 Å) [12]. The difference in the negative charges on the clusters does not affect the metal–metal bond lengths. Consequently, the metal–carbide bonds in **3** (mean 2.054 Å) are equivalent in length to the corresponding ones in **2**, **4**, and **5**.

There are sixteen carbonyl ligands in **3**. One carbonyl ligand, C(23)O(23), asymmetrically bridges the Ru(2)–Ru(3) edge, with the shorter metal–carbon bond lengths (2.05(1) Å) to Ru(2) atom and the longer metal–carbon interaction (2.16(1) Å) to Ru(3) atom. Another carbonyl ligand, C(42)O(42), also bridges the Ru(3)–Ru(4) edge, but highly asymmetrically (Ru(3)–C(42), 2.65(2) Å; Ru(4)–C(42), 1.93(1) Å; Ru(4)–C(42)–O(42), 162(1)°). The fourteen remaining carbonyl ligands are terminal with Ru–C distances 1.82(1)–1.97 Å (average 1.90 Å), C–O distances 1.09(2)–1.15(2) Å (average 1.12 Å), and Ru–C–O angles higher than 169°.

There are some differences in the number of bridging carbonyl ligands among **2**, **3**, **4**, and **5**; four for **5**, three for **4**, and only one for **2**, whereas two for **3**. The Ru–C distances of the terminal carbonyl ligands of **3** lie in the range 1.82(1)–1.97(1) Å (mean 1.90 Å); whereas those of the dianionic cluster **4** lie in the range 1.76(3)–1.86(3) Å (mean 1.81 Å). On the other hand, the C–O distances of the terminal carbonyl ligands lie in the range 1.09(2)–1.15(2) Å (mean 1.12 Å) for **3**; whereas those of the dianionic cluster **4** lie in the range 1.153–1.238 Å. Negative charges of the cluster caused the Ru–C distances to shorten and the C–O distances to lengthen. These findings show that an increase in the negative charge on the carbidocarbonyl clusters causes an increase in the metal–CO back bonding interactions without altering the size of metal skeleton.

The methyl group bonds directly to Ru(1) as an η^1-ligand showing no interaction with neighboring ruthenium atoms. The Ru(1)–methyl carbon distance is 2.194(12) Å. Thus cluster **3** presents one of the rare examples of alkyl derivatives of high-nuclearity metal cluster.

For the preparation of **3**, it is necessary to apply relatively severe reaction conditions. Heating of **1** in neat methyl iodide at 100 °C for 1 h resulted in the recovery of **1** almost quantitatively. Low reactivity of the dianion **1** probably explained by the poor nucleophilisity, because the negative charge disperses over the six ruthenium atoms and more probably to the carbonyl oxygen atoms through ruthenium–CO back bonding interactions.

It is well-known that the reaction of $[Fe_3(CO)_{11}]^{2-}$ with CH_3SO_3F at room temperature readily afforded the *O*-alkyl derivative $[Fe_3(CO)_{11}(COCH_3)]^-$ [18]. Formation of the same *O*-alkyl derivatives were also known on ruthenium and osmium clusters [19]. Protonation of $[HRu_3(CO)_{11}]^-$ at −60 °C gave *O*-protonated $HRu_3(CO)_{10}(COH)$ as the initial product, but at higher temperatures the rearrangement to $H_2Ru_3(CO)_{11}$ was observed [20]. These examples suggest that the initial electrophilic attack of methyl iodide occurs at a carbonyl oxygen of **1** and that the subsequent migration of the methyl group to the ruthenium skeleton results in the formation of **3**.

Synthesis of an acetylruthenium carbidocarbonyl cluster

The THF solution of **3** was treated with carbon monoxide under pressure (50 atm) at room temperature. Work up of the reaction mixture afforded deep-red crystals. The IR spectrum of the product was similar to that of **3** in the ν(C=O) region; a strong absorption appeared at 2013 cm^{-1} indicating that the product was a monoanionic hexanuclear ruthenium cluster. In addition a weak band at 1662 cm^{-1} was observed and assigned to an acetyl group, because similar weak bands at 1655–1670 cm^{-1} were observed in the cases of $[NMe_4][Rh_6(CO)_{15}(COEt)]$ and $[NMe_4][Rh_6(CO)_{15}(COPr)]$ [21]. The ^1H NMR spectrum of the product showed a singlet at δ 2.54 attributable to the protons of an acetyl group. Thus the complex was assumed to be an acetyl hexanuclear carbidocarbonyl cluster $[PPN][Ru_6C(CO)_{16}(COCH_3)]$ (**6**).

In order to obtain the exact molecular structure of **6** a single-crystal X-ray analysis was undertaken. The cluster **6** was isomorphous and isostructural with **3**, having an acetyl group in place of the methyl group of **3**. The structure is shown in Fig. 2. The selected interatomic distances and angles are presented in Tables 3 and 4, respectively.

The geometry of the metal framework of **3** was maintained during this carbonyl insertion reaction and the six ruthenium atoms of **6** form an octahedron as in **3**. The metal–metal distances (average 2.907 Å) in **6** are essentially the same as those in **3** (average 2.903 Å): the longest metal–metal bond is Ru(4)–Ru(6) and the shortest one is Ru(2)–Ru(3) for both **3** and **6**. The metal–carbide bonds in **6** (average 2.057 Å) are therefore almost equivalent in length to those of **3** (average 2.054 Å).

There are sixteen carbonyl ligands in **6**. Location of the carbonyls is quite the same as that of **3**. The Ru–C distances of the terminal carbonyl ligands lie in the range 1.80(1)–1.92(1) Å (average 1.87 Å), and the C–O distances of the terminal carbonyl ligand lie in the range 1.12(1)–1.18(1) Å (average 1.14 Å); these values are almost the same as those of **3**.

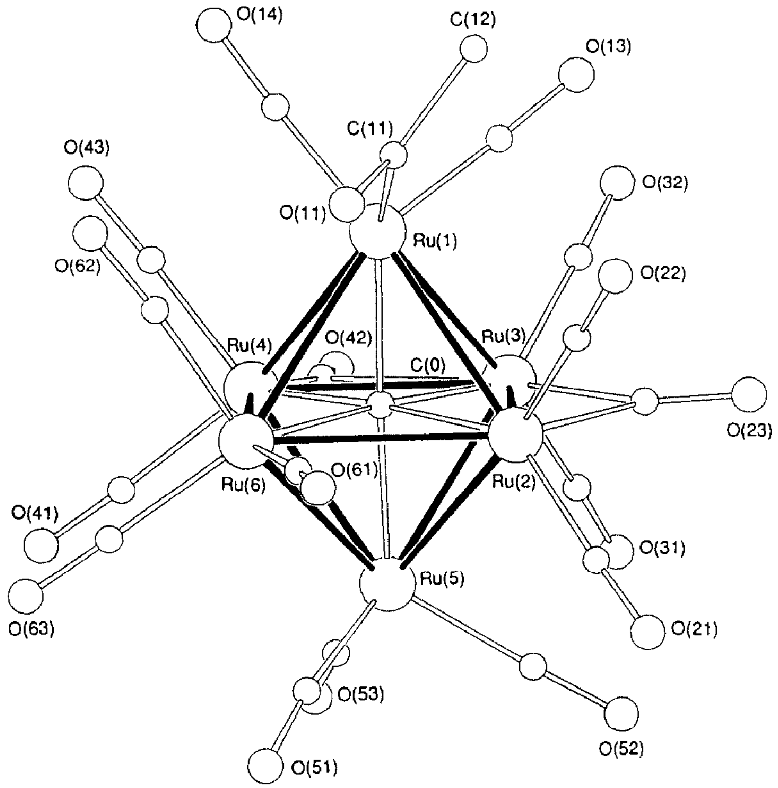

Fig. 2. The molecular structure of $[Ru_6C(CO)_{16}(COCH_3)]^-$ (anion of **6**) showing the atom numbering scheme.

The acetyl group coordinates to one ruthenium atom as in the case of **3**. The Ru(1)–C(11) (2.099(12) Å), C(11)–O(11) (1.204(15) Å), and C(11)–C(12) (1.539(17) Å) distances are practically the same as those calculated using covalent radii of the

Table 3

Selected interatomic distances (Å) and esd values for $[PPN][Ru_6C(COCH_3)]$ (**6**)

Ru(1)–Ru(2)	2.907(2)	Ru(4)–C(0)	2.057(10)
Ru(1)–Ru(3)	2.982(2)	Ru(5)–C(0)	2.095(9)
Ru(1)–Ru(4)	3.001(2)	Ru(6)–C(0)	2.036(9)
Ru(1)–Ru(6)	2.929(1)	Ru(1)–C(11)	2.099(12)
Ru(2)–Ru(3)	2.844(1)	Ru(2)–C(23)	2.018(9)
Ru(2)–Ru(5)	2.854(1)	Ru(3)–C(23)	2.109(10)
Ru(2)–Ru(6)	3.027(1)	Ru(3)–C(42)	2.733(12)
Ru(3)–Ru(4)	2.894(1)	Ru(4)–C(42)	1.929(11)
Ru(3)–Ru(5)	2.859(1)	Ru(6)–C(61)	1.894(11)
Ru(4)–Ru(5)	2.870(2)	O(11)–C(11)	1.204(15)
Ru(4)–Ru(6)	2.837(1)	O(23)–C(23)	1.181(11)
Ru(5)–Ru(6)	2.874(1)	O(42)–C(42)	1.127(14)
Ru(1)–C(0)	2.029(9)	O(61)–C(61)	1.151(14)
Ru(2)–C(0)	2.049(10)	C(11)–C(12)	1.539(17)
Ru(3)–C(0)	2.075(9)		

Table 4

Selected interatomic angles (deg) and esd values for [PPN][$Ru_6C(CO)_{16}(COCH_3)$] (**6**)

C(0)-Ru(1)-C(11)	127.9(4)	C(41)-Ru(4)-C(42)	101.4(4)
C(0)-Ru(1)-C(13)	119.7(4)	C(41)-Ru(4)-C(43)	89.7(4)
C(0)-Ru(1)-C(14)	136.4(4)	C(42)-Ru(4)-C(43)	95.0(5)
C(11)-Ru(1)-C(13)	86.9(5)	C(0)-Ru(5)-C(51)	118.6(4)
C(11)-Ru(1)-C(14)	81.7(5)	C(0)-Ru(5)-C(52)	121.4(4)
C(13)-Ru(1)-C(14)	89.2(5)	C(0)-Ru(5)-C(53)	125.2(4)
C(0)-Ru(2)-C(21)	140.1(4)	C(51)-Ru(5)-C(52)	95.3(5)
C(0)-Ru(2)-C(22)	129.5(5)	C(51)-Ru(5)-C(53)	96.2(4)
C(0)-Ru(2)-C(23)	94.4(4)	C(52)-Ru(5)-C(53)	93.2(5)
C(21)-Ru(2)-C(22)	87.9(5)	C(0)-Ru(6)-C(61)	114.5(4)
C(21)-Ru(2)-C(23)	95.4(4)	C(0)-Ru(6)-C(62)	112.5(4)
C(22)-Ru(2)-C(23)	95.4(5)	C(0)-Ru(6)-C(63)	138.3(4)
C(0)-Ru(3)-C(23)	91.0(4)	C(61)-Ru(6)-C(62)	95.7(5)
C(0)-Ru(3)-C(31)	131.8(4)	C(61)-Ru(6)-C(63)	95.8(5)
C(0)-Ru(3)-C(32)	137.4(4)	C(62)-Ru(6)-C(63)	91.0(4)
C(0)-Ru(3)-C(42)	85.2(3)	Ru(1)-C(11)-O(11)	118.1(8)
C(23)-Ru(3)-C(31)	95.0(4)	Ru(1)-C(11)-C(12)	122.5(9)
C(23)-Ru(3)-C(32)	96.5(4)	O(11)-C(11)-C(12)	118.9(11)
C(23)-Ru(3)-C(42)	174.2(3)	Ru(2)-C(23)-Ru(3)	87.1(4)
C(31)-Ru(3)-C(32)	89.3(5)	Ru(2)-C(23)-O(23)	139.9(8)
C(31)-Ru(3)-C(42)	84.3(4)	Ru(3)-C(23)-O(23)	133.0(8)
C(32)-Ru(3)-C(42)	89.3(4)	Ru(3)-C(42)-Ru(4)	74.5(4)
C(0)-Ru(4)-C(41)	128.0(4)	Ru(3)-C(42)-O(42)	121.7(8)
C(0)-Ru(4)-C(42)	111.2(4)	Ru(4)-C(42)-O(42)	163.6(10)
C(0)-Ru(4)-C(43)	124.9(4)	Ru(6)-C(61)-O(61)	173.1(10)

atoms involved. Thus, the overall structure of **6** is quite the same as that of **3**, except that the methyl group in **3** is replaced with the acetyl group. As far as we know, this is the first example of an η^1-acetyl derivative of a high nuclearity metal cluster which has been characterized by X-ray crystallography, although η^2-acyl derivatives of pentanuclear ruthenium clusters are known [22]. The present study also presents the first well characterized example of insertion of CO to metal–methyl bond in a high-nuclearity metal cluster, even though such an insertion was observed in the case of a triosmium carbonyl cluster [6] and, of course, is very common in the reaction of mononuclear metal-alkyl complexes.

Synthesis of an allylruthenium carbidocarbonyl cluster

A CH_2Cl_2 solution of **1** and allyl bromide was heated at 85 °C in a stainless steel pressure bottle. Work up of the resulting solution afforded deep-red crystals. The IR spectrum of the product showed a strong absorption at 1995 cm^{-1}, suggesting the product was a monoanionic hexanuclear ruthenium cluster. The ^1H NMR spectrum of the product showed the presence of an allyl group (vide infra). On the basis of these data and the elemental analysis the complex was assumed to be an allyl hexanuclear carbidocarbonyl cluster [PPN][$Ru_6C(CO)_{15}(C_3H_5)$] (**7**).

In order to elucidate the exact molecular structure of **7** a single-crystal X-ray analysis was undertaken. The structure of the anionic part of **7** is shown in Fig. 3. The selected interatomic distances and angles are presented in Tables 5 and 6, respectively.

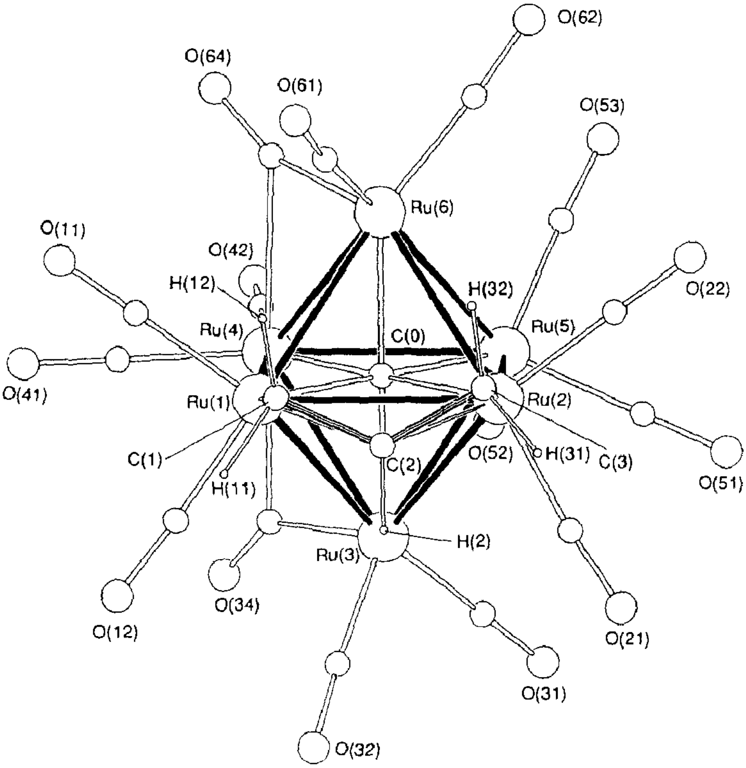

Fig. 3. The molecular structure of $[Ru_6C(CO)_{15}(C_3H_5)]^-$ (anion of 7) showing the atom numbering scheme.

Table 5

Selected interatomic distances (Å) and esd values for $[PPN][Ru_6C(CO)_{15}(C_3H_5)]$ (7)

Ru(1)-Ru(2)	2.954(1)	Ru(1)-C(1)	2.178(8)
Ru(1)-Ru(3)	2.925(1)	Ru(1)-C(2)	2.644(9)
Ru(1)-Ru(4)	2.868(1)	Ru(2)-C(2)	2.514(8)
Ru(1)-Ru(6)	2.904(1)	Ru(2)-C(3)	2.202(8)
Ru(2)-Ru(3)	2.942(1)	Ru(3)-C(34)	2.015(9)
Ru(2)-Ru(5)	2.854(1)	Ru(4)-C(34)	2.130(10)
Ru(2)-Ru(6)	2.910(1)	Ru(4)-C(64)	2.497(10)
Ru(3)-Ru(4)	2.843(1)	Ru(6)-C(64)	1.924(10)
Ru(3)-Ru(5)	2.846(1)	O(34)-C(34)	1.174(12)
Ru(4)-Ru(5)	2.923(1)	O(64)-C(64)	1.173(12)
Ru(4)-Ru(6)	2.895(1)	C(1)-C(2)	1.432(12)
Ru(5)-Ru(6)	2.894(1)	C(2)-C(3)	1.451(13)
Ru(1)-C(0)	2.010(8)	C(1)-H(11)	1.18(8)
Ru(2)-C(0)	2.028(9)	C(1)-H(12)	1.08(8)
Ru(3)-C(0)	2.050(9)	C(2)-H(2)	1.04(8)
Ru(4)-C(0)	2.082(9)	C(3)-H(31)	1.09(8)
Ru(5)-C(0)	2.084(8)	C(3)-H(32)	1.08(9)
Ru(6)-C(0)	2.041(9)		

Table 6

Selected interatomic angles (deg) and esd values for [PPN][$Ru_6C(CO)_{15}(C_3H_5)$] (7)

Ru(2)-Ru(1)-C(1)	82.3(2)	C(0)-Ru(3)-C(34)	95.4(4)
Ru(2)-Ru(1)-C(2)	53.0(2)	C(31)-Ru(3)-C(32)	90.0(4)
C(0)-Ru(1)-C(1)	124.3(3)	C(31)-Ru(3)-C(34)	96.1(4)
C(0)-Ru(1)-C(2)	96.2(3)	C(32)-Ru(3)-C(34)	99.4(4)
C(0)-Ru(1)-C(11)	127.6(4)	C(0)-Ru(4)-C(34)	91.1(3)
C(0)-Ru(1)-C(12)	125.8(4)	C(0)-Ru(4)-C(41)	129.2(3)
C(1)-Ru(1)-C(2)	32.8(3)	C(0)-Ru(4)-C(42)	139.9(4)
C(1)-Ru(1)-C(11)	86.4(3)	C(0)-Ru(4)-C(64)	85.8(3)
C(1)-Ru(1)-C(12)	90.5(4)	C(34)-Ru(4)-C(41)	88.0(4)
C(2)-Ru(1)-C(11)	118.6(3)	C(34)-Ru(4)-C(42)	94.7(4)
C(2)-Ru(1)-C(12)	96.1(3)	C(34)-Ru(4)-C(64)	176.8(3)
C(11)-Ru(1)-C(12)	90.2(4)	C(41)-Ru(4)-C(42)	90.7(4)
Ru(1)-Ru(2)-C(2)	57.2(2)	C(41)-Ru(4)-C(64)	93.5(3)
Ru(1)-Ru(2)-C(3)	87.3(2)	C(42)-Ru(4)-C(64)	88.1(4)
C(0)-Ru(2)-C(2)	99.9(3)	C(0)-Ru(5)-C(51)	121.0(4)
C(0)-Ru(2)-C(3)	128.1(3)	C(0)-Ru(5)-C(52)	122.3(4)
C(0)-Ru(2)-C(21)	121.9(4)	C(0)-Ru(5)-C(53)	125.7(4)
C(0)-Ru(2)-C(22)	125.7(4)	C(51)-Ru(5)-C(52)	95.8(4)
C(2)-Ru(2)-C(3)	35.1(3)	C(51)-Ru(5)-C(53)	92.7(5)
C(2)-Ru(2)-C(21)	90.3(3)	C(52)-Ru(5)-C(53)	91.1(4)
C(2)-Ru(2)-C(22)	117.6(3)	C(0)-Ru(6)-C(61)	120.2(4)
C(3)-Ru(2)-C(21)	90.3(4)	C(0)-Ru(6)-C(62)	138.4(4)
C(3)-Ru(2)-C(22)	82.9(3)	C(0)-Ru(6)-C(64)	104.2(4)
C(21)-Ru(2)-C(22)	97.1(4)	C(61)-Ru(6)-C(62)	90.6(4)
C(0)-Ru(3)-C(31)	130.2(4)	C(61)-Ru(6)-C(64)	98.9(4)
C(0)-Ru(3)-C(32)	135.1(4)	C(62)-Ru(6)-C(64)	96.9(4)
Ru(1)-C(1)-C(2)	91.8(5)	C(1)-C(2)-H(2)	114.5(44)
Ru(1)-C(1)-H(11)	103.1(41)	C(3)-C(2)-H(2)	117.4(45)
Ru(1)-C(1)-H(12)	114.0(40)	Ru(2)-C(3)-C(2)	84.3(5)
C(2)-C(1)-H(11)	100.6(42)	Ru(2)-C(3)-H(31)	101.2(40)
C(2)-C(1)-H(12)	121.6(42)	Ru(2)-C(3)-H(32)	111.5(42)
H(11)-C(1)-H(12)	120.8(56)	C(2)-C(3)-H(31)	102.5(42)
Ru(1)-C(2)-Ru(2)	69.8(21)	C(2)-C(3)-H(32)	112.9(46)
Ru(1)-C(2)-C(1)	55.4(43)	H(31)-C(3)-H(32)	133.3(64)
Ru(1)-C(2)-C(3)	120.3(5)	Ru(3)-C(34)-Ru(4)	86.6(4)
Ru(1)-C(2)-H(2)	106.7(45)	Ru(3)-C(34)-O(34)	139.5(8)
Ru(2)-C(2)-C(1)	118.0(6)	Ru(4)-C(34)-O(34)	133.9(7)
Ru(2)-C(2)-C(3)	60.7(4)	Ru(4)-C(64)-Ru(6)	80.7(3)
Ru(2)-C(2)-H(2)	106.6(40)	Ru(4)-C(64)-O(64)	124.4(8)
C(1)-C(2)-C(3)	125.5(8)	Ru(6)-C(64)-O(64)	154.9(9)

The metal framework geometry in **1** was again maintained during this reaction and the six ruthenium atoms of **7** form an octahedron. The metal-metal distances range from 2.843(1) (Ru(3)-Ru(4)) to 2.954(1) Å (Ru(1)-Ru(2)), and these values are almost the same as those in **2**, **3**, **4**, **5**, and **6**. The shortest edge is bridged by a carbonyl ligand, and the longest edge is bridged by the allyl ligand. The central carbide atom lies at a center of the octahedron but slightly moved toward the edge coordinated by the allyl ligand thus making Ru(1)-carbide (2.010(8) Å) and Ru(2)-carbide (2.028(9) Å) the shortest two, and Ru(4)-carbide (2.082(9) Å) and Ru(5)-carbide (2.084(8) Å) the longest two. There are fifteen carbonyl ligands in **7**. Two carbonyl ligands asymmetrically bridge the Ru(3)-Ru(4) and Ru(4)-Ru(6) edges; in both cases the longer metal–carbon interactions are with Ru(4). The thirteen remaining carbonyl ligands are terminal with Ru–C–O angles higher than 174°. The Ru–C and C–O distances of the terminal carbonyl ligands (Ru–C 1.794(8)–1.894(10) Å, average 1.82 Å; C–O 1.13(1)–1.19(1) Å, average 1.16 Å) are almost the same as those in **3** and **6**.

Cluster **7** is the first example of a μ,η^3-allylruthenium cluster of high nuclearity, although a simple η^3-allyl cluster $[PPh_4][Rh_6(CO)_{14}(\eta^3\text{-}C_3H_5)]$ [23] and mixed-metal allyl clusters $[Et_4N]_2[Re_7C(CO)_{21}Pd(\eta^3\text{-}CH_2CHCHC_6H_5)]$ [24] and $[Ph_4As]_2[Re_7C(CO)_{21}Pd(C_3H_5)]$ [10] have been reported. There are precedents for μ,η^3-allyl bonding in dinuclear palladium complexes [25,26]. The terminal carbon atoms C(1) and C(3) in **7** are bound to Ru(1) and Ru(2), respectively, and the central carbon atom C(2) is bound to each ruthenium atom with longer distances (2.644(9), and 2.514(8) Å). The central carbon atom C(2) lies 0.134(9) Å above the Ru(1)–Ru(2)–Ru(5)–Ru(4) mean plane, and the terminal carbon atoms C(1) and C(3) lie 0.465(9) and 0.587(9) Å below the plane, respectively. The C(1)–C(2)–C(3) plane is almost perpendicular to the mean Ru(1)–Ru(2)–Ru(5)–Ru(4) plane (dihedral angle 90.5(9)°). All of the hydrogen atoms bind to the allyl group lie 0.10(9)–0.56(9) Å above the C(1)–C(2)–C(3) plane away from the ruthenium atoms.

The ^1H NMR spectrum of **7** showed a doublet of doublets of doublets at δ 3.91 (J_{gem} 1.83 Hz, J_{cis} 7.02 Hz, and $^4J_{trans}$ 1.22 Hz) attributable to the *syn*-hydrogens, a triplet of triplets at δ 1.44 (J_{cis} 7.02 Hz and J_{trans} 12.21 Hz) attributable to the central hydrogen, and a doublet of doublets of doublets at δ 0.43 (J_{gem} 1.83 Hz, J_{trans} 12.21 Hz, and $^4J_{trans}$ 1.22 Hz) attributable to the *anti*-hydrogens.

The spectrum is interpreted on the basis of an AMM′XX′ spin system, and is not consistent with the solid-state structure of **7**. This suggests that the CO ligand scrambling probably involving the two bridging carbonyls occurs in solution.

An analogous 2-methylallyl derivative $[PPN][Ru_6C(CO)_{15}(C_4H_7)]$ (**8**) was prepared by the same procedure employed for **7**. The IR spectrum of this compound was the same as that of **7** in the ν(C=O) region. The ^1H NMR spectrum showed a typical pattern of a symmetrical η^3-2-methylallyl group: δ 4.14 (t, $J_{gem} = {}^4J_{trans} =$ 1.22 Hz, *syn*-H), 1.26 (s, CH_3), and 0.68 (t, $J_{gem} = {}^4J_{trans} =$ 1.22 Hz, *anti*-H). Similarities of the chemical shifts of *syn*- and *anti*-protons and the coupling constants to those of **7** suggests the μ,η^3-type coordination of 2-methylallyl ligand in **8**.

Experimental

$[PPN]_2[Ru_6C(CO)_{16}]$ [13] was prepared according to the reported methods. 2-Methylallyl bromide was prepared by halogen exchange reaction from 2-methylallyl chloride according to the literature [27]. Methyl iodide, allyl bromide, and solvents were used as received. All the reactions and subsequent procedures were carried out under argon. IR and ^1H NMR spectra were recorded on a Jasco A-202 spectrophotometer and a Jeol GSX-500 spectrometer, respectively.

Preparation of $[PPN][Ru_6C(CO)_{16}(CH_3)]$ (3)

Cluster **1** (100 mg, 0.047 mmol) was dissolved in neat methyl iodide and placed in a stainless pressure vessel equipped with an inner glass tube. The solution was heated at 120°C for 1 h, then the methyl iodide was removed under reduced pressure. The residue was subjected to an alumina (5% water) column chromatography (1.5 cm i.d. ×20 cm), eluting with benzene/dichloromethane (1/1 v/v). The eluate was evaporated to dryness and the residue was crystallized from methanol to give air-stable deep-red crystals of [PPN][$Ru_6C(CO)_{16}(CH_3)$] (30 mg, 0.0185 mmol, 40%). IR (CH_2Cl_2): ν(C=O) 2069w, 2045sh, 2011s, 1960w, and 1808m(br) cm^{-1}. ^1H NMR (acetone-d_6): δ 7.5–7.9 (30H, m, phenyl) and δ 1.10 (3H, s, CH_3). Anal. Found: C, 39.82; H, 2.04; N, 0.85. $C_{54}H_{33}NO_{16}P_2Ru_6$ calcd.: C, 40.03; H, 2.05; N, 0.86%.

Table 7

Crystal data and refinement details

	3	6	7
formula	$C_{54}H_{33}NO_{16}P_2Ru_6$	$C_{55}H_{33}NO_{17}P_2Ru_6$	$C_{55}H_{35}NO_{15}P_2Ru_6$
f_w	1620.22	1648.23	1618.25
crystal system	monoclinic	monoclinic	monoclinic
space group (No.)	$P2_1/n$ (14)	$P2_1/n$ (14)	$P2_1/a$ (14)
a, Å	18.785(4)	18.965(5)	19.343(3)
b, Å	17.762(5)	17.646(7)	19.099(3)
c, Å	17.085(4)	17.366(5)	15.802(3)
β, deg	94.42(2)	94.79(3)	98.50(2)
cell volume, $Å^3$	5684(2)	5791(3)	5774(2)
Z	4	4	4
D_{calcd}, g cm^{-3}	1.894	1.904	1.869
D_{measd}, g cm^{-3}	1.899	1.900	1.863
systematic absences	$h0l$, $h+l$ odd $0k0$, k odd	$h0l$, $h+l$ odd $0k0$, k odd	$h0l$, h odd $0k0$, k odd
temperature, °C	21	21	21
crystal size (mm)	0.22×0.30×0.42	0.12×0.26×0.32	0.21×0.32×0.37
λ(Mo-K_α), Å	0.71073	0.71073	0.71073
2θ limit, deg	55	55	55
scan method	ω ($2\theta \leq 30°$) $2\theta-\omega$ ($2\theta \geq 30°$)	ω ($2\theta \leq 30°$) $2\theta-\omega$ ($2\theta \geq 30°$)	ω ($2\theta \leq 30°$) $2\theta-\omega$ ($2\theta \geq 30°$)
scan range (ω), deg	1.2+0.35 tan θ	1.2+0.35 tan θ	1.2+0.35 tan θ
scan rate (2θ), deg min^{-1}	4	4	
collection region	$\pm h$, $+k$, $+l$	$\pm h$, $+k$, $+l$	$\pm h$, $+k$, $+l$
bkgd time at each side, s	5	5	5
reflections measured	14225	14175	14183
unique obsd reflections	5937	7156	6304
criterion for obsd F	$\geq 3\sigma$	$\geq 3\sigma$	$\geq 3\sigma$
no. of parameters	713	731	733
data/parameters	8.33	9.79	8.60
linear abs coeff μ, cm^{-1}	16.47	16.19	16.20
$F(000)$, e	3144	3200	3168
correction applied	Lz	Lz	Lz
correction made	no	no	no
decay	negligible	negligible	negligible
R, R_w ^{a}	0.059, 0.050	0.069, 0.040	0.054, 0.031
GOF ^{b}	3.27	2.38	1.44
mean shift/esd max, final cycle	0.201	0.421	0.363
$\delta\rho_{map}$, e $Å^{-3}$	1.81	0.97	1.00

^{a} $w = 1/\sigma^2(F_o)$. ^{b} $[\Sigma w(F_o - F_c)^2/(N_{obsd} - N_{param})]^{1/2}$.

Table 8

Atomic coordinates ($\times 10^5$) and equivalent temperature factors (Å^2) for [PPN][$Ru_6C(CO)_{16}(CH_3)$] (**3**) with esd values in parentheses

Atom	x	y	z	B_{eq} ^{a}
Ru(1)	11268(6)	93340(8)	14851(7)	4.2
Ru(2)	12763(6)	77528(8)	18850(7)	4.3
Ru(3)	4144(6)	86665(8)	28147(7)	4.3
Ru(4)	15770(6)	97035(7)	31436(7)	4.0
Ru(5)	17625(6)	81153(7)	34672(7)	4.2
Ru(6)	24886(6)	88289(8)	22388(7)	4.3
P(1)	−14985(19)	48047(23)	19293(22)	3.8
P(2)	−9495(20)	35836(24)	30116(22)	4.1
O(12)	−3171(58)	91744(81)	6536(69)	11.7
O(13)	11685(59)	109666(56)	9998(62)	7.7
O(21)	16481(63)	60938(63)	20664(68)	9.5
O(22)	9917(65)	75419(69)	1224(55)	9.3
O(23)	−2443(48)	72410(59)	20311(60)	6.8
O(31)	−1872(58)	80358(65)	42354(62)	8.4
O(32)	−9958(50)	94100(64)	23269(67)	8.4
O(41)	28152(49)	100226(63)	43578(57)	7.0
O(42)	3626(48)	100661(63)	41443(55)	6.8
O(43)	15983(63)	113314(60)	26947(65)	9.1
O(51)	32636(51)	74966(66)	37612(64)	8.4
O(52)	10533(58)	66193(62)	37947(63)	8.3
O(53)	16673(60)	85748(62)	51731(54)	7.8
O(61)	30411(54)	77134(66)	11327(62)	8.1
O(62)	28027(53)	101837(68)	12573(69)	9.2
O(63)	39634(56)	90300(82)	31224(71)	11.5
N	−9914(54)	41663(64)	23120(61)	4.7
C(0)	14471(62)	87498(77)	24611(64)	3.1
C(11)	14919(76)	92243(84)	3014(66)	4.9
C(12)	2248(75)	92284(102)	9860(102)	8.3
C(13)	11481(83)	103600(70)	12083(86)	5.7
C(21)	15452(76)	67168(74)	19871(81)	5.3
C(22)	10899(81)	76517(83)	7773(76)	5.4
C(23)	2415(66)	76284(76)	21699(81)	4.3
C(31)	371(75)	82992(95)	36894(83)	6.8
C(32)	−4866(71)	91368(83)	25024(91)	5.8
C(41)	23622(66)	98982(77)	39303(76)	4.2
C(42)	7433(65)	98437(97)	37205(80)	5.9
C(43)	15883(92)	107216(70)	28577(91)	7.4
C(51)	27242(73)	77351(99)	35842(91)	6.9
C(52)	12931(72)	71560(81)	36375(81)	5.3
C(53)	16873(77)	84229(77)	45338(71)	4.8
C(61)	27735(82)	80955(90)	15678(86)	7.4
C(62)	26601(79)	96642(89)	16105(90)	7.1
C(63)	34271(71)	89518(98)	28197(92)	7.0
C(A1)	−18662(64)	54701(74)	26228(67)	3.6
C(A2)	−24604(69)	52172(90)	30105(71)	5.1
C(A3)	−27298(77)	57244(87)	35531(81)	5.8
C(A4)	−23973(82)	64366(95)	36749(81)	6.7
C(A5)	−17935(80)	66633(94)	32958(84)	6.7
C(A6)	−15105(71)	61634(85)	27429(81)	5.4
C(B1)	−22596(69)	44176(73)	13020(70)	4.0
C(B2)	−21203(78)	37113(85)	9422(78)	5.5
C(B3)	−26759(85)	34122(89)	4134(85)	6.7

Table 8 (continued)

Atom	x	y	z	B_{eq} [a]
C(B4)	−33223(77)	38012(97)	3170(81)	6.6
C(B5)	−34615(75)	44742(95)	6916(79)	6.3
C(B6)	−29070(69)	48132(95)	11946(79)	5.8
C(C1)	−9798(67)	53469(80)	12796(70)	4.1
C(C2)	−13410(74)	58854(85)	8033(79)	5.3
C(C3)	−9414(85)	63008(98)	2916(83)	7.3
C(C4)	−1984(88)	61584(93)	2630(84)	7.3
C(C5)	1318(78)	56374(91)	7512(85)	6.3
C(C6)	−2423(71)	52018(86)	12930(75)	5.0
C(D1)	−7092(70)	26559(76)	26255(78)	4.7
C(D2)	−8880(73)	20126(84)	30742(91)	6.0
C(D3)	−6769(76)	13052(93)	27706(93)	6.7
C(D4)	−3281(76)	12750(96)	20752(93)	6.9
C(D5)	−1455(81)	19252(92)	16794(84)	6.4
C(D6)	−3596(75)	26404(95)	19297(84)	6.5
C(E1)	−17635(66)	34574(74)	35170(72)	3.8
C(E2)	−18079(77)	37393(80)	42768(80)	5.3
C(E3)	−24623(79)	36531(93)	46315(84)	6.2
C(E4)	−30305(72)	32686(85)	42427(83)	5.4
C(E5)	−29490(68)	30048(84)	34876(81)	5.0
C(C6)	−23245(68)	30693(82)	31127(77)	4.7
C(F1)	−2122(65)	38807(79)	37512(71)	4.0
C(F2)	645(74)	46120(80)	36860(83)	5.1
C(F3)	6059(73)	48128(87)	42457(88)	6.0
C(F4)	8689(72)	43045(81)	47950(84)	5.2
C(F5)	5971(77)	35832(84)	48489(86)	5.9
C(F6)	271(75)	33504(87)	43171(88)	6.5

[a] $B_{eq} = \frac{4}{3}(\Sigma_i \Sigma_j B_{ij} a_i a_j)$.

Preparation of $[PPN][Ru_6C(CO)_{16}(COCH_3)]$ *(6)*

Cluster **3** (507 mg, 0.31 mmol) was dissolved in THF (10 ml) and placed in an autoclave. After introduction of carbon monoxide (50 atm), it was kept for 2 h at room temperature with magnetic stirring. The solvent was removed in vacuo, and the residue was subjected to an alumina (5% water) column chromatography (2.5 cm i.d. ×25 cm). The first orange band, which contained small amount (ca. 15 mg) of $Ru_3(CO)_{12}$, was eluted with hexane. The second deep red band was eluted with benzene/CH_2Cl_2 (1/1 v/v), and the eluate was evaporated to dryness. The residue was crystallized from methanol to give deep-red crystals of $[PPN][Ru_6C(CO)_{16}(COCH_3)]$ (286 mg, 0.174 mmol, 56%). IR (CH_2Cl_2): ν(C=O) 2067w, 2013s, 1966w, 1805m(br), and 1662w(br) cm^{-1}. ^1H NMR (acetone-d_6): δ 7.4–7.9 (30H, m, phenyl), 2.54 (3H, s, $COCH_3$). Anal. Found: C, 39.72; H, 1.99; N, 0.78. $C_{55}H_{33}NO_{17}P_2Ru_6$ calcd.: C, 40.08; H, 2.02; N, 0.85%.

Preparation of $[PPN][Ru_6C(CO)_{15}(C_3H_5)]$ *(7)*

Cluster **1** (1.00 g, 0.466 mmol) and allyl bromide (2.0 ml, 23 mmol) were dissolved in CH_2Cl_2 (20 ml) and placed in a stainless steel pressure vessel equipped with an inner glass tube, and heated at 85 °C for 1 h. The solvent was removed from the resulting solution under reduced pressure and the residue was subjected to an alumina (5% water) column chromatography (2.5 cm i.d. ×25 cm). A red band was

Table 9

Atomic coordinates ($\times 10^5$) and equivalent temperature factors ($Å^2$) for [PPN][$Ru_6C(CO)_{16}(COCH_3)$] (**6**) with esd values in parentheses

Atom	x	y	z	B_{eq} [a]
Ru(1)	11287(5)	92173(5)	15232(5)	3.8
Ru(2)	12949(5)	76436(5)	20001(5)	3.9
Ru(3)	4503(5)	85924(5)	28756(5)	3.8
Ru(4)	16026(5)	96590(5)	31536(5)	3.6
Ru(5)	18023(5)	80850(5)	35280(5)	3.7
Ru(6)	24971(5)	87631(5)	22906(5)	3.8
P(1)	−15237(15)	47109(16)	19017(16)	3.6
P(2)	−9545(15)	35238(16)	29988(16)	3.8
O(11)	19383(46)	87140(53)	2954(47)	9.6
O(13)	−3635(44)	91488(63)	8923(51)	12.0
O(14)	11929(42)	107793(43)	8635(43)	7.2
O(21)	16022(47)	59870(43)	22646(50)	9.3
O(22)	9897(50)	72617(51)	3087(46)	10.3
O(23)	−2145(36)	71642(42)	21553(47)	7.2
O(31)	−797(46)	80025(53)	43485(48)	9.7
O(32)	−9810(37)	92838(48)	24649(46)	7.9
O(41)	28175(37)	100919(44)	42903(41)	6.5
O(42)	4181(38)	101212(45)	41211(42)	6.7
O(43)	16635(43)	112436(42)	25136(46)	8.0
O(51)	32860(38)	74674(44)	38096(43)	6.8
O(52)	11123(44)	66065(43)	39335(47)	8.2
O(53)	17342(42)	86489(45)	51776(41)	7.4
O(61)	30699(41)	75349(45)	12858(45)	7.6
O(62)	27995(39)	100262(46)	11940(46)	7.5
O(63)	39301(38)	90740(49)	31713(46)	8.1
N	−10170(39)	40830(43)	22911(43)	4.0
C(0)	14645(44)	86779(55)	25191(54)	3.2
C(11)	13550(60)	89445(70)	3933(65)	7.0
C(12)	7825(82)	89316(93)	−2891(72)	12.0
C(13)	2073(53)	91794(73)	11747(65)	6.7
C(14)	11744(58)	101805(64)	11416(63)	5.9
C(21)	15047(57)	66106(59)	21748(64)	5.7
C(22)	11095(60)	74122(68)	9688(64)	6.6
C(23)	2798(46)	75692(57)	22599(59)	4.2
C(31)	1139(59)	82268(62)	37924(64)	6.1
C(32)	−4447(50)	90146(62)	26015(60)	5.1
C(41)	23591(50)	99155(58)	38785(55)	4.3
C(42)	7987(55)	98558(68)	37348(63)	6.0
C(43)	16301(53)	106294(56)	27368(60)	4.8
C(51)	27485(50)	77260(59)	36481(61)	5.0
C(52)	13880(57)	71529(60)	37740(68)	6.2
C(53)	17825(54)	84684(54)	45582(60)	4.8
C(61)	28152(60)	79732(60)	16677(61)	5.8
C(62)	26477(57)	95388(60)	15991(60)	5.6
C(63)	33926(48)	89509(61)	28403(60)	4.8
C(A1)	−18678(49)	53745(52)	25840(53)	3.7
C(A2)	−24574(51)	51305(59)	29949(55)	4.5
C(A3)	−26973(59)	56328(63)	35498(60)	5.8
C(A4)	−23401(62)	63358(66)	36931(61)	6.5
C(A5)	−17582(59)	65436(61)	33108(61)	5.7
C(A6)	−15136(52)	60651(55)	27265(54)	4.2
C(B1)	−22685(51)	43129(53)	13067(52)	3.8

Table 9 (continued)

Atom	x	y	z	B_{eq} [a]
C(B2)	−21225(54)	36184(57)	9405(56)	4.6
C(B3)	−26614(63)	33102(62)	4236(62)	6.3
C(B4)	−32967(60)	36830(67)	2919(60)	6.4
C(B5)	−34550(56)	43740(67)	6607(56)	5.7
C(B6)	−29083(51)	46978(62)	11875(56)	4.8
C(C1)	−10221(54)	52724(55)	12586(54)	4.2
C(C2)	−13962(56)	57995(61)	7804(57)	5.2
C(C3)	−9934(62)	62372(66)	2930(63)	6.6
C(C4)	−2755(57)	61347(65)	2701(62)	6.2
C(C5)	893(58)	56126(65)	7478(60)	6.0
C(C6)	−2778(52)	51657(63)	12754(59)	5.2
C(D1)	−6878(49)	25882(53)	26754(56)	3.9
C(D2)	−8870(52)	19427(57)	30637(66)	5.5
C(D3)	−6264(56)	12300(60)	28341(66)	5.9
C(D4)	−1795(58)	12114(65)	22335(70)	6.7
C(D5)	73(63)	18556(64)	18594(69)	7.0
C(D6)	−2353(54)	25699(65)	20759(62)	5.5
C(E1)	−17553(48)	33972(54)	35117(57)	3.9
C(E2)	−18089(57)	37249(59)	42339(57)	5.1
C(E3)	−24451(57)	36451(65)	45868(59)	5.8
C(E4)	−30027(56)	32514(64)	41843(62)	5.7
C(E5)	−29545(55)	29414(60)	34556(63)	5.4
C(E6)	−23192(51)	30174(58)	31037(57)	4.6
C(F1)	−2472(50)	38413(56)	37031(52)	3.8
C(F2)	−67(58)	45799(57)	36470(66)	5.7
C(F3)	5559(60)	48102(66)	41834(67)	6.6
C(F4)	8487(57)	43196(67)	47341(67)	6.3
C(F5)	5907(60)	35818(67)	47912(65)	6.7
C(F6)	213(56)	33305(62)	42601(60)	5.7

[a] $B_{eq} = \frac{4}{3}(\Sigma_i \Sigma_j B_{ij} a_i a_j)$.

eluted with benzene/CH_2Cl_2 (1/1 v/v), and the eluate was evacuated to dryness. Crystallization of the residue from methanol yielded deep-red crystals of $[PPN][Ru_6C(CO)_{15}(C_3H_5)]$ (280 mg, 0.173 mmol, 37%). IR (CH_2Cl_2): ν(C=O) 2057w, 2007sh, 1995s, 1986sh, 1946w, 1796m(br), and 1779sh cm^{-1}. ^1H NMR (acetane-d_6): δ 7.4–7.9 (30H, m, phenyl), 3.91 (2H, ddd, J 7.02, 1.83, and 1.22 Hz, *syn*-H), 1.44 (1H, tt, J 12.21 and 7.02 Hz, central-H), and 0.43 (2H, ddd, J 12.21, 1.83, and 1.22 Hz, *anti*-H). Anal. Found: C, 40.95; H, 2.08; N, 0.99. $C_{55}H_{35}NO_{15}P_2Ru_6$ calcd.: C, 40.82; H, 2.18; N, 0.87%.

Preparation of [PPN][Ru$_6$C(CO)$_{15}$(C$_4$H$_7$)] (8)

Cluster **1** (1.50 g, 0.70 mmol) and 2-methylallyl bromide (3.0 ml, 34 mmol) were dissolved in CH_2Cl_2 (30 ml) and then treated in the same manner as described above. Crystallization of the product from methanol yielded deep-red crystals of $[PPN][Ru_6C(CO)_{15}(C_4H_7)]$ (460 mg, 0.28 mmol, 40%). IR (CH_2Cl_2): ν(C=O) 2057w, 2006sh, 1996s, 1943w, and 1796m(br) cm^{-1}. ^1H NMR (acetone-d_6): δ 7.4–7.9 (30H, m, phenyl), 4.14 (2H, t, J 1.22 Hz, *syn*-H), 1.26 (3H, s, CH_3), and 0.68 (2H, t, J 1.22 Hz, *anti*-H). Anal. Found: C, 41.20; H, 2.34; N, 0.87. $C_{56}H_{37}NO_{15}P_2Ru_6$ calcd.: C, 41.20; H, 2.29; N, 0.86%.

Table 10

Atomic coordinates [a] and equivalent temperature factors (Å^2) for [PPN][$Ru_6C(CO)_{15}(C_3H_5)$] (7) with esd values in parentheses

Atom	x	y	z	B_{eq} [b]
Ru(1)	29590(4)	39356(4)	71119(5)	3.1
Ru(2)	33579(4)	25653(4)	79038(5)	3.4
Ru(3)	43069(4)	33091(4)	69192(5)	3.6
Ru(4)	42458(4)	45214(4)	79491(5)	3.5
Ru(5)	46354(4)	31620(4)	87259(5)	3.3
Ru(6)	33243(4)	38120(4)	89557(5)	3.3
P(1)	8822(12)	30629(12)	39183(15)	3.0
P(2)	13359(12)	36278(12)	23347(15)	3.3
O(11)	21702(31)	52603(32)	73213(41)	6.3
O(12)	29301(33)	42987(41)	52728(40)	7.7
O(21)	37762(35)	13805(35)	68487(48)	7.9
O(22)	32541(35)	16701(40)	94374(43)	8.1
O(31)	56069(31)	24691(41)	68925(45)	8.4
O(32)	39412(36)	30395(45)	50454(42)	9.0
O(34)	51397(34)	45590(37)	65033(44)	7.6
O(41)	37417(32)	58443(32)	70190(41)	6.1
O(42)	54774(36)	52911(37)	88768(50)	9.3
O(51)	50754(38)	16418(36)	87483(58)	10.7
O(52)	60978(28)	36594(35)	86768(42)	6.1
O(53)	49056(34)	32150(41)	106552(39)	7.9
O(61)	17718(32)	39804(41)	88457(44)	8.0
O(62)	33260(35)	33831(47)	107780(43)	9.6
O(64)	35986(40)	53141(34)	95174(44)	8.4
N	13586(32)	33422(35)	32613(39)	3.3
C(0)	37714(45)	35414(45)	79101(55)	4.2
C(1)	19451(42)	34260(46)	68127(59)	4.6
C(2)	22600(43)	27459(46)	68589(56)	4.5
C(3)	22573(42)	22512(47)	75551(57)	4.4
C(11)	24636(43)	47532(49)	72463(57)	4.9
C(12)	29535(44)	41357(48)	60016(52)	4.3
C(21)	36302(49)	18607(53)	72284(57)	5.8
C(22)	32982(44)	20322(53)	88447(57)	5.1
C(31)	51174(43)	27930(51)	69079(57)	5.1
C(32)	40672(44)	31627(53)	57762(61)	5.5
C(34)	47595(46)	42573(48)	68898(58)	5.2
C(41)	39414(42)	53306(48)	73775(52)	4.4
C(42)	50070(48)	49922(51)	85391(63)	6.2
C(51)	48800(47)	22019(50)	87278(73)	6.9
C(52)	55365(43)	34991(47)	87029(58)	4.7
C(53)	47613(45)	32057(52)	99000(58)	5.4
C(61)	23737(45)	39242(52)	88602(56)	5.2
C(62)	33646(45)	35433(50)	100765(55)	4.9
C(64)	36034(50)	47695(51)	91756(62)	6.0
C(A1)	13329(40)	23345(42)	44801(46)	2.9
C(A2)	20478(42)	22568(46)	44655(53)	4.0
C(A3)	23979(48)	16993(52)	48958(61)	5.5
C(A4)	20484(51)	12231(49)	53139(64)	6.4
C(A5)	13493(51)	12944(50)	53176(64)	6.1
C(A6)	9862(46)	18444(48)	49107(57)	5.0
C(B1)	211(41)	27669(42)	34673(51)	3.3
C(B2)	−5610(42)	31976(47)	34389(55)	4.4
C(B3)	−12041(44)	29746(52)	30481(60)	5.4

Table 10 (continued)

Atom	x	y	z	B_{eq} [b]
C(B4)	−12753(44)	23424(53)	26416(58)	5.4
C(B5)	−7050(47)	19089(50)	26716(61)	5.9
C(B6)	−608(45)	21203(46)	30664(55)	4.5
C(C1)	7699(40)	37348(42)	46785(49)	3.1
C(C2)	3304(41)	36236(44)	53013(54)	3.9
C(C3)	2840(46)	41287(48)	59245(57)	4.9
C(C4)	6523(45)	47386(46)	59304(56)	4.7
C(C5)	10850(47)	48546(46)	53276(59)	5.0
C(C6)	11372(41)	43657(44)	46839(53)	3.8
C(D1)	5164(42)	39987(44)	18924(51)	3.6
C(D2)	3376(46)	46900(48)	20303(62)	5.4
C(D3)	−3217(51)	49470(54)	17517(71)	7.4
C(D4)	−8028(51)	45191(61)	13244(72)	8.4
C(D5)	−6587(53)	38403(60)	11528(65)	7.6
C(D6)	−24(46)	35722(49)	14360(60)	5.5
C(E1)	15358(39)	29514(42)	16262(47)	3.0
C(E2)	17560(44)	22975(45)	19564(55)	4.3
C(E3)	19486(48)	17800(49)	14358(58)	5.3
C(E4)	19150(46)	19063(47)	5784(60)	5.2
C(E5)	16929(49)	25450(53)	2337(55)	5.6
C(E6)	15044(47)	30683(47)	7634(54)	4.6
C(F1)	20249(42)	42768(41)	13531(51)	3.5
C(F2)	25526(44)	42662(47)	30454(56)	4.5
C(F3)	31305(46)	47048(49)	30642(65)	5.7
C(F4)	31508(48)	51602(50)	24002(67)	6.5
C(F5)	26373(51)	51709(52)	17144(65)	6.7
C(F6)	20476(49)	47360(50)	16899(60)	5.5
H(11)	1810(42)	3496(45)	6065(52)	10.8(3) [c]
H(12)	1574(39)	3576(41)	7229(49)	9.2(3) [c]
H(2)	2358(39)	2550(42)	6277(48)	8.9(3) [c]
H(31)	2314(39)	1751(43)	7243(48)	9.2(3) [c]
H(32)	1944(42)	2423(46)	8024(52)	10.6(3) [c]

[a] $\times 10^5$ for non-hydrogen atoms and $\times 10^4$ for hydrogen atoms. [b] $B_{eq} = \frac{4}{3}(\Sigma_i \Sigma_j B_{ij} a_i a_j)$. [c] Refined isotropically.

Structure determination

Data collection. A deep red single crystal of **3** for X-ray measurements obtained by recrystallization from methanol was fixed on the tip of a glass fiber with cyano acrylate adhesive. A deep red single crystal of **6** and **7** for X-ray measurements obtained by recrystallization from methanol was fixed with Apiezon grease N in a glass capillary which was filled with argon. Unit cell dimensions were derived from the least-squares fit of the angular settings of 20 reflections with $20° < 2\theta < 30°$. Intensity data were collected at 21°C by use of Rigaku AFC-4 fourcircle automated diffractometer with a graphite-monochromatized Mo-K_α radiation. Crystal data and experimental details are given in Table 7. Absorption corrections for these three crystals were not made, because deviations of Fo's for axial reflections at χ 90° were within ±5%.

Structure analysis and refinement for 3. Survey of the data set revealed the systematic extinctions $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$; the centrosymmetric monoclinic space group $P2_1/n$ was obtained. Complex neutral atom scattering factors were employed for all the atoms. The structure was solved by direct methods by use of the program MULTAN [28], which located six ruthenium atoms. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. They were refined by the block-diagonal least-squares method [29], with anisotropic thermal parameters for all atoms. The final R and R_w values are 0.059 and 0.050 with the weighting scheme $w = 1/\sigma^2$. The final difference Fourier synthesis showed noisy but uninformative backgrounds. The maximum peak (1.81 eÅ^{-3}) was located within the covalent radius of the ruthenium atom. Final atomic fractional coordinates are presented in Table 8.

Structure analysis and refinement for ***6***. Survey of the data set revealed the systematic extinctions $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$; the centrosymmetric monoclinic space group $P2_1/n$ was obtained. This space group was identical with that of complex **3**, and cell constants of **6** were almost the same as those of **3**. The indices of strong reflections of **6** and those of **3** were almost identical. Then **6** was found to be isomorphous with **3**. Atomic coordinates of six ruthenium atoms of **3** were adopted as such and refined by the block-diagonal least-squares method. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. They were refined by the block-diagonal least-squares method, with anisotropic thermal parameters for all atoms. The final R and R_w values are 0.069 and 0.040 with the weighting scheme $w = 1/\sigma^2$. The final difference Fourier synthesis showed noisy but uninformative backgrounds. The maximum peak (0.97 eÅ^{-3}) was located within the covalent radius of the ruthenium atom. Final atomic fractional coordinates are presented in Table 9.

Structure analysis and refinement for 7. Survey of the data set revealed the systematic extinctions $h0l$ for $h = 2n + 1$ and $0k0$ for $k = 2n + 1$; the centrosymmetric monoclinic space group $P2_1/a$ was obtained. The structure was solved by direct methods by use of the program MULTAN, which located six ruthenium atoms. The remaining non-hydrogen atoms and five hydrogen atoms of the allyl group were located from subsequent difference Fourier syntheses. They were refined by the block-diagonal least-squares method, with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. As refinement proceeded, the remaining hydrogen atoms in the phenyl groups of the counter cation were located in Fourier maps. Those atoms were included as fixed contributions in their idealized positions. The final R and R_w values are 0.054 and 0.031 with the weighting scheme $w = 1/\sigma^2$. The final difference Fourier synthesis showed noisy but uninformative backgrounds. The maximum peak (1.00 eÅ^{-3}) was located within the covalent radius of the ruthenium atom. Final atomic fractional coordinates are presented in Table 10.

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