A Dilithium *o*-Phenylenediphosphide $[Li(tmeda)]_2[C_6H_4(PR)_2\text{-}1,2]$ as a $[C_6H_4(PR^-)_2\text{-}1,2]$ or $[C_6H_4(P^{2-})_2\text{-}1,2]$ Synthon: the X-Ray Structures of $C_6H_4[PCH_2CHOCMe_2OCHCH_2\text{-}RR]_2\text{-}1,2$ and $[C_6H_4\{P(SiBu^t\text{-}P)\text{-}1,2\}]_3(\mu_3\text{-}SiBu^t)$ ($R = SiMe_3$, tmeda = $[Me_2NCH_2]_2$)†

Peter B. Hitchcock, Michael F. Lappert and Ping Yin
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

The crystalline dilithium diphosphide $[Li(tmeda)]_2[C_6H_4(PR)_2\text{-}1,2]$ **1** [$R = SiMe_3$, obtained from $C_6H_4(PRR'')_2\text{-}1,2$ ($R' = R'' =$ H or R, or $R' =$ H and $R'' =$ R)] reacts with H_2O, $SiCl_3Me$, or $[Zr(\eta\text{-}C_5H_3R_2\text{-}1,3)_2Cl_2]$ to yield *rac*- and *meso*-$C_6H_4(PHR)_2\text{-}1,2$, $C_6H_4(PR_2)_2\text{-}1,2$, or $[Zr(\eta\text{-}C_5H_3R_2\text{-}1,3)_2\{C_6H_4(PR)_2\text{-}1,2\}]$, respectively; whereas **1** with *RR*-$Me_2C(OCHCH_2OTs)_2$ (Ts = toluene-*p*-sulfonate) or $SiBu^tCl_3$ affords $C_6H_4[PCH_2CHOCMe_2OCHCH_2\text{-}RR]_2\text{-}1,2$ or $[C_6H_4\{P(SiBu^t\text{-}P)\text{-}1,2\}]_3(\mu_3\text{-}SiBu^t)$, respectively.

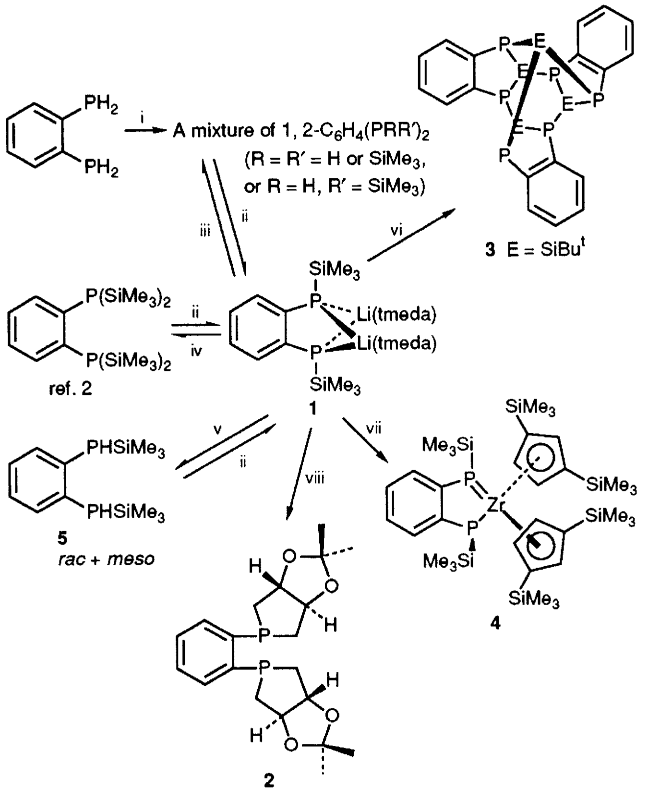
Crystalline $[Li(tmeda)]_2[C_6H_4(PR)_2\text{-}1,2]$ ($R = SiMe_3$) **1** has been obtained from three alternative starting materials: $C_6H_4(PH_2)_2\text{-}1,2$; $C_6H_4(PHR)_2\text{-}1,2$; or $C_6H_4(PR_2)_2\text{-}1,2$ (Scheme 1).

Compound **1** has a similar structure to $[Li(tmeda)]_2[C_6H_4(PPh)_2\text{-}1,2]$,[1] both in the crystal (X-ray) and in solution (variable temperature $^{31}P\{^1H\}$ and ^7Li NMR spectra‡). In its reactivity, however, it displays a unique feature by virtue of the electrophilic character of the $SiMe_3$ (≡ R) substituents. Thus, it acts as a $[C_6H_4(P^{2-})_2\text{-}1,2]$ synthon (class I behaviour) in its reactions with a bis(toluene-*p*-sulfonate) (reaction viii in Scheme 1) or $SiBu^tCl_3$ (reaction vi in Scheme 1), eliminating not only lithium but also the trimethylsilyl moiety. These reactions afforded $C_6H_4[PCH_2CHOCMe_2CHCH_2\text{-}RR]_2\text{-}1,2$ **2** or $[C_6H_4\{P(SiBu^t\text{-}P)\text{-}1,2\}]_3(\mu_3\text{-}SiBu^t)$ **3**, respectively; their X-ray structures are reported. Each compound is noteworthy: **2** for being a novel, readily accessible, optically active diphosphine derived (indirectly) from *RR*-tartaric acid, and **3** for having a P_6Si_4 skeleton comprising a hexagonal pyramidal P_3Si_4 *nido*-cluster with a $(PSi)_3$ base and an Si apex.

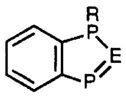
It is not inevitable that the $SiMe_3$ (≡ R) substituents of **1** be labile, as exemplified by its reactions with $[Zr(\eta\text{-}C_5H_3R_2\text{-}1,3)_2Cl_2]$, H_2O and $SiClMe_3$ (reactions vii, v and iv in Scheme 1, respectively) yielding $[Zr(\eta\text{-}C_5H_3R_2\text{-}1,3)_2\{C_6H_4(PR)_2\text{-}1,2\}]$ **4**, a mixture of *meso*- and *rac*-$C_6H_4(PHR)_2\text{-}1,2$ **5**, and $C_6H_4(PR_2)_2\text{-}1,2$, respectively with no loss of $SiMe_3$ groups. In this class II behaviour, **1** qualitatively resembles $[Li(tmeda)]_2[C_6H_4(PPh)_2\text{-}1,2]$.[1,3] It is likely, therefore, that in the class I reactions, elimination of LiX precedes that of $SiMe_3X$. However, the reaction of equimolar portions of **1** and a bis(toluene-*p*-sulfonate) (viii in Scheme 1) has a complicated stoichiometry, because the products comprised 2LiOTs and demimolar portions of each of **2** and $C_6H_4(PR_2)_2\text{-}1,2$. It is noteworthy that $SiMe_3OTs$ was not isolated; we assume that the latter was an intermediate but was readily consumed by $\frac{1}{2}$(**1**) to yield $\frac{1}{2}[C_6H_4(PR_2)_2\text{-}1,2]$ + LiOTs.

We suggest that the reaction sequence leading to formation of the cluster **3** from **1** and $SiBu^tCl_3$ may well have involved successively **6** and its cyclotrimer **7**; the final step would thus have been the ring-capping of **7** by its reaction with an equimolar portion of $SiBu^tCl_3$. The overall stoichiometry for reaction vi of Scheme 1 is thus $3(\mathbf{1}) + 4SiBu^tCl_3 \rightarrow \mathbf{7} + 6SiClMe_3 + 6LiCl$.

Compounds **1**–**5** were identified by elemental analyses and multinuclear NMR spectra and, for crystalline **1**–**4**, also by their X-ray structures; such data for **1** and **4** were similar[4] to those for their $(PPh)_2$-analogues,[1,3] and hence NMR spectral‡



Scheme 1 *Reagents and conditions*: i, (a) $2LiBu^n$, Et_2O, −35 °C, followed by (b) $2SiMe_3Cl$, Et_2O, −35 °C; ii, $2LiBu^n$, 2tmeda, $n\text{-}C_6H_{14}$, 0 °C; iii, 2HCl in Et_2O, 25 °C; iv, $2SiMe_3Cl$, $n\text{-}C_6H_{14}$, 25 °C; v, H_2O (excess), $n\text{-}C_6H_{14}$, 25 °C; vi, $SiBu^tCl_3$, THF, −78 °C; vii, (a) $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2X_2]$ (X = Cl or Br), THF, −78 °C, followed by (b) 25 °C for 16 h; viii, (−)-*RR*-$MeC(OCHCH_2OTs)_2$, THF, 25 °C; THF = tetrahydrofuran



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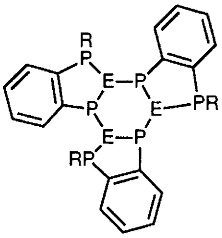

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† No reprints available.

‡ *Selected NMR data*: δ ($C_6D_5CD_3$, 298 K unless otherwise stated; ^1H, ^{13}C, ^{31}P, ^{29}Si, and ^7Li at 250, 62.90, 101.26, 46.70, and 97.21 MHz, respectively): **1** $^{31}P\{^1H\}$ δ −149.6 [septet at 263 K, $^1J(^{31}P^7Li)$ 38.3 Hz], $^7Li\{^1H\}$ δ 6.7 (t at 203 K). **2** ^1H δ 1.37 (q, Me), 1.64 and 1.73 (m, CH_2), 2.37, 3.73, and 4.10 (m, CH_2CH); ^{13}C δ 27.60 and 27.65 (Me), 20.63 and 24.64 (t, CH_2), 83.76 (t) and 84.65 (s, CH_2CH); $^{31}P\{^1H\}$ δ 5.32. **3** $^{31}P\{^1H\}$ δ −164.7 (brt) and −66.45 (brt). **4** $^{31}P\{^1H\}$ δ 37.3 (bs), and at 203 K −49.7(s) and 119.2(2); $^{29}Si\{^1H\}$ δ −6.68 (s, $CSiMe_3$), −6.68 [d, $PSiMe_3$, $^1J(^{29}Si^{31}P)$ 2.9 Hz]. **5** $^{31}P\{^1H\}$ δ −115.1 [$^3J(^{31}P^{31}P)$ 140.8 Hz] and −124.3 [$^3J(^{31}P^{31}P)$ 20 Hz]; $^{29}Si\{^1H\}$ δ 4.37 [t, $J(^{31}P^{29}Si)$ 20.6 Hz] and 4.65 [t, $J(^{31}P^{29}Si)$ 20.6 Hz].

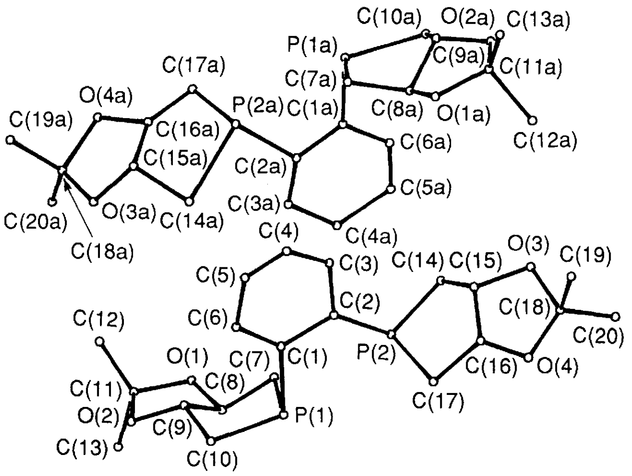

Fig. 1 The X-ray structure and atom labelling for $C_6H_4[PCH_2CHOCMe_2CHCH_2$-*RR*$]_2$-1,2 **2**

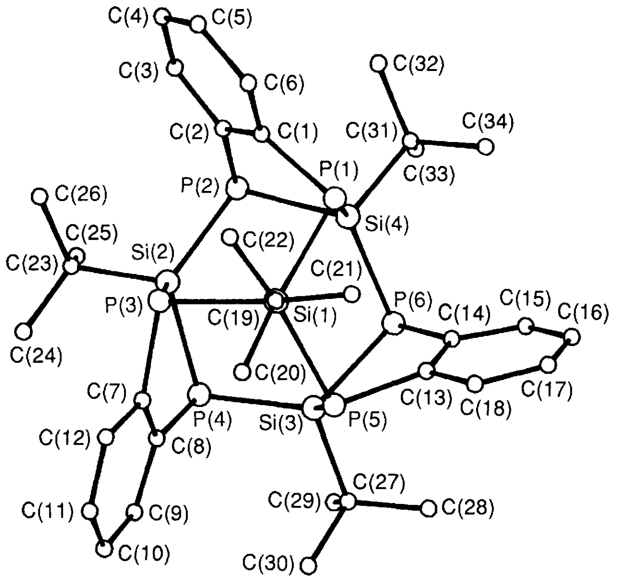

Fig 2 The X-ray structure and atom labelling for $[C_6H_4\{P(SiBu^t$-$P)$-$1,2\}]_3(\mu_3$-$SiBu^t)$ **3**

and X-ray§ details are provided here only for compounds **2** and **3**.

The X-ray structures of compounds **2** and **3** are illustrated in Figs. 1 and 2, respectively. The molecule $[C_6H_4\{P(SiBu^t$-$P)$-$1,2\}]_3(\mu_3$-$SiBu^t)$ **3** has approximate non-crystallographic C_3 symmetry. The Si_4P_6 cage contains four fused P_3Si_3 rings each with a chair conformation. The P–Si bond lengths fall into three distinct groups. As viewed in Fig. 2, the average P–Si bond length in the basal six-membered ring is 2.257(3) Å; the three bonds to Si(1) (the capping atom of the cage) are longer, averaging 2.277(3) Å; whilst the three *exo*-hexacyclic P–Si bonds [P(1)–Si(4), P(3)–Si(2) and P(5)–Si(3)] are shorter, averaging 2.245(3) Å.

These results show that $[Li(tmeda)]_2[C_6H_4(PR)_2$-1,2] (R = $SiMe_3$) has an interesting duality of reactivity, behaving as either a $[C_6H_4(PR^-)_2$-1,2] or a $[C_6H_4(P^{2-})_2$-1,2] synthon, the latter mode being particularly unusual and potentially valuable.

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§ *Crystal data* for **2**: $C_{20}H_{34}O_4P_2$, M = 400.4, monoclinic, space group $C2$ (No. 5), a = 21.988(3), b = 10.561(7), c = 19.596(8) Å, β = 113.58(3)°, U = 4170.5 Å^3, Z = 8, D_c = 1.27 g cm^{-3}, $F(000)$ = 1728, μ = 1.1 cm^{-1}.

For **3**: $C_{34}H_{48}P_6Si_4$, M = 755.0, triclinic, space group $P\bar{1}$ (No. 2), a = 10.601(3), b = 10.680(2), c = 19.557(5) Å, α = 78.93(2), β = 84.42(2), γ = 75.54(2)°, U = 2101.3 Å^3, Z = 2, D_c = 1.19 g cm^{-3}, μ = 3.8 cm^{-1}, $F(000)$ = 796.

For **2**, 7335 reflections were measured, giving 4980 unique reflections (R_{int} = 0.04), and 2578 with $I > 3\sigma(I)$ were used in the refinement. The rather high residuals R = 0.127. R_W = 0.167 with all atoms isotropic and H atoms calculated are a result of the pseudosymmetry. There are two independent molecules almost related by an inversion centre, making the least-squares matrix ill-conditioned. We include this structure only to confirm the identity of the compound and not to make any comment on the details of the geometry.

For **3**, 7433 unique reflections were measured, and 4547 reflections with $I > 2\sigma(I)$ were used in the refinement, giving R = 0.048, R_W = 0.060, with non-H atoms anisotropic and H atoms calculated.

For both structures intensities were measured for $2 < \theta < 25°$ on an Enraf-Nonius CAD4 diffractometer using monochromated Mo-Kα radiation (λ = 0.71069 Å). Structure solution was by direct methods using SHELXS-86.[5]

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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