

# Nitrosyl Ligand Related Metal Polyhedron Isomerism; Syntheses of $[N(PPh_3)_2][Ru_5C(CO)_{13}(NO)]$ and $[Ru_5C(CO)_{13}(NO)(AuPR_3)]$ ( $R = Et, Ph$ ) and the X-Ray Structure Analysis of $[Ru_5C(CO)_{13}(NO)(\mu_3-AuPEt_3)]$ and $[Ru_5C(CO)_{13}(NO)(\mu_2-AuPEt_3)]$ in One Crystal

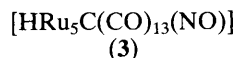
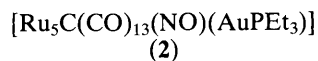
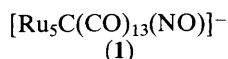
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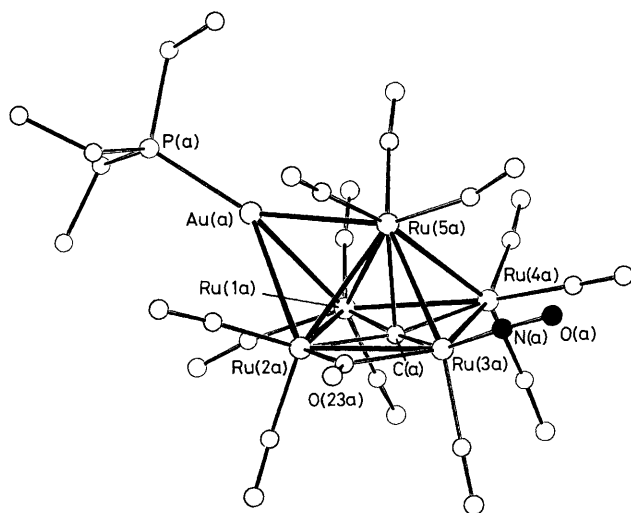
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The new nitrosyl monoanion  $[Ru_5C(CO)_{13}(NO)]^-$  (**1**) has been prepared by reaction of  $[Ru_5C(CO)_{15}]$  with  $[NO_2]^-$ , and it reacts with  $[AuPR_3]^+$  ( $R = Et, Ph$ ) to give  $[Ru_5C(CO)_{13}(NO)(AuPR_3)]$ ; X-ray structure analysis of one of these compounds  $[Ru_5C(CO)_{13}(NO)(AuPEt_3)]$  (**2**) shows that it exists as isomers (**2A**) and (**2B**) which differ in the bonding mode of the Au ligand and in its site relative to the nitrosyl ligand.

The first example of skeletal isomerism in a cluster compound in the solid state was reported recently for the molecule  $[Au_6\{P(C_6H_4OMe-p)_3\}_8(NO_3)_3]$ .<sup>1</sup> Although there are examples of heteronuclear cluster isomers in which the relative positions of two types of metal atom interchange within the metal core,<sup>2</sup> the reaction of the new nitrosyl cluster monoanion  $[Ru_5C(CO)_{13}(NO)]^-$  (**1**) with  $[AuPEt_3]^+$  has produced the first example of heteronuclear polyhedral isomerism, yielding two forms of  $[Ru_5C(CO)_{13}(NO)(AuPEt_3)]$  (**2**)<sup>†</sup> which are isomeric both in ligand distribution and in the geometric shape adopted by the metal atoms.



The nitrosyl cluster monoanion (**1**) was obtained in 88% yield as its  $[N(PPh_3)_2]^+$  salt from reaction of  $[Ru_5C(CO)_{15}]$  with  $[N(PPh_3)_2][NO_2]$  in tetrahydrofuran at room tempera-



**Figure 1.** The structure of isomer (**2A**)  $[Ru_5C(CO)_{13}(NO)(\mu_3-AuPEt_3)]$ . The principal bond lengths (Å) are: Au(a)-Ru(1a) 2.812, Au(a)-Ru(5a) 2.783, Au(a)-Ru(2a) 3.033, Ru(1a)-Ru(2a) 2.883, Ru(1a)-Ru(4a) 2.830, Ru(1a)-Ru(5a) 2.907, Ru(2a)-Ru(3a) 2.776, Ru(2a)-Ru(5a) 2.858, Ru(3a)-Ru(4a) 2.838, Ru(3a)-Ru(5a) 2.788, Ru(4a)-Ru(5a) 2.769, maximum e.s.d.; 0.002; Au(a)-P(a) 2.266(7); Ru(3a)-NO 1.76(2); Ru(2a)-C(23a) 1.99(2), Ru(3a)-C(23a) 2.13(2); mean Ru-C(carbido) 2.04.

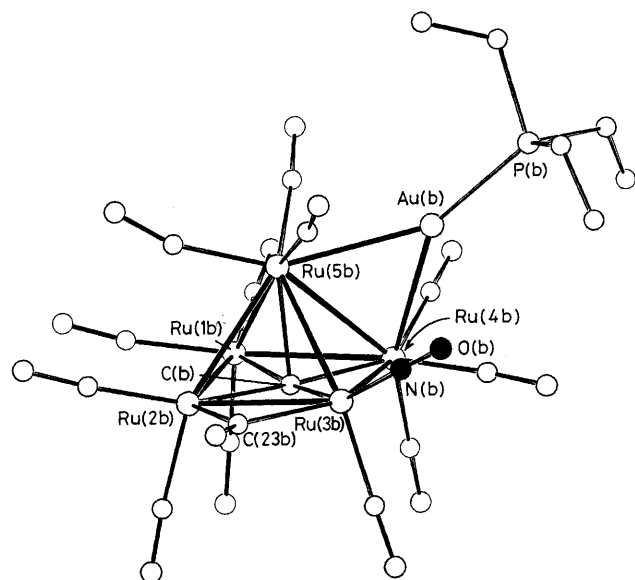
ture.<sup>†</sup> Acidification of (**1**) with concentrated sulphuric acid in  $CH_2Cl_2$  yields a compound (**3**) for which the i.r. spectrum<sup>†</sup> is consistent with formulation as the neutral hydride  $[HRu_5C(CO)_{13}(NO)]$ , as it shows evidence of the terminal NO group and of both terminal and bridging CO ligands. The identity of (**3**) has not been confirmed because its separation from the acid solution has not so far been possible. Reaction of the cation  $[AuPR_3]^+$  ( $R = Et, Ph$ ), formed from  $R_3PAuCl$  and  $Ag[ClO_4]$ , with the nitrosyl monoanion (**1**) in  $CH_2Cl_2$  solution is almost instantaneous, yielding ca. 70% of the neutral compounds  $[Ru_5C(CO)_{13}(NO)(AuPR_3)]$ .<sup>†</sup>

An X-ray analysis<sup>‡</sup> of compound (**2**) revealed two independent molecules, both having a square pyramidal  $Ru_5$  arrangement but distinctly different in the bonding mode of the  $AuPEt_3$  group. In the first isomer (**2A**) (Figure 1) the  $AuPEt_3$  ligand has a  $\mu_3$ -bonding mode, capping Ru(1a), Ru(2a), and Ru(5a) with two short distances [mean 2.798(2) Å] and one longer distance [Ru(2a)-Au 3.033(2) Å]. This type of asymmetric bonding for a  $AuPR_3$  group has been observed before and occurs, for example, in the neutral nitrosyl cluster  $[Ru_6C(CO)_{15}(NO)(AuPPh_3)]$ .<sup>3</sup> In the second isomer (**2B**) (Figure 2), the  $AuPEt_3$  group adopts a  $\mu_2$ -bonding mode, spanning Ru(4b) and Ru(5b) with mean Ru-Au distances of 2.770(2) Å. The distance between Au and Ru(3b) of 3.598(2) Å, is 0.565 Å longer than the longest Ru-Au distance in molecule (**2A**), and is non-bonding. The  $\mu_2$ -mode of Au bonding has been observed previously in several clusters of the iron triad and occurs, for example, in the monoanion  $[Os_{10}C(CO)_{24}(AuPPh_3)]^-$ .<sup>4</sup>

<sup>†</sup> Spectroscopic data: (**1**),  $\nu(CO)$   $CH_2Cl_2$ , 2061m, 2017vs, 2004s, 1963m, 1820w,  $\nu(NO)$  1724w; (**2**),  $\nu(CO)$  hexane, 2076m, 2038vs, 2025s, 2017s, 2007m, 1995w, 1988w(sh), 1976m, 1864w,  $\nu(NO)$  1763w; (**3**),  $\nu(CO)$   $CH_2Cl_2$ , 2097m, 2075vs, 2064vs, 2034s, 2002m, 1859w,  $\nu(NO)$  1770w;  $[Ru_5C(CO)_{13}(NO)(AuPPh_3)]$ ,  $\nu(CO)$  hexane, 2077m, 2034vs, 2026s, 2018s, 2008m(sh), 1997w, 1990w(sh), 1978m, 1863w,  $\nu(NO)$  1763w  $cm^{-1}$ ; mass spectrum (**2**)  $[M]^+$ ,  $m/z$ ,  $^{104}Ru$  1241.

<sup>‡</sup> Crystal Data for  $[Ru_5C(CO)_{13}(NO)(\mu_3-AuPEt_3)]$ :  $[Ru_5C(CO)_{13}(NO)(\mu_2-AuPEt_3)]$ ,  $[C_{20}H_{15}AuNO_{13}Ru_5]$ :  $[C_{20}H_{15}AuNO_{13}Ru_5]$ ,  $M = 1433.8$ , triclinic, space group  $P\bar{1}$ ,  $a = 20.364(3)$ ,  $b = 16.331(2)$ ,  $c = 9.992(2)$  Å,  $\alpha = 104.11(2)$ ,  $\beta = 89.89(2)$ ,  $\gamma = 105.39(2)^\circ$ ,  $Z = 2$ ,  $U = 3100.16$  Å<sup>3</sup>,  $D_c = 3.07$  g  $cm^{-3}$ ,  $I/\sigma(I) > 3.0$ ,  $R = 0.0882$  for 7763 reflections corrected for absorption [ $\mu(Mo-K\alpha) = 126.37$   $cm^{-1}$ ]. Data were collected with a Phillips PW 1100 diffractometer in the  $\theta$ -range 3–25°. The NO ligands were distinguished from the CO ligands on the basis of thermal parameters and of bond lengths. Mean Ru-N 1.79(2) Ru-CO(terminal) range 1.81–2.16(2) Å.

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



**Figure 2.** The structure of isomer (**2B**) [ $\text{Ru}_5\text{C}(\text{CO})_{13}(\text{NO})(\mu_2\text{-AuPPEt}_3)$ ]. The principal bond lengths ( $\text{\AA}$ ) are: Au(b)–Ru(4b) 2.792, Au(b)–Ru(5b) 2.748, Au(b)  $\cdots$  Ru(3b) 3.598, Ru(1b)–Ru(2b) 2.847, Ru(1b)–Ru(4b) 2.851, Ru(1b)–Ru(5b) 2.789, Ru(2b)–Ru(3b) 2.760, Ru(2b)–Ru(5b) 2.839, Ru(3b)–Ru(4b) 2.866, Ru(3b)–Ru(5b) 2.829, Ru(4b)–Ru(5b) 2.905, maximum e.s.d. 0.002; Au(b)–P(b) 2.263(8); Ru(3b)–NO 1.81(2); Ru(2b)–C(23b) 2.05(2), Ru(3b)–C(23b) 2.06(2); mean Ru–C(carbido) 2.03.

In several previously determined structures of ruthenium clusters, NO ligands have been observed in sites next to bridging CO ligands. By analogy with (**2A**) and (**2B**), it may be

assumed that in the precursor monoanion (**1**), there is one  $\mu\text{-CO}$  ligand, bridging the bond corresponding to Ru(2)–Ru(3) in (**2A**) and (**2B**), with the NO ligand bonded to Ru(3).

An important feature of the isomeric structures is the indication that the bonding mode of the gold atom is determined by the type of ligands present on the face of the pentanuclear precursor (**1**) attacked by the  $[\text{AuPPEt}_3]^+$  cation. It appears that formation of isomer (**2A**) with the  $\mu_3\text{-Au}$  atom bonded to Ru(1), Ru(2), and Ru(5) arises from attack on a face where only carbonyl ligands are present, whereas attack at the opposite side of the monoanion (**1**), where there is a  $\text{NO}^+$  ligand attached to Ru(3), leads to a  $\mu_2\text{-mode}$  of bonding for the  $[\text{AuEt}_3]^+$  ligand, attached only to Ru(4) and Ru(5), as in (**2B**).

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