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Preliminary Communication

1,8-Bis(diphenylphosphino)naphthalene: a rigid chelating, diphosphine analogue of proton sponge

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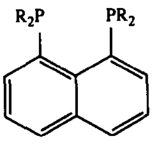
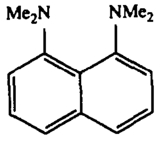
Abstract

The synthesis of the new diphosphine, 1,8-bis(diphenylphosphino)naphthalene (**1a**), and its X-ray crystal structure are reported. Protonation of **1a** gives a fluxional species to which a P–P bonded structure is assigned. Despite the strain apparent in the solid state due to the proximity of the diphenylphosphino groups, it appears that **1a** has a normal coordination chemistry with platinum(II) and palladium(II).

There is currently great interest in new diphosphine ligands with a C_3-backbone because the six-membered palladium(II) chelates which they form have been demonstrated to be extremely active catalysts for CO/ethylene co-polymerization [1]. We report here the new C_3-diphosphine ligand 1,8-bis(diphenylphosphino)naphthalene (**1a**), a phosphorus analogue of 1,8-bis(dimethylamino)naphthalene (**2**), which is also known as "proton sponge" because it is an effective non-nucleophilic base [2]. It might have been expected that diphosphine analogues of **2** would be confined to those having small substituents, and 1,8-bis(dimethylphosphino)naphthalene (**1b**) is known [3], but we have found that the bulky 1,8-bis(diphenylphosphino)naphthalene is surprisingly easily made and behaves as a normal chelating diphosphine towards palladium(II) and platinum(II).



1a R = Ph
1b R = Me
1c R = Cy



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Treatment of 1,8-dilithionaphthalene [3] with Ph_2PCl in diethyl ether at 0°C gave an 82% yield of diphosphine **1a** as a yellow, air-stable powder which has been fully characterised [4*]. It is readily made in this way on a 2 g scale. Clear yellow crystals of **1a** suitable for X-ray crystallography were grown from CH_2Cl_2/Et_2O. The crystal structure analysis [5*] confirms the identity of **1a** (see Fig. 1) and provides information on the distortions present in the molecule. In common with other 1,8-substituted naphthalenes, **1a** exhibits both out-of-plane and in-plane bending of the PPh_2 substituents away form one another as well as buckling of the C_{10} unit (mean carbon atom deviation from least-squares C_{10} plane 0.006 Å, phosphorus deviations: P(1) 0.50 Å, P(2) 0.34 Å). While these distortions lower the symmetry of the $C_{10}P_2$ nucleus from C_{2v} to approximately C_2, the orientations of the PPh_2 groups are such as to reduce the molecular symmetry to C_1 in the solid state. The net effect of these distortions is to generate a P(1) $\cdots$ P(2) distance of 3.052 Å, well within the sum of the van der Waals radii (3.80 Å). This distance is comparable with those in Pt^{II} or Pd^{II} complexes of conventional chelating diphosphines (*e.g.* P $\cdots$ P in $[PdCl_2(Ph_2PCH_2CH_2CH_2PPh)_2]$ is 3.193 Å [6]), and may explain the relatively orthodox coordinating properties of **1a** (see below).

The inequivalence of the two P atoms in **1a** in the solid state (see above) is confirmed by the MAS solid state $^{31}P\{^1H\}$ NMR spectrum which shows an AB pattern with $\delta(P_A)$ -18.0 and $\delta(P_B)$ -10.2. The J(PP) value of 199 Hz is unusually large for a ^4J(PP) coupling and indicates that there is a significant through-space component. In CD_2Cl_2 solution the $^{31}P\{^1H\}$ NMR spectrum of **1a** is a sharp singlet at -14.7 ppm even at -80°C indicating that either the structure is symmetrical in solution or there is rapid fluxionality on the NMR timescale leading to equivalence of the P atoms (the solution chemical shift is close to the average of the solid state shifts).

Addition of MeI to **1a** gave the monophosphonium salt **3**, the $^{31}P\{^1H\}$ NMR spectrum of which at $+28$°C was an AB pattern with ^4J(PP) of 24 Hz. Addition of one equivalent of $HBF_4 \cdot OMe_2$ to diphosphine **1a** in CD_2Cl_2 gave rise to a new species which from variable

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* Reference number with asterisk indicates a note in the list of references.

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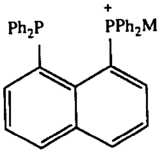
temperature ^{31}P NMR studies was found to be fluxional. At +28°C, the $^{31}P\{^1H\}$ NMR spectrum is a broad singlet ($w_{1/2} = 35$ Hz) at −4.9 ppm. The proton-coupled ^{31}P NMR spectrum is a doublet with $J(PH) = 288$ Hz. At −80°C the spectrum is an AB pattern, $\delta(P_A) = 8.2$ ppm, $\delta(P_B) = -19.6$ ppm, $J(P_AP_B) = 110$ Hz. The proton-coupled ^{31}P NMR spectrum at −80°C shows that only P_A is coupled to the proton with $J(P_AH) = 576$ Hz. $J(P_BH)$ must be less than the linewidth (20 Hz). The fluxionality of **4** is therefore proton exchange between the two phosphorus atoms and this is an intramolecular process since $J(PH)$ at ambient temperatures is half the low temperature $J(P_AH)$ value. The coalescence temperature is 275 K, corresponding to a $\Delta G^{\ddagger}$ of 49.5 kJ mol^{-1} as calculated by the Gutowsky–Holm method [7]. The large $J(PP)$ of 110 Hz for the protonated species contrast with that found for the phosphonium salt **3** and is consistent with the P–P bonded structure **4**, analogous to the recently reported [8] tricyclic compound **5**.



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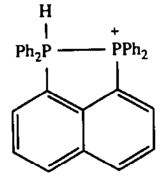

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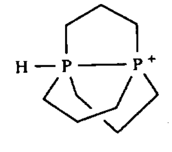

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Diphosphine **1a** reacts readily with $K[PtCl_3(C_2H_4)]$ or $[PdCl_2(NCPh)_2]$ to give the chelates **6** and **7**, respectively, in high yields (80–90%). The spectroscopic properties of these complexes are apparently normal. For example the ^{31}P coordination chemical shift (Δ) of 16.1 for **6** when compared with Δ for the monophosphine complex **8** yields a ring contribution (Δ_R) of −7.9, similar to the values for other six-membered chelates [9]. Hence, contrary to expectation, ligand **1a** has normal diphosphine coordination properties, and is a member of a potentially large class of ligands since preliminary studies indicate that the even bulkier cyclohexyl analogue, **1c**, is available by a similar route.

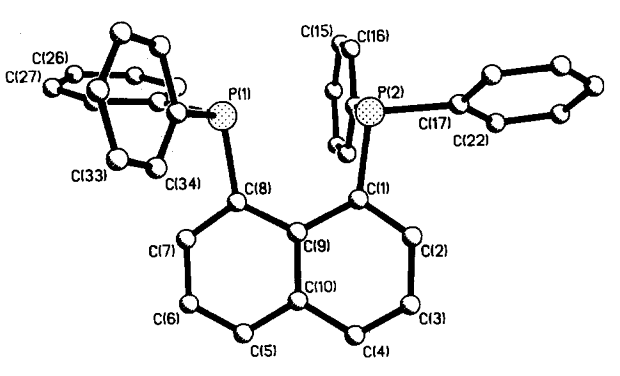
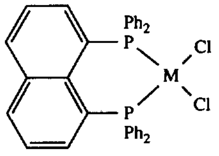
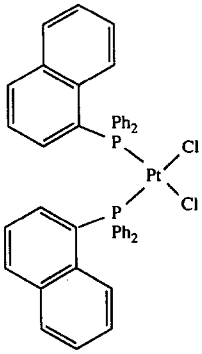


Fig. 1. Molecular geometry of **1a**, important molecular parameters include: bond lengths, P(1)–C(8) 1.844(6), P(1)–C(29) 1.828(5), P(1)–C(23) 1.837(5), P(2)–C(1) 1.848(6), P(2)–C(11) 1.839(5), P(2)–C(17) 1.839(5) Å; bond angles, P(1)–C(8)–C(9) 123.0(4), P(2)–C(1)–C(9) 124.5(3)°; torsion angles, C(1)–C(9)–C(8)–P(1) −13.4(7), C(8)–C(9)–C(1)–P(2) −7.7(7)°.



6 M = Pt
7 M = Pd



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Acknowledgements

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References and notes

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4 All isolated new compounds have been characterised by a combination of elemental analyses, IR, ^1H, ^{31}P and ^{13}C NMR spectroscopy. The ^{31}P NMR data for **3**–**9** (in $CDCl_3$) are: **1a**, $\delta(P)$ −14.7; **1c**, $\delta(P)$ −16.1; **3**, $\delta(P_A)$ +23.6, $\delta(P_B)$ −13.0, $^2J(P_AP_B)$ 24; **4**, $\delta(P_A)$ +8.2, $\delta(P_B)$ −19.6, $^2J(P_AP_B)$ 110; **6**, $\delta(P)$ +1.6, $^1J(PtP)$ 3318; **7**, $\delta(P)$ +20.8; and **8**, $\delta(P)$ +9.8, $^1J(PtP)$ 3656.

5 Crystal data for **3**: $C_{34}H_{26}P_2$, $M = 496.5$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.493(3)$, $b = 10.030(3)$, $c = 15.295(5)$ Å, $\alpha = 90.45(2)$, $\beta = 93.65(2)$, $\gamma = 117.70(2)°$, $V = 1285.5(6)$ Å^3, $Z = 2$, $D_x = 1.28$ g cm^{-3}, $\bar{\lambda} = 0.71069$ Å, μ(Mo-Kα) = 1.9 cm^{-1}, $F(000) = 520$, $T = 295$ K. Data were collected on a Siemens P3m diffractometer for $4 < 2\theta < 45°$. The structure was solved by direct methods and refined by least-squares to $R = 0.066$ for 2361 unique, observed ($I > \sigma(I)$) absorption corrected intensity data.
Table of atom coordinates, bond lengths, bond angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

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