Tetraruthenium Cluster Isomers containing Both C_6H_8 and [2.2]Paracyclophane Ligands: A New Face-bridging Co-ordination Mode for a C_6 Aromatic Ring†

Alexander J. Blake, Paul J. Dyson, Scott L. Ingham, Brian F. G. Johnson* and Caroline M. Martin
Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK

The reaction of $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ **1** with 2.2 molar equivalents of Me_3NO in dichloromethane containing cyclohexa-1,3-diene afforded the new tetrahedral complex $[Ru_4(CO)_9(\eta^4\text{-}C_6H_8)(\mu_3\text{-}C_{16}H_{16})]$ **2** in modest yield. The thermolysis of $[Ru_4(CO)_{12}(\mu_4\text{-}C_6H_8)]$ **3** in octane containing an excess of [2.2]paracyclophane ($C_{16}H_{16}$) and Me_3NO afforded the two new butterfly isomers $[Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\eta^6\text{-}C_{16}H_{16})]$ **4** and $[Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ **5**. Heating compound **4** results in its irreversible conversion to **5**. Compounds **2** and **4** have been characterised in the solid state by single-crystal X-ray diffraction and in **2** the [2.2]paracyclophane ring bonds to the cluster *via* an unusual $\mu_3\text{-}\eta^1:\eta^2:\eta^2$ bonding mode unseen before for an arene ring.

There is considerable interest in the synthesis of cyclophane–transition-metal complexes, and the majority of studies have focussed on complexes in which single metal atoms co-ordinate to either one or both of the cyclophane rings,[1] to form in some instances precursor units to polymeric systems.[2] However, it has been found that a metal can also be introduced into the cavity between the rings of a cyclophane system.[3] In complexes of [2.2]paracyclophane various features are consistently observed on co-ordination to a metal unit; for example the inter-arene distance contracts because of a reduction in the cofacial π repulsions as the metal unit(s) withdraw electron density, with the consequent redistribution of the remaining π-electron density.[4] This latter feature is apparent from the ^1H NMR spectra of these complexes; the frequencies of the unco-ordinated and co-ordinated ring protons increase and decrease respectively, relative to that observed in free [2.2]paracyclophane.[5]

Our interests in [2.2]paracyclophane have been concerned with the preparation, characterisation and reactivity of clusters bearing this compound as a ligand.[6–9] Compared to benzene and other simple arenes this ligand displays some unusual features. Whilst [2.2]paracyclophane has been observed to bond in the simple terminal mode (as it does in mononuclear complexes) it prefers to adopt multiple-bonding sites, and has been observed to bond along an edge in a $\mu\text{-}\eta^3:\eta^3$ mode in the binuclear complex,[8] and in clusters to form a triple bridge to a metal face in both the $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ mode,[6,7,9] and also a quasi-$\mu_3\text{-}\eta^1:\eta^1:\eta^1$ mode established in the solid state.[7]

In this paper we report the synthesis and characterisation of the tetrahedral cluster $[Ru_4(CO)_9(\eta^4\text{-}C_6H_8)(\mu_3\text{-}C_{16}H_{16})]$ **2** in which a new face-capping bonding type is observed for the [2.2]paracyclophane ligand in the solid state, and the butterfly clusters $[Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\eta^6\text{-}C_{16}H_{16})]$ **4** and $[Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ **5**; the former undergoes isomerisation to the latter species over a relatively short period at moderate temperatures.

Results and Discussion

To a solution of $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ **1** prepared from the thermolysis of $[Ru_3(CO)_{12}]$ with [2.2]paracyclophane in octane[7] in dichloromethane containing an excess of cyclohexa-1,3-diene at −78 °C, 2.2 molar equivalents of Me_3NO were added dropwise in dichloromethane. The solution was stirred at −78 °C for 20 min then allowed to warm slowly to room temperature and stirred for a further 3 h. Purification of the products was achieved by thin layer chromatography on silica, eluting with dichloromethane–hexane (3:7, v/v) which resulted in the isolation of yellow starting material and the new orange compound $[Ru_4(CO)_9(\eta^4\text{-}C_6H_8)(\mu_3\text{-}C_{16}H_{16})]$ **2** (*ca.* 10%).

Characterisation of compound **2** was initially based on spectroscopic evidence. The mass spectrum exhibits a parent peak at *m/z* 945 (calc. 946) followed by peaks which correspond to the loss of nine CO ligands (the largest peak is at *m/z* 862 which corresponds to the loss of three CO groups). The ^1H NMR spectrum contains resonances at δ 7.48 (s, 4 H), 5.75 (m, 2 H), 4.54 (m, 2 H), 3.32 (m, 4 H), 3.26 (s, 4 H), 2.47 (m, 4 H), 2.12 (m, 2 H) and 1.88 (m, 2 H). The signals at δ 7.48, 3.32, 3.26 and 2.47 are derived from the [2.2]paracyclophane moiety, the first and third corresponding to the aromatic protons of the unattached and co-ordinated rings respectively, the other two from the $-CH_2CH_2-$ linkages. These signals are typical for a $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ $C_{16}H_{16}$ system, similar spectra having been reported elsewhere.[9] A terminal $\eta^6\text{-}C_{16}H_{16}$ ligand contains a C–H singlet resonance at a higher frequency than that of a μ_3 ligand, typically between δ 4.5 and 6.[5] The remaining signals may be assigned to the cyclohexa-1,3-diene ring.

Crystals of compound **2** were grown from a solution of dichloromethane layered with octane after standing for several days at room temperature. X-Ray data were collected on a suitable crystal at 150 K. The molecular structure of **2** is shown in Fig. 1; selected bond lengths and fractional atomic coordinates are listed in Tables 1 and 2 respectively. The metal core consists of a tetrahedron of ruthenium atoms [range 2.780(2)–2.897(2) Å, mean 2.84(4) Å]. There are nine carbonyl ligands, three of which form bridging interactions. The most interesting feature of this cluster is the presence of the [2.2]paracyclophane ring which bonds to the cluster face defined by Ru(1)–Ru(2)–Ru(4) in a highly unusual manner more reminiscent of a μ_3-cyclohexadienyl ring.[10] In addition, a cyclohexa-1,3-diene moiety is bonded solely to Ru(3) in an η^4 mode. An alternative view of the C_6 ring–Ru_3 section of the molecule is presented in Fig. 2(*a*), and as mentioned above, the bonding is quite closely related to that observed in the facially bound cyclohexadienyl ring found in $[M_3H(CO)_9(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}$

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

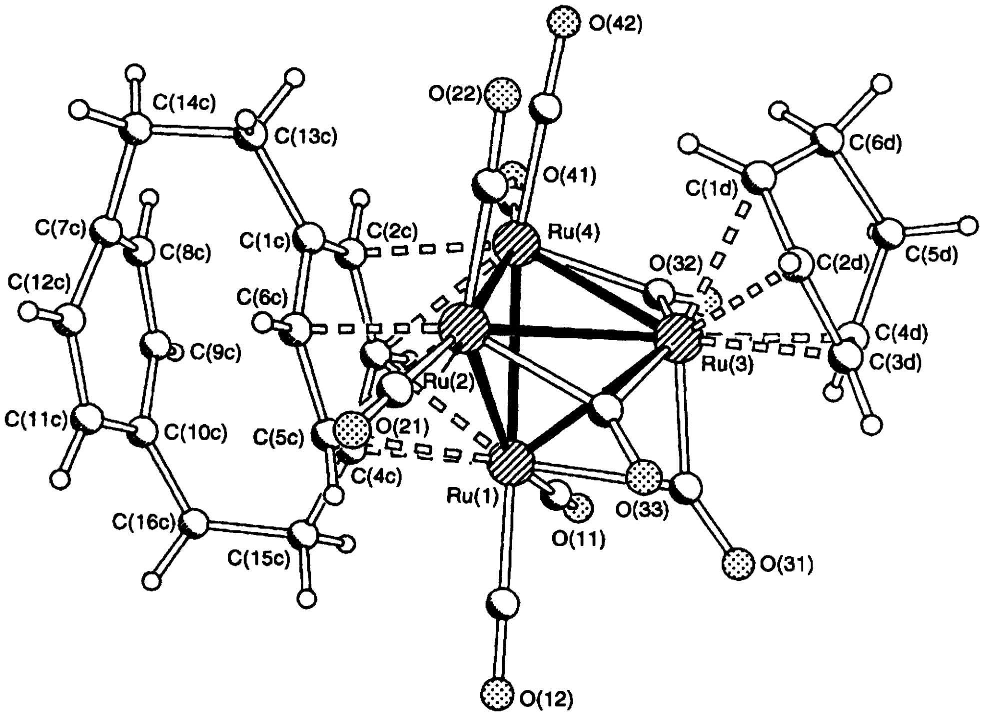

Fig. 1 The molecular structure of $[Ru_4(CO)_9(\eta^4\text{-}C_6H_8)(\mu_3\text{-}C_{16}H_{16})]$ **2** showing the atomic labelling scheme. Selected bond lengths are listed in Table 1

Table 1 Selected bond lengths (Å) for $[Ru_4(CO)_9(\eta^4\text{-}C_6H_8)(\mu_3\text{-}C_{16}H_{16})]$ **2**

Ru(1)–Ru(2)	2.868(3)	Ru(4)–C(2c)	2.173(10)	Ru(3)–C(1d)	2.296(10)
Ru(1)–Ru(3)	2.842(2)	C(1c)–C(2c)	1.434(14)	Ru(3)–C(2d)	2.227(11)
Ru(1)–Ru(4)	2.848(2)	C(2c)–C(3c)	1.444(14)	Ru(3)–C(3d)	2.152(11)
Ru(2)–Ru(3)	2.820(2)	C(3c)–C(4c)	1.443(14)	Ru(3)–C(4d)	2.223(10)
Ru(2)–Ru(4)	2.897(2)	C(4c)–C(5c)	1.467(14)	C(1d)–C(2d)	1.39(2)
Ru(3)–Ru(4)	2.780(2)	C(5c)–C(6c)	1.44(2)	C(1d)–C(6d)	1.524(13)
Ru(1)–C(3c)	2.529(11)	C(7c)–C(8c)	1.39(2)	C(2d)–C(3d)	1.43(2)
Ru(1)–C(4c)	2.116(10)	C(7c)–C(12c)	1.41(2)	C(3d)–C(4d)	1.44(2)
Ru(1)–C(5c)	2.506(9)	C(8c)–C(9c)	1.37(2)	C(4d)–C(5d)	1.49(2)
Ru(2)–C(5c)	2.473(10)	C(9c)–C(10c)	1.40(2)	C(5d)–C(6d)	1.54(2)
Ru(2)–C(6c)	2.179(10)	C(10c)–C(11c)	1.41(2)		
Ru(4)–C(3c)	2.478(10)	C(11c)–C(12c)	1.36(2)		

$C_6H_7)]$ (M = Ru or Os),[10] illustrated in Fig. 2(*b*). In cluster **2** Ru(1) bonds to C(4c) [2.116(10) Å] while longer interactions are also formed with C(3c) and C(5c) [2.529(11) and 2.506(9) Å, respectively], consequently, C(4c) is considered to form a σ bond with Ru(1) donating one electron. Two pairs of electrons are formally donated through the two η^2 C=C bonds with Ru(2) and Ru(4); each of these interactions consists of one long and one short bond, *viz.* Ru(2)–C(5c) 2.473(10), Ru(2)–C(6c) 2.179(10) and Ru(4)–C(3c) 2.478(10), Ru(4)–C(2c) 2.173(10) Å. While we have chosen to ascribe the $\eta^1:\eta^2:\eta^2$ nomenclature, an alternative description could also be used in which the ring forms an η^3 interaction with Ru(1) and two η^1 interactions, with distances of 2.721(11) and 2.804(9) Å being observed for Ru(2)$\cdots$C(1c) and Ru(4)$\cdots$C(1c) respectively, indicating little if any interaction between C(1c) and the metal framework. For a tetrahedral cluster a valence electron count of 60 is required to fulfil the electron atomic number rule, hence one further electron is required. A hydride bridging the edge Ru(2)–Ru(4), as observed in the analogous position in the dienyl species would be anticipated, especially as this is the longest Ru–Ru bond [2.897(2) Å]. However, a hydride has not been observed by ^1H NMR spectroscopy or located directly in the crystal structure.

In contrast to the solid-state structure, the ^1H NMR spectrum of **2** suggest that the ring behaves as a six-electron donor. The ring produces four signals in a typical pattern observed for rings attached to clusters in the $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ mode (see above). The singlet resonance of the co-ordinated C–H ring protons at δ 3.26 would not be anticipated from the bonding observed in the solid state, and it is possible that the ring is undergoing some type of dynamic behaviour in order to equilibrate all the C–H resonances. Nonetheless, a solution IR spectrum of the actual crystal used for the X-ray data collection is identical to that of the bulk solution, and it would appear that the solid-state structure consists of a conformation encountered in solution during rotation, merely frozen out by crystal-packing forces. As pointed out earlier, the unusual near-eclipsed $\mu_3\text{-}:\eta^1:\eta^1:\eta^1$ orientation has been observed for this ligand in the solid-state, and combined with the conventional $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ mode provides possible snapshots of the orientation of the ligand as it rotates over the metal face.

In the solid-state structure of [2.2]paracyclophane the arene rings adopt a non-planar boat configuration, whilst in **2** a similar deviation from planarity is only observed for one of the enyl units of the bound ring. The angles between the planes of the central rectangle and the triangle ends defined by C(2c)–C(1c)–C(6c) and C(5c)–C(4c)–C(3c) are 1(1) and 17(1)°, respectively (*cf.* 12.6° for the comparable angle in the free

Table 2 Atomic coordinates for $[Ru_4(CO)_9(\eta^4\text{-}C_6H_8)(\mu_3\text{-}C_{16}H_{16})]$ **2**

Atom	*x*	*y*	*z*
Ru(1)	0.661 13(8)	0.757 09(9)	0.179 21(5)
Ru(2)	0.939 94(8)	0.762 42(10)	0.282 02(5)
Ru(3)	0.683 96(8)	0.839 41(9)	0.344 46(5)
Ru(4)	0.718 13(8)	0.564 60(8)	0.308 61(5)
O(11)	0.345 2(8)	0.679 5(8)	0.123 6(5)
O(12)	0.657 2(8)	0.983 4(9)	0.055 0(5)
O(21)	1.192 5(8)	0.930 7(9)	0.236 1(5)
O(22)	1.117 1(8)	0.710 5(8)	0.448 9(5)
O(31)	0.498 0(8)	1.023 2(8)	0.226 0(4)
O(32)	0.412 3(8)	0.651 5(8)	0.333 1(4)
O(33)	0.881 0(8)	1.066 8(9)	0.296 7(4)
O(41)	0.517 6(8)	0.317 8(9)	0.306 6(5)
O(42)	0.868 3(8)	0.495 6(9)	0.479 4(5)
C(11)	0.464 4(11)	0.714 2(11)	0.144 2(7)
C(12)	0.661 1(11)	0.898 5(11)	0.103 1(6)
C(21)	1.098 1(11)	0.865 8(11)	0.252 6(6)
C(22)	1.048 0(11)	0.731 8(12)	0.386 7(7)
C(31)	0.572 4(10)	0.930 5(11)	0.250 3(6)
C(32)	0.539 9(11)	0.671 4(11)	0.331 6(6)
C(33)	0.860 9(11)	0.947 3(12)	0.304 0(6)
C(41)	0.594 5(11)	0.413 0(12)	0.306 8(6)
C(42)	0.811 8(11)	0.522 4(11)	0.414 4(6)
C(1c)	0.970 5(10)	0.495 0(11)	0.242 4(6)
C(2c)	0.824 2(10)	0.441 9(11)	0.225 3(6)
C(3c)	0.719 5(10)	0.506 5(11)	0.163 7(6)
C(4c)	0.758 9(11)	0.611 5(11)	0.110 0(6)
C(5c)	0.899 4(10)	0.677 2(11)	0.140 5(6)
C(6c)	1.006 6(11)	0.610 2(11)	0.199 1(6)
C(7c)	1.074 6(11)	0.301 5(11)	0.146 2(7)
C(8c)	0.939 9(11)	0.240 2(13)	0.119 0(6)
C(9c)	0.845 4(12)	0.291 4(12)	0.054 5(7)
C(10c)	0.879 2(12)	0.408 8(13)	0.013 3(7)
C(11c)	1.027 2(13)	0.451(2)	0.030 1(8)
C(12c)	1.121 2(13)	0.400 2(13)	0.094 0(7)
C(13c)	1.087 5(14)	0.404(2)	0.287 1(8)
C(14c)	1.145 2(14)	0.292 1(14)	0.234 7(8)
C(15c)	0.701 3(12)	0.604 8(13)	0.017 8(7)
C(16c)	0.766(2)	0.494(2)	−0.032 9(9)
C(1d)	0.759 8(10)	0.818 9(11)	0.481 7(6)
C(2d)	0.770 6(11)	0.953 8(12)	0.457 2(6)
C(3d)	0.638 8(10)	1.013 6(12)	0.415 8(6)
C(4d)	0.512 0(12)	0.926 5(13)	0.409 9(7)
C(5d)	0.489 5(12)	0.846 2(14)	0.483 3(7)
C(6d)	0.629 4(10)	0.768 5(14)	0.520 1(6)

molecule).[11] Hence, the angle of the unit involving the η^3 interaction has increased while the other has considerably decreased to such an extent that it is almost planar. Whilst it is possible that a hydrogen atom is connected to C(lc) thereby turning the ligand into a dienyl system, the approximate sp^2 hybridisation of this carbon atom tends to rule out this possibility, as does the ^1H NMR spectrum.

The formation of **2** from **1** involving an increase in nuclearity is not entirely unexpected. We have previously described the reaction of compound **1** with Me_3NO, triphenylphosphine and diphenylacteylene and observed that dinuclear products may be produced.[9] Hence, in this reaction fragmentation of **1** must occur, followed by recombination to form the tetrahedral cluster.

The thermolysis of the butterfly cluster $[Ru_4(CO)_{12}(\mu_4\text{-}C_6H_8)]$ **3** {prepared from the reaction of $[Ru_3(CO)_{12}]$ with cyclohexa-1,3-diene}[12] in octane containing an excess of [2.2]paracyclophane for 4 h results in the formation of a dark brown solution. Purification of the products from this reaction solution by thin layer chromatography using dichloromethane–hexane (2:2, v/v) as eluent resulted in the isolation of two new complexes $[Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\eta^6\text{-}C_{16}H_{16})]$ **4** and $[Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ **5**. Addition of 3.2 molar equivalents of Me_3NO to the reaction mixture improves the yield of these products. Characterisation of compounds **4** and **5** was based on spectroscopic evidence. Both compounds exhibit the same strong molecular ion in the mass spectrum at *m*/*z* 946 (calc. 946). Peaks corresponding to the loss of nine carbonyl groups are also present. The ^1H NMR spectrum of **4** is quite complicated since some of the signals overlap. However, experiments have shown that the [2.2]paracyclophane unit gives rise to three signals; singlet resonances at δ 6.80 and 4.34 for the C–H protons of the unco-ordinated and co-ordinated rings respectively and one mutiplet centred at δ 3.2 which integrates appropriately for all the protons in the $-CH_2CH_2-$ linkages. The cyclohexyne ring produces three multiplets centred at δ 3.29, 2.88 and 1.7, with relative intensities of 1:1:2. In **5** the ^1H NMR spectrum contains six signals of equal relative intensity, four of which can be attributed to the cyclophane moiety, the remaining two from the cyclohexyne unit. Singlet resonances at δ 7.21 and 3.16 result from the ring C–H protons of the unco-ordinated and co-ordinated rings, respectively. The latter value is low and comparable to that observed in **2** and indicative of a facially co-ordinated ligand. Multiplets at δ 3.17 and 2.56 can be assigned to the $-CH_2CH_2-$ linkages of the cyclophane ring system, the former corresponding to those closer to the co-ordinated ring. The hexyne entity produces two multiplets centred at δ 3.77 and 1.90, similar to that in **4**.

The molecular structure of compound **4** has been established in the solid state by an X-ray diffraction study on a crystal grown from a solution of dichloromethane–octane by slow

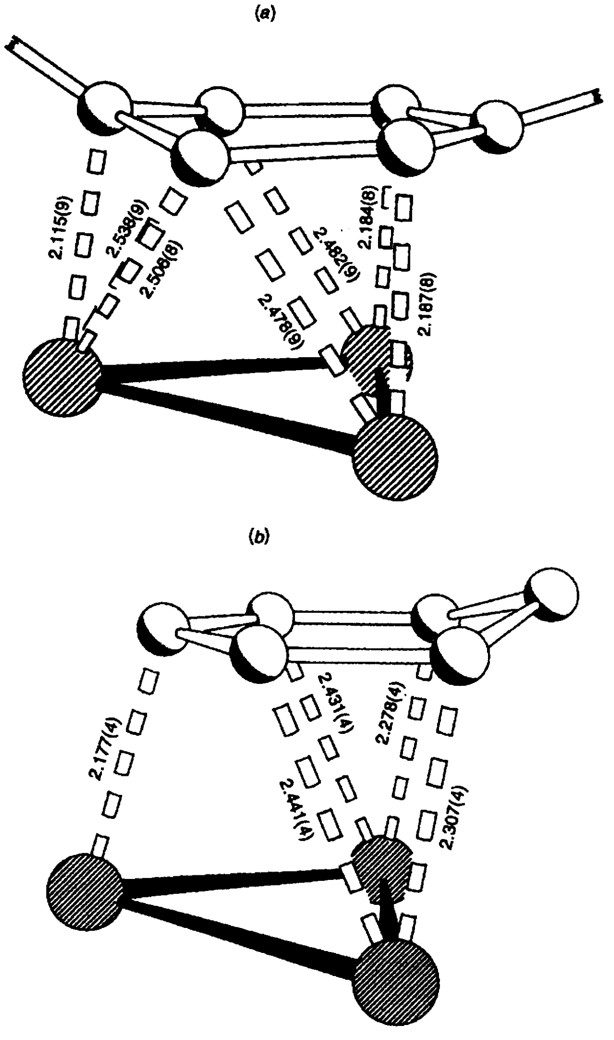

Fig. 2 Comparative views of the metal–ring interaction in $[Ru_4(CO)_9(\eta^4\text{-}C_6H_8)(\mu_3\text{-}C_{16}H_{16})]$ **2** (*a*) and $[Ru_3H(CO)_9\text{-}(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_6H_7)]$ (*b*); distances in Å

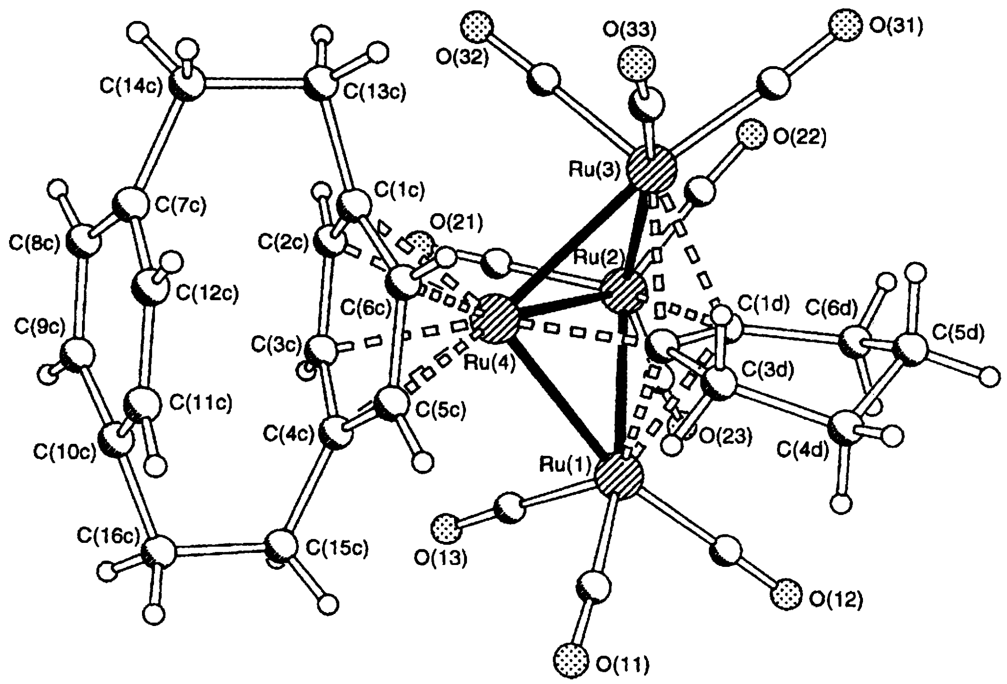

Fig. 3 The molecular structure of $[Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\eta^6\text{-}C_{16}H_{16})]$ **4** showing the atomic labelling scheme. Selected bond lengths are listed in Table 3

Table 3 Selected bond lengths (Å) for $[Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\eta^6\text{-}C_{16}H_{16})]$ **4**

Ru(1)–Ru(2)	2.712(2)	C(1c)–C(6c)	1.37(2)	Ru(1)–C(2d)	2.221(14)
Ru(1)–Ru(4)	2.635(2)	C(2c)–C(3c)	1.40(2)	Ru(2)–C(1d)	2.12(2)
Ru(2)–Ru(3)	2.729(2)	C(3c)–C(4c)	1.39(2)	Ru(3)–C(1d)	2.25(2)
Ru(2)–Ru(4)	2.844(2)	C(4c)–C(5c)	1.40(2)	Ru(3)–C(2d)	2.236(14)
Ru(3)–Ru(4)	2.636(2)	C(5c)–C(6c)	1.42(2)	Ru(4)–C(2d)	2.07(2)
Ru(4)–C(1c)	2.36(2)	C(7c)–C(12c)	1.35(2)	C(1d)–C(2d)	1.44(2)
Ru(4)–C(2c)	2.23(2)	C(7c)–C(8c)	1.38(2)	C(1d)–C(6d)	1.57(2)
Ru(4)–C(3c)	2.24(2)	C(8c)–C(9c)	1.38(2)	C(2d)–C(3d)	1.55(2)
Ru(4)–C(4c)	2.36(2)	C(9c)–C(10)	1.36(2)	C(3d)–C(4d)	1.54(2)
Ru(4)–C(5c)	2.19(2)	C(10c)–C(11c)	1.41(2)	C(4d)–C(5d)	1.51(2)
Ru(4)–C(6c)	2.164(14)	C(11c)–C(12c)	1.33(2)	C(5d)–C(6d)	1.49(2)
C(1c)–C(2c)	1.39(2)	Ru(1)–C(1d)	2.29(2)		

evaporation. Its molecular structure is illustrated in Fig. 3; selected bond lengths and fractional atomic coordinates are listed in Tables 3 and 4 respectively. This compound is an isomer of **2**, however, the four ruthenium atoms adopt a butterfly geometry rather than a tetrahedron since the C_6H_8 ligand constitutes that of a cyclohexyne ligand rather than a cyclohexa-1,3-diene moiety, thereby formally contributing six electrons to the cluster framework rather than four. The Ru–Ru bond lengths are rather unusual with the wing-tip ruthenium atoms being closer to the hinge ruthenium atom which carries the [2.2]paracyclophane ring. This unusual metal atom distribution is analogous to that found in the isostructural complex $[Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\eta^6\text{-}C_6H_6)]$,[13] but contrasts with that typically observed in butterfly clusters. The cyclohexyne unit lies between the wings of the butterfly *via* a $\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2$ interaction. The Ru(4) atom carries the [2.2]paracyclophane moiety, the remaining three Ru atoms each bearing three terminal carbonyl groups. The multiple bond of the cyclohexyne ring is short in comparison to the single bonds [1.44(2) Å *versus* a mean value of 1.53(3) Å for the five remaining bonds]. The [2.2]paracyclophane moiety is co-ordinated in a terminal fashion to Ru(4) *via* four short and two long interactions as the ring is not planar but boat shaped with four carbon atoms [C(2c), C(3c), C(5c) and C(6c)] lying closer to Ru(4) [mean 2.21(4) Å] than the two carbons to which the aliphatic bridges attach [C(1c) and C(4c), mean 2.36(2) Å]. The angle between the two enyl planes defined by C(2c)–C(1c)–C(6c) and C(3c)–C(4c)–C(5c) and the central rectangle are 18(1) and 15(2)°, respectively, these values being essentially the same within estimated errors. The angles are similar to that observed in free [2.2]paracyclophane, *viz.* 12.6°,[11] *albeit* slightly less acute. The angles between the enyl planes in the unattached ring defined by C(7c)–C(8c)–C(12c) and C(9c)–C(10c)–C(11c) are 11(2)°, relatively unperturbed from that of the free molecule.

Cluster **4** is the kinetic product from the thermolysis reaction, which is apparent from the fact that it undergoes isomerisation *via* migration of the [2.2]paracyclophane unit to the facial position affording the thermodynamic product **5**. This process has not been found to be reversible. For most arenes which can bond in both terminal and facial co-ordination sites the terminal bonding site is preferred. This is in contrast to the situation observed here with the face-capping ligand being most stable. However, [2.2]paracyclophane is unusual in this respect, and out of all the arene derivatives of $[Ru_6C(CO)_{14}(\text{arene})]$ [arene = $C_6H_{6-n}Me_n$ (n = 1–3), $C_6H_3Et_3$ or $C_{16}H_{16}$] the only species to contain a $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ ligand is the [2.2]paracyclophane derivative.[6]

Experimental

General Procedures and Materials.—All reactions were carried out using freshly distilled solvents under an atmosphere

Table 4 Atomic coordinates for $[Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\eta^6\text{-}C_{16}H_{16})]$ **4**

Atom	*x*	*y*	*z*
Ru(1)	0.109 18(12)	0.456 54(7)	0.862 30(8)
Ru(2)	0.019 19(11)	0.447 44(7)	0.694 19(8)
Ru(3)	0.247 29(12)	0.394 23(7)	0.648 51(9)
Ru(4)	0.263 41(11)	0.506 12(7)	0.750 92(8)
O(11)	0.286 9(11)	0.480 5(7)	1.024 2(8)
O(12)	−0.092 0(12)	0.374 2(7)	0.950 5(8)
O(13)	−0.025 1(11)	0.599 0(7)	0.863 5(7)
O(21)	−0.022 5(12)	0.595 3(7)	0.614 9(8)
O(22)	−0.097 8(12)	0.353 7(7)	0.549 4(9)
O(23)	−0.239 3(13)	0.445 5(7)	0.769 9(8)
O(31)	0.168 4(13)	0.263 0(8)	0.540 2(9)
O(32)	0.230 1(10)	0.500 1(7)	0.500 9(7)
O(33)	0.532 5(12)	0.366 8(7)	0.639 8(8)
C(11)	0.217(2)	0.469 5(9)	0.962 7(10)
C(12)	−0.013 9(14)	0.404 4(8)	0.917 4(10)
C(13)	0.027(2)	0.544 4(10)	0.861 7(10)
C(21)	−0.010(2)	0.538 5(10)	0.645 3(11)
C(22)	−0.053(2)	0.392 0(10)	0.602 2(11)
C(23)	−0.138(2)	0.447 4(9)	0.742 7(10)
C(31)	0.202(2)	0.312 4(11)	0.586 0(12)
C(32)	0.234 7(14)	0.458 8(9)	0.556 5(10)
C(33)	0.422(2)	0.374 8(9)	0.641 8(10)
C(1c)	0.423 5(14)	0.564 8(9)	0.679 0(10)
C(2c)	0.308 8(13)	0.602 7(8)	0.675 8(9)
C(3c)	0.260 0(14)	0.625 2(8)	0.752 3(9)
C(4c)	0.325 9(13)	0.609 1(8)	0.830 9(9)
C(5c)	0.419 4(14)	0.555 1(9)	0.833 5(10)
C(6c)	0.466 2(14)	0.532 1(9)	0.754 9(9)
C(7c)	0.599(2)	0.671 9(9)	0.692 1(11)
C(8c)	0.508(2)	0.725 3(9)	0.689 8(11)
C(9c)	0.460(2)	0.747 0(9)	0.765 0(10)
C(10c)	0.500(2)	0.716 8(9)	0.842 2(10)
C(11c)	0.610(2)	0.673 2(9)	0.842 3(11)
C(12c)	0.656(2)	0.651 8(9)	0.769 4(10)
C(13c)	0.506(2)	0.564 0(10)	0.602 0(11)
C(14c)	0.609(2)	0.628 2(10)	0.612 0(12)
C(15c)	0.312(2)	0.655 7(9)	0.910 0(10)
C(16c)	0.413(2)	0.715 7(10)	0.916 4(11)
C(1d)	0.1354(14)	0.369 9(8)	0.762 1(9)
C(2d)	0.2569(13)	0.401 3(8)	0.792 1(9)
C(3d)	0.3626(14)	0.359 1(8)	0.846 7(10)
C(4d)	0.307(2)	0.291 4(10)	0.884 6(12)
C(5d)	0.222(2)	0.250 5(10)	0.818 3(12)
C(6d)	0.104 7(14)	0.290 5(8)	0.784 3(10)

of nitrogen gas. Subsequent work-up of products was carried out using standard laboratory grade solvents without precautions to exclude air. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier-transform spectrometer. Positive ion mass spectra were obtained by fast atom bombardment on a Kratos MS50TC instrument. Proton NMR spectra were recorded using a Bruker AM360 or WM250 spectrometer.

The clusters $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ **1** and $[Ru_4(CO)_{12}(\mu_4\text{-}C_6H_8)]$ **3** were prepared according to literature methods.[7,12] Trimethylamine *N*-oxide (Me_3NO) and cyclohexa-1,3-diene were purchased from Aldrich, [2.2]paracyclophane from Fluka. The Me_3NO was dried and sublimed prior to use, whilst other materials were used without further purification.

Products were isolated by thin layer chromatography (TLC) using commercially prepared glass plates, precoated to 0.25 mm thickness with Merck Kieselgel 60G.

Reaction of $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ **1** *with* Me_3NO *and Cyclohexa*-1,3-*diene in Dichloromethane: Synthesis of* **2**.—Timethylamine *N*-oxide (2.2 equivalents, 11 mg) in dichloromethane (20 cm^3) was added dropwise to a solution of $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ **1** (50 mg) in dichloromethane (40 cm^3) containing excess cyclohexa-1,3-diene (2 cm^3) at −78 °C. The solution was allowed to warm to room temperature (1 h) where it was stirred for a further 3 h during which the colour of the solution darkened. The solvent was removed *in vacuo*, and the residue chromatographed using dichloromethane–hexane (3:7, v/v) as eluent. Two main products were observed which, in order of elution, were characterised by spectroscopic methods as starting material **1** (25%) and $[Ru_4(CO)_9(\eta^4\text{-}C_6H_8)(\mu_3\text{-}C_{16}H_{16})]$ **2** (orange, 10%).

Spectroscopic data for **2**: IR ν_{CO} (CH_2Cl_2): 2038m, 2014vs, 2005vs, 1973m, 1952m, 1852m, 1795m cm^{-1}. Positive ion FAB mass spectrum: *m*/*z* 945 (calc. 946) loss of 9 CO ligands observed; the largest peak at *m*/*z* 862 which corresponds to the loss of three CO groups. ^1H NMR ($CDCl_3$): δ 7.48 (s, 4 H), 5.75 (m, 2 H), 4.54 (m, 2 H), 3.32 (m, 4 H), 3.26 (s, 4 H), 2.47 (m, 4 H), 2.12 (m, 2 H), 1.88 (m, 2 H).

Thermolysis of $[Ru_4(CO)_{12}(\mu_4\text{-}C_6H_8)]$ **3** *with* $C_{16}H_{16}$ *in Octane: Synthesis of* **4** and **5**.—Compound $[Ru_4(CO)_{12}(\mu_4\text{-}C_6H_8)]$ **3** (30 mg) in octane (30 cm^3) containing an excess of $C_{16}H_{16}$ (15 mg) was heated to reflux for 4 h. Monitoring the reaction by spot TLC indicated this to be an optimum time in which the balance between remaining starting material and decomposition products was achieved. The solvent was removed *in vacuo*, and the residue purified by TLC, eluting with dichloromethane–hexane (2:3, v/v). Together with unreacted starting material (18%), two bands were characterised by spectroscopy, as $[Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\eta^6\text{-}C_{16}H_{16})]$ **4** (red, 14%) and $[Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ **5** (brown, 18%), respectively.

Spectroscopic data for **4**: IR ν_{CO} (CH_2Cl_2): 2069w, 2055m, 2030vs, 2004s, 1977s, 1960 (sh) cm^{-1}. Positive ion FAB mass spectrum: *m*/*z* 946 (calc. 946) loss of 9 CO ligands observed. ^1H NMR ($CDCl_3$): δ 6.80 (s, 4 H), 4.34 (s, 4 H), 3.29 (m, 2 H), 3.2 (m, 8 H), 2.88 (m, 2 H), 1.7 (m, 4 H).

Spectroscopic data for **5**: IR ν_{CO} (CH_2Cl_2): 2071m, 2030m, 2002vs, 1978m, (sh), 1937w cm^{-1}. Positive ion FAB mass spectrum: *m*/*z* 946 (calc. 946) loss of 9 CO ligands observed. ^1H NMR ($CDCl_3$): δ 7.21 (s, 4 H), 3.77 (m, 4 H), 3.17 (m, 4 H), 3.16 (s, 4 H), 2.56 (m, 4 H), 1.90 (m, 4 H).

Thermolysis of $[Ru_4(CO)_{12}(\mu_4\text{-}C_6H_8)]$ **3** *with* $C_{16}H_{16}$ *and* Me_3NO *in Octane: Synthesis of* **4** and **5**.—Compound $[Ru_4(CO)_{12}(\mu_4\text{-}C_6H_8)]$ **3** (50 mg) was suspended in octane (30 cm^3), and excess $C_{16}H_{16}$ (25 mg) and Me_3NO (15 mg, 3.2 mol equivalents) were added. The reaction mixture was heated to reflux for 4 h, by which stage IR spectroscopy indicated the complete consumption of starting material. The solvent was removed under reduced pressure and the products separated by TLC, using dichloromethane–hexane (2:3, v/v) as eluent. Two major bands were isolated and characterised by spectroscopy as $[Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\eta^6\text{-}C_{16}H_{16})]$ **4** (red 20%) and $[Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ **5** (brown, 28%), respectively.

Conversion of $[Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\eta^6\text{-}C_{16}H_{16})]$ **4** *to* $[Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ **5**.—A solution of $[Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\eta^6\text{-}C_{16}H_{16})]$ **4** (10 mg) in dichloromethane (20 cm^3) was heated to reflux for 2 h. IR spectroscopy and spot TLC indicated that complete conversion to $[Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ **5** had taken place.

Crystal-Structure Determination of Compound **2**.—A deep red crystal of **2** (approximate dimensions 0.08 × 0.12 × 0.31 mm) suitable for X-ray structural analysis was grown by layering a dichloromethane solution with octane.

Crystal data. $C_{31}H_{24}O_9Ru_4$, $M = 944.78$, monoclinic, space group $P2_1$, $a = 9.224(6)$, $b = 9.775(4)$, $c = 16.638(11)$ Å, $\beta = 98.59(7)°$, $U = 1483(2)$ Å^3 (from least-squares refinement of the 2θ values of 37 reflections; $26 > 2\theta > 30°$), Mo-Kα, radiation, $\lambda = 0.710\,73$ Å, $Z = 2$, $D_c = 2.115$ Mg m^{-3}, $F(000) = 916$, μ(Mo-Kα) = 2.053 mm^{-1}.

Data collection, structure solution and refinement. Stoë Stadi-4 diffractometer operating at 150 K, ω–2θ scan mode with graphite-monochromated Mo-Kα radiation and diffraction data measured to a maximum value for θ of 22.5°. Three standard reflections were monitored every 60 min and showed a 5% decrease in standard intensity during the data collection time (max. and min. corrections of 1.0510 and 0.9954). Absorption corrections were applied by the use of semi-empirical ψ scans (max. and min. transmission coefficients 0.844 and 0.741 respectively). A total of 4893 reflections were measured within the ranges $-9 < h < 9$, $0 < k < 10$, $0 < l < 17$ and averaged to yield 2065 unique reflections ($R_{int} = 0.0310$) of which 1923 were judged as significant by the criterion that $F_{obs}^2 > 2\sigma(F_{obs}^2)$. Corrections for Lorentz and polarisation effects were applied. Structure solution was by a combination of direct methods and Fourier techniques. Hydrogen atoms were placed in calculated positions and refined using a *riding* model. Anisotropic thermal motion was assumed for ruthenium atoms only. Full-matrix least-squares refinement on F_{obs}^2 for 2065 data, 197 parameters and one restraint converged to $wR2 = 0.0679$ (all data), conventional $R1 = 0.0288$ (observed data), $(\Delta/\sigma)_{max} = 0.001$, goodness-of-fit = 1.059. The function minimised was $\Sigma w(F_{obs}^2 - F_{calc}^2)^2$, $w = 1/[\sigma^2(F_{obs}^2) + (0.0381P)^2 + 2.2849P]$ where $P = (F_{obs}^2 + 2F_{calc}^2)/3$ and σ was obtained from counting statistics. A final difference electron density Fourier synthesis revealed maximum and minimum residual electron density peaks of 0.69 and −0.54 e Å^{-3}, respectively. The absolute configuration was assigned by the refinement of an absolute structure parameter[14] to a value of −0.06(6).

Crystal-structure Determination of Compound **4**.—A red crystal of **4** (approximate dimensions 0.06 × 0.16 × 0.16 mm) suitable for X-ray structural analysis was grown by slow evaporation of a dichloromethane–octane solution.

Crystal data. $C_{31}H_{24}O_9Ru_4$, $M = 944.78$, monoclinic, space group $P2_1/a$, $a = 10.419(2)$, $b = 18.787(3)$, $c = 15.589(3)$ Å, $\beta = 94.92(3)°$, $U = 3043.9(9)$ Å^3 (from least-squares refinement of the 2θ values of 30 reflections; $20 < 2\theta < 32°$), Mo-Kα radiation, $\lambda = 0.710\,73$ Å, $Z = 4$, $D_c = 2.064$ Mg m^{-3}, $F(000) = 1832$, μ(Mo-Kα) = 2.003 mm^{-1}.

Data collection, structure solution and refinement. Stoë Stadi-4 diffractometer operating at 295 K, ω–2θ scan mode with graphite-monochromated Mo-Kα radiation and diffraction data measured to a maximum value for θ of 20°. Three standard reflections were monitored every 60 min and showed no significant loss in standard intensity during the data collection time. Absorption corrections were applied by the use of semi-empirical ψ scans (max. and min. transmission coefficients 0.598 and 0.527 respectively). Corrections for Lorentz and polarisation effects were applied. A total of 3614 reflections were measured within the ranges $-10 < h < 9$, $0 < k < 18$, $0 < l < 15$ and averaged to yield 2806 unique reflections ($R_{int} = 0.0402$) of which 1940 were judged as significant by the criterion that $F_{obs}^2 > 2\sigma(F_{obs}^2)$. Structure solution was by a combination of direct methods and Fourier techniques. Hydrogen atoms were placed in calculated positions and refined using a *riding* model. Anisotropic thermal motion was assumed for the ruthenium atoms only. Full-matrix least-squares refinement on F_{obs}^2 for 2802 data and 197 parameters converged to $wR2 = 0.1080$ (all data), conventional $R1 = 0.0524$ (observed data), $(\Delta/\sigma)_{max} = 0.001$, goodness-of-fit = 1.088. The function minimised was $\Sigma w(F_{obs}^2 - F_{calc}^2)^2$, $w = 1/[\sigma^2(F_{obs}^2) + (0.0201P)^2 + 29.2266P]$ where $P = (F_{obs}^2 + 2F_{calc}^2)/3$ and σ was obtained from counting statistics. A final difference electron density Fourier synthesis revealed maximum and minimum residual electron density peaks of 0.85 and −0.54 e Å^{-3} respectively.

For both structures computations were performed with the SHELXTL-PC[15] package and SHELXL 93[16] program. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the University of Edinburgh, the EPSRC and ICI (Wilton) for financial assistance. We are grateful to Dr. S. Parsons for collection of single-crystal X-ray diffraction data.

References

1 D. J. Cram and D. I. Wilkinson, *J. Am. Chem. Soc.*, 1960, **82**, 5721; H. Ohno, H. Horita, T. Otsubo, Y. Sakata and S. Misumi, *Tetrahedron Lett.*, 1977, 265.
2 R. T. Swann, A. W. Hanson and V. Boekelheide, *J. Am. Chem. Soc.*, 1986, **108**, 3324.
3 C. Elschenbroich, R. Möckel and U. Zenneck, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 531.
4 Y. Kai and N. Kasai, *Acta Crystallogr., Sect. B*, 1978, **34**, 2840.
5 E. D. Laganis, R. H. Voegeli, R. T. Swann, R. G. Finke, H. Hopf and V. Boekelheide, *Organometallics*, 1982, **1**, 1415.
6 D. Braga, F. Grepioni, E. Parisini, P. J. Dyson, A. J. Blake and B. F. G. Johnson, *J. Chem. Soc., Dalton Trans.*, 1993, 2951.
7 P. J. Dyson, B. F. G. Johnson, C. M. Martin, A. J. Blake, D. Braga, F. Grepioni and E. Parisini, *Organometallics*, 1994, **13**, 2113.
8 A. J. Blake, P. J. Dyson, B. F. G. Johnson and C. M. Martin, *J. Chem. Soc., Chem. Commun.*, 1994, 1471.
9 A. J. Blake, P. J. Dyson, S. L. Ingham, B. F. G. Johnson and C. M. Martin, *Organometallics*, in the press.
10 D. Braga, F. Grepioni, E. Parisini, B. F. G. Johnson, C. M. Martin, J. G. M. Nairn, J. Lewis and M. Martinelli, *J. Chem. Soc., Dalton Trans.*, 1993, 1891.
11 H. Hope, J. Bernstein and K. N. Trueblood, *Acta Crystallogr., Sect. B*, 1972, **28**, 1733.
12 D. Braga, F. Grepioni, J. Byrne, C. M. Martin, B. F. G. Johnson and A. J. Blake, *Organometallics*, in the press.
13 S. Aime, L. Milone, D. Osella, G. A. Vaglio, M. Valle, A. Tiripicchio and M. Tiripicchio Camellini, *Inorg. Chim. Acta*, 1979, **34**, 49.
14 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.
15 G. M. Sheldrick, SHELXTL-PC, release 4.3, Siemens Analytical X-ray Instruments, Madison, WI, 1992.
16 G. M. Sheldrick, SHELXL 93, Program for structure refinement, University of Göttingen, 1993.

Received 12*th September* 1994; *Paper* 4/05509H