$Rh_4(\mu_4\text{-}PPh)_2$(cyclo-octa-1,5-diene)$_4$. A Doubly Co-ordinatively Unsaturated Phosphinidene-bridged Cluster without Carbonyl Ligands

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The new cluster $Rh_4(\mu_4\text{-}PPh)_2(cod)_4$ (cod = cyclo-octa-1,5-diene) has been prepared by the reaction of Li_2PPh with $Rh_2(\mu\text{-}Cl)_2(cod)_2$ or the reaction of $Rh_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)(cod)_2$ with $Li[BHEt_3]$ and has been spectroscopically and structurally characterized.

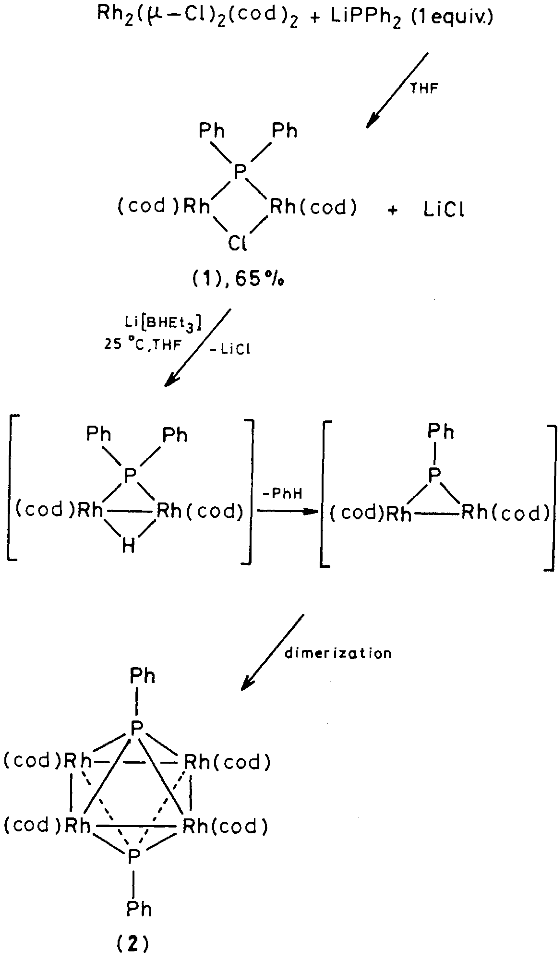
In order to assess fully the catalytic properties of polynuclear compounds, a need exists for the synthesis of new clusters which contain catalytically active metals and which are either co-ordinatively unsaturated, or have the means to generate easily open co-ordination sites. Polynuclear Rh complexes which possess phosphorus donor ligands, hydride, and/or polyolefin ligands, but no or few carbonyl groups, would appear ideal for such studies. Described herein is the synthesis and characterization of one such compound, $Rh_4(\mu_4\text{-}PPh)_2(cod)_4$ (cod = cyclo-octa-1,5-diene), (**2**), which we expect to show a rich derivative chemistry.

The synthesis of (**2**) first involves the preparation of the monophosphido-bridged Rh_2 complex (**1**) (Scheme 1). Complex (**1**) has been characterized spectroscopically and appears similar to the bis(diphenylphosphido)-bridged Rh_2 complexes previously described by Kreter and Meek:[1] $^{31}P\{^1H\}$ (C_6D_6, 22 °C) δ 23.2 p.p.m. [t, $J(^{31}P\text{–}^{103}Rh)$ 112.3 Hz]; *m/z* (fast atom bombardment) 642 (M^+), 607 ($M-Cl^+$), 565 ($M-Ph^+$), and 536 ($M-cod^+$). When (**1**) is treated with one equivalent of $Li[BHEt_3]$ in tetrahydrofuran (THF) an immediate green to red colour change occurs and red crystals of (**2**) slowly deposit upon solvent evaporation (Scheme 1). The mechanism of the (**1**) → (**2**) transformation is unknown but that outlined in Scheme 1 seems most reasonable. Replacement of Cl^- in (**1**) by hydride from $[BHEt_3]^-$ would be expected. Elimination of benzene (detected by g.c.) from the presumed hydride-phosphide complex with subsequent dimerization of the $Rh_2(\mu\text{-}PPh)(cod)_2$ intermediate would give (**2**). Cluster (**2**) has also been prepared by the direct reaction of $Rh_2(\mu\text{-}Cl)_2(cod)_2$ with Li_2PPh, equation (1). Although seemingly straightforward, this reaction actually gives a mixture of compounds of which (**2**) constitutes *ca.* 28% of the product mixture but is the only compound presently identified.

$$2Rh_2(\mu\text{-}Cl)_2(cod)_2 + 2Li_2PPh \longrightarrow (\mathbf{2}) + LiCl \qquad (1)$$

Cluster (**2**) has been spectroscopically and structurally characterized. Its $^{31}P\{^1H\}$ n.m.r. spectrum shows a quintet at δ + 65.75 p.p.m. with $J(^{31}P\text{–}^{103}Rh)$ 47.8 Hz, implying equivalent phosphorus nuclei coupling to four equivalent Rh atoms. An ORTEP drawing of (**2**) is shown in Figure 1.[†] The molecule consists of a planar array of four Rh atoms, capped above and below the plane by bridging μ_4-PPh ligands, and each Rh is further co-ordinated by a cod ligand. The Rh–Rh distances (2.843 Å average) are *ca.* 0.1 Å longer than typical Rh–Rh single bonds [*e.g.*, 2.732 Å average in $Rh_4(CO)_{12}$[2]] but are still consistent with direct Rh–Rh bonding in (**2**). Cluster (**2**) belongs to the growing family of $M_4(\mu_4\text{-}PR)_2$ clusters[3] first typified by $Co_4(\mu\text{-}PPh)_4(CO)_{10}$,[3a] but is the first such compound that does not possess carbonyl ligands.

[†] *Crystal data* for (**2**): $C_{44}H_{58}P_2Rh_4$, M = 1060, monoclinic, space group $P2_1/c$, a = 9.740(2), b = 18.919(4), c = 10.527(2) Å, β = 97.27(2)°, U = 1924.2(8) Å^3, Z = 4, D_c = 1.83 g cm^{-3}, $F(000)$ = 1228, $\mu(\text{Mo-}K_\alpha)$ = 17.88 cm^{-1}, Mo-K_α *X*-radiation, λ = 0.71073 Å. The structure was solved by a combination of direct methods and difference Fourier techniques. Refinement was carried out using blocked cascade least squares routines. For 2042 unique, absorption corrected, observed data [$I > 2\sigma(I)$], collected at 21(2) °C on a Nicolet R3 diffractometer in the range $3° < 2\theta < 45°$, the residuals were R = 0.042 and R_w = 0.038. The hydrogen atoms were calculated using a riding model [d (C–H) = 0.96 Å, U = 1.2 × U for attached carbon atoms] and fixed. The atomic co-ordinates for this work are available upon 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. The structure factor table is available as Supplementary Publication No. SUP 23798 (14 pp.) from the British Library Lending Division. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1983, issue 3, p. xvii.



Scheme 1

Cluster (**2**) has 60 valence electrons [4Rh (36) + 4cod (16) + 2PPh (8)]. It is thus 'doubly' co-ordinatively unsaturated since it is deficient by 4 electrons from the 64e$^-$ value calculated for 'saturated' square-planar tetranuclear clusters.[4] A valence bond description of (**2**) would require two formal Rh–Rh double bonds to satisfy the 18e$^-$ rule at each metal, but the Rh–Rh bond lengths determined for (**2**) do not support this view.

Complex (**2**) possesses many of the features that one would like to design into a catalytically active cluster: active metal atoms (Rh), capping μ_4-PPh ligands to retard cluster fragmentation (*e.g.*, ref. 5), co-ordinative unsaturation, and readily replaceable cod ligands. The latter should readily be effected by hydrogenation in the presence of other appropriate ligands. In related work we have shown that both cod ligands in $Rh_2(\mu\text{-}PPh_2)_2(cod)_2$[1] can be replaced by PEt_3 if the substitution reaction is conducted under an H_2 atmosphere, equation (2).[6]

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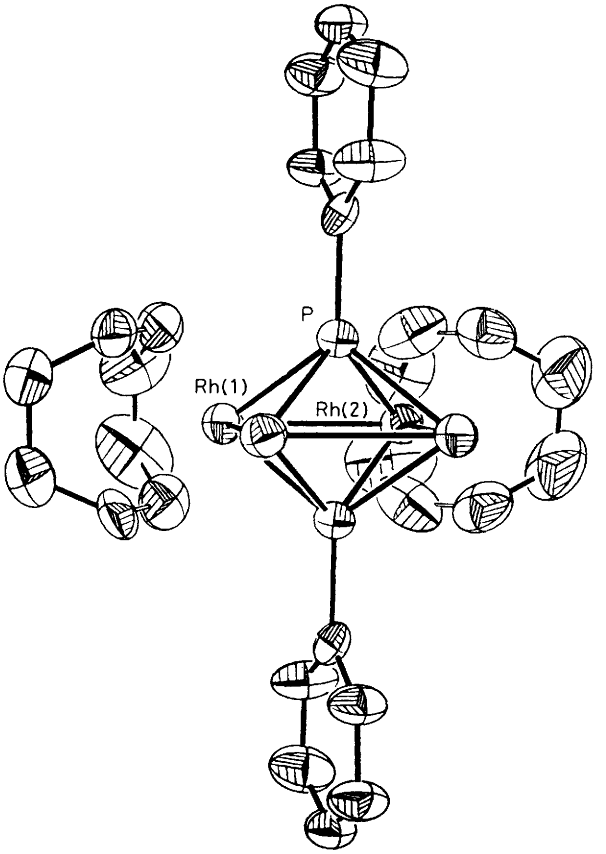
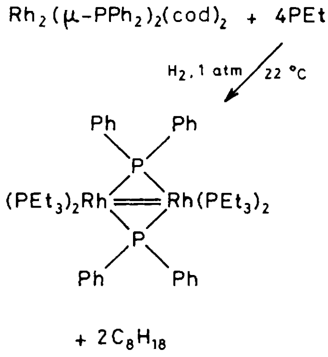


Figure 1. An ORTEP drawing of (**2**). The front cod ligands are omitted for clarity. Relevant bond distances (Å) are: Rh(1)–Rh(2) 2.836(1), Rh(1)–Rh(2′) 2.850(1), Rh(1)–P 2.423(2), Rh(1)–P′ 2.409(2), Rh(2)–P 2.415(2), Rh(2)–P′ 2.414(2), P · · · P′ 2.679(4), average Rh(2)–cod 2.157(9), and some angles (°) are: Rh(2′)–Rh(1)–Rh(2) 90.0(0), Rh(1)–Rh(2)–Rh(1′) 90.0(0).



(2)

References

1 P. E. Kreter and D. W. Meek, *Inorg. Chem.*, 1983, **22**, 319.
2 C. H. Wei, *Inorg. Chem.*, 1969, **8**, 2384.
3 (a) R. C. Ryan and L. F. Dahl, *J. Am. Chem. Soc.*, 1975, **97**, 1904; (b) H. Vahrenkamp, E. J. Wucherer, and D. Wolters, *Chem. Ber.*, 1983, **116**, 1219; H. Vahrenkamp and D. Wolters, *Organometallics*, 1982, **1**, 874; R. C. Ryan, C. U. Pittman, J. P. O'Connor, and L. F. Dahl, *J. Organomet. Chem.*, 1980, **193**, 247; J. S. Field, R. J. Haines, and D. N. Smit, *ibid.*, 1982, **224**, C49; J. S. Field, R. J. Haines, D. N. Smit, K. Natarajan, O. Scherdsteger, and G. Huttner, *ibid.*, 1982, **240**, C23.
4 J. W. Lauher, *J. Am. Chem. Soc.*, 1978, **100**, 5305.
5 G. Huttner, J. Schreider, H. D. Müller, G. Mohr, J. von Seyerl, and L. Wohlfahrt, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 76; G. Huttner, G. Mohr, and A. Frank, *ibid.*, 1976, **15**, 682.
6 E. W. Burkhardt and G. L. Geoffroy, *Inorg. Chem.*, submitted for publication.