Planar 64-Electron Butterfly Clusters with Elongated Metal–Metal Bonds: Synthesis and Molecular Structures of $Ru_4(CO)_{13}(\mu\text{-}PPh_2)_2$ and $Ru_4(CO)_{10}(\mu\text{-}PPh_2)_4$

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The 64-electron phosphido bridged clusters $Ru_4(CO)_{13}(\mu\text{-}PPh_2)_2$ and $Ru_4(CO)_{10}(\mu\text{-}PPh_2)_4$ have been synthesised and characterised by *X*-ray diffraction as consisting of quasiplanar Ru_4 butterfly polyhedra with unusually elongated metal–metal bonds.

One of the most interesting aspects of tetranuclear transition metal clusters is the structural diversity exhibited by molecules with formal 62- and 64-electron counts.[1] Within this electron counting regime lie molecules with 'normal' and 'flattened' butterfly or rhomboidal structures, square planar or rectangular systems, and metalloligated triangular geometries. Novel structural features have been observed for several Group 8 carbonyl clusters including patterns of M–M bond lengthening in 64-electron (5 M–M) systems[2] which have led to suggestions of three-centre, two-electron bonding.[3] A recent report on $Os_4(CO)_{16}$, a metal carbonyl analogue of cyclobutane with a puckered, open square metal framework[4] has prompted us to describe the synthesis and structures of two phosphido-bridged tetraruthenium clusters, $Ru_4(CO)_{13}(\mu\text{-}PPh_2)_2$ (**1**) and $Ru_4(CO)_{10}(\mu\text{-}PPh_2)_4$ (**2**). While quasi-isoelectronic with $Os_4(CO)_{16}$ they have quite different, and remarkable, M_4 frameworks.

The clusters (**1**) and (**2**) were synthesised as described in equations (1) and (2).

$$K_2[Ru_4(CO)_{13}] + 2Ph_2PCl \xrightarrow[\text{THF}]{298\,\text{K}} \underset{(\mathbf{1})\,(30\%)}{Ru_4(CO)_{13}(\mu\text{-}PPh_2)_2} + 2KCl \quad (1)$$

$$Ru_3(CO)_{12} + Ph_2P\text{-}PPh_2 \xrightarrow[\text{xylene}]{393\ K} Ru_4(CO)_{10}(\mu\text{-}PPh_2)_4 + \ldots \quad (2)$$

$$\underset{(2)\,(6\%)}{}$$

The synthesis of (**1**) represents a partial opening of the tetrahedral core of the anionic precursor $K_2[Ru_4(CO)_{13}]$.[5] A similar attempt to generate (**2**) from $M_4[Ru_4(CO)_{12}]$ [M = K or Na)[5] was unsuccessful. Complexes (**1**) and (**2**) are brick red air stable crystalline solids.† I.r. and ^{31}P n.m.r. spectra are indicative of high molecular symmetry.

In order to fully elucidate cluster geometries and bonding characteristics, the structures of both (**1**) and (**2**) were determined by single crystal *X*-ray diffraction studies, the results of which are illustrated in Figures 1 and 2 respectively.‡ It is immediately apparent that neither cluster has the square or spiked triangular geometry predicted by EAN rules for 64-electron tetranuclear species and found respectively in their quasi-isoelectronic osmium counterparts $Os_4(CO)_{16}$ (ref. 4) and $Os_4(CO)_{15}(PMe_3)$.[3] Rather, (**1**) and (**2**) are butterfly clusters characterised by planar triangulated Ru_4 cores with dihedral angles of 177.26° and 180° respectively between the Ru_3 triangles.

In cluster (**1**), the two phosphido ligands bridge adjacent ruthenium–ruthenium vectors, the phosphorus atoms showing a slight but significant deviation from the Ru(1)–Ru(2)–Ru(3) plane. In contrast, the Ru_4P_4 core of cluster (**2**) in which phosphido ligands span all four external ruthenium–ruthenium vectors, is rigorously planar being located about a crystallographic inversion centre. Also noteworthy are the carbonyl configurations. In both clusters, the axial groups are almost perfectly eclipsed, a feature which might be expected to incur unfavourable steric interactions but is probably imposed by the planar metal–phosphorus core arrangement.

The most interesting feature of these clusters is a remarkable elongation of certain of the metal–metal bonds within the planar core (Figure 3). Thus, in (**2**), all four external ruthenium–ruthenium vectors which are bridged by phosphorus show considerable elongation with respect to a normal Ru–Ru single bond, the average length of 3.050 Å being greater by ~0.23 Å than that of 2.8175(6) Å found in the

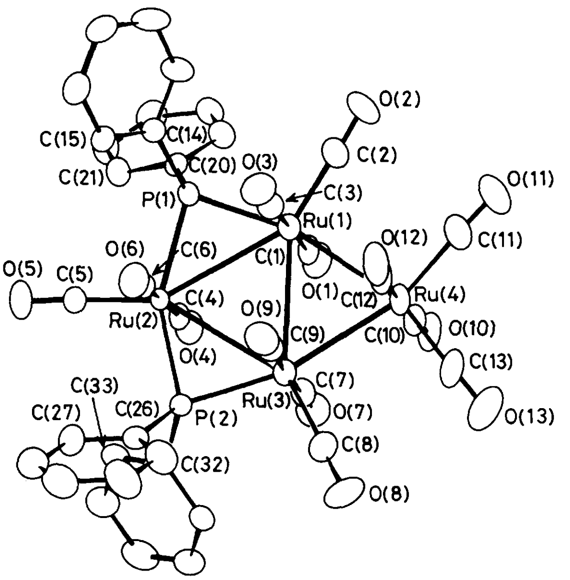

Figure 1. Molecular structure of cluster (**1**). Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 3.1594(4), Ru(1)–Ru(3) 3.1335(5), Ru(1)–Ru(4) 2.9098(4), Ru(2)–Ru(3) 3.1853(4), Ru(3)–Ru(4), 2.9170(4), Ru(1)–P(1) 2.317(1), Ru(2)–P(1) 2.350(1), Ru(2)–P(2) 2.355(1), Ru(3)–P(2) 2.315(1); Ru(1)–Ru(2)Ru(3) 59.19(1), Ru(1)–Ru(4)–Ru(3) 65.07(1), Ru(2)–Ru(1)–Ru(4) 118.34(1), Ru(2)–Ru(3)–Ru(4) 117.30(1), Ru(1)–P(1)–Ru(2) 85.21(2), Ru(2)–P(2)–Ru(3) 86.01(2).

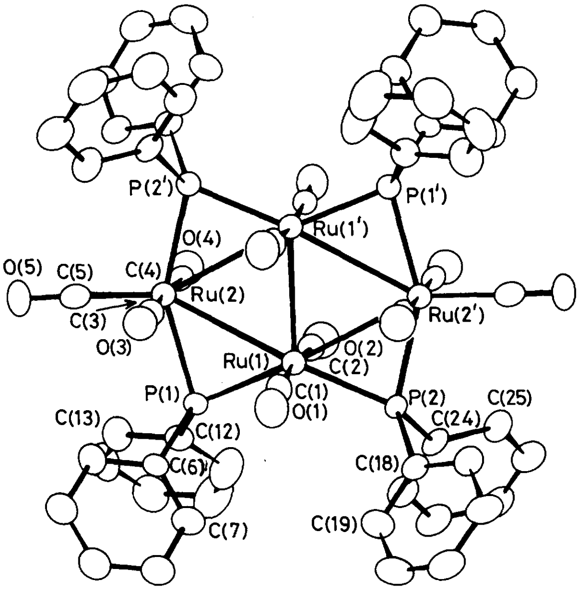

Figure 2. Molecular structure of cluster (**2**). Selected bond lengths (Å) and angles(°): Ru(1)–Ru(1') 2.8355(7), Ru(1)–Ru(2) 3.0610(7), Ru(1)–Ru(2') 3.0390(7), Ru(1)–P(1) 2.283(2), Ru(1)–P(2) 2.289(2), Ru(2)–P(1) 2.387(2), Ru(2)–P(2') 2.390(2); Ru(1)–Ru(2)–Ru(1') 55.40(1), Ru(2)–Ru(1)–Ru(2') 124.60(1), Ru(1')–Ru(1)–Ru(2) 61.91(1), Ru(1')–Ru(1)–Ru(2') 62.70(1), Ru(1)–P(1)–Ru(2) 81.89(4), Ru(1)–P(2)–Ru(2') 80.97(4), C(1)–Ru(1)–C(2) 173.5(3), C(3)–Ru(2)–C(4) 177.8(3), C(3)–Ru(2)–C(5) 90.2(3).

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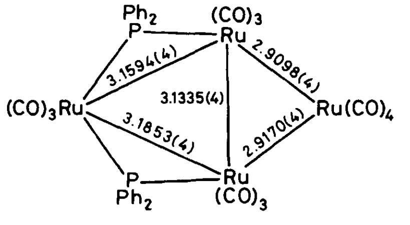
† The new clusters (**1**) and (**2**) were characterised by elemental analyses and i.r. and n.m.r. (^1H and ^{31}P) spectra. *Selected data* for (**1**): red crystals, i.r. $\nu_{CO}(C_6H_{12})$ 2075m, 2041s, 2030w, 2008m, and 1989m cm^{-1}; $^{31}P\text{-}\{^1H\}$ n.m.r. (C_6D_6) δ 118.8.

For (**2**): red crystals, i.r. $\nu_{CO}(CH_2Cl_2)$ 2062m, 2020s, 2004sh, 1979m, and 1949w; $^{31}P\text{-}\{^1H\}$ n.m.r. (CH_2Cl_2) δ 199.0.

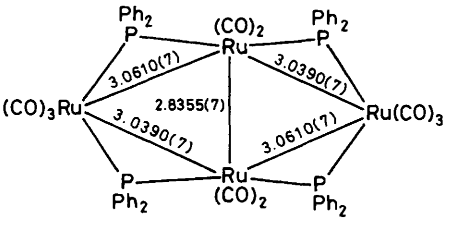
‡ *Crystal data* for (**1**): $Ru_4P_2O_{13}C_{37}H_{20}$, M = 1138.79, triclinic, space group $P\bar{1}$, a = 10.143(1), b = 12.860(2), c = 17.025(2) Å, α = 111.23(1), β = 90.64(1), γ = 102.54(1)°, U = 2010.8(5) Å^3, Z = 2, T = 294 K, D_c = 1.881 g cm^{-3}, $F(000)$ = 1104, λ = 0.71069 Å, μ(Mo-K_α) = 15.82 cm^{-1}. Intensity data were collected on a crystal of dimensions 0.22 × 0.25 × 0.25 mm mounted on a Syntex P2$_1$ diffractometer, by the ω scan technique ($2\theta \leqslant 50°$). From 7082 measured data, 5354 with $I \geqslant 3\sigma(I)$ were considered observed. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares to R and R_w values of 0.024 and 0.028.

For (**2**): $Ru_4P_4O_{10}C_{58}H_{40}\cdot 2CH_2Cl_2$, M = 1595.00, triclinic, space group $P\bar{1}$, a = 12.097(2), b = 14.385(3), c = 18.748(3) Å, α = 89.77(2), β = 102.55(1), γ = 92.90(1)°, U = 3180(1) Å^3, Z = 2**, D_c = 1.665 g cm^{-3}, $F(000)$ = 1576, T = 294 ± 1K, λ = 0.71069 Å, μ(Mo-K_α) = 12.32 cm^{-1}.

Intensity data were collected from an epoxy-coated crystal of dimensions 0.28 × 0.30 × 0.30 mm mounted on a Syntex P2$_1$ diffractometer using the θ–2θ scan method ($2\theta \leqslant 42°$). The structure was solved by Patterson and Fourier techniques using 5596 observed data [$I \leqslant 3\sigma(I)$] obtained from 6881 measured reflections. [**The structure contains two half-molecules per asymmetric unit located about inversion centres at 0,0,0 and 1/2,1/2,1/2. Structural parameters in the text and Figures 2 and 3 refer to one of these half molecules.] Full-matrix least-squares refinement gave R and R_w values of 0.032 and 0.038 respectively.



$Ru_4(CO)_{13}(\mu\text{-}PPh_2)_2$ (**1**)



$Ru_4(CO)_{10}(\mu\text{-}PPh_2)_4$ (**2**)

Figure 3. The central cores of (**1**) and (**2**) showing metal–metal distances.

phosphido-bridged ruthenium dimer $Ru_2(CO)_6(\mu\text{-}PPh_2)_2$.[6] In contrast, the hinge vector [Ru(1)–Ru(1′) = 2.8355(7) Å] is typical of an unsupported ruthenium–ruthenium single bond.

In cluster (**1**), a similar, though even more pronounced, metal–metal bond elongation is found. In contrast to (**2**), however, this feature is now confined to a triangle of ruthenium atoms, Ru(1)–Ru(2)–Ru(3), encompassing the two ruthenium–ruthenium vectors spanned by phosphido-bridge ligands and, perhaps surprisingly in light of the bonding characteristics of (**2**), the hinge vector Ru(1)–Ru(3). The average ruthenium–ruthenium distance within this triangle (3.160 Å) is now exceptionally long, being some 0.34 Å longer than is found in $Ru_2(CO)_6(\mu\text{-}PPh_2)_2$. The two remaining unsupported ruthenium–ruthenium bonds of 2.9098(4) Å [Ru(1)–Ru(4)] and 2.9170(4) Å [Ru(3)–Ru(4)] are close to values expected for ruthenium–ruthenium single bonds in electron precise tetraruthenium cluster complexes.[7]

In terms of a simple electron counting scheme, the butterfly configuration is associated with a 62-electron count and thus, clusters (**1**) and (**2**) formally represent electron rich members of this geometrical family. From the bonding characteristics discussed above, it is apparent that in both complexes the additional two electrons are placed in an orbital which contains a significant amount of metal–metal anti-bonding character. In cluster (**2**), this net anti-bonding effect is manifest in a lengthening of the four outer ruthenium–ruthenium bonds whereas in (**1**), the effect on the metal skeleton is restricted to one Ru_3 triangle. In this respect, (**1**) might be regarded as an electron rich 50-electron Ru_3 cluster in which two of the Ru–Ru bonds are bridged by $\mu\text{-}PPh_2$ moieties and one by an $Ru(CO)_4$ unit. We have carried out Extended Hückel Molecular Orbital calculations[8] on the model species $Ru_4(CO)_{13}(\mu\text{-}PH_2)_2$ and $Ru_4(CO)_{10}(\mu\text{-}PH_2)_4$ which indicate that 64-electron counts are favoured for these systems due to the near degeneracy of the two highest, doubly occupied MO's and the large energy gap between these HOMO's and the LUMO. There is a distinct analogy to $Pt_3(CO)_3(\mu\text{-}PH_2)_3{}^{3+}$ where the presence of phosphido bridges also generates a frontier orbital which is anti-bonding with respect to the metal framework.[9] Thus, it is clear that for these Ru_4 clusters, the phosphido bridging ligands play an important role in determining the detailed structural features and electron counts.

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References

1 (a) E. Sappa, A. Tiripicchio, A. J. Carty, and G. E. Toogood, *Prog. Inorg. Chem.*, 1987, **35**, 437; (b) D. G. Evans and D. M. P. Mingos, *Organometallics*, 1983, **2**, 435; (c) B. F. G. Johnson, 'Transition Metal Clusters,' Wiley, Chichester, 1980; (d) S. B. Colbran, B. F. G. Johnson, F. J. Lahoz, J. Lewis, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1988, 1199.

2 (a) A. J. Carty, S. A. MacLaughlin, J. Van Wagner, and N. J. Taylor, *Organometallics*, 1982, **1**, 1013; (b) R. D. Adams and L. W. Yang, *J. Am. Chem. Soc.*, 1983, **105**, 235; (c) M. R. Churchill, C. Bueno, and D. A. Young, *J. Organomet. Chem.*, 1981, **213**, 139.

3 L. R. Martin, F. W. B. Einstein, and R. K. Pomeroy, *Organometallics*, 1988, **7**, 294.

4 V. J. Johnson, F. W. B. Einstein, and R. K. Pomeroy, *J. Am. Chem. Soc.*, 1987, **109**, 8111.

5 A. K. Bhattacharyya, C. C. Nagel, and S. G. Shore, *Organometallics*, 1983, **2**, 1187.

6 F. Van Gastel, N. J. Taylor, and A. J. Carty, unpublished results.

7 D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.*, 1977, **16**, 2655.

8 Program ICONS: J. Howell, A. Rossi, D. Wallace, K. Haraki, and R. Hoffman, Q.C.P.E. 517, 1986, **6**, 100.

9 D. J. Underwood, R. Hoffman, K. Tatsumi, A. Nakamura, and Y. Yamamoto, *J. Am. Chem. Soc.*, 1985, **107**, 5968.

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