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# Isolation and structural characterisation of two sterically crowded diphosphanes

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**Abstract**

Under specific conditions the reduction of the chlorophosphanes $R(Me_2NCH_2-2-C_6H_4)PCl$ or $RPCl_2$ [$R = (Me_3Si)_2CH$] with $LiAlH_4$ gives the diphosphanes $\{R(Me_2NCH_2-2-C_6H_4)P\}_2$ (**2**) and RPH–PHR (**3**), respectively, in moderate to good yields. Compound **2** may be obtained in higher yield from the reaction of $\{R(Me_2NCH_2-2-C_6H_4)P\}Li$ with $PbI_2$. Compounds **2** and **3** have been characterised by multi-element NMR spectroscopy and the *meso*-diastereomers of both compounds have been characterised by X-ray crystallography. In the solid state both *meso*-**2** and *meso*-**3** adopt an antiperiplanar conformation. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* P-ligands; Crystal structures; P–P bond; Reduction

## 1. Introduction

Diphosphanes RR′P–PRR′ are accessible through a variety of synthetic procedures including: (i) reduction of a chlorophosphane with an alkali metal Eq. (1); (ii) oxidative coupling of a lithium phosphanide by a transition or main group metal centre Eq. (2); and (iii) oxidative coupling of a lithium phosphanide mediated by 1,2-dibromoethane Eq. (3). Such diphosphanes have been the subject of detailed NMR studies in solution and several have been structurally characterised by X-ray crystallography [1–6].

$$2RR'PCl + 2Na \rightarrow RR'P\text{–}PRR' + 2NaCl \qquad (1)$$

$$2(RR'P)Li + M^{n+} \rightarrow RR'P\text{–}PRR' + M^{(n-2)+} \quad [M = \text{e.g. } Zr^{IV},\ Hg^{II}] \qquad (2)$$

$$2(RR'P)Li + BrCH_2CH_2Br \rightarrow RR'P\text{–}PRR' + CH_2{=}CH_2 + 2LiBr \qquad (3)$$

The reduction of dichlorophosphanes, $RPCl_2$, and chlorophosphanes, $R_2PCl$, to the corresponding primary and secondary phosphanes $RPH_2$ and $R_2PH$ is typically achieved with high efficiency by their reaction with $LiAlH_4$ in ethereal solvents. However, in several recently reported instances it has been observed that such reductions proceed to give high yields of diphosphane products, RP(H)–P(H)R and $R_2P-PR_2$, as well as (or, in some cases, rather than) the expected phosphanes [4,7]. For example, whereas the reaction of $\{(2-C_5H_3N-6-Me)(Me_3Si)_2C\}AsCl_2$ with $LiAlH_4$ in ether at −78 °C yields the corresponding primary arsine $\{(2-C_5H_3N-6-Me)(Me_3Si)_2C\}AsH_2$, treatment of the dichlorophosphane $\{(2-C_5H_3N-6-Me)(Me_3Si)_2C\}PCl_2$ with $LiAlH_4$ under the same conditions yields the disecondary diphosphane $\{(2-C_5H_3N-6-Me)(Me_3Si)_2C\}P(H)-P(H)\{C(SiMe_3)_2(2-C_5H_3N-6-Me)\}$ [5]. Notably, when this reaction is carried out under the same conditions with THF as solvent the complexes $[\{(2-C_5H_3N-6-Me)(Me_3Si)_2C\}E(H)AlH_2]_2$ (E = P, As) are isolated [5], illustrating the sensitivity of reductions mediated by $LiAlH_4$ to the specific reaction conditions. The $LiAlH_4$-mediated oxidative coupling of chlorophosphanes is seemingly favoured when the chlorophosphane has sterically demanding substituents. We now report that, under certain conditions, reduction of the chlorophosphanes $PCl(R)(C_6H_4-2-CH_2NMe_2)$ and $RPCl_2$ [$R = (Me_3Si)_2CH$] by $LiAlH_4$ gives the corresponding diphosphanes as major by-products.

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## 2. Results and discussion

We recently reported that the reaction of $PCl\{CH(SiMe_3)_2\}(C_6H_4-2-CH_2NMe_2)$ with $LiAlH_4$ in ether–THF (2:5 ratio) under conditions of reflux gives the expected secondary phosphane $PH\{CH(SiMe_3)_2\}(C_6H_4-2-CH_2NMe_2)$ (**1**) in good yield [8]. However, when this reduction is carried out at low temperature (−78 °C) in the same solvent system in the presence of an excess of $LiAlH_4$, the diphosphane $\{P(CH[SiMe_3]_2)(C_6H_4-2-CH_2NMe_2)\}_2$ (**2**) is formed in moderate yield, along with variable amounts of **1**Eq. (4). These two products may be separated by crystallisation from cold ether, from which pale yellow crystals of **2** suitable for X-ray crystallography may be isolated after standing at −30 °C for 2 weeks. Compound **2** may be isolated more easily from the reaction of $Li[P\{CH(SiMe_3)_2\}(C_6H_4-2-CH_2NMe_2)]$ with $PbI_2$ at low temperatures. This yields **2** as the major product, along with elemental lead, lithium iodide and small amounts of the secondary phosphane **1** Eq. (5). Although certain lead(II) phosphanides $Pb(PR_2)_2$ are accessible [9–11], it has been noted that these are frequently thermally unstable, decomposing to the diphosphane $R_2P-PR_2$ and elemental lead. For example, the homoleptic, dimeric lead(II) diphosphanide $\{(Me_3Si)_2P\}Pb\{\mu\text{-}P(SiMe_3)_2\}_2Pb\{P(SiMe_3)_2\}$ may be isolated at ambient temperature; however, this compound decomposes to $\{(Me_3Si)_2P\}_2$ and elemental lead on heating under reflux in benzene solution for 10–15 min [9]. In the reaction between $Li[P\{CH(SiMe_3)_2\}(C_6H_4-2-CH_2NMe_2)]$ and $PbI_2$ it appears that the lead(II) diphosphanide intermediate, $Pb[P\{CH(SiMe_3)_2\}(C_6H_4-2-CH_2NMe_2)]_2$, is thermally unstable even at temperatures below ambient, decomposing to **2** and elemental lead in situ.

$$\begin{aligned}&PCl\{CH(SiMe_3)_2\}(C_6H_4\text{–}2\text{-}CH_2NMe_2)\\&\quad + LiAlH_4 \rightarrow x\{P(CH[SiMe_3]_2)\\&\quad \times (C_6H_4\text{–}2\text{-}CH_2NMe_2)\}_2\ (\mathbf{2})\\&+ y[PH\{CH(SiMe_3)_2\}(C_6H_4\text{–}2\text{-}CH_2NMe_2)]\ (\mathbf{1}) \qquad (4)\end{aligned}$$

$$\begin{aligned}&2Li[P\{CH(SiMe_3)_2\}(C_6H_4\text{–}2\text{-}CH_2NMe_2)]\\&\quad + PbI_2 \rightarrow \{P(CH[SiMe_3]_2)\\&\quad \times (C_6H_4\text{–}2\text{-}CH_2NMe_2)\}_2\ (\mathbf{2}) + 2LiI + Pb^0 \qquad (5)\end{aligned}$$

The $LiAlH_4$-mediated reduction of the related dichlorophosphane $RPCl_2$ [$R = (Me_3Si)_2CH$] in ether under reflux also gives substantial quantities of the diphosphane RP(H)–P(H)R (**3**), along with the expected primary phosphane $RPH_2$ (**4**). Compounds **3** and **4** are both highly soluble in hydrocarbon and ethereal solvents but may readily be separated by crystallisation from the extremely poor solvent hexamethyldisiloxane, from which colourless crystals of **3** may be isolated.

Both **2** and **3** crystallise as mixtures of *rac* and *meso* diastereomers; integration of the $^1H$-NMR spectra of both the re-dissolved crystalline materials and their precursor solutions shows that for **2** the *rac–meso* ratio is ca. 1:5, whilst for **3** this ratio is 2:3 and that these ratios are essentially unchanged upon crystallisation.

The $^1H$-, $^{13}C$- and $^{31}P$-NMR spectra of **2** are as expected and clearly show the presence of both diastereomers, although in the $^1H$ spectrum signals due to the two diastereomers overlap in several instances. Unusually, in the $^{13}C$-NMR spectrum of **2** $^{31}P-^{13}C$ coupling is resolved for the $SiMe_3$ carbons in both diastereomers, each signal appearing as a triplet due to coupling to the two phosphorus atoms, both of which appear to have similar coupling constants [$J_{PC}$(average) = 5.1 and 2.7 Hz (*meso*-isomer) and 2.2 Hz (*rac*-isomer, the signal due to the second of the diastereotopic $SiMe_3$ groups is obscured by signals due to the *meso*-diastereomer)].

The non-decoupled $^{31}P$-NMR spectrum of **3** comprises two sets of doublets of doublets, centred at −96.0 and −88.3 ppm (assigned to the *rac* and *meso* diastereomers, respectively), consistent with an AA′XX′′ spin system for each diastereomer [$^1J_{PH} = 120.0$ Hz (*rac*), 136.4 Hz (*meso*); $^2J_{PH} = 65.5$ Hz (*rac*), 58.1 Hz (*meso*)] (Fig. 1). The multiplet signal due to the *rac*-isomer also shows additional splitting due to coupling between each phosphorus and the α-proton of the adjacent $CH(SiMe_3)_2$ substituent [$^2J_{PH} = 7.5$ Hz]. The corresponding $^1H$-NMR spectrum of **3** exhibits complex doublet of doublet signals for the PH protons in both

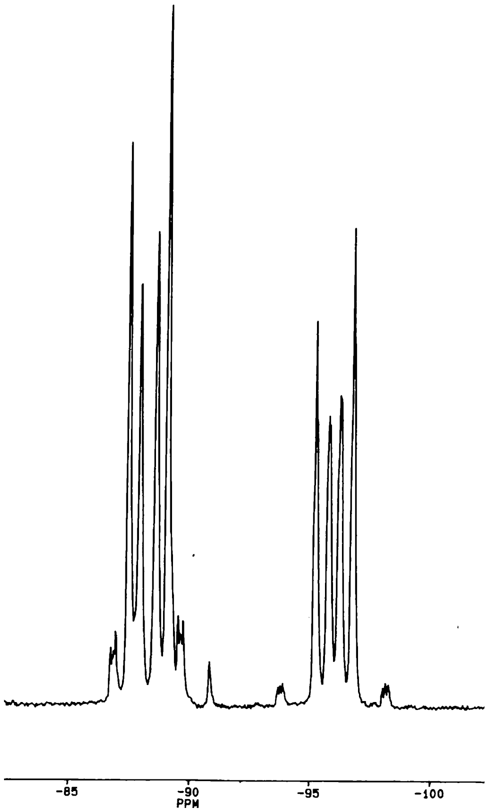
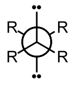


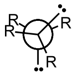
Fig. 1. Non-decoupled $^{31}P$-NMR spectrum of **3** in $d_8$-toluene.

diastereomers; further splitting due to additional coupling between the PH and $Si_2CH$ protons is also observed on these signals, although this is not completely resolved.

X-ray crystal structures were obtained for the *meso*-diastereomers of both **2** and **3** (in both cases crystals of the *rac* and *meso* forms adopt the same habit and are therefore impossible to distinguish by eye). The molecular structures of **2** and **3** are shown in Figs. 2 and 3, respectively and details of bond lengths and angles for both compounds are listed in Table 1. As far as we are aware **3** is only the third example of a disecondary diphosphane to be crystallographically characterised. The other two examples, (mes)PH–PH(mes) [3] and $\{(2\text{-}C_5H_3N\text{-}6\text{-}Me)(Me_3Si)_2C\}P(H)\text{–}P(H)\{C(SiMe_3)_2(2\text{-}C_5H_3N\text{-}6\text{-}Me)\}$ [5], also contain relatively bulky substituents at phosphorus [mes = $2,4,6\text{-}Me_3\text{–}C_6H_2$].

In spite of the large steric bulk of the substituents in **2** and **3**, the P–P distances of 2.2304(6) and 2.2086(8) Å, respectively, are well within the range of distances found for other diphosphanes, although, as expected, the P–P distance in the more sterically encumbered **2** is significantly greater than that in **3**. For example, the P–P distances in $(mes)_2P\text{–}P(mes)_2$, $Cy_2P\text{–}PCy_2$ and $Ph_4C_4P\text{–}PC_4Ph_4$ are 2.260(1), 2.215(3) and 2.2051(11) Å, respectively. In contrast, in the recently reported, closely related, ditertiary diphosphane $R_2P\text{–}PR_2$ [R = $CH(SiMe_3)_2$] the P–P distance is 2.3103(7) Å, the longest such distance to be reported, possibly due to steric interactions between the bulky substituents [2]. There is no contact between the N atoms of the benzylamine substituents and the P atoms in **3**.





Both **2** and **3** crystallise in an antiperiplanar conformation with a crystallographic centre of inversion midway between the two phosphorus atoms. This is in accord with the majority of diphosphanes for which a solid state structure has been obtained; for example, $(mes)_2P\text{–}P(mes)_2$ crystallises in an essentially antiperiplanar conformation with a dihedral angle of 158° between the nominal lone pair directions [1,12], whilst (mes)PH–PH(mes) crystallises with a crystallographic inversion centre [3] (however, there are several examples of diphosphanes which adopt an anticlinal conformation in the solid state [13–16]). Such an antiperiplanar arrangement is perhaps more likely in **2** and **3** due to the size of the substituents at phosphorus, although detailed NMR studies on the sterically encumbered diphosphane $(mes)_2P\text{–}P(mes)_2$ suggest that a synclinal conformation is favoured in solution for this molecule, i.e. in the absence of crystal packing forces [1]. The hydrogen atoms bonded to phosphorus in **3** appear to be disordered over the two possible positions that would give a pyramidal geometry at P, with small electron density peaks in these positions. These H atoms were not included in the refinement.

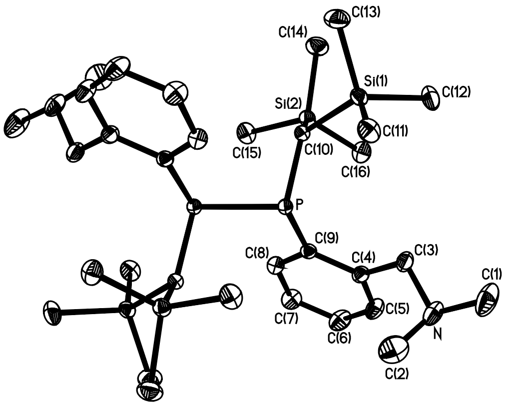


Fig. 2. Molecular structure of **2** with 40% probability ellipsoids and with H atoms omitted for clarity.

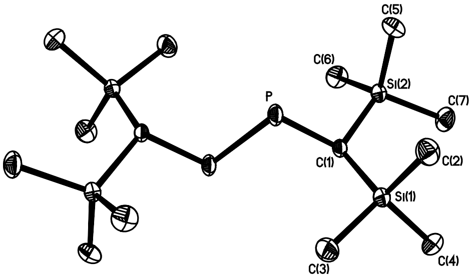


Fig. 3. Molecular structure of **3** with 40% probability ellipsoids and with H atoms omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for **2** and **3**

| **2** | | **3** | |
|---|---|---|---|
| *Bond lengths* (Å) | | | |
| P–P′ | 2.2304(6) | P–P′ | 2.2086(8) |
| C(10)–Si(1) | 1.9125(12) | C(1)–Si(2) | 1.8892(15) |
| Si(1)–C(12) | 1.8726(14) | Si(1)–C(4) | 1.8697(18) |
| Si(2)–C(15) | 1.8725(14) | Si(2)–C(7) | 1.8673(18) |
| P–C(9) | 1.8549(12) | P–C(1) | 1.8679(15) |
| C(10)–Si(2) | 1.8934(12) | Si(1)–C(2) | 1.8600(18) |
| Si(1)–C(13) | 1.8690(15) | Si(2)–C(5) | 1.8676(18) |
| Si(2)–C(16) | 1.8705(14) | C(1)–Si(1) | 1.8819(15) |
| P–C(10) | 1.8813(12) | Si(1)–C(3) | 1.8711(18) |
| S(1)–C(11) | 1.8791(14) | Si(2)–C(6) | 1.8685(17) |
| Si(2)–C(14) | 1.8755(14) | | |
| *Bond angles* (°) | | | |
| P′–P–C(10) | 99.70(4) | P′–P–C(1) | 100.14(5) |
| C(9)–P–C(10) | 107.80(5) | P–C(1)–Si(2) | 109.48(7) |
| P–C(10)–Si(2) | 120.07(6) | P–C(1)–Si(1) | 109.43(8) |
| P′–P–C(9) | 99.93(4) | Si(1)–C(1)–Si(2) | 119.11(7) |
| P–C(10)–Si(1) | 111.88(6) | | |
| Si(1)–C(10)–Si(2) | 115.71(6) | | |

Since the $LiAlH_4$-mediated reduction of **3** gives mixtures of primary phosphane and secondary diphosphane we were interested to see whether alternative reducing agents would have a similar effect on the dichlorophosphine $RPCl_2$. Alternative methods for the synthesis of primary phosphanes include the reduction of dichlorophosphanes with $Bu^n_3SnH$ [17]. We find that treatment of $RPCl_2$ [$R = (Me_3Si)_2CH$] with either $Bu^n_3SnH$ or $Ph_3SnH$ in ether yields a mixture of products containing $RPH_2$, RPH–PHR and the known cyclic triphosphane $(RP)_3$ [18,19] in the approximate ratio 8:11:1 Eq. (6).

$$RPCl_2 + 2Bu^n_3SnH \overset{Et_2O}{\rightarrow} xRPH_2 + yRPH\text{–}PHR + z(RP)_3$$

$$[R = CH(SiMe_3)_2] \qquad (6)$$

We attribute the formation of these three species to the radical-based nature of tin hydride reductions.

## 3. Conclusions

The products of the reduction of certain primary and secondary chlorophosphanes with lithium aluminium hydride are highly sensitive to the reaction conditions. Changes to either the reaction temperature or solvent may affect the ratio of the expected primary or secondary phosphane in comparison to diphosphane products: compound **2** may be isolated in moderate yield from the reduction of the respective chlorophosphane with $LiAlH_4$ at low temperature, whilst the same reaction carried out in refluxing ether–THF yields the secondary phosphane **1** as the exclusive product. The formation of diphosphane products appears to be favoured by sterically demanding substituents at phosphorus.

## 4. Experimental

### 4.1. General Comments

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Ether, THF and light petroleum (b.p. 40–60 °C) were distilled from sodium–potassium alloy under an atmosphere of dry nitrogen and stored over a potassium film (except THF which was stored over activated 4A molecular sieves). Hexamethyldisiloxane was distilled from $CaH_2$ under an atmosphere of dry nitrogen and was stored as for THF. Deuterated $C_6H_5CH_3$ was distilled from potassium and was deoxygenated by three freeze-pump-thaw cycles and stored over activated 4A molecular sieves. $PCl\{CH(SiMe_3)_2\}(C_6H_4\text{–}2\text{-}CH_2NMe_2)$ [8], $\{(Me_3Si)_2CH\}PCl_2$ [20] and $Li[P\{CH(SiMe_3)_2\}(C_6H_4\text{–}2\text{-}CH_2NMe_2)]$ [8] were prepared according to previously published procedures.

$^1H$- and $^{13}C$-NMR spectra were recorded on a Bruker Avance 300 spectrometer operating at 300.1 and 75.5 MHz, respectively, and chemical shifts are quoted in ppm relative to $Me_4Si$; $^{31}P$-NMR spectra were recorded on a Bruker AC300 spectrometer operating at 121.5 MHz and are quoted in ppm relative to external 85% $H_3PO_4$. Elemental analyses were obtained by Elemental Microanalysis Ltd., Okehampton, UK.

### 4.2. Preparation of $\{P(CH[SiMe_3]_2)(C_6H_4\text{–}2\text{-}CH_2NMe_2)\}_2$ (**2**)

#### 4.2.1. Method (a)

To a solution of $PCl\{CH(SiMe_3)_2\}(C_6H_4\text{–}2\text{-}CH_2NMe_2)$ (0.87 g, 2.416 mmol) in ether–THF (10 ml/25 ml) at −78 °C was added $LiAlH_4$ (0.09 g, 2.371 mmol). This mixture was allowed to attain room temperature (r.t.) and was stirred for 2 h. De-oxygenated water was carefully added and the organic phase was decanted and dried over activated 4A molecular sieves. Evaporation of the solvent under reduced pressure yielded a colourless oil containing both **1** and **2** from which crystals of **2** formed in ca. 10% yield after standing for 2 weeks at r.t.

#### 4.2.2. Method (b)

To a cold (−78 °C) suspension of $PbI_2$ (0.91 g, 1.974 mmol) in ether (30 ml) was added, dropwise, a solution of $Li[P\{CH(SiMe_3)_2\}(C_6H_4\text{–}2\text{-}CH_2NMe_2)]$ (1.19 g, 3.596 mmol) in ether (20 ml). This mixture was allowed to warm to r.t. and was stirred for 12 h. The dark reaction mixture was filtered and the filtrate was concentrated to ca. 10 ml and cooled to −30 °C for 12 h. The pale yellow crystals of **2** were isolated by filtration, washed with a little light petroleum and dried in vacuo. Yield: 0.91 g, 78%. Anal. Found: C, 57.57; H, 9.93; N, 4.14. Calc. for $C_{32}H_{62}N_2P_2Si_4$: C, 59.21; H, 9.63; N, 4.32%. $^1H$-NMR ($d_8$-$C_6H_5CH_3$, 295 K): *meso*-isomer: 0.10 (s, 9H, $SiMe_3$), 0.16 (s, 9H, $SiMe_3$), 0.41 (s, 1H, $Si_2CH$), 2.34 (s, 6H, $NMe_2$), 3.87 (d, $J_{HH} = 14.0$ Hz, 1H, $CH_2N$), 4.20 (d, $J_{HH} = 14.0$ Hz, 1H, $CH_2N$), 7.19 (m, 2H, ArH), 7.72 (m, 1H, ArH), 8.42 (m, 1H, ArH); *rac*-isomer: 0.14 (s, 9H, $SiMe_3$), 0.44 (s, 9H, $SiMe_3$), 0.77 (t, $J_{PH} = 3.6$ Hz, 1H, $Si_2CH$) 2.29 (s, 6H, $NMe_2$), 3.62 (d, $J_{HH} = 13.3$ Hz, 1H, $CH_2N$), 3.80 (d, $J_{HH} = 13.3$ Hz, 1H, $CH_2N$), 6.73 (m, 1H, ArH), 6.95 (m, 1H, ArH), 7.42 (m, 1H, ArH), 7.65 (m, 1H, ArH). $^{13}C\{^1H\}$-NMR ($d_8$-$C_6H_5CH_3$, 295 K): *meso*-isomer: 1.59 (t, $J_{PC} = 10.1$ Hz, $SiMe_3$), 2.17 (t, $J_{PC} = 2.7$ Hz, $SiMe_3$), 9.46 (t, $J_{PC} = 27.1$ Hz, $Si_2C$), 44.66 (s, $NMe_2$), 62.23 (t, $J_{PC} = 12.6$ Hz, $CH_2N$), 125.24 (Ar)128.07 (t, $J_{PC} = 3.0$ Hz, Ar), 128.22 (Ar), 135.37 (t, $J_{PC} = 12.1$ Hz, Ar), 144.93 (t, $J_{PC} = 13.8$ Hz, Ar); *rac*-isomer: 2.39 (t, $J_{PC} = 2.2$ Hz, $SiMe_3$), 8.27 (t, $J_{PC} = 19.2$ Hz, $Si_2C$), 44.31 ($NMe_2$), 61.18 (t, $J_{PC} =$

12.3 Hz, $CH_2N$), 124.47, 127.39 (Ar), 135.50 (t, $J_{PC} = 6.1$ Hz, Ar), 144.01 (t, $J_{PC} = 13.5$ Hz, Ar). $^{31}P\{^1H\}$-NMR ($d_8$-$C_6H_5CH_3$, 295 K): *meso*-isomer: −21.3; *rac*-isomer: −22.4.

### 4.3. Preparation of $\{PH(CH[SiMe_3]_2)\}_2$ (**3**)

To a solution of $\{(Me_3Si)_2CH\}PCl_2$ (1.98 g, 7.58 mmol) in ether (20 ml) was added $LiAlH_4$ (0.80 g, 21.1 mmol). This mixture was heated under reflux for 4 h, cooled and then de-oxygenated water was added (25 ml). The organic phase was extracted with light petroleum (3 × 10 ml) and dried over activated 4A molecular sieves. Solvent was removed in vacuo to give a colourless oil from which colourless crystals of *rac*–*meso*-**3** (ca. 2:3 ratio) appeared after standing for 16 h. Crystals of **3** suitable for X-ray crystallography were obtained from cold (−30 °C) hexamethyldisiloxane. Yield of crystalline *rac*–*meso*-**3**: 0.67 g, 46%. Anal. Found: C, 41.12; H, 10.55. Calc. for $C_{14}H_{40}P_2Si_4$: C, 43.93; H, 10.53%. $^1H$-NMR ($d_8$-$C_6H_5CH_3$, 295 K): *meso*-isomer: 0.15 (s, 9H, $SiMe_3$), 0.16 (s, 9H, $SiMe_3$), 0.29 (s, 1H, $CHSi_2$), 3.11 (dd, $^1J_{PH} = 136.4$ Hz, $^2J_{PH} = 58.1$ Hz, 1H, PH); *rac*-isomer: 0.13 (s, 9H, $SiMe_3$), 0.19 (s, 9H, $SiMe_3$), 0.32 (s, 1H, $CHSi_2$), 3.43 (dd, $^1J_{PH} = 120.0$ Hz, $^2J_{PH} = 66.5$ Hz, 1H, PH). $^{13}C\{^1H\}$-NMR ($d_8$-$C_6H_5CH_3$, 295 K): *meso*-isomer: 0.03 ($SiMe_3$), 5.03 (t, $J_{PC} = 18.6$ Hz, $CHSi_2$); *rac*-isomer: −0.10 ($SiMe_3$), 4.14 (d, $J_{PC} = 19.7$ Hz, $CHSi_2$). $^{31}P\{^1H\}$-NMR ($d_8$-$C_6H_5CH_3$, 295 K): *meso*-isomer: −96.0; *rac*-isomer: −88.3.

Table 2

Table 2

Crystallographic data for **2** and **3**

| | **2** | **3** |
|---|---|---|
| Empirical formula | $C_{32}H_{62}N_2P_2Si_4$ | $C_{14}H_{40}P_2Si_4$ |
| Formula weight | 649.14 | 382.76 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2_1/n$ | $P\bar{1}$ |
| $a$ (Å) | 12.6787(8) | 6.5376(7) |
| $b$ (Å) | 10.6897(7) | 8.1120(9) |
| $c$ (Å) | 14.8800(9) | 12.2027(13) |
| $\alpha$ (°) | | 106.375(2) |
| $\beta$ (°) | 102.631(12) | 93.835(2) |
| $\gamma$ (°) | | 103.031(2) |
| $V$ (Å$^3$) | 1967.9(2) | 598.99(11) |
| $Z$ | 2 | 2 |
| $D_{calc.}$ (g cm$^{-1}$) | 1.095 | 1.061 |
| $\mu$ (mm$^{-1}$) | 0.255 | 0.375 |
| Crystal size (mm) | 0.70 × 0.65 × 0.20 | 0.55 × 0.32 × 0.22 |
| Reflections | 16 462 | 5160 |
| Unique reflections | 4658 | 2732 |
| Reflections with $F^2 > 2\sigma$ | 4085 | 2421 |
| Parameters | 189 | 97 |
| $R$, $R_w$ [$F^2 > 2\sigma$] [a] | 0.0278, 0.0742 | 0.0358, 0.1034 |
| $R$, $R_w$ [all data] [a] | 0.0333, 0.0776 | 0.0395, 0.1064 |
| Goodness-of-fit on $F^2$ [b] | 1.042 | 1.077 |
| Largest difference peak/hole (e Å$^{-3}$) | 0.32, −0.22 | 0.68, −0.54 |

[a] $R = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|; R_w = [\Sigma\,w(F_o^2 - F_c^2)^2/(\Sigma\,wF_o^2)^2]^{1/2}$.

### 4.4. Reaction of $\{(Me_3Si)_2CH\}PCl_2$ with $Ph_3SnH$

To a solution of $\{(Me_3Si)_2CH\}PCl_2$ (0.73 g, 2.79 mmol) in cold (0 °C) ether (10 ml) was added, dropwise, a solution of $Ph_3SnH$ (1.96 g, 5.58 mmol) in ether (10 ml). This mixture was allowed to attain r.t. and was stirred for 16 h. Light petroleum (5 ml) was added and the solids were removed by filtration. The filtrate was concentrated to ca. 5ml and a $^{31}P\{^1H\}$-NMR spectrum was obtained, revealing the presence of $RPH_2$ (ca. 40%), RPH–PHR (ca. 55%) and $(RP)_3$ (ca. 5%). $^{31}P$-NMR (ether–light petroleum, 295 K): −155.2 (t, $J_{PP} = 198.5$ Hz, $(RP)_3$), −147.1 (s, $RPH_2$), −128.3 (d, $J_{PP} = 198.5$ Hz, $(RP)_3$), −96.0 (s, *meso*-RPH–PHR), −88.3 (s, *rac*-RPH–PHR).

A similar reaction between $\{(Me_3Si)_2CH\}PCl_2$ and $Bu^n_3SnH$ in ether at 0 °C gave substantially greater quantities of $RPH_2$ contaminated with RPH–PHR and $(RP)_3$.

### 4.5. Crystal structure determination of meso-2 and meso-3

Data were collected at 160 K on a Bruker AXS SMART CCD diffractometer with graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Structure solution was by direct methods and refinement was by full matrix least-squares on $F^2$. Absorption correction was by semi-empirical methods from equivalents and repeated reflections. Further details of data collection and refinement are given in Table 2 and in the supporting information. Programs used: BRUKER AXS SMART (diffractometer control), SAINT (data integration), and SHELXTL (structure solution and refinement).

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 179744 and 179743 for compounds **2** and **3**, respectively. Copies of this information are available free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (int. code) +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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