

# Metal selection of ligand functionality in $[(\text{mes})_2\text{P}(\ddot{\text{O}})_2\text{Li}\cdot 2\text{thf}]_2$ and $\{[(\text{Me}_3\text{Si})_2\text{N}\}\text{Cd}\{(\text{mes})_2\text{P}(\ddot{\text{O}})_2\text{Li}\cdot 2\text{thf}\}$ ( $\text{mes} = \text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$ )

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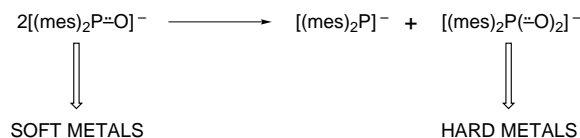
The reaction of  $\text{LiBu}^n$  with  $[(\text{mes})_2\text{P}(\text{H})=\text{O}]$  affords the diorganophosphate complex  $[(\text{mes})_2\text{P}(\ddot{\text{O}})_2\text{Li}\cdot 2\text{thf}]$  **1** and  $[(\text{mes})_2\text{PLi}]$ , however, addition of  $[\text{Cd}\{\text{N}(\text{SiMe}_3)_2\}_2]$  to the mixture gives the diorganophosphinite complex  $\{[(\text{Me}_3\text{Si})_2\text{N}\}\text{Cd}\{(\text{mes})_2\text{P}(\ddot{\text{O}})_2\text{Li}\cdot 2\text{thf}\}$  **2**; the formation of these complexes illustrates that the ligand functionality of **1** can be controlled by the character of the coordinated metal ion.

Although a large number of transition- and main-group metal complexes containing diorganophosphate ligands,  $[\text{R}_2\text{P}(\ddot{\text{O}})_2]^-$ , have been structurally characterised,<sup>1</sup> only transition-metal complexes of the diorganophosphinites,  $[\text{R}_2\text{P}(\ddot{\text{O}})]^-$ , have so far been investigated.<sup>2,3</sup> In comparison to the variety of metal coordination modes observed for  $[\text{R}_2\text{P}(\ddot{\text{O}})_2]^-$  [terminal metal–O, bridging ( $\mu\text{-O}$ ,  $\mu\text{-O}$ ), and bidentate], almost all of the structurally characterised  $[\text{R}_2\text{P}(\ddot{\text{O}})]^-$  complexes contain a ( $\mu\text{-O}$ ,  $\mu\text{-P}$ ) metal bridging mode. Our current interest in this ligand set is in its potential for forming stabilised main-group metal–P bonded complexes and heterobimetallic systems. As a prelude to more extensive studies, we embarked on an investigation of the influence of the character of main-group metal ions on the coordination mode of the  $[\text{R}_2\text{P}(\ddot{\text{O}})]^-$  ligand.

We report here the surprising finding that lithiation of  $[(\text{mes})_2\text{P}(\text{H})=\text{O}]$  with  $\text{LiBu}^n$  (1:1 equiv.) in thf affords the diorganophosphate complex  $[(\text{mes})_2\text{P}(\ddot{\text{O}})_2\text{Li}\cdot 2\text{thf}]$  **1**. However, addition of  $[\text{Cd}\{\text{N}(\text{SiMe}_3)_2\}_2]$  to the  $[(\text{mes})_2\text{P}(\text{H})=\text{O}]\text{-LiBu}^n$  mixture gives the heterobimetallic diorganophosphinite complex  $\{[(\text{Me}_3\text{Si})_2\text{N}\}\text{Cd}\{(\text{mes})_2\text{P}(\ddot{\text{O}})_2\text{Li}\cdot 2\text{thf}\}$  **2**.<sup>†</sup> The very different ligand functionalities exhibited appear to stem from the disproportionation reaction of the diorganophosphinite anion to the diorganophosphate anion in solution (Scheme 1).<sup>‡</sup> Although this disproportionation may be implicated in the formation of  $[\text{R}_2\text{PH}]$  and  $[\text{R}_2\text{P}(\text{OH})=\text{O}]$  during base hydrolysis of  $[\text{R}_2\text{PCI}]$ ,<sup>4</sup> the metal-dependent selection of these ligands (observed in **1** and **2**) has not previously been reported.

A low-temperature X-ray crystallographic study of **1**§ (Fig. 1) shows that the complex has the dimeric structure  $[(\text{mes})_2\text{P}(\ddot{\text{O}})_2\text{Li}\cdot 2\text{thf}]_2$ , composed of planar eight-membered  $[\text{LiO}_2\text{P}]_2$  rings. The Li–O bond lengths in **1** are similar to those occurring in lithium alkoxides and related compounds (Li–O av. 1.881 Å; cf. range 1.80–2.10 Å for other Li–O bonds).<sup>5</sup> The bridging mode of the  $[(\text{mes})_2\text{P}(\ddot{\text{O}})_2]^-$  anion and the dimeric structure of **1** are typical of a variety of diorganophosphate complexes containing a range of main-group and transition metals.<sup>1</sup>

A low-temperature X-ray crystallographic study of **2**§ shows it to have the heterobimetallic structure  $\{[(\text{Me}_3\text{Si})_2\text{N}\}\text{Cd}\{(\text{mes})_2\text{P}(\ddot{\text{O}})_2\text{Li}\cdot 2\text{thf}\}$  (Fig. 2). Molecules of **2** are composed



Scheme 1

of puckered heterocyclic  $[\text{Cd}(\text{PO})_2\text{Li}]$  rings, resulting from the bridging of the Cd and Li centres by the two  $[(\text{mes})_2\text{P}(\ddot{\text{O}})]^-$  ligands. The trigonal-planar Cd centre is attached slightly unsymmetrically to the P atoms of these bridging ligands [Cd–P(1) 2.579(5), Cd(1)–P(2) 2.609(3) Å] and to a terminal  $(\text{Me}_3\text{Si})_2\text{N}$  group [Cd–N(1) 2.136(7) Å]. Presumably, the distortion of the  $[\text{Cd}(\text{PO})_2\text{Li}]_2$  ring occurs principally in order to facilitate complexation of the pseudo-tetrahedral  $\text{Li}^+$  cation by the O atoms of the  $[(\text{mes})_2\text{PO}]^-$  ligands [1.90(2) Å] (while at the same time minimising the steric confrontation between the mesityl groups and the Li-attached thf ligands). Although a number of transition-metal complexes containing  $[\text{R}_2\text{P}(\ddot{\text{O}})]^-$  ligands have been structurally characterised,<sup>2,3</sup> **2** is the first non-transition-metal example and, to our knowledge, the first containing a  $\text{P}^{\text{V}}\text{-Cd}$  bond.<sup>6</sup>

The occurrence of the  $[(\text{mes})_2\text{P}(\ddot{\text{O}})_2]^-$  anion in **1** and the  $[(\text{mes})_2\text{P}(\ddot{\text{O}})]^-$  anion in **2** can be interpreted in terms of the way in which the underlying thermodynamics of metal–ligand bond formation affects the equilibrium between these anions. The presence of the small, highly charged  $\text{Li}^+$  cation will tend to shift this reaction towards the diorganophosphate, with strong Li–O bonding being maximised in **1**. In **2**, the scales are tipped towards the diorganophosphinite anion since the P/O donor set offered will provide optimum bonding with the soft Cd and hard Li metal cations. It is interesting, in the light of this current work, that the few synthetic studies of the oxidation of metal diorganophosphides indicate that the hardness or softness of the metal present has some bearing on the phosphorus oxyanions produced. Thus, oxidation of  $[\text{Me}_2\text{In}(\text{PPh}_2)]_2$  with pyridine-*N*-oxide gives the diorganophosphate  $[\text{Me}_2\text{In}\{(\text{O})_2\text{PPh}_2\}]_2$ ,<sup>11</sup> whereas the  $\text{O}_2$  oxidation of  $[\text{Pd}(\mu\text{-P}(\text{Bu}^t)_2)(\text{P}(\text{Bu}^t)_2\text{H})_2]$  gives the mixed-ligand complex  $[\text{Pd}(\text{Bu}^t_2\text{PO}_2)(\text{Bu}^t_2\text{PO})_2\text{H}]$ .<sup>10</sup>

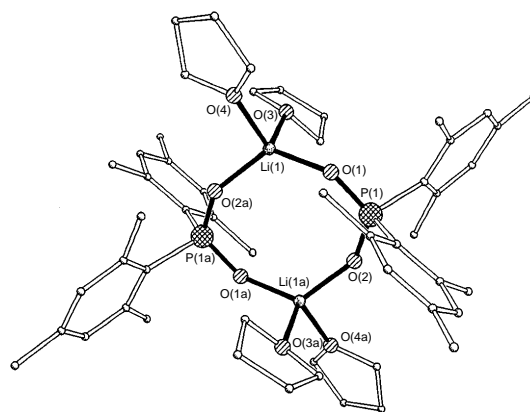
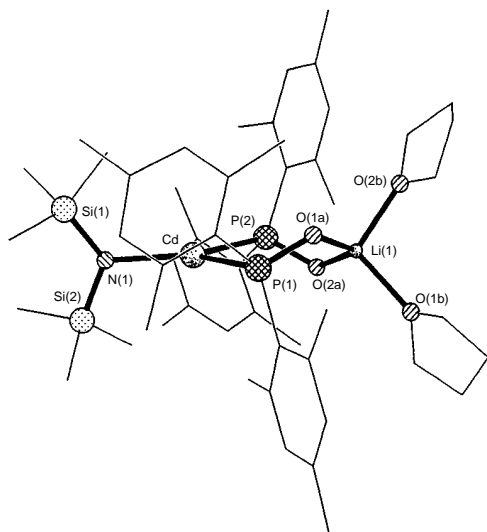


Fig. 1 Molecular structure of **1**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–O(1) 1.501(2), P(1)–O(2) 1.496(2), Li(1)–O(1) 1.878(4), Li(1)–O(2a) 1.884(4), Li(1)–O(3,4) 2.05; O(1)–P(1)–O(2) 117.39(9), av. angles about P 109.4, P(1)–O(1)–Li(1) 140.2(1), P(1)–O(2)–Li(1a) 143.4(1), O(1)–Li(1)–O(2a) 124.4(2), av. angles about Li 107.9.



**Fig. 2** Core structure of **2**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cd–N(1) 2.136(7), Cd–P(1) 2.579(3), Cd–P(2) 2.609(3), P(1)–O(1a) 1.512(8), P(1)–O(2a) 1.526(8), Li(1)–O(1a) 1.90(2), Li(1)–O(2a) 1.90(2), Li(1)–O(1b) 1.95(2), Li(1)–O(2b) 1.92(2), P(1)–Cd–P(2) 99.9, N(1)–Cd–P(1,2) (av.) 129.9, Cd–P(1,2)–O(1a,2a) (av.) 106.7, P(1,2)–O(1a,2a)–Li(1) (av.) 122.4, O(1a)–Li(1)–O(2a) 118(1); av. angles about Li 109.3.

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### Footnotes

† [(mes)<sub>2</sub>PH=O] was prepared by an alternative method to that reported in the literature, by the direct hydrolysis of [(mes)<sub>2</sub>PCl] [generated *in situ* from (mes)MgBr and PCl<sub>3</sub> (2:1 equiv.) in Et<sub>2</sub>O] with H<sub>2</sub>O. The crystalline phosphinous acid was obtained in 72% yield.

Syntheses: **1**: a solution of [(mes)<sub>2</sub>P(H)=O] (0.57 g, 2.0 mmol) in thf (10 ml) was reacted with LiBu<sup>n</sup> (1.3 ml, 2.0 mmol, 1.6 mol dm<sup>-3</sup> in hexanes) under argon. The yellow solution was reduced to dryness under vacuum, leaving a white solid. The solid was redissolved in hexane (10 ml) and a few drops of thf (*ca.* 0.5 ml). Storage at 20 °C (72 h) gave (reproducibly) large crystalline blocks of **1** {first batch, 0.14 g, 16%, based on [(mes)<sub>2</sub>P(H)=O] consumed}.

**2**: a solution of [(mes)<sub>2</sub>P(H)=O] (1.43 g, 5.0 mmol) in thf (10 ml) was reacted with LiBu<sup>n</sup> (6.3 ml, 5.0 mmol, 1.6 mol dm<sup>-3</sup> in hexanes) under argon. To the yellow solution produced was added neat [Cd{N(SiMe<sub>3</sub>)<sub>2</sub>}] (1.0 ml, 5 mmol). Stirring at room temp. (15 min) gave a colourless solution which was reduced *in vacuo* to *ca.* 10 ml. Storage at 5 °C (24 h), gave air-sensitive crystalline cuboids of **2** (2.00 g, 80%).

‡ Variable-temperature <sup>31</sup>P NMR studies show that the composition of the LiBu<sup>n</sup>–[(mes)<sub>2</sub>P(H)=O] reaction mixture is far from simple and that it changes with ageing. However, the intermediate formation of [(mes)<sub>2</sub>POLi] is confirmed by the observation of a weak 1:1:1:1 quartet (δ *ca.* –71.0) at –80 °C (<sup>1</sup>J<sub>31P7Li</sub> *ca.* 75 Hz). Storage under argon at 20 °C results in gradual broadening of the resonances originally at δ *ca.* –41 and another peak at δ –182.4 starts to predominate (after *ca.* 72 h). This is consistent with the formation of [(mes)<sub>2</sub>PLi], produced by the reaction shown in Scheme 1.

§ *Crystal data*: **1**: C<sub>52</sub>H<sub>76</sub>Li<sub>2</sub>O<sub>8</sub>P<sub>2</sub>, *M* = 904.95, triclinic, space group *P* $\bar{1}$ , *a* = 9.934(3), *b* = 11.423(4), *c* = 13.084(5) Å, α = 68.04(4), β = 68.91(4), γ = 71.09(4)°, *U* = 1233.6(8) Å<sup>3</sup>, *Z* = 1, *D<sub>c</sub>* = 1.199 Mg m<sup>-3</sup>, λ = 0.71073 Å, *T* = 153(2) K, μ(Mo-Kα) = 0.138 mm<sup>-1</sup>. Data were collected on a Siemens-Stoe AED diffractometer using an oil-coated rapidly cooled crystal<sup>8</sup> of dimensions 0.5 × 0.5 × 0.3 mm by the θ–ω method (3.69 ≤ θ ≤ 25.02°). Of a total of 5998 collected reflections, 4331 were independent. The structure was solved by direct methods and refined by full-matrix least-squares on *F*<sup>2</sup> to final values of *R*<sub>1</sub> [*F* > 4σ(*F*)] = 0.045 and *wR*<sub>2</sub> = 0.123 (all data);<sup>9</sup> largest peak, hole in the final difference map = 0.285, –0.321 e Å<sup>-3</sup>.

**2**: C<sub>50</sub>H<sub>78</sub>CdLiNO<sub>4</sub>P<sub>2</sub>Si<sub>2</sub>, *M* = 994.59, monoclinic, space group *C*2/*c*, *a* = 14.683(5), *b* = 22.611(5), *c* = 17.538(5) Å, β = 114.244(5)°, *U* = 5374(3) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.229 Mg m<sup>-3</sup>, λ = 0.71073 Å, *T* = 153(2) K, μ(Mo-Kα) = 0.550 mm<sup>-1</sup>. The procedure was identical to that for **1** with crystal dimensions 0.3 × 0.2 × 0.2 mm (2.50 ≤ θ ≤ 22.49°). Of a total of

4426 collected reflections, 3518 were independent. The structure was solved by direct methods and refined by full-matrix least-squares on *F*<sup>2</sup> to final values of *R*<sub>1</sub> [*F* > 4σ(*F*)] = 0.064 and *wR*<sub>2</sub> = 0.179 (all data). Largest peak, hole in the final difference map = 0.805, –1.788 e Å<sup>-3</sup>. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/377.

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