

**Synthesis of the Tetraruthenium Carbido Cluster  $[\text{Ru}_4(\text{H})_2\text{C}(\text{CO})_{12}]$  via Mixed Ruthenium–Gold Carbido Intermediates: X-Ray Crystal Structures of  $[\text{Ru}_4\text{C}(\text{CO})_{12}(\text{AuPMe}_2\text{Ph})_2]$ ,  $[\text{Ru}_4\text{C}(\text{CO})_{12}(\text{I})(\text{AuPEt}_3)]$ , and  $[\text{Ru}_4(\text{H})\text{C}(\text{CO})_{12}(\text{AuPPh}_3)]$**

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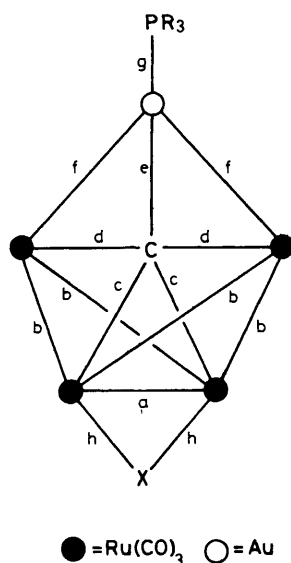
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The action of CO on the pentanuclear carbido cluster  $[\text{Ru}_5\text{C}(\text{CO})_{14}(\text{AuPR}_3)_2]$  [ $\text{PR}_3 = \text{PEt}_3$  (1),  $\text{PPh}_3$  (2),  $\text{PMe}_2\text{Ph}$  (3)] (80 atm, 60 °C) affords the tetranuclear carbido cluster  $[\text{Ru}_4\text{C}(\text{CO})_{12}(\text{AuPR}_3)_2]$  [ $\text{PR}_3 = \text{PEt}_3$  (4),  $\text{PPh}_3$  (5),  $\text{PMe}_2\text{Ph}$  (6)], which exhibits a carbide-centred, 'butterfly'  $\text{Ru}_4\text{C}$  core with both the 'wing-tip' and 'hinge' Ru atoms bridged by  $\text{AuPR}_3$  groups; the 'hinge' bridging  $\text{AuPR}_3$  group may be replaced by reaction with  $\text{I}_2$  or HI to give  $[\text{Ru}_4\text{C}(\text{CO})_{12}(\text{I})(\text{AuPR}_3)]$  [ $\text{PR}_3 = \text{PEt}_3$  (7),  $\text{PPh}_3$  (8)] and  $[\text{Ru}_4(\text{H})\text{C}(\text{CO})_{12}(\text{AuPR}_3)]$  [ $\text{PR}_3 = \text{PEt}_3$  (9),  $\text{PPh}_3$  (10)], respectively, and the subsequent reaction of (9) and (10) with  $[\text{BH}_4]^-$  removes the remaining  $\text{AuPR}_3$  group, acidification affording the tetraruthenium carbide  $[\text{Ru}_4(\text{H})_2\text{C}(\text{CO})_{12}]$  (11).

Much of the interest in carbido–carbonyl cluster chemistry has arisen from an anticipation of reactivity at the carbide atom. This type of reactivity has been observed in derivatives of the complex  $[\text{Fe}_4\text{C}(\text{CO})_{13}]$ ,<sup>1</sup> but neither the ruthenium analogue,  $[\text{Ru}_4\text{C}(\text{CO})_{13}]$ , nor any of its derivatives have previously been synthesized to provide a comparison with the iron system. Whereas complexes containing the  $\text{Fe}_4\text{C}$  core have been prepared from  $\text{Fe}_5\text{C}$  derivatives,<sup>2</sup> typical reactions of the

cluster  $[\text{Ru}_5\text{C}(\text{CO})_{15}]$ <sup>3</sup> include addition or substitution but not degradation to tetranuclear complexes. In an attempt to alter the above pattern of reactivity we have now studied mixed-metal derivatives of the pentanuclear ruthenium–carbido systems.

Treatment of  $[(\text{Ph}_3\text{P})_2\text{N}]_2[\text{Ru}_5\text{C}(\text{CO})_{14}]$ ,<sup>4</sup> in  $\text{CH}_2\text{Cl}_2$  solution, with  $[\text{AuPR}_3][\text{ClO}_4]$  (2 equiv.) ( $\text{PR}_3 = \text{PEt}_3$ ,  $\text{PPh}_3$ , or  $\text{PMe}_2\text{Ph}$ ) produces a deep red solution formulated as

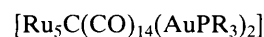


X	(10) H	(6) AuPR <sub>3</sub>	(7) I
a	2.856(1)	3.252(3)	3.427(1)
b(av.)	2.82	2.80	2.86
c(av.)	2.09	2.22	2.14
d(av.)	1.98	1.81	1.96
e	2.066(6)	2.104(25)	2.078(10)
f(av.)	2.95	2.86	2.92
g	2.270(2)	2.273(5)	2.278(3)
h(av.)	1.96	2.80	2.78
PR <sub>3</sub>	PPh <sub>3</sub>	PMe <sub>2</sub> Ph	PEt <sub>3</sub>

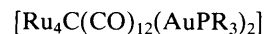
**Figure 1.** Structures of [Ru<sub>4</sub>C(CO)<sub>12</sub>(AuPMe<sub>2</sub>Ph)<sub>2</sub>] (6), [Ru<sub>4</sub>C(CO)<sub>12</sub>(I)(AuPEt<sub>3</sub>)] (7), and [Ru<sub>4</sub>C(CO)<sub>12</sub>(H)(AuPPh<sub>3</sub>)] (10). Interatomic distances are in Å.

[Ru<sub>5</sub>C(CO)<sub>14</sub>(AuPR<sub>3</sub>)<sub>2</sub>] [PR<sub>3</sub> = PEt<sub>3</sub> (1), PPh<sub>3</sub> (2), PMe<sub>2</sub>Ph (3)] on the basis of spectroscopic data.† The mass spectrum of (1) exhibited a 'parent ion' at *m/z* 1382, corresponding to [Ru<sub>4</sub>C(CO)<sub>12</sub>(AuPEt<sub>3</sub>)<sub>2</sub>] formed by pyrolysis on the instrument probe, and indicated the possibility of the preparation of tetraruthenium species from (1). Under a pressure of 80 atm of carbon monoxide at 60 °C a solution of [Ru<sub>5</sub>C(CO)<sub>14</sub>(AuPR<sub>3</sub>)<sub>2</sub>], [(1), (2), or (3)] in toluene is converted into

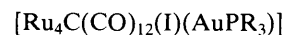
† (1): i.r. ν(CO)(CH<sub>2</sub>Cl<sub>2</sub>): 2060m, 2018s, 2005s, 1972m, 1954w,sh, 1833w,br cm<sup>-1</sup>; n.m.r. (CD<sub>2</sub>Cl<sub>2</sub>), <sup>31</sup>P-{<sup>1</sup>H}: -71.5(s), -117.6 p.p.m. (s), P(OMe)<sub>3</sub> standard; highest mass multiplet *m/z* 1382 (<sup>101</sup>Ru); (2): i.r. ν(CO)(CH<sub>2</sub>Cl<sub>2</sub>): 2066m, 2034m,sh, 2021s,sh, 2009s, 1976m, 1844w,br cm<sup>-1</sup>; (3): i.r. ν(CO)(CH<sub>2</sub>Cl<sub>2</sub>): 2062m, 2019s, 2007s, 1974m, 1954w,sh, 1836w,br cm<sup>-1</sup>; (4): i.r. ν(CO)(CH<sub>2</sub>Cl<sub>2</sub>): 2062vw, 2030s, 2021s,sh, 2007w,sh, 1988m, 1950w cm<sup>-1</sup>; n.m.r. (CD<sub>2</sub>Cl<sub>2</sub>), <sup>31</sup>P-{<sup>1</sup>H}: -74.7(s), -106.4 p.p.m. (s), P(OMe)<sub>3</sub> standard; highest mass multiplet *m/z* 1382 (<sup>101</sup>Ru); (5): i.r. ν(CO)(CH<sub>2</sub>Cl<sub>2</sub>): 2065vw, 2033s, 2026s,sh, 2013w, 1991m, 1954w cm<sup>-1</sup>; (6): i.r. ν(CO)(CH<sub>2</sub>Cl<sub>2</sub>): 2063vw, 2031s, 2024s,sh, 2010w,sh, 1990m, 1952w cm<sup>-1</sup>; highest mass multiplet *m/z* 1422 (<sup>101</sup>Ru); (7): i.r. ν(CO)(hexane): 2085w, 2060s, 2042s, 2004s, 1963m cm<sup>-1</sup>; n.m.r. (CD<sub>2</sub>Cl<sub>2</sub>), <sup>31</sup>P-{<sup>1</sup>H}: -106.6 p.p.m. (s), P(OMe)<sub>3</sub> standard; highest mass multiplet *m/z* 1194 (<sup>101</sup>Ru); (9): i.r. ν(CO)(hexane): 2087w, 2056s, 2045s, 2031w, 2013s, 1981vw, 1966w cm<sup>-1</sup>; n.m.r. (CD<sub>2</sub>Cl<sub>2</sub>), <sup>31</sup>P-{<sup>1</sup>H}: -106.1 p.p.m. (s), P(OMe)<sub>3</sub> standard; <sup>1</sup>H: δ 1.3 (m, 3H), 2.0 (m, 2H), -22.6 (s, 1H); highest mass multiplet *m/z* 1068 (<sup>101</sup>Ru); (10): i.r. ν(CO)(hexane): 2087w, 2056s, 2046s, 2031w, 2013s, 1982vw, 1969w cm<sup>-1</sup>; (11): i.r. ν(CO)(hexane): 2110vw, 2082m, 2067s, 2056s, 2046w, 2032m, 2022m, 2010w, 2005w, 1998w, 1992w cm<sup>-1</sup>; n.m.r. <sup>1</sup>H (CD<sub>2</sub>Cl<sub>2</sub>): δ -16.22 (d, *J* 2.9 Hz), -22.74 (d, *J* 2.9 Hz); highest mass multiplet *m/z* 754 (<sup>101</sup>Ru). Elemental analyses were consistent with the formulations.



- (1) PR<sub>3</sub> = PEt<sub>3</sub>  
 (2) PR<sub>3</sub> = PPh<sub>3</sub>  
 (3) PR<sub>3</sub> = PMe<sub>2</sub>Ph



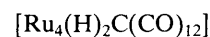
- (4) PR<sub>3</sub> = PEt<sub>3</sub>  
 (5) PR<sub>3</sub> = PPh<sub>3</sub>  
 (6) PR<sub>3</sub> = PMe<sub>2</sub>Ph



- (7) PR<sub>3</sub> = PEt<sub>3</sub>  
 (8) PR<sub>3</sub> = PPh<sub>3</sub>



- (9) PR<sub>3</sub> = PEt<sub>3</sub>  
 (10) PR<sub>3</sub> = PPh<sub>3</sub>



(11)

[Ru<sub>4</sub>C(CO)<sub>12</sub>(AuPR<sub>3</sub>)<sub>2</sub>] [PR<sub>3</sub> = PEt<sub>3</sub> (4), PPh<sub>3</sub> (5), PMe<sub>2</sub>Ph (6), respectively] in high yield (>80%). The formulation of (4), (5), and (6) was confirmed by spectroscopic and analytical data,† and X-ray analysis of [Ru<sub>4</sub>C(CO)<sub>12</sub>(AuPMe<sub>2</sub>Ph)<sub>2</sub>] (6) was performed on the orange crystals obtained from a hexane-dichloromethane solution.‡ The Ru atoms describe a 'butterfly' arrangement with the two gold-phosphine groups bridging across the 'wing-tips' and below the 'hinge' of the 'butterfly' (Figure 1). This contrasts with the structure of the iron analogue, [Fe<sub>4</sub>C(CO)<sub>12</sub>(AuPEt<sub>3</sub>)<sub>2</sub>],<sup>5</sup> in which the Fe<sub>4</sub> 'butterfly' forms part of a distorted octahedral structure with the gold atoms adjacent to each other. The room temperature <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum† exhibits one signal for the iron cluster but two for (4) and is therefore consistent with the observed difference in solid state structure.

Substitution of the 'hinge' bridging AuPR<sub>3</sub> group can be achieved by addition of solid I<sub>2</sub> or by bubbling HI gas through

‡ Crystal data for (6). C<sub>29</sub>H<sub>22</sub>Au<sub>2</sub>O<sub>12</sub>P<sub>2</sub>Ru<sub>4</sub>, *M* = 1411.54, monoclinic, space group *P2<sub>1</sub>/c* (from systematic absences), *a* = 13.796(3), *b* = 15.948(3), *c* = 18.929(5) Å, β = 108.62(2)°, *U* = 3946.7 Å<sup>3</sup>, *D<sub>c</sub>* = 2.375 g cm<sup>-3</sup>, *Z* = 4, *F*(000) = 2624, Mo-K<sub>α</sub> radiation, λ = 0.71069 Å, μ(Mo-K<sub>α</sub>) = 89.51 cm<sup>-1</sup>, 3378 observed diffractometer data [*F* > 5σ(*F*)]. Structure solved by direct methods and Fourier difference techniques, refined by blocked-cascade least squares (Au, Ru, P, O, and carbide C anisotropic) to *R* = 0.063, *R<sub>w</sub>* = 0.061.

Crystal data for (7). C<sub>10</sub>H<sub>15</sub>AuO<sub>12</sub>PRu<sub>4</sub>, *M* = 1194.43, monoclinic, space group *P2<sub>1</sub>/c* (from systematic absences), *a* = 11.692(1), *b* = 9.291(1), *c* = 28.669(2) Å, β = 96.82(1)°, *U* = 3092.3 Å<sup>3</sup>, *D<sub>c</sub>* = 2.565 g cm<sup>-3</sup>, *Z* = 4, *F*(000) = 2192, Mo-K<sub>α</sub> radiation, λ = 0.71069 Å, μ(Mo-K<sub>α</sub>) = 76.51 cm<sup>-1</sup>, 4842 observed diffractometer data [*F* > 4σ(*F*)]. Structure solved by direct methods and Fourier difference techniques, refined by blocked-cascade least squares (Au, Ru, I, P, O, and C anisotropic) to *R* = 0.050 and *R<sub>w</sub>* = 0.055.

Crystal data for (10). C<sub>31</sub>H<sub>16</sub>AuO<sub>15</sub>PRu<sub>4</sub>, *M* = 1212.66, triclinic, space group *P1̄* (No. 2), *a* = 10.074(2), *b* = 12.562(1), *c* = 15.182(2) Å, α = 103.14(1), β = 99.66(1), γ = 99.42(1)°, *U* = 1803.2 Å<sup>3</sup>, *D<sub>c</sub>* = 2.233 g cm<sup>-3</sup>, *Z* = 2, *F*(000) = 1136, Mo-K<sub>α</sub> radiation, λ = 0.71069 Å, μ(Mo-K<sub>α</sub>) = 57.19 cm<sup>-1</sup>, 5721 observed diffractometer data [*F* > 4σ(*F*)]. Structure solved by direct methods and Fourier difference techniques, refined by blocked-cascade least squares (Au, Ru, P, O, and carbonyl C anisotropic) to *R* = 0.031 and *R<sub>w</sub>* = 0.033. The atomic co-ordinates for the above structures 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.

a solution of (4) or (5) to produce the complexes  $[\text{Ru}_4\text{C}(\text{CO})_{12}(\text{I})(\text{AuPR}_3)]$  [ $\text{PR}_3 = \text{PEt}_3$  (7),  $\text{PPh}_3$  (8)] and  $[\text{Ru}_4\text{C}(\text{CO})_{12}(\text{H})(\text{AuPR}_3)]$  [ $\text{PR}_3 = \text{PEt}_3$  (9),  $\text{PPh}_3$  (10)], respectively. X-Ray crystal structure analysis of (7) and (10)<sup>‡</sup> indicate that the overall core geometry of (6) is retained (Figure 1), but that there are significant differences in certain of the metal-metal distances, in particular that between the two Ru atoms forming the 'hinge' of the 'butterfly' which is bridged by the different groups. In contrast to (6) and its iron analogue, the structure of (10) displays the same overall geometry as  $[\text{Fe}_4\text{C}(\text{CO})_{12}(\mu_2\text{-H})(\text{AuPPh}_3)]$ .<sup>5</sup>

In the structure of (10) the Ru-Ru 'hinge' distance is similar to that of  $\mu_2\text{-H}$  bridged bonds in pentanuclear ruthenium clusters.<sup>6</sup> On changing this bridging group from hydride to a  $\text{AuPMe}_2\text{Ph}$  unit there is an increase in the bridged Ru-Ru distance of ca. 0.40 Å, and in going from the bridging  $\text{AuPMe}_2\text{Ph}$  to a  $\mu_2\text{-I}$  ligand there is a further increase in bridged Ru-Ru distance of ca. 0.17 Å. In (6) and (7), therefore, this bridged 'hinge' Ru-Ru edge is lengthened to such an extent that little direct Ru-Ru bonding interaction can be present. A hydride ligand may act only as a one electron donor regardless of the mode of bonding, while an iodine ligand is capable of acting as a one, three, or five electron donor depending on the mode of co-ordination. A number of examples of a  $\mu_2\text{-I}$  iodine ligand, which is considered to act as a three-electron donor in ruthenium cluster chemistry, are known,<sup>7</sup> and in these cases there is an elongation of the bridged metal-metal bond similar to that observed in (7). Normally a single  $\text{AuPR}_3$  ligand is considered to act as a one electron donor and adopt a similar bonding mode to that of a hydride. Evidence for this comes from a number of mixed-metal tetra- and penta-nuclear clusters<sup>8</sup> in which the replacement of a bridging hydride by a  $\text{AuPR}_3$  group makes little difference to the bridged metal-metal distance. The unusual elongation of 0.40 Å observed for the bridged  $\text{AuPR}_3$  'hinge' bond in (10) is more consistent with the gold-phosphine ligand acting as a three electron donor in a manner similar to that of a bridging iodine.

Treatment of a  $\text{CH}_2\text{Cl}_2$  solution of (9) or (10) with  $[(\text{Ph}_3\text{P})_2\text{N}][\text{BH}_4]$  produces a yellow solution [i.r.  $\nu(\text{CO})$ : 2032s,sh, 2021s, 2007m,sh, 1985m, 1937w,br  $\text{cm}^{-1}$ ] and a layer of gold metal is deposited on the sides of the reaction flask. Acidification of this solution produces a bright yellow

compound formulated spectroscopically<sup>†</sup> as  $[\text{Ru}_4(\text{H})_2\text{C}(\text{CO})_{12}]$  (11). Both the i.r. and n.m.r. spectra of (11) show significant differences from those of the iron analogue  $[\text{HFe}_4\text{C}(\text{H})(\text{CO})_{12}]$ .<sup>3</sup> In particular the chemical shifts of the signals in the  $^1\text{H}$  n.m.r. spectrum of (11) do not indicate a large 'C-H' interaction as seen in  $[\text{HFe}_4\text{C}(\text{H})(\text{CO})_{12}]$ . This difference in the site of protonation is consistent with the expected greater metal-hydride bond strength of ruthenium compared to iron.<sup>9</sup>

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