Use of Phospha-alkynes in Metal Aggregate Synthesis. Crystal and Molecular Structure of the Remarkable Hexa-rhodium Complex $[Rh_2Cl_2\{Rh(\eta^5\text{-}C_5H_5)(P_2C_2Bu^t{}_2)\}_4]$

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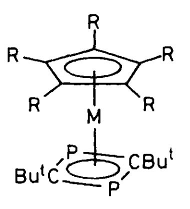
The remarkable hexa-rhodium compound $[Rh_2Cl_2\{Rh(\eta^5\text{-}C_5H_5)(P_2C_2Bu^t{}_2)\}_4]$ is obtained from the 1,3-diphosphacyclobutadiene complex $[Rh(\eta^5\text{-}C_5H_5)(P_2C_2Bu^t{}_2)]$ and $[RhCl(C_2H_4)_2]_2$.

In recent years there has been much interest in syntheses of transition metal cluster and aggregate compounds containing a variety of ligands.[1] More recent developments by Stone and co-workers[2] utilising carbyne complexes ($R{\equiv}CML_n$) have led to a variety of novel compounds containing chains of metal atoms culminating in the remarkable 'star' clusters possessing a ring of eight metals.[3]



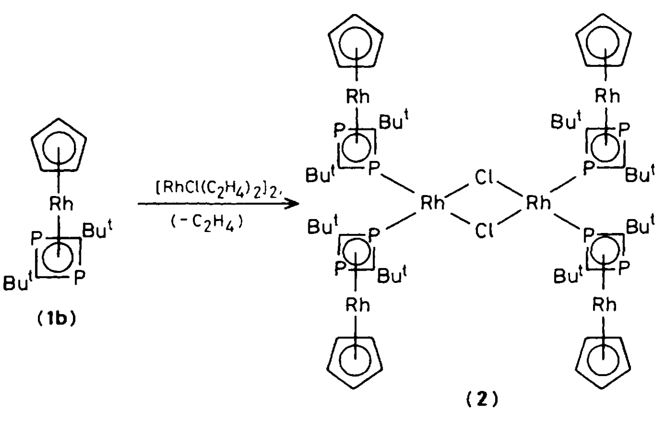
(1)

(**a**) R = H, M = Co
(**b**) R = H, M = Rh
(**c**) R = Me, M = Co
(**d**) R = Me, M = Rh
(**e**) R = Me, M = Ir

In previous papers[4—12] we have reported on the ligating ability of phospha-alkynes ($RC{\equiv}P$) and their use in cluster interlinkage.[8] Very recently[13] we described the first examples of the cyclodimerisation of $Bu^tC{\equiv}P$ to 2,4-di-t-butyl-1,3-diphosphacyclobutadiene in complexes of the type (**1a**—**e**).

We now find that (**1b**) reacts with $[RhCl(C_2H_4)_2]_2$ to afford the hexa-rhodium complex $[Rh_2Cl_2\{Rh(\eta^5\text{-}C_5H_5)(P_2C_2Bu^t{}_2)\}_4]$ (**2**) in which one of the ring phosphorus atoms in (**1b**) acts as a donor site for further ligation to interlink the metal–ligand fragments (see Scheme 1).

Compounds of type (**2**) are structurally related to other well known $[RhClL_2]_2$ complexes (L = CO, PF_3, PR_3 *etc.*) but this is the first time that such systems have been utilised in cluster synthesis.† The generality of this synthetic route to other metal systems is evident from our recent synthesis of the analogous $[Rh_2Cl_2\{Co(\eta^5\text{-}C_5Me_5)(P_2C_2Bu^t{}_2)\}_4]$ complex from (**1c**).



Scheme 1

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† *Crystal Data:* $C_{60}H_{92}Cl_2P_8Rh_6{\cdot}5CHCl_3$, M = 2346.4, monoclinic, space group $C2/c$, a = 21.807(13), b = 16.077(5), c = 28.649(14) Å, β = 104.51(4)°, U = 9723.7 Å^3, Z = 4, D_c = 1.60 g cm^{-3}. The molecule lies on a 2-fold rotation axis. Graphite monochromated Mo-K_α radiation (λ = 0.71069 Å), μ = 16.2 cm^{-1}; Enraf-Nonius CAD-4 diffractometer, θ–2θ mode, $2 < \theta < 22°$; 6663 reflections measured, 3534 unique reflections with $|F^2| > \sigma(F^2)$ used in the refinement; no absorption correction. The Rh atom positions were located by direct methods (MULTAN), and remaining non-hydrogen atoms found on difference maps. Three independent molecules of chloroform were located, one of which lies on a two-fold rotation axis and is disordered. Refinement by full-matrix least-squares with Rh, P, and Cl atoms anisotropic, omitting H atoms, led to R = 0.116, R_w = 0.147 [$w = 1/\sigma^2(F)$]. A final difference map had uninterpretable electron density of up to 2.1 e Å^{-3} near $\frac{1}{2}$, $\frac{1}{2}$, $\frac{3}{4}$, which is presumably due to further disordered solvent atoms. 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.

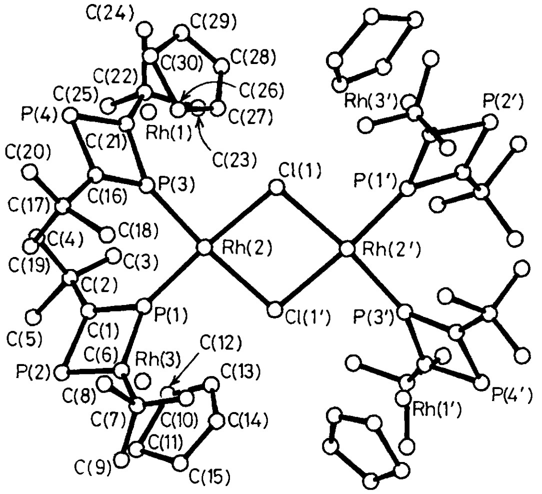

Figure 1. Molecular structure of complex (**2**). Important dimensions: Rh(1)–P(3) 2.317(7), Rh(1)–P(4) 2.333(9), Rh(2)–P(1) 2.174(8), Rh(2)–P(3) 2.178(7), Rh(3)–P(1) 2.339(7), Rh(3)–P(2) 2.351(9), P(1)–C(6) 1.84(3), P(1)–C(1) 1.79(3), P(2)–C(1) 1.84(3), P(2)–C(6) 1.83(3) Å.

Confirmation of the formulation of (**2**) comes from a single crystal *X*-ray diffraction study (Figure 1). Unfortunately the presence of $CHCl_3$ solvent molecules in disordered sites, which have so far proved difficult to model satisfactorily, is responsible for the currently high values of the residuals.

An additional feature of interest in (**2**) is the availability of four unused phosphorus donor sites at which co-ordination to other metal–ligand fragments (including clusters) might occur to give even larger metal aggregates, and additional studies on these systems are currently underway.

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