A Mixed Organozinc–Diorganophosphide Complex containing Protic Phosphine Ligands Bonded to Zinc

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Metallation of diphenylphosphine with $\mathrm{ZnEt_2}$ (5:3 equiv.) in thf produces $\{[\mathrm{EtZn}(\mu\text{-}\mathrm{PPh_2})]_3\cdot(\mathrm{HPPh_2})_2\cdot\mathrm{thf}\}$ **1**, which is shown by X-ray crystallography to have a $\mathrm{Zn_3P_3}$ core in which $\mathrm{Ph_2PH}$ ligands act as donors to two of the zinc centres.

Our interest in group 12 organophosphide complexes has been stimulated by their potential applications as precursors to semiconducting phases such as $\mathrm{M_3P_2}$ (M = Zn, Cd) and $\mathrm{CdP_2}$ for the doping of photoelectronic materials.[1,2] We recently reported the synthesis of $\{[\mathrm{EtZn}(\mu\text{-}\mathrm{PCy_2})]_3\cdot\mathrm{thf}\}\cdot2\mathrm{thf}$ (Cy = cyclohexyl) which was the first trimeric dialkyl or diaryl phosphide complex and the first mixed organometallic zinc phosphide to be characterised in the solid state.[3] Herein, we report the synthesis and structure of a mixed organozinc–diorganophosphide complex $\{[\mathrm{EtZn}(\mu\text{-}\mathrm{PPh_2})]_3\cdot(\mathrm{HPPh_2})_2\cdot\mathrm{thf}\}$ **1** which has a $\mathrm{Zn_3P_3}$ core solvated by neutral $\mathrm{Ph_2PH}$ ligands.

Complex **1** was first synthesised by the metallation reaction of $\mathrm{Ph_2PH}$ with $\mathrm{ZnEt_2}$ (2:1 equiv., respectively) in thf. The same complex is isolated in relatively low, though reproducible, yield from the reaction of $\mathrm{Ph_2PH}$ and $\mathrm{ZnEt_2}$ in the correct stoichiometric ratio (5:3 equiv., respectively).†

An X-ray crystallographic study of **1** shows it to be the trinuclear complex $\{[\mathrm{EtZn}(\mu\text{-}\mathrm{PPh_2})]_3\cdot(\mathrm{HPPh_2})_2\cdot\mathrm{thf}\}$.‡ There are two crystallographically independent but chemically equivalent molecules in the asymmetric unit, one of which is shown in Fig. 1. The complex has a $\mathrm{Zn_3P_3}$ core with one zinc centre [Zn(3)] solvated by thf and the other two zinc centres [Zn(1) and Zn(2)] solvated by neutral $\mathrm{Ph_2PH}$ groups. In both independent molecules, Zn(Et)(thf) fragments are similarly disordered on two positions [Fig. 1(*b*)]. The unusual stoichiometry of **1** appears to be the result of steric crowding whereby solvation by a third $\mathrm{Ph_2PH}$ group is unfavourable and a less bulky thf molecule fulfils the solvation role. In the only other complex containing a $\mathrm{Zn_3P_3}$ core, $\{[\mathrm{EtZn}(\mu\text{-}\mathrm{PCy_2})]_3\cdot\mathrm{thf}\}\cdot2\mathrm{thf}$, the presence of even more bulky cyclohexyl groups allows solvation of only one Zn centre (by thf).[3]

The tetranuclear zinc phosphide–hydroxide complex $[\mathrm{Zn_2(PBu^t{}_2)_2(OH)(\mu\text{-}OH)}]_2$,[4] the trinuclear $\{[\mathrm{EtZn}(\mu\text{-}\mathrm{PCy_2})]_3\cdot\mathrm{thf}\}\cdot2\mathrm{thf}$,[3] and the dimeric zinc disilylphosphide $\{\mathrm{Zn[P(SiMe_3)_2][\mu\text{-}P(SiMe_3)_2]}\}_2$[5,6] are the only examples of zinc phosphide complexes (containing $\mathrm{R_2P^-}$ ligands) that have been characterised by single-crystal X-ray crystallography. $[\mathrm{Zn(PBu^t{}_2)_2(OH)(\mu\text{-}OH)}]_2$ was prepared by a somewhat serendipitous route from $\mathrm{ZnCl_2}$ and $\mathrm{LiPBu^t{}_2}$ in which fortuitous entry of water allows crystallisation of this product.[4] It is interesting to note that the parent phosphine complex (without hydroxide inclusion) could not be crystallised in this previous work. Presumably the neutral $\mathrm{Ph_2PH}$ ligand of **1**, in addition to thf solvation, plays a similar role to the hydroxide ligands in the latter in facilitating crystallisation. In this context, a previous study of the metallation reaction of $\mathrm{Ph_2PH}$ with $\mathrm{ZnEt_2}$ in benzene gave only a polymeric powder identified as '$\mathrm{Zn(PPh_2)_2}$'.[7,8]

The μ-$\mathrm{Ph_2P}$–Zn bonds within the core of **1** (av. 2.44 Å) are shorter than the terminal $\mathrm{Ph_2(H)P}$–Zn bonds (av. 2.55 Å). The phosphino protons of the $\mathrm{Ph_2PH}$ groups were located on the electron density map, and revealed a tetrahedral environment for P(4) and P(5) respectively. The $\mathrm{Ph_2PH}$ groups can also be clearly seen spectroscopically. The phoshino protons are observed in the ^{1}H NMR spectrum of **1** in thf at δ 5.12 (doublet, $J_{\mathrm{P\text{-}H}}$ 216 Hz) [*cf.* δ 5.01 (doublet, $J_{\mathrm{P\text{-}H}}$ 216 Hz) for free $\mathrm{Ph_2PH}$ in the same solvent] (Fig. 2). Additionally, two peaks at δ −41.35 and −50.61 are observed in the ^{31}P NMR due to the terminal $\mathrm{Ph_2PH}$ and the bridging phosphido groups, respectively (Fig. 2). The P–H stretching vibration of the Zn bonded $\mathrm{Ph_2PH}$ of **1** (2343 cm^{-1}) is higher than that of free $\mathrm{Ph_2PH}$ (2301). The presence of such an acidic ligand directly attached to a group 12 organometallic complex is unprecedented, although group 13 organometallics are known to form simple adducts with acidic donor ligands.[9] This feature implies that, once one of the Et groups of $\mathrm{ZnEt_2}$ has reacted, the second is far less basic than one might have expected.

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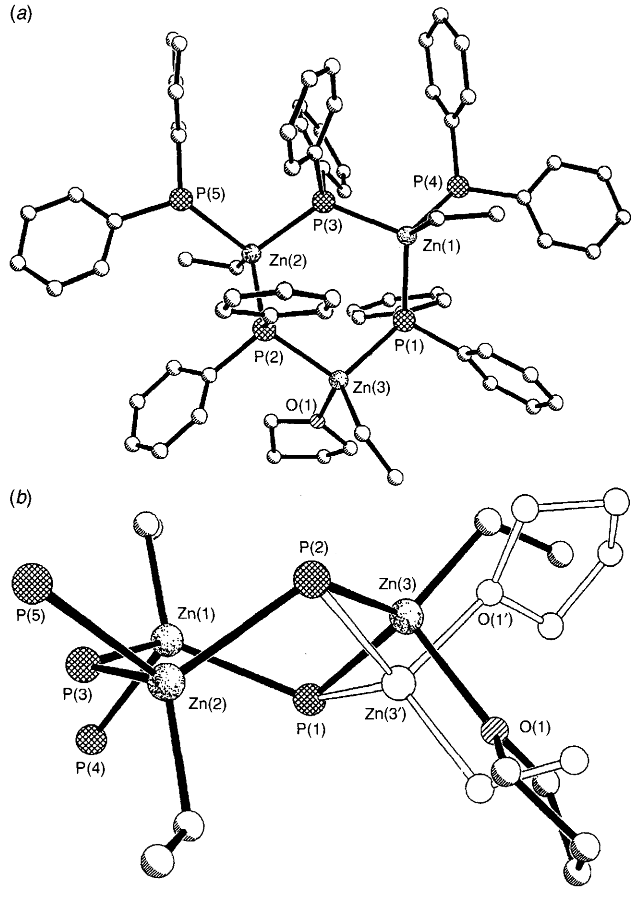

Fig. 1 (*a*) Molecular structure of **1**. Only one of the two crystallographically independent molecules is shown, and all hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°) averaged over both independent molecules for chemically unique bonds: Zn(1)–P(1) and Zn(2)–P(2) 2.42, Zn(1)–P(3) and Zn(2)–P(3) 2.45, Zn(1)–P(4) and Zn(2)–P(5) 2.55, Zn(3)–P(1) and Zn(3)–P(2) 2.47, Zn(1)–P(3)–Zn(2) 122, P(1)–Zn(3)–P(2) 108, Zn(1)–P(1)–Zn(3) and Zn(2)–P(2)–Zn(3) 115, P(1)–Zn(1)–P(3) and P(2)–Zn(2)–P(3) 104. (*b*) Core structure of one of the crystallographically independent molecules of **1**, illustrating the disorder of Zn(3) and the attached substituents over two sites.

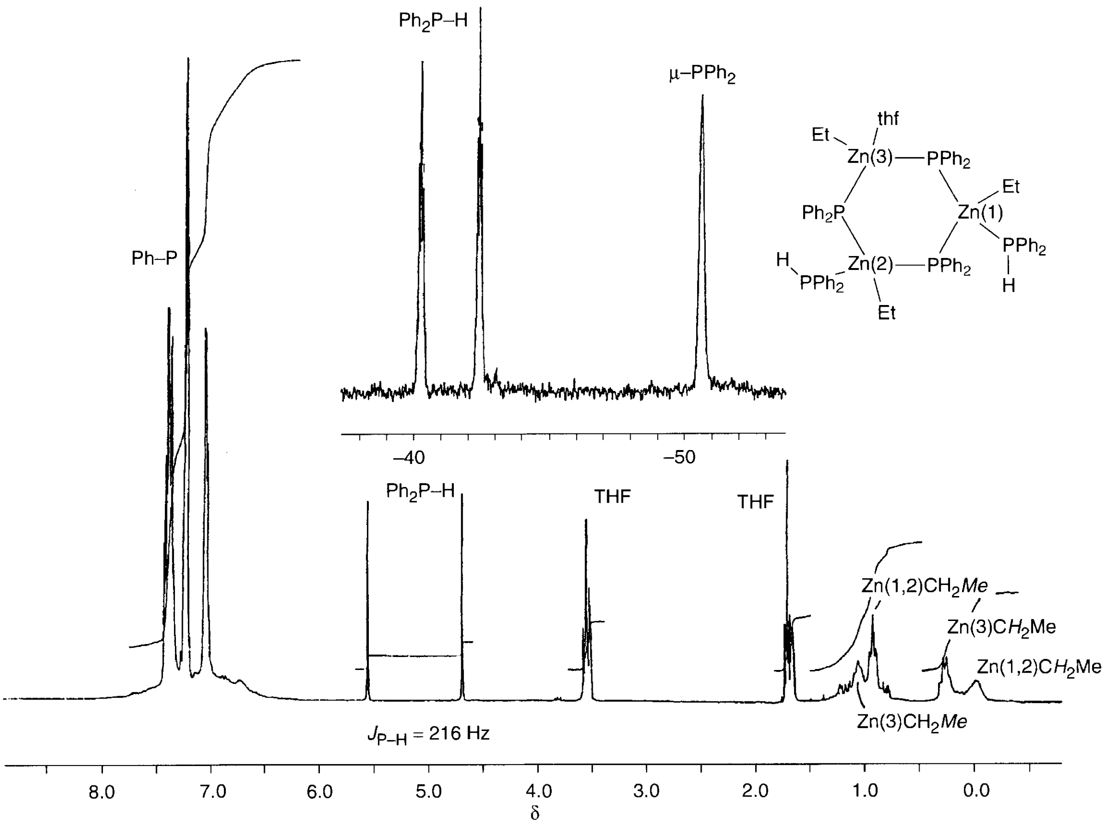

Fig. 2 ^{1}H NMR (250 MHz, [^{2}H$_8$]thf, 25 °C) of **1**. ^{31}P NMR (101.253 MHz, [^{2}H$_8$]thf, 25 °C) of **1** (insert).

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Footnotes

† ZnEt$_2$ (6.0 ml, 1.0 mol dm^{-3} in hexanes, 6.0 mmol) was added to a solution of Ph$_2$PH (1.94 ml, 10 mmol) in thf (10 ml) at 25 °C under N$_2$. Gentle heating to reflux precipitated a white solid which was dissolved by adding further thf (20 ml). Hexane (20 ml) was added and the colourless solution was reduced *in vacuo* to approximately 10 ml, whereupon the product precipitated and was gently heated back into solution. Storage at 5 °C (8 h) produced colourless highly air-sensitive cubic crystals of **1** in 23% yield. Originally **1** was prepared by a 1 : 2 reaction of ZnEt$_2$ and Ph$_2$PH in thf–hexane (1 : 1) and crystallised under the same conditions in a yield of 17%. Elemental analysis and spectroscopic work were hampered by loss of coordinated thf when **1** is placed under prolonged vacuum prior to isolation in a glove box, whereupon crystals of **1** are converted to a powder which is insoluble in thf. However, gentle drying of **1** under partial vacuum and transport into a glove box under N$_2$, allowed spectroscopic work and chemical analysis to be undertaken on crystalline samples of **1**; mp 86–88 °C (to a colourless oil, liberating solvated thf). (Found: C, 64.6; H, 5.9; P, 12.1. Calc: C, 65.6; H, 5.9; P, 11.9); ν_{max} (Nujol)/cm^{-1} 3046 m (aryl C–H), 2346w (P–H str); ^{1}H NMR ([^{2}H$_8$]thf, 25 °C, 250 MHz) δ 7.0–7.5 (several m, 50 H, Ph), 5.12 (d, J_{P-H} 216 Hz, 2 H, PH), 3.53 (m, 4 H, thf), 1.70 (m, 4 H, thf), 1.07 [t, 3 H, Zn(3)CH$_2$CH_3], 0.93 [t, 6 H, Zn(1,2)CH$_2$CH_3], 0.25 [q, 2 H, Zn(3)CH_2CH$_3$], −0.02 [q, 4 H, Zn(1, 2)CH_2CH$_3$]; ^{31}P NMR ([^{2}H$_8$]thf, 25 °C, 101.253 MHz) δ −41.35 (d qnt, $^1J_{P-H}$ 216 Hz, $^3J_{P-H}$ 7 Hz, PPh$_2$H), −50.61 (br s, PPh$_2$).

‡ *Crystal data* for **1**: C$_{70}$H$_{75}$OP$_5$Zn$_3$, M = 1283.26, T = 153(2) K, monoclinic, space group Cc, a = 13.937(2), b = 23.091(2), c = 39.389(6) Å, β = 92.42(2)°, V = 12664(3) Å^3, Z = 8, D_c = 1.346 Mg m^{-3}, Mo-Kα radiation (λ = 0.71073 Å), μ = 1.296 mm^{-1} and $F(000)$ = 5344. Data were collected on a Stoe–Siemens AED diffractometer using an oil-coated, rapidly cooled crystal of dimensions 0.41 × 0.38 × 0.32 mm by the ω method ($7 \leqslant 2\theta \leqslant 45°$). Of a total of 16408 collected 16397 were independent. The structure was solved by full-matrix least squares on F^2 with final R_1 ($F > 4\sigma F$) and wR_2 (all data) values of 0.070 and 0.196, respectively $\{R_1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}\}$ (G. M. Sheldrick, SHELXL-93, Göttingen, 1993). Largest peak and hole in the final difference map 0.736 and −0.719 e Å^{-3}. The crystal structure shows racemic twinning. The twinning factor, B, was refined to 0.67(2). Hydrogen atoms were placed in idealised positions and allowed to ride on the relevant atoms in the final stages of refinement, while anisotropic temperature factors were used for all other atoms except for the disordered thf and ethyl groups on Zn(3) and Zn(3′) in one independent molecule [and on Zn(6) and Zn(6′) in the other independent molecule]. The disordered groups were refined with distance restraints on two positions with occupation factors which refined to 52.6/47.4% for Zn(3)/Zn(3′) and 67.6/32.4% for Zn(6)/Zn(6′), respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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