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Monomeric alkali metal complexes of a sterically demanding, donor-functionalised secondary phosphide ligand

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The novel sterically demanding, amino-functionalised secondary phosphine (2-$Me_2NCH_2C_6H_4$)RPH [R = $CH(SiMe_3)_2$] was synthesized by the reaction of $RPCl_2$ with [Li{$C_6H_4CH_2NMe_2$-2}], followed by reduction with $LiAlH_4$. The compound is readily metallated with Bu^nLi to yield the lithium phosphide [Li{PR($C_6H_4CH_2NMe_2$-2)}$(THF)_2$] **1**·2THF, in which the ligand binds to Li through both its N and P. Metathesis between **1** and $NaOBu^t$ or $KOBu^t$ yielded the sodium and potassium phosphides [M{PR($C_6H_4CH_2NMe_2$-2)}] (M = Na **2** or K **3**), respectively. Compound **2** crystallises as the monomeric adduct [Na{PR($C_6H_4CH_2NMe_2$-2)}(tmen)], in which the formally four-co-ordinate Na exhibits a short contact with one of the *ipso*-carbons of the phosphide ligand. Compound **3** crystallises in the presence of pmdien as the mononuclear adduct [K{PR($C_6H_4CH_2NMe_2$-2)}(pmdien)] in which the potassium centre is only five-co-ordinate, although again showing a short $K \cdots C_{ipso}$ contact. The compounds have been characterised by multinuclear NMR spectroscopy, and **1**–**3** by X-ray crystallography.

Introduction

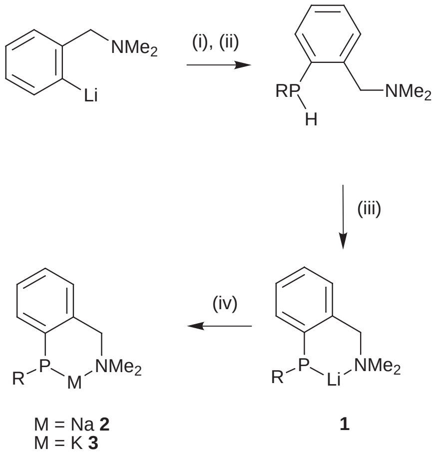
There is currently great interest in the reactivity and structural chemistry of alkali metal derivatives of uninegative ligands such as alkyls, alkoxides, amides and phosphides. However, whilst lithium primary and secondary phosphides have found widespread application as ligand transfer reagents for the synthesis of a wide array of transition metal and main group complexes, the chemistry of their heavier alkali metal analogues remains relatively unexplored.[1–6] The synthetic utility of such reagents has led to structural investigations of a number of simple alkali metal mono- and di-organophosphides. Their structures, in common with those of related amide, alkyl, and alkoxide complexes, are highly dependent upon the steric properties of substituents at the donor centre and the presence of additional donor ligands such as THF, tmen (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) or pmdien (*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine). Examples of lithium phosphides which are monomers, dimers, polymers or ladders in the solid state have been reported.[2] In contrast, structural studies on heavier alkali metal phosphides are limited to a handful of recent examples which include dimeric, tetrameric and polymeric species, but, to our knowledge, no monomeric complexes.[3–6]

Since the co-ordination of additional donor ligands to alkali metal complexes greatly enhances their reactivity by reducing the extent of aggregation we became interested in the effect on aggregation of incorporating additional donor functionality into a sterically demanding phosphide ligand. The chemistry of a range of alkali metal derivatives of variously functionalised phosphides has been investigated previously,[7,8] but only one such complex of a heavier alkali metal, [{Na[P(C_6H_4OMe-*o*$)_2$]-[MeO$(CH_2CH_2O)_2$Me]}$_2$],[3] has been structurally characterised to date. We herein describe the synthesis of a novel, sterically demanding, amino-functionalised, secondary phosphine and the preparation and structures of the corresponding lithium, sodium and potassium phosphides.

Results and discussion

Synthesis and characterisation of compounds 1–4

Treatment of {$(Me_3Si)_2CH$}PCl_2 with 1 equivalent of [Li{C_6H_4-CH_2NMe_2-2}] yields the chlorophosphine {$(Me_3Si)_2CH$}-(2-$Me_2NCH_2C_6H_4$)PCl, which, after subsequent reduction with $LiAlH_4$, gives the secondary phosphine {$(Me_3Si)_2CH$}(2-$Me_2NCH_2C_6H_4$)PH as a viscous, colourless oil in good yield (Scheme 1). Its ^1H, ^{13}C and ^{31}P NMR spectra exhibit the expected signals, the two diastereotopic Me_3Si groups appearing as a doublet in both the ^1H and ^{13}C spectra.



Scheme 1 *Reagents and conditions*: (i) $RPCl_2$, Et_2O–THF, −78 °C [R = $(Me_3Si)_2CH$]; (ii) $LiAlH_4$, THF, reflux; (iii) *n*-BuLi, light petroleum; (iv) $MOBu^t$, Et_2O (M = Na or K).

Treatment of {$(Me_3Si)_2CH$}(2-$Me_2NCH_2C_6H_4$)PH with Bu^nLi in light petroleum yields an orange oil which, in the presence of a small amount of THF, exhibits a 1 : 1 : 1 : 1 quartet in its ^{31}P-{^1H} NMR spectrum at δ −74.3 [$J(^7Li,^{31}P)$ = 39.1 Hz],

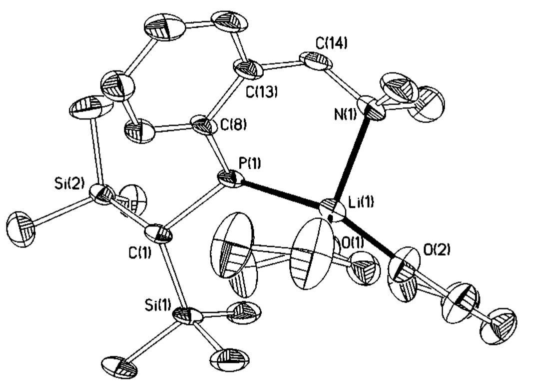


Fig. 1 Structure of one of the two independent molecules of **1**·2THF with selected atom labels, 40% probability ellipsoids, and with H atoms and second disorder components omitted for clarity.

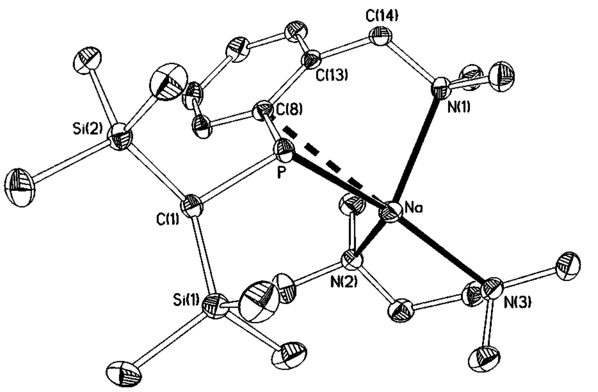


Fig. 2 Structure of complex **2**·tmem with 40% probability ellipsoids and no H atoms.

consistent with the formation of the lithium salt **1**. This oil is extremely soluble even in hydrocarbon solvents such as hexane. However, crystals of [Li{P[CH($SiMe_3$)$_2$]($C_6H_4CH_2NMe_2$-2)}(THF)$_2$] [**1**·2THF] suitable for an X-ray crystallographic study were obtained from a 10:1 mixture of the extremely poor solvent hexamethyldisiloxane and THF. The ^{1}H and ^{13}C NMR spectra of **1**·2THF are consistent with the crystal structure (see below); however, the two $SiMe_3$ groups, which are diastereotopic in the parent phosphine, give rise to a single resonance. This may be explained by rapid Li–P bond scission/re-co-ordination causing symmetrisation of the complex on the NMR timescale.

Synthetic approaches to heavier alkali metal phosphides include (i) P–C bond cleavage by an alkali metal,[3,7,8] (ii) direct metallation of a phosphine with an alkali metal or alkali metal hydride/alkyl,[4] (iii) P–Si bond cleavage by a heavier alkali metal alkoxide,[5,9] and (iv) metathesis between a lithium phosphide and an alkali metal amide.[6] We find that the lithium salt **1** undergoes a metathesis reaction, similar to (iv), with either sodium or potassium *tert*-butoxide to yield the heavier alkali metal phosphides [M{P[CH($SiMe_3$)$_2$]($C_6H_4CH_2NMe_2$-2)}] (M = Na **2** or K **3**), eqn. (1) [M = Na or K; R = CH($SiMe_3$)$_2$].

$$[\mathrm{Li\{PR(C_6H_4CH_2NMe_2\text{-}2)\}}] + \mathrm{MOBu^t} \longrightarrow [\mathrm{M\{PR(C_6H_4CH_2NMe_2\text{-}2)\}}] + \mathrm{LiOBu^t} \quad (1)$$

The facile preparation of the lithium salt **1** and the ease of separation of pure **2** and **3** from the lithium *tert*-butoxide by-product provides a convenient route to these materials. Both **2** and **3** are isolated as pyrophoric orange-yellow powders in high purity and moderate to good yield.

The ^{31}P, ^{1}H and ^{13}C NMR spectra of compound **2** in d_8-THF are similar in all major features to those of **3**. As was observed for **1**, the two $SiMe_3$ groups in both **2** and **3** are magnetically equivalent, possibly due to rapid M–P bond scission/re-co-ordination. In contrast to **1**, the sodium and potassium phosphides **2** and **3** are insoluble in all but the most co-ordinating solvents such as THF and, therefore, in order to obtain single crystals suitable for an X-ray crystallographic study it was necessary to solubilise the complexes by adding the co-ordinating amines tmen and pmdien respectively.

Solid state structures of compounds 1–3

Selected bond lengths and angles for **1**·2THF, **2**·tmen and **3**·pmdien are given in Table 1. The complex **1**·2THF crystallises as discrete monomers from solutions of **1** containing THF (Fig. 1). There are two crystallographically independent but essentially identical molecules in the unit cell; three out of the four THF ligands show two-fold disorder. The co-ordination geometry about the lithium is essentially distorted tetrahedral with the aminophosphide ligand binding through both its phosphorus and nitrogen centres to form a six-membered chelate ring with a ligand bite angle of 93.8(3) (molecule 1) and 94.5(3)° (molecule 2). Co-ordination about the lithium is completed by two molecules of THF. The six-membered chelate ring is puckered along the P–C(14) vector such that N(1) and Li(1) lie below the P(1)–C(8)–C(13)–C(14) plane, generating an angle of *ca.* 105° between the C(14)–C(13)–C(8)–P(1) and (best fit) C(14)–N(1)–Li(1)–P(1) planes; the corresponding angle in molecule 2 is *ca.* 110°. The Li–P distance of 2.535(8) (molecule 1) or 2.535(7) Å (molecule 2) is similar to those in a number of related lithium phosphides.[2] For example, a Li–P distance of 2.533(9) Å has been reported for the monomeric complex [Li{PH(mes)}(THF)$_3$] (mes = 2,4,6-$Me_3C_6H_2$).[2b] However, this distance is markedly longer than those in the closely related dimer [Li{P[CH($SiMe_3$)$_2$]$_2$}]$_2$ (average 2.473 Å),[2c] reflecting the higher co-ordination number of lithium in **1**·2THF. The Li(1)–N(1) distance of 2.124(9) Å [2.097(9) Å in molecule 2] is also typical of such distances; Li–N distances in tertiary amine-complexed organolithiums commonly fall in the range 2.01–2.21 Å.[10]

Compound **2** crystallises from toluene solutions containing tmen as the bright orange-yellow adduct **2**·tmen. The structure consists of discrete monomers in which the sodium atom is essentially four-co-ordinate, bound by the phosphorus and nitrogen atoms of the phosphide ligand and the two nitrogen atoms of the tmen co-ligand, in a distorted tetrahedral geometry (Fig. 2). A short Na···C(8) distance of 3.0040(18) Å, to the *ipso*-carbon directly bonded to phosphorus, suggests a weak supplementary interaction between these atoms, giving the sodium atom an effective co-ordination number of five. Such *ipso*-carbon interactions are a common feature of heavier alkali metal chemistry:[11] Na···C_{ipso} contacts are frequently observed in sodium complexes of benzylic carbanions, *e.g.* distances of 2.886(1) and 3.052(1) Å are reported for the Na···C_{ipso} separation in [Na(CPh_3)(tmen)].[12]

The six-membered chelate ring formed by the phosphide ligand [bite angle 81.40(4)°] is puckered along the P–C(14) vector in a similar manner to that in compound **1**·2THF; the folding angle is close to 90°, possibly as a consequence of the Na···C_{ipso} interaction. The Na–P distance of 2.8396(9) Å is at the shorter end of the range of such distances reported previously,[4a,c,f,g] as might be expected for such a chelating ligand. The Na–N(1) distance [2.4689(18) Å] lies between the two Na–N(tmen) distances [2.4533(18) and 2.5108(17) Å], and all three distances are typical of complexes in which sodium is co-ordinated by a chelating tertiary amine ligand.[4c,9,12]

Compound **3** crystallises from methylcyclohexane solutions containing pmdien as bright orange plates of the adduct **3**·pmdien. As for **1** and **2**, the phosphide ligand binds through both its P and N to form a puckered six-membered chelate ring (Fig. 3). The smaller bite angle of 75.53(3)° for the phosphide ligand in **3** reflects the increased ionic radius of potassium

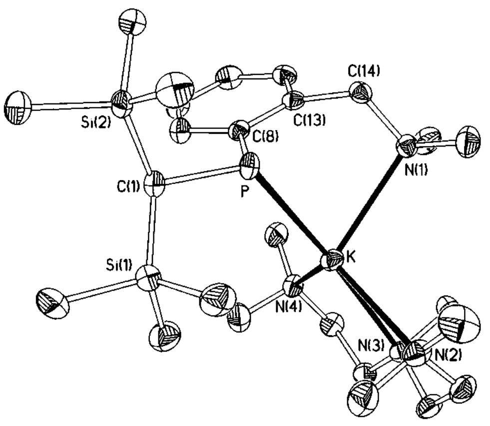


Fig. 3 Structure of complex **3**·pmdien with 40% probability ellipsoids and no H atoms.

Table 1 Selected bond lengths (Å) and angles (°) for compounds **1**·2THF, **2**·tmen and **3**·pmdien

1·2THF: Molecule 1			
Li(1)–P(1)	2.535(8)	N(1)–Li(1)–P(1)	93.8(3)
Li(1)–N(1)	2.142(9)	O(1)–Li(1)–O(2)	105.9(4)
Li(1)–O(1)	1.938(9)	O(1)–Li(1)–N(1)	110.3(4)
Li(1)–O(2)	1.973(8)	O(2)–Li(1)–N(1)	106.2(4)
P(1)–C(8)	1.816(4)	O(1)–Li(1)–P(1)	120.1(4)
P(1)–C(1)	1.895(4)	O(2)–Li(1)–P(1)	118.9(4)
C(1)–Si(1)	1.875(4)	Li(1)–P(1)–C(8)	84.9(2)
C(1)–Si(2)	1.874(5)	Li(1)–P(1)–C(1)	123.1(2)
		C(1)–P(1)–C(8)	103.6(2)
Molecule 2			
Li(2)–P(2)	2.535(7)	N(2)–Li(2)–P(2)	94.5(3)
Li(2)–N(2)	2.097(9)	O(3)–Li(2)–O(4)	109.7(4)
Li(2)–O(3)	1.965(8)	O(3)–Li(2)–N(2)	108.6(4)
Li(2)–O(4)	1.983(8)	O(4)–Li(2)–P(2)	107.1(4)
P(2)–C(32)	1.823(5)	O(3)–Li(2)–P(2)	115.3(4)
P(2)–C(25)	1.900(4)	O(4)–Li(2)–P(2)	119.7(3)
C(25)–Si(3)	1.868(5)	Li(2)–P(2)–C(32)	89.6(2)
C(25)–Si(4)	1.878(4)	Li(2)–P(2)–C(25)	123.6(2)
		C(25)–P(2)–C(32)	103.1(2)
2·tmen			
Na–P	2.8396(9)	N(1)–Na–P	81.40(4)
Na–N(1)	2.4689(18)	N(2)–Na–N(3)	74.91(6)
Na–N(2)	2.4533(18)	N(1)–Na–N(2)	122.37(6)
Na–N(3)	2.5108(17)	N(1)–Na–N(3)	106.11(6)
Na···C(8)	3.0040(18)	N(2)–Na–P	121.45(5)
P–C(1)	1.8980(18)	N(3)–Na–P	155.40(5)
P–C(8)	1.8171(18)	Na–P–C(1)	121.53(6)
C(1)–Si(1)	1.8731(18)	Na–P–C(8)	76.89(5)
C(1)–Si(2)	1.8811(18)	C(1)–P–C(8)	104.88(8)
3·pmdien			
K–P	3.2326(6)	N(1)–K–P	75.53(3)
K–N(1)	2.8008(16)	N(2)–K–N(3)	62.60(5)
K–N(2)	2.8565(17)	N(3)–K–N(4)	61.61(4)
K–N(3)	2.8590(15)	N(2)–K–P	107.09(4)
K–N(4)	2.8725(17)	N(3)–K–P	168.77(4)
K···C(8)	3.2854(17)	N(4)–K–P	126.31(3)
P–C(1)	1.9080(18)	N(1)–K–N(2)	100.87(5)
P–C(8)	1.8127(19)	N(1)–K–N(3)	109.77(5)
C(1)–Si(1)	1.870(2)	N(1)–K–N(4)	113.12(5)
C(1)–Si(2)	1.8705(19)	K–P–C(1)	124.55(6)
		K–P–C(8)	75.46(5)
		C(1)–P–C(8)	104.42(8)

over lithium and sodium. The potassium is essentially five-co-ordinate, its co-ordination sphere being completed by the three nitrogen atoms of the pmdien co-ligand. This low co-ordination number is somewhat surprising when compared to the four-co-ordinate lithium and pseudo-five-co-ordinate sodium complexes, but may be attributed to the steric requirements of the ligand. The co-ordination of potassium is supplemented by a short $K\cdots C_{ipso}$ contact [distance 3.2854(17) Å], which gives a folding angle close to 90°, as observed in **2**·tmen. The region of the co-ordination sphere of K opposite N(1) is largely empty, with no significant intermolecular contacts to K.

The K–P distance of 3.2326(6) Å is at the lower end of the range of such distances in the few previously reported structures of potassium phosphide complexes: 3.320(1), 3.271(2) and 3.181(2) Å for the dimeric compound $[\{K[P(SiBu^t{}_2F)(mes)]\}_2]$[4f] and the polymeric primary phosphide $[\{K[PH(C_6H_2Bu^t{}_3\text{-}2,4,6)]\}_x]$[4d] respectively, and from 3.306(2) to 3.451(1) Å in the polymeric complex $[\{K_3[PH(mes)]_3(THF)_2\}_x]$.[4e] The K–N(1) distance of 2.8008(16) Å is significantly shorter than the K–N (pmdien) distances [2.8565(17), 2.8590(15) and 2.8725(17) Å], but all lie within the range of typical K–N distances for complexes in which potassium is co-ordinated by tertiary amine ligands. For example, the K–N distances are 2.869(2), 2.848(2) and 3.028(2) Å in polymeric $[K(CH_2Ph)(pmdien)\cdot\frac{1}{2}C_6H_5CH_3]_n$,[13] and 2.819(3), 2.881(3) and 2.808(4) Å in monomeric $[K(CPh_3)(pmdien)(THF)]$.[14] These short K–P and K–N(1) distances reflect the low co-ordination number of potassium in **3**·pmdien.

Conclusion

The sterically demanding, donor-functionalised secondary phosphine $\{(Me_3Si)_2CH\}(2\text{-}Me_2NCH_2C_6H_4)PH$ is readily accessible *via* a simple synthetic procedure and undergoes facile deprotonation with *n*-butyllithium to give the corresponding lithium phosphide. Heavier alkali metal derivatives of this ligand may be prepared *via* a new route involving metathesis of the lithium salt with heavier alkali metal alkoxides, in a similar fashion to the well established route to heavier alkali metal organometallics.[11] By the inclusion of suitable co-ligands, monomeric heavier alkali metal phosphides have been obtained for the first time. Structural studies show that, as the alkali metal increases in size, the tendency towards $M\cdots C_{ipso}$ interactions increases, but that the steric bulk of the ligand nevertheless favours low co-ordination numbers even for the large potassium cation.

Compounds **1**–**3** are expected to prove useful ligand transfer reagents for the synthesis of transition metal and lanthanide derivatives; their metathesis chemistry and that of related compounds is currently under investigation.

Experimental

General

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen or argon. Diethyl ether, THF, light petroleum (bp 40–60 °C), methylcyclohexane and toluene were distilled from sodium, potassium or sodium/potassium alloy under an atmosphere of dry nitrogen and stored over a potassium film (with the exception of THF, which was stored over activated 4A molecular sieves). Hexamethyldisiloxane, tmen and pmdien were distilled from CaH_2 in a similar manner and stored over activated 4A molecular sieves. Deuteriated solvents were distilled from potassium and deoxygenated by three freeze–pump–thaw cycles and stored over activated 4A molecular sieves. The compounds $KOBu^t$ and $NaOBu^t$ were purchased from Aldrich and used without further purification, butyllithium was obtained from Aldrich as a 2.5 M solution in hexanes and $\{(Me_3Si)_2CH\}PCl_2$[15] and $[Li\{C_6H_4CH_2NMe_2\text{-}2\}]$[16] were prepared by published procedures.

Despite repeated attempts, satisfactory CHN analysis of compounds **1**–**3** could not be obtained due to their air sensitivity. However, all compounds were shown to be pure by multi-

Table 2 Crystallographic data

	1·2THF	**2**·tmen	**3**·pmdien
Empirical formula	$C_{24}H_{47}LiNO_2PSi_2$	$C_{22}H_{47}N_3NaPSi_2$	$C_{25}H_{54}KN_4PSi_2$
M	475.73	463.77	536.97
Crystal system	Triclinic	Triclinic	Monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	11.0847(15)	9.5849(15)	10.1740(2)
b/Å	15.223(2)	11.8767(18)	28.7226(6)
c/Å	17.755(3)	14.424(2)	12.1761(3)
α/°	95.503(3)	67.669(4)	
β/°	90.037(4)	87.913(4)	108.877(1)
γ/°	99.812(4)	71.329(3)	
U/Å^3	2983.1(7)	1432.1(4)	3366.77(13)
Z	4	2	4
D_c/g cm^{-3}	1.075	1.075	1.059
μ/mm^{-1}	0.194	0.208	0.295
T/K	160	160	160
$R(F)$ ('observed' data)	0.0884	0.0439	0.0447
$R_w(F^2)$ (all data)	0.2450	0.1164	0.1058
Collected/unique/observed reflections	20997/12641/5664	16581/6468/4790	21064/7949/5451

nuclear NMR methods. The ^{31}P NMR spectra were recorded on a Bruker WM300 spectrometer and ^1H and ^{13}C spectra on a Bruker AC200 spectrometer operating at 121.5, 200.1 and 50.3 MHz respectively; ^1H and ^{13}C chemical shifts are quoted in ppm relative to tetramethylsilane, ^{31}P chemical shifts relative to external 85% H_3PO_4.

Preparations

$\{(Me_3Si)_2CH\}(2\text{-}Me_2NCH_2C_6H_4)PH$. A cold (−78 °C) solution of 2-(*N*,*N*-dimethylaminomethyl)phenyllithium (0.87 g, 6.16 mmol) in THF (30 cm^3) was added to a cold (−78 °C) solution of $\{(Me_3Si)_2CH\}PCl_2$ (1.62 g, 6.20 mmol) in ether (20 cm^3) over 1 h. The reaction was stirred at this temperature for $\frac{1}{2}$ h and then allowed to warm to room temperature. The solvent was removed *in vacuo* and the residue extracted into light petroleum (30 cm^3) and filtered. The extract was evaporated under reduced pressure to yield a colourless oil.

This oil was dissolved in THF (30 cm^3) and added to a suspension of $LiAlH_4$ (0.27 g, 7.00 mmol) in THF (10 cm^3). The reaction mixture was heated under reflux for 2 h, cooled to room temperature, and then quenched by the careful addition of deoxygenated water (20 cm^3). Light petroleum (30 cm^3) was added and the organic layer decanted and dried over activated 4A molecular sieves. The solvent was removed *in vacuo* from the dried solution to give a colourless, viscous oil (1.47 g, 73%) (Found: C, 59.07; H, 10.06; N, 4.00. $C_{16}H_{31}NPSi_2$ requires C, 59.03; H, 9.91; N, 4.30%). δ_H ($CDCl_3$) 0.04 (9 H, s, $SiMe_3$), 0.10 (9 H, s, $SiMe_3$), 0.52 [1 H, dd, ^3J(HH) 5.8, J(PH) 1.8, CHP], 2.24 (6 H, s, NMe_2), 3.55 (2 H, s, CH_2N), 4.32 [1 H, dd, ^3J(HH) 5.8, J(PH), 216.4 Hz, PH] and 7.19–7.48 (4 H, m, aryl). δ_C ($CDCl_3$) 0.73 ($SiMe_3$), 0.93 ($SiMe_3$), 6.20 [d, J(PC) 41.8, CHP], 45.20 (NMe_2), 63.07 [d, J(PC) 11.4, CH_2N], 126.74, 127.53, 129.42, 132.94 (aryl), 137.50 [d, J(PC) 23.8 Hz, aryl] and 142.6 (aryl). δ_P ($CDCl_3$) −71.1 [d, J(PH) 216.4 Hz].

$[Li\{P[CH(SiMe_3)_2](C_6H_4CH_2NMe_2\text{-}2)\}(THF)_2]$, 1·2THF. To a solution of $\{(Me_3Si)_2CH\}(2\text{-}Me_2NCH_2C_6H_4)PH$ (1.16 g, 3.56 mmol) in light petroleum (10 cm^3) was added Bu^{n}Li (1.4 cm^3, 3.50 mmol). This mixture was stirred for 1 h, after which the solvent was removed *in vacuo* to give compound **1** as an extremely viscous orange oil. This was dissolved in 10:1 hexamethyldisiloxane–THF (5 cm^3) and cooled to −30 °C for 24 h to give yellow crystals of **1**·2THF (1.01 g, 58%). δ_H (C_6D_6) 0.45 (18 H, s, $SiMe_3$), 0.75 (1 H, s, CHP) 1.30 (8 H, m, THF), 1.89 (6 H, s, NMe_2), 3.32 (8 H, m, THF), 3.55 (2 H, s, br, CH_2N) and 6.64–7.41 (4 H, m, aryl). δ_C (C_6D_6) 1.90 ($SiMe_3$), 4.01 [d, J(PC) 64.7, CHP], 25.38 (THF), 45.35 (NMe_2), 65.93 [d, J(PC) 22.7, CH_2N], 68.33 (THF), 114.06, 126.90, 127.20, 130.00 (aryl), 131.79 [d, J(PC) 26.4, aryl] and 163.48 [d, J(PC) 66.1 Hz, aryl]. δ_P (C_6D_6) −74.3 [q, J(PLi) 39.1 Hz].

$[Na\{P[CH(SiMe_3)_2](C_6H_4CH_2NMe_2\text{-}2)\}]$ 2. To a slurry of NaOBu^t (0.28 g, 2.91 mmol) in ether (10 cm^3) was added a solution of compound **1** (2.80 mmol) in ether (15 cm^3). The reaction mixture was stirred for 1 h, filtered, and the solvent removed *in vacuo* from the filtrate to give a solid which was washed with light petroleum (5 × 20 cm^3) and dried under vacuum, giving **2** as a yellow-orange, pyrophoric powder (0.44 g, 45%). Crystals of the adduct **2**·tmen suitable for an X-ray crystallographic study were obtained from a cold (−30 °C) toluene solution containing tmen. δ_H ([$^2H]_8$THF) 0.13 (18 H, s, $SiMe_3$), 0.37 [1 H, d, J(PH) 1.8 Hz, Si_2CHP], 2.31 (6 H, s, NMe_2), 3.50 (2 H, s, CH_2N) and 6.21–7.04 (4 H, m, aryl). δ_C ([$^2H]_8$THF) 1.87 ($SiMe_3$), 5.05 [d, J(PC) 69.2, CSi_2], 46.06 (NMe_2), 66.36 [d, J(PC) 24.8 Hz, CH_2N], 113.48, 126.81, 127.11, 130.70 (aryl), 132.6 [d, J(PC) 27.9, aryl] and 165.42 [d, J(PC) 74.4 Hz, aryl]. δ_P ([$^2H]_8$THF) −75.7.

$[K\{P[CH(SiMe_3)_2](C_6H_4CH_2NMe_2\text{-}2)\}]$ 3. To a stirred solution of compound **1** (3.93 mmol) in ether (20 cm^3) was added a solution of KOBu^t (0.44 g, 3.90 mmol) in ether (10 cm^3). The bright orange precipitate was collected by filtration and washed with ether (3 × 10 cm^3). Removal of residual solvent under vacuum gave essentially pure **3** (1.26 g, 86%). Crystals of the adduct **3**·pmdien suitable for an X-ray diffraction study were grown from a hot methylcyclohexane solution containing pmdien. δ_H ([$^2H]_8$THF) 0.12 (18 H, s, $SiMe_3$), 0.35 [1 H, d, Si_2CHP, J(PH) 3.4 Hz], 2.26 (6 H, s, NMe_2), 3.44 (2 H, s, CH_2N) and 6.10–6.99 (4 H, m, aryl). δ_C ([$^2H]_8$THF) 1.45 ($SiMe_3$), 6.63 [d, CSi_2, J(PC) 69.2], 45.17 (NMe_2), 65.87 [d, CH_2N, J(PC) 24.8], 111.42, 125.51, 126.31, 129.55 (aryl), 132.51 [d, J(PC) 26.9, aryl] and 166.83 [d, J(PC) 76.5 Hz, aryl]. δ_P ([$^2H]_8$THF) −64.9.

X-Ray crystallography

Crystal data for the complexes **1**·2THF, **2**·tmen and **3**·pmdien are listed in Table 2. Crystals were examined on a Bruker AXS SMART CCD area detector diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å). Methods and programs were as described previously.[17] Semiempirical absorption corrections were applied. Twofold disorder was resolved for three of the four independent THF ligands in **1**·2THF with the aid of restraints.

CCDC reference number 186/1410.

See http://www.rsc.org/suppdata/dt/1999/1825 for crystallographic files in .cif format.

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