Synthesis, Molecular and Crystal Structures of Arene Derivatives of $[Ru_6C(CO)_{17}]$†

Dario Braga,*[,a] **Fabrizia Grepioni,**[a] **Emilio Parisini,**[a] **Paul J. Dyson,**[b] **Alexander J. Blake**[b] **and Brian F. G. Johnson***[,b]
[a] *Dipartimento di Chimica 'G. Ciamician', Università di Bologna, Via Selmi 2, 40126 Bologna, Italy*
[b] *Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK*

The complexes $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Me_2\text{-}1,3)]$ **1**, $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Et_3\text{-}1,3,5)]$ **2** and $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ **3** have been prepared from the reaction of $[Ru_3(CO)_{12}]$ and the appropriate arene. The molecular and crystal structures of the three derivatives have been established by single-crystal X-ray diffraction studies. Complexes **1** and **2** carry the arene fragment bound in a terminal fashion. Crystalline **1** contains two independent molecules showing different rotameric conformations of the xylene ligands. The [2.2]paracyclophane complex **3** provides the first example of a mono(arene) derivative of $[Ru_6C(CO)_{17}]$ to contain the $\mu_3\text{-}\eta^2:\eta^2:\eta^2$-bonding mode. The molecular organization in the crystal structures of **1**, **2** and **3** was also determined.

Among the earliest transition-metal clusters to contain arene ligands were those derived from the hexaruthenium carbidocarbonyl cluster $[Ru_6C(CO)_{17}]$,[1] in which the arene replaces the three carbonyl ligands bonded to one of the ruthenium atoms. The three derivatives $[Ru_6C(CO)_{14}(\eta^6\text{-arene})]$ (arene = C_6H_5Me, $C_6H_4Me_2$-1,3 or $C_6H_3Me_3$-1,3,5), together with $[Ru_6C(CO)_{17}]$, were initially prepared in modest yield from the thermolysis of $[Ru_3(CO)_{12}]$ in the appropriate arene.[2] The molecular structures of both the toluene[3] and mesitylene[4] derivatives have since been reported, and more recently their crystal structures examined in some detail.[5] The key interactions in these crystals involve preferential CO···CO interlocking and 'grouping' of the arene fragments in ribbons through the crystal.

Several bis(arene) derivatives of $[Ru_6C(CO)_{17}]$ have also been prepared and structurally chracterised by X-ray diffraction. Three different structural forms have been observed. First, in the cluster $[Ru_6C(CO)_{11}(\eta^6\text{-arene})(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (arene = C_6H_6,[6] C_6H_5Me[7] or $C_6H_4Me_2$-1,3[7]), the arene co-ordinates to a single metal atom in the η^6-bonding mode, whilst the benzene symmetrically caps ($\mu_3\text{-}\eta^2:\eta^2:\eta^2$) a triruthenium face; secondly, in *trans*-$[Ru_6C(CO)_{11}(\eta^6\text{-arene})_2]$ (arene = C_6H_6[8] or $C_6H_3Me_3$-1,3,5[9]) two terminally bound η^6-arene ligands 'sandwich' the entire cluster; finally in *cis*-$[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)(\eta^6\text{-}C_6H_6)]$ two η^6-arenes are co-ordinated to metal atoms adjacent to one another in the cluster framework.[10] Just as in the mono(arene) derivatives, in which CO···CO and arene···arene interactions have been maximised, the arene fragments in bis(arene) clusters show a clear tendency to establish graphitic-like interactions by pairing of arenes on neighbouring molecules. These observations have led us to examine a more extended series of these compounds in which the steric interactions between adjacent arene moieties within the lattice have been deliberately enhanced by employing the less symmetric $C_6H_4Me_2$-1,3 ligand and the more crowded $C_6H_3Et_3$-1,3,5 moiety. In addition a [2.2]paracyclophane complex, prepared as a possible precursor to polymeric materials containing $C_{16}H_{16}$ bridges, has also been examined.

Results and Discussion

The compound $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Me_2\text{-}1,3)]$ **1** was prepared by a literature method,[2] while $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Et_3\text{-}1,3,5)]$ **2** and $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ **3** were prepared by heating $[Ru_3(CO)_{12}]$ in refluxing octane in the presence of an excess of the appropriate arene. Relevant analytical and spectroscopic data are reported in Table 1.

Table 1 Spectroscopic and analytical data for complexes **1**–**3**

Complex	IR $\nu_{CO}{}^a$/cm^{-1}	Mass spectra m/z^b	^{1}H NMR^c	Analysis (%)^b C	H
1	2076m	1118	5.54 (m, 2 H)	24.72	1.11
	2024vs	(1117)	5.32 (d of d, 2 H)	(24.70)	(0.90)
	1982w		2.26 (s, 6 H)		
	1813w (br)				
2	2075m	1173	5.36 (s, 3 H)	27.95	1.60
	2023vs	(1173)	2.38 (m, 6 H)	(27.80)	(1.54)
	1997w		1.20 (m, 9 H)		
	1981w				
	1970w				
3	2076m	1219	7.44 (s, 4 H)	30.50	1.40
	2037s	(1219)	3.43 (s, 4 H)	(30.55)	(1.30)
	2024vs		3.40 (m, 4 H)		
	1982m		2.98 (m, 4 H)		
	1940m				
	1813w (br)				

[a] In CH_2Cl_2. [b] Calculated values in parentheses. [c] In $CDCl_3$.

Molecular and Crystal Structures of Complexes **1**, **2** *and* **3**.—The molecular structures of **1**, **2** and **3** in the solid state have been established by single-crystal X-ray diffraction. Relevant structural parameters are reported in Tables 2, 3 and 4, respectively. Each complex contains an octahedral metal-atom framework encapsulating a C (carbido) atom. In both **1** and **2** the arene fragment formally replaces three apical CO ligands of the parent cluster $[Ru_6C(CO)_{17}]$,[1] thus adopting the familiar η^6-apical bonding mode (see Figs. 1 and 2). The same type of co-ordination geometry had been previously observed in arene

---

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

Table 2 Relevant bond distances (Å) and angles (°) for the two asymmetric units of **1**

Ru(1)–Ru(2)	2.954(2)	Ru(7)–Ru(10)	2.975(3)
Ru(1)–Ru(4)	3.006(3)	Ru(7)–Ru(11)	2.837(2)
Ru(1)–Ru(5)	2.852(1)	Ru(7)–Ru(12)	2.844(3)
Ru(1)–Ru(6)	2.849(3)	Ru(8)–Ru(9)	2.949(3)
Ru(2)–Ru(3)	2.836(3)	Ru(8)–Ru(10)	2.822(2)
Ru(2)–Ru(5)	2.927(2)	Ru(8)–Ru(11)	2.879(3)
Ru(2)–Ru(6)	2.883(2)	Ru(8)–Ru(12)	2.959(2)
Ru(3)–Ru(5)	2.946(3)	Ru(9)–Ru(11)	2.853(2)
Ru(3)–Ru(6)	2.894(1)	Ru(9)–Ru(12)	2.876(2)
Ru(3)–Ru(4)	2.875(2)	Ru(10)–Ru(11)	2.868(2)
Ru(4)–Ru(5)	2.849(3)	Ru(10)–Ru(12)	2.912(2)
Ru(4)–Ru(6)	2.855(2)	Ru(7)–Ru(9)	2.932(2)
Ru(1)–C	2.051(5)	Ru(7)–C(45)	2.053(6)
Ru(2)–C	2.064(6)	Ru(8)–C(45)	2.082(6)
Ru(3)–C	2.091(5)	Ru(9)–C(45)	2.057(6)
Ru(4)–C	2.058(6)	Ru(10)–C(45)	2.070(6)
Ru(5)–C	2.107(5)	Ru(11)–C(45)	1.927(5)
Ru(6)–C	1.913(5)	Ru(12)–C(45)	2.082(5)
Ru(6)–C(15)	2.259(7)	Ru(11)–C(37)	2.233(8)
Ru(6)–C(16)	2.292(6)	Ru(11)–C(38)	2.295(7)
Ru(6)–C(17)	2.224(7)	Ru(11)–C(39)	2.236(6)
Ru(6)–C(18)	2.236(7)	Ru(11)–C(40)	2.265(7)
Ru(6)–C(19)	2.256(7)	Ru(11)–C(41)	2.239(8)
Ru(6)–C(20)	2.281(7)	Ru(11)–C(42)	2.215(8)
C(20)–C(21)	1.502(10)	C(38)–C(43)	1.542(13)
C(20)–C(22)	1.486(10)	C(40)–C(44)	1.473(12)
Ru(3)–C(3)	2.382(9)	Ru(8)–C(23)	2.082(7)
Ru(4)–C(3)	1.960(8)	Ru(10)–C(23)	2.035(7)
C(3)–O(3)	1.127(9)	C(23)–O(23)	1.152(8)
Ru(2)–C(5)	2.032(6)	Ru(9)–C(32)	1.930(7)
Ru(3)–C(5)	2.154(7)	C(32)–O(32)	1.130(9)
C(5)–O(5)	1.142(8)		
C(15)–C(16)–C(17)	118.2(6)	C(37)–C(38)–C(39)	118.4(8)
C(16)–C(17)–C(18)	120.7(7)	C(38)–C(39)–C(40)	123.6(7)
C(17)–C(18)–C(19)	119.9(7)	C(39)–C(40)–C(41)	113.9(8)
C(18)–C(19)–C(20)	120.9(7)	C(40)–C(41)–C(42)	120.7(8)
C(19)–C(20)–C(15)	117.4(7)	C(41)–C(42)–C(37)	120.3(8)
C(20)–C(15)–C(16)	122.7(7)	C(42)–C(37)–C(38)	122.8(9)
C(19)–C(20)–C(21)	120.2(8)	C(41)–C(40)–C(44)	122.7(9)
C(15)–C(16)–C(22)	120.2(7)	C(39)–C(38)–C(43)	119.3(8)

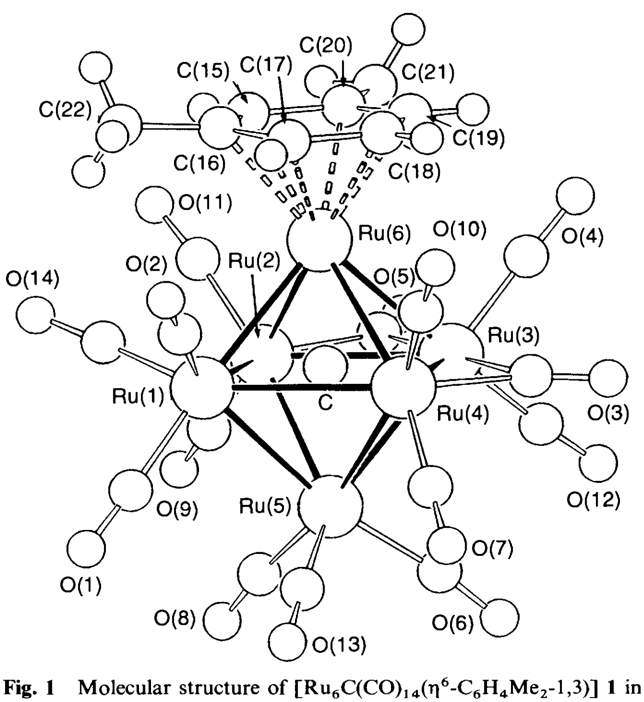

Fig. 1 Molecular structure of $[Ru_6C(CO)_{14}(\eta^6-C_6H_4Me_2-1,3)]$ **1** in the solid state. Only one of the two conformers present in the asymmetric unit is shown (**1A**). The C atoms of the CO groups bear the same labelling as the corresponding O atoms

Table 3 Relevant bond lengths (Å) and angles (°) for **2***

Ru(1)–Ru(3)	2.878(1)	C(1)–O(1)	1.131(8)
Ru(1)–Ru(4)	2.891(2)	C(2)–O(2)	1.141(9)
Ru(2)–Ru(4)	2.853(1)	C(3)–O(3)	1.140(7)
Ru(2)–Ru(3)	2.918(2)	C(4)–O(4)	1.138(6)
Ru(3)–Ru(3′)	2.855(1)	C(5)–O(5)	1.141(6)
Ru(3)–Ru(4)	2.962(1)	C(6)–O(6)	1.134(6)
Ru(4)–Ru(4′)	2.875(1)	C(7)–O(7)	1.140(7)
Ru(1)–C	1.928(6)	C(8)–O(8)	1.160(8)
Ru(2)–C	2.110(6)	Ru(1)–C(9)	2.235(6)
Ru(3)–C	2.063(3)	Ru(1)–C(10)	2.257(4)
Ru(4)–C	2.062(3)	Ru(1)–C(11)	2.306(4)
Ru(2)–C(1)	1.910(6)	Ru(1)–C(12)	2.260(6)
Ru(2)–C(2)	1.893(8)	C(9)–C(10)	1.425(5)
Ru(3)–C(3)	1.929(5)	C(9)–C(13)	1.493(9)
Ru(3)–C(4)	1.912(5)	C(10)–C(11)	1.413(6)
Ru(3)–C(5)	1.881(5)	C(11)–C(12)	1.430(5)
Ru(4)–C(6)	1.882(5)	C(11)–C(15)	1.505(6)
Ru(4)–C(7)	1.891(5)	C(13)–C(14)	1.490(11)
Ru(4)–C(8)	2.078(4)	C(15)–C(16)	1.519(8)
C(10′)–C(9)–C(10)	118.0(5)	C(12)–C(11)–C(15)	121.3(4)
C(10)–C(9)–C(13)	120.9(3)	C(15)–C(11)–Ru(1)	136.5(3)
C(13)–C(9)–Ru(1)	130.3(4)	C(11′)–C(12)–C(11)	121.3(5)
C(11)–C(10)–C(9)	122.0(4)	C(9)–C(13)–C(14)	113.1(6)
C(10)–C(11)–C(12)	118.2(4)	C(11)–C(15)–C(16)	109.5(4)
C(10)–C(11)–C(15)	120.2(4)		

* The primed atoms are related to the corresponding unprimed atoms by the symmetry operator *x*, 0.5 − *y*, *z*.

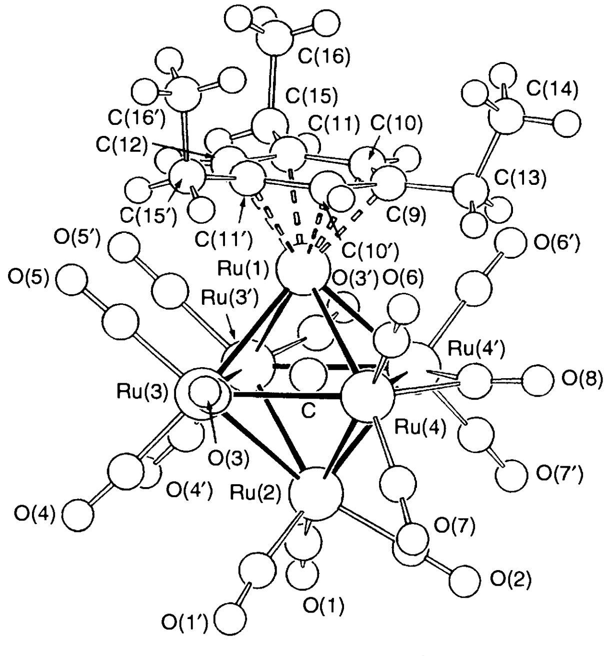

Fig. 2 Molecular structure of $[Ru_6C(CO)_{14}(\eta^6-C_6H_3Et_3-1,3,5)]$ **2** in the solid state

clusters of general formula $[Ru_6C(CO)_{14}(\eta^6\text{-arene})]$ (arene = C_6H_6,[11] C_6H_5Me[3] or $C_6H_3Me_3$-1,3,5[4]).

On the other hand, in cluster **3** one of the C_6 rings belonging to the [2.2]paracyclophane molecule is co-ordinated in a μ_3-facial mode, as shown in Fig. 3. This is the first example of a mono(arene)-substituted derivative of $[Ru_6C(CO)_{17}]$ in which this co-ordination mode has been observed. In fact, in the other face-capped arene derivatives previously characterized, namely $[Ru_6C(CO)_{11}(\eta^6\text{-arene})(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (arene = C_6H_6, C_6H_5Me or $C_6H_4Me_2$-1,3), face-capping occurs only after the apical site has been occupied by a terminal arene group. Two

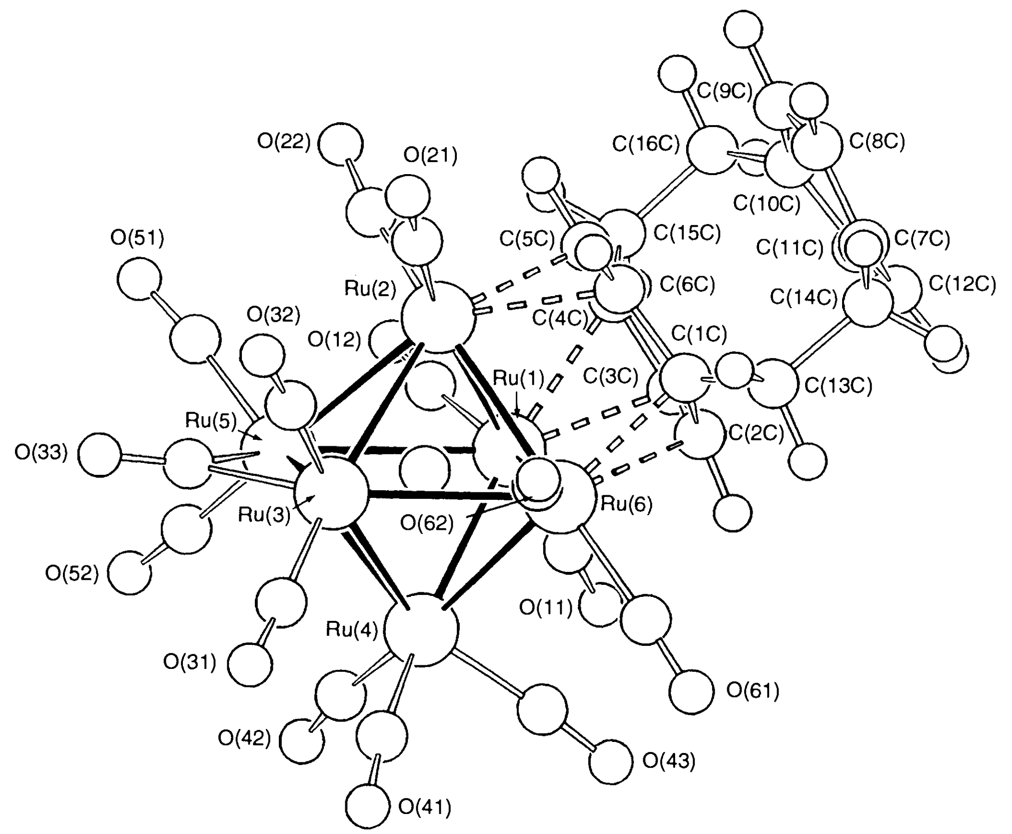

Fig. 3 Molecular structure of $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ **3** in the solid state

Table 4 Relevant bond distances (Å) and angles (°) for **3**

Ru(1)–Ru(2)	2.819(1)	Ru(3)–C(33)	2.056(9)	Ru(1)–C	2.039(8)	C(1C)–C(13C)	1.44(1)
Ru(1)–Ru(4)	2.832(1)	Ru(5)–C(33)	2.054(9)	Ru(2)–C	2.001(8)	C(13C)–C(14C)	1.58(1)
Ru(1)–Ru(5)	2.981(1)	C(33)–O(33)	1.167(12)	Ru(3)–C	2.080(8)	C(14C)–C(7C)	1.48(1)
Ru(1)–Ru(6)	2.933(1)	C(1C)–C(2C)	1.44(1)	Ru(4)–C	2.070(8)	C(12C)–C(7C)	1.41(1)
Ru(2)–Ru(3)	2.945(1)	C(2C)–C(3C)	1.43(1)	Ru(5)–C	2.068(8)	C(7C)–C(8C)	1.40(1)
Ru(2)–Ru(5)	2.922(1)	C(3C)–C(4C)	1.40(1)	Ru(6)–C	2.050(8)	C(9C)–C(8C)	1.40(1)
Ru(2)–Ru(6)	2.863(1)	C(4C)–C(5C)	1.45(1)	Ru(1)–C(4C)	2.359(9)	C(9C)–C(10C)	1.39(1)
Ru(3)–Ru(4)	2.990(1)	C(5C)–C(6C)	1.46(1)	Ru(1)–C(3C)	2.205(9)	C(10C)–C(11C)	1.37(1)
Ru(3)–Ru(5)	2.794(1)	C(1C)–C(6C)	1.42(1)	Ru(2)–C(5C)	2.212(9)	C(10C)–C(16C)	1.51(1)
Ru(3)–Ru(6)	2.935(1)	C(16C)–C(15C)	1.58(1)	Ru(2)–C(6C)	2.375(9)	C(11C)–C(12C)	1.42(1)
Ru(4)–Ru(5)	2.938(1)	C(4C)–C(15C)	1.53(1)	Ru(6)–C(2C)	2.365(8)		
Ru(4)–Ru(6)	2.869(1)			Ru(6)–C(1C)	2.195(9)		

C(1C)–C(2C)–C(3C)	121.5(8)	C(3C)–C(4C)–C(15C)	119.6(8)	C(12C)–C(7C)–C(8C)	117.8(8)
C(2C)–C(3C)–C(4C)	122.1(8)	C(5C)–C(4C)–C(15C)	118.2(8)	C(7C)–C(14C)–C(13C)	113.6(8)
C(3C)–C(4C)–C(5C)	117.4(8)	C(4C)–C(15C)–C(16C)	115.9(8)	C(1C)–C(13C)–C(14C)	114.7(8)
C(5C)–C(6C)–C(1C)	121.8(8)	C(7C)–C(8C)–C(9C)	120.7(8)	C(14C)–C(7C)–C(8C)	121.0(8)
C(6C)–C(1C)–C(2C)	115.9(8)	C(8C)–C(9C)–C(10C)	120.1(8)	C(14C)–C(7C)–C(12C)	120.8(8)
C(4C)–C(5C)–C(6C)	119.9(8)	C(9C)–C(10C)–C(11C)	118.2(8)	C(15C)–C(16C)–C(10C)	111.4(8)
C(6C)–C(1C)–C(13C)	119.3(8)	C(10C)–C(11C)–C(12C)	121.4(8)		
C(2C)–C(1C)–C(13C)	119.4(8)	C(11C)–C(12C)–C(7C)	118.5(8)		

isomers of the benzene–diene species $[Ru_6C(CO)_{12}(\mu\text{-}C_6H_8)(C_6H_6)]$ have also been isolated, one of which contains the benzene in a μ_3 mode.[11]

The two independent molecules present in the asymmetric unit of **1** (**1A** and **1B**) show far from negligible structural differences which deserve some comment. Fig. 4 shows a comparative projection of the two molecules perpendicular to the xylene ring plane. It can be easily appreciated that the xylene ligands in the two complexes possess different rotameric conformations with respect to the bridged octahedron equator. With reference to the quasi-symmetric bridging CO in the two molecules [C(4)O(4)], it can be seen that the conformations of the two xylene ligands differ, with respect to the bridged equator, by a rotation of *ca.* 120°, one CH_3 group in molecule **1A** being almost eclipsed on the C(4)O(4) ligand, while in molecule **1B** both CH_3 groups are on the opposite side with respect to the bridging ligand. The CO ligands in the two molecules also show different patterns of symmetric bridging, asymmetric bridging and bent terminal geometries. In this respect, it is appropriate to describe the crystal of **1** as a mixed crystal in which two structural isomers have co-crystallized. A similar observation has been made previously on the parent cluster $[Ru_6C(CO)_{17}]$, which is known to crystallize in two different isomeric forms containing conformational isomers related to those observed for **1**.[1] It is interesting to speculate on the analogy between different crystalline forms containing

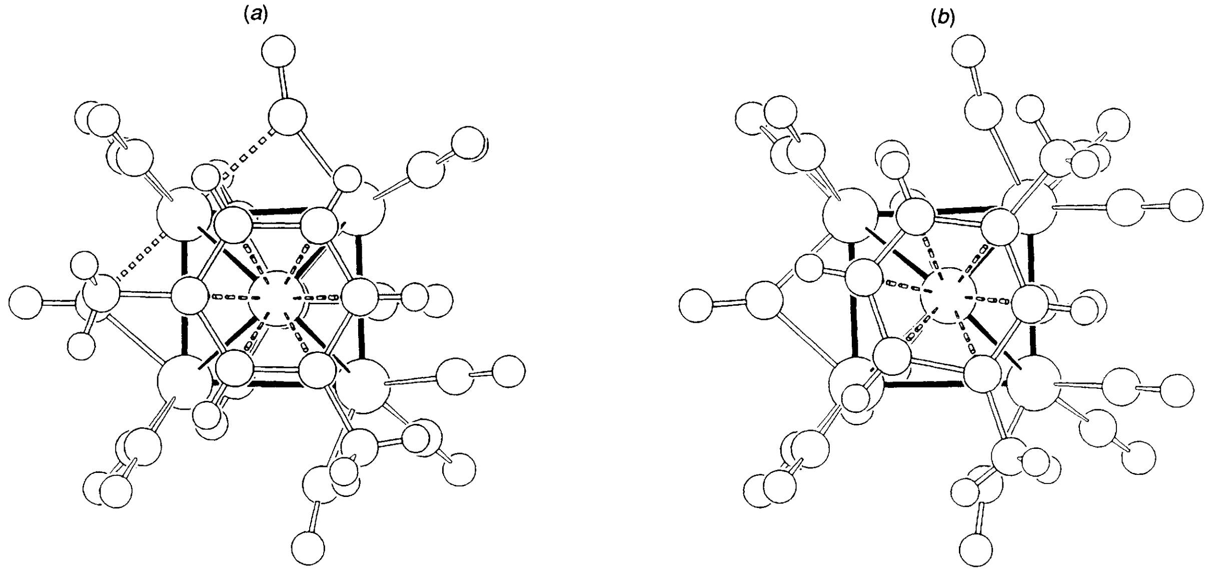

Fig. 4 Comparative projection of the two conformers **1A** (*a*) and **1B** (*b*) showing the different rotameric orientation of the xylene ligands with respect to the bridging CO

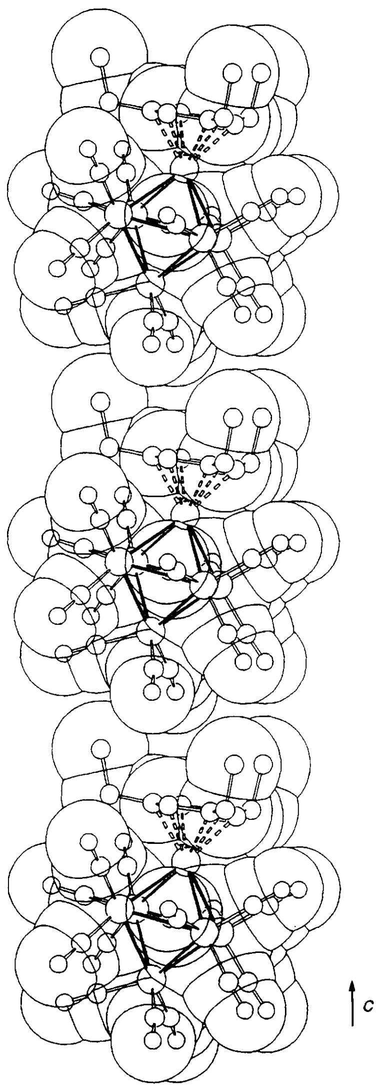

Fig. 5 Intermolecular interlocking in crystalline **2**: a molecular stack along the *c* axis. Note how the 'upward' orientation of the outer CH_3 groups provides an efficient clamping unit to lock a neighbouring molecule

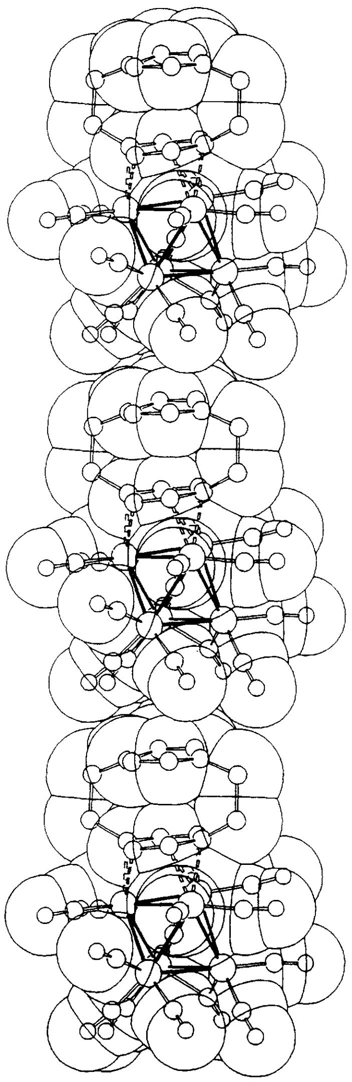

Fig. 6 Intermolecular interlocking in crystalline **3**: a molecular stack along the [110] cell diagonal. Note how the paracyclophane ligand interacts with the CO ligands bound to the opposite face of a neighbouring molecule along the stack

conformational isomers {such as the two crystals of [$Ru_6C(CO)_{17}$]} and the presence of conformational isomers within the same crystal structure (as in the present case). The two phenomena can be regarded as a manifestation of the same structural effect: the lack of a *unique* global energy minimum in which *both* conformational and packing energies are simultaneously minimized.

A simple calculation of the intramolecular van der Waals energy[12] for rotation of the $C_6H_4Me_2$ ligands about the co-ordination axis in the two independent molecules of **1** shows that, although separated by high energy barriers, three minima of comparable energy are present every 120° rotation in both plots. These minima correspond to the two different locations of the methyl groups shown in Fig. 4 for the two molecules. Given the high internal barrier to rotation, reorientation of the ligand in the solid state so as to *dynamically* occupy the three sites is regarded as improbable.

The crystal and molecular structure of **2** also deserves close examination. It is not surprising that all three ethyl groups point 'upwards', as shown in Fig. 2. This geometry, in fact, does not only minimize the *intramolecular repulsions* between the outermost CH_3 groups and the carbonyl ligands, but also allows an efficient *intermolecular interlocking* in the crystal lattice as shown in Fig. 5.

Unlike all other mono(arene) Ru_6C derivatives, **3** is unique in that the paracyclophane ligand adopts a μ_3-η^2:η^2:η^2-bonding mode. Fig. 3 shows the CO ligand distribution; it is reminiscent of that observed for most arene derivatives in this family, *i.e.* with one bridging ligand usually opposite to the Ru–Ru face involved in the interaction with the capping ligand. The co-ordination geometry of the paracyclophane ligand does not differ appreciably from that of benzene in face-capping bonding mode. The overall quality of the diffraction data is not sufficient to allow detection of 'long'–'short' C–C bond alternation within the C_6 ring bound to the metal framework. Carbon–carbon bonds range from 1.40(1) to 1.46(1) Å without a clear pattern. The strain in the molecule is clearly detectable in the C(ring)–C–C sp^3 angles [111.4(8)–115.9(8)°], as well as in the out-of-plane bending of the CH_2 groups (see Fig. 3). The average C–C bond length is slightly longer in the co-ordinated than in the unco-ordinated rings [1.43(2) and 1.40(2) Å, respectively]. This latter value is in agreement with the average C–C bond length observed in [2.2]paracyclophane itself (1.394 Å).[13] The remaining C–C bonds conform to the expected pattern of C(sp^2)–C(sp^3) and C(sp^3)–C(sp^3) bond lengths for this ligand.[13]

The molecular arrangement in the crystal of **3** is based on a direct interaction between the 'free' ring of the paracyclophane ligand and the CO groups bound to the opposite face of a neighbouring molecule (see Fig. 6). This arrangement is strictly comparable with that observed in crystalline **2**. It is interesting to speculate on the possibility of linking Ru_6 frames *via* paracyclophane bridges. Fig. 6 suggests that the hypothetical polymer *trans*-[{$Ru_6(C_{16}H_{16})$}$_n$] might show similar crystal packing to that seen in **3**.

Experimental

All reactions were carried out using freshly distilled solvents under an atmosphere of nitrogen. Subsequent work-up of products was achieved without precautions to exclude air and with standard laboratory-grade solvents. Infrared spectra were recorded on a Perkin Elmer 1600 Series FTIR spectrometer in CH_2Cl_2 solution using NaCl cells. Positive-ion fast atom bombardment mass spectra were obtained using a Kratos MS50TC spectrometer, with CsI as calibrant. Proton NMR spectra were recorded in $CDCl_3$ using a Bruker AM360 instrument, referenced to internal trimethylsilane. Products were separated by column chromatography on silica gel (60 mesh) using hexane (60%)–dichloromethane (40%) as eluent. The compound [$Ru_6C(CO)_{14}(\eta^6$-$C_6H_4Me_2$-1,3)] **1** was prepared according to the literature procedure.[2]

Preparation of [$Ru_6C(CO)_{14}(\eta^6$-$C_6H_3Et_3$-1,3,5)] **2**.—The compound [$Ru_3(CO)_{12}$] (500 mg) in octane (25 cm^3) containing an excess of 1,3,5-triethylbenzene (1.5 cm^3) was heated under reflux for 4 h. Infrared spectroscopy indicated complete consumption of the starting material after this time.

Table 5 Crystal data and details of measurements for **1**, **2** and **3**

	1	**2**	**3**
Formula	$C_{23}H_{10}O_{14}Ru_6$	$C_{27}H_{18}O_{14}Ru_6$	$C_{31}H_{16}O_{14}Ru_6$
M	1116.73	1172.83	1218.81
T/K	293	293	150
System	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/m$	$P\bar{1}$
a/Å	9.03(1)	9.481(4)	10.193(3)
b/Å	18.361(7)	15.931(4)	10.311(3)
c/Å	19.17(1)	11.505(8)	16.377(5)
α/°	114.65(4)		88.45(2)
β/°	90.31(7)	108.09(5)	87.52(2)
γ/°	100.44(6)		72.48(2)
U/Å^3	2827	1652	1638
Z	4	2	2
F(000)	2096	1112	1156
λ(Mo-Kα)/Å	0.710 69	0.710 69	0.710 73
μ(Mo-Kα)/cm^{-1}	31.9	27.4	27.2
θ Range/°	3–25	2.5–30	2.5–22.5
ω Scan width/°	0.70	0.70	variable[a]
Octants explored (*h*,*k*,*l*)	−10 to 10, −21 to 21, 0–22	−13 to 12, 0–22, 0–16	−10 to 10, −11 to 11, 0–17
Measured reflections	10 236	5180	5607
Unique observed reflections (R_{int})	9916 (0.047)	4943 (0.046)	4026 (0.030)
Unique observed reflections [$I_o > 2\sigma(I_o)$]	9151	4501	3594
No. of refined parameters	777	241	455
Goodness of fit on F^2	1.97	1.06	
Final *R* indices [$I > \sigma(I)$] R_1 (on *F*), wR_2 (on F^2)	0.046, 0.166	0.049, 0.137	
Final *R* indices (all data) R_1 (on *F*), wR_2 (on F^2)	0.050, 0.168	0.053, 0.148	
R,[b] R'[b,c], goodness of fit on *F*[b]			0.044, 0.056, 1.04

[a] Ref. 14. [b] Refinement on F_o with SHELX 76. [c] Weighting scheme: $w^{-1} = \sigma^2(F) + 0.0004F^2$.

Table 6 Atomic coordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for the two asymmetric units of **1**

Atom	x	y	z	Atom	x	y	z
Ru(1)	2 495(1)	8 376(1)	8 010(1)	Ru(7)	2 951(1)	3 332(1)	7 527(1)
Ru(2)	2 029(1)	6 578(1)	7 159(1)	Ru(8)	−925(1)	1 526(1)	6 863(1)
Ru(3)	5 057(1)	6 605(1)	7 586(1)	Ru(9)	2 286(1)	1 602(1)	7 240(1)
Ru(4)	5 684(1)	8 354(1)	8 446(1)	Ru(10)	−309(1)	3 187(1)	7 127(1)
Ru(5)	3 146(1)	7 430(1)	8 792(1)	Ru(11)	688(1)	2 743(1)	8 291(1)
Ru(6)	4 456(1)	7 650(1)	6 876(1)	Ru(12)	1 508(1)	2 117(1)	6 084(1)
C	3 820(6)	7 519(3)	7 775(3)	C(45)	1 039(6)	2 428(3)	7 224(3)
C(1)	1 310(9)	8 897(5)	8 826(5)	C(23)	−2 271(7)	2 350(4)	6 907(4)
O(1)	584(8)	9 204(4)	9 292(4)	O(23)	−3 557(6)	2 310(4)	6 856(5)
C(2)	3 286(8)	9 394(4)	7 980(5)	C(24)	3 561(8)	960(4)	6 560(4)
O(2)	3 743(8)	9 982(3)	7 943(4)	O(24)	4 320(7)	562(4)	6 193(4)
C(3)	7 133(8)	7 650(5)	8 355(5)	C(25)	4 421(8)	3 600(5)	6 915(4)
O(3)	8 277(6)	7 567(4)	8 510(5)	O(25)	5 312(7)	3 807(5)	6 579(4)
C(4)	6 371(9)	6 191(5)	6 847(4)	C(26)	2 382(8)	4 373(5)	7 940(5)
O(4)	7 205(8)	5 926(4)	6 404(4)	O(26)	2 260(6)	5 034(3)	8 260(4)
C(5)	3 196(8)	5 661(4)	6 874(4)	C(27)	3 378(8)	1 881(5)	5 680(4)
O(5)	3 051(6)	4 975(3)	6 496(3)	O(27)	4 454(7)	1 761(4)	5 399(3)
C(6)	4 132(10)	6 945(5)	9 313(5)	C(28)	−1 125(7)	4 016(4)	7 869(4)
O(6)	4 637(10)	6 684(5)	9 672(4)	O(28)	−1 596(7)	4 530(4)	8 322(3)
C(7)	6 187(9)	8 992(5)	9 515(5)	C(29)	−896(8)	3 573(5)	6 413(4)
O(7)	6 525(9)	9 388(5)	10 149(4)	O(29)	−1 275(8)	3 807(4)	6 007(3)
C(8)	1 199(9)	6 883(5)	8 906(4)	C(30)	1 425(9)	2 803(5)	5 586(4)
O(8)	113(7)	6 574(4)	9 033(3)	O(30)	1 478(9)	3 197(5)	5 253(4)
C(9)	278(8)	5 953(4)	7 330(4)	C(31)	4 482(8)	3 519(4)	8 289(4)
O(9)	−765(6)	5 546(4)	7 393(4)	O(31)	5 440(7)	3 652(4)	8 756(4)
C(10)	7 026(9)	9 149(5)	8 251(4)	C(32)	870(8)	644(4)	7 166(4)
O(10)	7 890(8)	9 632(4)	8 157(4)	O(32)	394(6)	34(3)	7 172(4)
C(11)	1 160(8)	6 224(4)	6 156(4)	C(33)	−2 300(7)	1 083(5)	7 365(5)
O(11)	518(8)	5 989(4)	5 559(4)	O(33)	−3 186(7)	825(5)	7 671(4)
C(12)	5 546(8)	5 920(4)	8 024(4)	C(34)	459(10)	1 210(5)	5 225(5)
O(12)	5 912(7)	5 522(4)	8 278(4)	O(34)	−174(7)	671(4)	4 659(3)
C(13)	3 118(10)	8 358(5)	9 717(5)	C(35)	3 602(8)	1 782(4)	8 102(4)
O(13)	3 099(8)	8 906(4)	10 299(4)	O(35)	4 424(8)	1 873(4)	8 590(4)
C(14)	784(9)	7 979(5)	7 284(5)	C(36)	−1 976(9)	672(6)	5 974(5)
O(14)	−270(7)	7 856(4)	6 885(4)	O(36)	−2 728(8)	150(5)	5 456(4)
C(15)	3 644(8)	7 332(4)	5 648(4)	C(37)	80(11)	3 781(7)	9 299(4)
C(16)	3 857(8)	8 170(5)	6 036(4)	C(38)	1 518(9)	3 721(5)	9 514(4)
C(17)	5 280(8)	8 609(4)	6 469(4)	C(39)	1 743(8)	2 969(4)	9 440(3)
C(18)	6 447(8)	8 209(5)	6 449(4)	C(40)	580(9)	2 272(5)	9 214(4)
C(19)	6 217(8)	7 349(5)	6 025(4)	C(41)	−942(10)	2 409(7)	9 038(5)
C(20)	4 815(9)	6 893(4)	5 622(4)	C(42)	−1 100(11)	3 156(9)	9 064(5)
C(21)	4 599(13)	5 984(5)	5 163(4)	C(43)	2 829(14)	4 471(6)	9 867(5)
C(22)	2 655(10)	8 600(6)	5 972(5)	C(44)	791(18)	1 509(7)	9 245(7)

Table 7 Atomic coordinates (× 10^4) with e.s.d.s in parentheses for **2**

Atom	x	y	z	Atom	x	y	z
Ru(1)	1 913(1)	2 500	8 997(1)	C(6)	−770(5)	4 131(3)	8 196(5)
Ru(2)	631(1)	2 500	5 306(1)	O(6)	−1 076(6)	4 598(3)	8 822(5)
Ru(3)	2 887(1)	3 396(1)	7 213(1)	C(7)	−1 520(6)	4 053(4)	5 803(5)
Ru(4)	−279(1)	3 402(1)	7 093(1)	O(7)	−2 274(7)	4 442(3)	5 026(5)
C	1 325(5)	2 500	7 235(5)	C(8)	−1 872(6)	2 500	7 065(5)
C(1)	1 004(8)	1 616(4)	4 318(5)	O(8)	−3 107(6)	2 500	7 032(6)
O(1)	1 128(8)	1 114(5)	3 661(5)	C(9)	703(6)	2 500	10 383(5)
C(2)	−1 411(8)	2 500	4 397(7)	C(10)	1 511(5)	1 733(3)	10 514(4)
O(2)	−2 630(7)	2 500	3 819(6)	C(11)	3 059(5)	1 717(3)	10 718(4)
C(3)	2 212(6)	4 506(3)	7 451(5)	C(12)	3 814(6)	2 500	10 765(6)
O(3)	2 090(6)	5 195(3)	7 672(6)	C(13)	−923(7)	2 500	10 217(6)
C(4)	3 855(5)	3 689(4)	6 038(5)	C(14)	−1 267(10)	2 500	11 396(9)
O(4)	4 499(6)	3 845(5)	5 381(5)	C(15)	3 897(6)	901(3)	10 994(5)
C(5)	4 726(5)	3 468(3)	8 449(4)	C(16)	4 285(8)	710(4)	12 351(6)
O(5)	5 860(4)	3 531(3)	9 173(4)				

The solvent was removed *in vacuo* and the products separated by column chromatography. The brown band was characterised as $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Et_3\text{-}1,3,5)]$ (127 mg).

Preparation of $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ **3**.—The compound $[Ru_3(CO)_{12}]$ (500 mg) in octane (25 cm^3) containing an excess of [2.2]paracyclophane (50 mg) was heated to a vigorous reflux for 3 h. Infrared spectroscopy indicated complete consumption of starting material after this time. The solvent was removed *in vacuo* and the products separated by column chromatography. The orange band was characterised as $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ (78 mg).

Table 8 Fractional coordinates of atoms with e.s.d.s in parentheses for **3**

Atom	*x*	*y*	*z*
Ru(1)	0.307 64(7)	0.543 62(7)	0.154 944)
Ru(2)	0.151 30(7)	0.446 01(7)	0.275 83(4)
Ru(3)	0.403 34(7)	0.281 85(7)	0.351 91(4)
Ru(4)	0.558 03(7)	0.403 31(7)	0.226 34(4)
Ru(5)	0.374 45(7)	0.245 23(7)	0.186 27(4)
Ru(6)	0.341 66(7)	0.577 06(7)	0.328 94(4)
C	0.353 3(7)	0.417 4(8)	0.254 1(5)
C(11)	0.419 6(9)	0.623 0(10)	0.082 3(6)
O(11)	0.483 5(7)	0.667 0(7)	0.038 3(5)
C(12)	0.254 6(8)	0.462 8(9)	0.066 1(6)
O(12)	0.212 7(6)	0.426 7(7)	0.009 4(4)
C(21)	0.053 5(9)	0.409 9(9)	0.373 9(6)
O(21)	−0.005 4(7)	0.392 8(8)	0.431 5(5)
C(22)	0.039 6(10)	0.381 0(9)	0.208 8(6)
O(22)	−0.036 2(7)	0.354 8(7)	0.168 2(5)
C(31)	0.553 8(10)	0.198 2(10)	0.415 4(6)
O(31)	0.639 3(7)	0.146 2(7)	0.458 2(4)
C(32)	0.298 6(10)	0.224 7(10)	0.436 3(7)
O(32)	0.240 0(8)	0.185 6(9)	0.487 2(5)
C(33)	0.412 7(9)	0.113 7(9)	0.284 5(6)
O(33)	0.427 8(7)	−0.001 9(7)	0.296 0(5)
C(41)	0.698 9(10)	0.331 1(9)	0.302 0(6)
O(41)	0.787 5(7)	0.300 5(7)	0.343 8(4)
C(42)	0.670 3(9)	0.309 8(9)	0.135 9(6)
O(42)	0.742 3(6)	0.265 0(6)	0.081 0(4)
C(43)	0.623 2(9)	0.555 6(10)	0.205 0(6)
O(43)	0.668 2(8)	0.641 7(7)	0.191 7(5)
C(51)	0.260 0(10)	0.157 9(10)	0.139 6(6)
O(51)	0.201 0(7)	0.096 2(8)	0.109 3(5)
C(52)	0.507 4(9)	0.132 4(9)	0.114 0(6)
O(52)	0.582 8(7)	0.062 7(7)	0.068 1(4)
C(61)	0.469 4(10)	0.671 9(9)	0.358 8(6)
O(61)	0.545 4(7)	0.721 1(7)	0.377 5(5)
C(62)	0.327 3(9)	0.530 9(9)	0.441 7(6)
O(62)	0.314 9(7)	0.521 6(7)	0.511 1(4)
C(1C)	0.152 0(9)	0.749 0(9)	0.329 0(6)
C(2C)	0.224 5(8)	0.774 2(8)	0.255 3(5)
C(3C)	0.180 6(9)	0.755 6(8)	0.176 6(6)
C(4C)	0.080 1(8)	0.691 0(8)	0.166 3(6)
C(5C)	0.016 9(9)	0.648 2(9)	0.239 3(6)
C(6C)	0.057 4(9)	0.674 6(9)	0.319 8(6)
C(7C)	−0.073 6(9)	0.988 5(8)	0.320 4(6)
C(8C)	−0.185 4(9)	0.938 7(8)	0.313 5(6)
C(9C)	−0.221 5(8)	0.908 0(8)	0.237 0(6)
C(10C)	−0.146 2(8)	0.927 2(9)	0.166 8(5)
C(11C)	−0.057 7(9)	1.003 7(9)	0.172 3(6)
C(12C)	−0.019 6(9)	1.036 8(8)	0.249 0(6)
C(13C)	0.129 1(10)	0.847 7(10)	0.401 9(6)
C(14C)	−0.003 6(10)	0.975 8(9)	0.398 3(6)
C(15C)	−0.000 4(9)	0.718 0(10)	0.088 5(6)
C(16C)	−0.135 9(9)	0.842 3(10)	0.091 7(6)

X-Ray Crystal Structure Determination of **1**, **2** *and* **3**.—Crystal data and details of measurements for compounds **1**, **2** and **3** are summarized in Table 5. Diffraction intensities were collected using Mo-Kα radiation and ω–2θ scans; at room temperature on an Enraf-Nonius CAD-4 for **1** and **2** and on a Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device[15] operating at 150 K for **3**; the intensities were reduced to F_o^2 in **1** and **2** and to F_o in **3**. An initial absorption correction based on ψ-scan correction and a decay correction of 26% were applied to **3**. The structures were solved by direct methods and refined by full-matrix least squares. For all calculations in **1** and **2** the crystallographic programs SHELXS 86[16a] and SHELXL 92[16b] were used, while SHELXS 86 and SHELX 76[16c] were used in **3**. A final absorption correction was applied in **3** using the Walker and Stuart method;[17] a similar treatment for **1** and **2** did not improve the data and was abandoned. All non-H atoms but the C(carbide) atom in **3** were allowed to vibrate anisotropically. In all species hydrogen atoms were added in calculated positions and refined 'riding' on the corresponding C atoms.

Fractional atomic coordinates of **1**, **2** and **3** are reported in Tables 6, 7 and 8, respectively.

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

Acknowledgements

Financial support by the Ministero dell'Universitá e della Ricerca Scientifica e Tecnologica is acknowledged. B. F. G. J., D. B. and F. G. thank NATO for a travel grant. P. J. D. thanks the SERC and British Petroleum for financial support.

References

1 A. Sirigu, M. Bianchi and E. Benedetti, *Chem. Commun.*, 1969, 596; D. Braga, F. Grepioni, P. Dyson, B. F. G. Johnson, P. Frediani, M. Bianchi and F. Piacenti, *J. Chem. Soc., Dalton Trans.*, 1992, 2565.
2 B. F. G. Johnson, R. D. Johnston and J. Lewis, *J. Chem. Soc., Chem. Commun.*, 1967, 1057; B. F. G. Johnson, R. D. Johnston and J. Lewis, *J. Chem. Soc. A*, 1968, 2865.
3 L. Farrugia, *Acta Crystallogr., Sect. C*, 1988, **44**, 997.
4 R. Mason and W. R. Robinson, *Chem. Commun.*, 1968, 468.
5 D. Braga, F. Grepioni, B. F. G. Johnson, H. Chen and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1991, 2559.
6 M. P. Gomez-Sal, B. F. G. Johnson, J. Lewis, P. R. Raithby and A. H. Wright, *J. Chem. Soc., Chem. Commun.*, 1985, 1682.
7 P. J. Dyson, B. F. G. Johnson, D. Reed, D. Braga, F. Grepioni and E. Parisini, *J. Chem. Soc., Dalton Trans.*, 1993, 2817.
8 R. D. Adams and W. Wu, *Polyhedron*, 1992, **21**, 23.
9 D. Braga, F. Grepioni, S. Righi, P. J. Dyson, B. F. G. Johnson, P. J. Bailey, J. Lewis and M. Martinelli, *J. Chem. Soc., Dalton Trans.*, 1992, 2121.
10 D. Braga, F. Grepioni, S. Righi, P. J. Dyson, B. F. G. Johnson, P. J. Bailey and J. Lewis, *Organometallics*, 1992, **11**, 4042.
11 P. J. Dyson, B. F. G. Johnson, J. Lewis, M. Martinelli, D. Braga and F. Grepioni, *J. Am. Chem. Soc.*, in the press.
12 D. Braga, F. Grepioni, B. F. G. Johnson, J. Lewis and M. Martinelli, *J. Chem. Soc., Dalton Trans.*, 1990, 1847.
13 H. Hope, J. Bernstein and K. N. Trueblood, *Acta Crystallogr., Sect. B*, 1972, **28**, 1733.
14 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
15 J. Cosier and A. M. Glayer, *J. Appl. Crystallogr.*, 1986, **19**, 105.
16 (*a*) G. M. Sheldrick, SHELXS 86, Program for the Solution of Crystal Structures, University of Göttingen, 1986; (*b*) G. M. Sheldrick, SHELXL 92, Program for Crystal Structure Determination (Gamma-test version), University of Göttingen, 1992; (*c*) G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.
17 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

Received 11*th May* 1993; *Paper* 3/02666C