Journal of Organometallic Chemistry, *443* (1993) C11–C13

JOM 23139PC

Preliminary Communication

Synthesis of bridged and linked ruthenium and osmium carbonyl clusters containing a $[Au_2(Ph_2PCH_2CH_2PPh_2)]^{2+}$ unit. The crystal and molecular structures of $Ru_5C(CO)_{14}Au_2(Ph_2PCH_2CH_2PPh_2)$ and $\{Os_4H_3(CO)_{12}\}_2Au_2(Ph_2PCH_2CH_2PPh_2)$

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(Received July 13, 1992)

Abstract

Treatment of $Au_2(Ph_2PCH_2CH_2PPh_2)Cl_2$ with one equivalent of the $[Ru_5C(CO)_{14}]^{2-}$ dianion in the presence of $TlPF_6$ gives $Ru_5C(CO)_{14}Au_2(Ph_2PCH_2CH_2PPh_2)$ (1) in good yield and the $[\{Ru_5C(CO)_{14}\}_2Au_2(Ph_2PCH_2CH_2PPh_2)]^{2-}$ (2) anion in low yield. Complex 2 becomes the major product if 2 equivalents of $[Ru_5C(CO)_{14}]^{2-}$ are used. Reaction of $[Au_2(Ph_2PCH_2CH_2PPh_2)Cl_2]$ with 3 equivalents of $[H_3Os_4(CO)_{12}]^-$ anion in the presence of $TlPF_6$ affords $\{H_3Os_4(CO)_{12}\}_2Au_2(Ph_2PCH_2CH_2PPh_2)$ (3) in reasonable yield. X-ray diffraction studies of 1 and 3 show that they contain the $[Au_2(Ph_2PCH_2CH_2PPh_2)]^{2+}$ fragment in different coordination modes.

The use of Group IB metal fragments for the metathetical formation of metal–metal bonds with anionic metal carbonyl clusters is well known [1]. However, the use of bimetallic cationic fragments, containing bidentate phosphine groups, such as $[Au_2(Ph_2PCH_2CH_2PPh_2)]^{2+}$, has been limited to a few cases in which both Au atoms are bonded to the same ruthenium or osmium cluster anion [2–4]. We decided to expand these studies in order to investigate the possibility of linking carbonyl cluster anions with this bidentate cation as a method of generating higher nuclearity cluster complexes, and we now report some preliminary results of these investigations. From the reactions of $Au_2(Ph_2PCH_2CH_2PPh_2)Cl_2$ with the anions $[Ru_5C(CO)_{14}]^{2-}$ and $[Os_4H_3(CO)_{12}]^-$ three complexes exhibiting two different coordination modes of the digold unit have been characterised: (i) a digold–pentaruthenium carbido cluster with a $[Au_2(Ph_2PCH_2CH_2PPh_2)]^{2+}$ unit bonded to one cluster anion *via* both Au atoms; (ii) a digold–decaruthenium cluster anion; and (iii) a digold–octaosmium cluster containing two monogold–tetraosmium units linked together *via* the $[Au_2(Ph_2PCH_2CH_2PPh_2)]^{2+}$ unit.

Treatment of a dichloromethane solution of the salt $[N(PPh_3)_2]_2[Ru_5C(CO)_{14}]$ with one equivalent of $Au_2(Ph_2PCH_2CH_2PPh_2)Cl_2$ in the presence of an excess of $TlPF_6$ at room temperature affords the dark red cluster $Ru_5C(CO)_{14}Au_2(Ph_2PCH_2CH_2PPh_2)$ (1), in 80% yield after chromatography on silica. A minor product (*ca.* 10% yield), found to be $[\{Ru_5C(CO)_{14}\}_2Au_2(Ph_2PCH_2CH_2PPh_2)]^{2-}$ (2), can be isolated as the $[N(PPh_3)_2]^+$ salt. When one half of an equivalent of the digold reagent was used, compound 2 was obtained in higher yield (*ca.* 60%) and compound 1 was isolated in 30% yield. Both compounds have been spectroscopically characterised. * In order to establish the coordination mode of the gold-diphenylphosphine fragment in the cluster 1, its structure has been determined by single crystal X-ray crystallography. ** The molecular structure of 1 is shown in Fig. 1, together with some important bond parameters. The metal core geometry of 1 can be described as a trigonal bipyramid fused with a square based pyramid sharing a common triangular face. The bidentate phosphine ligand bridges the Au–Au vectors, generating a six-membered ring. The Au–Au separation of 2.811(1) Å is similar to the corresponding distances in $Au_2Ru_4(\mu\text{-}H)(\mu_3\text{-}H)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{12}$, (2.823(1) Å [2]), $Au_2Ru_4(\mu\text{-}H)(\mu_3\text{-}H)(\mu\text{-}Ph_2AsCH_2PPh_2)(CO)_{12}$, (2.832(4) Å [3]), and $Au_2Ru_4(\mu_3\text{-}S)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_9$, (2.802(1) Å [4]). The cluster 1 has three carbonyls bridging three of the basal edges of the square based pyramid, and the remaining eleven are terminally coordinated to the metal core. The Ru_5Au_2 core geometry in 1 contrasts with that found in $Ru_5C(CO)_{14}(AuPEt_3)_2$, in which one gold atom caps

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the base of the square based pyramid and the other gold atom bridges one of the basal edges of the pyramid [5]. However, the orientations of the carbonyl ligands in the two compounds are very similar. The $^{31}P\{^1H\}$ NMR spectrum for **1**, in CD_2Cl_2 at room temperature shows two sharp singlets of equal intensity at δ -78.2 and δ -82.4 (relative to trimethylphosphite) which is consistent with the solid state structure of **1**. It has not been possible to obtain crystals of complex **2** suitable for crystallographic analysis, but from the spectroscopic data * the formulation is consistent with the presence of two $[Ru_5C(CO)_{14}]^{2-}$ dianions linked by a $[Au_2(Ph_2PCH_2CH_2PPh_2)]^{2+}$ cation.

The corresponding reaction of $[N(PPh_3)_2][Os_4H_3(CO)_{12}]$ with $Au_2(Ph_2PCH_2CH_2PPh_2)Cl_2$, in a 3 : 1 ratio, in the presence of excess $TlPF_6$, gives after chromatography on silica, the airstable yellow compound $\{Os_4H_3(CO)_{12}\}_2Au_2(Ph_2PCH_2CH_2PPh_2)$ (**3**) in quantitative yield based on the Au reagent used. Complex **3** has been characterised spectroscopically *, and by a single crystal X-ray study **, which showed that two tetraosmium units are linked together *via* the $[Au_2(Ph_2PCH_2CH_2PPh_2)]^{2+}$ fragment. The molecular structure of **3** is shown in Fig. 2, together with some selected bond parameters. The molecule lies on a crystallographic centre of symmetry located at the mid-point of the C(1)–C(1g) bond. The structural features of the unique $Os_4H_3(CO)_{12}AuPR_3$ unit in **3** are essentially the same as those reported for $Os_4H_3(CO)_{12}AuPEt_3$ [6]. The Au–P distance in **3** is not significantly different from the two values (2.280(5) and 2.293(4) Å) for the Au–P distances in **1**, although the mode of coordination of the $[Au_2(Ph_2PCH_2CH_2PPh_3)]^{2+}$ cation is different.

It has been demonstrated that with the careful choice of cluster and stoichiometry, the $[Au_2(Ph_2PCH_2CH_2PPh_2)]^{2+}$ unit exhibits different bonding modes. Currently we are investigating the chemistry of this cation with high nuclearity systems.

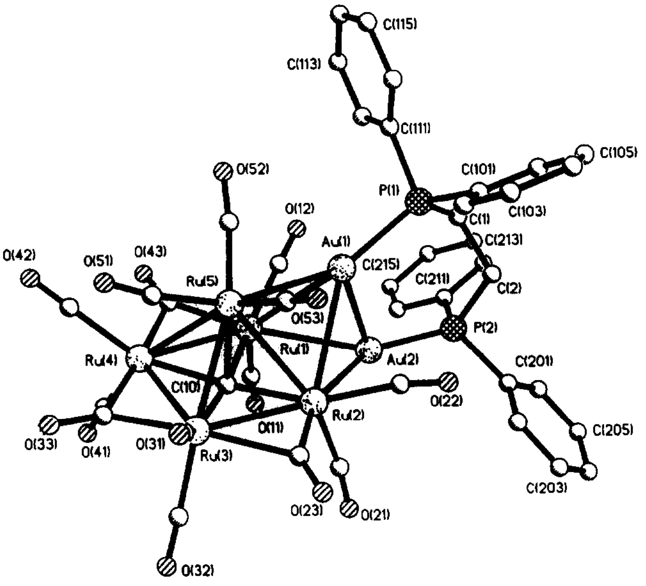

Fig. 1. The molecular structure of $[Ru_5C(CO)_{14}Au_2(Ph_2PCH_2CH_2PPh_2)]$ (**1**) showing the atom numbering scheme. Bond lengths: Au(1)–Au(2), 2.811(1); Au(1)–Ru(1), 3.084(2); Au(1)–Ru(2), 3.015(2); Au(1)–Ru(5), 2.722(2); Au(1)–P(1), 2.293(4); Au(2)–Ru(1), 2.796(2); Au(2)–Ru(2), 2.802(2); Au(2)–P(2), 2.280(5); Ru(1)–Ru(2), 3.006(2); Ru(1)–Ru(4), 2.793(2); Ru(1)–Ru(5), 2.900(3); Ru(2)–Ru(3), 2.804(2); Ru(2)–Ru(5), 2.898(2); Ru(3)–Ru(4), 2.796(3); Ru(3)–Ru(5), 2.813(2); Ru(4)–Ru(5), 2.827(2); Ru(1)–C(10), 2.02(2); Ru(2)–C(10), 2.01(2); Ru(3)–C(10), 2.03(2); Ru(4)–C(10), 2.04(2); Ru(5)–C(10), 2.21(2); P(1)–C(1), 1.82(2); P(2)–C(2), 1.81(2); C(1)–C(2), 1.54(3) Å. Bond angles: Ru(1)–Au(1)–Ru(2), 59.1(1); Ru(1)–Au(1)–Ru(5), 59.6(1); Ru(2)–Au(1)–Ru(5), 60.4(1); Au(2)–Au(1)–Ru(1), 56.4(1); Au(2)–Au(1)–Ru(2), 57.4(1); Au(2)–Au(1)–Ru(5), 106.0(1); Au(1)–Au(2)–Ru(1), 66.7(1); Au(1)–Au(2)–Ru(2), 65.0(1); Ru(1)–Au(2)–Ru(2), 65.0(1)°.

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* Spectroscopic data for **1**: IR ν(CO) (CH_2Cl_2): 2065m, 2034vs, 2008vs, 1972m, 1849br, sh cm^{-1}. MS: M^+ (obs.) *m/z* 1701 (calc.) 1702. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ -78.2(s, 1P), -82.4 (s, 1P). **2**: IR ν(CO) (CH_2Cl_2): 2066m, 2036s, 2017s, 1844br, sh cm^{-1}. MS: M^+ (obs.) *m/z* 2610 (calc.) 2611. **3**: IR ν(CO) (CH_2Cl_2): 2094m, 2071s, 2033vs, 2004m, 1970m, 1950m, br cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ -69.3 (s, 2P). ^1H NMR (CD_2Cl_2): δ -20.27 (s, 6H), 2.81 (s, br, 4H), 7.49 (m, 20H).

** Crystal data for **1**: $C_{41}H_{24}O_{14}P_2Ru_5Au_2$, M = 1701.8, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.772(1)$, $b = 14.829(2)$, $c = 16.084(3)$ Å, $\alpha = 102.04(1)$, $\beta = 93.82(1)$, $\gamma = 101.49(1)°$, $V = 2446(1)$ Å^3, $Z = 2$, $D_c = 2.31$ g cm^{-3}, $F(000) = 1580$, Mo Kα radiation, $\lambda = 0.71069$ Å, μ(Mo Kα) = 75.99 cm^{-1}, 4850 observed diffractometer data $[F > 4\sigma(F)]$. Structure solved by direct methods and Fourier difference techniques, refined by full-matrix least-squares analysis (Au, Ru, P, O and some C atoms anisotropic) to $R = 0.069$ and $R_w = 0.086$. Crystal data for **3**: $C_{50}H_{30}O_{24}P_2Os_8Au_2$, M = 2992.3, monoclinic, space group $P2_1/n$ (alternative setting $P2_1/c$, No. 14), $a = 18.502(5)$, $b = 8.934(1)$, $c = 21.156(5)$ Å, $\beta = 109.32(1)°$, $V = 3300(1)$ Å^3, $Z = 2$, $D_c = 3.010$ g cm^{-3}, $F(000) = 2636$, Mo Kα radiation, $\lambda = 0.71069$ Å, μ(Mo Kα) = 198.97 cm^{-1}, 3203 observed diffractometer data $[F > 3\sigma(F)]$. Structure solved by direct methods and Fourier difference techniques, refined by full-matrix least-squares analysis (Au, Os, P atoms anisotropic) to $R = 0.050$ and $R_w = 0.059$. Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre.

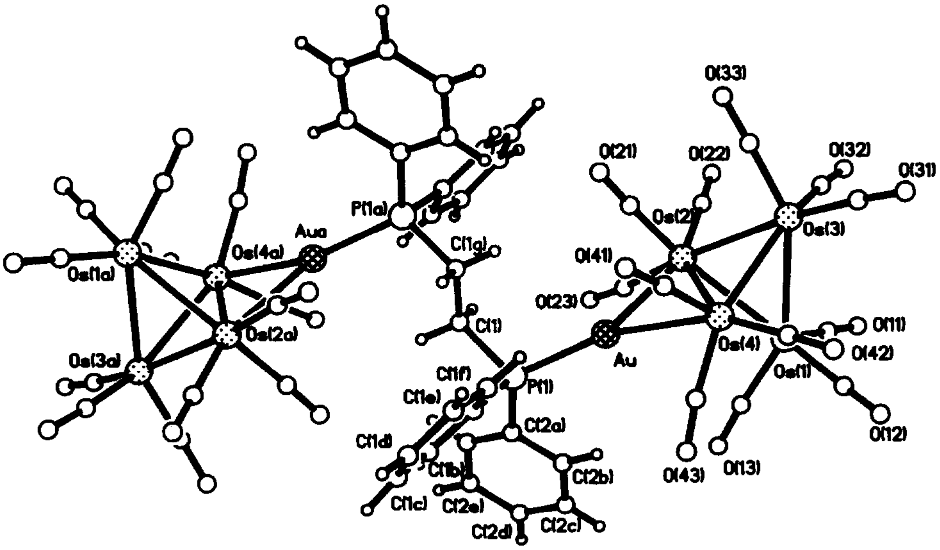

Fig. 2. The molecular structure of [$\{H_3Os_4(CO)_{12}\}_2Au_2(Ph_2PCH_2CH_2PPh_2)$] (3) showing the atom numbering scheme. Bond lengths: Au–Os(2), 2.778(2); Au–Os(4), 2.789(2); Os(1)–Os(2), 2.961(1); Os(1)–Os(3), 2.956(1); Os(1)–Os(4), 2.812(2); Os(2)–Os(3), 2.811(2); Os(2)–Os(4), 2.942(1); Os(3)–Os(4), 2.960(2); Au–P(1), 2.288(6); P(1)–C(1), 1.85(2); C(1)–C(1g), 1.56(3) Å. Bond angles: Os(2)–Au–Os(4), 63.8(1); Os(2)–Au–P(1), 143.4(1); Os(4)–Au–P(1), 152.8(1)°.

Acknowledgements

We thank the Royal Commission for the Exhibition of 1851 (W.T.W.), the Nehru Trust for Cambridge University, New Delhi, the Cambridge Commonwealth Trust, Cambridge (V.P.S.), the Committee of Vice-Chancellors and Principals (W.T.W. & V.P.S.), SERC (A.J.A.) and Ciba-Geigy (A.J.E.) for financial support.

References

1 C. E. Coffey, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, (1964) 1741; B. F. G. Johnson, J. Lewis, W. J. H. Nelson, P. R. Raithby and M. D. Vargas, *J. Chem. Soc., Chem. Commun.*, (1983) 608; B. F. G. Johnson, J. Lewis, W. J. H. Nelson, M. D. Vargas, D. Braga, K. Henrick and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, (1986) 975.
2 P. A. Bates, S. S. D. Brown, A. J. Dent, M. B. Hursthouse, G. F. M. Kitchen, A. G. Orpen, I. D. Salter and V. Sik, *J. Chem. Soc., Chem. Commun.*, (1986) 600.
3 P. A. Bates, S. S. D. Brown, D. B. Dyson, M. B. Hursthouse, R. V. Parish and I. D. Salter, *J. Chem. Soc., Dalton Trans.*, (1988) 1795.
4 S. S. D. Brown, S. Hudson, M. McPartlin and I. D. Salter, *J. Chem. Soc., Dalton Trans.*, (1987) 1967.
5 A. Cowie, B. F. G. Johnson, J. Lewis and P. R. Raithby, unpublished results.
6 B. F. G. Johnson, D. A. Kaner, J. Lewis, P. R. Raithby, M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, (1982) 314.