

Stepwise Formation of the Bis(benzene)hexaruthenium Carbido Carbonyl Cluster $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$ from $\text{Ru}_6\text{C}(\text{CO})_{17}$

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Contribution from the Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, U.K., University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U.K., and Dipartimento di Chimica G. Ciamician, Università di Bologna, Via Selmi 2, 40126 Bologna, Italy

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Abstract: A new stepwise synthetic pathway to the bis(benzene)hexaruthenium carbido carbonyl cluster $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$ is described. On treatment with 2 equiv of Me_3NO in the presence of 1,3- or 1,4-cyclohexadiene, the parent carbido cluster $\text{Ru}_6\text{C}(\text{CO})_{17}$ (**1**) affords the new cyclohexa-1,3-diene species $\text{Ru}_6\text{C}(\text{CO})_{15}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_8)$ (**2**) and the benzene derivative $\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_6)$ (**3**). Compound **2** may be converted into **3** by reaction with an additional equivalent of Me_3NO . Further treatment of **3** with either 1,3- or 1,4-cyclohexadiene affords three complexes, two new benzene/diene species, $\text{Ru}_6\text{C}(\text{CO})_{12}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_8)$ (**4**) and $\text{Ru}_6\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_8)$ (**5**), and the bis(benzene) cluster $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$ (**6**). Cluster **4** may be converted to **5** by heating in hexane. Compound **6** can also be generated from **5** by the addition of a second aliquot of Me_3NO or, alternatively, via the cationic benzene/dienyl intermediate $[\text{Ru}_6\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_7)]^+$ (**7**), formed on reaction with Ph_3C^+ . Compound **7** then reacts with DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) to afford **6**. The molecular structures of compounds **2**–**5** have been determined by single-crystal X-ray diffraction analysis. Compound **2** is monoclinic, space group $P2_1/C$, with $a = 17.723(3)$ Å, $b = 9.502(2)$ Å, $c = 18.443(5)$ Å, $\beta = 116.02(2)^\circ$, $Z = 4$; compound **3** is orthorhombic, space group $P2_12_12_1$, with $a = 8.924(6)$ Å, $b = 16.332(6)$ Å, $c = 18.299$ Å, $Z = 4$; compound **4** is orthorhombic, space group $Pna2_1$, with $a = 20.536(3)$ Å, $b = 9.843(3)$ Å, $c = 13.911(2)$ Å, $Z = 4$; compound **5** is triclinic, space group $P\bar{1}$, with $a = 10.314(9)$ Å, $b = 10.720(8)$ Å, $c = 15.23(1)$ Å, $\alpha = 74.24(5)^\circ$, $\beta = 79.59(5)^\circ$, $\gamma = 78.50(4)^\circ$, $Z = 2$.

Introduction

The benzene complex $\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_6)$ (**3**) was originally prepared in modest yield from the extended thermolysis of $\text{Ru}_3\text{-}(\text{CO})_{12}$ in benzene.¹ More recently a better yielding route has been described,² involving the ionic coupling of the pentanuclear dianion $[\text{Ru}_5\text{C}(\text{CO})_{14}]^{2-}$ with the mononuclear benzene dication $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{PhCN})_3]^{2+}$. In an extension of this method, the benzene cluster **3** was reduced with $\text{Na}_2\text{CO}_3/\text{MeOH}$ to produce the dianionic derivative $[\text{Ru}_6\text{C}(\text{CO})_{13}(\text{C}_6\text{H}_6)]^{2-}$, which on treatment with a further aliquot of $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{PhCN})_3]^{2+}$ resulted in the formation of $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$ (**6**). In this reaction a second benzene moiety has been introduced, and the integrity of the cluster framework has remained intact. A single-crystal X-ray analysis of cluster **6** showed that one of the benzene rings adopts the more common η^6 -coordination mode, while the other acquires the $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ -face-capping mode (Figure 1a). Examination of the face-capping benzene in this cluster reveals that the C–C bond lengths alternate around the C_6 ring. Three short bonds [average 1.39(2) Å] eclipse the Ru atoms, while the three remaining and unattached C–C bond lengths average 1.48(2) Å. These features accurately model benzene chemisorbed at the surface of metal atoms in low Miller index planes of close-packed arrays of a metallic lattice.³

We now report a new and systematic synthetic route to the bis(benzene) cluster **6**, directly from $\text{Ru}_6\text{C}(\text{CO})_{17}$ (**1**), in which

a series of stable intermediates **2**, **3**, **4**, **5**, and **7** have been isolated. The benzene cluster **3** has been characterized by both spectroscopic methods and single-crystal X-ray diffraction analysis, as have the new compounds $\text{Ru}_6\text{C}(\text{CO})_{15}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_8)$ (**2**), $\text{Ru}_6\text{C}(\text{CO})_{12}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_8)$ (**4**), and $\text{Ru}_6\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_8)$ (**5**). The novel cationic cyclohexadienyl cluster $[\text{Ru}_6\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_7)]^+$ (**7**) has been characterized by spectroscopic methods only.

Other bis(arene) clusters have been reported recently, including an isomer of **6**, formed when the $\mu_3\text{-C}_6\text{H}_6$ ligand undergoes isomerization at 150 °C to afford the "sandwich" complex $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_6)_2$, in which two η^6 -benzene groups bond to two *trans* ruthenium atoms within the Ru_6C cluster unit (Figure 1b).⁴ This structural type was previously found in the bis(mesitylene) complex $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)_2$, which is formed directly without the prior formation of $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_3\text{Me}_3)$ followed by ligand migration.^{5,6} A third structural form has been established for the mixed mesitylene/benzene hexaruthenium carbido carbonyl cluster $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\eta^6\text{-C}_6\text{H}_6)$, in which two terminally bonded arenes lie on *cis*-metal atoms (Figure 1c).⁶ This species was formed upon migration of the μ_3 -benzene ligand in $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$ to a single metal center on allowing the cluster to stand for a prolonged period.

We have also reported a similar chemistry associated with the pentaruthenium carbido carbonyl cluster $\text{Ru}_5\text{C}(\text{CO})_{15}$,^{7,8} in which the diene cluster, $\text{Ru}_5\text{C}(\text{CO})_{13}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_8)$, and two

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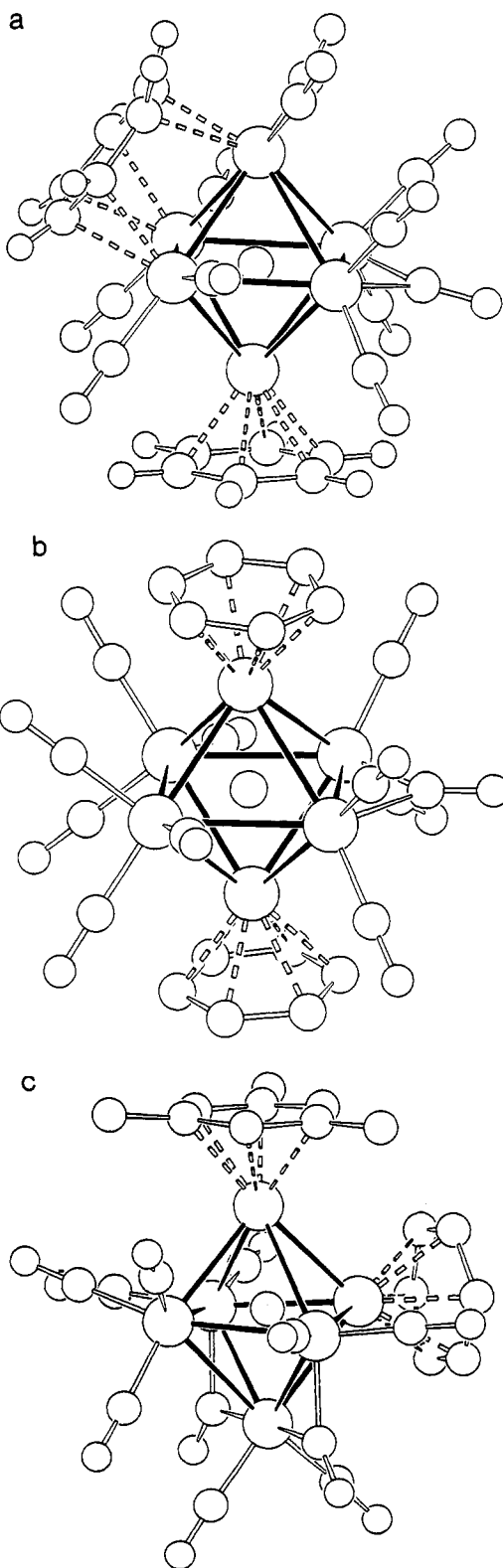


Figure 1. (a) $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$. (b) $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_6)_2$. (c) $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)(\eta^6\text{-C}_6\text{H}_6)$.

isomers of the benzene derivative, *viz.*, $\text{Ru}_5\text{C}(\text{CO})_{12}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$ and $\text{Ru}_5\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)$, have been prepared and structurally characterized. Thermolysis of $\text{Ru}_5\text{C}(\text{CO})_{12}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$ also results in migration of the face-capping benzene to the terminal site in $\text{Ru}_5\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)$.

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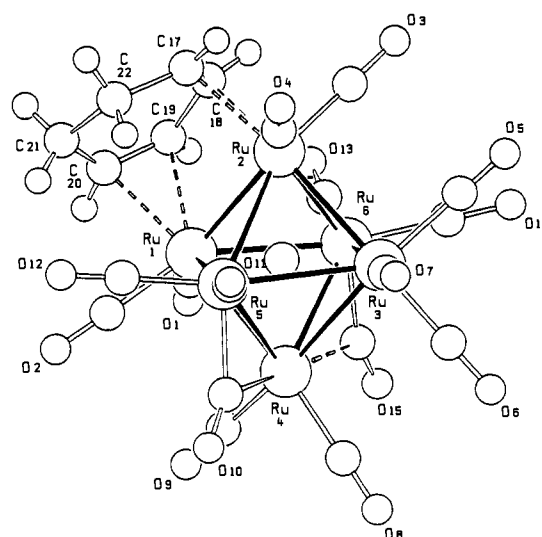


Figure 2. Molecular structure of **2**, showing the labeling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms.

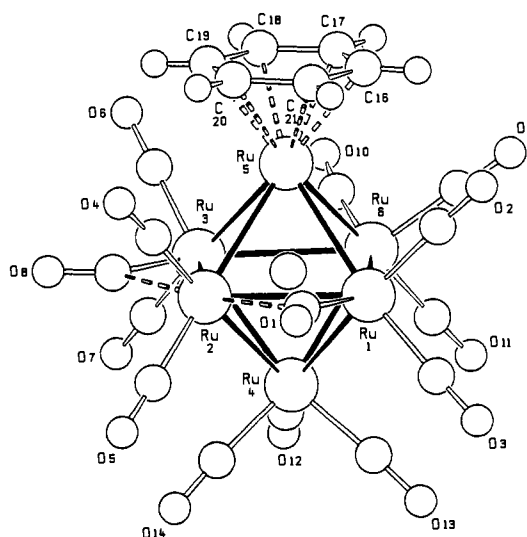
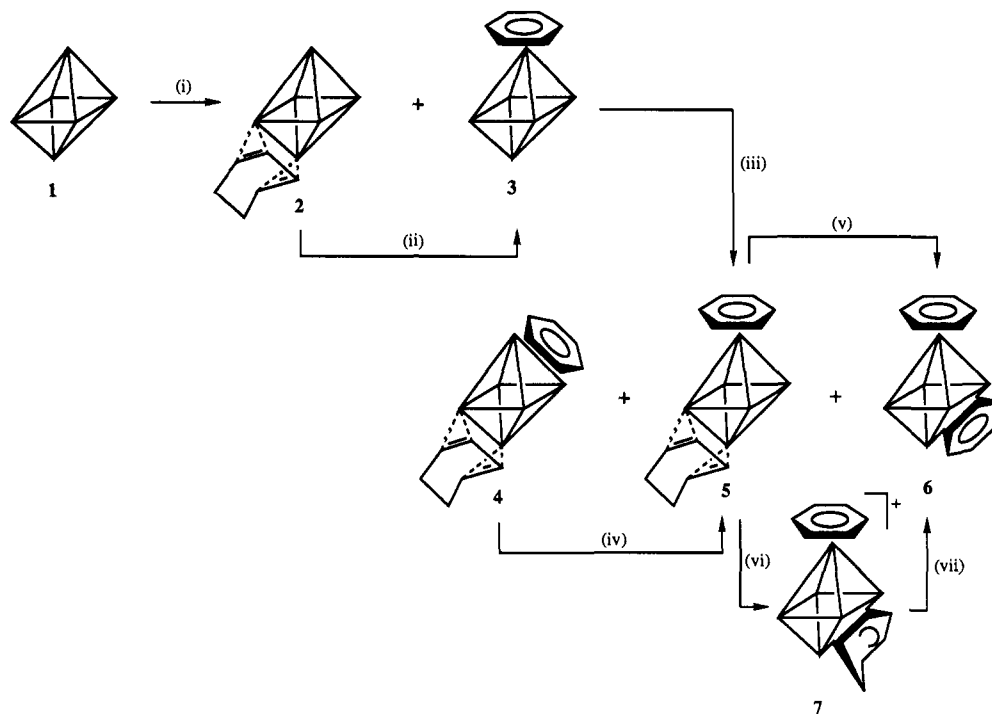


Figure 3. Molecular structure of **3**, showing the labeling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms.

Results and Discussion

The sequence of reaction utilized in the preparation of **6** involves the initial substitution of cyclohexadiene onto the Ru_6C framework, followed by "dehydrogenation" to yield a coordinated benzene. On repetition of this reaction sequence, a second benzene may be introduced into the system (Scheme I). Table I displays spectroscopic data for the compounds described.

The parent cluster $\text{Ru}_6\text{C}(\text{CO})_{17}$ (**1**) is readily activated toward reaction with either 1,3- or 1,4-cyclohexadiene upon treatment with 2 equiv of the oxidative decarbonylation reagent trimethylamine *N*-oxide (Me_3NO) in dichloromethane containing an excess of the diene, yielding $\text{Ru}_6\text{C}(\text{CO})_{15}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_8)$ (**2**) and $\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_6)$ (**3**). The molecular ion peaks in the mass spectrum of clusters **2** and **3** are consistent with the expected values. In **2** the ^1H NMR displays four multiplets at δ 5.06, 4.16, 2.16, and 0.95 ppm, of equal relative intensity, and may readily be assigned to the four distinct proton signals from the coordinated 1,3-cyclohexadiene moiety. The ^1H NMR of compound **3** is much simpler, consisting of a singlet at δ 5.56 ppm, indicative of a benzene ligand. The diene cluster **2** may be converted into **3** by the addition of an additional 1 equiv of Me_3NO . From this we can infer that in the previous reaction, in which both **2** and **3** are

Scheme I. Synthesis of $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$ from $\text{Ru}_6\text{C}(\text{CO})_{17}$ ^a

^a Reagents and conditions: (i) $\text{Me}_3\text{NO}/\text{CH}_2\text{Cl}_2$ added dropwise to a CH_2Cl_2 /cyclohexa-1,3-diene solution of **1**; (ii) $\text{Me}_3\text{NO}/\text{CH}_2\text{Cl}_2$ added dropwise to a CH_2Cl_2 solution of **2**; (iii) $\text{Me}_3\text{NO}/\text{CH}_2\text{Cl}_2$ added dropwise to a CH_2Cl_2 /cyclohexa-1,3-diene solution of **3**; (iv) heat **4** to reflux in hexane for 18 h; (v) $\text{Me}_3\text{NO}/\text{CH}_2\text{Cl}_2$ added dropwise to a CH_2Cl_2 solution of **5**; (vi) excess $[\text{Ph}_3\text{C}][\text{BF}_4]$ added to a CH_2Cl_2 solution of **5**; (vii) DBU added to a CH_2Cl_2 solution of **7**.

Table I. Spectroscopic and Microanalysis Data for Compounds 2–7^a

	IR (CH_2Cl_2), $\nu_{\text{CO}}/\text{cm}^{-1}$	MS	$^1\text{H NMR}$, $\delta(\text{CDCl}_3)$																																		
2	2082 (m), 2044 (s), 2030 (s), 1986 (m), 1836 (w, br)	1118 (calcd = 1119)	5.06 (m, 2H), 4.16 (m, 2H), 2.16 (m, 2H), 0.95 (m, 2H)																																		
3	2078 (m), 2026 (vs), 1816 (w, br)	1088 (calcd = 1089)	5.56 (s, 6H)																																		
4	2049 (m), 2018 (vs), 2007 (s), 1990 (m), 1875 (w, br), 1800 (w, br)	1116 (calcd = 1113)	5.03 (m, 1H), 4.80 (m, 1H), 4.22 (s, 6H), 4.07 (m, 1H), 3.62 (m, 1H), 2.46 (m, 1H), 2.02 (m, 1H), 1.13 (m, 1H), 0.95 (m, 1H)																																		
5	2044 (m), 2001 (s), 1966 (w), 1821 (w, br)	1112 (calcd = 1113)	5.56 (s, 6H), 4.95 (m, 1H), 4.90 (m, 1H), 4.26 (m, 1H), 3.53 (m, 1H), 2.10 (m, 1H), 1.97 (m, 1H), 1.00 (m, 1H), 0.83 (m, 1H)																																		
6	2039 (m), 2002 (s), 1995 (m), 1897 (w, br)	1082 (calcd = 1083)	5.54 (s, 6), 4.14 (s, 6H)																																		
7	2086 (m), 2047 (s), 1998 (w), 1900 (w, br)	1113 (calcd = 1112)	6.00 (s, 6H), 5.64 (m, 1H), 5.06 (m, 1H), 4.30 (m, 1H), 3.22 (m, 1H), 2.59 (m, 1H)																																		
	<table border="1"> <thead> <tr> <th rowspan="2"></th> <th colspan="2">% C</th> <th colspan="2">% H</th> </tr> <tr> <th>obsd</th> <th>calcd</th> <th>obsd</th> <th>calcd</th> </tr> </thead> <tbody> <tr> <td>2</td> <td>23.53</td> <td>23.62</td> <td>0.77</td> <td>0.72</td> </tr> <tr> <td>3</td> <td>25.90</td> <td>23.17</td> <td>1.69</td> <td>0.56</td> </tr> <tr> <td>4</td> <td>27.01</td> <td>26.98</td> <td>1.33</td> <td>1.27</td> </tr> <tr> <td>5</td> <td>26.44</td> <td>26.98</td> <td>1.11</td> <td>1.27</td> </tr> <tr> <td>7</td> <td>30.17</td> <td>25.05</td> <td>2.95</td> <td>1.09</td> </tr> </tbody> </table>			% C		% H		obsd	calcd	obsd	calcd	2	23.53	23.62	0.77	0.72	3	25.90	23.17	1.69	0.56	4	27.01	26.98	1.33	1.27	5	26.44	26.98	1.11	1.27	7	30.17	25.05	2.95	1.09	
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5	26.44	26.98	1.11	1.27																																	
7	30.17	25.05	2.95	1.09																																	

^a All IR spectra were recorded in dichloromethane, and NMR, in chloroform-*d*₁, except for **7**, in which the IR and NMR spectra were run in nitromethane and acetone-*d*₆, respectively.

generated, **2** is formed initially from **1**. We may reasonably assume that in this reaction the elimination of two carbonyl ligands (removed as CO_2 by Me_3NO) produces two vacant coordination sites on the surface of the cluster (possibly stabilized by the highly labile Me_3N group generated during the reaction) to which the cyclohexadiene ligates. Abstraction of hydrogen from the coordinated C_6H_8 must occur spontaneously (this being thermodynamically favorable) and is driven by the creation of a further vacant coordination site on the metal framework when an additional carbonyl group is removed by excess Me_3NO .

The molecular structures of both clusters **2** and **3** in the solid state have been established by single-crystal X-ray diffraction

techniques. The structure of $\text{Ru}_6\text{C}(\text{CO})_{15}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_8)$ (**2**) is depicted in Figure 2, and the relevant structural parameters are listed in Table II. The metal atom framework is the familiar octahedron established for $\text{Ru}_6\text{C}(\text{CO})_{17}$ (**1**),¹⁰ encapsulating a C(carbide) atom. The cyclohexadiene ligand replaces two CO 's, thus formally contributing four electrons to the cluster frame. The ligand is coordinated in a $\mu_2\text{-}\eta^2\text{:}\eta^2$ fashion, spanning an edge of the metal core. The CO ligand distribution is quite uneven: Ru(1) and Ru(2) bear the 1,3- C_6H_8 ligand and two terminal

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Table II. Relevant Bond Distances (Å) and Angles (deg) for **2**

Ru(1)–Ru(2)	2.890(1)	Ru(6)–C(16)	2.07(1)
Ru(1)–Ru(4)	2.857(1)	Ru(4)–C(10)	2.20(1)
Ru(1)–Ru(5)	2.936(1)	Ru(5)–C(10)	2.02(1)
Ru(1)–Ru(6)	2.876(1)	Ru(6)–C(15)	1.94(2)
Ru(2)–Ru(3)	2.846(1)	Ru(4)–C(15)	2.45(1)
Ru(2)–Ru(5)	2.927(1)	Ru(1)–C(19)	2.27(1)
Ru(2)–Ru(6)	2.926(1)	Ru(1)–C(20)	2.25(1)
Ru(3)–Ru(4)	2.949(1)	Ru(2)–C(17)	2.26(2)
Ru(3)–Ru(5)	2.928(1)	Ru(2)–C(18)	2.26(1)
Ru(3)–Ru(6)	2.829(1)	C(18)–C(19)	1.54(2)
Ru(4)–Ru(5)	2.834(1)	C(17)–C(18)	1.43(2)
Ru(4)–Ru(6)	2.887(1)	C(19)–C(20)	1.35(2)
Ru(1)–C(16)	2.01(1)	C(20)–C(21)	1.51(2)
Ru(2)–C(16)	2.02(1)	C(21)–C(22)	1.60(2)
Ru(3)–C(16)	2.07(1)	C(17)–C(22)	1.48(1)
Ru(4)–C(16)	2.07(1)	mean Ru–C _{CO(i)}	1.88(2)
Ru(5)–C(16)	2.04(1)	mean C _{CO} –O _{CO}	1.14(2)
Ru(4)–C(10)–O(10)	133(1)	Ru(4)–C(15)–O(15)	126(1)
Ru(5)–C(10)–O(10)	142(1)	Ru(6)–C(15)–O(15)	153(1)

Table III. Relevant Bond Distances (Å) and Angles (deg) for **3**

Ru(1)–Ru(2)	2.839(1)	Ru(4)–C(15)	2.069(6)
Ru(1)–Ru(4)	2.910(1)	Ru(5)–C(15)	1.935(6)
Ru(1)–Ru(5)	2.864(1)	Ru(6)–C(15)	2.053(6)
Ru(1)–Ru(6)	2.975(1)	Ru(5)–C(16)	2.221(8)
Ru(2)–Ru(3)	2.847(1)	Ru(5)–C(17)	2.240(8)
Ru(2)–Ru(4)	2.971(1)	Ru(5)–C(18)	2.220(8)
Ru(2)–Ru(5)	2.880(1)	Ru(5)–C(19)	2.205(9)
Ru(3)–Ru(4)	2.853(1)	Ru(5)–C(20)	2.240(9)
Ru(3)–Ru(5)	2.849(1)	Ru(5)–C(21)	2.200(8)
Ru(3)–Ru(6)	2.999(1)	Ru(1)–C(1)	1.954(8)
Ru(4)–Ru(6)	2.848(1)	C(1)–O(1)	1.156(9)
Ru(5)–Ru(6)	2.825(2)	Ru(2)···C(1)	2.322(8)
Ru(1)–C(15)	2.053(6)	Ru(3)–C(8)	2.022(9)
Ru(2)–C(15)	2.091(6)	C(8)–O(8)	1.123(11)
Ru(3)–C(15)	2.054(6)	Ru(2)···C(8)	2.196(8)
Ru(1)–C(1)–O(1)	149(1)	Ru(3)–C(8)–O(8)	142(1)
Ru(2)–C(8)–O(8)	133(1)		

CO's each; Ru(3) bears three terminal CO's; Ru(5) and Ru(6) bear two terminal CO's and one bridging CO ligand each; Ru(4) bears two terminal CO's and is involved in two interactions with bridging CO's. These latter ligands are not symmetrically bound, showing longer Ru–C distances from the common Ru(5) atom [2.20(1) and 2.45(1) Å *versus* 2.02(1) and 1.94(1) Å]. Ru–Ru bond lengths range from 2.834(1) to 2.949(1) Å. Although internuclear separations between light atoms in this structure are known with limited accuracy, it is worth noting that the two C=C double bonds within the C₆H₈ ligand that are eclipsed on the Ru atoms are consistently shorter than the other C–C bonds [1.42(2), 1.35(2) Å *versus* a mean value of 1.53(2) Å obtained from the remaining four bonds]. The ligand possesses a twisted conformation in agreement with the 1,3-multiple bond localization. A similar bonding pattern and mode of coordination has been observed in the related pentanuclear species Ru₅C(CO)₁₃(μ₂-η²-η²-C₆H₈), in which the C₆H₈ ligand replaces two radial CO's on two consecutive basal metal atoms of the square-pyramidal metal core.⁸

The molecular structure of **3** is depicted in Figure 3. Relevant structural parameters are listed in Table III. From a comparison of Figures 2 and 3, the structural relationship between the two molecules is easy to appreciate: the μ₂-η²-η² ligand spanning one octahedron edge in **2** formally migrates from the bridging position onto one apical atom in **3**. This is not to say that the reaction proceeds *via* this mechanistic pathway. It is important to stress that the formation of **3** from **2** necessitates not only CO loss but migration of one ligand to saturate the vacant site created on the molecular equator. It should also be taken into account that the CO ligands (and, perhaps, the benzene) are able to scramble around the metal framework in solution. This is substantiated

by the observation of an almost "continuous" distribution of metal–CO bonding geometries from symmetric bridging, *via* asymmetric bridging and "bent-terminal", to "straight" terminal ligands around the octahedral frame in the known mono- and bis-arene derivatives of Ru₆C(CO)₁₇ characterized to date.⁶ Ru–Ru bond lengths in **3** range from 2.825(1) to 2.999(1) Å, the two limits corresponding to two apex–equator edges, the shorter bond involving the arene-bound Ru(5) atom. This range is only slightly wider than that observed in **2**, with the diene-spanned bond showing an intermediate length [2.890(1) Å]. The solid-state molecular structure of **3** also confirms the C(carbide) "drift" toward the arene ligand previously detected in the related species Ru₆C(CO)₁₄(η⁶-C₆H₅Me)¹¹ and Ru₆C(CO)₁₄(η⁶-C₆H₃Me₃).¹² In fact, the Ru(5)–C(15) distance in **3** [1.935(6)] is noticeably shorter than all remaining five distances [range 2.053(6)–2.091(6) Å]. This "drifting" effect can be attributed to the need to "compensate" the substitution of benzene for three good π-acceptor CO ligands on going, ideally, from Ru₆C(CO)₁₇ to **3**.

Treatment of **3** with 2 molar equiv of Me₃NO in dichloromethane containing an excess of either 1,3- or 1,4-cyclohexadiene results in the isolation of three products, the major product being Ru₆C(CO)₁₂(η⁶-C₆H₆)(μ₂-η²-η²-C₆H₈) (**5**) and, in modest yield, Ru₆C(CO)₁₂(μ₃-η²-η²-η²-C₆H₆)(μ₂-η²-η²-C₆H₈) (**4**) and the bis(benzene) cluster Ru₆C(CO)₁₁(η⁶-C₆H₆)(μ₃-η²-η²-η²-C₆H₆) (**6**). The mass spectra of **4** and **5** are virtually identical, and in each case the molecular ion peaks are consistent with the calculated value. In the ¹H NMR of both compounds a singlet for the coordinated benzene is observed. In **4** this appears at δ 4.22 ppm, indicative of a face-capping ligand, while in **5** the signal at δ 5.56 ppm is entirely consistent with that of an η⁶-coordinated benzene. Both compounds also show eight signals deriving from the C₆H₈ ligand, each proton on the ring being chemically inequivalent (Table I). The spectroscopic data of **6** is in good agreement with that previously reported.²

It would appear that **5** is formed by a mechanism similar to that described for the formation of compound **2**. The reason that the benzene moiety in **4** adopts a face-capping bonding mode is not understood, but since there is no evidence that **3** is contaminated with the alternative facial isomer of Ru₆C(CO)₁₄-(C₆H₆) in which the benzene is μ₃-coordinated, the migration of the η⁶-benzene ligand to a face-capping site must occur upon substitution by the cyclohexadiene ligand. Mild thermolysis of **4** results in benzene migration and hence the generation of compound **5**. The migration of benzene from a trimetal face to a single metal atom has been observed in other systems.^{6,8}

The molecular structures of **4** and **5** have also been established by X-ray diffraction methods. The structures of the two isomers are closely related and will be illustrated together. Structural sketches are shown in Figures 4 and 5, respectively. Relevant structural parameters are listed together in Table IV for comparative purposes. The main difference between **4** and **5** arises primarily from the bonding fashion of the benzene fragment which is bound in the face-capping mode in **4**, while the ligand adopts the more common η⁶-bonding mode in **5**. The same type of structural relationship has already been observed in the Ru₅C family with the structures of Ru₅C(CO)₁₂(μ₃-η²-η²-η²-C₆H₆) and Ru₅C(CO)₁₂(η⁶-C₆H₆),⁸ and with the other pair of structural isomers described herein, namely, the bis(benzene) derivatives Ru₆C(CO)₁₁(η⁶-C₆H₆)(μ₃-η²-η²-η²-C₆H₆)² and Ru₆C(CO)₁₁(η⁶-C₆H₆)₂.⁴ It appears that, in both **4** and **5**, the benzene ligand is located as far as possible from the diene fragment. In **4** this latter ligand spans an apical–equator edge as observed in **2**, while the benzene covers the opposite triangular face, thus formally replacing one terminal CO from each Ru atom of the octahedron face.

(11) Farrugia, L. J. *Acta Crystallogr., Sect. C* 1988, C44, 997.(12) Braga, D.; Grepioni, F.; Johnson, B. F. G.; Hong, C.; Lewis, J. J. *Chem. Soc., Dalton Trans.* 1991, 2559.

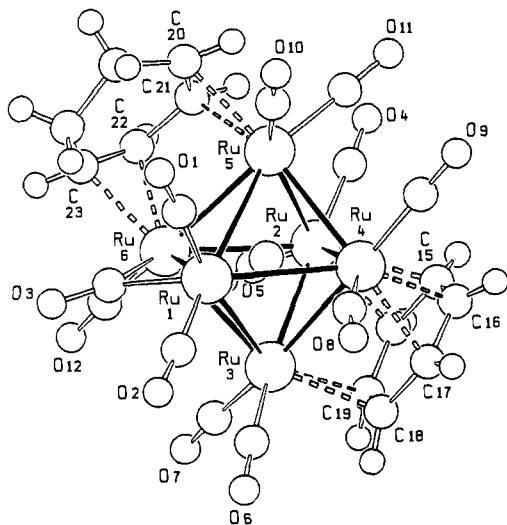


Figure 4. Molecular structure of **4**, showing the labeling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms.

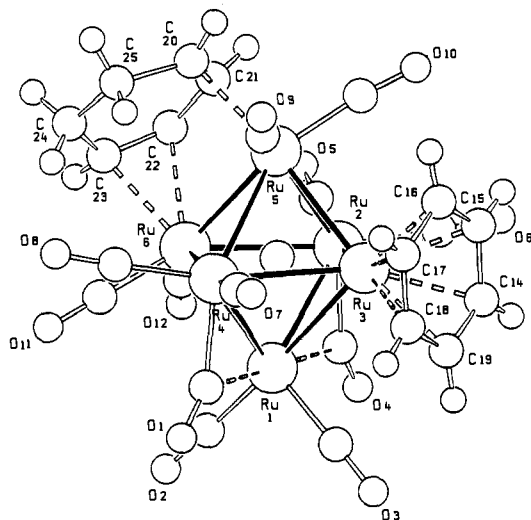


Figure 5. Molecular structure of **5**, showing the labeling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms.

The high quality of the diffraction data of **4** and **5** allowed direct location of the H atoms. The six H atoms of the benzene in **4** are bent out-of-plane, as previously observed in $\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$.¹³ The 1,3- C_6H_8 ligand adopts a twist conformation in both **4** and **5**. In keeping with the idea of rather fluxional molecules, it is noteworthy that the bridging CO involves atom Ru(6) in **4**, *i.e.* one Ru atom carrying the C_6H_8 ligand, while in **5** the bridging CO is on the opposite edge with respect to the diene ligand. From a close examination of Figures 4 and 5 it is, however, easy to appreciate that the presence of a bridging CO along the Ru(2)–Ru(4) bond in the structure of **4** is prevented by the presence of the face-capping benzene. It is not difficult to imagine that **5** can be generated from **4** by allowing the benzene ligand to slip from face-capping into apical position, this process also requiring CO ligand migration from the apical toward the equatorial Ru atoms.

The bis(benzene) cluster **6** may also be generated directly from **5** upon treatment with an additional 1 equiv of Me_3NO , or via the cationic benzene/dienyl species $[\text{Ru}_6\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_7)]^+$ (**7**), produced when a hydride is abstracted from **5** by treatment with $[\text{PhC}_3][\text{BF}_4]$. The profile of the infrared

Table IV. Relevant Bond Distances (Å) and Angles (deg) for the Two Isomers **4** and **5**

	4	5	
Ru(1)–Ru(3)	2.898(1)	Ru(1)–Ru(2)	2.860(1)
Ru(1)–Ru(4)	2.946(1)	Ru(1)–Ru(3)	2.917(1)
Ru(1)–Ru(5)	2.991(1)	Ru(1)–Ru(4)	2.871(1)
Ru(1)–Ru(6)	2.762(1)	Ru(1)–Ru(6)	2.846(1)
Ru(2)–Ru(3)	2.815(1)	Ru(2)–Ru(3)	2.834(1)
Ru(2)–Ru(4)	2.959(1)	Ru(2)–Ru(5)	2.948(1)
Ru(2)–Ru(5)	2.879(1)	Ru(2)–Ru(6)	2.881(1)
Ru(2)–Ru(6)	2.927(1)	Ru(3)–Ru(4)	2.841(1)
Ru(3)–Ru(4)	2.851(1)	Ru(3)–Ru(5)	2.820(1)
Ru(3)–Ru(6)	2.934(1)	Ru(4)–Ru(5)	2.926(1)
Ru(4)–Ru(5)	2.831(1)	Ru(4)–Ru(6)	2.929(1)
Ru(5)–Ru(6)	2.917(1)	Ru(5)–Ru(6)	2.857(1)
Ru(1)–C(13)	2.079(8)	Ru(1)–C(13)	2.077(6)
Ru(2)–C(13)	2.041(8)	Ru(2)–C(13)	2.045(6)
Ru(3)–C(13)	2.049(8)	Ru(3)–C(13)	1.953(5)
Ru(4)–C(13)	2.035(8)	Ru(4)–C(13)	2.073(6)
Ru(5)–C(13)	2.019(8)	Ru(5)–C(13)	2.013(6)
Ru(6)–C(13)	2.048(8)	Ru(6)–C(13)	2.048(6)
Ru(5)–C(20)	2.31(1)	Ru(5)–C(20)	2.268(8)
Ru(5)–C(21)	2.32(1)	Ru(5)–C(21)	2.280(7)
Ru(6)–C(22)	2.18(1)	Ru(6)–C(22)	2.347(7)
Ru(6)–C(23)	2.22(1)	Ru(6)–C(23)	2.284(7)
Ru(2)–C(14)	2.19(4)	Ru(3)–C(14)	2.233(6)
Ru(2)–C(15)	2.39(1)	Ru(3)–C(15)	2.238(6)
Ru(4)–C(16)	2.24(1)	Ru(3)–C(16)	2.231(7)
Ru(4)–C(17)	2.26(1)	Ru(3)–C(17)	2.234(7)
Ru(3)–C(18)	2.24(1)	Ru(3)–C(18)	2.239(6)
Ru(3)–C(19)	2.35(1)	Ru(3)–C(19)	2.249(6)
mean Ru–C _{CO(t)}	1.903	mean Ru–C _{CO(t)}	1.887
mean C _{CO} –O _{CO}	1.127	mean C _{CO} –O _{CO}	1.148
Ru(1)–C(3)–O(3)	137(1)	Ru(4)–C(1)–O(1)	143(1)
Ru(6)–C(3)–O(3)	138(1)	Ru(2)–C(4)–O(4)	149(1)
Ru(1)–C(1)–O(1)	132(1)		

$\nu(\text{CO})$ absorption band pattern of **7** is virtually identical to that of the starting material **5**, albeit shifted to higher wavenumbers by 30–45 cm^{-1} . For a hexaruthenium cluster this corresponds to an increase in positive charge of one unit. This evidence together with other spectroscopic data, including the correct mass spectrum value, m/z 1113, and a ^1H NMR showing the $\eta^6\text{-C}_6\text{H}_6$ singlet at δ 6.00 ppm and a series of signals indicative of a dienyl moiety, allows for the proposal of the cationic complex **7**; hence, this derivative represents another example of a dienyl bonded to a cluster unit. As far as we are aware, the only other previous examples are found in triruthenium and triosmium clusters.⁹ In all these examples the dienyl moiety is bonded above a triangle of three metal atoms. In the example reported here we cannot be certain of the bonding mode, as crystals of **7** suitable for X-ray analysis have not been grown. As far as we are aware, there are no further established examples of a dienyl unit bonded to one metal atom in a cluster. Deprotonation of this cationic cluster **7** with DBU affords the bis(benzene) cluster **6**.

Treatment of **4** with 1 equiv of Me_3NO does not result in the formation of the expected bis(benzene) species in which both ligands adopt face-capping coordination modes; instead, the formation of **6** is observed. Here there are two possible mechanisms which may be in play. First, the diene may undergo dehydrogenation (driven from the creation of a vacant coordination site on the cluster core by removal of CO by Me_3NO) directly onto a single metal atom (similar to the mechanism which we believe occurs in the formation of **3** from **2**). Alternatively, the diene may initially convert to a μ_3 -benzene which then rapidly migrates to a terminal site, this being an isomerization step observed in similar systems,⁹ but as yet unobserved in this instance.

Experimental Section

All reactions were carried out with the exclusion of air using freshly distilled solvents under an atmosphere of nitrogen. Subsequent workup of products was achieved without precautions to exclude air with standard

(13) Braga, D.; Grepioni, F.; Johnson, B. F. G.; Housecroft, C. E.; Lewis, J.; Martinelli, M. *Organometallics* 1991, 10, 1260.

Table V. Crystal Data and Details of Measurements for 2, 3, 4, and 5

	2	3	4	5
formula	C ₂₂ H ₈ O ₁₅ Ru ₆	C ₂₁ H ₆ O ₁₄ Ru ₆	C ₂₅ H ₁₄ O ₁₂ Ru ₆	C ₂₅ H ₁₄ O ₁₂ Ru ₆ CH ₂ Cl ₂
mol wt	1118.72	1088.69	1112.80	1197.73
crystal size (mm)	0.15 × 0.25 × 0.10	0.12 × 0.20 × 0.10	0.18 × 0.25 × 0.13	0.43 × 0.31 × 0.08
temp (K)	296	296	296	150
system	monoclinic	orthorhombic	orthorhombic	triclinic
space group	P2 ₁ /c	P2 ₁ 2 ₁ 2 ₁	Pna2 ₁	P $\bar{1}$
a (Å)	17.723(3)	8.924(6)	20.536(3)	10.314(9)
b (Å)	9.502(2)	16.332(6)	9.843(3)	10.720(8)
c (Å)	18.443(5)	18.299(9)	13.911(2)	15.23(1)
α (deg)				74.24(5)
β (deg)	116.02(2)			79.59(5)
γ (deg)				78.50(4)
V (Å ³)	2792	2667	2812	1574
Z	4	4	4	2
F(000)	2096	2032	2096	1132
λ(Mo Kα) (Å)	0.710 69	0.710 69	0.710 69	0.710 69
μ(Mo Kα) (cm ⁻¹)	29.41	30.74	29.13	27.65
θ range (deg)	3–25	2.5–25	2.5–20	2.5–22.5
ω scan width (deg)	1.40	0.80	0.70	1.20
requested counting σ(I)/I	0.02	0.02	0.01	0.05
prescan rate (deg min ⁻¹)	5	5	8	5
prescan acceptance σ(I)/I	0.5	0.5	0.5	0.5
max scan time (s)	100	100	60	66
octants explored				
(h _{min} h _{max} , k _{min} k _{max} , l _{min} l _{max})	±21, 0 15, 0 21	0 10, 0 19, 0 21	0 19, 0 13, 0 9	±10, ±10, 0 16
measd reflns	5384	4352	3744	4033
unique obsd reflns				
[I ₀ > 2σ(I ₀)]	2879	3375	3079	3497
no. of refined params	389	372	421	459
R, R _w , ^a S	0.043, 0.046, 1.35	0.024, 0.025, 1.04	0.026, 0.029, 1.41	0.045, 0.048, 1.00
K, g ^a	1.1947, 0.0015	1.028, 0.0005	0.9971, 0.0027	1.0000, 0.0037

$$^a R_w = \sum [(F_o - F_c)w^{1/2}] / \sum F_o w^{1/2}, \text{ where } w = k / [\sigma(F) + |g|F^2].$$

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 by thin layer chromatography (TLC) on plates supplied by Merck coated with a 0.25-mm layer of Kieselgel 60 F₂₅₄, using hexane (70%)/dichloromethane (30%) as eluent. Ru₆C(CO)₁₇ was prepared according to the literature procedure.¹⁴ Cyclohexa-1,3-diene and cyclohexa-1,4-diene were purchased from Aldrich Chemical Co. and used without further purification. Trimethylamine N-oxide (Me₃NO) was sublimed prior to reaction. Spectroscopic details and microanalytical data of the species described below can be found in Table I.

Reaction of Ru₆C(CO)₁₇ (1) with 1,3- or 1,4-Cyclohexadiene and Me₃NO. Ru₆C(CO)₁₇ (1) (100 mg) in CH₂Cl₂ (30 mL) containing excess 1,3- or 1,4-cyclohexadiene (1.5 mL) was cooled to -78 °C and treated with Me₃NO (15 mg, 2.1 mol equiv) added dropwise in CH₂Cl₂ (5 mL) over a 5-min period. The reaction mixture was stirred for 25 min and brought to room temperature, after which time the color had changed from purple to dark brown. The solvent was removed *in vacuo*, and the products were separated by TLC. The two brown bands are characterized (in order of elution) as Ru₆C(CO)₁₅(μ₂-η²-η²-C₆H₈) (2) (19 mg) and Ru₆C(CO)₁₄(η⁶-C₆H₆) (3) (24 mg), respectively. Crystallization was achieved by slow evaporation from dichloromethane/hexane.

Reaction of Ru₆C(CO)₁₅(μ₂-η²-η²-C₆H₈) (2) with Me₃NO. Ru₆C(CO)₁₅(μ₂-η²-η²-C₆H₈) (2) (10 mg) in CH₂Cl₂ (20 mL) was treated with Me₃NO (1 mg, 1.1 molar equiv) added dropwise in CH₂Cl₂ (3 mL) over 5 min. The reaction mixture was stirred for 15–20 min, and the solvent was removed *in vacuo*. The products were separated by TLC and the two brown bands characterized spectroscopically as the starting material, Ru₆C(CO)₁₅(μ₂-η²-η²-C₆H₈) (2) (5 mg), and Ru₆C(CO)₁₄(η⁶-C₆H₆) (3) (3 mg).

Reaction of Ru₆C(CO)₁₄(η⁶-C₆H₆) (3) with 1,3- or 1,4-Cyclohexadiene and Me₃NO. Ru₆C(CO)₁₄(η⁶-C₆H₆) (3) (30 mg) in CH₂Cl₂ (20 mL) containing a large excess of 1,3- or 1,4-cyclohexadiene (2 mL) was cooled to -78 °C and treated with Me₃NO (5 mg, 2.1 molar equiv) added dropwise in CH₂Cl₂ (5 mL). The reaction mixture was stirred for 30 min, during which time it was brought to room temperature. The solvent was removed *in vacuo*, and the products were separated by TLC. In order of elution,

the major brown band and the minor orange and red bands were characterized as Ru₆C(CO)₁₂(η⁶-C₆H₆)(μ₂-η²-η²-C₆H₈) (11 mg) (5), Ru₆C(CO)₁₂(μ₃-η²-η²-η²-C₆H₆)(μ₂-η²-η²-C₆H₈) (4 mg) (4), and Ru₆C(CO)₁₁(η⁶-C₆H₆)(μ₃-η²-η²-η²-C₆H₆) (6) (4 mg), respectively. Products 4 and 6 were crystallized from dichloromethane, into which pentane diffused, while compound 5 was crystallized over several weeks at -20 °C from dichloromethane/hexane.

Thermolysis of Ru₆C(CO)₁₂(μ₃-η²-η²-η²-C₆H₆)(μ₂-η²-η²-C₆H₈) (4). Ru₆C(CO)₁₂(μ₃-η²-η²-η²-C₆H₆)(μ₂-η²-η²-C₆H₈) (4) (4 mg) was heated in hexane (15 mL) under reflux for 18 h, during which period the reaction mixture darkened from orange to brown. IR spectroscopy indicated complete conversion of the starting material to Ru₆C(CO)₁₂(η⁶-C₆H₆)(μ₂-η²-η²-C₆H₈) (5) (3 mg). Spot TLC was used to ensure that only one product had resulted.

Reaction of Ru₆C(CO)₁₂(η⁶-C₆H₆)(μ₂-η²-η²-C₆H₈) (5) with Me₃NO. Ru₆C(CO)₁₂(η⁶-C₆H₆)(μ₂-η²-η²-C₆H₈) (5) (13 mg) in CH₂Cl₂ (20 mL) was treated with Me₃NO (1 mg, 1.1 molar equiv) added dropwise in CH₂Cl₂ (3 mL) over a few minutes. The reaction mixture was stirred for a further 15 min. The solvent was removed *in vacuo*, and the products were separated by TLC. In order of elution, the two bands were identified spectroscopically as the brown starting material, Ru₆C(CO)₁₂(η⁶-C₆H₆)(μ₂-η²-η²-C₆H₈) (5) (6 mg), and Ru₆C(CO)₁₁(η⁶-C₆H₆)(μ₃-η²-η²-η²-C₆H₆) (6) (2 mg).

Reaction of Ru₆C(CO)₁₂(η⁶-C₆H₆)(μ₂-η²-η²-C₆H₈) (5) with [Ph₃C][BF₄]. Ru₆C(CO)₁₂(η⁶-C₆H₆)(μ₂-η²-η²-C₆H₈) (5) (18 mg) in CH₂Cl₂ (10 mL) was treated with an excess of [Ph₃C][BF₄] (approximately 0.5 g) and the reaction mixture heated to reflux for 25 min. A dark suspension can be seen in the solution, which is allowed to settle for a few minutes. The solvent was decanted, leaving a brown precipitate on the walls of the vessel, which was washed with hexane (four 2-mL aliquots) and then dichloromethane (three 2-mL aliquots) and redissolved in acetone or nitromethane. Slow evaporation from these solvents, as well as other attempts at crystallization, led only to the formation of a brown powder. The brown solid was characterized by spectroscopic methods as [Ru₆C(CO)₁₂(η⁶-C₆H₆)(μ₃-η¹-η²-η²-C₆H₇)]⁺ (7) (6 mg).

Reaction of [Ru₆C(CO)₁₂(η⁶-C₆H₆)(μ₃-η¹-η²-η²-C₆H₇)]⁺ (7) with DBU. [Ru₆C(CO)₁₂(η⁶-C₆H₆)(μ₃-η¹-η²-η²-C₆H₇)]⁺ (7) (5 mg) was suspended in CH₂Cl₂ (10 mL). DBU (3 drops) was added and the mixture stirred for 15 min. Purification by filtration through silica followed by removal

(14) Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Nelson, W. J. H.; Sankey, S. W.; Wong, K. J. *Organomet. Chem.* 1980, 191, C3.

of the solvent *in vacuo* afforded a red-brown solid characterized by spectroscopic methods as $\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$ (**6**) (6 mg).

Structural Characterization

Diffraction data for species **2**, **3**, and **4** were collected on an Enraf-Nonius CAD-4 diffractometer, and data for species **5**, on a Stadi-4 diffractometer. Diffraction intensities were collected in $\omega/2\theta$ scan mode at room temperature for **2**, **3**, and **4** and at 150 K in an oil drop for **5**, due to crystal instability out of solution. Crystal data and details of measurement are summarized in Table V. The structures were solved by direct methods, which allowed location of the Ru atoms, followed by difference Fourier syntheses and subsequent least-squares refinement. Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography*.^{15a} For all calculations the SHELX76 program was used.^{15b} All atoms except the H atoms were treated anisotropically. The H atoms of the C_6H_6 ligands as well as

those of the face-capping benzene ligand in **4** were directly located from the final Fourier maps and refined by constraining the positions to an average C–H bond distance of 0.95 Å, while the H atoms of the terminal ligands (perhaps because of the more extensive vibrational motion of the ligands) could not be located and were added in calculated positions (C–H 0.95 Å) and refined “riding” on their respective C atoms. Common isotropic thermal factors were refined for the H(CH₂) and H(CH) atoms.

Acknowledgment. We would like to thank Dr. Alexander J. Blake (Edinburgh) for collecting data on the crystal of **5**. We are grateful to the SERC and British Petroleum (P.J.D.) for financial assistance. Financial support by MURST (Italy) is also acknowledged (D.B., F.G.). D.B., F.G., and B.F.G.J. acknowledge NATO for a travel grant.

Supplementary Material Available: Tables of anisotropic thermal parameters, thermal parameters and fractional atomic coordinates for the hydrogen atoms, and a complete list of bonds and angles for all crystallographically characterized species discussed (61 pages); listing of observed and calculated structure factors for **2–5** (62 pages). Ordering information is given on any current masthead page.

(15) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, pp 99–149. (b) Sheldrick, G. M. *SHELX76, Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.