THE SYNTHESIS, MOLECULAR STRUCTURE AND CRYSTAL ORGANIZATION OF HRu$_5$C(CO)$_{13}$(η^5-C$_5$H$_5$)*

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Abstract—Reaction of the square-pyramidal cluster Ru$_5$C(CO)$_{15}$ with NaC$_5$H$_5$ followed by HBF$_4$ affords the wingtip-bridged butterfly cluster HRu$_5$C(CO)$_{13}$(η^5-C$_5$H$_5$) (1) in high yield. Compound 1 has been characterized by spectroscopy and in the solid-state by a single crystal X-ray diffraction study. The cyclopentadienyl ring is coordinated to the bridging metal atom and the hydride bridges the Ru—Ru hinge. The molecular organization of 1 has been analysed and an intricate network of intra- and intermolecular hydrogen bonding is observed. Chemical and structural features of 1 are compared with those of the related benzene cluster, Ru$_5$C(CO)$_{13}$(η^6-C$_6$H$_6$) (2).

The interaction of clusters with unsaturated organic ligands constitutes a major area of exploration within the field of cluster science.[1] Such studies are a natural progression from traditional organo-metallic chemistry and it has been found that the interaction of an unsaturated organic moiety with a cluster of metals is often strikingly different from that in a mononuclear complex. These differences are borne out in both the structure and reactivity of the organo-unit.

The synthesis and characterization of clusters having carbocycles with ring sizes ranging from four to eight has been well developed.[2] For rings of five atoms and upwards multicentre bonding has been observed in clusters, although only terminal coordination has been observed with four-membered rings.

Solid-state studies have not only focused on the molecular structure of these molecules, they have also examined their intermolecular organization.[3] It has been shown recently that CO ligands establish networks of intermolecular C—H $\cdots$ O interactions in which the CO ligand acts as a hydrogen bonding acceptor from organic ligands. Therefore, the synthesis and structural characterization of clusters with five-membered carbocyclic rings offers an interesting opportunity to study the participation of these ligands in intermolecular networks.

RESULTS AND DISCUSSION

The reaction of Ru$_5$C(CO)$_{15}$ with an excess of NaC$_5$H$_5$ at room temperature in tetrahydrofuran results in the formation of a bright yellow solution. Addition of a slight excess of HBF$_4$ in ether to this solution produces a neutral yellow compound which may be purified by filtration through silica gel, eluting with dichloromethane–hexane (1:1, v/v). The yellow compound has been characterized
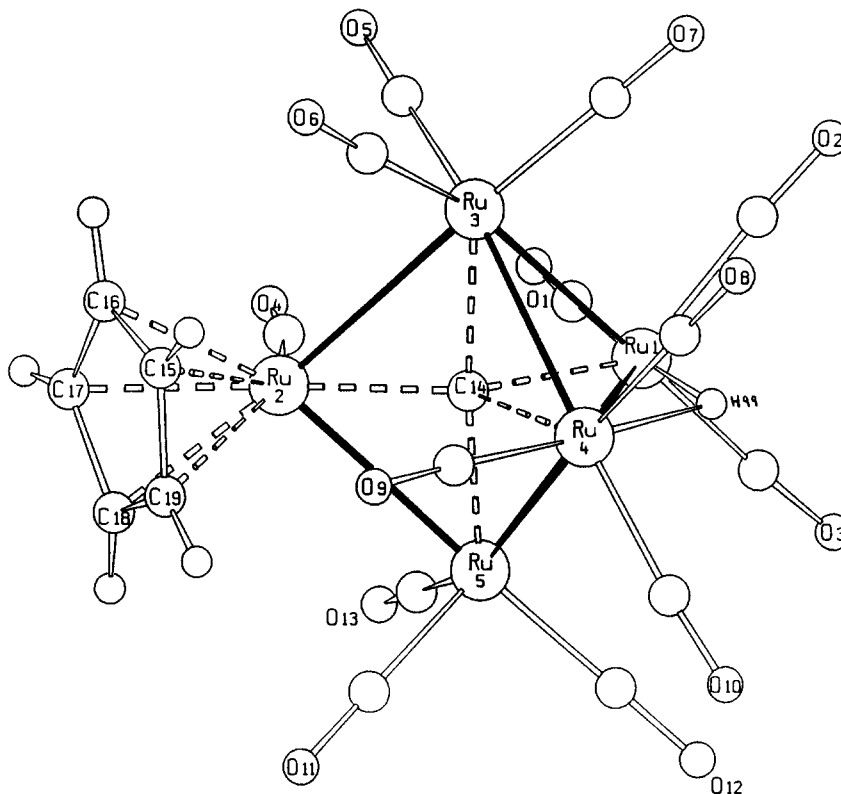

Fig. 1. The molecular structure of 1 in the solid state showing the atomic labelling scheme. The carbon atoms bear the same numbering system as their corresponding oxygen atoms.

as $HRu_5C(CO)_{13}(\eta^5\text{-}C_5H_5)$ (1) from spectroscopic analysis and a single-crystal X-ray diffraction study. The IR spectrum contains stretches at wavenumbers indicative of terminal carbonyl ligands, namely between 2093 and 1934 cm^{-1}. The mass spectrum of 1 contains a parent peak at 949 (calc. 948 amu). The ^1H NMR spectrum exhibits just two singlet resonances at δ 5.19 and -22.30 ppm with relative intensities of 5:1, respectively. Assignment of these signals is straightforward; the former signal is derived from the ring protons of the cyclopentadienyl moiety and the latter from a hydride.

Crystals of 1 were grown from a solution of dichloromethane by vapour diffusion with pentane. On removal of the crystals from the mother liquor they rapidly deteriorated and were therefore frozen in a droplet of mineral oil and data were collected at 150 K. The metal atom framework of 1 comprises of a Ru_4 butterfly unit, in which the wingtip ruthenium atoms are bridged by a fifth ruthenium atom to give the bridged butterfly structure shown in Fig. 1. The bridging metal atom has a C_5H_5 ligand and one carbonyl ligand coordinated, whilst each of the four ruthenium atoms in the butterfly unit carry three carbonyl groups with a hydride bridge located on the hinge. Viewing the molecule graphically (Fig. 2) one can appreciate that the

carbonyl ligands on the hinge ruthenium atoms are bent away from the hinge; this presumably minimizes steric interaction with the hydride.

The cluster has essentially the same metallic core as $Ru_5C(CO)_{13}(\eta^6\text{-}C_6H_6)$ (2; see Fig. 3) and Table 1
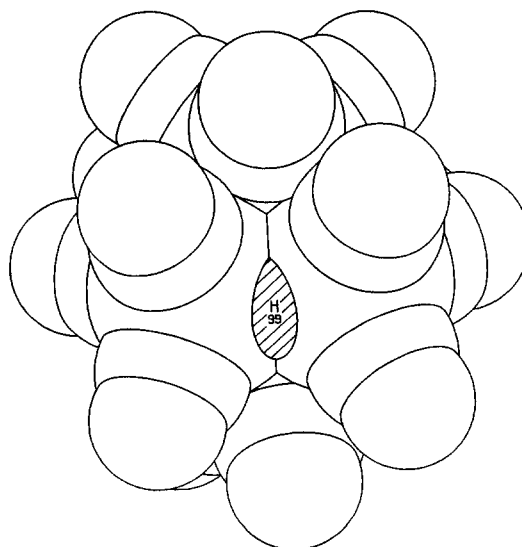

Fig. 2. Space filling representation of structure 1 showing that the carbonyls on hinge ruthenium atoms are bent away from the hinge.
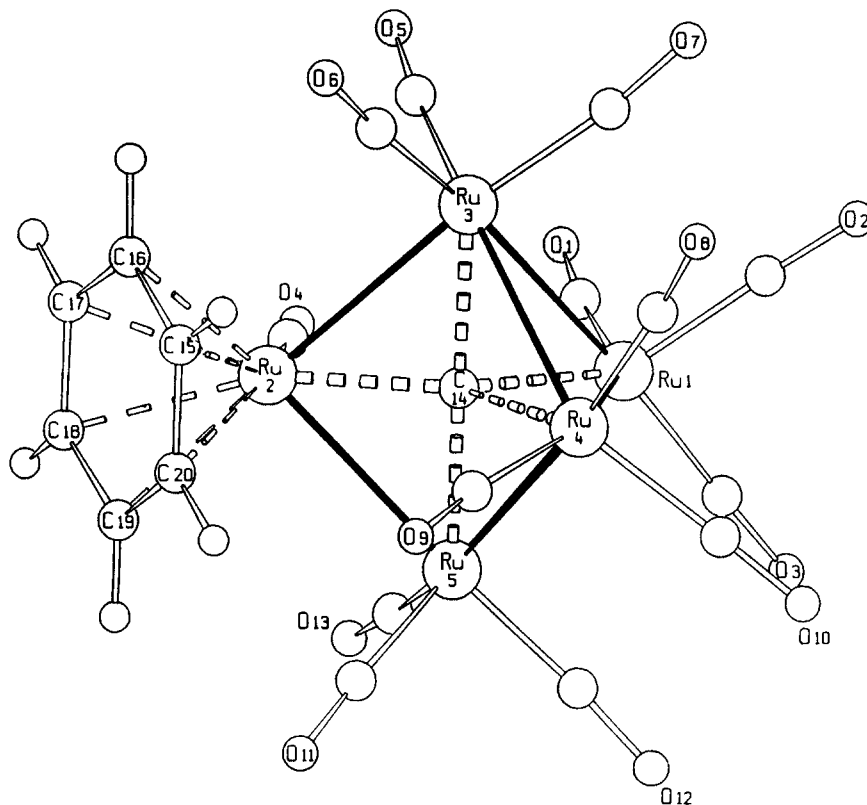
Fig. 3. The molecular structure of **2** in the solid state showing the atomic labelling scheme. The carbon atoms bear the same numbering system as their corresponding oxygen atoms.

compares principal bond lengths in **1** and **2**.[4] The main difference between the two complexes arises from the fact that in **2**, the bridging ruthenium atom [Ru(2)] carries a six-membered ring, whereas **1** has a five-membered ring. In **1** the dihedral angle of the butterfly is smaller than that of **2** with the resulting extrusion of C(14) from its interstitial position. The dihedral angle in **1** is 174.0° compared to 177.1° in **2**. With respect to compound **2** the carbide atom is closer to the bridging ruthenium atom of structure **1**. The Ru(2)—CO bond in **1** is significantly shorter [1.82(1) Å] than the other Ru—C(CO) bond distances [range 1.88(1)–1.94(1) Å, average 1.91(1) Å] and the C—O distance [1.16(2) Å] is at the far end of the range of the C—O bond lengths [1.13(2)–1.16(2) Å]. It was also noted in the previously reported isolobal structure, Ru₅C(CO)₁₃(η⁵-C₅H₅)(AuPPh₃),[5] that the Ru—C(CO) distance of the ruthenium atom bearing the cyclopentadienyl ligand [1.84(3) Å] is considerably shorter than the other Ru—C(CO) distances [1.91(4) Å], although the larger estimated standard deviations associated with these latter parameters make comparisons less significant. Both the Ru(2)—Ru(3) and Ru(2)—Ru(5) bond lengths are longer in **1** than in **2** [2.903(2) and 2.891(2) versus 2.872(2) and 2.859(2) Å, respectively]. The addition of the

hydride across the Ru(1)—Ru(4) hinge also causes an elongation of the bond [2.849(2) versus 2.732(2) Å in **2**]. Another structural difference between **1** and **2** is the outward direction of the carbonyls on Ru(1) and Ru(4) due to accommodation of the hydride (Fig. 2).

An examination of the crystal structures of **1** and **2** using the program PLATON-90[6] has revealed the presence of an intricate network of hydrogen bonds; SCHAKAL92[7] was used for the graphical representation of these results. In order to have hydrogens located at their nuclei, all C—H bond distances were normalized to 1.08 Å with a cut-off distance of 2.6 Å applied for intramolecular hydrogen bonds and any contacts below the O—H van der Waals distance were considered to be a possible intermolecular H···O interaction. As in the previous cases, where the hydrogen atoms were in calculated positions, close attention was paid to the donor–acceptor C(CH)···O distances (range 3.290–3.732 Å). Table 2 lists the short C—H···O contacts found. In both structures all the aromatic hydrogen atoms are involved in C—H···O interactions. In both cases there is only one ruthenium atom which has no COs involved in C···H—O interactions. In **2** this is Ru(5), and in **1** it is Ru(2). In **1** the solvent molecule, when present, is also

Table 1. Selected bond lengths (Å) for **1** and **2**

	1	**2**
Ru(1)—Ru(3)	2.850(2)	2.837(2)
Ru(1)—Ru(4)	2.849(2)	2.732(2)
Ru(1)—Ru(5)	2.842(2)	2.870(2)
Ru(2)—Ru(3)	2.903(2)	2.872(2)
Ru(2)—Ru(5)	2.891(2)	2.859(2)
Ru(3)—Ru(4)	2.858(2)	2.877(2)
Ru(4)—Ru(5)	2.867(2)	2.865(2)
Ru(1)—C(14)	2.14(1)	2.10(1)
Ru(2)—C(14)	2.01(1)	2.07(1)
Ru(3)—C(14)	1.99(1)	1.97(1)
Ru(4)—C(14)	2.11(1)	2.04(1)
Ru(5)—C(14)	1.98(1)	1.99(1)
Ru(1)—H(99)	1.65(1)	
Ru(4)—H(99)	1.88(1)	
Ru(2)—C(15)	2.289(12)	2.32(1)
Ru(2)—C(16)	2.213(14)	2.27(1)
Ru(2)—C(17)	2.229(13)	2.23(1)
Ru(2)—C(18)	2.222(13)	2.24(1)
Ru(2)—C(19)	2.297(13)	2.29(1)
Ru(2)—C(20)		2.33(1)
Ru(2)—$C_{CO(mean)}$	1.91(1)	1.88(2)
C—$O_{CO(mean)}$	1.14(2)	1.15(2)

cyclopentadienyl cluster based on a square-pyramidal Ru_5C unit has been prepared by an alternative route. Reaction of $Ru_5C(CO)_{15}$ with Me_3NO in the presence of C_5H_6 affords the bis(cyclopentadienyl) complex, $Ru_5C(CO)_{10}(\eta^5-C_5H_5)_2$.[8]

EXPERIMENTAL

General procedures and materials

Reactions were carried out using freshly distilled solvents under an atmosphere of dry nitrogen gas. Subsequent purification of products were carried out using standard laboratory grade solvents without precautions to exclude air. IR spectra were recorded on a Perkin–Elmer 1710 Fourier-Transform spectrometer. Mass spectra were obtained by positive ion fast atom bombardment on a Kratos MS50TC calibrated with CsI. ^1H NMR spectra were recorded using a Bruker WM250 spectrometer referenced to internal TMS.

The cluster $Ru_5(CO)_{15}$ was prepared from $Ru_6C(CO)_{17}$ according to the literature method.[9] NaC_5H_5 was prepared by the conventional procedure and HBF_4 was used as purchased from Aldrich Chemicals.

involved in C—H $\cdots$ O interactions. Figure 4 shows the network of C—H $\cdots$ O interactions in compound **1**.

There is no evidence for a preference for a certain type of CO involvement; instead it seems most likely that the crystal packing may be organized in such a way as to maximize these C—H $\cdots$ O interactions.

The chemistry of **1** and **2** is very different. The benzene cluster **2** is prepared from the square-pyramidal cluster $Ru_5C(CO)_{12}(\eta^6-C_6H_6)$ upon reaction with a steady stream of CO at atmospheric pressure.[4] The reaction takes place rapidly and in quantitative yields and involves nucleophilic attack by CO at the basal ruthenium atom which carries the benzene ligand; this is accompanied by cleavage of an apex-to-basal Ru—Ru bond and formation of the bridged-butterfly cluster **2**. A similar transformation is observed for the parent cluster $Ru_5C(CO)_{15}$ under more forcing conditions, *ca* 10 atmospheres of CO. Both $Ru_5C(CO)_{16}$ and **2** readily lose CO, reverting back to their precursor materials. In **1**, the open bridged-butterfly structure has not been found to undergo rearrangement to a square-pyramidal structure with the expulsion of CO. A

Reaction of $Ru_5C(CO)_{15}$ with NaC_5H_5 and HBF_4— synthesis of $HRu_5C(CO)_{13}(\eta^5-C_5H_5)$ (1)

To a solution of $Ru_5C(CO)_{15}$ (100 mg) in thf (20 cm³) an excess of NaC_5H_5 (10 mg, 1.1 mol. equiv.) was added with stirring at room temperature. The solution turned from dark red to bright yellow and HBF_4 in ether (1 cm³, 1% solution, w/w) was added. The solution was stirred for a further 30 min and then filtered through a short column containing silica gel (60 mesh), eluting with dichloromethane–hexane (1:1, v/v). The solvent was removed *in vacuo* and the yellow microcrystalline solid characterized as $HRu_5C(CO)_{13}(\eta^5-C_5H_5)$ (**1**; 85 mg). Crystals of **1** suitable for X-ray diffraction analysis were grown from dichloromethane–pentane by vapour diffusion. The crystals collapsed upon removal from the mother liquor, presumably due to the presence of dichloromethane in the lattice.

Spectroscopic data for $HRu_5C(CO)_{13}(\eta^5-C_5H_5)$ (**1**). IR [CH_2Cl_2, $v(CO)$]: 2093 (m), 2063 (s), 2052 (vs), 2040 (sh), 2019 (m), 1982 (w), 1934 (w) cm^{-1}. Positive FAB mass spectrum: 949 (calc. 948) amu. ^1H NMR ($CDCl_3$): δ 5.19 (s, 5H), -22.30 (s, 1H) ppm.
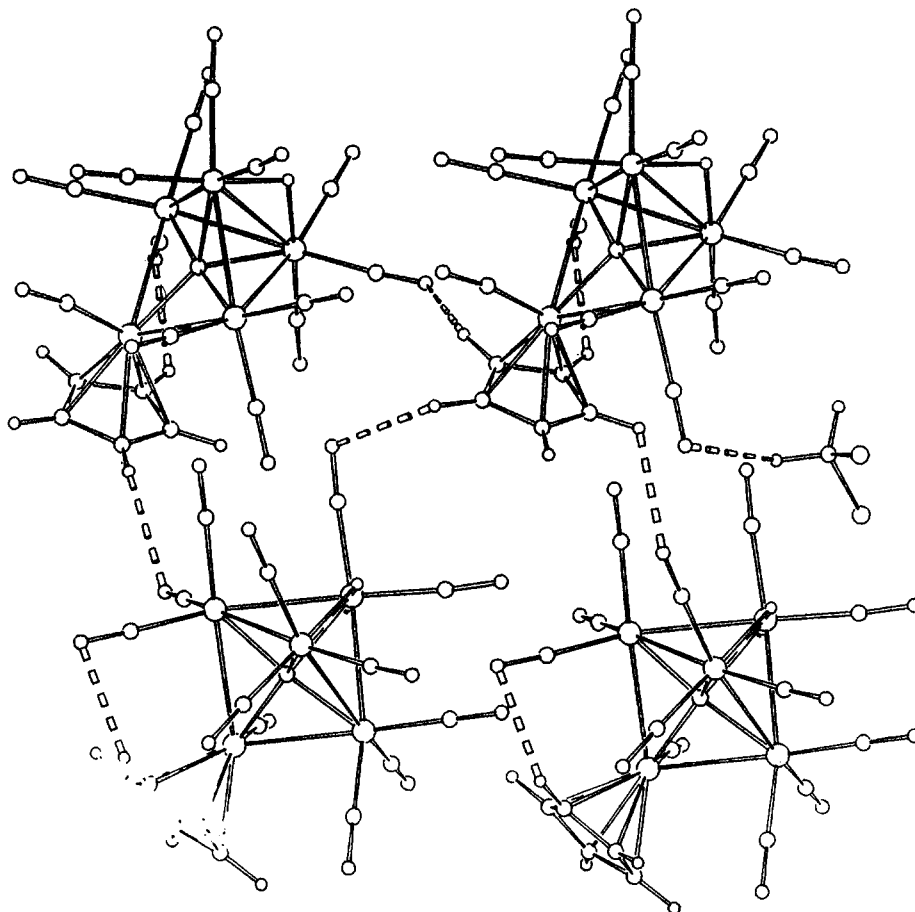
Fig. 4. The network of C—H $\cdots$ O interactions for **1** is shown.

Table 2. Analysis of possible hydrogen bonds

No.	Type	Res	Donor H $\cdots$ Acceptor	D$\cdots$A (Å)	H$\cdots$A (Å)	D—H$\cdots$A (Å)
HRu$_5$C(CO)$_{13}$(η^5-C$_5$H$_5$) (1)						
1	intra	2	C(15)—H(15)$\cdots$O(6)	3.290	2.513	128.1
2		2	C(16)—H(16)$\cdots$O(10)	3.452	2.461	152.0
3		2	C(17)—H(17)$\cdots$O(2)	3.264	2.454	130.9
4		2	C(19)—H(19)$\cdots$O(8)	3.242	2.583	118.6
5		1	C(20)—H(20)$\cdots$O(11)	3.455	2.579	137.7
6		2	C(18)—H(18)$\cdots$O(5)	3.619	2.713	114.3
Ru$_5$C(CO)$_{13}$(η^6-C$_6$H$_6$) (2)						
1		1	C(17)—H(17)$\cdots$O(1)	3.388	2.463	143.1
2		1	C(17)—H(17)$\cdots$O(4)	3.325	2.424	140.0
3		1	C(18)—H(18)$\cdots$O(5)	3.250	2.485	126.9
4	intra	1	C(20)—H(20)$\cdots$O(9)	3.391	2.583	131.0
5		1	C(19)—H(19)$\cdots$O(7)	3.732	2.683	163.8
6		1	C(16)—H(16)$\cdots$O(10)	3.297	2.685	115.5
7		1	C(20)—H(20)$\cdots$O(3)	3.536	2.720	132.0

Structure determination

Diffraction data were collected on a Stoe Stadi-4 circle diffractometer at 150 K using an Oxford Cryosystems low temperature device.[10] Crystallographic data and details of measurements are given in Table 3. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and the refinement was carried out by least squares full-matrix cycles using the SHELXL-93 system of computer programs,[11] initially with isotropic and finally with anisotropic thermal parameters for all non-hydrogen atoms. Solvent molecules of CH_2Cl_2 were found to be present with one-third occupancy. Attempts to locate the hydrogen atoms from Fourier difference maps were unsuccessful and in the case of the ring hydrogens these were added in calculated positions and refined "riding" on their respective carbon atoms. Common isotropic thermal parameters were refined for the cyclopentadienyl hydrogen atoms. Potential energy minimization calculations performed using XHYDEX[12] indicated only one possible site [bridging the hinge Ru(1)—Ru(4) bond] was obtained

Table 3. Crystal data and details of measurements for 1

Formula	$C_{19}H_6O_{13}Ru_5 \cdot$ $1/3CH_2Cl_2$
Mol. wt	1003.1
Temperature	150
System	monoclinic
Space group	Cc
a (Å)	10.156(6)
b (Å)	16.050(7)
c (Å)	17.488(7)
β (°)	99.93(5)
V (Å^3)	2808
Z	4
$F(000)$	1886
λ(Mo-K_α) (Å)	0.71073
μ(Mo-K_α) (cm^{-1})	2.81
θ-range ($\cdot$)	2.5-25
Octants explored	$-12,11$
$(h_{min}h_{max},k_{min}k_{max},l_{min}l_{max})$	0,19
	0,20
Measured reflections	2552
Unique observed reflections	2460
Unique observed reflections $[I_o > 2\sigma(I_o)]$	2436
No. of refined parameters	365
GOF on F^2	1.250
Final R indices $[I > \sigma(I)]$ R_1 (on F), R_w2 (on F^2)	0.0286,0.0981
Final R indices (all data) R_1 (on F), R_w2 (on F^2)	0.0297,0.1081

Table 4. Atomic coordinates ($\times 10^4$) for structure 1

	x	y	z
Ru(1)	$-9464(1)$	$-2448(1)$	$-1955(1)$
Ru(2)	$-11303(1)$	$-2032(1)$	$-198(1)$
Ru(3)	$-11597(1)$	$-1359(1)$	$-1758(1)$
Ru(4)	$-8886(1)$	$-861(1)$	$-1248(1)$
Ru(5)	$-8548(1)$	$-2348(1)$	$-327(1)$
C(14)	$-10122(11)$	$-1845(7)$	$-996(7)$
C(1)	$-10512(12)$	$-3442(8)$	$-1962(7)$
O(1)	$-11124(11)$	$-4028(6)$	$-1983(7)$
C(2)	$-9996(12)$	$-2285(8)$	$-3061(8)$
O(2)	$-10240(10)$	$-2187(8)$	$-3712(5)$
C(3)	$-7873(12)$	$-3060(8)$	$-2045(8)$
O(3)	$-6939(11)$	$-3430(8)$	$-2148(7)$
C(4)	$-11864(13)$	$-3076(8)$	$-512(9)$
O(4)	$-12309(12)$	$-3741(6)$	$-628(7)$
C(5)	$-13114(14)$	$-2074(8)$	$-1969(8)$
O(5)	$-14031(11)$	$-2500(7)$	$-2101(8)$
C(6)	$-12584(13)$	$-429(8)$	$-1448(8)$
O(6)	$-13182(12)$	$115(7)$	$-1290(7)$
C(7)	$-11711(13)$	$-921(9)$	$-2806(8)$
O(7)	$-11795(12)$	$-646(8)$	$-3402(6)$
C(8)	$-9099(15)$	$-9(9)$	$-2042(9)$
O(8)	$-9216(13)$	$487(8)$	$-2512(7)$
C(9)	$-9308(14)$	$-127(8)$	$-489(8)$
O(9)	$-9526(14)$	$328(8)$	$-10(8)$
C(10)	$-6977(13)$	$-712(9)$	$-945(8)$
O(10)	$-5854(10)$	$-619(8)$	$-808(7)$
C(11)	$-8083(12)$	$-1970(8)$	$710(9)$
O(11)	$-7794(11)$	$-1762(8)$	$1348(6)$
C(12)	$-6735(14)$	$-2535(8)$	$-451(8)$
O(12)	$-5641(10)$	$-2663(7)$	$-517(6)$
C(13)	$-8888(13)$	$-3466(8)$	$-35(8)$
O(13)	$-9091(11)$	$-4124(6)$	$134(7)$
C(15)	$-11989(13)$	$-846(8)$	$344(8)$
C(16)	$-12986(14)$	$-1456(11)$	$262(9)$
C(17)	$-12519(14)$	$-2128(10)$	$745(8)$
C(18)	$-11146(14)$	$-1959(9)$	$1084(8)$
C(19)	$-10874(14)$	$-1149(9)$	$850(8)$
Cl(1)	$142(6)$	$-4519(4)$	$-3579(4)$
Cl(2)	$-1072(9)$	$-5967(3)$	$-3006(4)$
C(20)	$-1265(20)$	$-5159(13)$	$-3667(12)$

for the hydride ligand, which was supported by the longer Ru(1)—Ru(4) bond distance of 2.849(2) Å. This hydrogen atom was included in the calculation of structure factors, but its position was not refined. Fractional atomic coordinates are reported in Table 4.

REFERENCES

1. For example, see (a) P. R. Raithby and M. J. Rosales, *Adv. Inorg. Chem. Radiochem.* 1985, **29**, 169; (b) D.

Braga, P. J. Dyson, F. Grepioni and B. F. G. Johnson, *Chem. Rev.* 1994, **94**, 1585.

2. While there are numerous examples of clusters with five-, six-, seven- and eight-membered rings, one with a four-membered ring system has only recently been published: P. J. Bailey, A. J. Blake, P. J. Dyson, S. L. Ingham and B. F. G. Johnson, *J. Chem. Soc., Chem. Commun.* 1994, 2233.

3. (a) D. Braga, F. Grepioni, P. Sabatino and G. R. Desiraju, *Organometallics* 1994, **13**, 3532; (b) D. Braga and F. Grepioni, *Accts Chem. Res.* 1994, 27.

4. D. Braga, F. Grepioni, P. Sabation, P. J. Dyson, B. F. G. Johnson, J. Lewis, P. J. Bailey, P. R. Raithby and D. Stalke, *J. Chem. Soc., Dalton Trans.* 1993, 985.

5. A. G. Cowie, B. F. G. Johnson, J. N. Lewis, P. R. Raithby and A. G. Swanson, *J. Chem. Soc., Chem. Commun.* 1984, 637.

6. A. L. Spek, PLATON90, *Acta Cryst.* 1990, **A46**, C31.

7. E. Keller, SCHAKAL92, Graphical Representation of Molecular Models, University of Frieiburg, Germany (1992).

8. A. J. Blake, P. J. Dyson, R. C. Gash, B. F. G. Johnson and P. Trickey, *J. Chem. Soc., Dalton Trans.*, 1994, 1105.

9. D. H. Farrar, P. F. Jackson, B. F. G. Johnson, J. Lewis, J. N. Nicholls and M. McPartlin, *J. Chem. Soc., Chem. Commun.* 1981, 415.

10. J. Cosier and A. M. Glazer, *J. Appl. Cryst.* 1986, **19**, 105.

11. G. M. Sheldrick, SHELXL-93, Program for Crystal Structure Determination, Göttingen, Germany (1993).

12. A. G. Orpen, *J. Chem. Soc., Dalton Trans.* 1980, 2509.