The Synthesis and Characterisation of [$Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_{16}H_{16}\text{-}\mu_2\text{-}O)$]: an Intermediate in the Formation of the Carbido-cluster [$Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})$]

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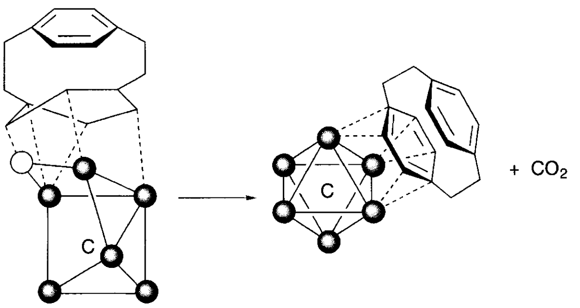
The complex $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_{16}H_{16}\text{-}\mu_2\text{-}O)$ **1** is isolated and fully characterised in solution and in the solid-state by a single crystal X-ray diffraction analysis: it constitutes a rare example of a molecular system containing both the carbido- and oxo-ligand of a cleaved carbonyl group which are trapped within a metal cluster framework; on heating **1** undergoes quantitative conversion to the carbido-cluster, $Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})$ **2**, with the elimination of CO_2.

The discovery of $Fe_5C(CO)_{15}$[1] and $Ru_6C(CO)_{17}$[2] led to a widespread interest in carbido-clusters and provoked studies into the origin of the carbido-atom. The isolated C-atom was found to be derived from a coordinated CO ligand in which the cluster unit brought about the disproportionation of carbon monoxide (2CO → 'C' + CO_2).[3]

The relevance that these discoveries bore on the activation of CO on metal surfaces was immediately recognised but the precise method by which the C–O bond cleavage occurs is still a matter of some debate, although it is generally accepted that the cluster unit activates the CO moiety by interaction of both the C and O with a number of metal atoms simultaneously. The significance of this observation was soon appreciated by surface chemists who correlated this observation with the formation of a carbide on the surface.[4] Here we report further studies on hexaruthenium-cluster systems which shed further light on this intriguing chemistry.

We have recently observed that three clusters containing the [2.2]paracyclophane ligand, *viz.* $Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})$, $Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})$ **2** and $Ru_6C(CO)_{11}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})(\eta^6\text{-}C_{16}H_{16})$, may be obtained from the thermolysis of $Ru_3(CO)_{12}$ with [2.2]paracyclophane in octane.[5] An additional product has also been isolated from the same reaction, albeit in modest yield.† This new product has been fully characterised in solution‡ by ^1H NMR studies and in the solid phase by single-crystal X-ray diffraction§ as the open cluster, $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_{16}H_{16}\text{-}\mu_2\text{-}O)$ **1**.



1 **2**

Fig. 1 The molecular structure of **2** in the solid state showing the atomic labelling scheme. The carbonyl C-atoms bear the same numbering system as their corresponding O-atoms. Relevant bond distances (Å): Ru(1)–Ru(2) 2.868(3), Ru(1)–Ru(3) 2.913(3), Ru(1)–Ru(4) 2.817(3), Ru(1)–Ru(5) 2.847(3), Ru(2)–Ru(4) 2.707(3), Ru(2)–Ru(6) 2.864(3), Ru(3)–Ru(4) 2.782(3), Ru(4)–Ru(6) 2.933(3), Ru(5)–Ru(6) 2.846(3), Ru(1)–C(99) 1.94(3), Ru(2)–C(99) 2.17(2), Ru(4)–C(99) 2.09(2), Ru(5)–C(99) 2.04(2), Ru(6)–C(99) 1.97(3), Ru(3)–O(99) 2.14(2), Ru(5)–O(99) 2.06(2), O(99)–C(20) 1.40(3), Ru–C(7) mean 2.15(3), C(7)–O(7) 1.13(3), Ru–C(mean CO terminal) 1.90(3), C–O(mean CO terminal) 1.14(3), Ru(1)–C(17) 2.22(2), Ru(3)–C(18) 2.60(2), Ru(3)–C(19) 2.20(2), Ru(3)–C(20) 2.70(2), Ru(5)–C(16) 2.38(2), Ru(5)–C(20) 2.67(2), Ru(5)–C(21) 2.23(2), C(16)–C(17) 1.48(3), C(16)–C(21) 1.34(3), C(17)–C(18) 1.38(3), C(18)–C(19) 1.49(3), C(18)–C(31) 1.52(3), C(19)–C(20) 1.54(3), C(20)–C(21) 1.56(3), C(21)–C(22) 1.53(3), C(22)–C(23) 1.55(3), C(23)–C(24) 1.52(4), C(24)–C(25) 1.39(3), C(24)–C(29) 1.37(3), C(25)–C(26) 1.38(3), C(26)–C(27) 1.37(3), C(27)–C(28) 1.44(3), C(27)–C(30) 1.51(3), C(28)–C(29) 1.36(4), C(30)–C(31) 1.55(3).

The molecular structure of **1** is illustrated in Fig. 1. The metal atoms adopt an open octahedral arrangement in which three Ru–Ru edges are open with respect to an ideal octahedron. The interstitial carbido-atom lies in the centre of the cavity formed by Ru-atoms 1, 2, 4, 5 and 6. The open edge between Ru(3) and Ru(5) is spanned by a bridging O-atom. The interstitial carbido-atom sits in the middle of a bridged-butterfly sub-system defined by Ru(1) and Ru(6) (wing-tip atoms) and Ru(2) and Ru(4) (hinge atoms), the wing-tips being bridged by Ru(5). The distances between the carbido-atom and the wing-tip ruthenium atoms [1.94(3), 1.97(3) Å] are shorter than those from the bridging atom [Ru(5)–C(99) 2.04(2) Å] and from the hinge atoms [2.09(2) and 2.17(2) Å]; Ru(3) is at 3.11 Å.

The PCP-type ligand interacts with three metal atoms of the cluster. While the C_6-ring is severely distorted, it clearly shows the presence of a delocalized bonding pattern. First, C(16)–C(21) establishes a 'conventional' π-interaction with both C atoms bonding to Ru(5) [Ru(5)–C(16) 2.38(2), Ru(5)–C(21) 2.23(2) Å] and second, instead of eclipsing a Ru-atom, C(17)–C(18) lies *quasi*-parallel to the bond, with only one C-atom, C(17), interacting with Ru(1) [Ru(1)–C(17) 2.22(2) Å]. Interactions also occur between C(19) and Ru(3) [2.20(2) Å] and C(18) and Ru(3) [2.60(2) Å]. The distribution of bond lengths and angles is in agreement with the assignment of an sp^3 hybridisation to atom C(20) which also forms a σ-bond with the O-atom. The other five atoms can be considered to have an sp^2 hybridisation. The PCP-type moiety therefore contributes a total of five electrons and can be represented more adequately with the delocalised π-allyl type and π-ene bonding.

The bridging O-atom is pyramidal; the C–O distance of 1.40(3) Å is in agreement with a C–O single bond length and the two Ru–O interactions are slightly different in length [Ru(3)–O(99) 2.14(2), Ru(5)–O(99) 2.06(2) Å] with an inner angle at the O-atom of 117.2(7)°. The O-atom is required to contribute

Table 1 Assignments of the ^1H NMR spectrum of **1**

H position	δ	Multiplicity and $J_{H\text{-}H}$/Hz
H(16)	3.78	dd, 5.8, 2.1
H(17)	4.18	dd, 5.8, 1.6
H(19)	4.08	dd, 6.2, 1.6
H(20)	5.91	dd, 6.2, 2.1
H(22a)	1.64	ddd, 13.8, 9.7, 7.8
H(22b)	2.4–2.55	overlapping multiplet
H(23a)	3.2–3.5	overlapping multiplet
H(23b)	3.2–3.5	overlapping multiplet
H(25)	7.46	dd, 7.9, 1.6
H(26)	7.05	dd, 7.9, 1.6
H(28)	7.46	dd, 7.9, 1.6
H(29)	7.79	dd, 7.9, 1.6
H(30a)	2.95	dt, 13.6, 8.6
H(30b)	3.2–3.5	overlapping multiplet
H(31a)	3.68	ddd, 14.0, 8.8, 1.6
H(31b)	2.4–2.55	overlapping multiplet

three electrons to the cluster leaving one 'unused' lone-pair, and the total electron count for the cluster is therefore 90.

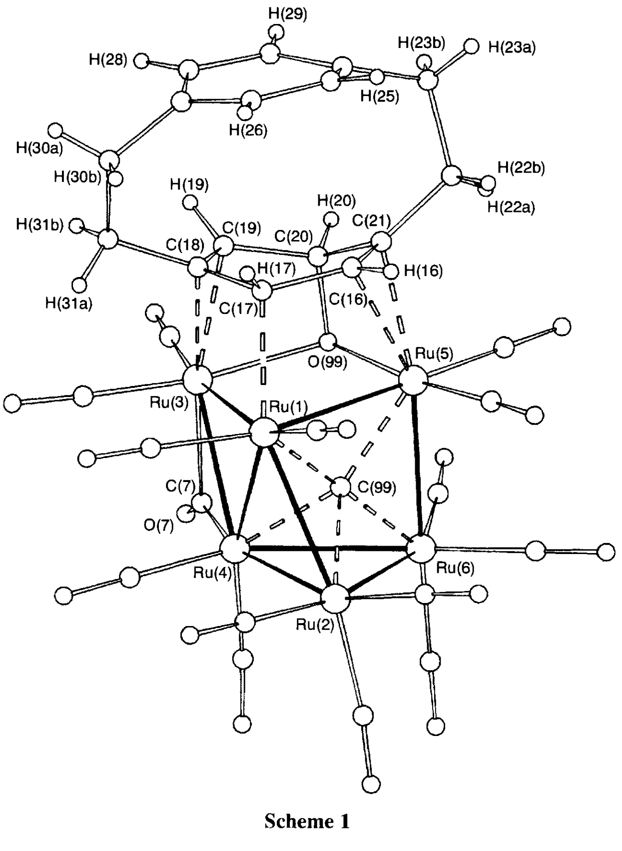
The ^{1}H NMR spectrum of **1** is noteworthy, it comprises of 16 multiplets, some of which overlap, as indicated in Table 1.

There is also spectroscopic evidence for the presence of a second isomeric form of **1**. Isolation of this isomer and preliminary spectroscopic analysis reveal that it is very similar to **1**, possibly differing only in the interaction of the $C_{16}H_{16}O$ moiety with the Ru_6C cluster unit.

We have found that on heating $Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^1\text{-}C_{16}H_{16})$ with an equimolar quantity of $Ru_3(CO)_{12}$ both the open cluster **1** and the octahedral carbido species **2** are observed. Furthermore, thermolysis of compound **1** in octane or its pyrolysis in a gas cell, yields **2** and CO_2 almost quantitatively. Hence, it follows that **1** is an intermediate in the formation of **2**, merely requiring the loss of CO_2 and a re- arrangement of the hexaruthenium polyhedron (see Scheme 1).

As already outlined, it has been proposed that carbido-atoms may be introduced into metal cluster compounds by the thermally induced cleavage of a coordinated carbon monoxide ligand. Carbon dioxide is usually detected as a by-product from these reactions, indicating that the disproportionation of two carbonyl groups has occurred. The multi-hapto coordination of a carbonyl ligand leads to a considerable elongation and weakening of the C–O bond facilitating such a cleavage.[6] Additionally, this coordination mode increases the nucleophilicity of the carbonyl oxygen, enabling attack at the electrophilic carbon of a terminal carbonyl necessary for the formation of CO_2. One might, therefore, expect to form an ester-type intermediate which then converts into CO_2 and the observed cluster carbide, which is similar to a mechanism proposed earlier by Deeming.[7]

We believe that cluster **1** models the stage in the above reaction sequence after C–O bond cleavage of a di-hapto carbonyl ligand has taken place, but before the oxygen atom has been expelled from the cluster as CO_2. Since the cluster has a particularly open geometric framework, an intramolecular mechanism for the conversion of **1** to **2** can be envisaged in which CO_2 is generated (initially by the attack of the nucleophilic oxygen with a ring carbon of the cyclophane moiety) and is then rapidly expelled from the cluster core together with rearrangement of the metal atom network thereby affording **2**. The stability of the octahedrally encapsulated carbido-atom in this system, together with the production of CO_2 undoubtedly contribute to the driving force for the C–O cleavage process.



Scheme 1

We wish to thank the EPSRC and ICI (Wilton) (C. M. M.) for financial assistance. Financial support by MURST (Italy) is also acknowledged (D. B., F. G.) and NATO is thanked for a travel grant (D. B., F. G. and B. F. G. J.).

Received, 13th January 1995; Com. 5/00220F

Footnotes

† A suspension of $Ru_3(CO)_{12}$ (500 mg) in octane (30 ml) containing a large excess of [2.2]paracyclophane (200 mg) was heated to reflux for 2 h. After this time the solvent was removed *in vacuo*, and the products separated by column chromatography, using a solution of dichloromethane–hexane (3 : 7) as eluent. In order of elution, the products were characterised spectroscopically as $Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})$ (yellow, 15%), $Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})$ **2** (red, 20%), $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_{16}H_{16}\text{-}\mu_2\text{-}O)$ **1** (purple, 5%) and $Ru_6C(CO)_{11}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})(\eta^6\text{-}C_{16}H_{16})$ (brown, 3%).

Compounds **1** and **2** are also produced in 8 and 26% yields, respectively, on heating $Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})$ (50 mg) and $Ru_3(CO)_{12}$ (42 mg, 1 mol equiv.) in octane (30 ml) at reflux for 3 h.

‡ *Spectroscopic data* for **1**: IR ν_{CO}/cm^{-1} (CH_2Cl_2) 2084 m, 2053 s, 2037 vs, 2016 m, 2008 m, 1067 w, 1866 w. MS: *m/z* 1262 (calc. = 1263). ^{1}H NMR ($CDCl_3$) see Table 1. ^{13}C NMR ($CDCl_3$), ([2.2]paracyclophane resonances only) δ 138.2(q), 136.9(q), 133.8(CH), 133.6(CH), 133.4(CH), 130.1(CH), 109.2(q), 88.3(CH), 74.4(CH), 65.1(q), 47.4(CH), 39.8(CH_2), 35.8(CH_2), 34.6(CH_2), 34.3(CH_2), 21.6(CH).

§ *X-Ray data* for compound **1**: Data were collected on a Stoë Stadi-4 four-circle diffractometer equipped with a graphite monochromator (Mo-Kα radiation, λ = 0.71073 Å). Formula $C_{33}H_{18}Cl_2O_{16}Ru_6$ (including CH_2Cl_2 solvate) M = 1347.8, T = 150.0(1) K, orthorhombic, space group $Pca2_1$, a = 18.270(4), b = 10.432(6), c = 19.825(6) Å, U = 3781(2) Å^3, Z = 4, μ(Mo-Kα) = 2.368 cm^{-1}, $F(000)$ = 2568, red tablet, 0.19 × 0.23 × 0.04 mm, $2\theta_{max}$ 45, wR_2 (on F^2, all data) = 0.1168, R_1 [on F, for 2162 unique reflections with $I > 2\sigma(I)$] = 0.0543, 2849 collected reflections, 2581 unique reflections used in the refinement, S (on F^2) = 1.052. The structure was solved by direct methods,[8] and a series of Fourier difference maps were used to locate all light atoms except the H-atoms. These atoms were placed in geometrically calculated positions. All other calculations were performed using SHELX93.[9] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 E. H. Braye, L. F. Dahl, W. Hübel and D. L. Wampler, *J. Am. Chem. Soc.*, 1962, **84**, 4633.
2 B. F. G. Johnson, R. D. Johnston and J. Lewis, *Chem. Commun.*, 1967, 1057.
3 S. Martinengo, B. T. Heaton, R. J. Goodfellow and P. Chini, *J. Chem. Soc., Chem. Commun.*, 1977, 39; I. A. Oxton, S. F. A. Kettle, P. F. Jackson, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Chem. Commun.*, 1979, 687.
4 V. Ponec, *Catal. Rev. Sci. Eng.*, 1978, **18**, 151; W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 117.
5 P. J. Dyson, B. F. G. Johnson, C. M. Martin, A. J. Blake, D. Braga, F. Grepioni and E. Parisini, *Organometallics*, 1994, **13**, 2113.
6 E. L. Muetteries, *Bull. Soc. Chim. Belg.*, 1975, **85**, 959; 1976, **85**, 451; M. L. Chisholm, C. E. Hammond, V. J. Johnston, W. E. Streib and J. C. Huffman, *J. Am. Chem. Soc.*, 1992, **114**, 7056.
7 A. J. Deeming, in *Transition Metal Clusters*, ed. B. F. G. Johnson, Wiley, New York, 1980, p. 415.
8 G. M. Sheldrick, SHELXS 86, Program for Crystal Structure Solution, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
9 G. M. Sheldrick, SHELXL 93, Program for Crystal Structure Refinement, University of Göttingen, 1993.