A New Rh_6 Geometry in the First Rh_6 Phosphido-bridged Cluster: Synthesis and Structure of $Rh_6(\mu\text{-}Bu^t_2P)_4(CO)_6(\mu\text{-}CO)_2(\mu\text{-}H)_2$

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Reaction of $Rh_4(CO)_{12}$ with Bu^t_2PH (Rh : P = 3 : 2) in toluene under reflux yields the Rh_6 phosphido-bridged cluster $Rh_6(\mu\text{-}Bu^t_2P)_4(CO)_6(\mu\text{-}CO)_2(\mu\text{-}H)_2$ (60%) which has an unusual Rh_6 core geometry consisting of a Rh_4 tetrahedron bridged on opposite edges by two more Rh atoms.

Large metal clusters (M ≥ 6) bearing phosphido (R_2P^-) or phosphinidene (RP^-) ligands or their arsenic analogues are of considerable interest since they frequently exhibit unusual and interesting structures and chemical reactivities.[1] We recently noted that the use of sterically demanding phosphides or arsenides particularly $Bu^t_2P^-$ and $Bu^t_2As^-$ can dramatically alter the molecular geometries of larger metal clusters.[2] We report here the facile high yield synthesis of $Rh_6(\mu\text{-}Bu^t_2P)_4(CO)_6(\mu\text{-}CO)_2(\mu\text{-}H)_2$ (**1**) which is unique for several reasons. To our knowledge, (**1**) is the first Rh_6 phosphido-bridged cluster to be reported, and it has a unique central Rh_6 framework. With the exception of $Rh_6(CO)_{11}(\mu\text{-}Bu^t_2As)_2(\mu_4\text{-}Bu^tAs)$,[3] in which the structure is based on a pentagonal pyramid, the Rh_6 clusters structurally characterized have so far had a closed octahedral or trigonal-prismatic geometry.[4] However, the Rh_6 core of (**1**) consists of a central Rh_4 tetrahedron with two further Rh atoms bridging two of its edges. Four Bu^t_2P units bridge the four Rh–Rh bonds formed by the two edge-bridging Rh atoms (Figure 1).

Reaction of $Rh_4(CO)_{12}$ with Bu^t_2PH (Rh : P = 3 : 2) in toluene under reflux (2.5 h) gives a deep red solution from which deep red, almost black, crystals of (**1**) can be isolated in *ca.* 60% yield, equation (1). It appears that the stoicheiometry of the reaction is a key factor in determining the nature of the product. If a Rh : P ratio of 2 : 3 is employed, high yields of yellow–orange $[Rh(CO)(Bu^t_2PH)]_2(\mu\text{-}H)(\mu\text{-}Bu^t_2P)$ can be isolated (80% yield), equation (2). This complex has been described elsewhere.[5]

A general view of the molecule and one of the central Rh_6P_4 core are shown in Figure 1 (a) and (b) respectively.† There are two bridging CO groups which bridge two edges of the central Rh_4 tetrahedron. In addition, each Rh atom bears a terminal CO ligand. The spectroscopic data are in accord with the structure determined by *X*-ray diffraction although it is not particularly informative.‡ The ^1H n.m.r. spectrum shows two multiplets (rel. areas 72 : 2) for the Bu^t_2P groups (δ 1.42) and the hydrides (δ −16.2). The $^{31}P\{^1H\}$ n.m.r. spectrum contains a single complex multiplet to low field (δ 323.92) indicative of phosphido groups bridging metal–metal bonds.[6] The hydride ligands could not be located in the *X*-ray structure, and their positions cannot be interpreted from the complex signal in the

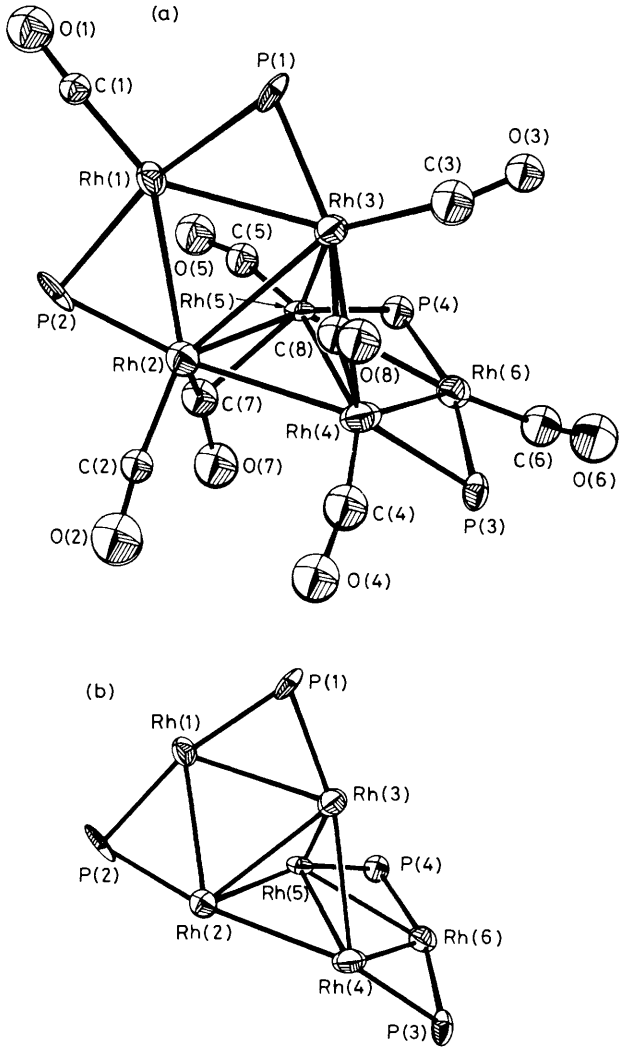


Figure 1. (a) Overall ORTEP view of (**1**). Typical bond lengths (Å): Rh(1)–Rh(3) 2.852(3), Rh(1)–Rh(2) 2.877(3), Rh(2)–Rh(3) 3.104(4), Rh(2)–Rh(4) 2.905(4), Rh(3)–Rh(5) 3.118(4), Rh(4)–Rh(5) 3.184(3), Rh(1)–P(1) 2.282(10), Rh(3)–P(1) 2.285(8), Rh(6)–P(4) 2.289(10), Rh(1)–C(1) 1.81(2), Rh(2)–C(7) 1.86(7), Rh(5)–C(7) 2.21(9). Angles (°): Rh(1)–P(1)–Rh(3) 77.3(3), Rh(2)–Rh(1)–Rh(3) 65.44(8), Rh(2)–Rh(4)–Rh(3) 64.8(1), Rh(2)–C(7)–Rh(5) 90(3).(b) View of the Rh_6P_4 core of (**1**).

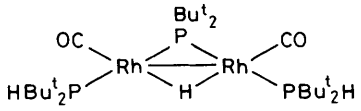
† *Crystal data* for (**1**): $C_{40}H_{74}O_8P_4Rh_6$, *M* = 1424.34, monoclinic, space group, *Cc*, *a* = 24.002(2), *b* = 11.957(3), *c* = 22.399(6) Å, β = 111.805 (3)°; *U* = 5968.2 (5) Å^3, *Z* = 4, D_c = 1.583 g cm^{-3}, λ(Mo-K_α) = 0.71073 Å (graphite monochromator), μ(Mo-K_α) = 17.401 cm^{-1}. Methods: MULTAN, difference Fourier, full matrix least squares. Refinement of 3032 reflections [$I > 3\sigma(I)$] out of 4680 unique observed reflections (3° < 2θ < 48°) collected on an Enraf–Nonius CAD-4 diffractometer at 23 ± 2 °C gave *R* and R_w values of 0.0696 and 0.0750 respectively. Data/parameter ratio = 9.625, maximum peak in final difference Fourier = 0.894 eÅ^{-3}. There is one badly disordered molecule of toluene solvent in the symmetric unit. This, and the poor quality of the data, have led to some unusual C–C and C–O distances. 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, 1986.

‡ Evaporation to dryness followed by recrystallization from toluene (−40 °C) gives (**1**). M.p. 104—106 °C (decomp.). A satisfactory elemental analysis (C and H) has been obtained. ^1H N.m.r. ([$^2H_8$]PhMe, 360 MHz), δ 1.42 (m, Bu^t_2P), −16.16 (m, μ-H); $^{31}P\{^1H\}$ (in C_6D_6) δ 323.92 (m) p.p.m.; i.r. (hexane, KBr) 2045 w, 2020 m, 1995 s, 1972 s, 1843, br m cm^{-1}, (Nujol, NaCl) 2018 sh, 2010 m, 1988 s, 1965 s, 1840 br m, 1361 m, 1168 m, 1015 w, 805 m, 690 w cm^{-1}.

$$3\ Rh_4(CO)_{12} + 8\ Bu^t_2PH \xrightarrow{2.5\ h,\ toluene} 2\ Rh_6(\mu\text{-}Bu^t_2P)_4(CO)_6(\mu\text{-}CO)_2(\mu\text{-}H)_2 + 20\ CO\uparrow \quad (1)$$

(1)

+ other products

$$Rh_4(CO)_{12} + 6\ Bu^t_2PH \xrightarrow{2.5\ h,\ toluene} 2 \quad \text{  } \quad + 8\ CO\uparrow \quad (2)$$

^{1}H n.m.r. spectrum. However, considering the central Rh_4 core of the molecule, two edges are bridged by Rh atoms and two by CO ligands. This leaves two remaining edges. For geometrical reasons, it seems reasonable to propose that the H atoms are bridging these bonds [Rh(3)–Rh(5) and Rh(2)–Rh(4)]. The key structural parameters of the molecule all fall within normal limits. Thus, the Rh–Rh bonds range from 3.184(4) to 2.852(3) Å and average 2.954 Å. The Rh–P distances are also fairly similar ranging from 2.234(7) to 2.289(10) Å. These values are comparable to analogous ones found in other Bu^t_2P bridged rhodium species such as $[Rh(\mu\text{-}Bu^t_2P)(CO)]_3$[7] and $[Rh(\mu\text{-}Bu^t_2P)(CO)_2]_2$.[8] It is interesting to note that the overall Rh_6P_4 core may be viewed as being formed from the intersection of two Rh_4P_2 planes, *i.e.* Rh(1)–Rh(2)–Rh(3)–Rh(4)–P(1)–P(2) intersects with Rh(2)–Rh(5)–Rh(4)–Rh(6)–P(4)–P(3) by the sharing of one edge [Rh(2)–Rh(4)] and the linking of Rh(3) to Rh(5) to form the central Rh_4 tetrahedron. Each Rh_4P_2 plane bears a strong resemblance to the core of the planar Ir_4 complex $[Ir(\mu\text{-}Bu^t_2As)](CO)_2(\mu\text{-}CO)_2$ which we recently described.[2] In this case, the unusual planar nature of the Ir_4As_4 core was attributed to the influence of the bulky $Bu^t_2As^-$ ligands. The cluster (**1**) has a formal electron count of 84 with six skeletal bonding electron pairs for the Rh_6 core. A capped *closo* or capped trigonal-bipyramid such as that found for $Os_6(CO)_{18}$ would be expected based on Wade's Rules.[9] The further opening up of the core geometry may be due to the steric demands of the $Bu^t_2P^-$ groups. Control of cluster geometry in heteronuclear systems has recently been described for $[Au_2Ru_4(\mu\text{-}H)(\mu_3\text{-}H)_9(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{12}]$ and $[Ag_2Ru_4(\mu_3\text{-}H)_2(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{12}]$.[10]

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