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Preliminary communication

SYNTHESIS AND X-RAY STRUCTURE ANALYSIS OF THE NEUTRAL NITROSYL HYDRIDO CLUSTER $HRu_6C(CO)_{15}(NO)$

BRIAN F.G. JOHNSON, JACK LEWIS*, WILLIAM J.H. NELSON, JOSE PUGA,
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain)
MARY McPARTLIN and ANGELO SIRONI
School of Chemistry, The Polytechnic of North London, London, N7 8DB (Great Britain)
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Summary

Protonation of the anion $[Ru_6C(CO)_{15}(NO)]^-$, formed from the reaction of $Ru_6C(CO)_{17}$ with $[N(PPh_3)_2][NO_2]$, gives the neutral nitrosyl hydrido cluster $HRu_6C(CO)_{15}(NO)$; X-ray analysis shows that the overall structure of this compound is very similar to that of the previously reported derivative $Ru_6C(CO)_{15}(NO)(AuPPh_3)$.

The synthesis of nitrosyl containing clusters is currently receiving a great deal of attention because of their greater reactivity compared with binary carbonyl clusters. Recently we reported the synthesis of the first hexaruthenium nitrosyl cluster species, $[Ru_6C(CO)_{15}(NO)]^-$, $Ru_6C(CO)_{14}(NO)_2$ and $Ru_6C(CO)_{15}(NO)(AuPPh_3)$ [1]. Attempts to isolate the hydrido analogue of the gold triphenylphosphine derivative, $HRu_6C(CO)_{15}(NO)$, failed due to the ready dissociation of the compound back to $[Ru_6C(CO)_{15}(NO)]^-$, even in non-coordinating solvents.

We now find that addition of one drop of concentrated H_2SO_4 to a solution of $[N(PPh_3)_2][Ru_6C(CO)_{15}(NO)]^-$ in CH_2Cl_2, followed by slow evaporation of the acid-containing solution, yields $HRu_6C(CO)_{15}(NO)$ (I) in good yield. The hydride I was characterised by IR (ν(CO), CH_2Cl_2, 2100w, 2069m, 2054s, 2031mw, and 1859w(br) cm^{-1}; ν(NO), 1774w(br) cm^{-1}) and ^1H NMR spectroscopy (hydride at τ 31.38, CD_2Cl_2, room temperature and microanalysis.

X-ray analysis of $HRu_6C(CO)_{15}NO$ (I) shows that it has the structure shown in Fig. 1 and confirms the presence of a terminal NO group. The environment of the NO ligand is very similar to that found in $Ru_6C(CO)_{14}(NO)_2$ and

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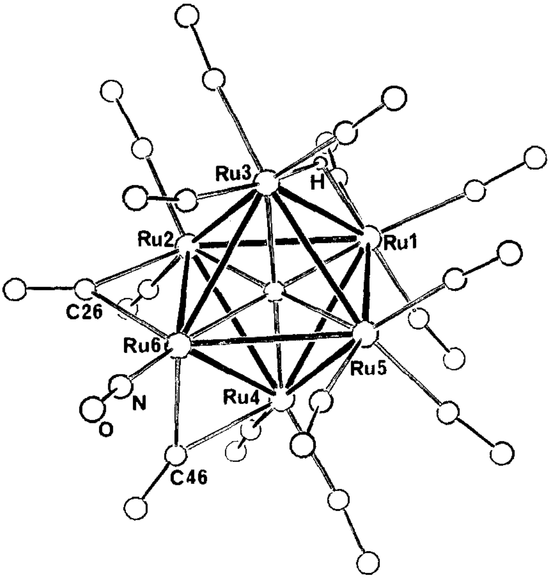

Fig. 1. The structure of the neutral nitrosyl hydrido cluster $HRu_6C(CO)_{15}(NO)$ (I). Important bond lengths (Å) are: Ru—Ru (1)—(2) 2.947, (1)—(3) 2.918, (1)—(4) 2.993, (1)—(5) 2.851, (2)—(3) 2.915, (2)—(4) 2.934, (2)—(6) 2.816, (3)—(5) 2.875, (3)—(6) 2.957, (4)—(5) 2.918, (4)—(6) 2.815, (5)—(6) 2.968, maximum e.s.d. 0.003 Å; (Ru(6)—N 1.77(2), N—O 1.17(2), mean Ru—C (carbido) 2.06.

$Ru_6C(CO)_{15}(NO)AuPPh_3$ (II) [1]; in all three compounds a Ru atom bonded to a nitrosyl ligand is also bonded to two μ-CO groups which bridge adjacent edges of one triangular face.

In several cases it has been found that $AuPR_3$ ligands can replace H ligands in polynuclear carbonyl compounds and adopt similar bonding modes [2,3]. Due to initial difficulties in obtaining crystals of the hydride (I) X-ray analysis of the $AuPPh_3$ analogue $Ru_6C(CO)_{15}(NO)AuPPh_3$ (II) was undertaken [1]. This revealed that the $AuPPh_3$ ligand adopts an unusual asymmetric μ_3-bonding mode (Fig. 2) with two short Ru—Au distance (mean of Ru(1)—Au and Ru(3)—Au 2.782 Å) and a very long bond (Ru(2)—Au 3.19 Å). At that time it was concluded that the parent monohydride $HRu_6C(CO)_{15}(NO)$ (I) would probably have a similar structure with the asymmetric μ_3-Au ligand replaced by an asymmetric μ_3-H atom [1].

In the present X-ray analysis of I the position of the H ligand could not readily be deduced from the usual indirect criteria of M—M bond lengthening and carbonyl ligand displacement [4]. However computer diagrams [5] of space-filling models of the molecule revealed only one "hole" in the close-packed surface ligands large enough to accommodate a hydrogen ligand. This "hole", above the Ru(1),Ru(2),Ru(3) face, was too asymmetric to be attributed to a μ_3-H atom and it was concluded that the H ligand was in a μ_2-site bridging the Ru(1)—Ru(3) bond but leaning over the Ru(1),Ru(2),Ru(3) face. After full refinement of the structure the highest peak in the final difference Fourier (ca. 1 $eÅ^{-3}$) corresponded to a reasonable position for this μ-H atom and is included in Fig. 2. Comparison of Fig. 1 and 2 shows that, allowing

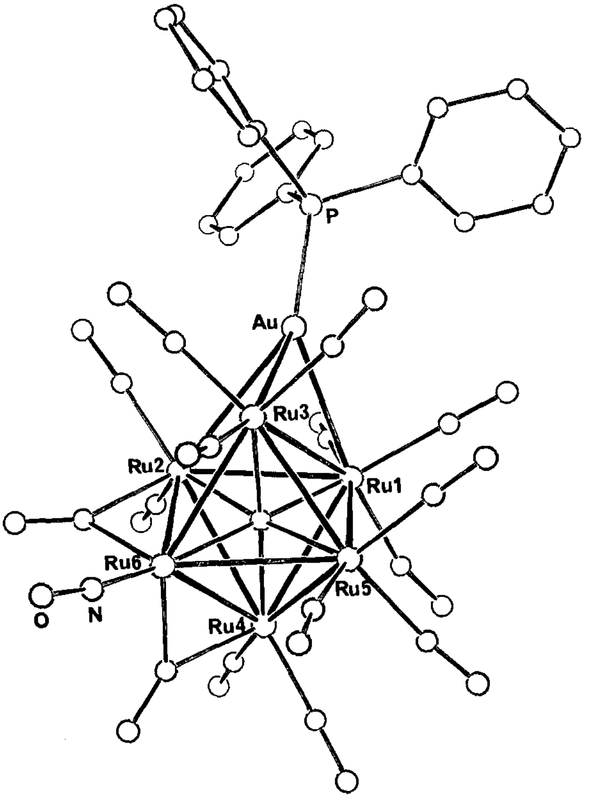

Fig. 2. The structure of the neutral cluster $Ru_6C(CO)_{15}(NO)AuPPh_3$ (from ref. 1) showing the similarity of the Au bonding site to that of the μ-H in $HRu_6C(CO)_{15}NO$ (I), illustrated in Fig. 1.

for the differences in Ru—H and Ru—Au bond lengths, the hydrogen and gold ligands have in fact adopted very similar bonding sites. In an interesting reversal of the normal procedure one can perhaps conclude that the Ru(2)—Au distance of 3.19 Å [1] maybe due to accidental proximity rather than bonding preference and that, by analogy with the hydride structure (I), the structure of II should be regarded as having a μ-Au ligand bridging Ru(1) and Ru(3).

Crystal data for I: $C_{16}HNO_{16}Ru_6$, M = 1 069.19, Monoclinic, space group $P2_1/n$, a 16.247(3), b 10.255(2), c 15.315(3) Å, β 98.31(2)°, U 2524.9 Å, $Z = 4$, D_c 2.81 g cm^{-3}, $I/\sigma(I) \geqslant 3.0$, present R factor 0.0553 for 1951 reflections corrected for absorption (μ(Mo-K_α) 32.52 cm^{-1}). Data were collected on a Philips PW1100 diffractometer in the θ range 3—25°*.

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*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this communication.

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