

[2.2]Paracyclophane as a Face-Capping Ligand: Conformational Variability over the Ruthenium Triangle

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Summary: The three new [2.2]paracyclophane clusters $Ru_3(CO)_9(\mu_3-\eta^2:\eta^2-C_{16}H_{16})$ (1), $Ru_6C(CO)_{11}(\mu_3-\eta^2:\eta^2-C_{16}H_{16})(\eta^6-C_{16}H_{16})$ (3), and $Ru_6C(CO)_{12}(\mu_3-\eta^2:\eta^2-C_{16}H_{16})(\mu_2-\eta^2-C_6H_6)$ (4) have been prepared and characterized spectroscopically. The structures of compounds 3 and 4 have also been analyzed by X-ray diffraction methods. A comparison of the face-capping ligand in these species, together with the known complex $Ru_6C(CO)_{14}(\mu_3-\eta^2:\eta^2-C_{16}H_{16})$ (2) leads to the observation that the [2.2]-paracyclophane ring bonds to the triruthenium face in a range of differing orientations, from near-staggered to near-eclipsed.

Introduction

There has been considerable interest in the structure and properties of the unusual, strained hydrocarbon [2.2]-paracyclophane. The crystal structure of this molecule was initially established on two separate occasions,^{1,2} but there was a significant variance between the two sets of results. It was generally considered that the observed differences arose from the poor quality of the data accessible at the time, and later studies led to the apodictic molecular structure and enabled an analysis of the observed thermal motion.³ In 1960 Cram and Wilkinson prepared the first complex of paracyclophane, *viz.* tricarbonyl(η^6 -[2.2]paracyclophane)chromium,⁴ and in 1978 the molecular and crystal structure of this intriguing complex was established by single crystal X-ray analysis.⁵ A feature of this latter work was the investigation into the nature of the interaction between the two arene moieties. In general, it has been argued that the distance between the two parallel rings arises from a combination of two opposite effects. Firstly, the strain imposed on the bridging CH_2-CH_2 units, and secondly, the π -electron repulsion of the rings. It was clearly demonstrated that the distance between the two arene rings was shortened considerably when one of the rings was coordinated to the $Cr(CO)_3$ unit. This is not unexpected since $Cr(CO)_3$ is a good π -electron withdrawing group, thereby diminishing the π -repulsion term described above.

The work described in this paper originally had a somewhat different set of objectives. First, we had established in earlier work,⁶ that for the Ru_6C cluster

system interaction with a single arene ligand always led to the η^6 -bonding form irrespective of the nature of the arene. The one exception was found to be the [2.2]-paracyclophane ligand which was observed to adopt the less common $\mu_3-\eta^2:\eta^2$ bonding configuration. The reasons for this difference in bonding arrangement are unclear, but it may be reasonably assumed that they are essentially nonsteric in origin.^{6,7} It therefore occurred to us that given this predisposition toward the facial bonding mode, it might be possible to prepare a "sandwich" cluster similar to that which we reported earlier, *viz.* $Ru_6C(CO)_{11}(\eta^6-C_6H_3Me_3)_2$,⁸ but with the two paracyclophane ligands facially coordinated. However, this has eluded us to date. Secondly, given that the extent of the π -interaction between the two rings is apparently diminished on coordination to the $Cr(CO)_3$ unit, there existed the distinct possibility of preparing compounds in which the [2.2]-paracyclophane might serve as a bridge between cluster systems. As a third objective we were concerned with the nature of the packing that arene clusters show in the solid. The derivatives of [2.2]paracyclophane were obvious and attractive candidates for this effect.

In this paper we report the preparation and full characterization of three new [2.2]paracyclophane derivatives based on the Ru_3 and Ru_6C cluster units, *viz.* $Ru_3(CO)_9(\mu_3-\eta^2:\eta^2-C_{16}H_{16})$ (1), $Ru_6C(CO)_{11}(\mu_3-\eta^2:\eta^2-C_{16}H_{16})(\eta^6-C_{16}H_{16})$ (3), and $Ru_6C(CO)_{12}(\mu_3-\eta^2:\eta^2-C_{16}H_{16})(\mu_2-\eta^2-C_6H_6)$ (4). From a detailed and systematic study of the molecular structures possessed by these species and that previously reported, *viz.* $Ru_6C(CO)_{14}(\mu_3-\eta^2:\eta^2-C_{16}H_{16})$ (2),⁶ we have been able to show that the $C_{16}H_{16}$ moiety undergoes significant distortions on coordination, giving rise to a variation in coordination mode from the nearly perfectly staggered to the nearly eclipsed conformation of the ring with respect to the cluster triangular face.

Results and Discussion

Preparation and Chemical Characterization. Direct reaction of $Ru_3(CO)_{12}$ in heptane or octane over a moderately short period with $C_{16}H_{16}$ affords compound 1 in good yield. In contrast, heating $Ru_3(CO)_{12}$ with $C_{16}H_{16}$ in octane for several hours gives two principal products, these being the hexanuclear derivatives 2 and 3. In turn,

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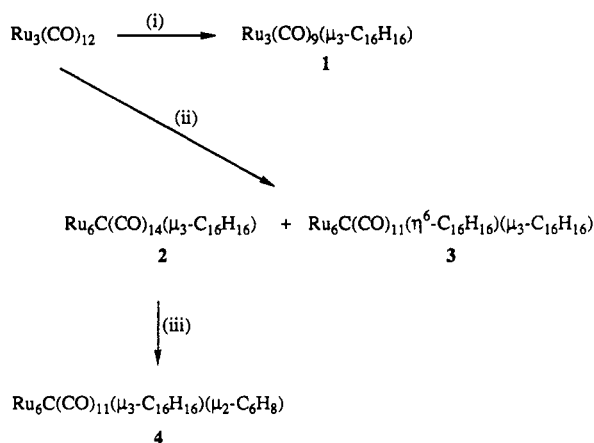
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Scheme 1. Preparation of Clusters 1-4^a

^a Reaction key: (i) octane/ C_6H_6 , reflux for 1 h; (ii) octane/ C_6H_6 , reflux for 4 h; (iii) 2 equiv of Me_3NO in CH_2Cl_2 added dropwise to a $\text{CH}_2\text{Cl}_2/1,3\text{-C}_6\text{H}_8$ solution of **2**.

treatment of **2** with Me_3NO in the presence of cyclohexa-1,3-diene yields the mixed cyclophane-diene complex **4**. All compounds were initially characterized on the basis of the customary analytical and spectroscopic techniques (see Experimental Section), while compounds **3** and **4** were also subjected to single crystal X-ray diffraction analysis. In each case, the established structure agreed with that derived on the basis of the observed spectroscopic properties (see below).

The ^1H NMR spectrum of the new compound **1** is similar to that reported for **2** in that two singlet resonances are observed at δ 7.22 and 3.76 ppm for the ring protons of the unattached and coordinated rings, respectively. Multiple resonances are also observed at δ 3.23 and 2.67 ppm, these corresponding to the CH_2 protons. It is clear that on coordination one ring exhibits a C-H resonance to a lower field and the other to a higher field than the parent. This observation may be taken to indicate a synergic interaction between the two rings; it has been recorded earlier that on coordination of the metal unit the π -electron interaction between the two arenes is diminished. The extent of these shifts is difficult to rationalize on a quantitative basis, but further studies of this interesting phenomenon are in hand. NMR studies of **3** and **4** have been hampered by the poor solubility of the crystalline sample required for clean spectra.

The IR spectra (ν_{CO} region) of **1**, **3**, and **4** are similar to those of their benzene relatives.⁹ Some slight shifts in ν_{CO} values are noted for the clusters, possibly indicating the difference in π -bonding capabilities of the cyclophane, but these changes may not be of significance. The profile in the ν_{CO} region of the triruthenium μ_3 -benzene cluster is virtually identical to that of **1**.^{9a} The only difference is that the peaks in **1** occur at slightly lower wavenumbers. The diagnostic pattern observed in all the monoarene derivatives based on the hexaruthenium cluster system, *viz.* $\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-arene})$,^{9b} is not apparent in the infrared spectrum of **2**, yet the wavenumbers of the strongest absorptions are compatible. This is not surprising given the nature of the arene-cluster interaction in **2**, *i.e.* facial

as opposed to terminal. As for the triruthenium analogue, the carbonyl region of the hexaruthenium bis(paracyclophane) spectrum is very similar to that of its bis(benzene) analogue.^{9c} The shift to lower wavenumbers is quite distinct in this case, in which a lowering in wavenumber of about 6 cm^{-1} has taken place. The infrared spectrum of compound **4** also shows a good relationship with its benzene analogue $\text{Ru}_6\text{C}(\text{CO})_{12}(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_6)(\mu_2\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_8)$.^{9c}

The mass spectra of compounds **1-4** show similarities and can therefore be discussed together. Each cluster exhibits a strong parent peak within 1 amu of the calculated value. Parent peaks are observed at 763, 1219, 1344, and 1242 amu for compounds **1-4**, respectively. Below the parent peak, the sequential loss of carbonyl groups is apparent, but peaks corresponding to the loss of the paracyclophane ligands cannot be appreciated.

Structural Characterization of $\text{Ru}_6\text{C}(\text{CO})_{11}(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_6)(\eta^6\text{-C}_6\text{H}_6)$ (3**) and $\text{Ru}_6\text{C}(\text{CO})_{12}(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_6)(\mu_2\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_8)$ (**4**).** The molecular structure of **2** has been previously described.⁶ It is only necessary to recall here that **2** represents the only example of a monoarene substituted Ru_6C cluster with the ligand in a facial ($\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2$) bonding mode. All other examples of the type $\text{Ru}_6\text{C}(\text{CO})_{14}(\text{arene})$ (arene = C_6H_6 , $\text{C}_6\text{H}_5\text{Me}$, $\text{C}_6\text{H}_4\text{Me}_2$, $\text{C}_6\text{H}_3\text{Me}_3$, and $\text{C}_6\text{H}_3\text{Et}_3$) carry the arene ligand terminally bound to an apex of the octahedral core.¹⁰ One of the rings of the paracyclophane ligand (PCP hereafter) in **2** interacts with three metal atoms *via* three π -interactions. The bonding is of the same type as that of benzene in $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_6)$ and in $\text{Ru}_6\text{C}(\text{CO})_{11}(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_6)(\eta^6\text{-C}_6\text{H}_6)$ with the midpoints of alternating C-C bonds in the ring eclipsed over the Ru atoms (but see below).^{11,12} The molecular structures of compounds **3** and **4** are shown in Figures 1 and 2 respectively. The molecular structure of **3** is reminiscent of that of the bis(benzene) derivative $[\text{Ru}_6\text{C}(\text{CO})_{11}(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_6)(\eta^6\text{-C}_6\text{H}_6)]$: one PCP ligand is, in fact, apically bound to one cluster apex; the second PCP ligand is capping one cluster face as in **2**. The PCP ligand in **4** is facially bound as in **2** and **3**, whereas the cyclohexadiene C_6H_8 ligand adopts the edge-bridging ($\mu_2\text{-}\eta^2\text{-}\eta^2$) coordination mode, shown by all 1,3- C_6H_8 derivatives of the hexanuclear cluster $\text{Ru}_6\text{C}(\text{CO})_{17}$. The C_6H_8 ligand spans one edge opposite to the PCP-bound cluster face.

In all species the octahedron equator carries one bridging CO (a feature common to most derivatives of $\text{Ru}_6\text{C}(\text{CO})_{17}$, while two other CO ligands are in asymmetric bridging positions. Ru-Ru bond lengths range from 2.827(2) to 3.045(2) Å in **3** and from 2.778(3) to 3.036(3) Å in **4**, thus being comparable to the values observed in **2** [2.836(3) and 3.006(3) Å]. Relevant structural parameters for **3** and **4** are reported in Tables 1 and 2, respectively. The C(carbide) atoms in both **3** and **4** roughly occupy the center of the octahedral cavities. In **3**, however, the carbide "drift" toward the Ru atom carrying the apical PCP is observed [Ru(4)-C 1.93(2) Å *vs* the range 2.04(2)-2.09(2) Å for the other Ru-C(carbide) distances]. This effect is invariably observed when an apical tricarbonyl unit is substituted by an apical arene, which is a poorer π -acceptor ligand.

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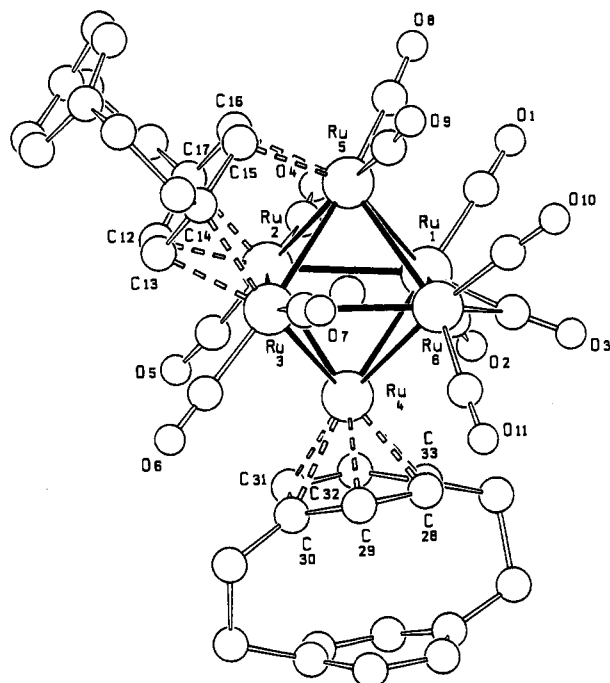


Figure 1. Molecular structure of $\text{Ru}_6\text{C}(\text{CO})_{11}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{16}\text{H}_{16})(\eta^6\text{-C}_{16}\text{H}_{16})$ (**3**) in the solid state. The C atoms of the CO ligands bear the same numbering as the corresponding O atoms. H atoms are omitted for clarity.

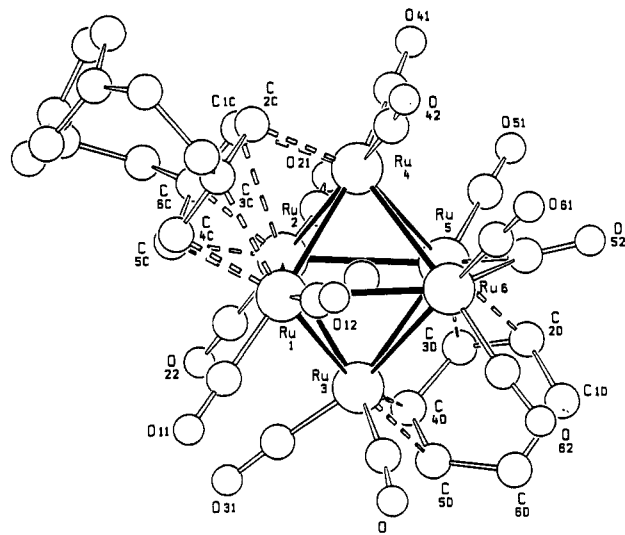


Figure 2. Molecular structure of $\text{Ru}_6\text{C}(\text{CO})_{12}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{16}\text{H}_{16})(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_8)$ (**4**) in the solid state. The C atoms of the CO ligands bear the same numbering as the corresponding O atoms. H atoms are omitted for clarity.

Apart from these general features the structures of **2–4** offer the opportunity to study the coordination of PCP in different crystalline environments. The C_6 rings in free PCP deviate from planarity toward a boat conformation with four atoms coplanar and the two C atoms bound to the CH_2CH_2 bridges elevated from the plane. This geometry is observed in all "free" rings of the PCP ligands in **2**, **4**, and **3**, and is also retained upon apical coordination in **3** [Ru(4)–C(30) 2.38(2), Ru(4)–C(33) 2.39(2) Å vs an average of 2.22(2) Å for the remaining four Ru–C bond distances]. In the facial ($\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$) coordination, on the contrary, the spread of the Ru–C bond distances [from 2.20(2) to 2.34(2) Å] arises from different types of deformation (see below). The most important structural

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **3**

Ru(1)–Ru(2)	2.884(2)	C(17)–C(18)	1.54(2)
Ru(1)–Ru(4)	2.853(2)	C(18)–C(19)	1.56(3)
Ru(1)–Ru(5)	2.957(2)	C(19)–C(20)	1.55(3)
Ru(1)–Ru(6)	2.827(2)	C(20)–C(21)	1.37(3)
Ru(2)–Ru(3)	2.909(2)	C(20)–C(25)	1.38(3)
Ru(2)–Ru(4)	2.908(2)	C(21)–C(22)	1.36(3)
Ru(2)–Ru(5)	2.857(2)	C(22)–C(23)	1.43(3)
Ru(3)–Ru(4)	2.847(2)	C(23)–C(24)	1.37(3)
Ru(3)–Ru(5)	2.835(2)	C(23)–C(26)	1.49(3)
Ru(3)–Ru(6)	3.045(2)	C(24)–C(25)	1.37(3)
Ru(4)–Ru(6)	2.879(2)	C(26)–C(27)	1.57(3)
Ru(5)–Ru(6)	2.871(2)	Ru(4)–C(28)	2.22(2)
Ru(1)–C	2.08(2)	Ru(4)–C(29)	2.20(2)
Ru(2)–C	2.05(2)	Ru(4)–C(30)	2.38(2)
Ru(3)–C	2.04(2)	Ru(4)–C(31)	2.22(2)
Ru(4)–C	1.93(2)	Ru(4)–C(32)	2.22(2)
Ru(5)–C	2.08(2)	Ru(4)–C(33)	2.39(2)
Ru(6)–C	2.09(2)	C(28)–C(29)	1.40(2)
Ru–C(mean)	1.89(2)	C(28)–C(33)	1.45(3)
C–O(mean)	1.14(2)	C(29)–C(30)	1.43(2)
Ru(1)–C(3)	2.07(2)	C(30)–C(31)	1.37(3)
Ru(6)–C(3)	2.09(2)	C(30)–C(43)	1.55(2)
C(3)–O(3)	1.14(2)	C(31)–C(32)	1.41(3)
Ru(2)–C(12)	2.33(2)	C(32)–C(33)	1.41(3)
Ru(2)–C(17)	2.20(2)	C(33)–C(34)	1.51(3)
Ru(3)–C(13)	2.26(2)	C(34)–C(35)	1.64(3)
Ru(3)–C(14)	2.34(2)	C(35)–C(36)	1.48(3)
Ru(5)–C(15)	2.23(2)	C(36)–C(37)	1.37(3)
Ru(5)–C(16)	2.34(2)	C(36)–C(41)	1.38(3)
C(12)–C(13)	1.42(2)	C(37)–C(38)	1.42(3)
C(12)–C(17)	1.43(2)	C(38)–C(39)	1.32(3)
C(13)–C(14)	1.43(2)	C(39)–C(40)	1.35(3)
C(14)–C(15)	1.49(2)	C(39)–C(42)	1.59(3)
C(14)–C(27)	1.53(3)	C(40)–C(41)	1.38(3)
C(15)–C(16)	1.41(3)	C(42)–C(43)	1.57(3)
C(16)–C(17)	1.49(2)		
O–C–Ru(mean)	175(2)	C(25)–C(20)–C(19)	119(2)
O(3)–C(3)–Ru(1)	139(2)	C(28)–C(29)–C(30)	120(2)
O(3)–C(3)–Ru(6)	135(2)	C(28)–C(33)–C(34)	119(2)
C(12)–C(13)–C(14)	120(2)	C(29)–C(28)–C(33)	120(2)
C(12)–C(17)–C(16)	115(2)	C(29)–C(30)–C(43)	120(2)
C(12)–C(17)–C(18)	121(2)	C(30)–C(31)–C(32)	120(2)
C(13)–C(12)–C(17)	124(2)	C(30)–C(43)–C(42)	112(2)
C(13)–C(14)–C(15)	117(2)	C(31)–C(30)–C(29)	118(2)
C(13)–C(14)–C(27)	121(2)	C(31)–C(30)–C(43)	122(2)
C(14)–C(27)–C(26)	113(2)	C(32)–C(33)–C(28)	116(2)
C(15)–C(14)–C(27)	116(2)	C(32)–C(33)–C(34)	125(2)
C(15)–C(16)–C(17)	122(2)	C(33)–C(32)–C(31)	121(2)
C(16)–C(15)–C(14)	121(2)	C(33)–C(34)–C(35)	107(2)
C(16)–C(17)–C(18)	118(2)	C(36)–C(35)–C(34)	115(2)
C(17)–C(18)–C(19)	117(2)	C(36)–C(37)–C(38)	119(2)
C(20)–C(19)–C(18)	113(2)	C(36)–C(41)–C(40)	121(2)
C(21)–C(20)–C(19)	122(2)	C(37)–C(36)–C(35)	121(2)
C(21)–C(20)–C(25)	118(2)	C(37)–C(36)–C(41)	117(2)
C(21)–C(22)–C(23)	121(2)	C(38)–C(39)–C(40)	120(2)
C(22)–C(21)–C(20)	121(2)	C(38)–C(39)–C(42)	123(2)
C(22)–C(23)–C(26)	120(2)	C(39)–C(38)–C(37)	120(2)
C(23)–C(24)–C(25)	121(2)	C(39)–C(40)–C(41)	119(2)
C(23)–C(26)–C(27)	114(2)	C(40)–C(39)–C(42)	116(2)
C(24)–C(23)–C(22)	116(2)	C(41)–C(36)–C(35)	121(2)
C(24)–C(23)–C(26)	123(2)	C(43)–C(42)–C(39)	109(2)
C(24)–C(25)–C(20)	121(2)		

parameters concerning the PCP ligands are compared in Table 3. The structural features of free PCP in its crystal are also reported for comparison. From Table 3 the following general considerations can be appreciated.

(i) The C–C bond lengths within the ring tend to be longer in their mean values for the rings bound to the cluster than for the free rings. In these latter rings C–C bond lengths are comparable to those in free PCP. In **3**, in particular, the mean C–C bond length for the η^6 and μ_3 coordinated rings are both longer than in free PCP, whereas in the unattached rings they are both smaller.

(ii) The C–C–C angles of the aliphatic bridges between coordinated and uncoordinated rings are comparable with

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4

Ru(1)–Ru(2)	2.922(3)	C(1C)–C(2C)	1.41(3)
Ru(1)–Ru(3)	2.821(3)	C(1C)–C(6C)	1.44(3)
Ru(1)–Ru(4)	2.848(2)	C(2C)–C(3C)	1.43(3)
Ru(1)–Ru(6)	3.036(3)	C(3C)–C(4C)	1.42(3)
Ru(2)–Ru(3)	2.908(2)	C(3C)–C(16C)	1.45(3)
Ru(2)–Ru(4)	2.844(3)	C(4C)–C(5C)	1.43(3)
Ru(2)–Ru(5)	2.929(3)	C(5C)–C(6C)	1.43(3)
Ru(3)–Ru(5)	2.908(2)	C(6C)–C(7C)	1.50(3)
Ru(3)–Ru(6)	3.007(3)	C(7C)–C(8C)	1.53(3)
Ru(4)–Ru(5)	2.952(3)	C(8C)–C(9C)	1.47(3)
Ru(4)–Ru(6)	2.878(2)	C(9C)–C(10C)	1.44(3)
Ru(5)–Ru(6)	2.778(3)	C(9C)–C(14C)	1.32(3)
Ru(1)–C	2.06(2)	C(10C)–C(11C)	1.37(3)
Ru(2)–C	2.06(2)	C(11C)–C(12C)	1.41(3)
Ru(3)–C	2.02(2)	C(12C)–C(13C)	1.40(3)
Ru(4)–C	2.05(2)	C(12C)–C(15C)	1.48(3)
Ru(5)–C	2.03(2)	C(13C)–C(14C)	1.43(3)
Ru(6)–C	2.10(2)	C(15C)–C(16C)	1.57(3)
Ru–C(mean)	1.87(3)	Ru(3)–C(4D)	2.36(3)
C–O(mean)	1.16(3)	Ru(3)–C(5D)	2.28(2)
Ru(5)–C(52)	2.02(3)	Ru(5)–C(2D)	2.26(2)
Ru(6)–C(52)	2.03(3)	Ru(5)–C(3D)	2.23(2)
C(52)–O(52)	1.21(3)	C(1D)–C(2D)	1.54(3)
Ru(1)···C(3C)	2.49(2)	C(1D)–C(6D)	1.55(4)
Ru(1)–C(4C)	2.21(2)	C(2D)–C(3D)	1.37(3)
Ru(2)···C(5C)	2.41(2)	C(3D)–C(4D)	1.50(3)
Ru(2)–C(6C)	2.14(2)	C(4D)–C(5D)	1.38(3)
Ru(4)···C(1C)	2.44(2)	C(5D)–C(6D)	1.54(4)
Ru(4)–C(2C)	2.15(2)		
O–C–Ru(mean)	175(2)	C(10C)–C(9C)–C(8C)	118(3)
O(52)–C(52)–Ru(5)	139(2)	C(10C)–C(11C)–C(12C)	123(2)
O(52)–C(52)–Ru(6)	134(2)	C(11C)–C(10C)–C(9C)	118(2)
C(1C)–C(2C)–C(3C)	119(2)	C(11C)–C(12C)–C(15C)	121(2)
C(1C)–C(6C)–C(7C)	120(2)	C(12C)–C(13C)–C(14C)	121(2)
C(2C)–C(1C)–C(6C)	126(2)	C(12C)–C(15C)–C(16C)	111(2)
C(2C)–C(3C)–C(16C)	120(2)	C(13C)–C(12C)–C(11C)	115(2)
C(3C)–C(4C)–C(5C)	121(2)	C(13C)–C(12C)–C(15C)	121(2)
C(3C)–C(16C)–C(15C)	115(2)	C(14C)–C(9C)–C(8C)	122(3)
C(4C)–C(3C)–C(2C)	118(2)	C(14C)–C(9C)–C(10C)	120(2)
C(4C)–C(3C)–C(16C)	119(2)	C(2D)–C(1D)–C(6D)	116(2)
C(4C)–C(5C)–C(6C)	123(2)	C(2D)–C(3D)–C(4D)	121(2)
C(5C)–C(6C)–C(1C)	112(2)	C(3D)–C(2D)–C(1D)	122(2)
C(5C)–C(6C)–C(7C)	119(2)	C(4D)–C(5D)–C(6D)	123(2)
C(6C)–C(7C)–C(8C)	118(2)	C(5D)–C(4D)–C(3D)	119(2)
C(9C)–C(8C)–C(7C)	113(2)	C(5D)–C(6D)–C(1D)	114(2)
C(9C)–C(14C)–C(13C)	120(2)		

those of free PCP although the angles involving the face-capping ligand are slightly larger (on the average) than those involving the unattached rings.

(iii) No C–C bond length alternation is observed within the face-capping rings in 2–4. This is contrary to what is usually observed with face-capping arenes when diffraction data of reasonable quality are available.¹⁰

(iv) Interestingly, the μ_3 -rings show a different degree of torsion with respect to the underlying Ru₃ fragments in the three complexes, as represented in Figure 3. This is reflected in the value of the Ru–C distances which alternate in their mean length, the difference increasing in the order 3 < 2 < 4 [in 3 2.23(2) vs 2.34(2) ($\Delta = 0.11$), in 2 2.20(1) vs 2.37(1) ($\Delta = 0.17$), and in 4 2.17(2) vs 2.45(2) Å ($\Delta = 0.28$ Å)]. The fact that on going from 3 to 2 and to 4 the "short" Ru–C bond distances become progressively shorter, while the "long" Ru–C distance increases, clearly indicates that the separation between the ring and the metal triangle planes is retained while the ligand moves toward a near eclipsing of the C atoms over the Ru atoms.

The comparative analysis of compounds 2–4 offers an important indication of the fact that the face-capping interaction is highly deformable. This is not so evident when the ligand is benzene, which is almost completely embedded within the carbonyl shell, but becomes more

evident with the bulky PCP ligand which protrudes from the cluster surface. It seems reasonable then to attribute the deformation effects to extra molecular forces that act on the molecules embedded in their crystalline field.

Experimental Section

Synthesis. All reactions were carried out with the exclusion of air using solvents freshly distilled under an atmosphere of nitrogen. Subsequent workup of products was achieved without precautions to exclude air with standard laboratory grade solvents. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR in CH₂Cl₂ using NaCl cells. Positive fast atom bombardment mass spectra were obtained using a Kratos MS50TC spectrometer, with CsI as calibrant. ¹H NMR spectra were recorded in CDCl₃ using a Bruker AM360 instrument, referenced to internal TMS. Products were separated chromatographically by either using a column fitted with nitrogen pressurization containing silica 60 mesh or by thin layer on plates supplied by Merck coated with a 0.25-mm layer of Kieselgel 60 F₂₅₄. [2,2]-Paracyclophane and cyclohexa-1,3-diene were purchased from Fluka Chemicals and Aldrich Chemicals, respectively, and used without further purification. Trimethylamine *N*-oxide (Me₃NO) was sublimed prior to reaction.

Thermolysis of Ru₃(CO)₁₂ with C₁₆H₁₆: Preparation of Ru₃(CO)₉(μ_3 - η^2 : η^2 : η^2 -C₁₆H₁₆) (1), Ru₆C(CO)₁₄(μ_3 - η^2 : η^2 : η^2 -C₁₆H₁₆) (2), and Ru₆C(CO)₁₁(μ_3 - η^2 : η^2 : η^2 -C₁₆H₁₆)(η^6 -C₁₆H₁₆) (3). In a typical reaction, a suspension of Ru₃(CO)₁₂ (0.5 g) in octane (30 mL) containing a large excess of [2,2]paracyclophane (0.1 g) was heated to reflux. Depending on the reaction time, the distribution of the products 1–3 can be optimized. A reaction period of 1 h yields mostly 1, while a reaction time of 4 h affords mostly 2, and as the time increases beyond 4 h, increased quantities of 3 are produced. If the thermolysis is carried out in heptane, compound 1 is the major product. In each case, the resulting reaction solution is treated through a silica column, using dichloromethane–hexane (3:7) as eluent. In order of elution, the yellow, orange, and brown products, *viz.* 1–3 are extracted.

Reaction times and typical corresponding yields are as follows:

solvent	time	product (yield)
in heptane	3 h	1 (30%), 2 (10%)
in octane	1 h	1 (25%), 2 (15%)
	4 h	1 (10%), 2 (25%), 3 (5%)
	7 h	1 (5%), 2 (15%), 3 (10%)

Spectroscopic and analytical data for 1: IR (CH₂Cl₂) ν_{CO} 2067 (s), 2024 (vs), 1993 (m), 1980 (m), 1959 (w, sh) cm⁻¹; ¹H NMR (CDCl₃) δ 7.22 (s, 4H), 3.76 (s, 4H), 3.23 (m, 4H), 2.67 (m, 4H) ppm; MS M⁺ = 763 (calc = 763) amu. Anal. Found (Calc): C, 41.12 (39.32); H, 2.31 (2.10).

Spectroscopic and analytical data for 2: IR (CH₂Cl₂) ν_{CO} 2076 (w), 2039 (s), 2024 (vs), 1982 (w, br), 1940 (w, br), 1814 (w, br) cm⁻¹; ¹H NMR (CDCl₃) δ 7.44 (s, 4H), 3.43 (s, 4H), 3.40 (m, 4H), 2.98 (m, 4H) ppm; MS M⁺ = 1219 (calc = 1219) amu. Anal. Found (Calc): C, 30.51 (30.54); H, 1.38 (1.31).

Spectroscopic and analytical data for 3: IR (CH₂Cl₂) ν_{CO} 2031 (s), 1995 (vs), 1944 (w), 1786 (w, br) cm⁻¹; MS M⁺ = 1344 (calc = 1343) amu. Anal. Found (Calc): C, 39.44 (39.35); H, 2.43 (2.40).

Reaction of Ru₆C(CO)₁₄(μ_3 - η^2 : η^2 : η^2 -C₁₆H₁₆) (2) with Cyclohexa-1,3-diene and Me₃NO: Preparation of Ru₆C(CO)₁₄(μ_3 - η^2 : η^2 : η^2 -C₁₆H₁₆)(μ_2 - η^2 : η^2 -C₆H₈) (4). The compound Ru₆C(CO)₁₄(μ_3 - η^2 : η^2 : η^2 -C₁₆H₁₆) (2) (50 mg) was dissolved in dichloromethane (20 mL) containing an excess of cyclohexa-1,3-diene (1.5 mL), and the solution was cooled to -78 °C. Me₃NO (5 mg, 2.1 mol equiv) was added dropwise, and the reaction mixture was allowed to slowly warm to room temperature. After 25 min, IR spectroscopy indicated that the reaction had reached completion and the reaction was stopped. The solvent was removed *in vacuo*, and the products were isolated by TLC, eluting with dichlo-

Table 3^a

	C ₁₆ H ₁₆	3							
		2		μ_3 -C ₁₆ H ₁₆		η^6 -C ₁₆ H ₁₆		4	
		A	B	A	B	A	B	A	B
C(ring)-CH ₂ -CH ₂ (deg)	113.7	115(1)	113(1)	115(2)	114(2)	110(2)	112(2)	117(2)	112(2)
CH ₂ -CH ₂ (Å)	1.562	1.58(1)		1.57(3)		1.61(3)		1.55(3)	
C(ring)-CH ₂ (Å)	1.509	1.49(1)	1.50(1)	1.54(3)	1.52(3)	1.53(3)	1.54(3)	1.48(3)	1.50(1)
C-C(ring) (Å)	1.385	1.43(1)	1.40(1)	1.45(3)	1.38(3)	1.41(3)	1.36(3)	1.43(3)	1.40(3)
C(ring)-Ru "long" (Å)		2.37(1)		2.34(2)		2.39(2)		2.45(2)	
C(ring)-Ru "short" (Å)		2.20(1)		2.23(2)		2.22(2)		2.17(2)	
ring A-ring B (Å)	3.09	3.00		2.99		3.02		3.01	

^a "A" denotes the coordinated ring, while "B" refers to the unattached ring.

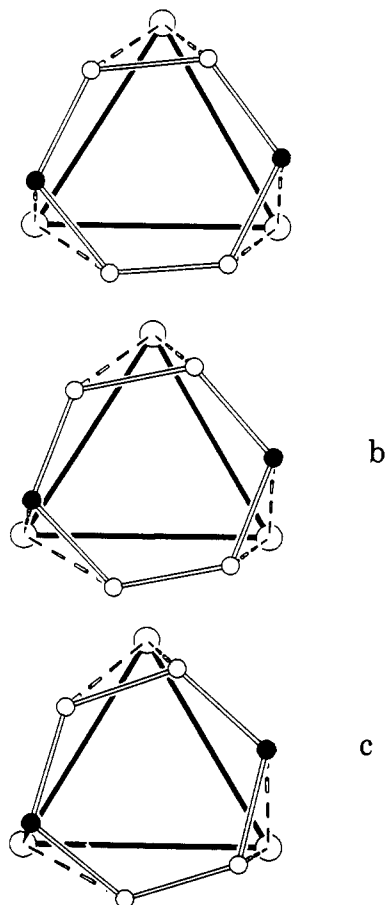


Figure 3. Comparative projections of the PCP-coordination planes in **3**, **2**, and **4** showing the progression from near-eclipsing to near-staggering of the C=C midpoints over the Ru atoms. The remaining portions of the clusters and of the ligands have been omitted for clarity. Filled C atoms are those connected to the aliphatic chains.

romethane-hexane (40:60) as eluent. An orange band was extracted and characterized spectroscopically as [Ru₆C(CO)₁₂(μ_3 - η^2 : η^2 : η^2 -C₁₆H₁₆)(μ_2 - η^2 : η^2 -C₆H₆)] (**4**) (14 mg).

Spectroscopic and analytical data for **4**: IR (CH₂Cl₂) ν_{CO} 2015 (vs), 2005 (s, sh), 1893 (w, br), 1786 (w, br) cm⁻¹; MS M⁺ = 1242 (calc = 1243) amu. Anal. Found (Calc): C, 33.02 (33.82); H, 2.07 (1.95).

Crystal Structure Determination. The diffraction data for the species discussed herein were collected on a Stoe four-circle diffractometer equipped with a graphite monochromator (Mo K α radiation, λ = 0.710 73 Å). Crystal data and details of measurements are summarized in Table 4. The structures were solved by direct methods,¹³ followed by difference Fourier and subsequent least-squares refinements. Scattering factors for neutral atoms were taken from the appropriate tables.¹⁴ Both

Table 4. Crystal Data and Details of Measurements for **3** and **4**

	3	4
formula	C ₄₄ H ₃₂ O ₁₁ Ru ₆	C ₃₅ H ₂₄ O ₁₂ Ru ₆
mol wt	1343.12	1242.96
temp (K)	150	293
system	monoclinic	monoclinic
space group	P2 ₁ /a	P2 ₁ /a
a (Å)	19.295(23)	19.819(10)
b (Å)	10.487(19)	9.887(5)
c (Å)	20.19(4)	20.864(10)
β (deg)	93.74(14)	111.78(4)
V (Å ³)	4076.7	3796.5
Z	4	4
F(000)	2592	2376
λ (Mo K α) (Å)	0.710 69	0.710 69
μ (Mo K α) (mm ⁻¹)	2.05	2.20
θ range (deg)	3–22.5	3–22.5
octants explored	–20 to +18,	–21 to +19,
(h_{min} – h_{max} , k_{min} – k_{max} , l_{min} – l_{max})	0–11, 0–21	0–10, 0–22
no. of measured reflns	5609	5032
no. of unique reflns	5152	4890
no. of refined paramtrs	330	479
GOF on F ²	1.044	1.049
R ₁ (on F, I > 2 σ (I))	0.0678	0.0623
wR ₂ (on F ² , all data)	0.2532	0.2048

structural models were refined on F² by means of SHELXL93.¹⁵ All atoms except the H atoms were treated anisotropically. The H atoms in both species were added in calculated positions [CH₂ 0.97 Å, CH(rings) 0.93 Å] and refined "riding" on their respective C atoms.

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Supplementary Material Available: Tables of anisotropic thermal parameters and fractional atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms, tables of fractional atomic coordinates for the hydrogen atoms, complete lists of bond lengths and angles, and ORTEP drawings of **3** and **4** (16 pages). Ordering information is given on any current masthead page.

OM930872S

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