^{31}P N.M.R. Studies on Trialkylphosphinegold(I) Derivatives of Ruthenium Carbide Clusters: Synthesis and *X*-Ray Crystal Structures of $[Ru_6C(CO)_{16}(AuPMePh_2)_2]$ and $[Ru_5WC(CO)_{17}(AuPEt_3)_2]$

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Reaction of the anions $[Ru_6C(CO)_{16}]^{2-}$ and $[Ru_5WC(CO)_{17}]^{2-}$ with $ClAuPR_3$ (R = alkyl, aryl) yields $[Ru_6C(CO)_{16}(AuPR_3)_2]$ and $[Ru_5WC(CO)_{17}(AuPR_3)_2]$, respectively; *X*-ray crystallography has shown that the two gold atoms adopt a different geometry in each case and subsequent low-temperature $^{31}P\{^1H\}$ n.m.r. studies have shown that these compounds exist as isomeric species in solution.

The similarity between the structures of some hydrido–metal complexes and the corresponding $AuPR_3$ derivatives has resulted in much interest in the preparation and characterisation of complexes containing the gold moiety. Although H and $AuPR_3$ may be described as isolobal,[1] the wider range of bonding modes available to $AuPR_3$ means that the analogy must be applied with care. Further interest in such complexes is generated by the possibility that introduction of 14- or 16-electron metal centres and/or heteropolar metal–metal bonds might *influence* the reactivity of such species.

X-Ray crystallography has been used extensively to characterise clusters of this type, and in a few cases ^{31}P n.m.r. spectra have been recorded. In all reported cases it has been found that the ^{31}P n.m.r. spectra were in agreement with the solid-state structures, although in one case the operation of a low-energy process equilibrating two phosphorus environments was observed.[2] We report here n.m.r. spectroscopic evidence which demonstrates for the first time the existence of a number of rapidly interchanging isomers in solution.

The anions $[Ru_5MC(CO)_{17}]^{2-}$ (M = Cr, Mo, W) have been prepared by reaction of $[PPN]_2[Ru_5C(CO)_{14}]$ [PPN = $(Ph_3P)_2N$] with the mono-nuclear species $L_3M(CO)_3$ (M = Cr, L = pyridine; M = Mo, W, L = acetonitrile) in refluxing tetrahydrofuran (THF). Reaction of $[PPN]_2[Ru_6C(CO)_{16}]$ and $[PPN]_2[Ru_5WC(CO)_{17}]$ with $[AuPR_3]^+$ gave the respective title compounds; the products were isolated in 60—90% yield by t.l.c.

The complexes $[Ru_6C(CO)_{16}(AuPEt_3)_2]$ (**1**) and $[Ru_5MC(CO)_{17}(AuPEt_3)_2]$ [(**2**), M = W; (**3**), M = Mo; (**4**), M = Cr] were prepared and identified by mass spectrometry and micro-analysis. The ν_{CO} i.r. spectrum of (**1**) in CH_2Cl_2 shows bands at 2066 (w), 2047 (s), 2014 (vs), 1961 (w), and 1820 cm^{-1} (m, br.) and that of (**2**) in CH_2Cl_2, bands at 2070 (m), 2043 (vs), 2015 (vs), 2012 (s, sh), 1975 (w), 1936 (vw), 1908 (vw), 1865 (vw), and 1823 cm^{-1} (m, br.). The spectra of (**3**) and (**4**) are similar to that of (**2**). The i.r. spectra recorded in cyclohexane are much more complex, consistent with the presence of more than one isomer in solution. The triphenyl-, methyldiphenyl-, and trimethyl-phosphine analogues of $[Ru_6C(CO)_{16}(AuPR_3)_2]$ [(**5**), (**6**), and (**7**), respectively] have been prepared in similar fashion. The complexes $[Ru_6C(CO)_{16}(AuPEt_3)(AuPPh_3)]$ (**8**) and $[Ru_6C(CO)_{16}\{Au_2(Ph_2PCH_2)_2\}]$ (**9**) have also been prepared.

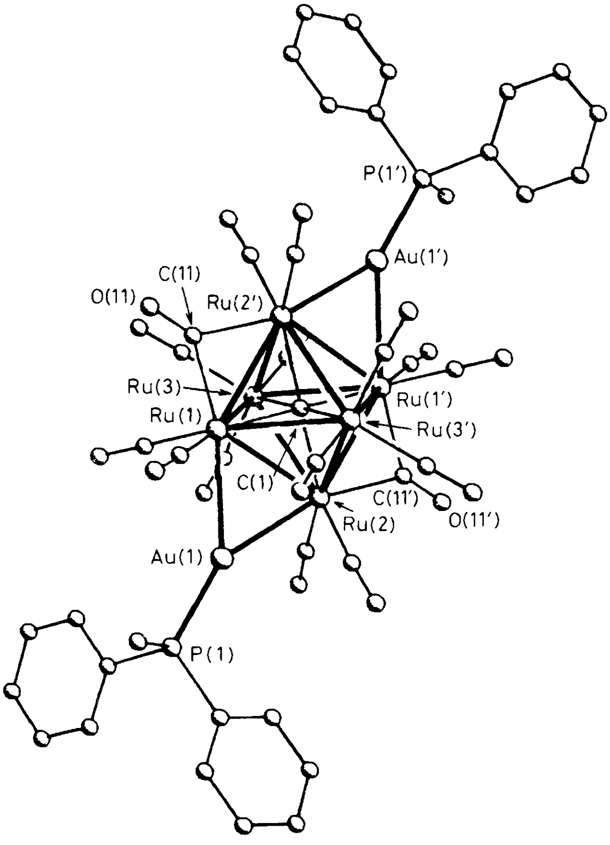

Figure 1. Molecular structure of $[Ru_6C(CO)_{16}(AuPMePh_2)_2]$. Bond lengths: Ru(1)–Ru(2), 2.758(1); Ru(2)–Ru(3), 2.936(1); Ru(1)–Ru(3), 2.868(1); Ru(1)–Ru(2'), 2.832(1); Ru(2)–Ru(3'), 2.950(1); Ru(1)–Ru(3'), 2.874(1); Ru(1)–C(1), 2.080(1); Ru(2)–C(1), 2.074(1); Ru(3)–C(1), 2.034(1); Ru(1)–Au(1), 2.788(1); Ru(2)–Au(1), 2.758(1); Au(1)–P(1), 2.288(3) Å.

Crystals of (**1**), (**2**), and (**6**) which were suitable for *X*-ray analysis were obtained by recrystallisation from a mixture of C_6H_{14}–CH_2Cl_2 at −20 °C.

The molecular structure of $[Ru_6C(CO)_{16}(AuPMePh_2)_2]$†‡ is shown in Figure 1 along with some bond lengths. The six ruthenium atoms define a slightly distorted octahedron with the carbide atom C(1) lying at a crystallographic centre of symmetry. The bond Ru(1)–Ru(2) is bridged by the gold-phosphine ligand; Au(1) lies 0.185 Å above the plane defined by Ru(1), Ru(2), Ru(1'), and Ru(2'). The bond Ru(1)–Ru(2') is bridged by a carbonyl ligand. The remaining carbonyls are terminally co-ordinated, two each to Ru(1) and Ru(2) and three to Ru(3).

A preliminary photographic study of (**1**)§ suggests that the molecules lie on crystallographic centres of symmetry and thus that (**1**) and (**6**) have similar structures.

The molecular structure of $[Ru_5WC(CO)_{17}(AuPEt_3)_2]$‡¶ is shown in Figure 2 together with some important bond lengths. The five Ru atoms define a square-based pyramid with the carbido atom C(100) lying just below the square base. The W(1) atom also caps this square plane to form a distorted octahedron and is bonded to the carbide. The Au(1) atom caps the Ru(1)Ru(2)Ru(5) face, while the Au(2) atom is bonded to the Ru(1) and Ru(5) atoms of the octahedron and to Au(1) thus forming the second cap. Bridging carbonyl groups span the W(1)–Ru(1) and Ru(3)–Ru(5) edges. The W(1) atom is also bonded to three terminal carbonyl ligands as are Ru(2) and Ru(4), while Ru(1), Ru(3), and Ru(5) are bonded to two each.

Thus (**1**) and (**6**) have similar solid-state structures in which there are no Au–Au interactions. In (**2**), however, the Au–Au

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† *Crystal data* for (**6**): $C_{43}H_{26}Au_2O_{16}P_2Ru_6$, $M = 1860.54$, monoclinic, space group $P2_1/c$, $a = 14.811(6)$, $b = 9.698(4)$, $c = 18.031(11)$ Å, $\beta = 106.39(42)°$, $U = 2484.6$ Å^3, $D_c = 2.49$ g cm^{-3} for $Z = 2$, $F(000) = 1728.0$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 76.99$ cm^{-1}. 2946 unique, observed $[F > 3\sigma(F)]$ reflections were measured on a Syntex $P2_1$ diffractometer. The structure was solved by a combination of direct methods and Fourier difference techniques and refined by blocked full-matrix least squares (all atoms anisotropic except for the phenyl and methyl carbon and hydrogen atoms) to $R = R_w = 0.044$.

‡ The atomic co-ordinates for the structures of (**2**) and (**6**) 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.

§ *Crystal data* for (**1**): $C_{29}H_{30}Au_2O_{16}P_2Ru_6$, $M = 1696.83$, monoclinic, space group $P2_1/c$, $a = 9.52(6)$, $b = 15.73(4)$, $c = 14.25(4)$ Å, $\beta = 105.0(1)°$, $U = 2062.0$ Å^3, $D_c = 2.73$ g cm^{-3} for $Z = 2$.

¶ *Crystal data* for (**2**): $C_{30}H_{30}Au_2O_{17}P_2Ru_5W$, $M = 1807.62$, orthorhombic, space group $P2_12_12_1$, $a = 13.217(3)$, $b = 16.265(4)$, $c = 19.422(8)$ Å, $U = 4431.9$ Å^3, $D_c = 2.708$ g cm^{-3} for $Z = 4$, $F(000) = 3312$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 109.45$ cm^{-1}. 3093 unique, observed $[F > 6\sigma(F)]$ reflections were measured on a Stoe diffractometer. The structure was solved by a combination of direct methods and Fourier difference techniques and refined by blocked full-matrix least squares (Au, P, Ru, and W anisotropic) to $R = 0.079$ and $R_w = 0.078$.

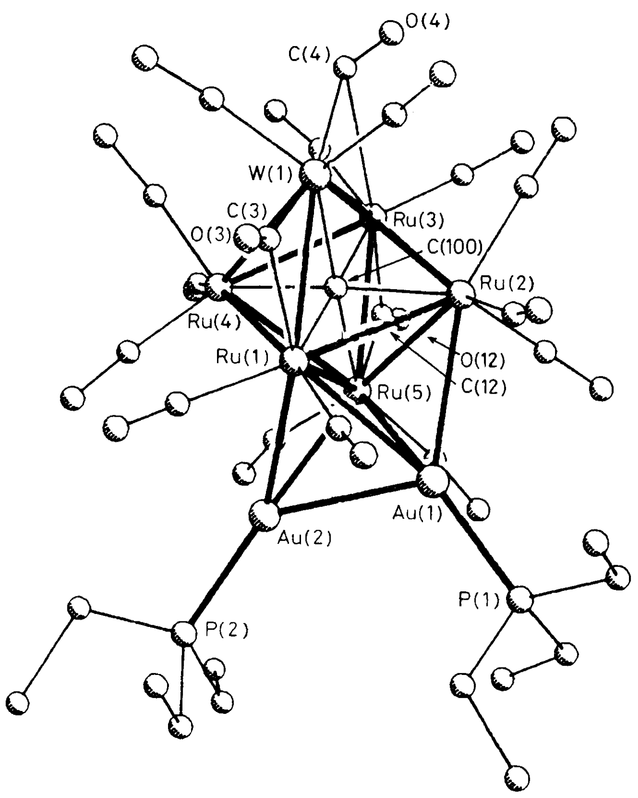

Figure 2. Molecular structure of $[Ru_5WC(CO)_{17}(AuPEt_3)_2]$. Bond lengths: Au(1)–Au(2), 2.808(3); Au(1)–Ru(1), 2.886(5); Au(1)–Ru(2), 2.935(4); Au(1)–Ru(5), 2.907(5); Au(2)–Ru(1), 2.840(4); Au(2)–Ru(5), 2.865(5); W(1)–R(1), 2.900(4); W(1)–Ru(2), 2.966(5); W(1)–Ru(3), 2.953(5); W(1)–Ru(4), 3.038(5); Ru(1)–Ru(2), 2.957(6); Ru(1)–Ru(4), 2.971(6); Ru(1)–Ru(5), 3.109(6); Ru(2)–Ru(3), 2.892(6); Ru(2)–Ru(5), 2.935(6); Ru(3)–Ru(4), 2.863(6); Ru(3)–Ru(5), 2.865(5); Ru(4)–Ru(5), 2.845(6); W(1)–C(100), 2.05(4); Ru(1)–C(100), 2.03(4); Ru(2)–C(100), 2.04(5); Ru(3)–C(100), 2.12(4); Ru(4)–C(100), 2.09(5); Ru(5)–C(100), 2.18(4); Au(1)–P(1), 2.29(1); Au(2)–P(2), 2.27(1) Å.

distance is 2.808(3) Å, within a normal bond distance, and the arrangement of metal atoms is similar to that in $[Ru_6C(CO)_{16}(CuMeCN)_2]$[3] where the Cu–Cu distance is 2.691(1) Å.

The $^{31}P\{^1H\}$ n.m.r. spectrum of (**1**) in CH_2Cl_2 at room temperature exhibits a single sharp resonance at δ −72.1 p.p.m. (relative to trimethylphosphite). On cooling, this resonance broadens and splits until, at −70 °C, resonances at δ −69.8 (A) and −76.2 (B) p.p.m. (intensity 2 : 1) are observed. These changes are fully reversible over the temperature range. The relative intensities of resonances (A) and (B) vary with the solvent employed (*e.g.* 3 : 1 in THF). The observed spectrum may be explained by assigning the two resonances to two different isomers of (**1**) which rapidly interconvert at room temperature. Consistent with the presence of two forms, the i.r. spectrum shows a reversible temperature dependence, becoming more complex on cooling implying conversion of one isomeric form to another. Also, the average signal in the $^{31}P\{^1H\}$ n.m.r. spectrum at room temperature does not lie at the weighted mean position suggested by the two signals resolved at low temperature. The presence of a temperature-dependent equilibrium between the two forms obviously complicates the interpretation of the n.m.r. data. However, we propose that in one isomer the gold moieties are arranged as shown in the crystal structure (Figure 1) and in the other as in (**2**) (Figure 2). A low-energy process involving Ru–Au bond breaking/making which equilibrates the two signals may be invoked to explain the observation of only a single resonance in the spectrum of the latter. Such a process is consistent with the observation that weak tangential gold–gold bonds in homonuclear gold clusters allow facile skeletal rearrangements[4] and would be similar to the proposal of Stone and co-workers[2] that a Berry pseudo-rotation exchange process accounts for the ^{31}P n.m.r. spectrum of $[Ru_3S(CO)_8L(AuPPh_3)_2]$ (L = PPh_3, CO). However, they found no evidence for isomeric species in their systems. $^{31}P\{^1H\}$ N.m.r. studies on (**2**), (**3**), and (**4**) have revealed similar behaviour, although in these cases the limiting low-temperature spectra are more complex.

$[Ru_6C(CO)_{16}(AuPEt_3)_2]$ $[Ru_5MC(CO)_{17}(AuPEt_3)_2]$
(**1**) (**2**), M = W; (**3**), M = Mo;
(**4**), M = Cr

$[Ru_6C(CO)_{16}(AuPR_3)_2]$
(**5**), R = Ph; (**6**), R_3 = Me Ph_2;
(**7**), R = Me

$[Ru_6C(CO)_{16}(AuPEt_3)(AuPPh_3)]$
(**8**)

$[Ru_6C(CO)_{16}\{Au_2(Ph_2PCH_2)_2\}]$
(**9**)

The process by which these isomers interconvert is of some interest. We have found that simple exchange with PPh_3 does not occur. Instead, irreversible extrusion of $[AuPEt_3]^+$ results and generates $[Ru_6C(CO)_{16}(AuPEt_3)]^-$. Interpretation of the ^{31}P n.m.r. results in terms of an intermolecular exchange process can also be ruled out since a mixture of $[Ru_6C(CO)_{16}(AuPEt_3)_2]$ and $[Ru_6C(CO)_{16}(AuPPh_3)_2]$ only slowly generates $[Ru_6C(CO)_{16}(AuPEt_3)(AuPPh_3)]$, equilibrium being attained in *ca.* 8 h. The interconversion of isomers is therefore the result of an intramolecular rearrangement of metal atoms.

It is apparent that the solid-state structures of these complexes do not adequately describe the structures of species present in solution and that the distribution of isomers may vary with the solvent. This must be an important consideration in any studies of the chemistry or catalytic properties of such species.

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