

# Effect of peripheral donor substituents on the binding modes of phosphinomethanide ligands. Synthesis and crystal structures of alkali metal derivatives of an O-functionalised phosphinomethanide ligand

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The O-functionalised tertiary phosphine  $\{(Me_3Si)_2CH\}P(C_6H_4-2-CH_2OMe)_2$  (**9**) is accessible *via* the reaction of  $\{(Me_3Si)_2CH\}PCl_2$  with two equivalents of *in situ* generated 2-LiC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OMe. Phosphine **9** is readily deprotonated by Bu<sup>n</sup>Li to give the lithium phosphinomethanide  $[\{(Me_3Si)_2C\}P(C_6H_4-2-CH_2OMe)_2]Li$  (**13**), which undergoes metathesis reactions with the alkoxides MOR [M = Na, K, R = Bu<sup>n</sup>; M = Rb, R = 2-ethylhexyl] to give the heavier alkali metal phosphinomethanides  $[\{(Me_3Si)_2C\}P(C_6H_4-2-CH_2OMe)_2]M$  in good yields [M = Na (**14**), *n* = 2; M = K (**15**), Rb (**16**), *n* = ∞]. Compounds **9**,  $[\{(Me_3Si)_2CH\}P(C_6H_4-2-CH_2OMe)_2LiBr]_2$  (**10**), and **14–16** have been studied by X-ray crystallography; in the solid state **14** adopts a dimeric structure, whereas **15** and **16** crystallise as one-dimensional polymers.

## Introduction

Phosphorus-stabilised carbanions (phosphinomethanides,  $[R_2P-CR_2]^-$ ) constitute an interesting class of ambidentate ligands. Their ambidentate nature may be attributed to extensive delocalisation of charge from the carbanion to the phosphorus centre(s) and the similar electronegativities of phosphorus and carbon, allowing the P and C atoms to compete as nucleophiles for metal centres. Phosphinomethanides thus adopt a wide variety of coordination modes in their complexes with main group and transition metals, ranging from monodentate C- or P-donation through to  $\eta^2$ -PC and  $\eta^3$ -PCP heteroallyl coordination and bridging modes.<sup>1</sup> The coordination mode adopted is dependent on a variety of factors, including the nature of the substituents at the P and C centres, the nature of the metal and the presence of co-ligands. In addition, we have recently shown that the incorporation of donor functionality at the periphery of tertiary phosphines has a dramatic effect on both their deprotonation behaviour and the binding modes of the subsequent phosphinomethanide ligands.<sup>2</sup>

In this context, we have reported that the amino-functionalised tertiary phosphine  $\{(Me_3Si)_2CH\}P(C_6H_4-2-CH_2NMe_2)_2$  undergoes complete deprotonation on treatment with Bu<sup>n</sup>Li in a matter of minutes at room temperature.<sup>2a</sup> This is in stark contrast to  $\{(Me_3Si)_2CH\}PMe_2$ , which undergoes deprotonation with Bu<sup>n</sup>Li only over a period of several days in refluxing hexane.<sup>3</sup> The peripheral amino groups also engender a novel PN<sub>2</sub>-coordination mode in the corresponding phosphinomethanide derivatives,  $[\{(Me_3Si)_2C\}P(C_6H_4-2-CH_2NMe_2)_2M(L)_n]_x$  [M = Li (**1**), *n* = 0, *x* = 1; M = Na (**2**), (L)<sub>*n*</sub> = (Et<sub>2</sub>O)<sub>0.5</sub>(DME)<sub>0.5</sub>, *x* = 1; M = K (**3**), Rb (**4**), *n* = 0, *x* = ∞; M = Cs (**5**), (L)<sub>*n*</sub> = (PhMe), *x* = ∞], enabling the synthesis of the first complexes (**2–5**) containing a direct bond between a heavier alkali metal and a formally tertiary phosphine centre.<sup>2b–d</sup> There is a remarkable structural diversity amongst these alkali metal complexes, which range from non-solvated monomers to one-dimensional polymers.

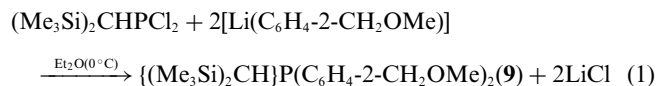
In addition, we have demonstrated that the related tertiary phosphine MeP(C<sub>6</sub>H<sub>4</sub>-2-CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub> (**6**) undergoes selective deprotonation at a benzylic site on treatment with Bu<sup>n</sup>Li to give the unusual dimer  $[MeP\{C_6H_4-2-CH(Li)NMe_2\}(C_6H_4-2-CH_2NMe_2)]_2$  (**7**),<sup>4</sup> but that treatment of **6** with Bu<sup>n</sup>Li under the same conditions results in deprotonation at the methyl

group adjacent to phosphorus to give a tetrameric phosphinomethanide complex  $[LiCH_2P(C_6H_4-2-CH_2NMe_2)_2]_4 \cdot (PhMe)_3$  (**8**).<sup>5</sup> The benzyllithium species **7** isomerises slowly in toluene solution to give **8**; both **7** and **8** are unstable in THF, yielding the same secondary phosphide complex  $[MeP\{C_6H_4-2-CH(C_6H_4-2-CH_2NMe_2)\}Li(THF)_2]$  *via* an unusual Smiles rearrangement.<sup>6</sup>

The foregoing prompted us to consider to what extent changing the peripheral donor groups in these ligands from nitrogen- to oxygen-donors would affect their reactivities and structures. We herein report the synthesis and structural characterisation of the new O-functionalised tertiary phosphine  $\{(Me_3Si)_2CH\}P(C_6H_4-2-CH_2OMe)_2$  (**9**) and its alkali metal derivatives  $[\{(Me_3Si)_2C\}P(C_6H_4-2-CH_2OMe)_2]M$  [M = Na, K, Rb].

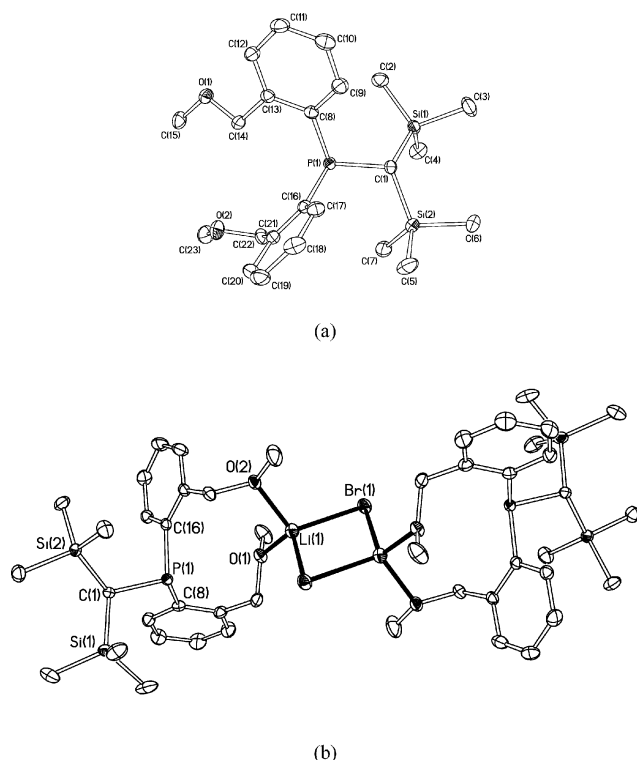
## Results and discussion

Metalation of 2-bromobenzyl methyl ether with Bu<sup>n</sup>Li at 0 °C cleanly gives the corresponding lithium salt, which reacts *in situ* with half an equivalent of  $\{(Me_3Si)_2CH\}PCl_2$  to give the tertiary phosphine  $\{(Me_3Si)_2CH\}P(C_6H_4-2-CH_2OMe)_2$  (**9**) in good yield, according to eqn. (1).



Compound **9** is isolated as a viscous oil which slowly crystallises on standing for several days at room temperature. In contrast to previous reports,<sup>7</sup> we found that, if the reaction between Bu<sup>n</sup>Li and 2-bromobenzyl methyl ether was allowed to warm to room temperature, a side reaction occurred that greatly diminished the yield of **9**. This is most likely due to the formation of butyl-substituted benzyl ethers and LiBr; interestingly, isolation of the expected tertiary phosphine from these reactions yielded a novel tertiary phosphine–LiBr adduct  $[\{(Me_3Si)_2CH\}P(C_6H_4-2-CH_2OMe)_2LiBr]_2$  (**10**) as a significant by-product.

The <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **9** and **10** in CDCl<sub>3</sub> are essentially identical, suggesting that the LiBr fragment in **10** is only weakly bound by the ligand; indeed, dissolution of **10** in this solvent is accompanied by the precipitation of a small amount of solid, which we attribute to the elimination of LiBr under these conditions. Compounds **9** and **10** were characterised by



**Fig. 1** Molecular structures of (a) **9** and (b) **10** with 40% probability ellipsoids and with H atoms omitted for clarity.

X-ray crystallography; the molecular structures of **9** and **10** are shown in Fig. 1 and details of bond lengths and angles are given in Table 1. The structure of **9** is as expected; the P atom is three-coordinate with P–C bond lengths of 1.8480(14), 1.8529(14) and 1.8514(14) Å [P–C(1), P–C(8), and P–C(16), respectively]. This contrasts with the crystal structures of several related

**Table 1** Selected bond lengths (Å) and angles (°) for **9** and **10**

<b>9</b>			
P(1)–C(1)	1.8480(14)	P(1)–C(8)	1.8529(14)
P(1)–C(16)	1.8514(14)	Si(1)–C(1)	1.9126(15)
Si(1)–C(2)	1.8619(17)	Si(1)–C(3)	1.8696(17)
Si(1)–C(4)	1.8719(18)	Si(2)–C(1)	1.9063(15)
Si(2)–C(5)	1.8699(18)	Si(2)–C(6)	1.8730(17)
Si(2)–C(7)	1.8710(17)		
C(1)–P(1)–C(8)	105.59(6)	C(1)–P(1)–C(16)	105.56(6)
C(8)–P(1)–C(16)	97.17(6)	P(1)–C(1)–Si(1)	107.53(7)
Si(1)–C(1)–Si(2)	113.34(7)	P(1)–C(1)–Si(2)	112.94(7)
<b>10</b>			
Br(1)–Li(1)	2.482(4)	Br(1)–Li(1A)	2.465(4)
P(1)–C(1)	1.854(2)	P(1)–C(8)	1.854(2)
P(1)–C(16)	1.855(2)	Si(1)–C(1)	1.906(2)
Si(1)–C(2)	1.877(3)	Si(1)–C(3)	1.872(3)
Si(1)–C(4)	1.858(3)	Si(2)–C(1)	1.908(2)
Si(2)–C(5)	1.867(3)	Si(2)–C(6)	1.867(2)
Si(2)–C(7)	1.871(3)	O(1)–C(14)	1.433(3)
O(1)–C(15)	1.427(3)	O(1)–Li(1)	1.940(4)
O(2)–C(22)	1.448(3)	O(2)–C(23)	1.427(3)
O(2)–Li(1)	1.963(5)		
Li(1)–Br(1)–Li(1A)	76.12(15)	C(1)–P(1)–C(8)	103.51(10)
C(1)–P(1)–C(16)	104.16(10)	C(8)–P(1)–C(16)	98.09(10)
P(1)–C(1)–Si(1)	107.42(11)	P(1)–C(1)–Si(2)	114.99(11)
Si(1)–C(1)–Si(2)	113.34(11)	Br(1)–Li(1)–Br(1A)	103.88(15)
Br(1)–Li(1)–O(1)	115.2(2)	Br(1A)–Li(1)–O(1)	113.69(19)
Br(1)–Li(1)–O(2)	111.37(19)	Br(1A)–Li(1)–O(2)	110.21(19)
O(1)–Li(1)–O(2)	102.7(2)		

Symmetry operator (inversion): A,  $2 - x, 2 - y, -z$ .

benzylamine- or naphthylamine-substituted tertiary phosphines such as  $\text{P}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)_3$  (**11**) and  $\text{P}(\text{C}_{10}\text{H}_6\text{-8-NMe}_2)_3$  (**12**), for which X-ray crystallography suggests significant  $\text{P} \cdots \text{N}$  contacts.<sup>8,9</sup> For example, compound **11** crystallises in four, structurally different, forms which have either two or three  $\text{P} \cdots \text{N}$  contacts, giving a pseudo-hexacoordinate or pseudo-heptacoordinate phosphorus centre.<sup>9</sup> The lack of any corresponding  $\text{P} \cdots \text{O}$  contact in **9** is most likely due to the weaker donor strength of the ether O atom and the large degree of steric hindrance about the phosphorus atom in this compound.

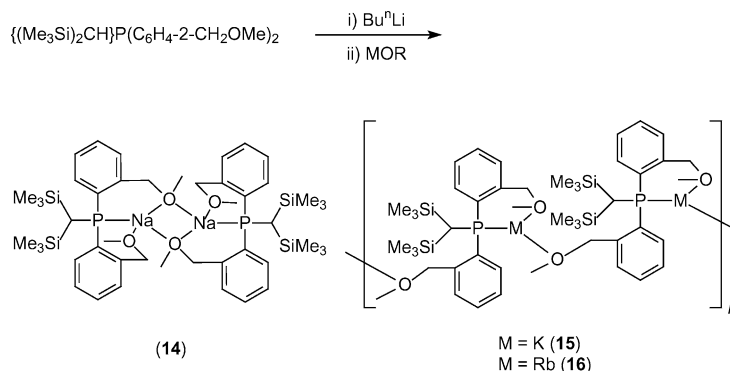
Compound **10** crystallises as discrete dimers with a crystallographic centre of inversion and a central  $\text{Li}_2\text{Br}_2$  rhombus-shaped core. It is to be expected that the hard lithium cations will favour interactions with the hard oxygen donor groups over interactions with the soft tertiary phosphine centres and, in accord with this, there are no short contacts between the lithium and phosphorus atoms in **10**. The coordination sphere of each lithium is comprised of two bromide ions and two oxygen atoms from the benzyl ether substituents of an adjacent phosphine, giving a four-coordinate, distorted tetrahedral lithium centre. Thus, the tertiary phosphine ligands chelate the lithium atoms *via* their two ether donor groups, generating 10-membered chelate rings. The Li–Br distances of 2.465(4) and 2.482(4) Å and the Li–O distances of 1.940(4) and 1.963(5) Å are typical for these types of contact.

Treatment of **9** with one equivalent of  $\text{Bu}^n\text{Li}$  in diethyl ether yields a red solution containing the lithium phosphinomethanide  $[\{(\text{Me}_3\text{Si})_2\text{C}\}\text{P}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{OMe})_2]\text{Li}$  (**13**). Despite repeated attempts, we were unable to obtain a sample of **13** suitable for analysis; this compound is always isolated as a viscous oil. However, the identity of **13** may be inferred from the large change in  $^{31}\text{P}$  chemical shift from  $-46.6$  to  $-11.8$  ppm on metalation of **9** with  $\text{Bu}^n\text{Li}$  and the subsequent successful isolation of the heavier alkali metal compounds  $[\{(\text{Me}_3\text{Si})_2\text{C}\}\text{P}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{OMe})_2]\text{M}_n$  *via* the *in situ* formation of **13** (Scheme 1) [ $\text{M} = \text{Na}$  (**14**),  $n = 2$ ;  $\text{M} = \text{K}$  (**15**),  $\text{Rb}$  (**16**),  $n = \infty$ ]. In contrast to **1**,  $^{31}\text{P}$ – $^7\text{Li}$  coupling was not resolved in either the  $^{31}\text{P}$  or  $^7\text{Li}$  NMR spectra of crude solutions of **13** in either toluene or THF.<sup>2a</sup>

A straightforward metathesis reaction between *in situ* formed **13** and the alkali metal alkoxides MOR [ $\text{M} = \text{Na}$ ,  $\text{K}$ ,  $\text{R} = \text{Bu}^i$ ;  $\text{M} = \text{Rb}$ ,  $\text{R} = 2\text{-ethylhexyl}$ ] yields the heavier alkali metal phosphinomethanides **14–16** as orange crystalline solids, after work-up (Scheme 1). A similar reaction between **13** and caesium 2-ethylhexoxide yields an orange oil, which we were unable to crystallise, but which has  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra consistent with the formation of a caesium phosphinomethanide  $[\{(\text{Me}_3\text{Si})_2\text{C}\}\text{P}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{OMe})_2]\text{Cs}$ . Compounds **14–16** are soluble in ethereal and aromatic solvents but are insoluble in light petroleum and were obtained as single crystals suitable for X-ray crystallography from hot toluene.

The  $^{31}\text{P}\{^1\text{H}\}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectra of **14–16** are consistent with the formation of solvent-free phosphinomethanide complexes; the  $^{31}\text{P}\{^1\text{H}\}$  spectra exhibit singlets at  $-12.4$ ,  $-6.2$  and  $-17.1$  ppm, respectively, whereas the  $^1\text{H}$  NMR spectra are very broad at room temperature, consistent with the operation of one or more dynamic processes in solution. This behaviour parallels that of the amino-functionalised compounds **1–5** and may be attributed to rapid, reversible M–O or M–P cleavage and/or changes in chelate ring conformation.<sup>2b</sup>

Compound **14** crystallises from toluene as solvent-free centrosymmetric dimers containing an  $\text{Na}_2\text{O}_2$  rhombus-shaped core; the molecular structure of **14** is shown in Fig. 2 and details of bond lengths and angles are given in Table 2. Each sodium is bound by the phosphorus and the two ether oxygen atoms of a phosphinomethanide ligand, generating two puckered six-membered chelate rings [O–Na–P bite angles:  $81.57(5)$  and  $86.48(5)^\circ$ ]. Each sodium is further coordinated by an oxygen atom from an adjacent ligand in the dimer; thus one ether oxygen in each ligand acts as a bridge between the two sodium

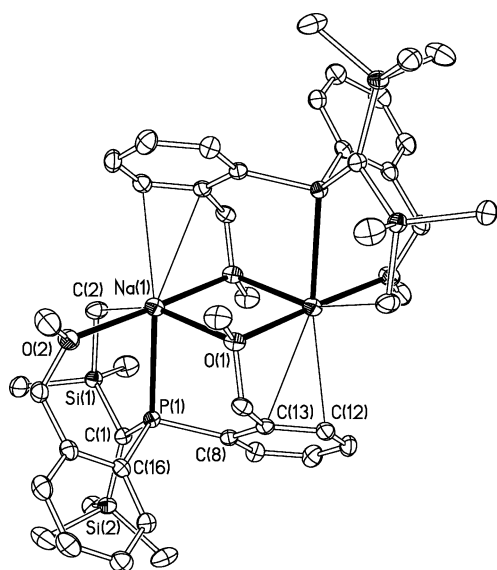


**Scheme 1** M = Na, K, R = Bu<sup>n</sup>; M = Rb, R = 2-ethylhexyl [principal contacts only shown].

**Table 2** Selected bond lengths (Å) and angles (°) for **14**

P(1)–Na(1)	2.8144(16)	P(1)–C(1)	1.7499(18)
P(1)–C(8)	1.866(2)	P(1)–C(16)	1.8501(19)
Si(1)–C(1)	1.8198(18)	Si(1)–C(2)	1.897(2)
Si(1)–C(3)	1.887(2)	Si(1)–C(4)	1.883(2)
Si(2)–C(1)	1.829(2)	Si(2)–C(5)	1.876(2)
Si(2)–C(6)	1.886(2)	Si(2)–C(7)	1.893(2)
Na(1)–O(1)	2.4327(17)	Na(1)–O(1A)	2.4543(18)
Na(1)–O(2)	2.3182(18)	Na(1)–C(12A)	2.859(2)
Na(1)–C(13A)	2.945(2)		
P(1)–Na(1)–O(1)	86.48(5)	P(1)–Na(1)–O(1A)	96.04(5)
P(1)–Na(1)–O(2)	81.57(5)	O(1)–Na(1)–O(1A)	84.37(6)
O(1)–Na(1)–O(2)	102.79(6)	O(1A)–Na(1)–O(2)	172.24(5)
Na(1)–O(1)–Na(1A)	95.63(6)	P(1)–C(1)–Si(1)	114.43(10)
P(1)–C(1)–Si(2)	124.79(10)	Si(1)–C(1)–Si(2)	118.72(10)

Symmetry operator (inversion): A,  $-x, 1-y, -z$ .



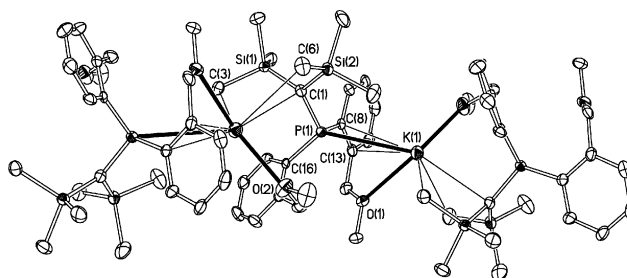
**Fig. 2** Molecular structure of **14** with 40% probability ellipsoids and with H atoms omitted for clarity.

atoms. The Na–P distance of 2.8144(16) Å is somewhat longer than the same distance in **2** [2.8004(10) Å],<sup>2d</sup> but is shorter than the Na–P distances in the only other reported sodium phosphinomethanides [ $\{\text{CH}_2\text{C}(\text{PR}_2)_2\}\text{NaL}_2$  [R = Ph, L = pmdeta; R = Pr<sup>i</sup>, L = (THF)<sub>3</sub>; pmdeta = *N,N,N',N',N''*-pentamethyldiethylenetriamine], which range from 2.877(2) to 3.0451(11) Å;<sup>10,11</sup> the Na–P distance falls in the typical range of distances found for Na–P contacts in sodium phosphides.<sup>1a</sup>

In addition to these contacts there is a short intramolecular Si–Me...Na contact to one of the SiMe<sub>3</sub> groups in the chelating ligand [Na...C(2) 3.003(2) Å] and an η<sup>2</sup>-interaction between the sodium and an aryl ring in the other half of the dimer

[Na...C(12A) 2.859(2), Na...C(13A) 2.945(2) Å]. There is no contact between the sodium atom and the essentially planar carbanion centre [sum of angles at C(1) = 357.94°].

Compounds **15** and **16** are both isostructural and isomorphous and crystallise from hot toluene as one-dimensional polymers. The polymeric structure of **15** is shown in Fig. 3 and details of bond lengths and angles for both **15** and **16** are given in Table 3.



**Fig. 3** Structure of **15** with 40% probability ellipsoids and with H atoms omitted for clarity.

The coordination mode of the phosphinomethanide ligands in **15** and **16** is significantly different from the PO<sub>2</sub> coordination mode observed in **14**. Each ligand binds the potassium or rubidium atom *via* its phosphorus and one of its oxygen atoms to give a single, puckered, six-membered chelate ring [P–M–O bite angle 58.10(6)° (**15**), 57.58(4)° (**16**)]; in addition, the metal has an η<sup>2</sup>-interaction with two of the aryl carbons of this ligand. The metal atoms are further coordinated by the oxygen atom of a second ligand in the polymeric chain, and have short contacts to the carbanion centre and to one methyl from each of the two SiMe<sub>3</sub> groups of this second ligand, along with an η<sup>2</sup>-interaction with an aryl ring in the second ligand. Thus, the overall binding mode of the ligand more closely resembles the bridging mode observed in the cyclic tetramer [LiCH<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>-2-CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]<sub>4</sub>·(PhMe)<sub>n</sub> (**8**), in which each amino-functionalised arm of the ligand binds a different metal centre, than the doubly chelating PN<sub>2</sub>/PO<sub>2</sub> modes observed in **1–5** and **14**.

The M–P(1) distances of 3.6836(15) and 3.7328(8) Å for **15** and **16**, respectively are substantially longer than the corresponding distances in the amino-functionalised phosphinomethanides **3** and **4** [3.2227(5) and 3.3437(8) Å, respectively],<sup>2c</sup> consistent with the significantly different binding mode, but lie within the range of distances typically found for potassium and rubidium phosphides.<sup>1a</sup> The M...C(1) distances of 3.291(4) Å (**15**) and 3.418(3) Å (**16**) are at the longer end of the usual range for K–C and Rb–C σ-bonds [K–C 2.91–3.10, Rb–C 3.29–3.51 Å]<sup>12</sup> and the carbanion centres are essentially planar in both compounds [sum of angles at C(1) = 359.2° (**15**), 358.9° (**16**); displacement of C(1) from the PSi<sub>2</sub> plane towards K/Rb: 0.094 Å (**15**), 0.108 Å (**16**)]; this suggests that any M...carbanion interactions in these compounds are relatively weak. For comparison,



**Table 3** Selected bond lengths (Å) and angles (°) for **15** (M = K) and **16** (M = Rb)

	15	16		15	16
M(1)–C(1A)	3.291(4)	3.418(3)	M(1)–C(21A)	3.604(4)	3.657(3)
M(1)–O(2A)	2.669(3)	2.783(2)	M(1)–O(1)	2.825(3)	2.973(2)
M(1)–C(13)	3.258(4)	3.326(3)	M(1)–C(8)	3.293(4)	3.335(3)
M(1)–C(16A)	3.630(4)	3.677(3)	M(1)–C(14)	3.580(4)	3.729(3)
M(1)–P(1)	3.6836(15)	3.7328(8)	M(1)–P(1A)	3.8948(15)	3.9979(8)
P(1)–C(1)	1.767(4)	1.769(3)	P(1)–C(16)	1.846(4)	1.849(3)
P(1)–C(8)	1.879(4)	1.875(3)	Si(1)–C(1)	1.832(4)	1.836(3)
Si(1)–C(4)	1.887(4)	1.891(3)	Si(1)–C(3)	1.898(4)	1.891(3)
Si(1)–C(2)	1.892(4)	1.902(3)	Si(2)–C(1)	1.837(4)	1.834(3)
Si(2)–C(5)	1.894(5)	1.883(3)	Si(2)–C(6)	1.883(4)	1.888(4)
Si(2)–C(7)	1.879(4)	1.889(3)			
O(2A)–M(1)–O(1)	144.61(10)	145.49(7)	C(1A)–M(1)–P(1)	149.42(8)	146.14(5)
O(2A)–M(1)–C(1A)	84.92(10)	82.65(7)	O(1)–M(1)–C(1A)	106.42(9)	103.75(7)
O(2A)–M(1)–P(1)	123.52(8)	129.45(5)	O(1)–M(1)–P(1)	58.10(6)	57.58(4)
O(2A)–M(1)–P(1A)	61.07(7)	59.60(5)	O(1)–M(1)–P(1A)	132.87(6)	129.56(4)
C(1A)–M(1)–P(1A)	26.81(7)	26.13(5)	Si(2)–C(1)–Si(1)	121.8(2)	121.66(17)
P(1)–C(1)–Si(2)	110.6(2)	110.90(15)	P(1)–C(1)–Si(1)	126.8(2)	126.37(18)

Symmetry operator (screw axis): A,  $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$ .

the sum of angles at the carbanion centre in  $\{(\text{Me}_3\text{Si})_3\text{C}\}\text{Cs}(\eta^6\text{-C}_6\text{H}_6)_3$ , which contains a genuine C–Cs  $\sigma$ -bond, is 351.79° and the central C atom is displaced some 0.304 Å out of the  $\text{Si}_3$  plane towards the Cs ion.<sup>13</sup>

The P–C(1) distances in **14**, **15**, and **16** [1.7499(18), 1.767(4) and 1.769(3) Å, respectively] are considerably shorter than expected for a P–C single bond, consistent with some degree of multiple bond character, associated with the extensive delocalisation of charge from the carbanion centre to phosphorus *via* negative hyperconjugation. For comparison, the P–C(8) distances in **14**, **15** and **16** are 1.866(2), 1.879(4) and 1.875(3) Å, respectively and the P–C(1) distances in the tertiary phosphine **9** and its LiBr complex **10** are 1.8480(14) and 1.854(2) Å, respectively.

In summary, we have shown that subtle changes in the donor groups at the periphery of a phosphinomethanide ligand can have significant consequences for the binding mode and aggregation state of its complexes. The coordination chemistry of these ligands with alternative metal centres is currently under investigation.

## Experimental

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen or argon. THF, diethyl ether, toluene and light petroleum (bp 40–60 °C) were distilled under nitrogen from potassium or sodium/potassium alloy. THF was stored over activated 4A molecular sieves; all other solvents were stored over a potassium film. Deuterated toluene, THF and benzene were distilled from potassium and  $\text{CDCl}_3$  was distilled from  $\text{CaH}_2$ ; all NMR solvents were deoxygenated by three freeze–pump–thaw cycles and were stored over activated 4A molecular sieves. The compounds  $\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PCl}_2$ <sup>14</sup> and 2- $\text{BrC}_6\text{H}_4\text{CH}_2\text{OMe}$ <sup>15</sup> were prepared by previously published procedures. Rubidium 2-ethylhexoxide was prepared by the direct reaction between rubidium metal and 2-ethylhexanol in THF.  $\text{Bu}^n\text{Li}$  was purchased from Aldrich as a 2.5 M solution in hexanes. All other compounds were used as supplied by the manufacturer.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Jeol Lambda 500 spectrometer operating at 500.16 and 125.78 MHz, respectively, or a Bruker Avance 300 spectrometer operating at 300.15 and 75.47 MHz, respectively; chemical shifts are quoted in ppm relative to tetramethylsilane. <sup>31</sup>P NMR spectra were recorded on a Jeol Lambda 500 spectrometer operating at 202.35 MHz and chemical shifts are quoted relative to external 85%  $\text{H}_3\text{PO}_4$ .

Elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University.

## Preparation of $\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{OMe})_2$ (**9**)

To a cold (0 °C) solution of 2- $\text{BrC}_6\text{H}_4\text{CH}_2\text{OMe}$  (2.5 g, 12 mmol) in ether (50 ml) was added  $\text{Bu}^n\text{Li}$  (4.8 ml, 12 mmol). The temperature of the reaction mixture was maintained at 0 °C for 3 h whilst stirring and then a solution of  $\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{PCl}_2$  (1.3 g, 5 mmol) in ether (30 ml) was added, dropwise. This mixture was allowed to attain room temperature and was stirred for 12 h. The solution was filtered and solvent was removed *in vacuo*. The oily product was extracted into light petroleum (30 ml), filtered and solvent was removed *in vacuo* from the filtrate to yield **9** as a viscous pale yellow oil, which crystallised on standing at room temperature for several days. Isolated yield 1.69 g (78%). <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$  at 25 °C):  $\delta$  0.10 (s, 18H,  $\text{SiMe}_3$ ), 1.40 (d, <sup>2</sup> $J(\text{P},\text{H})$  = 1.42 Hz, 1H, CHP), 3.35 (s, 6H, OMe), 4.97 (dd, <sup>2</sup> $J(\text{H},\text{H})$  = 12.48 Hz, <sup>4</sup> $J(\text{P},\text{H})$  = 1.94 Hz, 2H,  $\text{CH}_2\text{O}$ ), 5.09 (dd, <sup>2</sup> $J(\text{H},\text{H})$  = 12.48 Hz, <sup>4</sup> $J(\text{P},\text{H})$  = 2.36 Hz, 2H,  $\text{CH}_2\text{O}$ ), 7.13–7.64 (m, 8H, ArH). <sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{CDCl}_3$  at 25 °C):  $\delta$  0.85 ( $\text{SiMe}_3$ ), 12.07 (d, <sup>1</sup> $J(\text{P},\text{C})$  = 25.50 Hz, CHP), 56.31 (OMe), 72.52 (d, <sup>3</sup> $J(\text{P},\text{C})$  = 14.63 Hz,  $\text{CH}_2\text{O}$ ), 123.72 (Ar), 125.72 (d, <sup>2</sup> $J(\text{P},\text{C})$  = 3.00 Hz, Ar), 128.81, 130.71 (Ar), 136.09, (d, <sup>2</sup> $J(\text{P},\text{C})$  = 10.05 Hz, Ar), 139.92 (d, <sup>1</sup> $J(\text{P},\text{C})$  = 12.79 Hz, Ar). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CDCl}_3$  at 22 °C):  $\delta$  –46.6 (br).

## Preparation of $[\{(\text{Me}_3\text{Si})_2\text{C}\}\text{P}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{OMe})_2]\text{Na}]_2$ (**14**)

To a solution of **9** (2.6 g, 6.02 mmol) in ether (30 ml) was added  $\text{Bu}^n\text{Li}$  (2.4 ml, 6.02 mmol) and this mixture was stirred for 1 hour. This solution was added to a solution of  $\text{NaOBu}^t$  (0.58 g, 6.02 mmol) in ether (30 ml) and was stirred for 3 h. Solvent was removed *in vacuo* to leave a brown solid which was washed with light petroleum (3 × 20 ml) and residual solvent was removed *in vacuo*. Crystals of **14** suitable for X-ray crystallography were obtained from cold (–30 °C) toluene. Isolated yield 2.13 g (78%). Found (%): C, 60.85; H, 8.00. Calc. (%): C, 60.76; H, 7.98. <sup>1</sup>H NMR ( $d_8$ -toluene at 21 °C):  $\delta$  0.45 (br s, 18H,  $\text{SiMe}_3$ ), 2.92 (br s, 6H, OMe), 4.87 (s, 4H,  $\text{CH}_2\text{O}$ ), 7.05–7.50 (m, 8H, ArH). <sup>13</sup>C{<sup>1</sup>H} NMR ( $d_8$ -THF at 25 °C):  $\delta$  2.54 ( $\text{SiMe}_3$ ), 10.99 (d, <sup>1</sup> $J(\text{P},\text{C})$  = 26.07 Hz, PCH), 58.61 (OMe), 73.58 (d, <sup>1</sup> $J(\text{P},\text{C})$  = 7.26 Hz,  $\text{CH}_2\text{O}$ ), 127.76 (Ar), 128.54, 129.35, 133.91 (Ar), 139.21 (d, <sup>2</sup> $J(\text{P},\text{C})$  = 10.11 Hz, Ar), 143.58 (d, <sup>1</sup> $J(\text{P},\text{C})$  = 12.88 Hz, Ar). <sup>31</sup>P{<sup>1</sup>H} NMR ( $d_8$ -toluene at 21 °C):  $\delta$  –12.4 (br).

**Table 4** Crystallographic data for **9**, **10**, **14**, **15** and **16**

Compound	<b>9</b>	<b>10</b>	<b>14</b>	<b>15</b>	<b>16</b>
Formula	C <sub>23</sub> H <sub>37</sub> O <sub>2</sub> PSi <sub>2</sub>	C <sub>46</sub> H <sub>74</sub> Br <sub>2</sub> Li <sub>2</sub> O <sub>4</sub> P <sub>2</sub> Si <sub>4</sub>	C <sub>46</sub> H <sub>72</sub> Na <sub>2</sub> O <sub>4</sub> P <sub>2</sub> Si <sub>4</sub>	C <sub>23</sub> H <sub>36</sub> KO <sub>2</sub> PSi <sub>2</sub>	C <sub>23</sub> H <sub>36</sub> O <sub>2</sub> PRbSi <sub>2</sub>
<i>M</i>	432.7	1039.1	909.3	470.8	517.1
Crystal system	Triclinic	Monoclinic	Triclinic	Orthorhombic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> /Å	7.2142(4)	12.0404(6)	9.235(4)	11.0925(19)	11.122(1)
<i>b</i> /Å	11.2764(6)	9.4535(5)	11.043(4)	14.177(3)	14.430(1)
<i>c</i> /Å	16.3272(8)	24.4234(12)	13.945(7)	16.388(3)	16.248(1)
<i>a</i> /°	73.502(1)		85.58(4)		
<i>β</i> /°	86.635(1)	95.371(1)	80.06(4)		
<i>γ</i> /°	77.341(1)		69.33(3)		
<i>V</i> /Å <sup>3</sup>	1242.57(11)	2767.8(2)	1310.4(10)	2577.1(8)	2607.6(3)
<i>Z</i>	2	2	1	4	4
<i>μ</i> /mm <sup>−1</sup>	0.223	1.645	0.229	0.377	2.068
Data collected	11239	23677	7484	13124	20240
Unique data	5839	6579	4388	4511	5239
<i>R</i> <sub>int</sub>	0.023	0.045	0.018	0.068	0.050
Refined parameters	261	279	270	270	270
<i>R</i> (on <i>F</i> , <i>F</i> <sup>2</sup> > 2σ)	0.035	0.036	0.032	0.050	0.037
<i>R</i> <sub>w</sub> (on <i>F</i> <sup>2</sup> , all data)	0.095	0.086	0.083	0.102	0.061
Goodness of fit on <i>F</i> <sup>2</sup>	1.037	1.028	1.042	1.071	1.064
min, max electron density/e Å <sup>−3</sup>	0.32, −0.19	0.78, −0.49	0.32, −0.19	0.32, −0.28	0.31, −0.33
Absolute structure parameter				−0.06(7)	−0.014(5)

**Preparation of [(Me<sub>3</sub>Si)<sub>2</sub>C]P(C<sub>6</sub>H<sub>4</sub>-2-CH<sub>2</sub>OMe)<sub>2</sub>][K] (**15**)**

To a solution of **9** (2.4 g, 5.56 mmol) in ether (30 ml) was added Bu<sup>n</sup>Li (2.2 ml, 5.56 mmol). This solution was added to a solution of KOBu<sup>t</sup> (0.62 g, 5.56 mmol) in ether (30 ml) and this mixture was stirred for 3 h. After this period the ether was removed *in vacuo* to leave a brown solid. This was washed with light petroleum (3 × 20 ml) and residual solvent was removed *in vacuo* to give **15** as an orange solid. Single crystals of **15** suitable for X-ray crystallography were obtained from cold (−30 °C) toluene. Yield 1.63 g (62%). Found (%): C, 57.35; H, 7.84. Calc. (%): C, 58.68; H, 7.71. <sup>1</sup>H NMR (*d*<sub>8</sub>-toluene at 21 °C): δ 0.36 (br s, 18H, SiMe<sub>3</sub>), 3.38 (br s, 6H, OMe), 4.00 (br s, 2H, CH<sub>2</sub>O), 4.27 (br d, <sup>4</sup>*J*(P,H) = 6.10 Hz, 2H, CH<sub>2</sub>O), 7.05–7.49 (m, 8H, ArH). <sup>13</sup>C{<sup>1</sup>H} NMR (*d*<sub>8</sub>-toluene at 21 °C): δ 2.62 (SiMe<sub>3</sub>), 11.02 (d, <sup>1</sup>*J*(P,C) = 25.1 Hz, CHP), 58.36 (OMe), 75.59 (d, <sup>1</sup>*J*(P,C) = 4.58 Hz, CH<sub>2</sub>O), 128.31, 131.43, 133.41, 138.94 (Ar), 142.80 (d, <sup>2</sup>*J*(P,C) = 12.93 Hz, Ar), 150.24 (d, <sup>1</sup>*J*(P,C) = 13.73 Hz, Ar). <sup>31</sup>P{<sup>1</sup>H} NMR (*d*<sub>8</sub>-toluene at 21 °C): δ −6.17 (br).

**Preparation of [(Me<sub>3</sub>Si)<sub>2</sub>C]P(C<sub>6</sub>H<sub>4</sub>-2-CH<sub>2</sub>OMe)<sub>2</sub>][Rb] (**16**)**

To a solution of **9** (2.6 g, 6.02 mmol) in ether (30 ml) was added Bu<sup>n</sup>Li (2.41 ml, 6.02 mmol) and this mixture was stirred for 1 h. The resulting solution was added to rubidium 2-ethylhexoxide (6.02 mmol, 6.02 ml of a 1.0 M solution in THF) and stirred overnight. Solvent was removed *in vacuo* and the sticky solid was washed with light petroleum (3 × 20 ml). The resulting dark red solid was recrystallised from cold (−30 °C) toluene. Yield 1.2 g (39%). Found (%): C, 53.20; H, 6.67. Calc. (%): C, 53.42; H, 7.02. <sup>1</sup>H NMR (*d*<sub>8</sub>-toluene at 21 °C): δ 0.37 (br s, 18H, SiMe<sub>3</sub>), 2.90 (br s, 6H, OMe), 4.27 (br d, 2H, CH<sub>2</sub>O), 4.92 (d, 2H, CH<sub>2</sub>O), 7.10–7.52 (m, 8H, ArH). <sup>13</sup>C{<sup>1</sup>H} NMR (*d*<sub>8</sub>-toluene at 21 °C): δ 2.06 (SiMe<sub>3</sub>), 10.76 (d, <sup>1</sup>*J*(P,C) = 25.45 Hz, CHP), 58.12 (OMe), 73.42 (d, <sup>1</sup>*J*(P,C) = 2.65 Hz, CH<sub>2</sub>O), 127.21, 129.50, 131.46, 137.61 (Ar), 138.61 (d, <sup>2</sup>*J*(P,C) = 10.13 Hz, Ar), 142.98 (d, <sup>1</sup>*J*(P,C) = 12.95 Hz, Ar). <sup>31</sup>P{<sup>1</sup>H} NMR (toluene/light petroleum at 21 °C): δ −17.1 (br).

**Crystal structure determinations of **9**, **10**, **14**, **15** and **16****

Measurements were made at 150 K on Bruker AXS SMART or Nonius KappaCCD diffractometers using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). For all compounds cell parameters were refined from the observed positions of all strong reflections in each data set. Intensities were

corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and were refined on *F*<sup>2</sup> values for all unique data. Table 4 gives further details. All non-hydrogen atoms were refined anisotropically, and H atoms were constrained with a riding model; *U*(H) was set at 1.2 (1.5 for methyl groups) times *U*<sub>eq</sub> for the parent atom. None of the structures is disordered. Compounds **15** and **16** are both isostructural and isomorphous (in space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>), the relationship between the reported coordinates for these compounds is such that (*x*, *y*, *z*) for **15** transforms as (*x*,  $\frac{1}{2} - y$ , *z*) for **16**.

Programs were Bruker AXS SMART (control) and SAINT (integration), Nonius COLLECT and associated HKL DENZO and SCALEPACK, and SHELXTL for structure solution, refinement, and molecular graphics.<sup>16</sup>

CCDC reference numbers 263835–263839.

See <http://www.rsc.org/suppdata/dt/b5/b502416a/> for crystallographic data in CIF or other electronic format.

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