

Synthesis and Structural Characterization of Diene and Benzene Pentaruthenium Clusters†

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Reaction of the square-pyramidal cluster $[\text{Ru}_5\text{C}(\text{CO})_{15}]$ **1** with cyclohexa-1,3-diene and Me_3NO in CH_2Cl_2 at ambient temperature affords the novel species $[\text{Ru}_5\text{C}(\text{CO})_{13}(\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_8)]$ **2** which has been fully characterized by X-ray diffraction studies [monoclinic, space group $P2_1/n$, $a = 16.193(3)$, $b = 9.897(2)$, $c = 19.536(4)$ Å, $\beta = 98.80(3)^\circ$ and $Z = 4$]. Further reaction of compound **2** with Me_3NO in the same solvent results in the dehydrogenation of the C_6H_8 ligand and the production of two isomers **3a** and **3b** of the benzene derivative $[\text{Ru}_5\text{C}(\text{CO})_{12}(\text{C}_6\text{H}_6)]$. In agreement with mass spectroscopic and ^1H NMR data, the X-ray diffraction analysis shows that the benzene ligand is bound in a face-capping mode in $[\text{Ru}_5\text{C}(\text{CO})_{12}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$ **3a** and in a terminal mode in $[\text{Ru}_5\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)]$ **3b**, respectively. Compound **3a** is triclinic, space group $P\bar{1}$, $a = 9.525(2)$, $b = 14.574(3)$, $c = 9.484(4)$ Å, $\alpha = 96.29(2)$, $\beta = 112.37(3)$, $\gamma = 82.33(2)^\circ$ and $Z = 2$; **3b** is monoclinic, space group $P2_1/c$, $a = 15.26(2)$, $b = 16.675(9)$, $c = 19.016(9)$ Å, $\beta = 96.04(7)^\circ$ and $Z = 8$. On heating **3a** in hexane a quantitative and irreversible conversion to **3b** is observed. Treatment of **3b** with carbon monoxide produces the adduct $[\text{Ru}_5\text{C}(\text{CO})_{13}(\eta^6\text{-C}_6\text{H}_6)]$ **4a**, which, on the basis of a single crystal X-ray diffraction study, has been shown to contain a 'bridged-butterfly' arrangement of five ruthenium atoms. Compound **4a** is monoclinic, space group $P2_1/n$, $a = 9.792(4)$, $b = 15.718(2)$, $c = 16.446(3)$ Å, $\beta = 96.37(2)^\circ$ and $Z = 4$. On standing in CH_2Cl_2 , **4a** undergoes loss of carbon monoxide to give the apical isomer $[\text{Ru}_5\text{C}(\text{CO})_{12}(\text{C}_6\text{H}_6)]$ **3c**. On heating in hexane over a prolonged period **3c** undergoes quantitative isomerization to **3b**.

In the course of our studies on the synthesis and structure of arene clusters, we have been able to show that benzene readily forms complexes with a wide range of cluster systems.¹⁻⁶ We have reported the synthesis and full structural characterization by single crystal X-ray diffraction studies of a variety of arene derivatives based on Ru_3 ,¹ Os_3 ,^{2,3} Os_4 ⁴ or Ru_6C cluster units.⁵ Formal donation of six electrons from the cyclic system to the cluster orbitals can be achieved either *via* conventional η^6 bonding, in which the benzene fragment formally replaces a tricarbonyl unit bound to a single metal atom, or *via* the less common 'face-capping' of a cluster triangular face. In this latter type of bonding extensive localization of single and double bonding is usually observed within the carbon six-membered ring.^{1,5}

The isolation of the first arene clusters containing terminal arene ligands, *viz.* $[\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-arene})]$ (where arene = $\text{C}_6\text{H}_3\text{Me}_3$, $\text{C}_6\text{H}_4\text{Me}_2$ and $\text{C}_6\text{H}_5\text{Me}$) was reported in 1967;⁶ the bonding mode was established by an X-ray diffraction study of the mesitylene derivative.⁷ The face-capping bonding mode has been ascertained in the trimetallic species $[\text{M}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$ ($\text{M} = \text{Ru}^1$ or Os^8). These species are of special interest because of the relevance they bear to the chemisorption of benzene on a $\text{Rh}(111)$ ⁹ or $\text{Os}(001)$ ¹⁰ single-crystal surface and also, possibly more significantly, because the benzene molecule apparently bonds in a manner more closely resembling that of a triene than a fully delocalized ring system. In this respect the cluster $[\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$ is exceptional in that it contains two benzene moieties each bonded in a different manner, *viz.* one face-capping and one terminal.⁸

Further studies have revealed that the face-capping benzene in $[\text{M}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$ ($\text{M} = \text{Ru}$ or Os) can be displaced to a terminal bonding position on reaction of the cluster with an alkyne.³ Thus, it is clear that a systematic and diverse chemistry of arene clusters is emerging which is of relevance not only to the organometallic chemistry of cluster compounds but also to the chemisorption of arenes on the metal surface. Furthermore, the investigation of the crystal structures of some of these carbonyl-arene clusters has afforded insights into the factors controlling the reorientational motion of the arene fragments in the solid state.¹¹ We have been able to show that benzene in either co-ordination mode is able to undergo $2\pi/6$ reorientational jumping motion in the solid state with relatively low energy barriers at room temperature, while toluene or mesitylene is blocked in its motion by the surrounding ligands and molecules.⁵ It has also been shown that precise relationships exist between the shape of the arene fragments and the molecular self organization within the solid lattice.¹²

In this paper we report a systematic study of the synthesis and structural chemistry of some benzene derivatives of the square-pyramidal carbidocarbonyl cluster $[\text{Ru}_5\text{C}(\text{CO})_{15}]$.¹³ A review on arene cluster chemistry has recently appeared.¹⁴

Results and Discussion

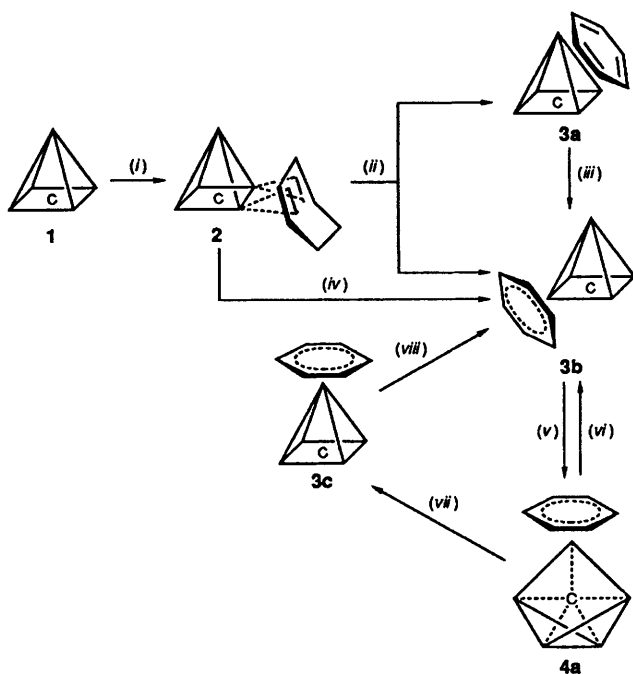
The addition of two equivalents of Me_3NO to $[\text{Ru}_5\text{C}(\text{CO})_{15}]$ **1** in dichloromethane in the presence of cyclohexa-1,3-diene produces red $[\text{Ru}_5\text{C}(\text{CO})_{13}(\text{C}_6\text{H}_8)]$ **2** (Scheme 1), which may be separated in moderate yield after thin-layer chromatography (TLC) on silica using dichloromethane-ethyl acetate-hexane (2:1:17 v/v) as eluent. The molecular formula of **2** was initially established from the mass and ^1H NMR spectra. The mass

† *Supplementary data available: see Instructions for Authors, J. Chem. Soc., Dalton Trans., 1993, Issue 1, pp. xxiii-xxviii.*

Table 1 Spectroscopic data for compounds 2–4^a

Compound	$\nu(\text{CO})^a/\text{cm}^{-1}$	$^1\text{H NMR}^b$	Mass spectrum m/z^c
2 $[\text{Ru}_5\text{C}(\text{CO})_{13}(\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_8)]$	2083m	5.42 (2 H, m)	961 (961)
	2051s	4.36 (2 H, m)	
	2032w (sh)	2.74 (2 H, m)	
	2020s	1.80 (2 H, m)	
3a $[\text{Ru}_5\text{C}(\text{CO})_{12}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$	2085m	4.12 (6 H, s)	931 (931)
	2063s		
	2028w (sh)		
	2014s		
	1890w (br)		
3b $[\text{Ru}_5\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)]$	2077m	5.93 (6 H, s)	931 (931)
	2048s		
	2033m (sh)		
	2010s		
3c $[\text{Ru}_5\text{C}(\text{CO})_{12}(\text{C}_6\text{H}_6)]$	2078m	5.93 (6 H, s)	931 (931)
	2068s		
	2050s		
	2035s		
	2011s		
4a $[\text{Ru}_5\text{C}(\text{CO})_{13}(\eta^6\text{-C}_6\text{H}_6)]$	2076m	6.36 (6 H, s)	959 (959)
	2045s		
	2023s		
	1982w		

^a Measured in CH_2Cl_2 . ^b Measured in CDCl_3 . ^c Calculated values given in parentheses.



Scheme 1 (i) $\text{Me}_3\text{NO-CH}_2\text{Cl}_2$ added dropwise to a CH_2Cl_2 -cyclohexa-1,3-diene solution; (ii) $\text{Me}_3\text{NO-CH}_2\text{Cl}_2$ added dropwise to a CH_2Cl_2 solution; (iii) refluxing hexane for 4 h; (iv) refluxing hexane for 18 h; (v) CO bubbled through a CH_2Cl_2 solution; (vi) allowed to stand under N_2 immediately after preparation of compound 4; (vii) allowed to stand under N_2 after storing compound 4 at -20°C for 24 h; (viii) refluxing hexane for 40 h

spectrum exhibited a strong parent peak together with peaks corresponding to the sequential loss of thirteen CO groups. The $^1\text{H NMR}$ spectrum displayed four multiplets of equal intensity which may be readily assigned to the four different protons of the co-ordinated diene (see Table 1).

The molecular structure of compound 2 has been established by single crystal X-ray diffraction and is shown in Fig. 1 together with the atomic labelling scheme. Relevant structural parameters are listed in Table 2. The metal-atom polyhedron in compound 2 comprises the familiar square-pyramidal frame-

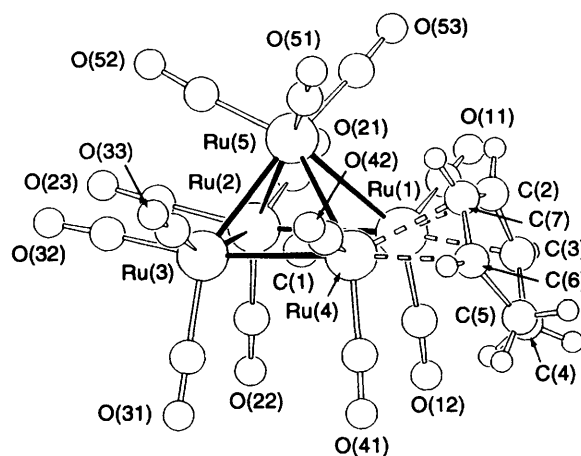


Fig. 1 The solid-state molecular structure of compound 2, showing the atomic labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms

work of $[\text{Ru}_5\text{C}(\text{CO})_{15}]$.¹³ Ruthenium–ruthenium bond lengths range from 2.772(2) to 2.909(2) Å [mean 2.831(2) Å] and are comparable to the values reported for compound 1 [2.800(2)–2.882(2) Å, mean 2.840(2) Å]. The cyclohexadiene ligand occupies a radial position with respect to the cluster square base. The ligand clearly interacts in $\mu\text{-}\eta^2\text{:}\eta^2$ mode with the metal atoms by spanning one basal edge, thus formally replacing one radial CO on two consecutive Ru atoms in the parent $\text{Ru}_5\text{C}(\text{CO})_{15}$ molecule. The 1,3 C=C double-bond localization is reflected in the C–C distances [C(2)–C(3) 1.39(2) and C(6)–C(7) 1.40(2) Å versus an average of 1.46(2) Å for the other C–C distances]. In agreement with this bonding pattern the C–C–C angles at the sp^3 -hybridized carbon atoms are significantly smaller than 120° [116(1) and 116(1) $^\circ$ at C(5) and C(4), respectively]. The Ru–C(diene) distances are slightly different, the separation from atoms C(3) and C(6) [mean 2.33(1) Å] being slightly longer than that from atoms C(7) and C(2) [mean 2.28(1) Å].

The formation of compound 2 from the reaction of cyclohexa-1,3-diene is not unexpected and is similar to the behaviour

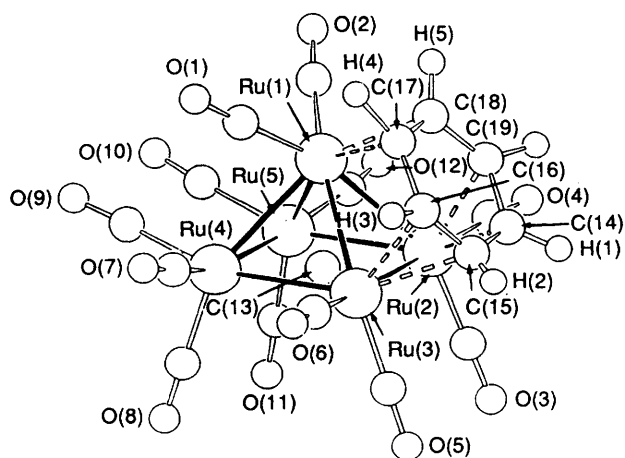


Fig. 2 The solid-state molecular structure of compound **3a**, showing the atomic labelling scheme; other detail as in Fig. 1

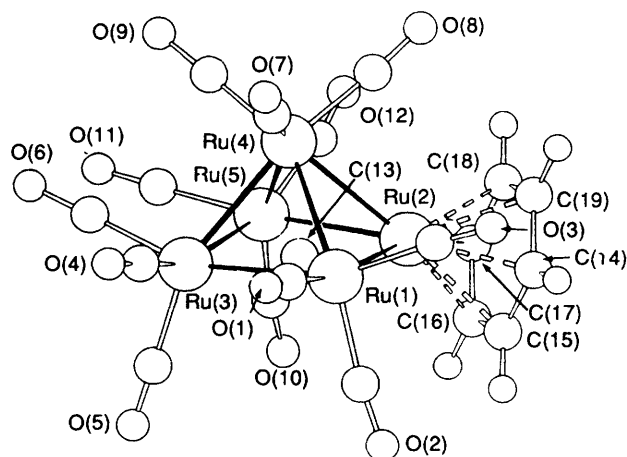


Fig. 3 The solid-state molecular structure of one of the two independent molecules present in the asymmetric unit of compound **3b**, showing the atomic labelling scheme; other detail as in Fig. 1

Table 2 Relevant bond distances (Å) and angles (°) for compound **2**

Ru(1)–Ru(2)	2.840(2)	Ru(1)–C(2)	2.28(2)
Ru(2)–Ru(3)	2.909(2)	Ru(1)–C(3)	2.30(1)
Ru(3)–Ru(4)	2.831(3)	Ru(4)–C(7)	2.28(1)
Ru(1)–Ru(4)	2.795(2)	Ru(4)–C(6)	2.36(2)
Ru(1)–Ru(5)	2.844(2)	C(2)–C(3)	1.39(2)
Ru(2)–Ru(5)	2.772(2)	C(3)–C(4)	1.50(2)
Ru(3)–Ru(5)	2.793(2)	C(4)–C(5)	1.43(2)
Ru(4)–Ru(5)	2.864(2)	C(5)–C(6)	1.48(2)
Ru(1)–C(1)	2.01(1)	C(6)–C(7)	1.40(2)
Ru(2)–C(1)	2.03(1)	C(2)–C(7)	1.43(2)
Ru(3)–C(1)	2.01(1)		
Ru(4)–C(1)	2.02(1)	Ru–C _{co} (mean)	1.91(2)
Ru(5)–C(1)	2.12(1)	C _{co} –O _{co} (mean)	1.13(2)
C(2)–C(3)–C(4)	120(1)	C(5)–C(6)–C(7)	120(1)
C(3)–C(4)–C(5)	116(1)	C(6)–C(7)–C(2)	119(1)
C(4)–C(5)–C(6)	116(1)	C(7)–C(2)–C(3)	121(1)

Table 3 Relevant bond distances (Å) for compound **3a**

Ru(1)–Ru(2)	2.827(1)	Ru(1)–C(18)	2.23(1)
Ru(1)–Ru(3)	2.829(1)	Ru(2)–C(19)	2.31(1)
Ru(1)–Ru(4)	2.800(1)	Ru(2)–C(14)	2.21(1)
Ru(1)–Ru(5)	2.811(1)	Ru(3)–C(15)	2.26(1)
Ru(2)–Ru(3)	2.845(1)	Ru(3)–C(16)	2.25(1)
Ru(2)–Ru(5)	2.841(1)		
Ru(3)–Ru(4)	2.843(1)	C(14)–C(15)	1.45(1)
Ru(4)–Ru(5)	2.827(1)	C(15)–C(16)	1.34(1)
Ru(1)–C(13)	2.09(1)	C(16)–C(17)	1.46(2)
Ru(2)–C(13)	2.02(1)	C(17)–C(18)	1.36(2)
Ru(3)–C(13)	2.00(1)	C(18)–C(19)	1.42(1)
Ru(4)–C(13)	2.02(1)	C(14)–C(19)	1.38(1)
Ru(5)–C(13)	2.01(1)	Ru–C _{co} (mean)	1.90(1)
Ru(1)–C(17)	2.31(1)	C _{co} –O _{co} (mean)	1.13(1)

Table 4 Relevant bond distances (Å) for compound **3b**

	Molecule A	Molecule B
Ru(1)–Ru(2)	2.847(2)	2.873(2)
Ru(1)–Ru(3)	2.800(2)	2.769(2)
Ru(1)–Ru(4)	2.774(2)	2.793(2)
Ru(1)–Ru(5)	2.744(2)	2.732(2)
Ru(2)–Ru(3)	2.807(2)	2.797(2)
Ru(3)–Ru(4)	2.856(2)	2.858(2)
Ru(4)–Ru(5)	2.865(2)	2.887(2)
Ru(2)–Ru(5)	2.791(2)	2.797(2)
Ru(1)–C(13)	2.09(2)	2.13(2)
Ru(2)–C(13)	1.93(2)	1.86(2)
Ru(3)–C(13)	2.00(2)	2.04(2)
Ru(4)–C(13)	2.02(2)	2.07(2)
Ru(5)–C(13)	2.07(2)	2.07(2)
Ru(2)–C(14)	2.25(1)	2.21(2)
Ru(2)–C(15)	2.23(1)	2.21(2)
Ru(2)–C(16)	2.21(1)	2.22(2)
Ru(2)–C(17)	2.21(1)	2.24(1)
Ru(2)–C(18)	2.22(1)	2.24(1)
Ru(2)–C(19)	2.24(1)	2.23(2)
Ru–C _{co} (mean)	1.90(2)	1.91(2)
C _{co} –O _{co} (mean)	1.14(3)	1.13(3)

observed in the formation of cyclohexa-1,3-diene derivatives of the mononuclear unit $M(\text{CO})_3$ ($M = \text{Fe}, \text{Ru}$ or Os). The simplest mechanistic pathway might be taken to involve the sequential removal of a co-ordinated CO (by oxidation to CO_2 by Me_3NO) followed by the addition of the diene *via* one olefin fragment in the first instance. The formation of **2**, in which the diene spans two ruthenium atoms, may reflect the activation by Me_3NO of co-ordination sites on two adjacent ruthenium atoms rather than at a single metal site.

Compound **2** was found to react with a further equivalent of Me_3NO in CH_2Cl_2 at ambient temperature to give the two isomeric benzene products, red $[\text{Ru}_5\text{C}(\text{CO})_{12}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$ **3a** and black $[\text{Ru}_5\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)]$ **3b**. After removal of solvent under vacuum these isomers were readily separated by TLC on silica using dichloromethane–ethyl acetate–hexane (2:1:17 v/v). On warming, isomer **3a** readily and irreversibly converts to **3b**. The observation that isomer **3a** appears to be the first product of the reaction may be taken to reflect the co-ordination mode of the diene in **2** (see above).

The solid-state structures of the isomers **3a** and **3b**, as established by single crystal X-ray diffraction,¹⁵ are shown in Figs. 2 and 3, respectively. Relevant bond distances are listed in Tables 3 and 4. Since the important structural features of the two complexes have been previously described in a preliminary report,¹⁵ the following section will only briefly summarize the main structural differences between the two species. Both clusters are based on the same square-pyramidal metal framework seen in compounds **1** and **2**, with the C(carbide) atom roughly occupying the middle of the square base (but see also

below). The most striking difference between the two structures arises essentially from the mode of co-ordination of the benzene fragment, which is face-capping (μ_3 bonding) in **3a** and terminal (η^6 bonding) in **3b**. This is the first report of the synthesis and full structural characterization of two structural isomers containing benzene in both bonding modes.

Face-capping of a cluster frame by benzene is not very common. This co-ordination mode has been previously observed only in the trinuclear species $[M_3(CO)_9(\mu_3-\eta^2:\eta^2-C_6H_6)]$ ($M = Ru^1$ and Os^8) and $[Os_3(CO)_8(\eta^2-C_2H_2)(\mu_3-\eta^2:\eta^2:\eta^2-C_6H_6)]^2$ and in the hexanuclear carbido-carbonyl cluster $[Ru_6C(CO)_{11}(\eta^6-C_6H_6)(\mu_3-\eta^2:\eta^2:\eta^2-C_6H_6)]^8$. A face-capping arene has also been observed in the cobalt cluster $[Co(\eta^5-C_5H_5)_3(\mu_3-\eta^2:\eta^2:\eta^2-C_6H_5CH=CHMe)]^{16}$. The η^6 co-ordination found in compound **3b** is more common. The benzene ligand formally replaces one tricarbonyl unit in the ligand envelope as observed in several arene derivatives of the octahedral cluster $[Ru_6C(CO)_{17}]$ {including $[Ru_6C(CO)_{11}(\eta^6-C_6H_6)(\mu_3-\eta^2:\eta^2:\eta^2-C_6H_6)]$ mentioned above⁸} and in the recently reported trinuclear species $[Ru_3(CO)_7(\mu_3-\eta^2-C_2-Ph_2CO)(\eta^6-C_6H_6)]^{3b}$ and $[Os_3(CO)_8(\mu_3-\eta^2-C_2Me_2)(\eta^6-C_6H_6)]^{3a}$.

At no stage during the formation of compounds **3a** and **3b** from compound **2** was observed the formation of the expected hexadienyl derivative $[Ru_5HC(CO)_{12}(C_6H_7)]$ **5**. The first step in this reaction sequence may be envisaged as the creation of a vacant co-ordination site within the Ru_5C unit by the oxidation of CO to CO_2 by Me_3NO , followed by the oxidative addition of a C-H bond of the diene to generate the hydridohexadienyl cluster **5**. The required second C-H bond cleavage must occur

by an alternative route since only one equivalent of Me_3NO is required. We may speculate that this essential second cleavage is brought about by an initial cluster rearrangement, possibly a square-pyramidal to bridged-butterfly interconversion, during which an activated co-ordination site is generated, which is then followed by the required C-H bond cleavage. This process will generate the second possible bridged-butterfly intermediate $[Ru_5H_2C(CO)_{12}(C_6H_6)]$. Dihydrogen is then evolved and the square-pyramidal Ru_5C unit regenerated. In this overall mechanistic pathway the dienyl derivative **5** is expected to be μ_3 bonded across a Ru_3 triangular face.

Treatment of compound **3b** with carbon monoxide under ambient conditions produces the new cluster $[Ru_5C(CO)_{13}(\eta^6-C_6H_6)]$ **4a**. In this reaction CO addition has apparently occurred at the basal ruthenium atom which supports the benzene molecule. Just as in the reaction of $[Ru_5C(CO)_{15}]$ with CO or MeCN, we have been able to establish by single

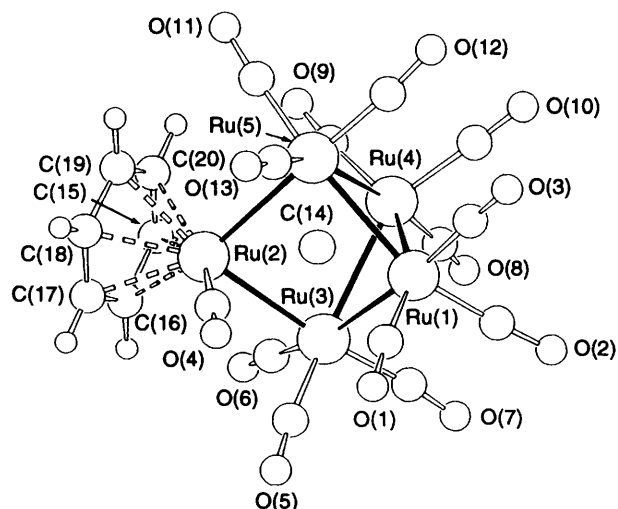


Fig. 4 The solid-state molecular structure of compound **4a**, showing the atomic labelling scheme; other detail as in Fig. 1

Table 5 Relevant bond distances (Å) for compound **4a**

Ru(1)–Ru(3)	2.837(2)	Ru(1)–Ru(4)	2.732(2)
Ru(1)–Ru(5)	2.870(2)	Ru(2)–Ru(3)	2.872(2)
Ru(2)–Ru(5)	2.859(2)	Ru(3)–Ru(4)	2.877(2)
Ru(4)–Ru(5)	2.865(2)		
Ru(1)–C(14)	2.10(1)	Ru(2)–C(14)	2.07(1)
Ru(3)–C(14)	1.97(1)	Ru(4)–C(14)	2.04(1)
Ru(5)–C(14)	1.99(1)	Ru(2)–C(15)	2.32(1)
Ru(2)–C(16)	2.27(1)	Ru(2)–C(17)	2.23(1)
Ru(2)–C(18)	2.24(1)	Ru(2)–C(19)	2.29(1)
Ru(2)–C(20)	2.33(1)		
Ru–C _{CO} (mean)	1.88(2)	C _{CO} –O _{CO} (mean)	1.15(2)

Table 6 Crystal data and measurement details for compounds **2**, **3a**, **3b** and **4a**^a

	2	3a	3b	4a
Formula	$C_{20.25}H_{8.5}Cl_{0.5}O_{15}Ru_5$	$C_{19}H_6O_{12}Ru_5$	$C_{19}H_6O_{12}Ru_5$	$C_{20}H_6O_{13}Ru_5$
M_r	1014.5	931.6	931.6	959.6
Crystal size/mm	0.25 × 0.27 × 0.42	0.13 × 0.16 × 0.14	0.12 × 0.11 × 0.15	0.2 × 0.25 × 0.13
System	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
$a/\text{Å}$	16.193(3)	9.525(2)	15.26(2)	9.792(4)
$b/\text{Å}$	9.897(2)	14.574(3)	16.675(9)	15.718(2)
$c/\text{Å}$	19.536(4)	9.484(4)	19.016(9)	16.446(3)
$\alpha/^\circ$		96.29(2)		
$\beta/^\circ$	98.80(3)	112.37(3)	96.04(7)	96.37(2)
$\gamma/^\circ$		82.33(2)		
$U/\text{Å}^3$	3092	1204	4812	2515
Z	4	2	8	4
$F(000)$	1962	872	3488	1800
$D_c/g\text{ cm}^{-3}$	2.19	2.57	2.57	2.54
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	24.3	28.40	28.43	27.2
2θ Range/ $^\circ$	7–45	6–56	5–50	6–50
ω Scan width/ $^\circ$	1.40	1.40	0.90	1.2
Maximum scan time/s		90	90	100
Measured reflections	5113	6415	7726	4752
Unique observed reflections [$I > 2\sigma(I)$]	2886	4114	3951	2037
No. of refined parameters	256	331	571	302
R, R' ^b	0.061, 0.78	0.040, 0.040	0.058, 0.060	0.039, 0.042
Goodness of fit	1.4	1.1	2.5	1.3
g	0.002	0.0010	0.0009	0.0004
k	1	0.7	1.01	1.12

^a Details common to the determinations of **3a**, **3b** and **4a**: requested counting $[\sigma(I)/I] = 0.02$, prescan rate = 3° min^{-1} and prescan acceptance $[\sigma(I)/I] = 0.5$. ^b $R' = \Sigma[(F_o - F_c)w^2]/\Sigma F_o w^2$, where $w = k/[\sigma(F) + |g|F^2]$.

Table 7 Fractional atomic coordinates ($\times 10^4$) for compound **2**

Atom	x	y	z
Ru(1)	1259(1)	1062(1)	3564(1)
Ru(2)	392(1)	642(1)	2846(1)
Ru(3)	-774(1)	3424(1)	3163(1)
Ru(4)	901(1)	3755(1)	3815(1)
Ru(5)	518(1)	2775(1)	2423(1)
C(1)	212(8)	2177(14)	3398(7)
C(2)	2492(9)	2217(15)	3695(8)
C(3)	2513(10)	1348(16)	4258(8)
C(4)	2442(11)	1914(16)	4960(8)
C(5)	2541(11)	3346(17)	5035(9)
C(6)	2259(10)	4163(16)	4409(8)
C(7)	2291(9)	3619(15)	3750(8)
C(11)	1736(9)	-435(16)	3098(7)
O(11)	2033(8)	-1277(11)	2845(6)
C(12)	1076(10)	-14(16)	4300(8)
O(12)	912(7)	-669(11)	4753(6)
C(21)	66(11)	-776(17)	2384(9)
O(21)	307(8)	-1623(15)	2104(8)
C(22)	-810(10)	-452(17)	3533(8)
O(22)	-1055(8)	-1075(12)	3937(6)
C(23)	-1404(10)	511(16)	2195(8)
O(23)	-1975(8)	387(13)	1803(6)
C(31)	-1266(10)	3416(16)	4006(9)
O(31)	-1539(8)	3510(13)	4504(6)
C(32)	-1794(11)	3204(16)	2541(8)
O(32)	-2422(8)	3124(14)	2185(7)
C(33)	-842(10)	5352(17)	3006(8)
O(33)	-898(8)	6467(11)	2896(7)
C(41)	674(9)	3696(15)	4739(8)
O(41)	509(7)	3646(11)	5269(5)
C(42)	864(9)	5707(16)	3752(8)
O(42)	837(8)	6849(11)	3704(6)
C(51)	958(10)	4536(17)	2305(8)
O(51)	1220(7)	5558(11)	2202(6)
C(52)	-349(10)	2777(17)	1656(8)
O(52)	-834(8)	2762(16)	1171(6)
C(53)	1340(10)	1830(16)	1999(8)
O(53)	1813(8)	1318(12)	1721(6)
Cl(1)	8073(17)	6184(27)	1179(14)
Cl(2)	8345(21)	7291(34)	-61(16)
C(100)	8738(64)	7137(106)	677(52)

crystal X-ray diffraction studies that the Ru_5C polyhedron undergoes conversion from a square-based pyramid to a bridged-butterfly arrangement.

The molecular structure of compound **4a** is shown in Fig. 4 together with the atomic labelling scheme. Relevant bond distances are listed in Table 5. The metal-atom framework can be described as a bridged-butterfly. This cluster can be seen as being formally derived from the square-pyramidal geometry of compound **3b** by opening up one apex-to-base linkage upon CO insertion on the basal Ru atom bearing the benzene ligand. The bridging Ru(2) atom is almost equidistant from the two ruthenium atoms of the butterfly hinge [Ru(1)···Ru(2) 3.919(2) and Ru(2)···Ru(4) 3.819(2) Å]. The Ru–Ru bond lengths in **4a** range from 2.732(2) to 2.877(2) Å and are slightly longer, in their mean value, than in **3b** [2.844(2) versus 2.812(2) Å]. Each ruthenium atom, except Ru(2), bears three CO groups as in the parent molecule. The Ru(2) atom formally receives two electrons more than the other metal atoms (six from benzene and two from the single CO ligand) but is involved in only two metal–metal interactions. Interestingly, the drift of the C(carbide) atom towards the arene-co-ordinated metal atom, observed in compound **3b**, is not seen in **4a**. This observation confirms that the C(carbide) atom ‘comes to help’ if complete substitution of CO ligands for the less efficient π -acceptor benzene ligand deprives the metal atom of electron density. This is not so for Ru(2) in **4a**, where the presence of the extra CO

Table 8 Fractional atomic coordinates for compound **3a**

Atom	x	y	z
Ru(1)	0.706 95(5)	0.352 48(3)	0.736 43(5)
Ru(2)	0.949 13(5)	0.213 79(3)	0.859 52(6)
Ru(3)	0.641 78(5)	0.169 49(3)	0.742 43(6)
Ru(4)	0.591 48(5)	0.245 23(3)	0.461 39(5)
Ru(5)	0.898 52(5)	0.285 99(3)	0.575 95(6)
C(1)	0.511 5(8)	0.414 1(4)	0.629 2(8)
O(1)	0.394 6(6)	0.452 3(4)	0.571 2(7)
C(2)	0.806 8(8)	0.458 9(5)	0.747 7(9)
O(2)	0.866 6(8)	0.523 9(4)	0.762 8(8)
C(3)	1.034 0(9)	0.090 5(5)	0.864 1(9)
O(3)	1.083 5(9)	0.014 8(5)	0.868 3(9)
C(4)	1.150 4(9)	0.246 7(6)	0.965 9(9)
O(4)	1.272 3(7)	0.262 5(7)	1.028 7(8)
C(5)	0.694 4(9)	0.040 3(5)	0.740 2(11)
O(5)	0.728 7(9)	-0.037 5(4)	0.738 5(10)
C(6)	0.433 3(8)	0.148 1(5)	0.684 3(10)
O(6)	0.312 4(6)	0.134 2(5)	0.658 1(9)
C(7)	0.378 4(8)	0.247 4(5)	0.418 6(8)
O(7)	0.249 3(6)	0.252 4(4)	0.384 3(7)
C(8)	0.596 9(8)	0.138 6(5)	0.330 4(9)
O(8)	0.604 6(9)	0.074 8(4)	0.255 1(8)
C(9)	0.551 8(8)	0.330 0(5)	0.307 0(7)
O(9)	0.520 2(7)	0.379 7(4)	0.213 4(6)
C(10)	0.866 3(8)	0.374 7(5)	0.425 4(8)
O(10)	0.856 4(8)	0.426 7(4)	0.344 2(7)
C(11)	0.971 4(8)	0.183 1(6)	0.474 4(9)
O(11)	1.005 9(7)	0.119 3(5)	0.413 5(8)
C(12)	1.094 7(8)	0.327 9(6)	0.687 8(9)
O(12)	1.207 6(7)	0.357 9(5)	0.743 6(9)
C(13)	0.773 6(6)	0.221 2(3)	0.656 2(6)
C(14)	0.881 6(10)	0.213 3(6)	1.057 9(9)
C(15)	0.729 0(11)	0.184 8(6)	0.999 9(9)
C(16)	0.606 0(9)	0.246 2(8)	0.946 7(10)
C(17)	0.625 4(14)	0.342 1(8)	0.933 6(11)
C(18)	0.767 5(15)	0.370 6(6)	0.988 9(9)
C(19)	0.895 5(11)	0.305 3(8)	1.050 5(10)

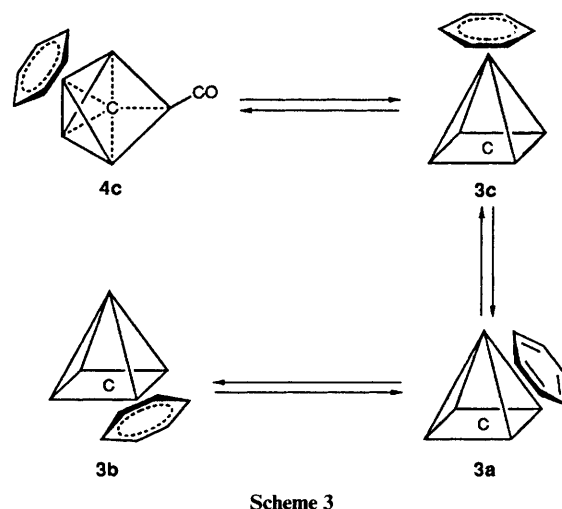
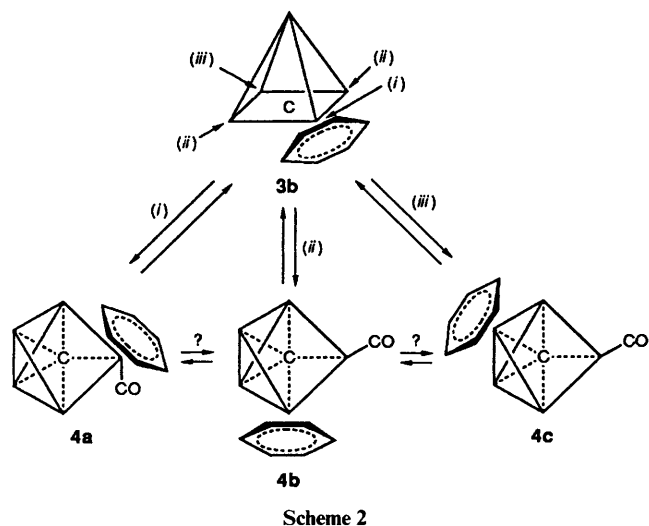
ligand appears to compensate for this effect, or in the face-capped **3a** where the effect is distributed over three metal atoms. Consistent with this, Ru–C(benzene) distances in **4a** appear to be slightly longer, in their mean value, than in **3b** [2.28(1) versus 2.23(1) Å].

On standing, freshly prepared samples of compound **4a** readily evolve carbon monoxide to regenerate the initial compound **3b**. If, however, **4a** is prepared and stored at -20°C for 24 h under a CO atmosphere, on removal of the CO at the same temperature under nitrogen, a third, new isomer of $[\text{Ru}_5\text{C}(\text{CO})_{12}(\text{C}_6\text{H}_6)]$ **3c** is produced. All attempts to obtain crystals of this new isomer have failed and have led to the isolation of crystals of the established isomer **3b**. However, since the IR spectra of the compounds are clearly different, we are inclined to suggest that the new isomer **3c** is based on the same square-pyramidal Ru_5 unit but that the benzene molecule is co-ordinated to the apical ruthenium atom. Alternatively, **3c** may possess a structure simply derived from **3b** by opening one Ru–Ru edge to form a bridged-butterfly Ru_5C arrangement which is stabilized by donation of a carbonyl oxygen to form a Ru–C–O–Ru bridge. It would appear that the thermodynamically stable isomer is **3b** but that isomer **3c** is the kinetically controlled product. If **3c** is heated in hexane for ca. 40 h then conversion to the isomer **3b** is observed.

It is clear that, given these observations, the reaction of isomer **3b** with CO is not simple. This leads us to suggest that attack by CO may occur either at more than one ruthenium site (Scheme 2) at substantially different rates or that CO attack initially occurs at one site and is followed by a slow isomerisation process involving CO migration. Possible mechanistic pathways are shown in Schemes 2 and 3. Given that compound **3b** appears to be the thermodynamically stable

Table 9 Fractional atomic coordinates for compound **3b**

Atom	x	y	z	Atom	x	y	z
Ru(1A)	0.951 85(10)	0.307 20(8)	0.771 75(9)	Ru(1B)	0.289 72(10)	0.272 10(8)	0.409 29(9)
Ru(2A)	0.855 73(10)	0.170 44(8)	0.809 91(9)	Ru(2B)	0.319 82(10)	0.283 40(8)	0.560 66(9)
Ru(3A)	0.854 10(10)	0.312 99(9)	0.888 25(9)	Ru(3B)	0.300 61(10)	0.135 09(8)	0.492 02(9)
Ru(4A)	0.796 72(10)	0.395 20(8)	0.759 86(9)	Ru(4B)	0.442 90(10)	0.179 79(9)	0.413 70(10)
Ru(5A)	0.813 57(10)	0.250 11(9)	0.681 75(9)	Ru(5B)	0.441 37(10)	0.339 62(9)	0.471 92(10)
O(1A)	1.058 5(10)	0.425 5(9)	0.868 9(10)	O(1B)	0.211 0(9)	0.153 6(9)	0.300 9(8)
O(2A)	1.087 9(10)	0.174 6(9)	0.772 1(11)	O(2B)	0.125 8(9)	0.356 0(10)	0.449 1(10)
O(3A)	1.005 6(11)	0.381 9(9)	0.636 2(10)	O(3B)	0.326 5(11)	0.391 3(8)	0.298 9(7)
O(4A)	0.887 8(15)	0.464 2(8)	0.973 0(9)	O(4B)	0.257 7(10)	-0.014 6(7)	0.405 4(9)
O(5A)	0.690 7(12)	0.272 3(16)	0.957 4(14)	O(5B)	0.377 4(12)	0.040 8(11)	0.619 6(9)
O(6A)	0.972 9(9)	0.223 4(10)	0.996 3(10)	O(6B)	0.110 6(10)	0.147 2(8)	0.524 6(10)
O(7A)	0.838 8(12)	0.550 4(7)	0.835 9(8)	O(7B)	0.395 7(12)	0.043 7(11)	0.310 7(11)
O(8A)	0.599 6(11)	0.414 9(9)	0.752 4(11)	O(8B)	0.578 8(12)	0.086 9(11)	0.504 9(14)
O(9A)	0.816 4(15)	0.494 3(9)	0.625 2(10)	O(9B)	0.549 9(13)	0.252 9(12)	0.303 4(12)
O(10A)	0.638 4(11)	0.174 1(10)	0.659 6(10)	O(10B)	0.586 8(11)	0.350 7(11)	0.589 4(8)
O(11A)	0.791 5(11)	0.348 1(10)	0.543 6(10)	O(11B)	0.543 8(13)	0.420 9(11)	0.361 0(11)
O(12A)	0.924 7(13)	0.124 8(9)	0.615 3(10)	O(12B)	0.350 4(11)	0.498 7(8)	0.496 6(8)
C(1A)	1.015 3(14)	0.380 8(12)	0.829 8(13)	C(1B)	0.241 3(12)	0.194 7(9)	0.342 6(9)
C(2A)	1.035 5(13)	0.222 2(11)	0.773 4(13)	C(2B)	0.186 4(15)	0.324 3(13)	0.435 1(12)
C(3A)	0.985 2(13)	0.352 7(12)	0.688 3(16)	C(3B)	0.315 1(13)	0.350 7(9)	0.349 1(9)
C(4A)	0.875 7(16)	0.410 8(8)	0.938 9(11)	C(4B)	0.274 8(13)	0.042 0(8)	0.434 8(9)
C(5A)	0.749 7(17)	0.292 3(16)	0.931 1(15)	C(5B)	0.347 0(13)	0.073 3(13)	0.570 5(13)
C(6A)	0.932 7(16)	0.256 1(12)	0.956 5(14)	C(6B)	0.179 1(13)	0.144 1(11)	0.511 2(12)
C(7A)	0.825 3(14)	0.491 3(8)	0.810 4(9)	C(7B)	0.412 6(13)	0.095 2(12)	0.349 8(13)
C(8A)	0.671 9(14)	0.406 3(11)	0.754 2(12)	C(8B)	0.535 0(16)	0.120 8(13)	0.468 1(10)
C(9A)	0.810 7(15)	0.456 1(13)	0.677 2(14)	C(9B)	0.512 5(16)	0.226 5(15)	0.348 6(13)
C(10A)	0.701 8(16)	0.205 0(13)	0.664 4(12)	C(10B)	0.537 9(10)	0.346 0(11)	0.542 9(8)
C(11A)	0.797 8(15)	0.312 3(11)	0.593 6(14)	C(11B)	0.506 9(15)	0.385 6(15)	0.401 8(13)
C(12A)	0.885 2(14)	0.168 3(11)	0.644 3(9)	C(12B)	0.379 7(16)	0.437 2(12)	0.488 7(11)
C(13A)	0.822 0(9)	0.279 7(10)	0.787 9(10)	C(13B)	0.381 6(12)	0.232 8(10)	0.494 2(11)
C(14A)	0.871 7(9)	0.087 5(8)	0.903 5(6)	C(14B)	0.254 2(9)	0.238 1(6)	0.651 0(8)
C(15A)	0.783 2(9)	0.088 6(8)	0.876 3(6)	C(15B)	0.343 4(9)	0.249 4(6)	0.673 2(8)
C(16A)	0.759 4(9)	0.071 0(8)	0.805 1(6)	C(16B)	0.382 2(9)	0.324 2(6)	0.665 3(8)
C(17A)	0.824 1(9)	0.052 4(8)	0.761 1(6)	C(17B)	0.331 8(9)	0.387 7(6)	0.635 2(8)
C(18A)	0.912 6(9)	0.051 3(8)	0.788 3(6)	C(18B)	0.242 6(9)	0.376 4(6)	0.613 0(8)
C(19A)	0.936 4(9)	0.068 8(8)	0.859 5(6)	C(19B)	0.203 8(9)	0.301 6(6)	0.620 9(8)



isomer, we tend to believe that the former pathway is the more appropriate.

The precise mechanism of the isomer interconversion has not been established. Nevertheless, since both isomers **3a** and **3c** convert irreversibly to **3b** (in the absence of external CO), it is not unreasonable to conclude that the process occurs *via* benzene slippage, first from a η^6 mode (as in **3c**) to a μ_3 - η^2 : η^2 : η^2 mode (as in **3a**) and finally to the alternative η^6 mode as in **3b**. Such slippage would also necessitate a considerable and simultaneous movement of the bonded CO

ligands. An alternative mechanism, in which the isomer interconversion is brought about by a mechanism related to that postulated for the reaction with CO, cannot be ruled out. In this alternative the initial step may be envisaged as involving solvent addition to a ruthenium atom *via* any of the three steps described above. However, the likelihood that this reaction would occur in hexane must be remote and it is more likely that some decomposition occurs to produce CO which reacts to bring about this isomerization according to the suggested route.

Table 10 Fractional atomic coordinates for compound **4a**

Atom	x	y	z
Ru(1)	0.178 15(12)	0.242 60(8)	0.323 88(8)
Ru(2)	-0.155 02(12)	0.166 48(8)	0.414 24(8)
Ru(3)	-0.030 95(13)	0.124 36(8)	0.269 20(8)
Ru(4)	-0.056 33(12)	0.304 17(8)	0.238 55(8)
Ru(5)	-0.018 90(12)	0.327 27(8)	0.412 42(8)
O(1)	0.342 0(11)	0.111 3(7)	0.429 9(7)
O(2)	0.328 6(15)	0.218 5(13)	0.176 1(9)
O(3)	0.369 7(14)	0.388 4(9)	0.373 5(12)
O(4)	0.089 1(12)	0.099 4(8)	0.520 1(7)
O(5)	0.100 2(12)	-0.034 0(8)	0.348 8(7)
O(6)	-0.294 0(14)	0.046 0(8)	0.184 5(9)
O(7)	0.100 3(16)	0.092 3(9)	0.113 5(9)
O(8)	-0.084 8(13)	0.249 5(9)	0.062 0(7)
O(9)	-0.353 5(12)	0.360 4(8)	0.229 7(8)
O(10)	0.095 0(14)	0.468 1(8)	0.205 7(10)
O(11)	-0.275 9(14)	0.424 3(8)	0.442 1(8)
O(12)	0.112 4(14)	0.499 0(9)	0.395 2(10)
O(13)	0.098 3(15)	0.301 3(10)	0.589 6(8)
C(1)	0.276 6(15)	0.163 2(10)	0.393 7(10)
C(2)	0.274 5(19)	0.225 0(14)	0.234 3(13)
C(3)	0.291 4(17)	0.333 5(11)	0.353 8(13)
C(4)	-0.004 3(17)	0.123 3(11)	0.477 0(10)
C(5)	0.004 7(13)	0.024 2(10)	0.320 6(10)
C(6)	-0.196 1(18)	0.076 0(10)	0.219 5(11)
C(7)	0.060 6(19)	0.107 6(11)	0.174 6(12)
C(8)	-0.069 7(17)	0.271 7(11)	0.127 4(10)
C(9)	-0.245 5(16)	0.335 1(10)	0.232 5(9)
C(10)	0.038 4(19)	0.407 7(13)	0.216 7(13)
C(11)	-0.180 9(18)	0.384 7(12)	0.431 5(11)
C(12)	0.066 1(20)	0.431 2(12)	0.398 7(12)
C(13)	0.056 8(15)	0.312 6(12)	0.521 9(12)
C(14)	-0.030 2(13)	0.226 8(9)	0.338 6(9)
C(15)	-0.374 3(10)	0.156 6(7)	0.344 8(5)
C(16)	-0.335 7(10)	0.078 1(7)	0.379 7(5)
C(17)	-0.294 6(10)	0.072 3(7)	0.463 5(5)
C(18)	-0.292 1(10)	0.145 0(7)	0.512 4(5)
C(19)	-0.330 7(10)	0.223 4(7)	0.477 5(5)
C(20)	-0.371 8(10)	0.229 2(7)	0.393 7(5)

Experimental

Synthesis and Characterization.—All syntheses were performed with the exclusion of air using solvents dried by conventional procedures. Product separation was achieved by thin-layer chromatography using plates supplied by Merck pre-coated with a 0.25 mm layer of Kieselgel 60F₂₅₄. Eluents were mixed from standard laboratory-grade solvents. Infrared spectra were recorded in CH₂Cl₂ using NaCl cells (0.5 mm path length) on a Perkin Elmer 1710 Fourier-transform spectrometer using carbon monoxide gas as calibrant. Mass spectra were obtained by electron-impact ionisation on a Kratos-AEI-MS12 instrument, using bis(perfluoroheptyl)-s-triazene as calibrant. Proton NMR spectra were recorded using a Bruker WM250 spectrometer using an internal deuterium lock.

The [Ru₅C(CO)₁₅] cluster was prepared according to the literature method.¹³ Trimethylamine *N*-oxide was sublimed immediately prior to use and cyclohexa-1,3-diene was used as received (Aldrich).

Reaction of [Ru₅C(CO)₁₅] 1. An excess of cyclohexa-1,3-diene (0.5 cm³) was added to a solution of [Ru₅C(CO)₁₅] **1** (100 mg) in CH₂Cl₂ (70 cm³). A solution of Me₃NO (16 mg, 2 mol equivalents) in CH₂Cl₂ (10 cm³) was added dropwise over a period of 5 min. The mixture was stirred for 30 min at room temperature and the reaction monitored by IR spectroscopy until complete conversion of the starting material was ensured. The solvent was removed *in vacuo* and the residue separated by TLC using dichloromethane–ethyl acetate–hexane (2:1:17 v/v) as eluent. The red band was extracted as the major product and characterized as [Ru₅C(CO)₁₃(μ-η²:η²-C₆H₈)] **2** (32 mg) by spectroscopy.

Reaction of [Ru₅C(CO)₁₃(μ-η²:η²-C₆H₈)] 2. Trimethylamine *N*-oxide (3 mg, 1.1 mol equivalent) in CH₂Cl₂ (5 cm³) was added dropwise over a period of 5 min to a solution of [Ru₅C(CO)₁₃(μ-η²:η²-C₆H₈)] **2** (32 mg) in CH₂Cl₂ (50 cm³). The mixture was stirred for 15 min at room temperature and the reaction monitored by IR spectroscopy, until complete conversion of the starting material was observed. The solvent was removed under a stream of nitrogen and the products extracted by TLC using dichloromethane–ethyl acetate–hexane (2:1:17 v/v) as eluent. The red and black bands were extracted and spectroscopically characterized as [Ru₅C(CO)₁₂(μ₃-η²:η²:η²-C₆H₆)] **3a** (14 mg) and [Ru₅C(CO)₁₂(η⁶-C₆H₆)] **3b**, respectively.

Thermolysis of compound 2. Compound **2** (24 mg) was dissolved in hexane (80 cm³) and heated under reflux for 18 h during which time the solution changed from red to black. Infrared spectroscopy used to monitor the thermolysis indicated that no starting material remained. The solvent was removed *in vacuo* and the residue separated by TLC using CH₂Cl₂–hexane (3:7 v/v) as eluent. The black band was extracted as the major product and characterized as [Ru₅C(CO)₁₂(η⁶-C₆H₆)] **3b** (20 mg) by IR spectroscopy.

Thermolysis of [Ru₅C(CO)₁₂(μ₃-η²:η²:η²-C₆H₆)] 3a. Compound **3a** (10 mg) was heated under reflux in hexane (30 cm³) for 4 h. During this time the colour changed from red to black and the IR spectrum indicated complete conversion of the starting material to [Ru₅C(CO)₁₂(η⁶-C₆H₆)] **3b**. This was confirmed by spot TLC which showed no other products present.

Preparation of [Ru₅C(CO)₁₂(C₆H₆)] 3c. Crystals of [Ru₅C(CO)₁₃(η⁶-C₆H₆)] **4a** (10 mg) were dissolved in CH₂Cl₂ (30 cm³) and on standing under a nitrogen atmosphere for 30 min the colour changed from yellow to black. Infrared spectroscopy showed that no starting material remained and spot TLC demonstrated only one product had formed which was characterized by mass spectroscopy as [Ru₅C(CO)₁₂(η⁶-C₆H₆)] **3c**.

Reaction of compound 3c with CO. A steady stream of CO was bubbled through a solution of [Ru₅C(CO)₁₂(C₆H₆)] **3c** (20 mg) in CH₂Cl₂ (30 cm³). After 5 min the solution had changed from black to yellow. Complete consumption of the starting material was indicated by IR spectroscopy. The reaction vessel was sealed and stored at -20 °C for 5 d during which time yellow crystals of [Ru₅C(CO)₁₃(η⁶-C₆H₆)] **4a** were obtained. Spot TLC indicated that the reaction was quantitative.

Thermolysis of compound 3c. Compound **3c** (8 mg) was refluxed in hexane (25 cm³) for 40 h. Infrared spectroscopy indicated complete conversion to [Ru₅C(CO)₁₂(η⁶-C₆H₆)] **3b** (8 mg). This was confirmed by spot TLC which showed that no other products were present.

X-Ray Structure Determination.—The diffraction data for all species discussed herein were collected on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo-Kα radiation, λ = 0.710 69 Å). Diffraction intensities were collected in the ω-2θ scan mode at room temperature for compounds **3a**, **3b** and **4a**, while data for compound **2** were measured at 200 K. Crystal data and measurement details are summarized in Table 6. The structures were solved by means of direct methods followed by Fourier difference syntheses and subsequent least-squares refinement. Scattering factors for neutral atoms were taken from ref. 17(a) and the SHELX 76 program^{17b} was used for all calculations. Absorption corrections for **3a**, **3b** and **4a** were applied using the Walker and Stuart method^{17c} once complete structural models were available and all atoms refined isotropically. All non-H atoms were treated anisotropically for **3a** and **4a**, while in **3b** the benzene groups were refined isotropically. Two independent molecules are present in the asymmetric unit of **3b**: structural parameters discussed in the text are given as pairs of chemically corresponding values in the two molecules. A fraction of CH₂Cl₂ solvent molecule was found

in the lattice of compound **2**, the site occupation factor for the two chlorine and the carbon atoms converged to *ca.* 0.25. The benzene H atoms in compounds **2**, **3b** and **4a** were added in calculated positions and refined 'riding' on their respective C atoms; those in **3a** were found in the final Fourier difference maps and refined with C–H bond length constraints. Common isotropic thermal parameters were refined for the benzene H atoms in compounds **3b** and **4a** [0.10(2) and 0.10(3) Å², respectively]. Fractional atomic coordinates are reported in Tables 7–10 for compounds **2**, **3a**, **3b** and **4a**, respectively.

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

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