The Interconversion of Quasi-planar Butterfly and Tetrahedral Tetraruthenium Cluster Geometries: *X*-Ray Crystal Structure of Tetrahedral $[H_2Ru_4(CO)_{10}(\mu\text{-}PPh_2)_2]$

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The quasi-planar 64-electron butterfly cluster $[Ru_4(CO)_{13}(\mu\text{-}PPh_2)_2]$ reacts with dihydrogen under photolysis giving the 60-electron tetrahedral cluster $[H_2Ru_4(CO)_{10}(\mu\text{-}PPh_2)_2]$, a transformation which can be reversed under a pressure of carbon monoxide; the two hydride ligands in the unsymmetric $[H_2Ru_4(CO)_{10}(\mu\text{-}PPh_2)_2]$ have been located *via* a single crystal *X*-ray analysis.

Despite the importance of the reversible formation and cleavage of metal–metal bonds in dinuclear and cluster chemistry there are still only a relatively small number of well characterised examples of this phenomenon.[1] In this context the reversible addition of dihydrogen to a transition-metal cluster resulting in concomitant metal–metal bond cleavage–formation is perhaps the most important example in view of the catalytic implications of such a transformation. Only recently have processes involving the activation of dihydrogen at room temperature by transition-metal clusters been described.[2]

We have recently reported the synthesis and *X*-ray crystal structures of two 64-electron tetraruthenium cluster complexes $[Ru_4(CO)_{13}(\mu\text{-}PPh_2)_2]$ and $[Ru_4(CO)_{10}(\mu\text{-}PPh_2)_4]$, both of which adopt unusual quasi-planar butterfly geometries, a facet ascribed to the π-donor properties of the bridging phosphido ligand.[3] In our continuing studies in this area, we were interested in investigating the reactivity of these electron-rich molecules particularly with regard to their conversion to M_4 clusters with 62- or 60-electron counts and normal M–M bonds. We report here the addition of H_2 to the quasi-planar butterfly cluster $[Ru_4(CO)_{13}(\mu\text{-}PPh_2)_2]$ (**1**) which surpisingly leads to metal–metal bond formation. This represents an unprecedented example of dihydrogen activation with a net 4-electron loss and the transformation of a planar butterfly to a tetrahedral cluster.

Irradiation of a toluene solution of (**1**) whilst it was purged with a slow stream of dihydrogen (298 K; 25 min) resulted in the formation of two complexes, the known trinuclear cluster $[H_2Ru_3(CO)_8(\mu\text{-}PPh_2)_2]$(**2**)[4] (25%) and a new tetranuclear dihydride cluster (**3**)† (50%). Identification of (**3**) as a dihydride complex was based on the ^1H NMR spectrum, a triplet of doublets and a doublet of doublets being observed at high field [δ – 15.92, dt, *J* 18 and 2 Hz (H_A); –19.9, dt, *J* 9 and 2 Hz (H_B)]. The ^{31}P NMR spectrum (85% H_3PO_4 reference) exhibited doublets at 290 and 320 ppm (*J* 170 Hz) shifted considerably to low field with respect to the equivalent phosphido-bridges of the 64-electron (**1**) which are at high field (δ 119 ppm) as a result of the considerable elongation of the μ-PPh_2-bridged metal–metal vectors. Thus, while suggesting that (**3**) might be an electron-precise species, the NMR and analytical data did not allow an unequivocal structural assignment. An *X*-ray crystallographic study carried out on crystals grown from toluene–hexane provided further insight.‡

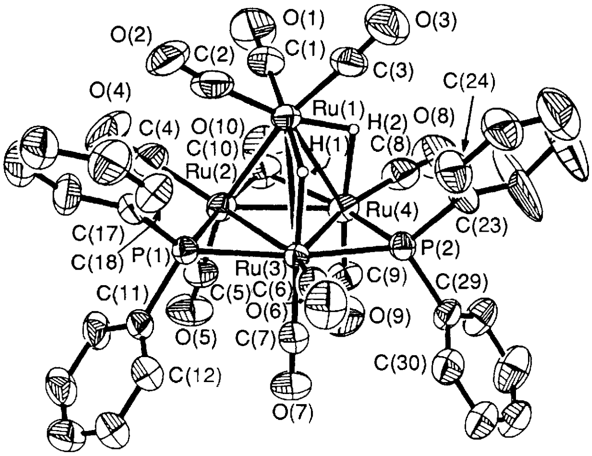

Figure 1. The molecular structure of $[H_2Ru_4(CO)_{10}(\mu\text{-}PPh_2)_2]$ (**3**). Important bond lengths and angles not mentioned in the text are: Ru(1)–Ru(2) 2.794(1); Ru(2)–P(1) 2.329(2); Ru(3)–P(1) 2.326(2); Ru(3)–P(2) 2.342(2); Ru(4)–P(2) 2.271(2) Å; Ru(2)–C(10)–Ru(4) 76.5(3); Ru(2)–P(1)–Ru(3) 75.3(1); Ru(3)–P(2)–Ru(4) 75.3(1)°.

As shown in Figure 1, complex (**3**) is identified as $[H_2Ru_4(CO)_{10}(\mu\text{-}PPh_2)_2]$ with a tetrahedral array of ruthenium atoms and associated with an outer valence electron count of 60. Two of the Ru–Ru vectors [Ru(2)–Ru(3) 2.844(1) Å and Ru(3)–Ru(4) 2.820(1) Å] are bridged by phosphido ligands whilst the third vector in the 'basal' plane, namely Ru(2)–Ru(4) [2.719(1) Å], is bridged unsymmetrically by a CO group [Ru(2)–C(10) 1.996(9) Å and Ru(4)–C(10) 2.370(11) Å]. The fourth ruthenium atom, Ru(1), caps this plane and is unique in that it carries three terminal carbonyl ligands. The *X*-ray analysis allowed the location of the two hydrides which bridge the Ru(1)–Ru(3) and Ru(1)–Ru(4) edges. These two hydride-bridged metal–metal bonds [Ru(1)–Ru(3) 3.021(1) Å and Ru(1)–Ru(4) 2.942(1) Å] are somewhat elongated when compared to the four remaining Ru–Ru distances. It is significant that the molecule is asymmetric and that at room temperature the hydrides are non-fluxional since transfer of a hydride from the Ru(1)–Ru(3) or Ru(1)–Ru(4) edges to the Ru(1)–Ru(2) vector would effectively create a plane of symmetry bisecting the tetrahedron. That such a process does not occur presumably indicates that a transition

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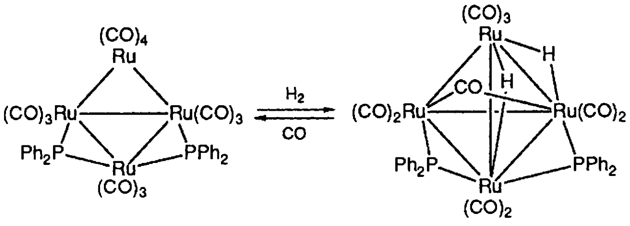
† The new cluster (**3**) was characterised by its IR and NMR (^1H and ^{31}P) spectra. Selected data for (**3**): IR, ν_{CO} (CH_2Cl_2) 2122w, 2076w, 2045vs, 2023s, 1987m, 1975m, and 1961m cm^{-1}.

‡ *Crystal data* for (**3**): $C_{34}H_{22}O_{10}P_2Ru_4$, M = 1056.78, orthorhombic, space group $P2_12_12_1$, a = 12.980(2), b = 14.112(2), c = 20.366(4) Å, U = 3709.8(11) Å^3, Z = 4, T = 295 K, D_c = 1.89 g cm^{-3}, $F(000)$ = 2048, λ = 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ = 17.05 cm^{-1}. Intensity data were collected on a crystal of dimensions 0.29 × 0.27 × 0.30 mm mounted on a Nicolet R_3m diffractometer, by the ω scan technique ($2\theta < 55°$). From 4738 measured data, 3875 with $I > 3\sigma(I)$ were considered observed. The structure was solved by Patterson and Fourier methods and refined by full matrix least-squares analysis to R and R_w values of 0.0314 and 0.0347. Refinement of the other enantiomorph (the space group is polar) gave R = 0.0325. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



(1) (3)

$[H_2Ru_3(CO)_8(\mu\text{-}PPh_2)_2]$

(2)

Scheme 1

state in which one of the hydrides H(1) or H(2) triply bridges a face of the tetrahedron is energetically disfavoured. Few triply bridging hydride ligands are known in clusters of high nuclearity.[5]

Complex (**3**) is formally derived from (**1**) by loss of three CO ligands, addition of H_2, and formation of a 'new' metal–metal bond, Ru(1)–Ru(3). In view of these pronounced changes it is even more remarkable that (**3**) can be transformed back to (**1**) upon addition of carbon monoxide (Scheme 1). Thus, exposure of (**3**) to carbon monoxide (70 atm) at 25 °C resulted in the formation of (**1**) in 35% isolated yield as the major product. While examples of the reversible interconversion of tetranuclear clusters upon addition–elimination of carbon monoxide and dihydrogen are known,[6] interconversions have not previously been accompanied by geometrical rearrangement of the metal core.

The isolation of $[H_2Ru_3(CO)_8(\mu\text{-}PPh)_2)_2]$ (**2**) from the UV-mediated hydrogenation of (**1**) indicates the competitive nature of the metal–metal bond formation–cleavage processes. It is interesting that (**2**) formally results from the cleavage of the two strongest ruthenium–ruthenium bonds in (**1**) *i.e.* those to the $Ru(CO)_4$ moiety; however, whether this occurs before or after hydrogen addition cannot be ascertained. Indeed, the observation that the reaction is UV-mediated (in the absence of UV irradiation no reaction was observed after 1 week) is suggestive of the latter, that is with the initial formation of a species '$H_2Ru_4(CO)_{13\text{-}n}(\mu\text{-}PPh_2)_2$' ($n$ = 0 or 1) which reacts further *via* metal–metal bond cleavage or formation.

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