Measurement of an Exceedingly Long Metal Carbonyl C–O Bond by Single Crystal X-Ray Diffraction in $Ru_8(\mu\text{-}H)_2(\mu_6\text{-}\eta^2\text{-}CO)(CO)_{19}(\eta^6\text{-}C_{16}H_{16})$

Caroline M. Martin, Alexander J. Blake, Paul J. Dyson, Scott L. Ingham and Brian F. G.Johnson*

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ

The [2.2]paracyclophane octaruthenium cluster, $Ru_8(\mu\text{-}H)_2(\mu_6\text{-}\eta^2\text{-}CO)(CO)_{19}(\eta^6\text{-}C_{16}H_{16})$ **1**, is isolated from the thermal reaction between $Ru_3(CO)_{12}$ and [2.2]paracyclophane in *n*-heptane; a single crystal X-ray structure analysis reveals that one of the carbon monoxide groups bonds to six of the Ru atoms *via* a μ_6-η^2 interaction resulting in possibly the longest metal–carbonyl C–O bond recorded thus far.

The chemistry of the carbon monoxide ligand is of fundamental importance and a plethora of information regarding the bonding capabilities of this ligand may be found in the literature.[1] Since the preparation of $Ni(CO)_4$, a large and diverse range of metal carbonyl compounds have been reported, and systematic studies of carbonyl clusters have revealed that carbon monoxide may bond to the cluster unit in a variety of different bridging coordination modes including the *dihapto* (M–C–O–M) arrangement.[2] As such, these studies have greatly aided the characterisation of chemisorbed CO on the single crystal metal surface.[3] On coordination in the *dihapto* fashion, the carbon–oxygen bond is weakened considerably and readily undergoes cleavage to form an isolated carbido atom, a process important in both cluster and surface chemistry.[4] We now report the isolation of the octaruthenium cluster $Ru_8(\mu\text{-}H)_2(\mu_6\text{-}\eta^2\text{-}CO)(CO)_{19}(\eta^6\text{-}C_{16}H_{16})$ **1** from the reaction of $Ru_3(CO)_{12}$ with [2.2]paracyclophane in *n*-heptane,† which contains a *dihapto* CO ligand interacting with six ruthenium atoms, resulting in a considerably reduced C–O bond order as evidenced by a bond length of 1.378(11) Å.

After separation and purification, the new cluster **1** was characterised initially by the usual spectroscopic methods.‡ However, the highly unusual *dihapto* bonding mode and central cluster unit were established only as a result of a detailed single crystal X-ray structural analysis.§

The molecular structure of **1** is depicted in Fig. 1, together with relevant bond parameters. The cluster framework may best be described as a square pyramidal Ru_5 unit onto which is fused a Ru_3 triangle. This highly unusual 'open' framework of eight ruthenium atoms clearly shows the basic framework of the Ru_5C square pyramid and may be viewed, for electron counting purposes, either as an edge-bridged *nido*-dodecahedron or as derived from a bicapped octahedron by the cleavage of the three appropriate Ru–Ru edges. In either way, the observed electron count of 116 may be understood.

The metal framework is significantly distorted, with Ru–Ru distances varying from 2.684(2) to 2.946(2) Å. The cyclophane ligand is terminally bound to the only basal vertex of the square pyramid not involved in edge-bridging to the Ru_3 component [Ru(1)]. The cyclophane ring is not coordinated symmetrically over Ru(1). Rather, it is off-centred in such a fashion that the ring is displaced slightly to one side, as reflected by the variations observed in the Ru–C(ring) bond distances of the non-bridgehead C-atoms [Ru(1)–C(2C) 2.261(10), Ru(1)–C(3C) 2.247(10), Ru(1)–C(5C) 2.157(10) and Ru(1)–C(6C) 2.167(10) Å]. The bridgehead atoms are not in the same plane as the other four and the arene adopts a boat-shaped geometry characteristic of paracyclophane in an η^6 bonding mode.[5] The *dihapto*-carbonyl ligand sits in a central cavity where it bridges six metal atoms, the carbon coordinating to the four square pyramidal basal rutheniums, and the oxygen to the two fused edge-bridging ruthenium atoms. The carbon atom is displaced below the plane of the four rutheniums by 0.966(9) Å and is displaced from the centre of the square base, being shifted slightly towards the cyclophane-bound Ru atom [Ru(1)–C 2.042(9); av. 2.22(1) Å].

The C–O ligand acts as a six-electron donor, and it appears that compound **1** provides the first example of a carbonyl coordinated to six metal atoms in a μ_6-η^2 mode. The C atom bonds to four Ru atoms [Ru(1)–C 2.042(9), Ru(2)–C 2.170(9), Ru(3)–C 2.280(9), Ru(4)–C 2.197(9) Å] and the O atom interacts with two [Ru(6)–O 2.149(7), Ru(8)–O 2.125(6) Å]. The C–O bond length of this multi-briding carbonyl is 1.378(11) Å, possibly the longest metal–carbonyl C–O distance observed thus far. The only other known example of a six electron donating carbonyl ligand is found in $[(C_5H_5)_3Nb_3(CO)_7]$ which contains a carbonyl ligand with a bond length of 1.30 Å.[2] The remaining nineteen carbonyls in **1** are terminally bonded and essentially linear, and are distributed between the seven ruthenium atoms not involved in bonding to the cyclophane moiety. Two carbonyls are attached to each of the three atoms Ru(3), Ru(6) and Ru(8), three carbonyls are

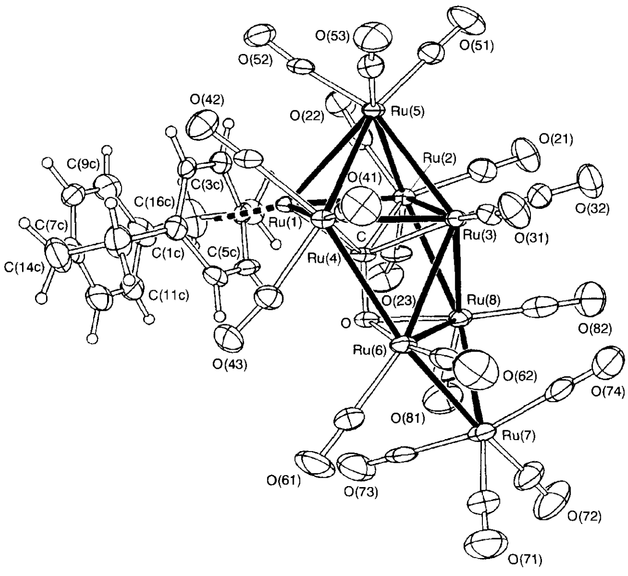

Fig. 1 Molecular structure of **1** in the solid state showing the atomic labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atom. Relevant bond distances (Å) and angles (°): Ru(1)–Ru(2) 2.691(2), Ru(1)–Ru(4) 2.684(2), Ru(1)–Ru(5) 2.9322(14), Ru(2)–Ru(3) 2.810(2), Ru(2)–Ru(5) 2.828(2), Ru(2)–Ru(8) 2.931(2), Ru(3)–Ru(4) 2.821(2), Ru(3)–Ru(5) 2.8618(14), Ru(3)–Ru(6) 2.850(2), Ru(3)–Ru(8) 2.882(2), Ru(4)–Ru(5) 2.834(2), Ru(4)–Ru(6) 2.983(2), Ru(6)–Ru(7) 2.768(2), Ru(6)–Ru(8) 3.019(2), Ru(7)–Ru(8) 2.773(2), Ru(1)–C 2.042(9), Ru(2)–C 2.170(9), Ru(3)–C 2.280(9), Ru(4)–C 2.197(9), Ru(6)–O 2.149(7), Ru(8)–O 2.125(6), C–O 1.378(11), Ru(1)–C–Ru(2) 79.4(3), Ru(1)–C–Ru(4) 78.5(3), Ru(2)–C–Ru(3) 78.3(3), Ru(3)–C–Ru(4) 78.1(3), Ru(1)–C–O 121.2(6), Ru(2)–C–O 117.5(6), Ru(3)–C–O 109.8(6), Ru(4)–C–O 117.1(6), C–O–Ru(6) 95.5(5), C–O–Ru(8) 95.2(5), Ru(6)–O–Ru(8) 89.9(2), mean Ru–C_{CO} 1.90, mean C–O_{CO} 1.14, Ru(1)–C(1C) 2.399(10), Ru(1)–C(2C) 2.261(9), Ru(1)–C(3C) 2.247(10), Ru(1)–C(4C) 2.379(10), Ru(1)–C(5C) 2.157(10), Ru(1)–C(6C) 2.167(10), C(1C)–C(2C) 1.410(14), C(1C)–C(6C) 1.413(14), C(1C)–C(13C) 1.51(2), C(2C)–C(3C) 1.419(14), C(3C)–C(4C) 1.411(14), C(4C)–C(5C) 1.407(14), C(4C)–C(15C) 1.489(14), C(5C)–C(6C) 1.39(2), C(7C)–C(8C) 1.39(2), C(7C)–C(12C) 1.39(2), C(7C)–C(14C) 1.52(2), C(8C)–C(9C) 1.39(2), C(9C)–C(10C) 1.40(2), C(10C)–C(11C) 1.39(2), C(10C)–C(16C) 1.48(2), C(11C)–C(12C) 1.35(2), C(13C)–C(14C) 1.56(2), C(15C)–C(16C) 1.59(2).

situated on Ru(2), Ru(4) and Ru(5), and four carbonyls are coordinated to the unique atom Ru(7). The two hydride ligands could not located experimentally.

A closely related complex is also isolated in low yields together with **1**, but we are still in the process of fully characterising this new and intriguing compound. One would also anticipate that the bridging CO in **1** would be prone to cleavage with the probable formation of a carbido atom, and whilst we have not observed this to take place, we are currently attempting to bring about such a transformation.

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Footnotes

† We have previously described the thermolysis of $Ru_3(CO)_{12}$ and [2.2]paracyclophane under a number of different reactions conditions resulting in the isolation of a series of clusters with nuclearities ranging from three to eight, all of which carry a coordinated paracyclophane ligand, *viz.* $Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})$,[6] $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_{16}H_{16}\text{-}\mu_2\text{-}O)$,[5] $Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})$,[7] $Ru_6C(CO)_{11}(\eta^6\text{-}C_{16}H_{16})(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})$[6] and $Ru_8(\mu\text{-}H)_4(CO)_{18}(\eta^6\text{-}C_{16}H_{16})$.[8] Cluster **1** and a closely related species **1a** can be isolated using the following reaction conditions: $Ru_3(CO)_{12}$ (250 mg) and [2.2]paracyclophane (100 mg) are heated to reflux in *n*-heptane (30 ml) for 3 h. The solvent is removed *in vacuo* and the products separated by TLC eluting with dichloromethane–hexane (3:7, *v*/*v*). A number of products elute in the sequence: $Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})$ (yellow, 32%), **1** (purple, 2%), **1a** (purple, 1%), $Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})$ (red, 18%) and $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_{16}H_{16}\text{-}\mu_2\text{-}O)$ (purple, 12%).

‡ *Spectroscopic data* for **1**: IR (CH_2Cl_2): ν_{CO}/cm^{-1} 2101m, 2062s, 2034vs, 1984w, 1957w; ^1H NMR ($CDCl_3$): δ 6.89 (s, 4H), 4.40 (s, 4H), 3.38 (br s, 8H), −11.67 (s, 1H), −15.37 (s, 1H); *MS*: M^+ = 1580 (calc. 1579).

§ *Crystal data* for **1**: $Ru_8O_{20}C_{57}H_{42}$ (including three solvated molecules of toluene, two of which exhibit 50% disorder), monoclinic, space group $P2_1/n$, a = 14.088(6), b = 25.134(12), c = 17.834(8) Å, β = 109.54(5)°, M = 1855.47, U = 5951(5) Å^3, Z = 4, D_c = 2.071 g cm^{-3}, T = 150(2) K, $F(000)$ = 3584, $R1$ = 0.0496 [5946 reflections with $F_o > 4\sigma(F_o)$], $wR2$ = 0.11315 for 7725 independent reflections corrected for absorption [μ(Mo-Kα) = 1.845 mm^{-1}] and 720 parameters. In the refinement process it was possible to distinguish between the oxygen and carbon atoms of the $\mu_6\text{-}\eta^2$-CO ligand, thus directly confirming the assignment. 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.

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