# Bis(phospha-adamantyl)alkanes: a new class of very bulky diphosphines

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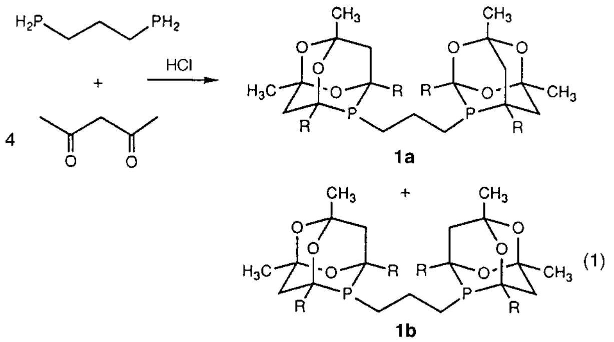
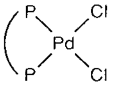
**Adamantane-like cages are formed when $H_2P(CH_2)_nPH_2$ ($n$ = 2 or 3) react with acetylacetone or trifluoroacetylacetone and the crystal structures of the dichloropalladium(II) complexes of the $C_3$-diphosphine ligands show that their cone angles are much larger than $Bu^t_2P(CH_2)_3PBu^t_2$; a diphospha-adamantane derived from $o$-$C_6H_4(PH_2)_2$ is also described.**

Bulky alkyl diphosphines of the type $R_2P(CH_2)_nPR_2$, ($n$ = 1–5, R = $Bu^t$, $Pr^i$ or Cy) have been at the heart of many key developments in transition metal chemistry over the last 25 years[1–7] including the stabilisation of unusual oxidation states and low coordination numbers,[1,2] formation of agostic alkyls, activation of C–H and C–C bonds,[3,4] and preparation of polyhydride complexes.[1,3,5] Recently bulky alkyl diphosphine complexes of palladium have attracted attention as carbonylation catalysts[6] and as catalysts for the Heck reaction.[7] We report here a simple route to a new class of very bulky alkyl diphosphines which are air-stable.

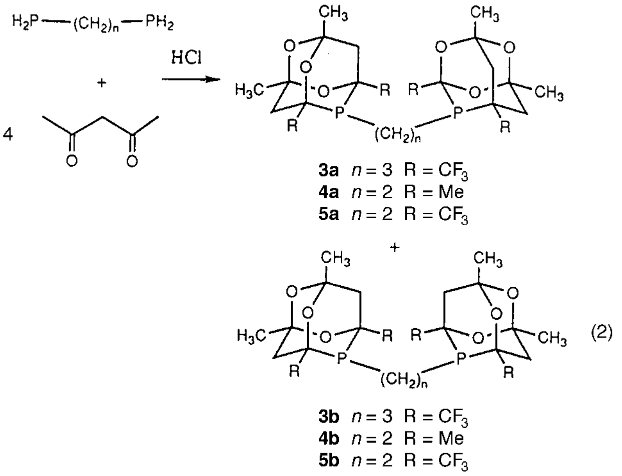
It has been reported that $PH_3$ reacts with acetylacetone[8] or trifluoroacetylacetone[9] to give adamantane-like cage secondary phosphines although no coordination chemistry of these ligands has been reported. This prompted us to attempt the synthesis of bis(phospha-adamantyl)alkanes from diprimary phosphines. Thus $H_2P(CH_2)_3PH_2$ was reacted with acetylacetone in the presence of HCl and this gave an air-stable, crystalline product which was identified as a mixture of the diastereomeric phospha-adamantane diphosphines **1a** and **1b** [eqn. (1)] on the basis of elemental analysis, mass spectrometry, $^{31}P$ and $^1H$ NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of the product in $CDCl_3$ showed two singlets at −31.0 and −30.2 ppm in the ratio of *ca.* 1 : 1, consistent with the presence of *rac* (**1a**) and *meso* (**1b**) diastereoisomers. Addition of MeOH to a $CH_2Cl_2$ solution of the mixture of ligands **1a** and **1b** leads to selective crystallisation of the *rac* isomer **1a**; in this way samples of **1a** and **1b** in purity of > 95% are readily obtained.





**2a** diphosphine = **1a**
**6a** diphosphine = **3a**
**7a** diphosphine = **4a**
**8a** diphosphine = **5a**
**2b** diphosphine = **1b**
**6b** diphosphine = **3b**
**7b** diphosphine = **4b**
**8b** diphosphine = **5b**

The dichloropalladium(II) chelates **2a** and **2b** were made by treatment of $[PdCl_2(NCPh)_2]$ with **1a** and **1b** respectively and the crystal structure of **2a**, as determined by X-ray crystallography,† is illustrated in Fig. 1. The bulk of the phospha-adamantane diphosphines is evident and the estimated cone angle[10] is 173° (*cf.* 155° for $Bu^t_2PCH_2CH_2CH_2PBu^t_2$ in its $PtCl_2$ complex[11]); furthermore there is no possibility of



**3a** $n = 3$ R = $CF_3$
**4a** $n = 2$ R = Me
**5a** $n = 2$ R = $CF_3$

**3b** $n = 3$ R = $CF_3$
**4b** $n = 2$ R = Me
**5b** $n = 2$ R = $CF_3$

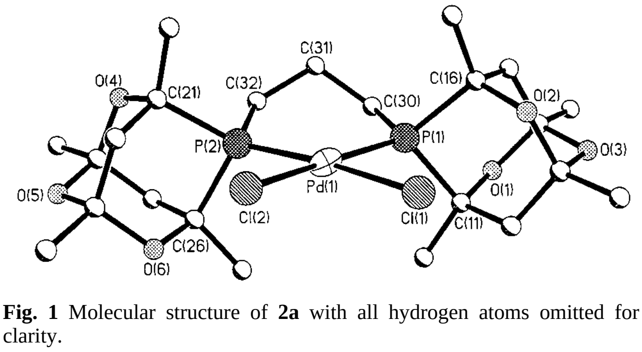


**Fig. 1** Molecular structure of **2a** with all hydrogen atoms omitted for clarity.

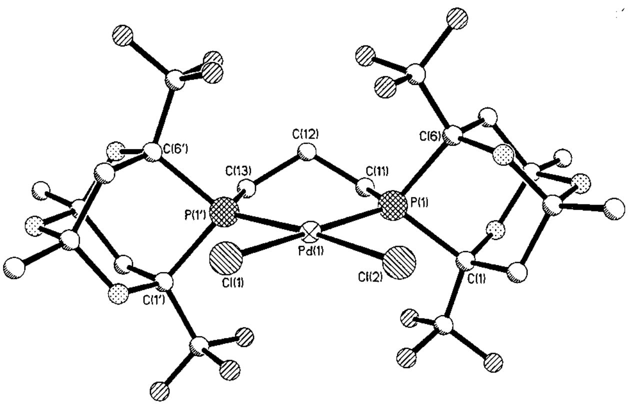
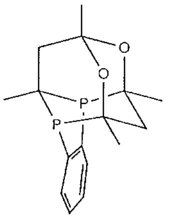


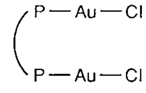
**Fig. 2** Molecular structure of **6a** with all hydrogen atoms omitted for clarity. Primed atoms are related by non-crystallographic mirror symmetry.

reduction of the bulk of this ligand by intermeshing. The most unusual aspect of the geometry is the long intra-cage P–C distances and small C–P–C angles (Fig. 1). The electronic consequences of this geometric distortion at phosphorus on the metal–phosphine bond and its chemistry is currently under investigation. Methoxycarbonylation of alkenes catalysed by derivatives of **2a** and **2b** has recently been reported.[12]

The condensation reaction shown in eqn. (1) can be generalised to other diphosphines and other acetylacetones [eqn. (2)]. Hence the ligands **3–5a**,**b** have been made in high yield as mixtures of diastereoisomers using the appropriate $H_2P(CH_2)_nPH_2$ and 1,3-diketone. Preliminary results show that the corresponding dichloropalladium chelates **6–8a**,**b** can be made and the crystal structure of **6a** (Fig. 2)† reveals the great steric bulk of the coordinated diphosphine **3a**, with an estimated cone angle of 192°.



**9**



**10** diphosphine = **9**

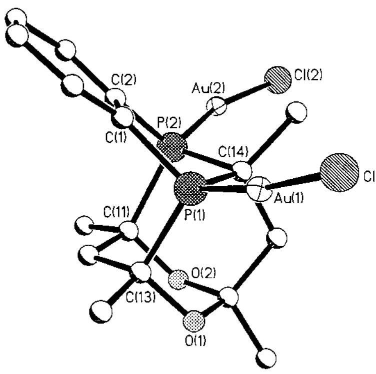
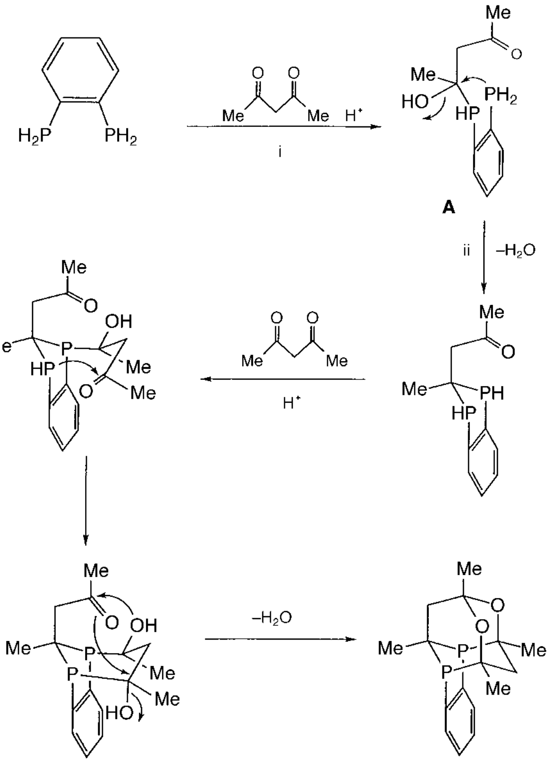


**Fig. 3** Structure of **10** with all hydrogen atoms omitted for clarity.



**Scheme 1** Suggested mechanism for the formation of the diphospha-adamantane **6**.

A different type of product was obtained when 1,2-diphosphinobenzene was added to acetylacetone in the presence of HCl. The structure of the product was assigned to the diphospha-adamantane **9** on the basis of the symmetry of its $^1$H, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR spectra and the structure was confirmed by X-ray crystallography.† The diphosphine **9** reacts with [AuCl(tht)] to give the binuclear gold(I) complex **10** which has also been characterised by X-ray crystallography (Fig. 3).†

The mechanism for the formation of the monophospha-adamantanes has been previously discussed[9] and a mechanism for the formation of the diphospha-adamantane cage **9** is suggested in Scheme 1. The rigidity of the phenylene backbone promotes the formation of **9** because the pendant $PH_2$ group in **A** is held in close proximity to the electrophilic carbon thus facilitating the ring closure step ii.

We have shown that diphosphines featuring very bulky, rigid, phospha-adamantane cages are readily accessible in one step from primary diphosphines. The extension of this work to other diprimary phosphines and other 1,3-diketones is being explored alongside investigation of the coordination chemistry and applications of these remarkable ligands. We thank EPSRC, Albright and Wilson and Shell International for supporting this work and Johnson Matthey for a loan of palladium compounds.

## Notes and references

† Crystal structures were determined from data collected on a Siemens SMART diffractometer for $2.0 < \theta < 27.5°$ ($\lambda = 0.71073$ Å), at 173 K. The structures were solved by direct and Fourier methods and refined by least-squares against all unique $F^2$ data corrected for absorption. *Crystal data*: for **2a**: $C_{23}H_{38}Cl_2O_6P_2Pd$, $M = 649.8$, monoclinic, space group $P2_1/c$ (no. 14), $a = 13.402(5)$, $b = 14.735(3)$, $c = 14.150(3)$ Å, $\beta = 103.48(2)°$, $V = 2717.3(13)$ Å$^3$, $Z = 4$, $\mu = 1.033$ mm$^{-1}$, 6219 unique data, $R1 = 0.059$. For **3a**·$CHCl_3$: $C_{24}H_{27}Cl_5F_{12}O_6P_2Pd$, $M = 985.05$, monoclinic, space group $Cc$ (no. 9), $a = 13.142(2)$, $b = 11.987(2)$, $c = 22.167(3)$ Å, $\beta = 102.419(8)°$, $V = 3410.4(9)$ Å$^3$, $Z = 4$, $\mu = 1.135$ mm$^{-1}$, 7771 unique data, $R1 = 0.026$. For **9**: $C_{16}H_{20}O_2P_2$, $M = 306.26$, orthorhombic, space group $Pnma$ (no. 62), $a = 17.491(3)$, $b = 12.133(2)$, $c = 7.347(2)$ Å, $V = 1559.1(6)$ Å$^3$, $Z = 4$, $\mu = 0.277$ mm$^{-1}$, 1882 unique data, $R1 = 0.047$. For **10**: $C_{16}H_{20}Au_2Cl_2O_2P_2$, $M = 771.1$, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.934(2)(3)$, $b = 8.2681(12)$, $c = 15.118(2)$ Å, $\alpha = 85.449(13)$, $\beta = 87.77(2)$, $\gamma = 76.846(12)°$, $V = 962.4(3)$ Å$^3$, $Z = 2$, $\mu = 15.68$ mm$^{-1}$, 4343 unique data, $R1 = 0.020$. CCDC 182/1219. See http://www.rsc.org/suppdata/cc/1999/901/ for crystallographic files in .cif format.

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