Journal of Organometallic Chemistry, 377 (1989) C17–C22
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20347PC

Preliminary communication

The first decaruthenium hydrido cluster: synthesis and crystal structure of $[N(PPh_3)_2]_2[Ru_{10}C(CO)_{24}] \cdot C_6H_{14}$ and $[N(PPh_3)_2][HRu_{10}C(CO)_{24}]$

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(Received April 10th, 1989)

Abstract

X-ray structural studies of new thermolysis products from the reaction of $Ru_3(CO)_{12}$ in heptane in the presence of 1,3,5-trimethylbenzene (mesitylene) confirm that they are the decaruthenium carbido-cluster dianion $[Ru_{10}C(CO)_{24}]^{2-}$ (I) and the hydrido decaruthenium carbido-cluster monoanion $[HRu_{10}C(CO)_{24}]^-$ (II). Both anions have the giant tetrahedral Ru_{10} metal framework, and the monohydride provides the first example of a hydrido ligand in a tetrahedral Ru_4 cavity.

A tetrahedral site for a hydrido ligand was first deduced from the X-ray structure determination of the tetracapped octahedral decaosmium monohydride anion $[HOs_{10}C(CO)_{24}]^-$, in which the distorted close packing of the carbonyl ligands precluded a surface location for the hydrido ligand and indicated that it was inside one of the Os_4 caps, since the octahedral cavity was occupied by the carbide ligand [1]. This type of site symmetry for a hydrido ligand is still very rare; although the

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* Crystal data for the dianion $[Ru_{10}C(CO)_{24}]^{2-}$ (I); $C_{97}H_{60}N_2O_{24}P_4Ru_{10} \cdot C_6H_{14}$, $M = 2858.63$, monoclinic, space group $C2/c$, a 17.349(5), b 27.443(6), c 21.570(6) Å, β 92.74(1)°, U 10257.82 Å^3, $F(000) = 5592$, μ(Mo-K_α) 14.09 cm^{-1}, $Z = 4$, D_c 1.85 g cm^{-3}. In the true space group $C2$, location of three phenyl rings and the hexane molecule could not be achieved satisfactorily because of pseudo symmetry (a 'c-glide') relating the two independent molecules, each of exact C_2 symmetry. Consequently the structure was refined in the space group $C2/c$ resulting in an apparent disorder of the counterion and solvent. Present $R = 0.1455$ and $R' = 0.1471$ for 2549 reflections with $I/\sigma(I) > 3$.

Crystal data for the anion $[HRu_{10}C(CO)_{24}]^-$ (II); $C_{61}H_{31}NP_2Ru_{10} \cdot CH_2Cl_2$, $M = 2341.39$, monoclinic, space group $P2_1/c$, a 11.777(2), b 17.805(4), c 35.365(5) Å, β 94.03(1)°, U 7397.33 Å^3, $F(000) = 4476$, μ(Mo-K_α) 19.45 cm^{-1}, $Z = 4$, D_c 2.10 g cm^{-3}. Final $R = 0.0725$ and $R' = 0.0650$ for 3555 reflections with $I/\sigma(I) > 3$.

0022-328X/89/$03.50

hexaruthenium monoanion $[HRu_6(CO)_{18}]^-$ provided the first example of an interstitial hydrido ligand in a carbonyl cluster; this was octahedrally sited [2]. There has been no example of a hydride ligand inside a tetrahedron of ruthenium atoms until now.

The thermolysis of $Ru_3(CO)_{12}$ in mesitylene was shown in early work to lead to $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)]$, the first example of a metal cluster containing an interstitial carbide [3]. We reported recently on the isolation and structural characterisation of an intermediate in its formation, namely $[Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)]$, together with the unusual edge bridged trigonal bipyramidal cluster $[HRu_6(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{13}(\mu_2\text{-}\eta^7\text{-}C_6H_3Me_2CH_2)]$ [4]. Further investigation of the solid residues from this reaction has led to the isolation of the decaruthenium carbidocluster anions $[Ru_{10}C(CO)_{24}]^{2-}$ (I) and $[HRu_{10}C(CO)_{24}]^-$ (II), which may be isolated in reasonable yield. An X-ray diffraction study * has shown that these complexes are isostructural with their respective osmium analogues $[Os_{10}C(CO)_{24}]^{2-}$ (III) and $[HOs_{10}C(CO)_{24}]^-$ (IV) [1,5], and both therefore have the giant tetrahedral metal framework, well known for a range of decaosmium clusters, which for many years has eluded detection in studies of ruthenium clusters by several workers [6]. Remarkably, since our isolation of these two clusters there has been an independent report of the synthesis of the decaruthenium dianion (I) by a different route, and of the X-ray characterisation of its unsolvated $[N(PPh_3)_2]^+$ salt [7].

The ^1H NMR spectrum of I shows no resonances other than those due to the $[N(PPh_3)_2]^+$ counterion, whilst that of II has an additional singlet at -13.5 ppm corresponding to a hydrido ligand *. The negative ion fast atom bombardment (FAB) mass spectrum of II shows a strong molecular ion at $m/z = 1695$, succesive loss of 24 carbonyl ligands, and a weak isotopic envelope at $m/z = 1032$ corresponding to the $Ru_{10}C$ metal core. Treatment of II with base results in complete conversion to I; this reaction can be reversed quantitatively by protonation of I.

The crystal of the $[N(PPh_3)_2]^+$ salt of the monohydrido cluster II are isomorphous with those of the analogous osmium monoanion IV; the crystals of these salts suffer from a relatively serious pseudo-symmetry problem which causes all reflections with $k + l = 2n + 1$ to be very weak. Consequently in our earlier studies with the osmium cluster two X-ray analyses were carried out using the better crystals of the salts of the $[Ph_4As]^+$ and $[Ph_3PMe]^+$ cations. So far alternative crystals of the ruthenium cluster II have not been obtained, but careful structural analysis of the $[N(PPh_3)_2]^+$ salt has established the overall features satisfactorily. Significantly the structure of the non-hydrido dianion I is indistinguishable from that of the hydrido cluster II (Fig. 1). In the structure of II, as in its osmium analogue IV, the entire surface of the cluster is covered with close-packed carbonyl ligands (Fig. 2), and there is no space to accommodate an external hydrido ligand; this is consistent only with the location of the H ligand in one of the tetrahedral caps of the cluster. The relatively high estimated standard deviations, resulting from pseudo-symmetry and the consequent small number of data, do not allow distinction of the four caps on the criterion of bond lengths.

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* Spectroscopic data for $[PPN]_2[Ru_{10}C(CO)_{24}]$ (I): IR (CH_2Cl_2): ν(CO) 2027(vs), 2000(m), 1983(s) cm^{-1}; ^1H NMR (CD_2Cl_2): δ 7.70 ppm (multiplet).

Spectroscopic data for $[PPN][HRu_{10}C(CO)_{24}]$ (II): IR (CH_2Cl_2): ν(CO) 2053(vs), 2009(s) cm^{-1}; ^1H NMR (CD_2Cl_2): δ 7.70 ppm (multiplet, 30H), -13.5 ppm (s, 1H).

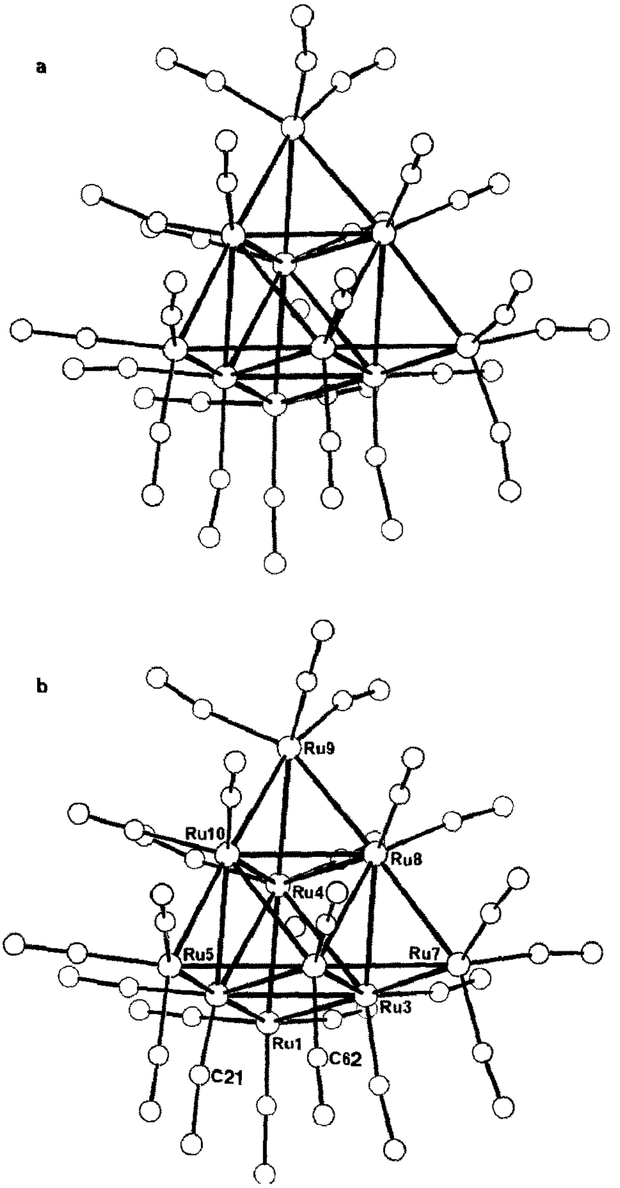

Fig. 1. (a) The molecular structure of the anion $[Ru_{10}C(CO)_{24}]^{2-}$ (I), showing the similarity of the carbonyl ligand distribution to that of the monohydride II. (b) The molecular structure of the anion $[HRu_{10}C(CO)_{24}]^-$ (II). Principle bond distances (Å) are: Ru–Ru (1)–(2) 2.778, (1)–(3) 2.795, (1)–(4) 2.780, (2)–C(3) 2.875, (2)–(4) 2.845, (2)–(5) 2.785, (2)–(6) 2.850, (2)–(10) 2.847, (3)–(4) 2.850, (3)–(6) 2.849, (30–(7) 2.783, (3)–(8) 2.873, (4)–(8) 2.874, (4)–(9) 2.794, (4)–(10) 2.859, (5)–(6) 2.774, (5)–(10) 2.799, (6)–(7) 2.793, (6)–(8) 2.860, (6)–(10) 2.855, (7)–(8) 2.782, (8)–(9) 2.789, (8)–(10) 2.852, (9)–(10) 2.840. Maximum e.s.d. 0.004 Å. Mean Ru–C (carbonyl) 1.83(6), mean C–O (carbonyl) 1.18(7).

As the solution infrared spectrum of II has two absorptions in the carbonyl stretching region and I has three, the structure of I might have been expected to have lower symmetry than that of II. Since a cluster $[M_{10}C(CO)_{24}]^{2-}$ of *Td* symmetry has four IR active $\nu(CO)$ modes, it would appear that there is accidental

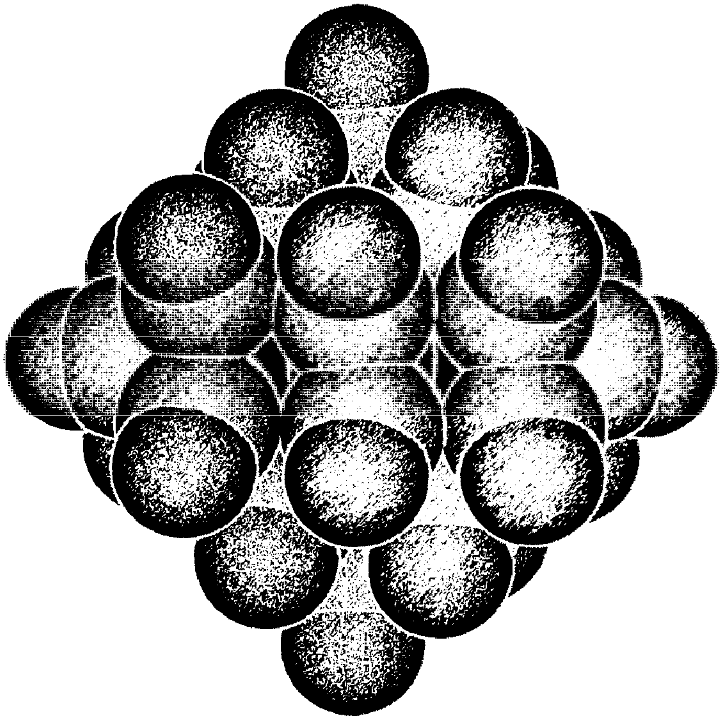

Fig. 2. Computed space filling model for the monohydride II, viewed onto the Ru(1)–Ru(2)–Ru(5) edge, showing the close packing of the carbonyl ligands. The metal atoms are calculated with covalent radii for clarity, and carbon and oxygen with Van der Waals' radii of 1.40 and 1.60 Å, respectively.

coincidence of IR absorptions and that this, rather than small perturbations in the cluster symmetry, governs the number of bands resolved in the spectra.

The clusters I and II enriched with ca. 30% ^{13}C were prepared from ^{13}CO enriched $Ru_3(CO)_{12}$, and their variable temperature (VT) ^{13}C NMR spectra were recorded. The spectra of both anions are temperature dependent, and stacked plots of the spectra obtained are shown in Fig. 3. The spectrum of I at 290 K shows a broad singlet at 204.4 ppm, which on cooling broadens further and separates into two singlets. On further cooling to 200 K two sharp resonances of equal intensity at 213.7 and 192.7 ppm are obtained; the carbido-resonance is observed at 362 ppm in this cluster. These spectra are entirely consistent with the solid state structure of I since there are only two carbonyl environments, viz. four apical "$Ru(CO)_3$" caps and six "$Ru(CO)_2$" fragments at the apices of the central octahedron. It is clear from the spectra that at 290 K there is complete carbonyl fluxionality, which is reduced at lower temperatures, until at 200 K the structure is static on the NMR timescale.

The VT spectra of the anion II are somewhat more complex owing to the assymmetry introduced into the structure by the hydrido ligand. The spectrum at 290 K shows four broad resonances at 189.9, 206.7, 209.5 and 211.3 ppm, and a shoulder on the high field side of the resonance at 189.9 ppm. As the temperature is decreased the resonances sharpen, but no new resonances are observed, except that the shoulder is resolved into a sharp singlet. The spectrum observed at 200 K thus shows five resonances at 188.1, 189.2, 206.4, 209.1, and 211.2 ppm in the intensity

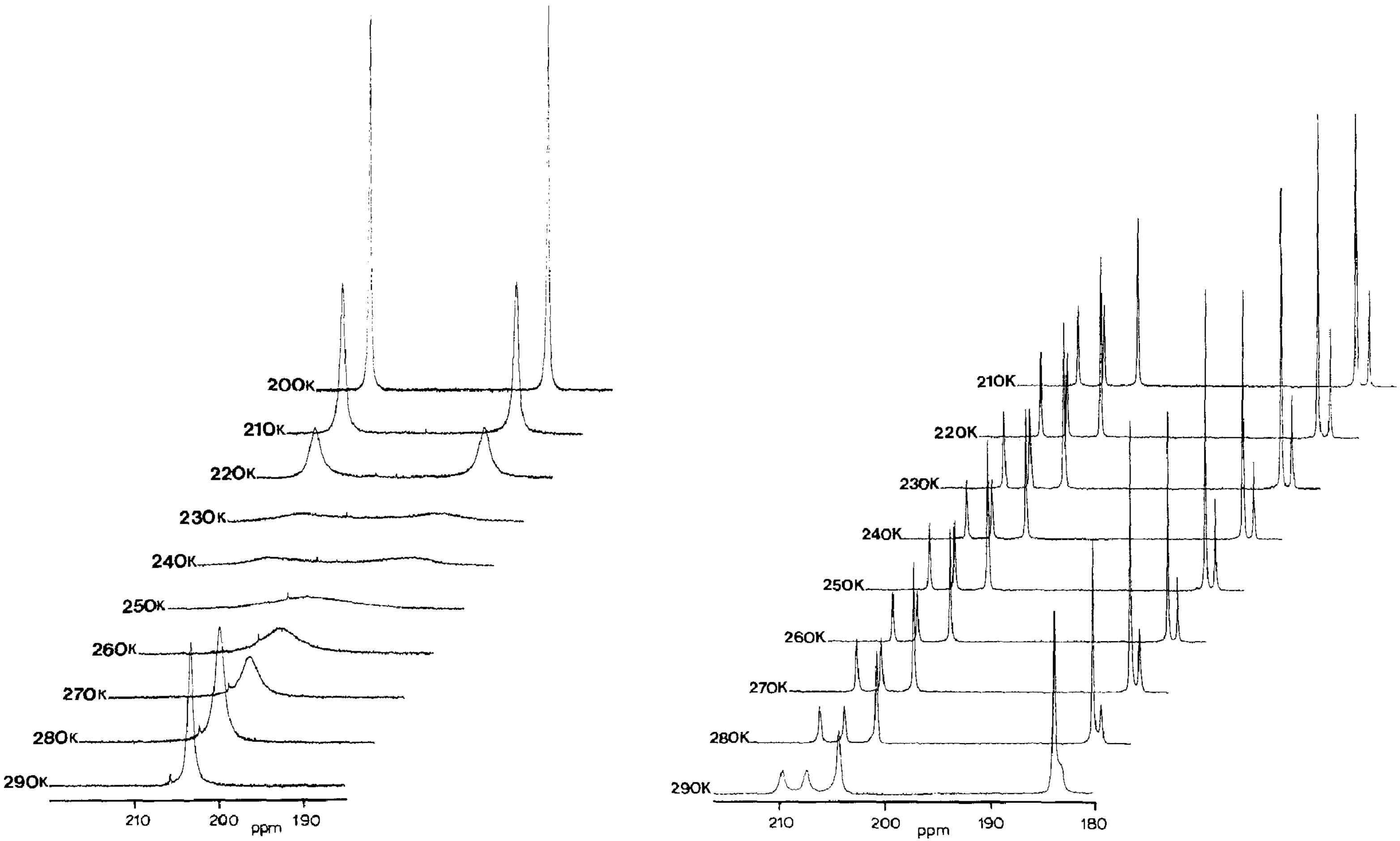

Fig. 3. Variable temperature ^{13}C NMR spectra of the anions (a) $[Ru_{10}C(CO)_{24}]^{2-}$ (I) and (b) $[HRu_{10}C(CO)_{24}]^{-}$ (II) in CD_2Cl_2 solution.

ratio 1/3/2/1/1, the carbido-resonance in this anion is observed at 374.5 ppm. This spectrum is consistent with the structural formulation in which the hydrido ligand is located in one of the interstitial tetrahedral sites provided by the "$Ru(CO)_3$" fragments capping the central octahedron, resulting in a structure of C_{3v} symmetry. The five carbonyl environments may be identified as follows: (i) a unique apical $Ru(CO)_3$ fragment of the cap containing the hydrido ligand, (ii) three equivalent apical $Ru(CO)_3$ fragments at the corners of the basal Ru_6 plane relative to the cap containing the hydride, (iii) six equivalent carbonyls situated equatorially around the base of the tetrahedron containing the hydrido ligand, (iv) three equatorial carbonyls on the $Ru(CO)_2$ fragments of the central triangle of the basal Ru_6 plane and (v) three axial carbonyls on the same $Ru(CO)_2$ fragments. It is clear that the broadening of the resonances as the temperature increases indicates some form of fluxional behaviour within the cluster, however whether this is due solely to motion of the carbonyls, or whether the hydride ligand is also fluctional is unclear from these data. We will be reporting further on this aspect of the fluxionality of the cluster elsewhere [8]. These interpretations of the ^{13}C NMR spectra assume that the carbonyls of the capping $Ru(CO)_3$ fragments are equivalent by virtue of rapid equilibration between the three environments relative to the rest of the cluster, which has proved to be valid for the spectroscopic investigations of other cluster carbonyl systems.

We thank S.E.R.C. (P.J.B. and H.R.P.) and British Petroleum plc. (P.J.B.) for financial support, and Johnson Matthey plc. for generous loans of ruthenium trichloride.

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