

Preliminary communication

Conversion of a phenylphosphinidene-capped ruthenium cluster compound with a *closo*-octahedral Ru_4P_2 framework to one with a *closo*-trigonal prismatic skeleton by the addition of carbon monoxide and protons

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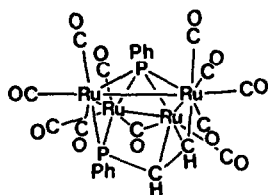
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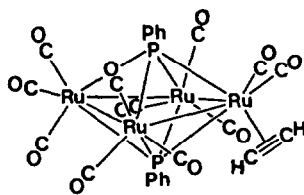
Abstract

Treatment of $[\text{Ru}_4(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(\text{CO})_{10}]$ with NaBH_4 leads to the formation of $[\text{Ru}_4(\mu_4\text{-PPh})_2(\mu_2\text{-H})(\mu_2\text{-CO})_2(\text{CO})_8]^-$ which readily adds protons and carbon monoxide to produce $[\text{Ru}_4(\mu_3\text{-PPh})_2(\mu_2\text{-H})_2(\text{CO})_{12}]$; X-ray crystallographic studies have revealed that while the Ru_4P_2 framework adopts a *closo* octahedral geometry in $[\text{Ru}_4(\mu_4\text{-PPh})_2(\mu_2\text{-H})(\mu_2\text{-CO})_2(\text{CO})_8]^-$, it adopts a *closo* trigonal prismatic one in $[\text{Ru}_4(\mu_3\text{-PPh})_2(\mu_2\text{-H})_2(\text{CO})_{12}]$

We have previously established that the seven skeletal electron pair (S.E.P.) species $[\text{Ru}_4(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(\text{CO})_{10}]$ (I) containing a *closo*-octahedral skeletal framework [1] reacts readily with both carbon monoxide and acetylene under mild conditions, reversibly in the case of the former, to produce the nine S.E.P. derivative $[\text{Ru}_4(\mu_3\text{-PPh})_2(\text{CO})_{13}]$ (III) [2] and the ten S.E.P. product $[\text{Ru}_4(\mu_4\text{-PPh})\{\mu_4\text{-}\eta^3\text{-P(Ph)CHCH}\}(\mu_2\text{-CO})(\text{CO})_{10}]$ (IV) [3], respectively; the latter results from the formal insertion of the acetylene into one of the capping phosphinidene ligands. The



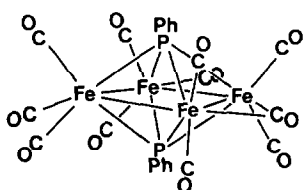
(IV)



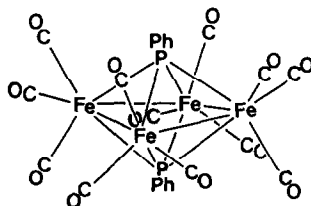
(V)

obvious intermediates in these reactions viz. the eight S.E.P. species $[\text{Ru}_4(\mu_4\text{-PPh})_2(\text{CO})_{12}]$ (II) and $[\text{Ru}_4(\mu_4\text{-PPh})_2(\text{CO})_{11}(\eta^2\text{-C}_2\text{H}_2)]$ (V), could not be detected.

This behaviour contrasts with that of $[\text{Fe}_4(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(\text{CO})_{10}]$ (VI) which gives solely the eight S.E.P. derivative $[\text{Fe}_4(\mu_4\text{-PPh})_2(\text{CO})_{12}]$ (VII) on reaction with



(VI)



(VII)

carbon monoxide [4,5]. Halet, Hoffmann and Saillard have analysed the electronic structures of octahedral clusters with $M_4(\mu_4\text{-E})_2$ frameworks (M = transition metal, E = PPh, S, etc.) and shown that systems with eight S.E.P.'s are favoured for more electronegative metals such as cobalt while those with seven S.E.P.'s are favoured for less electronegative metals such as ruthenium [6,7]. With the object of establishing whether an eight S.E.P. product could be obtained using a much smaller ligand, notwithstanding the above, the reaction of compound I with BH_4^- (source of H^-) was investigated.

Treatment of the purple undecacarbonyl with the borohydride in THF gave a red-brown reaction mixture which contained two products according to ^{31}P NMR spectroscopic evidence. Dissolution of the residue from this reaction in methanol followed by addition of $[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ resulted in the separation of a dark blue precipitate, shown to be the bis(triphenylphosphine)iminium salt of one of the products and characterised as $[(\text{Ph}_3\text{P})_2\text{N}][\text{Ru}_4(\mu_4\text{-PPh})_2(\mu_2\text{-H})(\mu_2\text{-CO})_2(\text{CO})_8]$ (PPN, IX). The second product could not be isolated sufficiently pure for characterisation, but is believed to be $[\text{Ru}_4(\mu_3\text{-PPh})_2(\mu_2\text{-H})(\text{CO})_{12}]^-$ (X) (vide infra).

The structure of IX has been determined X-ray crystallographically * and the geometry of the anion is illustrated in Fig. 1. As in compound I the the Ru_4P_2 framework adopts a *closo*-octahedral configuration but with two opposite Ru-Ru edges being bridged by two carbonyl groups. The hydride ligand, identified spectroscopically (^1H NMR), is presumed to bridge a third Ru-Ru edge; the equal distances of the opposite edges, crystallographically imposed, is reconciled in terms of the bridging hydrogen atom being disordered as described in the footnote.

* *Crystal data:* $\text{C}_{58}\text{H}_{41}\text{NO}_{10}\text{P}_2\text{Ru}_4$. $M = 1439.80$, triclinic, $P\bar{1}$, a 9.152(6), b 12.067(8), c 13.556(9) Å, α 93.72(2); β 98.55(2); γ 92.06(2)°, U 1475.81 Å³. D_c 1.62 g cm⁻³ for $Z = 1$. $F(000) = 712$, $\lambda(\text{Mo-K}\alpha)$ 0.71069 Å, $\mu(\text{Mo-K}\alpha)$ 10.41 cm⁻¹. 4735 unique reflections were measured on a Nonius CAD-4 diffractometer in the range $3 \leq \theta \leq 25^\circ$ (N.C.R.L., C.S.I.R., Pretoria) 3858 of which were classed as observed ($I > 4\sigma(I)$). The structure was solved using the automatic Patterson routine of SHELXS-86 [8] and refined (SHELX-76 [9]) by full-matrix least-squares methods to $R = 0.072$ ($R_w = 0.084$), with anisotropic temperature factors for the Ru and P atoms, and individual isotropic temperature factors for the remaining non-H atoms. The phenyl rings in the cation were refined as rigid hexagons. Both the cation and the anion are located on centres of symmetry in the crystal. This implies that the H atom in the anion is disordered, probably by bridging opposite edges of the Ru_4 square alternately. Convergence was achieved with the final refinement and a final difference map was featureless with a maximum peak height of 1.5 eÅ⁻³. Tables of atomic coordinates and full lists of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Center.

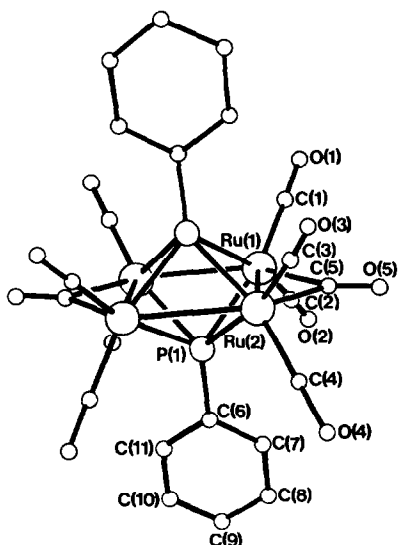
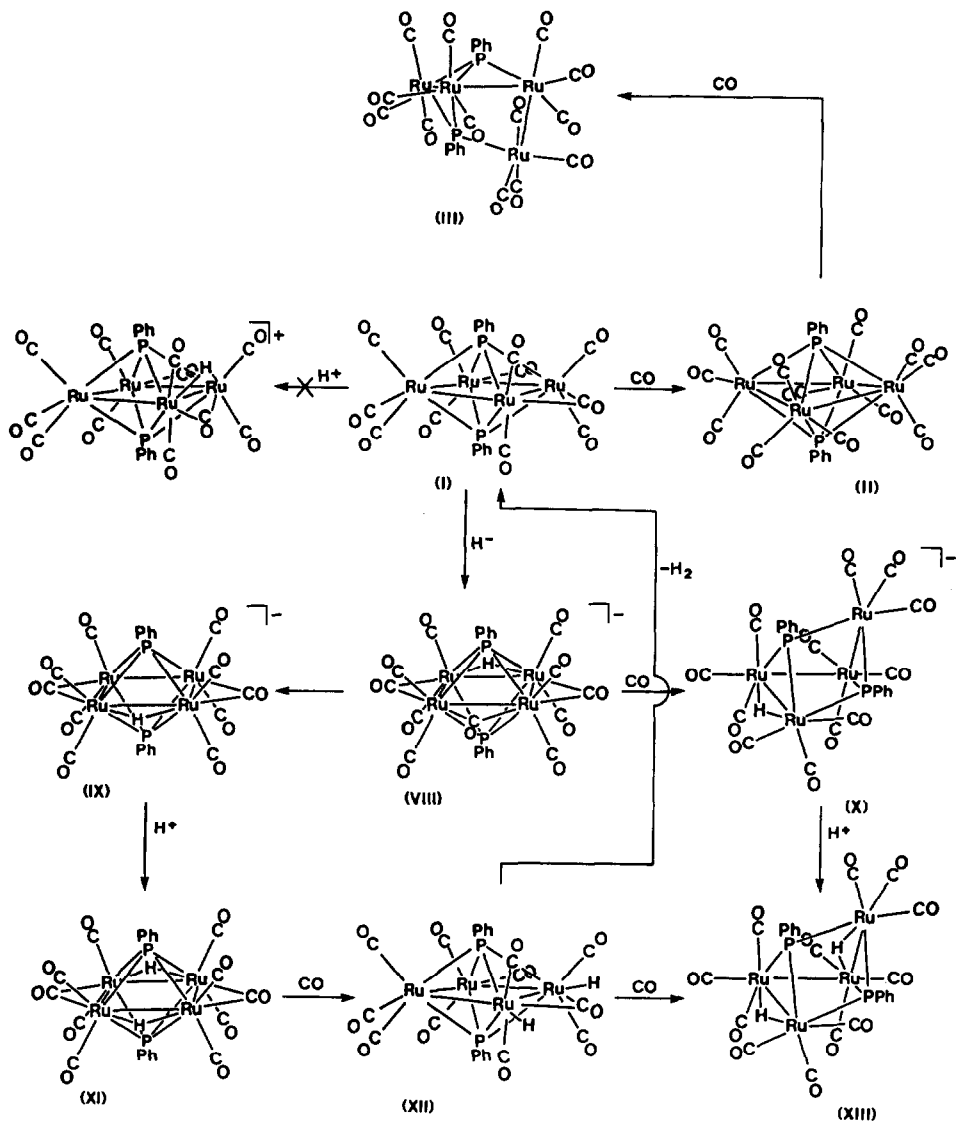


Fig. 1. The stereochemistry of the $[\text{Ru}_4(\mu_4\text{-PPh})_2(\mu_2\text{-H})(\mu_2\text{-CO})_2(\text{CO})_8]^-$ anion. The anion possesses a crystallographically imposed centre of symmetry (see text). Relevant interatomic distances (\AA): Ru(1)–Ru(2), 2.770(1); Ru(1)–Ru(2)', 2.922(1); Ru(1)–P(1), 2.443(2); Ru(2)–P(1), 2.453(1); Ru(1)–P(1)', 2.440(2); Ru(2)–P(1)', 2.450(1); Ru(1)–C(5), 2.059(9); Ru(2)–C(5), 2.081(9).

Compound IX is readily protonated and on reaction with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ gives a reaction mixture from which purple $[\text{Ru}_4(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(\text{CO})_{10}]$ (I) and a yellow product characterised as $[\text{Ru}_4(\mu_3\text{-PPh})_2(\mu_2\text{-H})_2(\text{CO})_{12}]$ (XIII) could be isolated. Decomposition of some $[\text{Ru}_4(\mu_4\text{-PPh})_2(\mu_2\text{-H})(\mu_2\text{-CO})_2(\text{CO})_8]^-$ was observed to occur during the reaction, explaining the source of CO for the formation of XIII, but products which could be assigned as the seven and eight S.E.P. species of formulation $[\text{Ru}_4(\mu\text{-PPh})_2(\mu\text{-H})_2(\text{CO})_{10}]$ and $[\text{Ru}_4(\mu_4\text{-PPh})_2(\mu\text{-H})_2(\text{CO})_{11}]$ and of possible structures XI and XII respectively (see Scheme 1), could not be detected in the reaction mixture. Nevertheless it is proposed that the protonation of IX produces the dihydride XI which rapidly scavenges CO to give $[\text{Ru}_4(\mu\text{-PPh})_2\text{H}_2(\text{CO})_{11}]$ (XII). It is also suggested that the latter rapidly reacts further, either reductively eliminating H_2 to give the parent species $[\text{Ru}_4(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(\text{CO})_{10}]$ (I) or scavenging CO to produce $[\text{Ru}_4(\mu_3\text{-PPh})_2(\mu_2\text{-H})_2(\text{CO})_{12}]$ (XIII). Significantly, previous studies have shown that compound I is unreactive towards hydrogen at pressures up to ten atmospheres [2] and even with CO/ H_2 mixtures only affords $[\text{Ru}_4(\mu_3\text{-PPh})_2(\text{CO})_{13}]$ (III).

A crystal structure determination on compound XIII* has revealed that the

* *Crystal data:* $\text{C}_{24}\text{H}_{12}\text{O}_{12}\text{P}_2\text{Ru}_4 \cdot \text{C}_6\text{H}_{14}$. $M = 1044.45$, triclinic, $P\bar{1}$, a 10.533(6), b 13.069(7), c 14.279(8) \AA , α 62.28(2); β 84.27(2); γ 84.54(2) $^\circ$, U 1728.6 \AA^3 . D_c 2.00 g cm^{-3} for $Z = 2$. $F(000) = 1016$, $\lambda(\text{Mo-K}\alpha)$ 0.71069 \AA , $\mu(\text{Mo-K}\alpha)$ 16.28 cm^{-1} . 9447 unique reflections were measured on a Nonius CAD-4 diffractometer in the range $3 \leq \theta \leq 25^\circ$ (N.C.R.L., C.S.I.R., Pretoria), 8281 of which were classed as observed ($I > 3\sigma(I)$). Data were corrected for Lorentz and polarisation effects and also for absorption using the empirical method. The structure was solved by direct methods and refined (SHELX-76 [9]) by full-matrix least-squares methods to $R = 0.046$ ($R_w = 0.053$), with anisotropic temperature factors for the Ru and P atoms, and individual isotropic temperature factors for the remaining non-H atoms. Convergence was achieved with the final refinement and a final difference map was featureless with a maximum peak height of 1.5 $\text{e}\text{\AA}^{-3}$.



Scheme 1. The structure depicted for each of VIII and XII is only one of a number of possibilities.

Ru₄P₂ framework adopts a slightly distorted trigonal prismatic structure with the phosphorus atom occupying opposite vertices of one of the square faces (see Fig. 2). The two hydride ligands could not be detected crystallographically but are equivalent and presumably bridging on the basis of the ¹H and ³¹P NMR spectroscopic results and are assumed to bridge the Ru-Ru edges of both triangular faces. The structure of XIII is analogous to those of [Os₄(μ₃-S)₂(μ₂-H)₂(CO)₁₂] and [Os₄(μ₃-Se)₂(μ₂-H)₂(CO)₁₂] [10].

Compound IX also readily adds carbon monoxide in the absence of protons. Attempts to isolate the carbonylation product pure for characterisation purposes

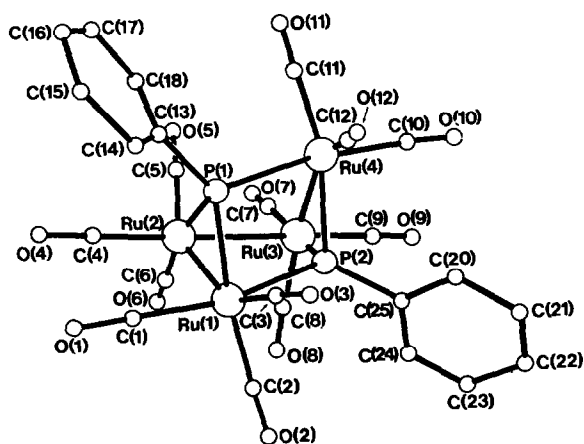


Fig. 2. The molecular stereochemistry of $[\text{Ru}_4(\mu_3\text{-PPh})_2(\mu_2\text{-H})_2(\text{CO})_{12}]$. Relevant interatomic distances (Å): Ru(1)–Ru(2), 3.000(1); Ru(2)–Ru(3), 2.886(1); Ru(3)–Ru(4), 2.993(1); Ru(1)–P(1), 2.380(1); Ru(2)–P(1), 2.338(1); Ru(4)–P(1), 2.406(1); Ru(1)–P(2), 2.405(1); Ru(3)–P(2), 2.337(1); Ru(4)–P(2), 2.371(1).

proved unsuccessful; however it is assumed to have the stoichiometry $[(\text{Ph}_3\text{P})_2\text{N}][\text{Ru}_4(\mu\text{-PPh})_2(\mu\text{-H})(\text{CO})_{12}]$ (PPN,X) with a trigonal prismatic geometry for the anion based on IR and ^1H and ^{31}P NMR spectroscopic evidence and by analogy with the above results. The anion X is also formed as one of the products of the reaction of $[\text{Ru}_4(\mu_4\text{-PPh})_2(\mu_2\text{-CO})(\text{CO})_{10}]$ with NaBH_4 (vide supra).

The reactions described in this communication are summarised in Scheme 1. Although not all compounds illustrated in the scheme were isolated, it is significant that all those that were characterised are either seven or nine S.E.P. species and, furthermore, it is particularly significant that no eight S.E.P. system could be detected in the reaction of compound IX with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in the presence of a limited amount of CO. This is consistent with our previous findings that eight S.E.P. Ru_4P_2 compounds are unstable with respect to their corresponding seven or nine/ten S.E.P. derivatives. The change in geometry of the Ru_4P_2 framework in $[\text{Ru}_4(\mu_4\text{-PPh})_2(\mu_2\text{-H})(\mu_2\text{-CO})_2(\text{CO})_8]^-$ from octahedral to trigonal prismatic, by addition of CO and H^+ under very mild conditions, is most unusual, although it has been predicted that while nine S.E.P. $\text{M}_4(\mu_4\text{-E})_2$ cluster systems containing more electronegative metals will adopt a *nido*-pentagonal bipyramidal structure, as found for $[\text{Co}_4(\mu_4\text{-PPh})_2(\text{CO})_3\{\mu\text{-F}_2\text{PN}(\text{Et})\text{PF}_2\}_4]$ [11], those with less electronegative metals will adopt trigonal prismatic geometries [6].

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