

Preliminary communication

THE SYNTHESIS OF THE FIRST HEXARUTHENIUM NITROSYL CLUSTER SPECIES; X-RAY ANALYSIS OF $\text{Ru}_6\text{C}(\text{CO})_{14}(\text{NO})_2$ AND $\text{Ru}_6\text{C}(\text{CO})_{15}(\text{NO})(\text{AuPPh}_3)$

BRIAN F.G. JOHNSON, JACK LEWIS, WILLIAM J.H. NELSON, JOSE PUGA,
 PAUL R. RAITHBY,

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain)

DARIO BRAGA, MARY McPARTLIN,

School of Chemistry, The Polytechnic of North London, London N7 8DB (Great Britain)

and WILLIAM CLEGG

Anorganisch-Chemisches Institut der Universität, Tammannstrasse 4, D-3400 Göttingen (F.R.G.)

(Received November 2nd, 1982)

Summary

Reaction of $\text{Ru}_6\text{C}(\text{CO})_{17}$ with $[(\text{Ph}_3\text{P})_2\text{N}][\text{NO}_2]$ has given the anion $[\text{Ru}_6\text{C}(\text{CO})_{15}(\text{NO})]^-$ (I) which reacts with $[\text{NO}]^+$ to give $\text{Ru}_6\text{C}(\text{CO})_{14}(\text{NO})_2$ (II) and with Ph_3PAuCl to give $\text{Ru}_6\text{C}(\text{CO})_{15}(\text{NO})\text{AuPPh}_3$ (III); X-ray analysis of II and III confirms the presence of terminal NO-ligands as indicated by the IR spectra, and shows that the AuPPh_3 ligand in III adopts a μ_3 -bonding mode.

A problem often encountered with metal carbonyl cluster compounds containing more than three metal atoms has been their relative lack of reactivity. In an attempt to overcome this problem we are synthesising and studying nitrosyl clusters of osmium and ruthenium [1].

The reaction of the carbido cluster $\text{Ru}_6\text{C}(\text{CO})_{17}$ with $[(\text{Ph}_3\text{P})_2\text{N}][\text{NO}_2]$ in THF has led to the formation of the first hexaruthenium nitrosyl cluster species $[\text{Ru}_6\text{C}(\text{CO})_{15}\text{NO}]^-$ (I), which was isolated in 85% yield as the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ salt. Reaction of I with $[\text{NO}]^+$ gave the dinitrosyl derivative $\text{Ru}_6\text{C}(\text{CO})_{14}(\text{NO})_2$ (II). The IR spectra* of I and II were consistent with the presence of both bridging and terminal carbonyl ligands and reveal that the NO ligands are terminal.

*IR spectra in CH_2Cl_2 : I: $\nu(\text{CO})$ 2067m, 2022s, 2007sh, and 1824mbr, $\nu(\text{NO})$ 1726mbr; II: $\nu(\text{CO})$ 2092w, 2068s, 2052vs, 2038sh, and 1874mbr, $\nu(\text{NO})$ 1774mbr; III: $\nu(\text{CO})$ 2080m, 2043s, 2023sh, and 1850mbr, $\nu(\text{NO})$ 1760mbr; IV: $\nu(\text{CO})$ 2100m, 2068s, 2058vs, 2031sh, and 1858mbr; $\nu(\text{NO})$ 1774mbr cm^{-1} .

X-ray analysis of II* shows that it has the structure illustrated in Fig. 1, with the nitrosyl ligands attached to opposite vertices (Ru(5) and Ru(6)) of a carbido-centred octahedral Ru_6 core. This species is of considerable importance, because in principle two separate metal centres are activated by coordination to an NO ligand. Therefore II may be expected to show greater reactivity than the mononitrosyl hexaruthenium systems. Further, as has been pointed out previously [2], the presence of two nitrosyl ligands in a cluster molecule is of interest in relation to the surface-catalysed oxidation of CO with 2NO which gives CO and N_2O :



Protonation of I by concentrated H_2SO_4 in dichloromethane gives the neutral monohydride derivative $HRu_6C(CO)_{15}(NO)$ IV. The IR spectrum of IV is also consistent with the presence of a terminal nitrosyl and both terminal and bridging carbonyl ligand. The 1H NMR spectrum of IV, in CD_2Cl_2 at $30^\circ C$,

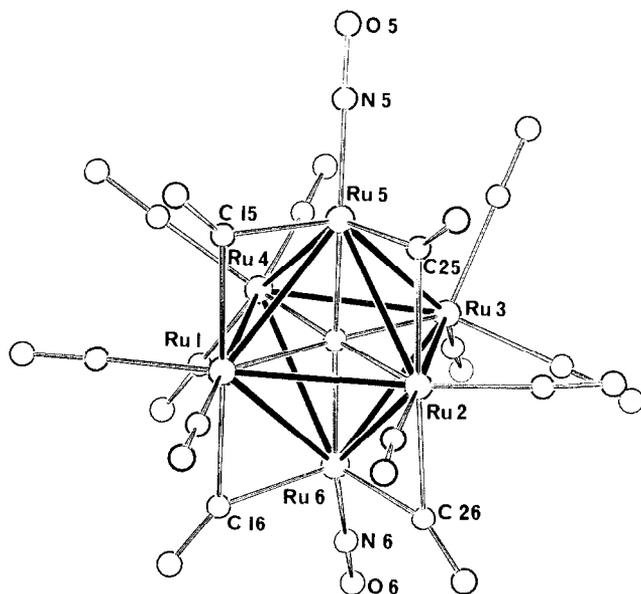


Fig. 1. The structure of the neutral nitrosyl cluster $Ru_6C(CO)_{14}(NO)_2$ (II). Important bond lengths (\AA) are: Ru(1)—Ru(2) 2.940, Ru(1)—Ru(4) 2.873, Ru(1)—Ru(5) 2.881, Ru(1)—Ru(6) 2.840, Ru(2)—Ru(3) 2.912, Ru(2)—Ru(5) 2.830, Ru(2)—Ru(6) 2.855, Ru(3)—Ru(4) 2.835, Ru(3)—Ru(5) 2.971, Ru(3)—Ru(6) 2.839, Ru(4)—Ru(5) 2.878, Ru(4)—Ru(6) 2.957; maximum e.s.d. 0.003 \AA ; mean Ru—N 1.78(1), mean N—O 1.14(2), mean Ru—C (carbido) 2.04(1) \AA .

*Crystal data: II: $C_{15}N_2O_{16}Ru_6$, $M = 1070.59$, Monoclinic, space group $P2_1/n$, a 14.547(3), b 11.851(2), c 14.674(3) \AA , β 91.01(2) $^\circ$, U 2529.4 \AA^3 , $Z = 4$, D_c 2.81 g cm^{-3} , $I/\sigma(I) \geq 2.0$, present R factor 0.0530 for 4893 reflections corrected for absorption ($\mu(\text{Mo-K}\alpha)$ 34.76 cm^{-1}). Data were collected on a Stoe four-circle diffractometer in the θ -range 2.5–25 $^\circ$.

III: $C_{34}H_{15}AuNO_{16}PRu_6$, $M = 1555.87$, Triclinic, space group $P\bar{1}$, a 17.211(2), b 11.851(2), c 10.949(2) \AA , α 84.43(3), β 107.2(3), γ 104.79(3) $^\circ$, $Z = 2$, U 2061.97 \AA^3 , D_c 2.5 g cm^{-3} , $I/\sigma(I) \geq 3.0$, present R factor 0.0708 for 5284 reflections ($\mu(\text{Mo-K}\alpha)$ 54.54 cm^{-1}). Data were collected on a Philips PW1100 diffractometer in the θ -range 3–25 $^\circ$. In both II and III the NO groups were readily distinguished from the CO groups by inspection of thermal parameters, and satisfactory refinement.

shows a singlet at -21.38 ppm which has been assigned to the hydride ligand.

In several cases it has recently been found that AuPPR_3 ligands can replace H ligands in polynuclear carbonyl clusters and adopt similar bonding modes [3,4]; both ligands formally donate $1e$ to the cluster. As initial attempts to grow crystals of IV suitable for X-ray analysis were unsuccessful, we prepared the neutral mixed metal cluster $\text{Ru}_6\text{C}(\text{CO})_{15}(\text{NO})(\text{AuPPh}_3)$ III by treating I with triphenylphosphinegold(I) chloride in the presence of thallium hexafluorophosphate. The IR spectrum reveals that the terminal mode of nitrosyl bonding has been maintained, and that both bridging and terminal CO ligands are still present.

X-ray analysis of III shows that the AuPPh_3 ligand adopts an unusual asymmetric μ_3 -bonding mode with two short Ru—Au distances (mean 2.782 Å) and one long (3.19 Å) (Fig. 2). The overall metal polyhedron is therefore capped octahedral, a geometry which has no analogue in homonuclear Ru clusters (the largest has a Ru_6 core) but is similar to that observed for $\text{Os}_7(\text{CO})_{21}$ [5].

The μ_3 -bridging mode is well established for H ligands on cluster surfaces [6]; the presence of a μ_3 - AuPPh_3 ligand bridging the three Co atoms in $\text{FeCo}_3(\text{CO})_{12}\text{AuPPh}_3$ has been cited [3] as supporting spectroscopic evidence

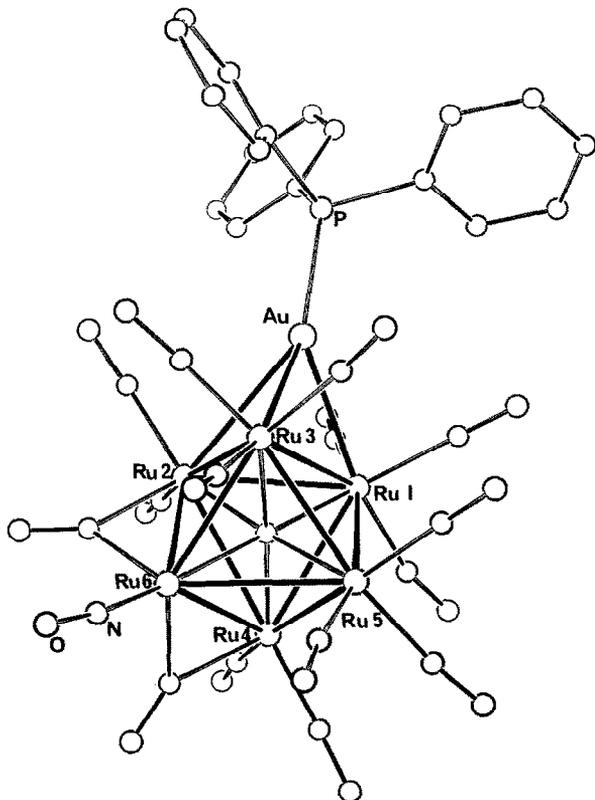


Fig. 2. The structure of the mixed-metal nitrosyl cluster $\text{Ru}_6\text{C}(\text{CO})_{15}(\text{NO})\text{AuPPh}_3$ (III). Important bond lengths (Å) are: Ru(1)—Ru(2) 2.930, Ru(1)—Ru(3) 3.053, Ru(I)—Ru(4) 2.930, Ru(1)—Ru(5) 2.839, Ru(2)—Ru(3) 2.926, Ru(2)—Ru(4) 3.017, Ru(2)—Ru(6) 2.841, Ru(3)—Ru(5) 2.843, Ru(3)—Ru(6) 2.894, Ru(4)—Ru(6) 2.803, Ru(5)—Ru(6) 3.099, Ru(4)—Ru(5) 2.929; maximum e.s.d. 0.002 Å; Ru(1)—Au 2.763(2), Ru(2)—Au 3.159(2), Ru(3)—Au 2.801(2), Au—P 2.296(5), Ru—N 1.720(15), N—O 1.20(2), mean Ru—C (carbido) 2.07(2) Å.

that in the monohydride $\text{HFeCo}_3(\text{CO})_{12}$ the H ligand is similarly situated. By the same argument it seems probable that the parent monohydride $\text{HRu}_6\text{C}(\text{CO})_{15}\text{NO}$ has structure similar to that of III, with the μ_3 -Au ligand replaced by a μ_3 -H atom. Dark red crystals of IV have now been obtained by slow evaporation of a dichloromethane solution in the presence of sulphuric acid and an X-ray analysis will be undertaken to see if this prediction is correct.

The mean Ru—Ru distance for the Au-bridged face is 2.970 Å similar to the mean value of 2.954 Å for the two H-bridged faces in $\text{H}_2\text{Ru}_6(\text{CO})_{18}$ [7]. The asymmetric nature of the μ_3 -Au bridge is reflected in a longer bond between the two Ru atoms which are closest to the Au atom (Ru(3)—Ru(4) 3.053 Å). This is one of three remarkably long Ru—Ru bonds found in this structure; they are in the range 3.017—3.099 Å, significantly longer than the range of the other Ru—Ru distances, 2.803—2.930 Å. These three long bonds do not share a common vertex and are related by an approximate c_3 axis (through the mid-point of the Ru(1)—Ru(2)—Ru(3) face and the carbido C atom) giving an alternation of long and short bond lengths similar to that observed in other octahedral clusters in which a significant distortion of the M_6 core from O_h to D_3 symmetry has been observed [8].

There is some similarity between the environment of the terminal nitrosyl ligand in III and those in II. In both structures the Ru atoms bonded to the nitrosyl ligands are each also bonded to two μ -CO ligands which bridge adjacent edges of one triangular face. The two bridging CO ligands in III are symmetrically bonded with Ru—C distances in the range 2.03–2.06(2) Å, whereas the four μ -CO groups in II are asymmetrically bonded being in each case nearer to the Ru atom attached to the nitrosyl ligand. The mean values for the long and short bridging bonds in II are 2.23 and 2.04 Å, respectively, similar to the values found [9] for the bridging bonds in the dianion $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ V, although the overall arrangement of the four μ -CO ligands is different in II and V.

We thank the S.E.R.C. (D.B.) and I.C.I. (W.J.H.N.) for financial support, and Consejo Nacional de Investigaciones Cientificas y Tecnologicas for a grant (J.P.).

References

- 1 B.F.G. Johnson, J. Lewis, P.R. Raithby, C. Zuccaro, *J. Chem. Soc., Dalton Trans.*, (1980) 99; S. Bhaduri, B.F.G. Johnson, J. Lewis, D.J. Watson, and C. Zuccaro, *J. Chem. Soc., Chem. Commun.*, (1979) 557; D. Braga, B.F.G. Johnson, J. Lewis, J.M. Mace, M. McPartlin, J. Puga, W.J.H. Nelson, P.R. Raithby, K.H. Whitmire, *J. Chem. Soc., Chem. Commun.*, (1982) 1081.
- 2 B.F.G. Johnson and S. Bhaduri, *J. Chem. Soc., Chem. Commun.*, (1973) 650; S. Bhaduri, B.F.G. Johnson, C.J. Savory, J.A. Segal, and R.H. Walter, *ibid.*, (1974) 809; D.E. Fjare, and W.L. Gladfelter, *Inorg. Chem.*, 20 (1981) 3533.
- 3 J.W. Lauher, and K. Wald, *J. Amer. Chem. Soc.*, 103 (1981) 7648.
- 4 B.F.G. Johnson, D.A. Kaner, J. Lewis, P.R. Raithby, and M.J. Taylor, *J. Chem. Soc., Chem. Commun.*, (1982) 314; L.W. Bateman, M. Green, J.A.K. Howard, K.A. Meady, R.M. Mills, I.D. Salter, F.G.A. Stone, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, (1982) 773.
- 5 C.R. Eady, B.F.G. Johnson, J. Lewis, R. Mason, P. Hitchcock, and K.M. Thomas, *J. Chem. Soc., Chem. Commun.*, (1977) 385.
- 6 R.G. Teller and R. Bau, *Struct. Bonding (Berlin)*, 44 (1981) 1.
- 7 M.R. Churchill and J. Wormald, *J. Amer. Chem. Soc.*, 93 (1971) 5670.
- 8 M. McPartlin, C.R. Eady, B.F.G. Johnson, J. Lewis, *J. Chem. Soc., Chem. Commun.*, (1976) 883.
- 9 B.F.G. Johnson, J. Lewis, M. McPartlin, W.J.H. Nelson, *J. Organometal. Chem.*, 191 (1980) C3.