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Erratum

Erratum to "The role of lithium 1,3-bis(trimethylsilyl)-1-aza-allyls in phosphorus chemistry" [J. Organometallic Chem. 529 (1997) 243–255]☆

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The role of lithium 1,3-bis(trimethylsilyl)-1-aza-allyls in phosphorus chemistry

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Abstract

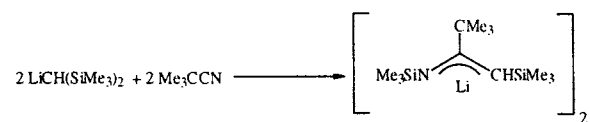
Treatment of the lithium 1-aza-allyl $[Li\{N(R)C(^tBu)CHR\}]_2$ **1**, abbreviated as $[Li(LL')]_2$, with PCl_3 gave in poor yields the *trans-P,P'*-dichlorodiazaphosphetidine $ClPN(R')P(Cl)NR'$ **3** ($R = SiMe_3$, $R' = C(^tBu)=C(H)SiMe_3$). An improved route to **3** was based on $[\{Cu(\mu - LL')\}_2]$ and PCl_3. However, the method of choice involved conversion of **1** into successively the imine $RN=C(^tBu)CHR_2$ **4** (which upon heating gave the isomeric enamine **5**) and $Cl_2PN=C(^tBu)CHR_2$ **6** and thermolysis of **6**. The imine $RN=C(^tBu)CH(R)PPh_2$ **7**, obtained from $[Li(LL')]_2$ **1** and Ph_2PCl, was isomerised into the *Z*-enamine $R_2NC(^tBu)=C(H)PPh_2$ **8**, which upon irradiation gave a mixture of **8** and its *E*-isomer **9**. Treatment of **7** with $R''PCl_2$ or PCl_3 gave the cyclic phosphonium chlorides $[Ph_2PP(R'')N(H)C(^tBu)=CH]Cl$ (**10** $R'' = Ph$, or **11** $R'' = Et$) or $[Ph_2PP(Cl)N(R)C(^tBu)=CH]Cl$ **12**; **12** with $AgOSO_2CF_3$ or $Na[BPh_4]$ afforded $[Ph_2PP(Cl)N(R)C(^tBu)=CH]A$ (**13** $A = CF_3SO_3$, or **14** $A = BPh_4$). The enamines $RN=C(^tBu)CH(X)R$ (**15** $X = Cl$, or **16** $X = I$) were obtained from **1** and $POCl_3$ or ICl, respectively, and the enamine $R_2NC(Ph)=CR_2$ **17** was obtained from the lithium 1-aza-allyl $[Li\{N(R)C(Ph)CR_2\}(THF)]$ and $CF_3SO_3SiMe_3$. Compounds **3–17** were characterised by multinuclear NMR spectroscopy and (in most cases) MS, while single crystal X-ray diffraction data are provided for **3** and **10**. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium; Phosphorus; Aza-allyl; Phosphetidine; Phosphonium salt; Crystal structure

1. Introduction

We recently reviewed the synthesis and reactions of alkali metal α,ω-bis(trimethylsilyl)-1-aza-allyl and -β-diketiminates, including their role as precursors for preparing unusual transition metal and main group element complexes [1]. A major topic of this paper concerns reactions of the 1-aza-allyllithium complex $[Li(LL')]_2$ **1** ($LL' = N(R)C(^tBu)CHR$, $R = SiMe_3$) in the context of phosphorus chemistry.

Complex **1** is readily obtained from $LiCHR_2$ and ^{t}BuCN in diethyl ether or pentane under ambient conditions, see Reaction (1) [2], and has already successfully been used to obtain $[K(LL')]_n$, *rac*-$[Zr(LL')Cl_2]$ [2], *rac*-$[Yb(LL')_2]$ [3] and $[Zr(LL')Cl_3]$ [4]; experiments are in hand on derivatives of tin(II), lead(II), iron(II) and cobalt(II), using $[LL']^-$ or a closely related ligand [5]. Among the general features of interest are: (i) the variety of bonding modes of $[LL']^-$, including η^3-chelating, η^2-bridging and η^1-enamido; (ii) the lability of the Me_3Si substituents; and (iii) the chiral nature, at C-3, of the metal-bound η^3-1-aza-allyl ligand.



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2. Results and discussion

2.1. Synthesis of the 1,3,2-λ^3,4-λ^3-diazadiphosphetidine 3

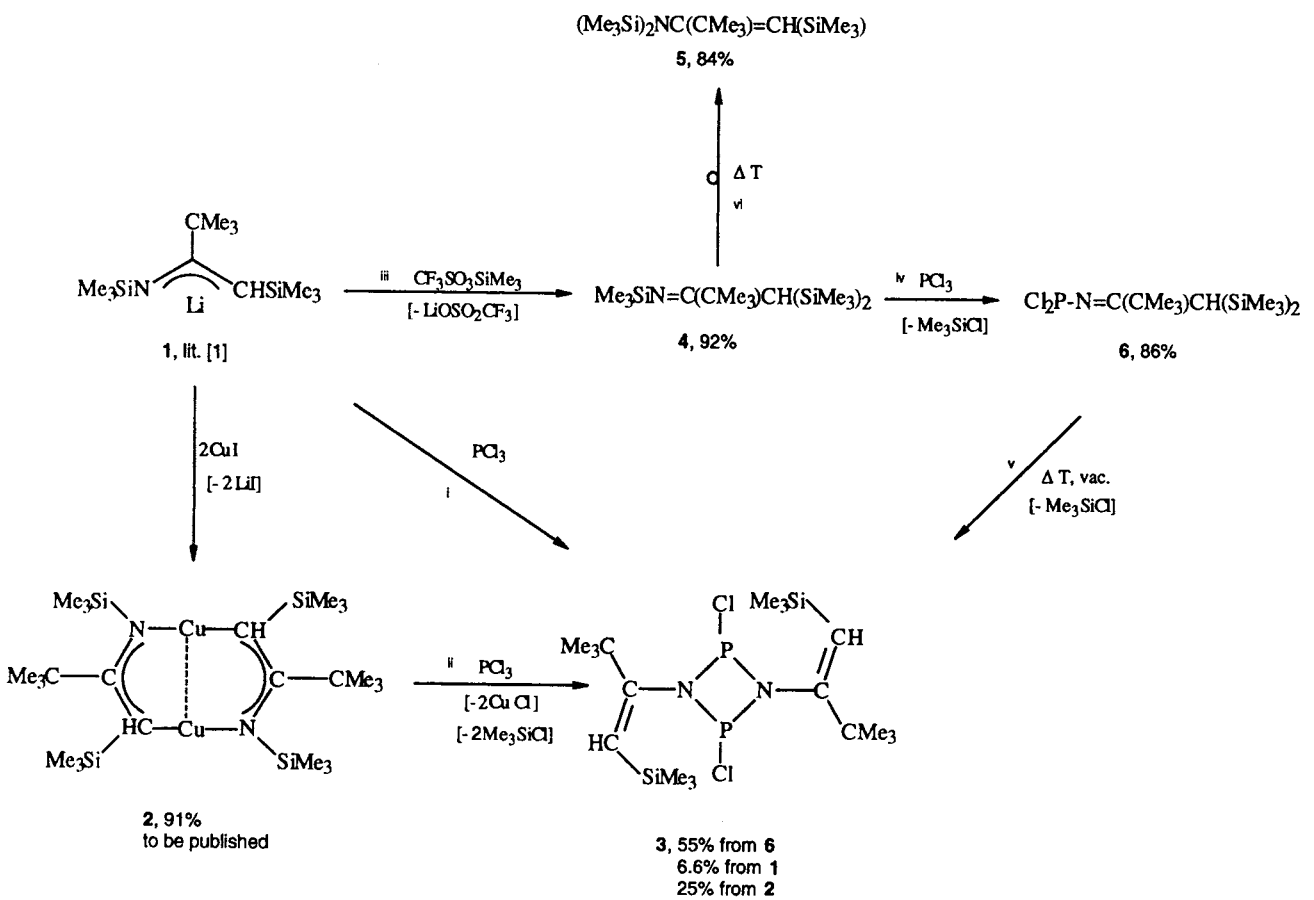
Three alternative routes to the *P,P′-trans*-dichlorodiazaphosphetidine **3**, from (i) PCl_3 and $[\overline{Li(LL')}]_2$ **1**, (ii) $[\{Cu(\mu\text{-}LL')\}_2]$ **2** (details of which will be published elsewhere) or (iii) $RN{=}C(^tBu)CHR_2$ **4** are illustrated in Scheme 1, which also shows the thermal isomerisation of the ketimine **4** into the enamine $R_2NC(^tBu){=}CHR$ **5**.

First we attempted to introduce the $[LL']^-$ ligand to a phosphorus(III) centre, by using $[\overline{Li(LL')}]_2$ **1** as a ligand transfer reagent. When **1** was treated with PCl_3 in a Li:P ratio of 3:1, in a variety of solvents and under differing reaction conditions, an orange–red solution and a large quantity of a similarly coloured precipitate were obtained; the latter was insoluble in several common aprotic solvents and it probably consisted of a mixture of LiCl and oligomeric phosphorus-containing species. In one experiment, however, we were able to isolate a small amount of colourless crystals of **3** from the reaction mixture ((i) in Scheme 1), which was fully characterised by microanalysis, NMR and MS spectra and single crystal X-ray diffraction (Section 2.4).

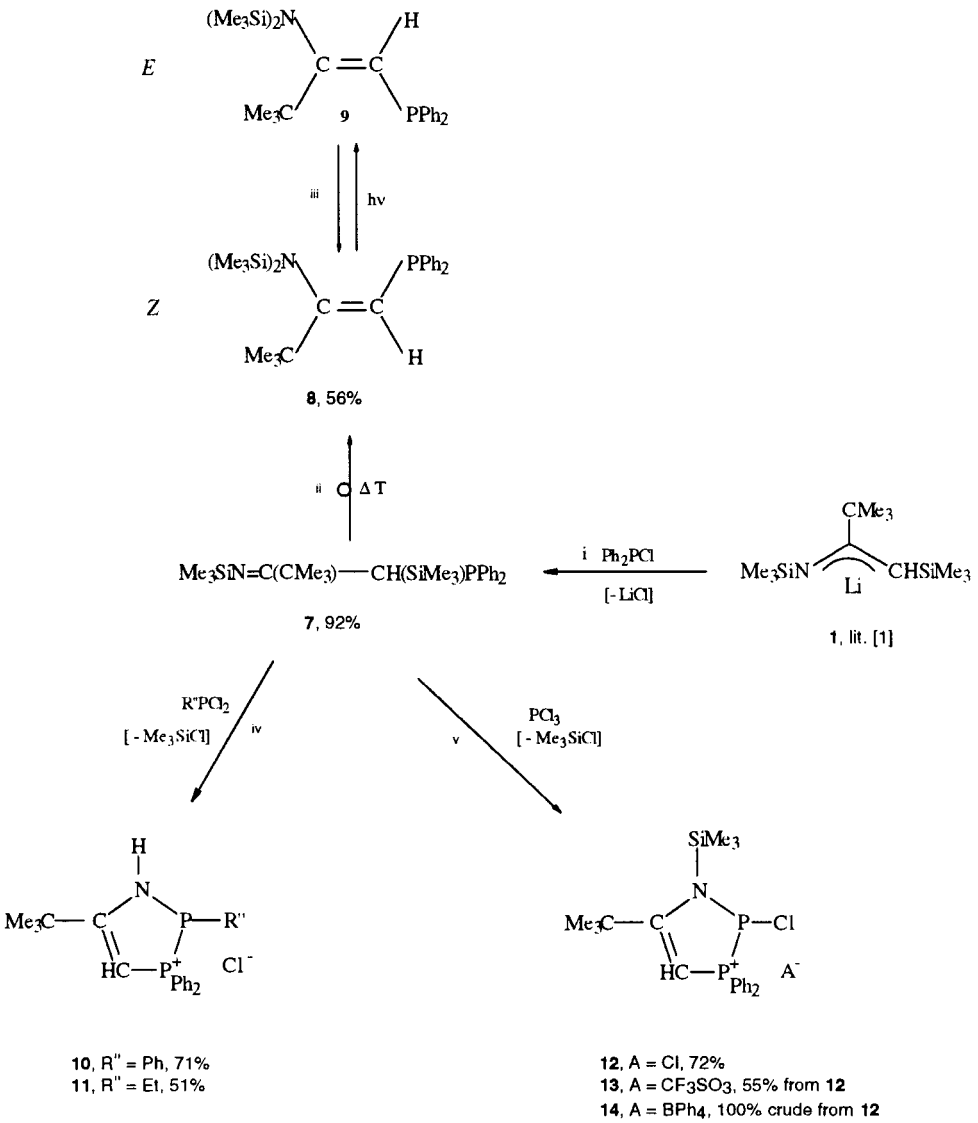
The pathway to **3** from **1** probably involves $[LL']^-$ behaving as an *N*-centred nucleophile in attacking PCl_3 to give $Cl_2PN(R)C(^tBu){=}CHR$, which then eliminates Me_3SiCl to give $ClP{=}NC(^tBu){=}CHR$; the latter probably has various oligomerisation routes available, one of which is the 2 + 2 cyclodimerisation to yield **3**. There are precedents for an iminophospine being dimerised [6].

For an ambidentate *N,C*-monoanionic ligand, *N*- over *C*-centred nucleophilicity is often favoured by using a silver(I), rather than a lithium, salt. In another investigation, we had made the 1-aza-allylcopper(I) compound **2** in high yield from **1** (the Ag(I) analogue was unstable); from **2** and PCl_3 ((ii) in Scheme 1), the yield of **3** was still modest (25%), but was an improvement compared with the lithium route.

The method of choice for converting **1** into **3** proved to be one in which $[\overline{Li(LL')}]_2$ **1** was first converted into the ketimine $RN{=}C(^tBu)CHR_2$ **4**. The latter with PCl_3 afforded $Cl_2PN{=}C(^tBu)CHR_2$ **6** ((iv) in Scheme 1), which on heating ((v) in Scheme 1) gave **3** in 55% yield. However, even this route was not without difficulty. Thus, $[\overline{Li(LL')}]_2$ **1** proved to be unreactive towards Me_3SiCl in boiling toluene. Converting **1** into $[K(LL')]_n$



Scheme 1.



Scheme 2.

and treating the latter with Me_3SiCl gave a mixture of the ketimine **4** and its isomer, the enamine $R_2NC(^tBu)$=CHR **5**, in a ratio of ca. 1:3. Compound **4** was finally made in good yield from **1** and trimethylsilyl triflate ((iii) in Scheme 1). Heating the ketimine **4** above 130°C gave the thermodynamically favoured product, the isomeric enamine **5** ((vi) in Scheme 1). The latter was unreactive towards PCl_3 and various other phosphorus chlorides. This behaviour seems to be a characteristic of *N*,*N*-bis(trimethylsilyl)enamines (cf. **8** and **17**).

Attempts to make a *P*,*P*′-dihydrocarbyl or -bis(-dimethylamino) analogue of **3**, by treating **1** or **4** with $PhPCl_2$ or R_2CHPCl_2, or **1** with $(Me_2N)PF_2$, invariably gave a mixture of products, as was also the case when **1** was treated with $(Me_2N)_2PCl$. However, from **1** and Ph_2PCl, the ketimine $RN=C(^tBu)CH(R)PPh_2$ **7** ((i) in Scheme 2) was obtained in high yield, and this compound proved to be a key starting material for obtaining a range of heterocyclic compounds, as shown in Scheme 2.

A further item of interest is that heating the ketimine **7** yielded the isomeric *Z*-enamine **8** ((ii) in Scheme 2), which upon photolysis gave a mixture of **8** and its *E*-isomer **9**.

2.2. Synthesis of the salts $[Ph_2\overline{PP(X)N(Y)C(^tBu)=C}\text{-}H]A$ **10–14**

The synthesis of the phosphonium salts **10–14** is illustrated in Scheme 2 together with the isomerisations **7**→**8**→**9** ((ii) and (iii), respectively, in Scheme 2).

Treament of **7** with $PhPCl_2$ ((iv) in Scheme 2) readily afforded in high yield the phosphonium salt $[Ph_2\overline{PP(Ph)N(H)C(^tBu)=CH}]Cl$ **10**, which was insoluble in pentane or diethyl ether, but soluble in

dichloromethane or hot toluene; X-ray quality crystals were grown from the latter. The salt **10** was fully characterised by microanalysis, NMR and MS spectra and single crystal X-ray diffraction (Section 2.5).

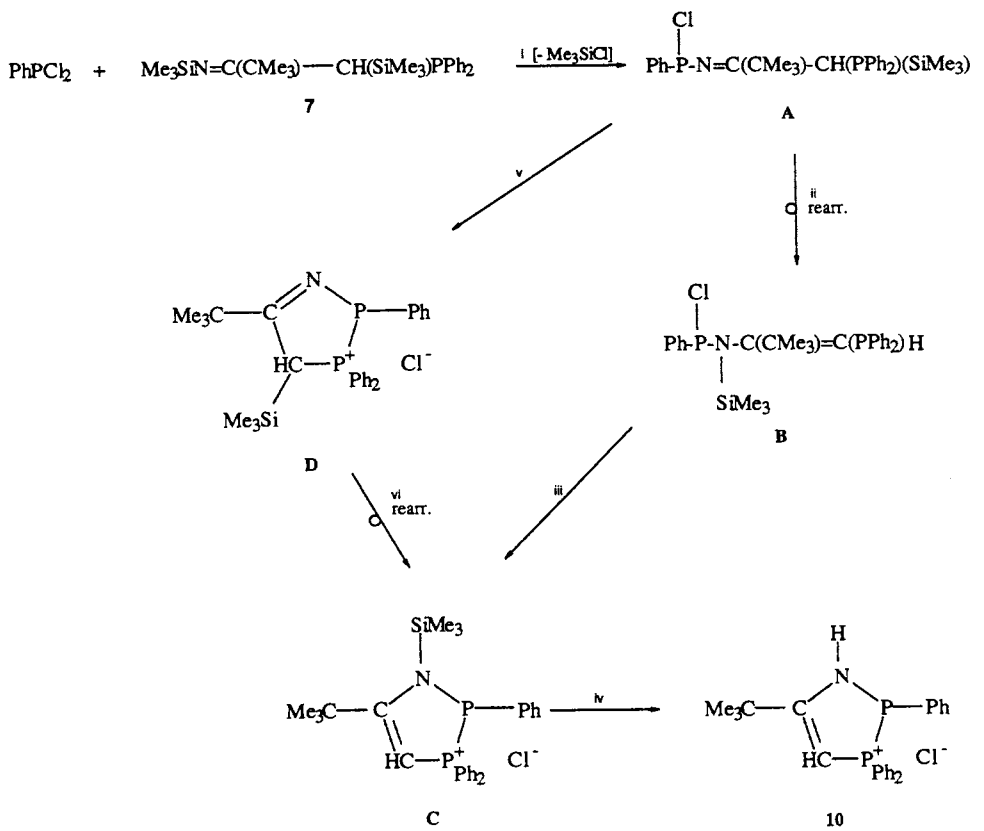
The formation of **10** from **7** involves one or other of the sequence of reactions of Scheme 3. The first step ((i) in Scheme 3) is the *N*-centred nucleophilic attack of **7** at the phosphorus of $PhPCl_2$, yielding the ketimidophosphorus(III) chloride $PhP(Cl)N{=}C(^tBu)CH(R)PPh_2$ **A** with concomitant Me_3SiCl elimination, a process which is similar to the formation of **6** + Me_3SiCl from **4** + PCl_3 ((iv) in Scheme 1). The second step is either ((ii) in Scheme 3) the transformation of **A** into the isomeric enamidophosphorus(III) chloride $PhP(Cl)N(R)C(^tBu){=}C(^tBu)PPh_2$ **B**, which has analogy with the isomerisations **7** → **8** → **9** ((ii) and (iii) in Scheme 2) and **4** → **5** ((iv) in Scheme 1). The third step is the cyclisation ((iii) in Scheme 3) effected as a consequence of the nucleophilic intramolecular displacement of the chloride as the anion in **C**; related cyclisations involving nucleophilic displacement of Cl^- from a chlorophosphine by a phosphine are well established [7]. The final, probably inadvertent, hydrolysis ((iv) in Scheme 3) converts **C** into **10**. Further support for **C** as an intermediate came from the observation that the ketimine **7** with PCl_3, in pentane at low temperature, yielded the labile salt $[Ph_2PP(Cl)N(R)C(^tBu){=}CH]Cl$ **12** ((v) in Scheme 2), which with silver triflate or sodium tetraphenylborate gave the stable analogues $[Ph_2PP(Cl)N(R)C(^tBu){=}CH]A$ (**13** $A = CF_3SO_3$, or **14** BPh_4). An alternative pathway to **10** from **7** via **A** involves as the second step the cyclisation of **A** ((v) in Scheme 3) to give the cyclo-ketimidophosphonylphosphonium salt $[Ph_2PP(Ph)N{=}C(^tBu)CHR]Cl$ **D**, followed by its rearrangement ((vi) in Scheme 3).

In a process similar to the reaction between **7** and $PhPCl_2$ → **10**, the former compound with $EtPCl_2$ gave ((iv) in Scheme 2) $[Ph_2PP(Et)N(H)C(^tBu){=}CH]Cl$ **11**.

Despite repeating several times the reaction ((iv) in Scheme 2) between **7** and $RPCl_2$, the isolated product was invariably **10** (R = Ph) or **11** (R = Et); the fate of the initially *N*-bound trimethylsilyl group (cf. **C** in Scheme 3) remains a mystery.

2.3. Further reactions of 1-aza-allyllithium compounds

Treatment of $[Li(LL')]_2$ with $POCl_3$ or ICl, in a Li:P ratio of 2:1 or Li:I ratio of 1:1 in pentane or diethyl ether, respectively, gave, after distillation, the ketimine $RN{=}C(^tBu)CH(X)R$ **15** (X = Cl, Reaction (2)) or **16** (X = I, Reaction (3)), respectively. Compounds **15** and **16** were obtained as air-sensitive, yellow, distillable liquids, which gave reasonably satisfactory microanalysis and NMR and MS (**16** only) data.



Scheme 3.

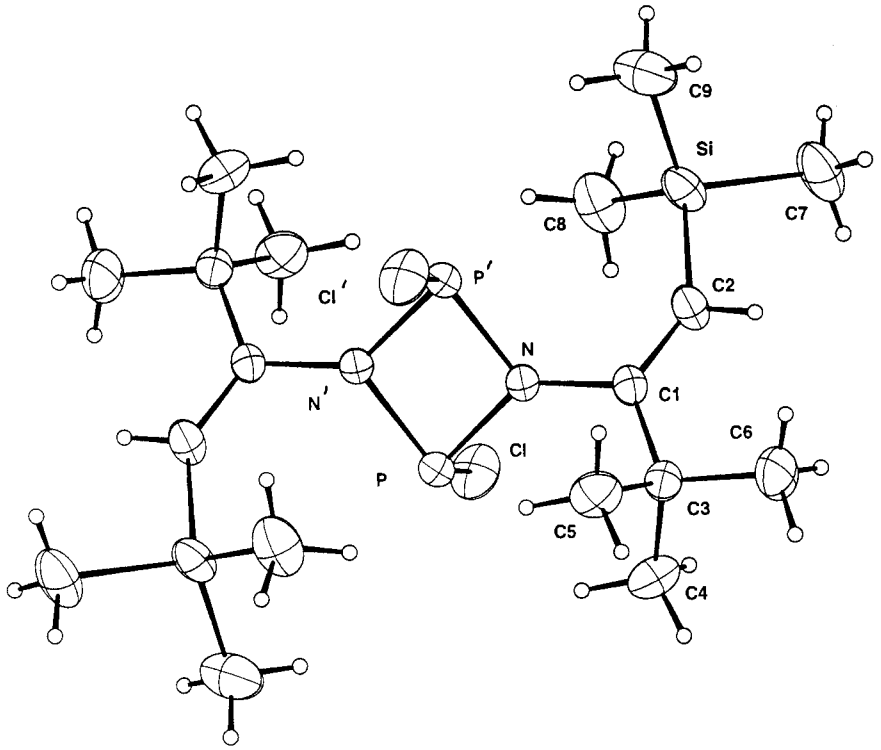
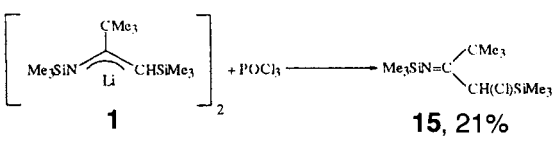


Fig. 1. Molecular structure of **3**.



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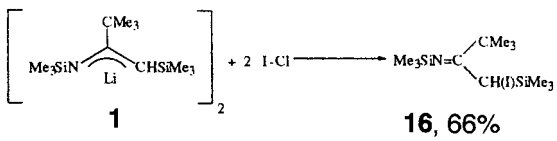
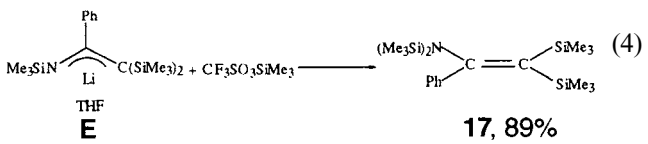


(3)

We have recently prepared the lithium complex of a trimethylsilyl derivative of the ligand $[LL']^-$, Li{N(R)C(Ph)CR_2}(THF) **E** (details of which will be published elsewhere). The ligand $[N(R)C(Ph)CR_2]^-$ is even more bulky than $[LL']^-$. Having had only limited success with converting $[\overline{Li(LL')}]_2$ **1** directly into the phosphetidine **3**, but having obtained satisfactory results by transforming **1** into the imine RN=C(^{t}Bu)CHR_2 **4** and reacting **4** (rather than **1**) with PCl_3, we treated **E** with trimethylsilyl triflate. This afforded the enamine $R_2NC(Ph)=CR_2$ **17**, rather then the isomeric ketimine $RN=C(Ph)CR_3$, Reaction (4). It may well be that the latter is too sterically hindered to be thermally stable, and even if it had been the kinetic product it must rapidly have rearranged into **17**. The enamine **17** proved to be inert not only to PCl_3 (at 80°C) but also to $PhPCl_2$ at 120°C and $PhPF_2$ at 50°C; in this respect the enamine **17** behaves similarly to **5** and **8** (see Section 2.1).



(4)

2.4. The structure of the diazadiphosphetidine *3*

The X-ray molecular structure of the crystalline *P,P′-trans*-dichlorodiazadiphosphetidine **3** is illustrated in Fig. 1, including the atom numbering scheme. Selected bond lengths and angles are listed in Tables 1 and 2 (with comparative data on three analogues) and the non-hydrogen atom coordinates in Table 3.

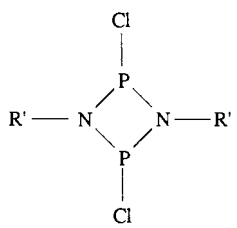
The crystalline compound **3** is centrosymmetric. It has a planar $\overline{PNPN}$ ring, with the *N*-ligating sp^2-carbon atoms also coplanar, the sum of the angles at nitrogen (ΣN) being 360°. The endocyclic ring angle at nitrogen, 98.46(9)°, is significantly greater than that at phosphorus, 81.54(9)°. The Cl–P–N and Cl–P–N′ bond angles are significantly narrower than tetrahedral; the mutually *trans*-lone pairs at phosphorus appear to be very much stereochemically active. The alkenyl groups have the *E*-configuration, so as to minimise steric effects, the *t*-butyl groups being *trans* to $SiMe_3$. As a consequence, there are close contacts between the $SiMe_3$ groups and the phosphorus atoms, P···C(8) 4.50 Å, an effect which persists in solution as evident from the observed ^1H- and $^{13}C\{^1H\}$-NMR spectra of **3** in $[^2H_8]$toluene.

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

Bond length (Å)			
Cl–P	2.107(1)	Si–C(8)	1.856(3)
Si–C(9)	1.857(3)	Si–C(7)	1.868(3)
Si–C(2)	1.873(3)		
P–N	1.707(2)	N–C(1)	1.434(3)
N–P′	1.699(2)	C(1)–C(2)	1.326(3)
C(1)–C(3)	1.526(3)	C(3)–C(6)	1.525(4)
C(3)–C(5)	1.526(4)	C(3)–C(4)	1.541(4)
Bond angle (°)			
C(8)–Si–C(9)	110.8(2)	C(8)–Si–C(7)	108.1(2)
C(9)–Si–C(7)	108.7(2)	C(8)–Si–C(2)	114.15(13)
C(9)–Si–C(2)	111.11(14)	C(7)–Si–C(2)	103.52(14)
N[a]–P–N	81.54(9)	N[a]–P–Cl	102.97(7)
N–P–Cl	102.49(7)	C(1)–N–P′	126.49(14)
C(1)–N–P	135.0(2)	P[a]–N–P	98.46(9)
C(2)–C(1)–N	119.9(2)	C(2)–C(1)–C(3)	125.6(2)
N–C(1)–C(3)	114.5(2)	C(1)–C(2)–Si	137.7(2)
C(6)–C(3)–C(5)	108.2(3)	C(6)–C(3)–C(1)	111.4(2)
C(5)–C(3)–C(1)	110.3(2)	C(6)–C(3)–C(4)	107.6(2)
C(5)–C(3)–C(4)	109.7(2)	C(1)–C(3)–C(4)	109.7(2)

[a] Symmetry transformations used to generate equivalent atoms: $1-x, -y, -z$.

The skeletal geometry of the diazadiphosphetidine **3** is broadly similar to those of three other *P*,*P*′-dichlorodiazadiphosphetidines **F** [8], **G** [9] and **H** [10], which have been crystallographically characterised, except in one important aspect i.e. the chlorides in **F**–**H** are arranged in a *cis* manner, Table 2.



F, R′ = Bu^t
G, R′ = Ph
H, R′ = $C_6H_2Pr^i_3$-2,4,6

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **3**

Atom	*x*	*y*	*z*	U_{eq}[a]
Cl	−1361(1)	221(1)	1849(1)	70(1)
Si	−3119(1)	1977(1)	−1761(1)	54(1)
P	500(1)	100(1)	1078(1)	41(1)
N	1(2)	877(1)	−101(1)	37(1)
C(1)	−63(2)	1997(2)	−313(2)	38(1)
C(2)	−1218(3)	2409(2)	−1023(2)	49(1)
C(3)	1297(3)	2612(2)	294(2)	46(1)
C(4)	1378(4)	2578(3)	1588(2)	68(1)
C(5)	2709(3)	2133(3)	19(3)	64(1)
C(6)	1219(4)	3773(2)	−66(3)	88(1)
C(7)	−4242(3)	3221(3)	−1844(3)	80(1)
C(8)	−3982(3)	973(3)	−967(3)	77(1)
C(9)	−3114(4)	1514(4)	−3229(3)	87(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonilised U_{ij} tensor.

Two recently reported monochloro analogues ClPN(t-Bu)P(N^{i}Pr$_2$)NC$_6$H$_2$^{t}Bu$_3$-2,4,6 [11] and ClPN(SiMe$_3$)P(NHC$_6$H$_2^t$Bu$_3$-2,4,6)NC$_6$H$_2^t$Bu$_3$-2,4,6 [12], were also shown to have *cis*-geometry. There has been much interest in *cis* → *trans* isomerism in this class of compounds; the *trans*-isomer appears generally to be kinetically favoured and often isomerises to the thermodynamically preferred *cis*-product [9]. A contrary view has been put forward for Me$_2$NPN(SiMe$_3$)P(NMe$_2$)NSiMe$_3$, which on the basis of NMR spectroscopic data was assigned to be the *cis*-kinetic product; upon heating it gave a mixture of *cis*- and *trans*-isomers [13]. It may well be that bulky amido substituents at P and P′ favour the *trans* isomer, since *cis*-ClPN(Ph)P(Cl)NPh upon aminolysis afforded exclusively *trans*-R$'_2$NPN(Ph)P(NR$'_2$)NPh (R′ = ^{n}Bu or Ph) [9]. In contrast, crystalline Ph(H)NPN(Ph)P{N(H)Ph}NPh was shown to be the *cis*-isomer [14]; other pertinent data are listed in Ref. [15].

Table 2
Some comparative structural data on four crystalline *P*,*P*′-dichlorodiazadiphosphetidines

Parameter	ClPN(R′)P(Cl)NR **3**[a]	ClPN(tBu)P(Cl)N(^{t}Bu) **F**[b]	ClPN(Ph)P(Cl)NPh **G**[c]	ClPN(Ar)P(Cl)NAr **H**[d]
l(P–N) (Å)	1.699(2)	1.687(9), 1.681(9)	1.698(10), 1.691(10)	1.698(3), 1.704(3), 1.701(3), 1.703(3)
l(P–Cl) (Å)	2.107(1)	2.114(7), 2.096(7)	2.075(6), 2.099(9)	2.091(1), 2.103(1)
l(N–C_{sp^2}) (Å)	1.434(3)	–	1.423(9)	1.444(4), 1.449(4)
NPN (°)	81.54(9)	82.3(4), 82.6(4)	80.1(3). 80.5(4)	81.5(9), 81.4(1)
PNP′ (°)	98.46(9)	97.6(5), 96.9(5)	99.7(4)	97.8(1), 97.9(1)
ΣN (°)	360	360, 352.7	359.9	356.6, 356.8
Disposition of Cl$^-$ ligands	*trans*	*cis*	*cis*	*cis*

[a] R′ = C(^{t}Bu)=CHSiMe$_3$; this work.
[b] Ref. [8].
[c] Ref. [9].
[d] Ar = C$_6$H$_2^t$Pr$_3$-2,4,6 [10].

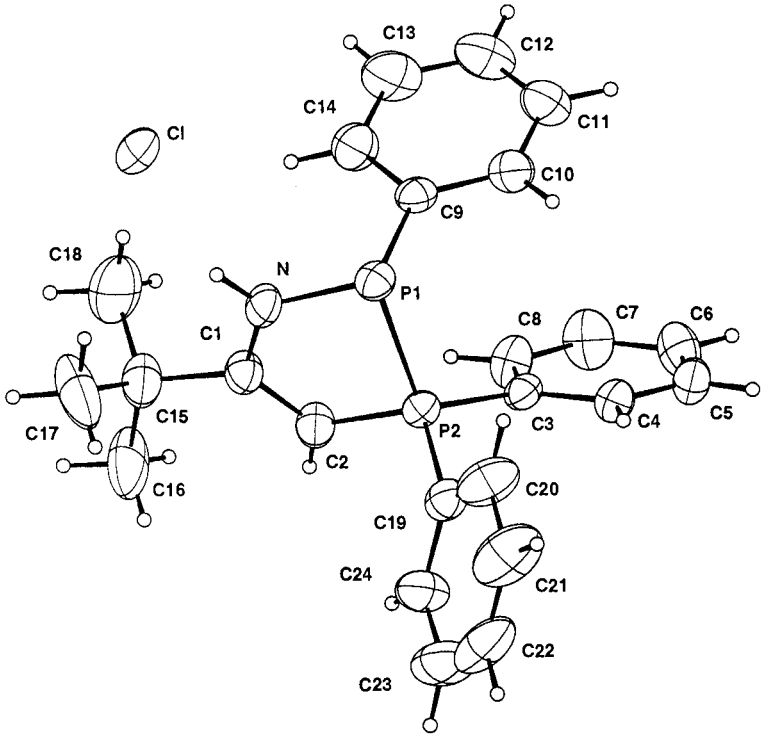


Fig. 2. Molecular structure of **10**.

When a sample of the *trans*-diazadiphosphetidine **3** in C_6D_6 in an NMR spectroscopic tube was either (i) set aside for 7 days at ambient temperature or (ii) heated for several hours, there was no evidence of isomerisation. This thermal stability of **3** is attributed to steric effects (cf. the *E* configuration in the alkenyl group and the proximity of the $SiMe_3$ group to the phosphorus atoms).

The high ^{31}P-NMR spectroscopic chemical shift value, δ 268.2, for a solution of **3** in [$^2H_8$]toluene showed that the *trans*-configuration of **3** was retained in solution. It had previously been established that this is a feature which distinguishes *trans*- from *cis*-isomers [6–16]. Furthermore, the stereochemical rigidity of **3** in solution was demonstrated by the proton–phosphorus coupling involving the $SiMe_3$ protons, giving rise to a virtual triplet $J(^1H-^{31}P) = 1.3$ Hz (which disappeared in the $^1H\{^{31}P\}$-NMR spectrum) and the corresponding $J(^{13}C-^{31}P) = 5.8$ Hz observed for the $SiMe_3$ carbons. In the $^{31}P\{^1H\}$-NMR spectrum, a single broad ($\omega_{1/2} = 180$ Hz) signal at δ 268 was detected. The $^{29}Si\{^1H\}$-NMR spectrum also showed a singlet signal.

2.5. The structure of the phosphonium salt *10*

The X-ray structure of the cation salt [Ph_2PP(Ph)N(H)C(^{t}Bu)=CH]Cl **10** is illustrated in Fig. 2, with the atom numbering scheme. Selected bond lengths and angles are listed in Table 4 and the non-hydrogen atom coordinates in Table 5.

The P(2)P(1)NC(1)C(2) ring in **10** is almost planar, with P(1) and C(2) 0.09 Å on one side, and P(2) (0.09 Å), N (0.08 Å) and C(1) (0.05 Å) on opposite sides of the plane, and C(9) (attached to P(1)) −1.90 Å and C(15) (attached to C(1)) 0.05 Å out of the plane. The PPNCC framework appears to have only a single structurally characterised precedent in **I** [17]. There are four cyclic ureido-phosphonium salts [X(Y)PP(R′)N(Me)C(O)Ne][A] **J** (X = Me = R′, Y = NEt_2 and A = Cl) [18], **K** (X = Ph, R′ = $CHCl_2$, Y = ^{t}Bu and A = BPh_4) [19] and [Me-NC(O)N(Me)PP (NEt_2)N(Me)C(O)NMe]A (**L** A = PF_6, or **M** A = Cl) [20], which have cations related to those in **10** and **I**, for which there are X-ray crystallo-

Table 4
Selected bond lengths (Å) and angles (°) for **10**

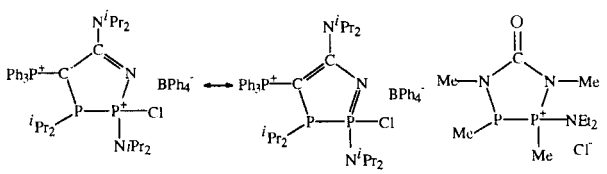
Bond length (Å)			
P(1)–N	1.694(4)	P(1)–C(9)	1.826(4)
P(1)–P(2)	2.208(2)	P(2)–C(2)	1.737(5)
P(2)–C(19)	1.780(5)	P(2)–C(3)	1.784(4)
N–C(1)	1.375(5)	C(1)–C(2)	1.343(6)
Bond angle (°)			
N–P(1)–C(9)	103.4(2)	N–P(1)–P(2)	87.51(13)
C(9)–P(1)–P(2)	97.66(14)	C(2)–P(2)–C(19)	112.9(2)
C(2)–P(2)–C(3)	114.9(2)	C(19)–P(2)–C(3)	108.8(2)
C(2)–P(2)–P(1)	95.7(2)	C(19)–P(2)–P(1)	110.5(2)
C(3)–P(2)–P(1)	113.59(14)	C(1)–N–P(1)	122.6(3)
C(2)–C(1)–N	118.6(4)	C(2)–C(1)–C(15)	124.3(4)

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **10**

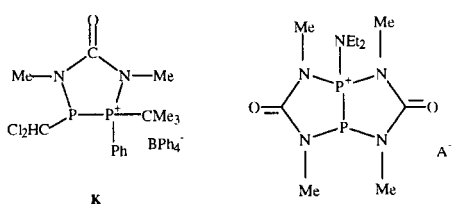
Atom	*x*	*y*	*z*	U_{eq}[a]
Cl	3808.5(5)	3343(2)	−437.2(7)	79(1)
P(1)	3810.9(4)	1763(1)	1803.8(7)	52(1)
P(2)	3940.4(4)	2527(1)	3111.2(7)	49(1)
N	3883(1)	3478(4)	1499(2)	59(1)
C(1)	3903(2)	4616(5)	2047(3)	58(1)
C(2)	3902(1)	4344(5)	2867(3)	61(1)
C(3)	3564(1)	1898(5)	3765(2)	48(1)
C(4)	3620(1)	591(5)	4176(3)	57(1)
C(5)	3312(2)	81(6)	4619(3)	68(1)
C(6)	2945(2)	825(6)	4643(3)	79(2)
C(7)	2884(2)	2115(6)	4229(4)	87(2)
C(8)	3194(2)	2658(6)	3800(3)	69(1)
C(9)	3231(1)	1606(5)	1749(2)	50(1)
C(10)	3065(2)	402(6)	2093(3)	70(1)
C(11)	2629(2)	192(7)	2040(4)	86(2)
C(12)	2358(2)	1159(7)	1618(4)	93(2)
C(13)	2516(2)	2306(7)	1252(4)	98(2)
C(14)	2954(2)	2571(6)	1323(3)	75(2)
C(15)	3926(2)	6111(6)	1677(3)	81(2)
C(16)	3997(3)	7246(6)	2353(4)	132(3)
C(17)	4286(2)	6177(7)	1147(4)	137(3)
C(18)	3504(3)	6394(7)	1114(5)	147(3)
C(19)	4463(2)	2008(6)	3563(3)	62(1)
C(20)	4632(2)	698(7)	3389(4)	94(2)
C(21)	5031(2)	336(10)	3775(4)	128(3)
C(22)	5259(2)	1268(12)	4310(5)	125(4)
C(23)	5092(2)	2558(11)	4492(4)	128(3)
C(24)	4696(2)	2951(7)	4110(3)	93(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonilised U_{ij} tensor.

graphic data; some comparative parameters are in Table 6.



I J



K

L, A = PF_6
M, A = Cl

Bond distances to the λ^4P^+, probably due to the positive charge at this phosphorus atom, are generally shorter than those to λ^3P. In **10**, an additional slight shortening of the endocyclic λ^4P^+–C distance compared with the exocyclic distances is observed, which may indicate a degree of delocalisation in the ring system. Another interesting feature of the structure is the fact that the chloride anion is bonded to the cation via a nearly linear N–H···Cl hydrogen bridge N···Cl: 3.096(4) Å, NHCl 158(1)°, **10** being a tight ion pair. This structural element is unique for these ring systems, because with substituents other than hydrogen at N, the chloride is close to the λ^4P^+ (cf. **K**). In the case of more bulky anions (**I**, **J**, **L** or **M**) than chloride, well separated ion pairs are observed instead.

Solutions of **10–14** in $CDCl_3$ show chemical shifts in the $^{31}P\{^1H\}$-NMR spectrum for the λ^4P^+ of δ 39–63 with coupling constants $^1J(^{31}P-{}^{31}P)$ in the range of 228–279 Hz, which are in the lower range of reported values [7,18,19,21].

3. Experimental details

All manipulations were carried out under argon, using standard Schlenk techniques. Solvents were distilled from drying agents and degassed. The NMR spectra were recorded in C_6D_6 or $CDCl_3$ at 298 K using the following Bruker instruments: AC-P 250 (^{1}H, 250.1; ^{11}B, 80.3; ^{13}C, 62.9; ^{31}P 101.2; ^{29}Si 49.7 MHz), DPX 300 (^{1}H, 300.1; ^{13}C 75.5; ^{31}P, 121.5 MHz) and AMX 500 (^{1}H, 500.1; ^{13}C, 125.7 MHz) and referenced internally to residual solvent resonances (data in δ) in the case of ^{1}H- and ^{13}C-spectra. The ^{31}P, ^{29}Si and ^{11}B spectra were referenced externally to H_3PO_4, $SiMe_4$ and $BF_3(OEt_2)$, respectively. Unless otherwise stated, all NMR spectra other than ^{1}H were proton-decoupled. Electron impact mass spectra were taken from solid samples using a Kratos MS 80 RF instrument. Melting points were taken in sealed capillaries and are uncorrected.

3.1. Reaction of [Li{N(R)C(tBu)CHR}]2 1 with PCl_3

A solution of $[\overline{Li(LL')}]_2$ **1** (1.61 g, 3.2 mmol) in pentane (15 cm^3) was added dropwise to PCl_3 (0.44 g, 3.2 mmol) in pentane (20 cm^3) at −25°C. The reaction mixture was allowed to warm to room temperature (r.t.) and then was stirred for another 90 min. The volatiles were removed under vacuum and the residue was extracted with pentane (20 cm^3). The extract was freed from solvent and crystallised from diethyl ether, to yield colourless crystals of the diazadiphosphetidine **3** (0.05 g, 6.6%), m.p. 139–142°C (decomp.). Anal. Found: C, 45.8: H, 8.09; N, 5.81. $C_{18}H_{38}Cl_2N_2P_2Si_2$. Calc.: C, 45.9: H, 8.12; N, 5.94%. MS *m*/*z* (%): 470/2 (40) $[M_2]^+$, 455 (22) $[M_2-Me]^+$, 435 (52) $[M_2-Cl]^+$, 413 (100) $[M_2-{}^tBu]^+$, 400 (12) $[M_2-2Cl]^+$, 235/7 (65) $[M]^+$. ^{1}H-NMR (C_7D_8): δ 0.31 (virtual t, $SiMe_3$, $J(^1H-{}^{31}P)$ 1.3 Hz), δ 1.13 (s, ^{t}Bu), δ 5.14 (s, CH). ^{31}P-NMR (C_7D_8): δ 268.2. ^{13}C-NMR (C_7D_8): δ 1.1 (t,

$SiMe_3$, $J(^{13}C-^{31}P)$ 5.8 Hz), δ 29.6 (t, $C(CH_3)_3$, $^4J(^{13}C-^{31}P)$ 5.0 Hz), δ 38.2 (t, $C(CH_3)_3$, $^3J(^{13}C-^{31}P)$ 1.2 Hz), δ 113.7 (s, b, CH), δ 156.1 (t, CN, $^2J(^{13}C-^{31}P)$ 2.3 Hz). ^{29}Si-NMR ($CDCl_3/C_7H_8$): δ −10.9 (s, $SiMe_3$).

3.2. Reaction of $[Cu\{N(R)C(^tBu)CHR\}]_2$ **2** with PCl_3

A solution of [{Cu(μ-LL′)] **2** (1.05 g, 1.71 mmol) in pentane (25 cm^3) was added slowly to a solution of PCl_3 (0.30 cm^3, 3.42 mmol) in pentane (50 cm^3) at −70°C. The reaction mixture was allowed to warm to r.t. and stirred for 1 h. Filtration from a voluminous white precipitate and removal of volatiles from the filtrate gave a yellow oil. After recrystallisation from Et_2O, colourless crystals of **3**, (0.21 g, 25%) were obtained. The characterisation of **3** is described in Section 3.1.

3.3. Preparation of $Me_3SiN=C(^tBu)CH(SiMe_3)_2$ **4**

A solution of trimethylsilyl triflate (0.69 g, 3.1 mmol) in pentane (10 cm^3) was added to $[Li(LL')]_2$ **1** (0.77 g, 1.55 mmol) in pentane (30 cm^3) at −30°C. The mixture was allowed to warm to r.t. and was stirred for 3 h, then filtered. Volatiles were removed in vacuo from the combined filtrate and washings. The residual colourless oily imine **4** (0.9 g, 92%) slowly solidified at r.t.; m.p. 25–30°C. Anal. Found: C, 57.0; H, 11.8; N, 4.49. $C_{15}H_{37}NSi_3$. Calc.: C, 57.1; H, 11.8; N, 4.44%. MS m/z (%): 300 (58) $[M-Me]^+$, 258 (100) $[M-CMe_3]^+$, 242 (29) $[M-SiMe_3]^+$. IR: ν(C=N), 1679 cm^{-1}. ^{1}H-NMR (C_6D_6): δ 0.12 (s, $NSiMe_3$), δ 0.33 (s, $SiMe_3$), δ 1.01 (s, ^{t}Bu), δ 2.39 (s, CH). ^{13}C-NMR (C_6D_6): δ 1.5 (s, $SiMe_3$), δ 3.2 (s, $SiMe_3$), δ 29.9 (s, $C(CH_3)_3$), δ 35.0 (s, CH), δ 43.4 (s, $C(CH_3)_3$), δ 187.4 (s, CN).

3.4. Preparation of $(Me_3Si)_2N(^tBu)C=CH(SiMe_3)$ **5**

Thermolysis of the imine **4**, either by heating **4** for 90 min in refluxing xylene, or heating pure **4** at 130°C for 30 min, yielded the enamine **5** in essentially quantitative yield; it sublimed at ca. 130°C/10^{-3} Torr. MS m/z (%): 300 (17) $[M-Me]^+$, 258 (100) $[M-Me]^+$, 242 (5) $[M-SiMe_3)^+$. ^{1}H-NMR (C_6D_6): δ 0.21 (s, $SiMe_3$), δ 0.26 (s, $NSiMe_3$), δ 1.14 (s, ^{t}Bu), δ 5.41 (s, CH). ^{13}C-NMR (C_6D_6): δ 1.0 (s, $SiMe_3$), δ 3.6 (s, $NSiMe_3$), δ 32.0 (s, $C(CH_3)_3$), δ 40.2 (s, $C(CH_3)_3$), δ 119.5 (s, CH), δ 168.4 (s, CN).

3.5. Preparation of $Cl_2PN=C(^tBu)CH(SiMe_3)_2$ **6**

Phosphorus(III) chloride (0.41 cm^3, 0.65 g, 4.75 mmol) was added by pipette to the imine **4** (1.50 g, 4.75 mmol) at r.t.; the reaction was exothermic, but the mixture was stirred at 50°C for a further 60 min. Volatiles were removed under vacuum; the residue was redissolved in diethyl ether (10 cm^3) and removal of volatiles in vacuo yielded the colourless solid imidophosphorus(III) chloride **6** (1.4 g, 86%). MS m/z (%): 343 (0.4) $[M]^+$, 328 (0.8) $[M-Me]^+$, 308 (50) $[M-Cl]^+$, 286 (54) $[M-CMe_3]^+$. ^{1}H-NMR (C_6D_6): δ 0.06 (s, $SiMe_3$), δ 1.00 (s, ^{t}Bu), δ 2.22 (d, CH, $^4J(^1H-^{31}P)$ 4.1 Hz). ^{31}P-NMR (C_6D_6): δ 109.5. ^{13}C-NMR (C_6D_6): δ 1.2 (s, $SiMe_3$), δ 28.9 (d, $C(CH_3)_3$, $^4J(^{13}C-^{31}P)$ 5.2 Hz), δ 38.3 (d, CH, $^3J(^{13}C-^{31}P)$ 5.0 Hz), δ 43.7 (s, $C(CH_3)_3$), δ 199.0 (d, CN, $^2J(^{13}C-^{31}P)$ 8.6 Hz).

Further purification of **6** was not attempted, since it slowly decomposed at r.t., yielding the diazadiphosphetidine **3**; see Section 3.6.

3.6. Synthesis of the diazadiphosphetidine **3** from **6**

The solid imidophosphorus(III) chloride **6**, obtained from the imide **4** (1.18 g, 3.77 mmol) and PCl_3 (0.52 g,

Table 6
Some comparative data on five cyclic phosphonium cations

Parameter	**10**	**I**	**J**	**K**	**L**
l(P–P) (Å)	2.208(2)	2.228(2)	2.191(2)	2.223(2)	2.193
$l(P^{III}–C_{exo})$ (Å)	1.826(4)	–	1.840(5)	1.863(3)	–
$l(P^{III}–N)$ (Å)	1.694(4)	1.677(4)	1.761(3)	1.704(3)	1.713, 1.714
$l(P^{V}–C_{exo})$ (Å)	1.780(5), 1.784(4)	–	1.781(4)	1.828(4), 1.788(4)	–
$l(P^{V}–C_{endo})$ (Å)	1.737(5)	–	–	–	–
$l(P^{V}–N_{endo})$ (Å)	–	1.605(3)	1.670(2)	1.658(3)	1.647, 1.630
C_{sp^2}–N(ring)(Å)	1.375(5)	1.352(8)	1.363(5), 1.389(3)	1.407(5), 1.389(5)	1.413, 1.361
$C_{sp^2}–C_{sp^2}$ (Å)	1.343(6)	1.476(6)	–	–	–
$P^{V}P^{III}N$ (°)	87.5(1)	80.1(1)	88.4(1)	88.6(1)	87.8, 87.3
$P^{III}P^{V}(C/N)_{endo}$ (°)	110.5(2)	103.1(1)	95.4(1)	94.7(1)	97.0, 96.7
ΣP^{III}	288.6	294.7	286.5	290.8	283.5

3.77 mmol), was heated to 70°C/10^{-2} Torr for 45 min. The solid was observed to melt at ca. 60°C; the pressure increased as the elimination of Me_3SiCl commenced. The melt solidified and the pressure reverted back to 10^{-2} Torr. The cooled solid was dissolved in diethyl ether (25 cm^3); cooling to −30°C afforded colourless crystals of the diazadiphosphetidine **3** (0.35 g, 40%), while the mother liquor yielded a further crop (0.13 g, 15%). The characterisation of **3** is described in Section 3.1.

3.7. Reaction of $[Li\{N(R)C(^tBu)CHR\}]_2$ **1** with Ph_2PCl

A solution $[\overline{Li(LL')}]_2$ **1** (1.58 g, 3.15 mmol) in pentane (20 cm^3) was added slowly (10 min) dropwise to a solution of Ph_2PCl (1.39 g, 6.3 mmol) in pentane (40 cm^3) at −70°C. The reaction mixture was allowed to warm to r.t. and was then stirred for 60 min. The colourless precipitate was filtered off. The volatiles were removed from the filtrate in vacuo. The residual pale yellow oil was identified as the imine $Me_3SiN{=}C(^tBu)CH(SiMe_3)PPh_2$ **7** (2.48 g, 92%). It melted just above r.t. MS m/z (%): 428 (3) $[M+H]^+$, 412 (13) $[M-Me]^+$, 370 (100) $[M-CMe_3]^+$, 349 (10) $[M-C_6H_6]^+$. ^{1}H-NMR (C_6D_6): δ 0.08 (d, $SiMe_3$, $^4J(^1H-^{31}P)$ 1.1 Hz), δ 0.48 (s, $NSiMe_3$), δ 0.73 (s, ^tBu), δ 3.95 (d, CH, $^2J(^1H-^{31}P)$ 5.7 Hz), δ 6.99 (m, Ph), δ 7.10 (m, Ph), δ 7.60 and 7.72 (t, *o*-Ph). ^{31}P-NMR (C_6D_6): δ −1.5. ^{13}C-NMR (C_6D_6): δ 0.7 (d, $SiMe_3$, $^3J(^{13}C-^{31}P)$ 6.7 Hz), δ 3.0 (s, $NSiMe_3$), δ 28.6 (s, $C(CH_3)_3$), δ 40.7 (d, CH, $^1J(^{13}C-^{31}P)$ 27.8 Hz), δ 43.6 (s, $C(CH_3)_3$), δ 128.0 (d, *m*-C, $^3J(^{13}C-^{31}P)$ 7 Hz); δ 128.5 (d, *m*-C, $^3J(^{13}C-^{31}P)$ 7.7 Hz), δ 128.9 (s, *p*-C), δ 129.3 (s, *p*-C), δ 134.6 (d, *o*-C, $^2J(^{13}C-^{31}P)$ 11 Hz), δ 135.0 (d, *o*-C, $^2J(^{13}C-^{31}P)$ 7.9 Hz), δ 138.8 (d, *ipso*-C, $^1J(^{13}C-^{31}P)$ 16.6 Hz), δ 140.8 (d, *ipso*-C, $^1J(^{13}C-^{31}P)$ 29.7 Hz), δ 183.0 (d, CN).

3.8. Isomerisation of the imine **7** into the enamines $(Me_3Si)_2NC(^tBu){=}C(H)PPh_2$ **8** and **9**

Attempts to distil the imine **7** at 10^{-2} Torr, with the heating bath at 150°C, gave the colourless *Z*-enamine **8** (1.55 g, 56%), m.p. 90°C. Anal. Found: C, 67.3; H, 8.96; N, 3.22. $C_{24}H_{38}NPSi_2$. Calc.: C, 67.4; H, 8.96; N, 3.28%. MS m/z (%): 427 (10) $[M]^+$, 412 (12) $[M-Me]^+$, 370 (85) $[M-CMe_3]^+$. ^{1}H-NMR (C_6D_6): δ 0.28 (s, $NSiMe_3$), δ 1.16 (s, ^tBu), δ 6.33 (d, CH, $^2J(^1H-^{31}P)$ 4.8 Hz), δ 7.10 (Ph, 6H), δ 7.50 (t, *o*-Ph, 2H, δ 7.51 (t, *o*-Ph, 2H). ^{31}P-NMR (C_6D_6): δ −31.8. ^{13}C-NMR (C_6D_6): δ 3.7 (d, $SiMe_3$, $^5J(^{13}C-^{31}P)$ 3.1 Hz), δ 31.7 (s, $C(CH_3)_3$), δ 39.7 (d, $C(CH_3)_3$, $^3J(^{13}C-^{31}P)$ 3.8 Hz), δ 120.0 (s, CH), δ 128.1 (s, *p*-C), δ 128.6 (d, *m*-C, $^3J(^{13}C-^{31}P)$ 6.0 Hz), δ 133.0 (d, *o*-C, $^2J(^{13}C-^{31}P)$ 18.8 Hz), δ 142.2 (d, *ipso*-C, $^1J(^{13}C-^{31}P)$ 12.6 Hz), δ 171.9 (d, CN, $^2J(^{13}C-^{31}P)$ 21.9 Hz).

Irradiation of the *Z*-enamine **8** in C_6D_6, in an NMR spectroscopic tube, using a medium pressure mercury lamp at r.t. for 1.5 h, afforded a mixture of **8** (2.4 parts) and its *E*-isomer **9** (1 part); this ratio remained unchanged after 12 h of further irradiation.

Compound **9**: ^{1}H-NMR (C_6D_6): δ 0.11 (s, $SiMe_3$), δ 1.45 (s, ^tBu), δ 5.93 (d, CH, $^2J(^1H-^{31}P)$ 6.0 Hz) (phenyl region was superimposed by signals of **8**). ^{31}P-NMR (C_6D_6): δ −25.9. ^{13}C-NMR (C_6D_6): δ 3.3 (s, $SiMe_3$), δ 32.4 (d, $C(CH_3)_3$, $^4J(^{13}C-^{31}P)$ 11.8 Hz), δ 38.7 (s, $C(CH_3)_3$), δ 123.4 (d, CH, $^1J(^{13}C-^{31}P)$ 18.2 Hz), δ 131.2 and 130.8 (d, *o*-Ph, d, $^2J(^{13}C-^{31}P)$ 8.8 and 8.7 Hz), δ 141.1 (d, *ispo*-Ph, $^1J(^{13}C-^{31}P)$ 10.9 Hz), other signals in the phenyl region were superimposed by **8**, δ 169.8 (d, CN, $^2J(^{13}C-^{31}P)$ 25.9 Hz).

3.9. Synthesis of the phosphonium chlorides $[Ph_2\overline{PP(R)N(H)C(^tBu){=}CH}]Cl$ **10** (*R* = Ph) and **11** (*R* = Et)

Phenylphosphorus(III) chloride (0.14 cm^3, 1.03 mmol) was added by pipette to the imine **7** (0.44 g, 1.03 mmol) at r.t.; the reaction was exothermic and the initially mobile oil became increasingly viscous. The mixture was stirred at 50°C for 30 min. Volatiles were removed in vacuo and the residue was washed with pentane (10 cm^3). Recrystallisation from boiling toluene yielded colourless crystals of the phosphonium chloride **10** (0.31 g, 71%), which decomposed in the range 130–165°C. Anal. Found: C, 68.2; H, 6.25; N, 2.96. $C_{24}H_{26}ClNP_2$. Calc.: C, 67.7; H, 6.15; N, 3.29%. MS m/z (%): 389 (72) $[M-HCl]^+$, 347 (37) $[M-C_6H_6]^+$, 313 (100) $[M-Cl-Ph]^+$. ^{1}H-NMR ($CDCl_3$): δ 1.43 (s, ^tBu), δ 4.60 (d, NH, $^4J(^1H-^{31}P)$ 16.0 Hz), δ 6.84–7.18 (10 H), δ 7.54–7.77 (5H), δ 10.09 (dd, CH, $^3J(^1H-^{31}P)$ 32.3 Hz, $^2J(^1H-^{31}P)$ 21.4 Hz). ^{31}P-NMR ($CDCl_3$): δ 15.0 (d, λ^3P, $^1J(^{31}P-^{31}P)$ 238.5 Hz), δ 43.8 (d, λ^4P^+, $^1J(^{31}P-^{31}P)$ 238.5 Hz). ^{13}C-NMR ($CDCl_3$): δ 29.3 (s, $C(CH_3)_3$; proton coupled q $^1J(^{13}C-^1H)$ 129.8 Hz) δ 38.1 (d, $C(CH_3)_3$, $^3J(^{13}C-^{31}P)$ 11.6 Hz), δ 64.8 (d, CH, $^1J(^{13}C-^{31}P)$ 72.6 Hz: proton coupled q, $^3J(^{13}C-^1H)$ 178.9 Hz), δ 118.5 (d, *ipso*-C, $^1J(^{13}C-^{31}P)$ 79.5 Hz), δ 123.4 (dd, *ipso*-C, $^2J(^{13}C-^{31}P)$ 75.5 Hz, $^3J(^{13}C-^{31}P$ 18.8 Hz), δ 125.1 (s, *ipso*-C), δ 128.0–134 (multiple multiplets of aromatic carbons), δ 186.4 (dd, CN, $^2J(^{13}C-^{31}P)$ 13.6 and 14.1 Hz).

The ethyl analogue $[Ph_2\overline{PP(Et)N(H)C(^tBu){=}CH}]Cl$ **11** of compound **10** was prepared in a similar manner from $EtPCl_2$ (0.11 cm^3, 1.1 mmol) and the imine **7** (0.47 g, 1.1 mmol); colourless crystals of **11** (0.21 g, 51%), decomposing at 100–108°C, were obtained after recrystallisation from hot toluene. Anal. Found: C, 61.2; H, 7.16; N, 3.77. $C_{20}H_{26}ClNP_2$. Calc.: C, 63.6, H, 6.94; N, 3.71%. MS m/z (%): 343 (5) $[MH-Cl]^+$, 283 (12) $[MH-Cl-PEt]^+$, 220 (25) $[Ph_2PCl]^+$. ^{1}H-NMR ($CDCl_3$): δ 0.78 (dt, CH_2CH_3, $^3J(^1H-^{31}P)$ 18.1 Hz,

$^3J(^1H-{}^1H)$ 7.8 Hz), δ 1.38 (s, ^{t}Bu), δ 1.59 and 1.94 (multiple multiplets, CH_2CH_3), δ 4.72 (d, NH, $^4J(^1H-{}^{31}P)$ 15.4 Hz), δ 7.53 – 7.78 (Ph, 10 H), δ 9.44 (dd, CH, $^3J(^1H-{}^{31}P)$ 29.5 Hz, $^2J(^1H-{}^{31}P)$ 22.6 Hz). ^{31}P-NMR ($CDCl_3$): δ 28.6 (d, λ^3P, $^1J(^{31}P-{}^{31}P)$ 245.4 Hz; δ 39.6 (d, λ^4P^+, $^1J(^{31}P-{}^{31}P)$ 245.4 Hz). ^{13}C-NMR ($CDCl_3$): δ 7.7 (d, CH_2CH_3, $^2J(^{13}C-{}^{31}P)$ 16.6 Hz), δ 21.6 (d, CH_2CH_3, $^1J(^{13}C-{}^{31}P)$ 32.5 Hz), δ 29.3 (s, $C(CH_3)_3$, δ 38.0 (d, $C(CH_3)_3$, $^3J(^{13}C-{}^{31}P)$ 11.3 Hz), δ 63.7 (d, CH, $^1J(^{13}C-{}^{31}P)$ 67.8 Hz), δ 125.2 (s, *ipso*-C) δ 128.6 (d, *ipso*-C, $^1J(^{13}C-{}^{31}P)$ 61.1 Hz), δ 129.9–134.2 (aromatic C), δ 185.8 (s, CN).

3.10. Synthesis of the N-trimethylsilyphosphonium chlorides $[Ph_2\overline{PP(Cl)N(R)C(^tBu)}{=}\overline{CH}]A$ 12 (A = Cl), 13 ($A = CF_3SO_3$) and 14 ($A = BPh_4$)

Phosphorus(III) chloride (0.14 cm^3, 1.57 mmol) was added by pipette to the imine **7** (0.67 g, 1.57 mmol) in hexane (20 cm^3) at −30°C. While warming up to r.t., formation of a pale yellow precipitate was observed. The reaction mixture was stirred for 1 h, then filtered. The precipitate was dried in vacuo and identified as **12** (0.52 g, 72%). ^{1}H-NMR ($CDCl_3$): δ 0.18 (s, $SiMe_3$), δ 1.60 (s, ^{t}Bu), δ 7.61 – 7.72 (Ph, 4H), δ 7.75 – 7.81 (Ph, 6H), δ 10.26 (dd, CH, $^2J(^1H-{}^{31}P)$ 30.8 Hz, $^3J(^1H-{}^{31}P)$ 21.5 Hz). ^{31}P-NMR ($CDCl_3$): δ 54.9 (d, λ^4P^+, $^1J(^{31}P-{}^{31}P)$ 227.9 Hz), δ 69.2 (d, λ^3P, $^1J(^{31}P-{}^{31}P)$ 227.9 Hz). ^{13}C-NMR ($CDCl_3$): δ 4.7 (s, $SiMe_3$), δ 30.4 (s, $C(CH_3)_3$), δ 40.8 (d, $C(CH_3)_3$, $^3J(^{13}C-{}^{31}P)$ 14.9 Hz), CH not observed, δ 117.7 (dd, *ipso*-C, $^1J(^{13}C-{}^{31}P)$ 70.9 Hz $^2J(^{13}C-{}^{31}P)$ 12.8 Hz), δ 130.0 and 133.3 (d, Ph, $^2J(^{13}C-{}^{31}P)$ 12.2 and 8.8 Hz) δ 134.8 (s, *p*-Ph), δ 191.0 (d, CN, $^2J(^{13}C-{}^{31}P)$ 16.2 Hz). Attempts at recrystallisation, from mixtures of hot CH_2Cl_2 and C_5H_{12} or PhMe, led to decomposition of **12**.

Silver triflate (0.27 g, 1.05 mmol) was added to a solution of the phosphonium chloride **12** (0.48 g, 1.05 mmol) in CH_2Cl_2 (15 cm^3) at −40°C. The reaction mixture was allowed to warm to r.t. and stirred for 12 h, then filtered. Volatiles were removed from the filtrate in vacuo, and the colourless solid residue was recrystallised from a mixture of CH_2Cl_2 and Et_2O to give colourless crystals of **13** (0.33 g, 55%), decomposing in the range 130–190°C. MS *m*/*z* (%): 419 (7) [*M* (cation) − H]$^+$, 385 (8) [*M* (cation) − Cl]$^+$, 363 (15) [*M* (cation) − CMe_3]$^+$. ^{1}H-NMR ($CDCl_3$): δ 0.21 (s, $SiMe_3$), δ 1.52 (s, ^{t}Bu), δ 7.65–7.86 (Ph, 10H), δ 8.77 (dd, CH, $^2J(^1H-{}^{31}P)$ 32.3 Hz, $^3J(^1H-{}^{31}P)$ 25.6 Hz). ^{31}P-NMR ($CDCl_3$): δ 61.7 (d, λ^4P^+, $^1J(^{31}P-{}^{31}P)$ 233.5 Hz), δ 73.0 (d, λ^3P, $^1J(^{31}P-{}^{31}P)$ 233.5 Hz). ^{13}C-NMR ($CDCl_3$): δ 4.8 (s, $SiMe_3$), δ 30.1 (s, $C(CH_3)_3$), δ 40.9 (d, $C(CH_3)_3$, $^3J(^{13}C-{}^{31}P)$ 15.0 Hz), δ 78.2 (d, CH, $^1J(^{13}C-{}^{31}P)$ 16.8 Hz), δ 116.2 (d, *ipso*-C, $^1J(^{13}C-{}^{31}P)$ 76.1 Hz), δ 120.5 (q, CF_3, $^1J(^{13}C-{}^{19}F)$ 320.3 Hz), δ 130.1 and 130.4 (d, Ph, $^2J(^{13}C-{}^{31}P)$ 12.8 and 12.1 Hz), δ 133.1 and 133.8 (d, Ph, $^3J(^{13}C-{}^{31}P)$ 5.4 and 9.1 Hz), δ 135.3 (s, *p*-C), δ 191.5 (d, CN, $^2J(^{13}C-{}^{31}P)$ 18.2 Hz).

Solid sodium tetraphenylborate (0.35 g, 1.07 mmol) was added to a solution of the phosphonium chloride **12** (0.49 g, 1.07 mmol) in CH_2Cl_2 (20 cm^3) at −40°C. The reaction mixture was allowed to warm to r.t. and stirred for 1 h. Initially the $Na[BPh_4]$ floated on top of the mixture, but gradually a denser precipitate (NaCl) settled at the bottom of the reaction vessel, and was filtered off. Volatiles were removed from the filtrate in vacuo, leaving a residue of crude **14** (0.80 g, 100%); attempts to crystallise **14**, by dissolving it in CH_2Cl_2 and adding PhMe, C_5H_{12} or Et_2O, proved to be unsuccessful. ^{1}H-NMR ($CDCl_3$): δ 0.18 (s, $SiMe_3$), δ 1.27 (s, ^{t}Bu), δ 6.15 (dd, CH, $^{2/3}J(^1H-{}^{31}P)$ 27.6 and 25.6 Hz); δ 6.86–7.00 and 7.27–7.78 (Ph, 30H). ^{31}P-NMR ($CDCl_3$): δ 63.1 (d, λ^4P^+, $^1J(^{31}P-{}^{31}P)$ 241.0 Hz), δ 69.5 (d, λ^3P, $^1J(^{31}P-{}^{31}P)$ 241.0 Hz). ^{11}B-NMR ($CDCl_3$): δ −9.2 (s, BPh_4).

3.11. Reactions of $[Li\{N(R)C(^tBu)CHR\}]_2$ 1 with $POCl_3$ or ICl

A solution of $[\overline{Li(LL')}]_2$ **1** (3.0 g, 6.0 mmol) in pentane (15 cm^3) was slowly added to $POCl_3$ (0.55 cm^3, 6.0 mmol) in pentane (30 cm^3) at −60°C. The reaction mixture was allowed to warm to r.t. and stirred for 12 h. Removal of volatiles and distillation of the residue afforded the pale yellow liquid imine $Me_3SiN{=}C(^tBu)\{CH(Cl)SiMe_3\}$ **15** (0.70 g, 21%), b.p. 60–64°C/10^{-1} Torr. Anal. Found: C, 51.7; H, 10.1; N, 5.07. $C_{12}H_{28}ClNSi_2$. Calc.: C, 51.9; H, 10.2; N, 5.04%. ^{1}H-NMR (C_6D_6): δ 0.12 (s, $SiMe_3$), δ 0.30 (s, $SiMe_3$), δ 1.01 (s, ^{t}Bu), δ 4.2 (s, CH). ^{13}C-NMR (C_6D_6): δ −1.8 (s, $SiMe_3$), δ 2.3 (s, $SiMe_3$), δ 28.7 (s, $C(CH_3)_3$), δ 43.9 (s, $C(CH_3)_3$), δ 49.2 (s, CH), δ 180.4 (s, CN).

Similarly, from $[\overline{Li(LL')}]_2$ **1** (1.23 g, 2.46 mmol) and ICl (0.80 g, 4.93 mmol) in pentane (55 cm^3), and stirring at r.t. for 2 h and then for a further 60 h, upon addition of Et_2O (4 cm^3), the initially red reaction mixture had become pale yellow with a yellow precipitate. Removal of the solvent from the filtrate and distillation of the residue yielded the air-sensitive, yellow liquid imine $Me_3SiN{=}C(^tBu)\{CH(I)SiMe_3\}$ **16** (1.1 g, 60%), b.p. 70–74°C/10^{-2} Torr. Anal. Found: C, 37.8; H, 7.58; N, 3.86. $C_{12}H_{28}INSi_2$. Calc: C, 39.0; H, 7.64; N, 3.79%. MS *m*/*z* (%): 354 (20) [*M* − Me]$^+$, 312 (98) [*M* − CMe_3]$^+$, 242 (7) [*M* − I]$^+$. ^{1}H-NMR (C_6D_6): δ 0.16 (s, $SiMe_3$), δ 0.26 (s, $SiMe_3$), δ 1.04 (s, ^{t}Bu), δ 3.94 (s, CH). ^{13}C-NMR (C_6D_6): δ −0.7 (s, $SiMe_3$), δ 2.2 (s, $SiMe_3$), δ 15.2 (s, CH), δ 29.5 (s, $C(CH_3)_3$), δ 44.6 (s, $C(CH_3)_3$), δ 182.6 (s, CN).

3.12. Reaction of $[Li\{N(R)C(Ph)CR_2\}(THF)]$ ($R = SiMe_3$) E with $CF_3SO_3SiMe_3$

Trimethylsilyl triflate (1.40 cm^3, 7.3 mmol) in pentane (10 cm^3) was added to a suspension of the 1-aza-allyl-

Table 7
Crystallographic data for compounds **3** and **10**

Compounds	**3**	**10**
Formula	$C_{18}H_{38}Cl_2N_2P_2Si_2$	$C_{24}H_{26}ClNP_2$
M_w	471.5	425.8
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.171073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)
a (Å)	9.187(2)	31.552(7)
b (Å)	12.606(2)	9.310(2)
c (Å)	12.005(1)	16.088(7)
α (°)	101.60(1)	97.39(2)
V (Å^3)	1361.9(4)	4687(3)
Z	2	8
$D_{calc.}$ (Mg m^{-3})	1.15	1.21
$F(000)$	504	1792
μ (mm^{-1})	0.45	0.31
Crystal size (mm^3)	$0.4\times0.4\times0.2$	$0.3\times0.2\times0.2$
θ min and max (°)	2–30	2–25
Index ranges	$0\le h\le12$, $0\le k\le17$, $-16\le l\le16$	$0\le h\le37$, $0\le k\le11$, $-19\le l\le18$
Reflections collected	4161	4179
Independent reflections	3947 ($R_{int}=0.039$)	4108 ($R_{int}=0.022$)
Reflections with $I>2\sigma(I)$	2525	2256
No. of variables	124	253
R_1 ($I>2\sigma(I)$)	0.052	0.061
wR_2 (all data)	0.146	0.156
Largest difference peak (e Å^{-3})	0.46	0.24

lithium compound **E** (3.05 g, 7.3 mmol) in pentane (50 cm^3) at −40°C. The reaction mixture was allowed to warm to r.t. and stirred for 12 h, then filtered. Removal of volatiles from the filtrate in vacuo yielded the colourless, waxy solid **17** (2.66 g, 89%). Anal. Found: C, 57.7; H, 10.0; N, 3.70. $C_{20}H_{41}NSi_4$. Calc.: C, 58.9; H, 10.1; N, 3.43%. MS m/z (%): 407 (35) $[M]^+$, 392 (18) $[M-Me]^+$, 334 (63) $[M-SiMe_3]^+$. ^{1}H-NMR (C_6D_6): δ −0.06 (s, $SiMe_3$), δ 0.16 (s, $NSiMe_3$), δ 0.43 (s, $SiMe_3$), δ 7.02 (m, *p*-Ph, 3H). δ 7.28 (*o*-Ph, 2H). ^{13}C-NMR (C_6D_6): δ 1.2 (s, $NSiMe_3$), δ 1.4 (s, $SiMe_3$), δ 1.6 (s, $SiMe_3$), δ 125.6 (s, *m*-C), δ 126.7 (s, *p*-Ph), δ 128.1 (s, CSi_2), δ 129.3 (s, *o*-Ph), δ 145.5 (s, *ipso*-C), δ 166.1 (s, CN).

*3.13. X-ray structure determination of the diazadiphosphetidine **3** and the phosphonium chloride **10***

Data were collected on an Enraf–Nonius CAD4 diffractometer using monochromatic Mo–K_α radiation and crystals sealed under argon in Lindemann capillaries. Cell dimensions were calculated from the setting angles for 25 reflections with $9<\theta<13°$. Intensities were measured by an $\omega-2\theta$ scan. Corrections were made for Lorentz and polarisation effects but not for absorption. There was no crystal decay as measured by two standard reflections. Positions of non-hydrogen atoms were derived by direct methods using SHELXLS-86 and refined on F^2 with anisotropic thermal parameters by full-matrix least squares using SHELXL-93.

Further details are in Table 7. Hydrogen atom positions, anisotropic thermal parameters and structure factors are available from P.B. Hitchcock upon request.

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