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Preliminary communication

THE ABILITY OF CAPPING PHENYLPHOSPHINIDENE LIGANDS TO CONFER THE TRIGONAL PRISMATIC GEOMETRY ON HEXARUTHENIUM FRAMEWORKS

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Summary

Reaction of $[Ru_3(CO)_{12}]$ with a three-fold molar amount of $PPhH_2$ in toluene under reflux affords a range of products including two hexaruthenium species, $[Ru_6(\mu_4\text{-PPh})_2(\mu_3\text{-PPh})_2(CO)_{12}]$ and $[Ru_6(\mu_4\text{-PPh})_3(\mu_3\text{-PPh})_2(CO)_{12}]$, established X-ray crystallographically to have distorted trigonal prismatic skeletal geometries.

It is our contention that metal cluster compounds with strained, non-regular skeletal frameworks will be more reactive than related clusters with stable skeletal geometries and as a consequence will have more potential as homogeneous catalysts. We are employing edge-bridging and face-capping ligands to confer unusual and strained geometries on metal cluster frameworks and with the object of synthesising capped higher nuclearity clusters of ruthenium we have investigated the reaction of $[Ru_3(CO)_{12}]$ with $PPhH_2$.

As described previously, reaction of equimolar amounts of these precursors in toluene under reflux affords a range of products including $[Ru_3(\mu_3\text{-PPh})(\mu_2\text{-H})_2(CO)_9]$ (1), $[Ru_4(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(CO)_{10}]$ (2), $[Ru_5(\mu_4\text{-PPh})(CO)_{15}]$ (3), and a green product partially characterised as $[Ru_6(\mu\text{-PPh})_2(CO)_n]$ (n = 15 or 16) [1]. It has now been established that the corresponding reaction involving a three-fold molar amount of $PPhH_2$ affords a range of different products* which has been found to include $[Ru_3(\mu_3\text{-PPh})_2(CO)_9]$ (4), $[Ru_4(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(CO)_{10}]$ (2), $[Ru_4(\mu_4\text{-PPh})_2(\mu_2\text{-PPhH})_2(CO)_8]$ (5) and two hexanuclear compounds characterised as $[Ru_6(\mu_4\text{-PPh})_2(\mu_3\text{-PPh})_2(CO)_{12}]$ (6) and $[Ru_6(\mu_4\text{-PPh})_3(\mu_3\text{-PPh})_2(CO)_{12}]$ (7).

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*The reaction time was 8 h while separation of the products was effected column chromatographically (silica gel) using mixtures of CH_2Cl_2 and petroleum ether in varying proportions as eluents.

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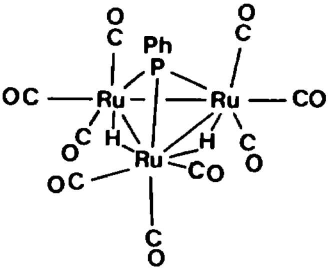
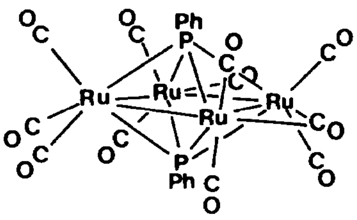


(1)



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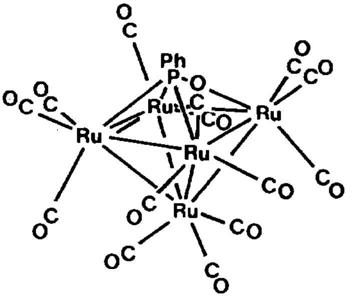

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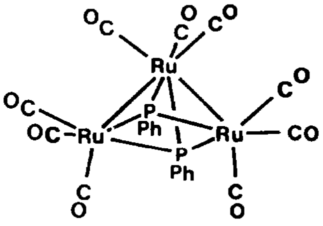

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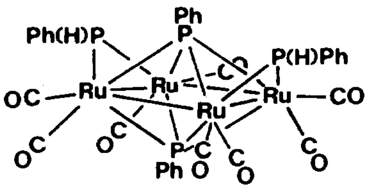

(5)

The molecular structures of both hexanuclear compounds have been determined by X-ray crystallography* and are illustrated in Fig. 1 and 2 and 2 and 3 respectively; in each case only one of the two crystallographically independent molecules per asymmetric unit is shown. Since, for both compounds, the two independent molecules are geometrically very similar, the following discussion

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*Crystal data for **6**: $C_{36}H_{20}O_{12}P_4Ru_6$. M = 1374.66, triclinic, space group $P\bar{1}$, a 21.88(3), b 21.13(3), c 9.98(1) Å, α 93.1(1), β 90.3(1), γ 98.6(1)°, U 4553 Å^3. D_c 2.0 g cm^{-3} for Z = 4. F(000) = 2800, λ(Mo-K_α) = 0.71069 Å, μ(Mo-K_α) = 21 cm^{-1}. 12076 reflections were measured on a Philips PW1100 diffractometer (N.P.R.L., C.S.I.R., Pretoria), 10078 of which were classed as observed ($I > 3\sigma(I)$). Data were corrected for Lorentz and polarisation effects but not absorption. The structure was solved by standard direct and Fourier methods and refined by full-matrix least-squares methods to R = 0.067 with the Ru and P atoms being assigned anisotropic temperature factors, and the O and C atoms averaged isotropic temperature factors

Crystal data for **7**: $C_{42}H_{25}O_{12}P_5Ru_6$. M = 1482.69, monoclinic, space group Cc, a 23.82(3), b 23.36(3), c 23.60(3) Å, β 103.0(1)°, U 12802 Å^3. D_c = 1.54 g cm^{-3} for Z = 8. F(000) = 5120, λ(Mo-K_α) 0.71069 Å, μ(Mo-K_α) 15 cm^{-1}. Of the 8883 reflections measured (as for **6**), 7446 were classed as observed ($I > 3\sigma(I)$). The structure was solved by multisolution tangent refinement and Fourier techniques and refined by full-matrix least-squares methods to R = 0.102 with Ru atoms being assigned anisotropic temperature factors, the P, O and carbonyl C atoms individual isotropic temperature factors and the phenyl C atoms averaged isotropic temperature factors.

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

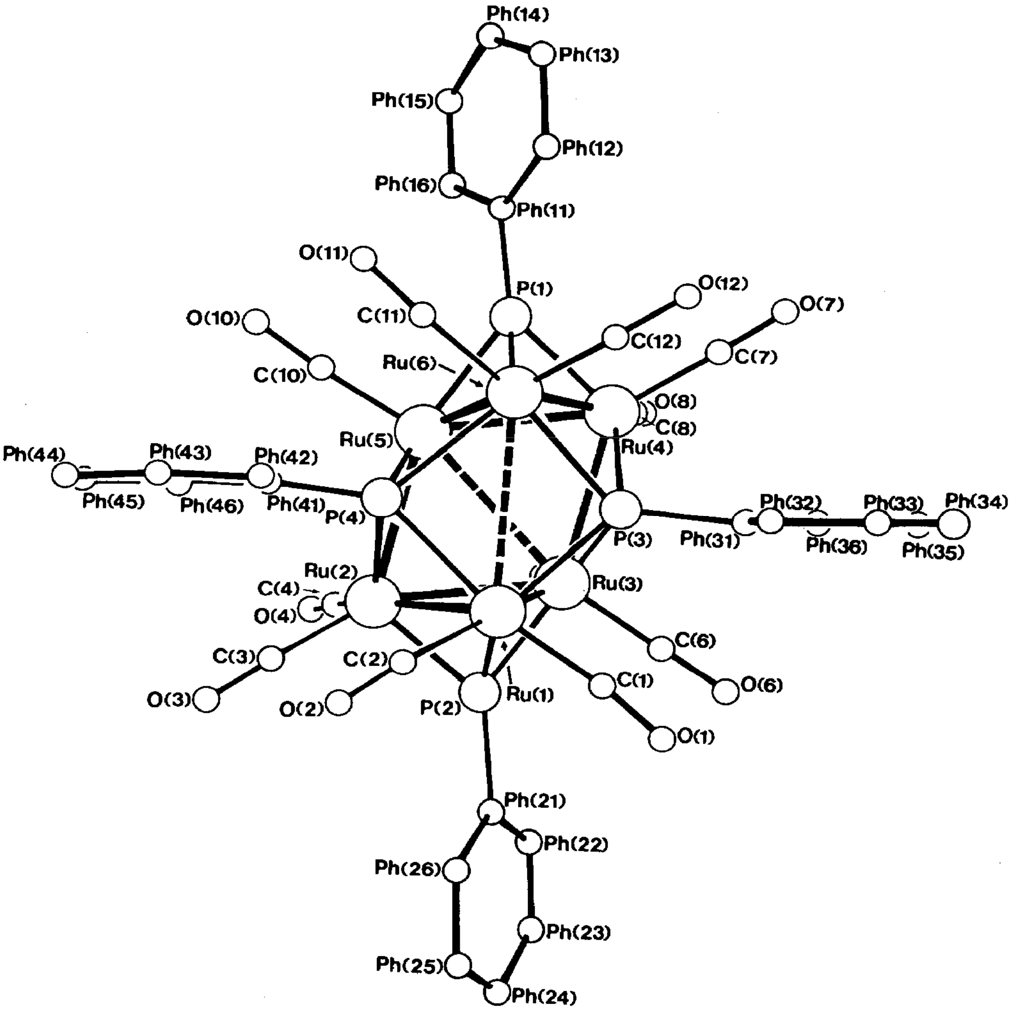

Fig. 1. The molecular stereochemistry of [$Ru_6(\mu_4\text{-PPh})_2(\mu_3\text{-PPh})_2(CO)_{12}$]. Relevant interatomic distances: Ru(1)—Ru(2), 2.860(2); Ru(1)—Ru(3), 2.855(2); Ru(1)—Ru(6), 3.248(2); Ru(2)—Ru(3), 2.876(2); Ru(2)—Ru(5), 2.808(2); Ru(3)—Ru(4), 2.836(2); Ru(3)—Ru(5), 3.233(2); Ru(4)—Ru(5), 2.867(2); Ru(4)—Ru(6), 2.861(2); Ru(5)—Ru(6), 2.857(2) Å.

is based on mean values for chemically equivalent distances and angles. The six ruthenium atoms in both compounds adopt a distorted trigonal prismatic geometry with both triangular faces and two of the three square faces being capped by a phenylphosphinidene ligand in the case of compound 6 and all five faces being capped by this ligand in the case of compound 7. For both compounds the coordination to each ruthenium is completed by two terminal carbonyl groups. The distortion in 6 can be described to a first approximation in terms of a torsional twist of the Ru(1)Ru(2)Ru(3) plane through an angle of 12° about the approximate three-fold axis, away from the eclipsed, trigonal prismatic geometry towards the staggered octahedral configuration; the square planar faces of the hypothetical trigonal prism are present as rhomboidal non-planar moieties with the folding about the Ru(3)—Ru(5) diagonal being 12.3°, that about the Ru(2)—Ru(6) diagonal being 18.5° and that about the Ru(1)—Ru(4)

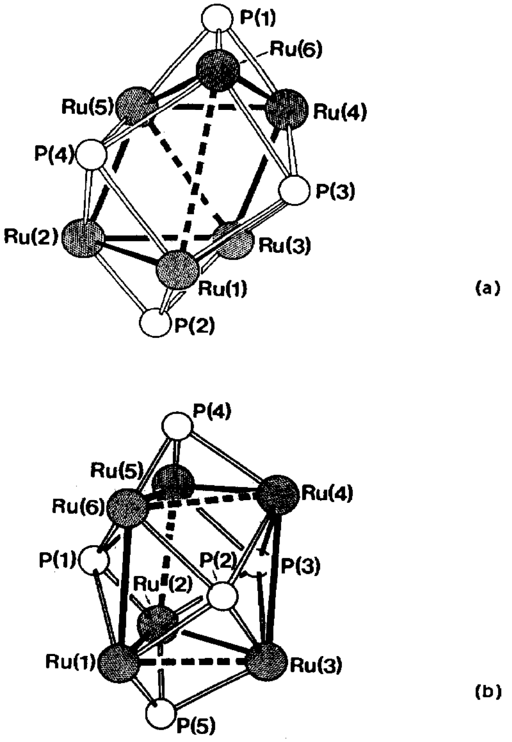

Fig. 2. (a) The geometry of the Ru_6P_4 framework in $[Ru_6(\mu_4\text{-}PPh)_2(\mu_3\text{-}PPh)_2(CO)_{12}]$; (b) The geometry of the Ru_6P_5 framework in $[Ru_6(\mu_4\text{-}PPh)_3(\mu_3\text{-}PPh)_2(CO)_{12}]$.

diagonal being 19.0°. The skeletal framework is subjected to further perturbation as reflected by the two triangular faces not being parallel to each other (dihedral angle 13.1°) and by eight of the ruthenium—ruthenium distances being short (2.808(2)—2.876(2) Å), two being intermediate (3.233(2) and 3.248(2) Å, and five being long (3.938(2)—4.659(2) Å) (see Fig. 1); a trigonal prismatic skeletal framework has nine short and six long metal—metal distances whereas an octahedral framework has twelve short and three long ones.

The distortion of the metal atom framework in compound **7** is different from that in compound **6** in that it can be described in terms of a simple expansion of the skeletal polyhedron. However, this expansion does not correspond to a symmetric elongation along the three-fold axis (cf. $[Pt_6(\mu_2\text{-}CO)_6(CO)_6]^{2-}$ [2]) but to a lengthening of two corresponding edges of the two triangular faces, one to a greater extent than the other (Ru(1)—Ru(3) 3.325(5), Ru(4)—Ru(6) 3.515(5) Å), and to an elongation of the axial ruthenium—ruthenium vector directly opposite to the two longer equatorial ruthenium—ruthenium distances (Ru(2)—Ru(5) 3.239(6) Å). This distortion results in a lowering of the symmetry of the metal atom framework from D_{3h} to C_{2v}; in contrast to that found in compound **6** there is effectively no torsional twist about the three-fold axis.

Although hexanuclear clusters with trigonal prismatic geometries are known, all, apart from $[Pt_6(\mu_2\text{-}CO)_6(CO)_6]^{2-}$ [2], contain encapsulated atoms as in $[M_6(N)(\mu_2\text{-}CO)_9(CO)_6]^-$ (M = Co or Rh) [3] and $[Rh_6(C)(\mu_2\text{-}CO)_9(CO)_6]^{2-}$

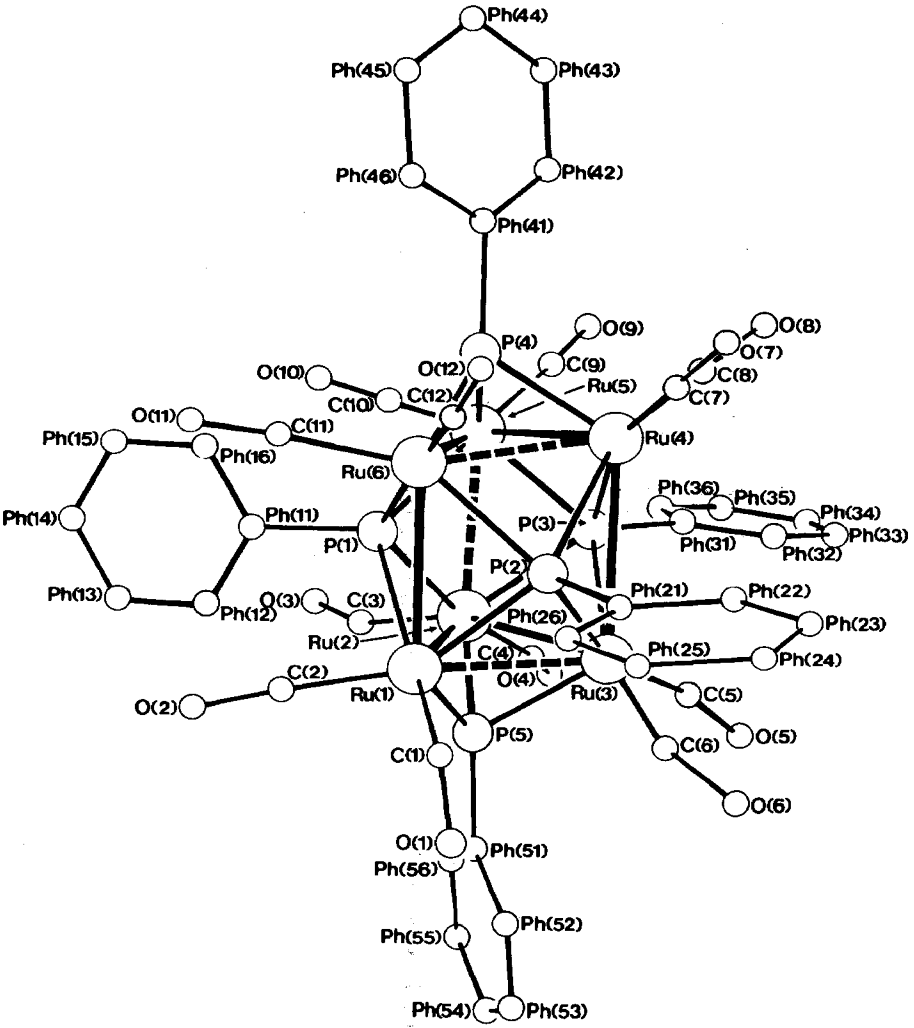

Fig. 3. The molecular stereochemistry of [Ru$_6$(μ_4-PPh)$_3$(μ_3-PPh)$_2$(CO)$_{12}$]. Relevant interatomic distances: Ru(1)—Ru(2), 2.921(5); Ru(1)—Ru(3), 3.325(5); Ru(1)—Ru(6), 2.920(6); Ru(2)—Ru(3), 2.851(5); Ru(2)—Ru(5), 3.239(5); Ru(3)—Ru(4), 2.957(5); Ru(4)—Ru(5), 2.831(5); Ru(4)—Ru(6), 3.515(5); Ru(5)—Ru(6), 2.959(5) Å.

[4]). Furthermore the former has four electrons less than the ninety valence electrons normally associated with a trigonal prismatic configuration [5]. Compounds 6 and 7 are thus unusual in adopting this geometry and are the first examples of hexaruthenium clusters with trigonal prismatic frameworks.

[Ru$_6$(μ_4-PPh)$_2$(μ_3-PPh)$_2$(CO)$_{12}$] has 88 valence electrons and, on the basis that a capped polyhedral cluster has the same number of bonding skeletal molecular orbitals as the parent uncapped polyhedron, would be predicted to adopt a metal framework structure intermediate between octahedral and trigonal prismatic [6]. The description given above of the solid state structure of this compound is indeed consistent with this prediction but only to a first approximation since additional perturbations were also noted. Compound 7 contains 92 valence electrons and, again on the basis that the capping ligands will not influence the number of bonding skeletal molecular orbitals, would be expected to adopt a trigonal prismatic geometry, but distorted due to the occupancy of an anti-bonding orbital by the two electrons in excess of 90. However, Mingos and Forsyth have calculated that capped metal cluster compounds containing a "larger" number of capping ligands do not have the same number of bonding skeletal molecular orbitals as their uncapped parent clusters [5]. On this basis compound 7 should rather be described in terms of a tricapped trigonal prismatic skeletal framework and because of the presence of ten skeletal pairs of electrons, a regular trigonal prismatic disposition of the six ruthenium atoms would be predicted, contrary to that observed.

It is thus apparent that while current bonding theories can predict the geometries of the metal atom framework of compounds 6 and 7, they can only do so to a first approximation and cannot account for the various distortions observed. These are considered to be imposed by the capping phenylphosphinidene ligands, although the origin of the imposition cannot be ascertained at this stage. Significantly, increased donation of electron density to the metal core of butterfly complexes has been found to lead to an increase in the dihedral angle and to an unequal lengthening of some of the edges [7]. However, steric effects have also been established to play an important role in the determination of the geometry of clusters [8].

The low temperature (−90°C) ^{31}P nuclear magnetic resonance spectrum of compound 7 is consistent with the solid state structure exhibiting a triplet of doublets at δ 503.0, an overlapping triplet of doublets at 407.4 and an overlapping triplet of triplets at −141.7 ppm (relative to H_3PO_4) assigned to the two equivalent quadruply capping, to the two equivalent triply capping and to the unique quadruply capping phenylphosphinidene ligands respectively. Increase in temperature to 30°C leads to the collapse of the two outer sets of resonances while further increase leads to the formation of a new multiplet at 281 ppm (the weighted average). It is thus apparent that at room temperature the quadruply capping phenylphosphinidene ligands are equivalent on the NMR time scale. It is unlikely that these ligands migrate around the skeletal framework as frequently observed for carbon monoxide and hydrogen and as a consequence this fluxional process must involve the metal atom core. Although the facile rearrangement of the skeletal frameworks of metal clusters has been noted previously, established examples thereof are limited to clusters of rhodium and platinum [9—11] or to homo- or hetero-nuclear species containing gold [12—17].

The ^{31}P NMR spectrum of compound 6 exhibits two triplets both at room temperature (578 and 415 ppm) and at −90°C, consistent with the solid state structure, assigned to the two equivalent quadruply capping and the two equivalent triply capping phenylphosphinidene ligands respectively.

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