The Role of 1-Azaallyllithium Compounds in Phosphorus Chemistry, 2[◇]

Aspects of the Chemistry of the Cyclic Phosphonium Salt $[Ph_2P^aP(Cl)N(SiMe_3)C(tBu)=C^bH(P^a–C^b)]Cl$ and the Related Diazadiphosphetidine $[ClP^aN(R)P(Cl)N^bR(P^a–N^b)]$ [R = C(*t*Bu)=C(H)SiMe$_3$]

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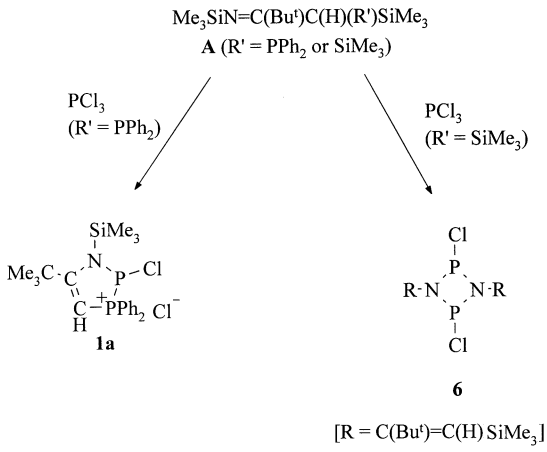
We report the preparation of the novel phosphonium salts $[Ph_2P^aP(NR'_2)N(R)C(tBu)=C^bH]A(P^a–C^b)$ (**2a**; R′ = Et, R = SiMe$_3$, A = Cl; **2b**: R′ = Me, R = SiMe$_3$, A = Cl; **2c**: R = Et, R′ = SiMe$_3$, A = [OSO_2CF_3]; **2d**: R′ = Et, R = SiMe$_3$, A = [BPh_4]; **4**: R′ = Et, R = H, A = Cl) and *trans*-1,3,2,4-diazadiphosphetidines $R'_2NP^aN(R)P(NR'_2)N^c(R)(P^a–N^c)$ [**3a**: R′ = Et, R = C(*t*Bu)=C(H)PPh_2; **3b**: R′ = Me, R = C(*t*Bu)=C(H)PPh_2; **7**: R′ = Me, R = C(*t*Bu)=C(H)SiMe$_3$]. Reaction of **3a** with Cu_2I_2 led to the *P*- and *P,P′*-centred complexes [Cu(I)(**3a**)] (**5a**) and [{Cu(I)}$_2$(**3b**)] (**5b**) [R = C(*t*Bu)=C(H)PPh_2]. The phosphazole $N^aC(tBu)C(H)C^cP^aN(Me)(CH_2)_2N^cMe(N^a–P^a)(C^c–N^c)$ (**8**) was obtained by a remarkable heterocycloaddition reaction from the diazadiphosphetidine $ClP^aN(R)P(Cl)N^bR(P^a–N^b)$ [**6**: R = C(*t*Bu)=C(H)SiMe$_3$] and the electron-rich olefin $[=C^aN(Me)(CH_2)_2N^aMe(C^a–N^a)]_2$ and was oxidised with S_8 yielding $N^aC(tBu)C(H)C^cP^a(S)N(Me)(CH_2)_2N^cMe(N^a–P^a)(C^c–N^c)$ (**9**). Compounds **2–9** were characterised by multinuclear NMR spectroscopy, mass spectrometry for **5–9**, while single-crystal X-ray diffraction data are provided for **3a** and **5a**.

Introduction

Recently we reported that treatment of the ketimine $Me_3SiN=C(Bu^t)CH(R')SiMe_3$ (**A**: R′ = PPh_2; **B**: R′ = SiMe$_3$) with PCl_3 gave the novel phosphonium salt $[Ph_2P^aP(Cl)N(SiMe_3)C(tBu)=C^bH]Cl(P^a–C^b)$ (**1a**) or the *trans*-1,3,2,4-diazadiphosphetidine **6** (Scheme 1)[1].

Scheme 1



The chloride **1a** was thermolabile and decomposed during attempted recrystallisation, whereas the corresponding triflate or tetraphenylborate was stable. We now present further reactions of the two phosphorus-containing heterocycles **1a** and **6**.

[◇] Part 1: Ref.[1].

Results and Discussion

The reaction of **1a** with $Me_3SiNR'_2$ led (step i in Scheme 2), by Me_3SiCl elimination, to the P^{III}-dialkylamino derivatives **2a** and **2b**. Both compounds were thermally labile and were isolated as crude materials from the reaction mixture by removing the solvent and washing the residue with pentane. They were characterised solely by multinuclear NMR spectroscopy.

After resolvation in hot toluene, **2a** or **2b** eliminated a second equivalent of Me_3SiCl and cooling gave (step ii in Scheme 2) colourless crystals of the *trans*-diazadiphosphetidine **3a** or **3b** in nearly quantitative yield. Each gave satisfactory (parent ion) mass spectra and microanalyses. NMR-spectroscopic studies showed that the *P,P′*-bis(diethylamino) compound **3a** existed in solution as mixture of two *trans* isomers, which only differed in the orientation of their substituents at the endocyclic nitrogen atom. In the minor isomer (henceforth identified as *syn*), both diphenylphosphane end groups were close to the same endocyclic phosphorus atom (this conformation is also adopted in the CuI complex **5a**, see Figure 3), while in the major (*anti*) isomer they were close to endocyclic phosphorus atoms of adjacent molecules (as in the crystal, Figure 2). The bis(dimethylamino) analogue **3b**, by contrast, was found to exist solely as the *anti* isomer.

Replacing Cl^- of **2a** by a bulkier anion by treatment with $Ag[OSO_2CF_3]$ or $Na[BPh_4]$ gave (step iii in Scheme 2) the thermally stable five-membered heterocycle **2c** or **2d**. Each was recrystallised from a mixture of CH_2Cl_2 and pentane

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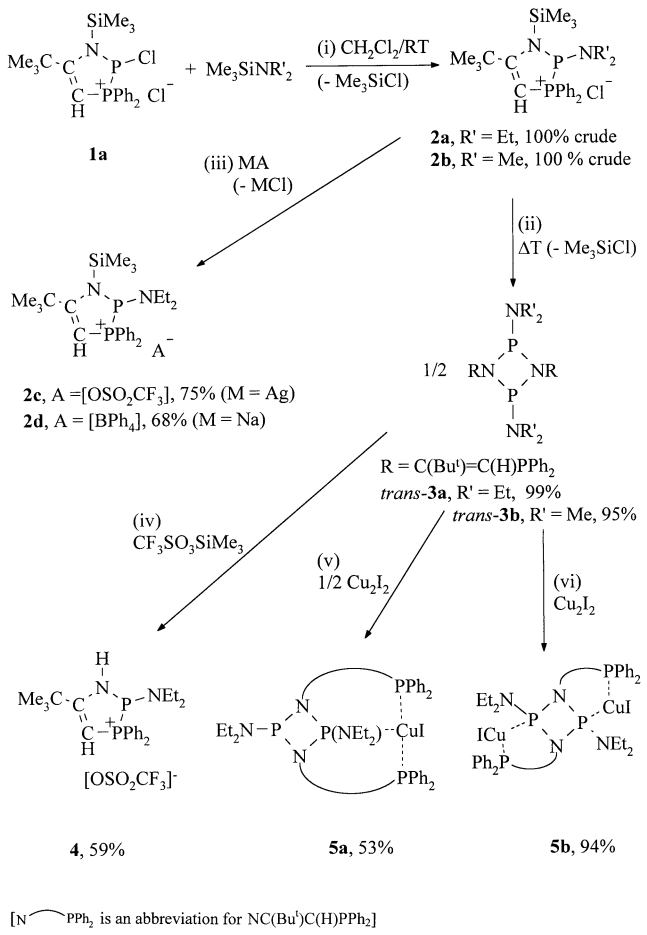
Scheme 2. Some reactions of the phosphonium salt **1a**

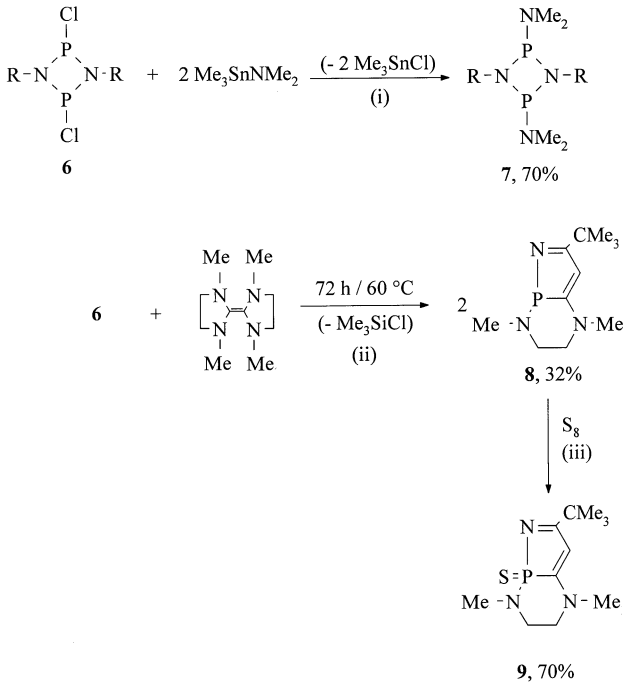


and was fully characterised. Remarkably, the conversion of the phosphonium chloride **2a** into the diazadiphosphetidine **3a** proved to be quasi-reversible as was shown by treatment of **3a** with $CF_3SO_3SiMe_3$ in hot toluene (80°C, 96 h) which yielded (step iv in Scheme 2) the phosphonium triflate **4**; the cation is the desilylated analogue of that in **2a**. The fate of the Me_3Si group at N was not established. A similar observation had, however, been made for the reaction of $Me_3SiN{=}C(t\text{Bu})CH(PPh_2)SiMe_3$ (**A**: R′ = PPh_2) with $PhPCl_2$ or $EtPCl_2$ (cf. Scheme 1) giving $Ph_2P^aP(R'')N(H)C(t\text{Bu}){=}C^bH(P^a{-}C^b)Cl$ (R'' = Ph or Et), with no trace of the $SiMe_3$-substituted product being detected[1].

The ability of a diazaphosphetidine to act as ligand is well documented[2] and is now demonstrated for **3a** by the synthesis (steps v or vi of Scheme 2) of the iodocopper(I) complexes **5a** or **5b** from a mixture of **3a** and Cu_2I_2 in hot toluene. Thus, compound **3a** behaved as a novel terminal tridentate (**5a**) or bridging bis(bidentate) (**5b**) ligand. The related reaction of **3b** with AgI led, under similar reaction conditions, to the disappearance of AgI, and the formation of a white precipitate, presumably an Ag analogue of **5b**, but its extreme insolubility in standard solvents including hot $CHCl_3$ or CH_3CN prevented its characterisation. This was not surprising, as even **5b** was only very sparingly soluble in hot toluene or $CHCl_3$, which may be due to its being a polymer of infinite chain length, with **5b** moieties bridging CuI units (*anti* isomer). The *syn* isomer of **5a** was, by contrast, a monomer both in the gas phase (parent ion in the mass spectrum) and in the crystal (see Figure 3). As a consequence, **5a** was much more soluble than **5b** in, for example, hot toluene.

Further reactions of the diazadiphosphetidine **6** are illustrated in Scheme 3. Treatment of **6** with Me_3SnNMe_2 led (i in Scheme 3) in a clean reaction to the *trans*-diazadiphosphetidine **7**, which with $LiNEt_2$ gave an inseparable mixture of products, whereas Me_3SiNEt_2 proved to be unreactive. The treatment of **6** with the electron-rich olefin [$=C^aN(Me)(CH_2)_2N^aMe(C^a{-}N^a)]_2$[3] led not, as we had anticipated, by chlorine abstraction to a stable phosphorus-centred radical, as had been reported for formation of PR'_2 from $ClPR'_2$ [R′ = $CH(SiMe_3)_2$][4], but (step ii in Scheme 3) to the fused bicyclic compound $N^aC(t\text{Bu})C(H)C^cP^aN(Me)(CH_2)_2N^cMe(N^a{-}P^a)(C^c{-}N^c)$ (**8**). The latter was distillable in a vacuum at 130°C and crystallised at room temperature after several days. Compound **8** was converted (step iii in Scheme 3) into its P^V derivative **9** by treatment with S_8 and crystallisation from Et_2O.

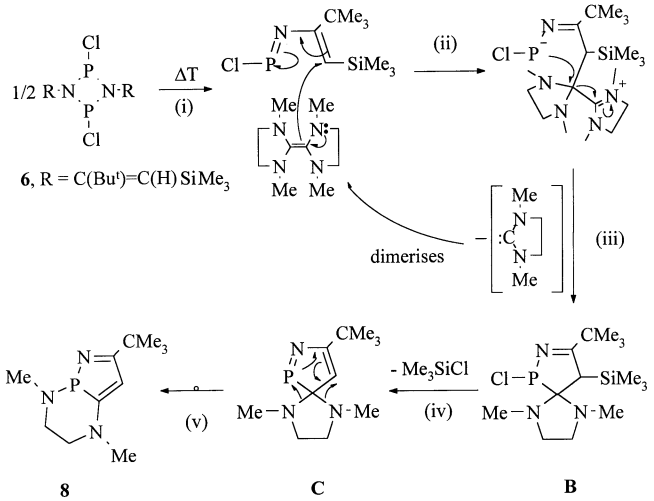
Scheme 3. Some reactions of the *trans*-diazadiphosphetidine **6** [R = C(*t*Bu)C(H)$SiMe_3$]



A plausible reaction pathway for the formation of **8** is outlined in Scheme 4. The first step (i in Scheme 4) is the dissociation of **6** into the transient monomer, the iminophosphane, which is subjected to nucleophilic attack (step ii in Scheme 4) by the electron-rich olefin known[5] to be a powerful C-centred nucleophile. A reversible dimerisation of an iminophosphane has been reported for *t*BuP=N*t*Bu[6]. In step (iii) (which may be synchronous with ii), a *spiro* bycyclic compound **B** is formed with electron-rich

carbene elimination (this can dimerise to reform the electron-rich olefin). Loss of Me_3SiCl from **B** thus leads (step iv in Scheme 4) to **C**, which isomerises (step v in Scheme 4) into the more stable bicyclic compound **8**.

Scheme 4. Proposed reaction pathway from **6** + [=$C^aN(Me)(CH_2)_2$-$N^aMe(C^a-N^a)]_2$ to **8**



NMR-Spectra and Solution Behaviour

In the following discussion of the NMR spectra of the new cyclic phosphonium salts **2** and **4** we also include data on five related compounds $[Ph_2P^aP(R'')N(R')C(t\text{Bu})=C^bH(P^a-C^b)]$A {R′ = $SiMe_3$, R″ = Cl and A = Cl (**1a**), $[OSO_2CF_3]$ (**1b**), $[BPh_4]$ (**1c**); A = Cl, R′ = H, R″ = Ph (**10a**), Et (**10b**)} which had been reported earlier[1]. The data are summarised in Table 1. Each was insoluble in hydrocarbons or Et_2O, but readily soluble in CH_2Cl_2. As a general rule, the NH compounds (i.e., R′ = H) **4**, **10a** and **10b** were thermally stable and were easily crystallised from aromatic solvents, while solutions of the $NSiMe_3$ derivatives **1a**−**2d** were much less so and, in particular for A = Cl, decomposed at room temperature. Compounds with the bulkier anions (A = $[OSO_2CF_3]$ or $[BPh_4]$) were sufficiently stable to be purified by recrystallisation from mixtures of CH_2Cl_2 and Et_2O or pentane.

The ^{31}P-NMR spectral shift values for the λ^4P^+ (Table 1) were in the region reported for typical phosphonium salts[7]. The assignments of individual ^{31}P-NMR spectroscopic shift values and $J_{H\text{-}P}$ coupling constants were made on the basis of 2D-^{31}P-^{1}H correlation experiments for **2d**, **4**, **10a**, and **10b** (as an example, see Figure 1). These showed cross-peaks for NH, CH, and for each set of *o*-hydrogen atoms at the benzene rings of the λ^4P^+ and hence established the identity of the λ^4P^+. The remaining doublet is consequently attributed to λ^3P, an assignment further supported by its broadening attributable to the quadrupolar moment of the adjacent nitrogen atom.

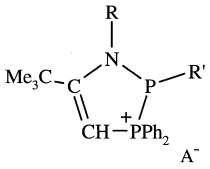
The $^1J_{PP}$ coupling constants were on the low side of previously reported values (240−424 Hz)[8][9][10] in related systems, but showed the general trend[8] of increasing with increasing electron-donating strength of the substituent at the λ^3P (**2c** being an exception).

The comparatively small effect of changing the anion A^- (compounds **1a**−**1c**, **2a**, **2c**, **2d**) on the ^{31}P-NMR shift value for λ^3P, and in particular on the size of the $^1J_{PP}$ coupling constants makes it plausible to assume that in solution the phosphonium salts exist as separated ion pairs even for the comparatively small chloride anion. Larger differences in ^{31}P-NMR spectroscopic shifts {$\Delta\delta[^{31}P(\lambda^3P)]$ = 6−18 ppm} and coupling constants (Δ^1J_{PP} = 35−58 Hz) in the related urea-bridged derivatives [*t*Bu(Ph)P^aP(R)N(Me)-C(O)N^b(Me)(P^a-N^b)]A (R = Me, Et, *i*Pr, *t*Bu, Ph, Xyl, 9-Anth, $CHCl_2$, or CH_2SiMe_3) have been attributed to a change in structure from a zwitterionic form for the chloride to a separated ion pair for the tetraphenylborate[8].

Other interesting features were: (i) the ^{1}H-NMR spectroscopic shift of the ring C*H* adjacent to λ^4P^+ seemed to depend mainly on the nature of the counterion. Independent of other substituents they varied from $\delta \approx 10$ for A = Cl, through $\delta \approx 8$ for A = $[OSO_2CF_3]$ to $\delta \approx 6$ for A = $[BPh_4]$; (ii) the large $^4J_{H\text{-}\lambda^4P}$ coupling constants of 10−16 Hz for the NH compounds **4** and **10**; and (iii) $\delta[^{13}C\{^1H\}]$ = 78 for the ring *C*H and δ = 190 for the ring *C*N, a value usually associated with a carbon atom doubly bonded to an oxygen or nitrogen atom. Items (ii) and (iii) indicate a considerable delocalisation of π-electron density in the heterocycle between N and λ^4P^+.

The ^{31}P-NMR spectroscopic shift of $\delta \approx 186$ for the endocyclic phosphorus atom of the diazadiphosphetidine **3a**, **3b**, or **7** in $CDCl_3$ solution is appropriate for each having *trans*-orientated substituents at the phosphorus atom[11][12][13][14][15][16][17][18][19][20][21]. While **7** showed only a singlet for the magnetically equivalent phosphorus atoms of the PN heterocycle, the spectrum of **3a** indicated the presence of two isomers in a ratio of approximately 3:1. The set of signals of the major isomer assigned to be of the *anti* isomer (as in the crystal) showed an AA′XX′ spectral pattern with two pseudo triplets, one for the PPh_2 (X) groups at δ = −29.4 and the other for the ring phosphorus (A) at δ = 186.6. The spectrum was readily simulated on the basis of J_{AX} = 202.6 and $J_{AA'}$ = 20.4 Hz. The CP-MAS ^{31}P-NMR spectrum of **3a** showed the signals only of the major (δ = −29.4 and δ = 186.6, J_{PP} = 190 Hz), but not of the minor, isomer. It is, however, not inevitable that the minor isomer exists only in solution and not in the solid, because the larger line width and the less favourable signal-to-noise ratio of the solid-state NMR spectrum compared to that in solution may have obscured the CP-MAS signals of the minor isomer. The solution ^{31}P-NMR spectrum of the latter showed features consistent with its being the *syn* isomer, having a conformation similar to **5a**. Only a doublet was observed for the PPh_2 groups, while the ring phosphorus atom close to the PPh_2 groups gave rise to a triplet of doublets due to a coupling with *P*Ph_2 and the other endocyclic phosphorus atom, respectively. Variable-temperature solution ^{31}P-NMR spectroscopic studies on the isomeric mixture of **3a** showed no temperature dependence for the ratio

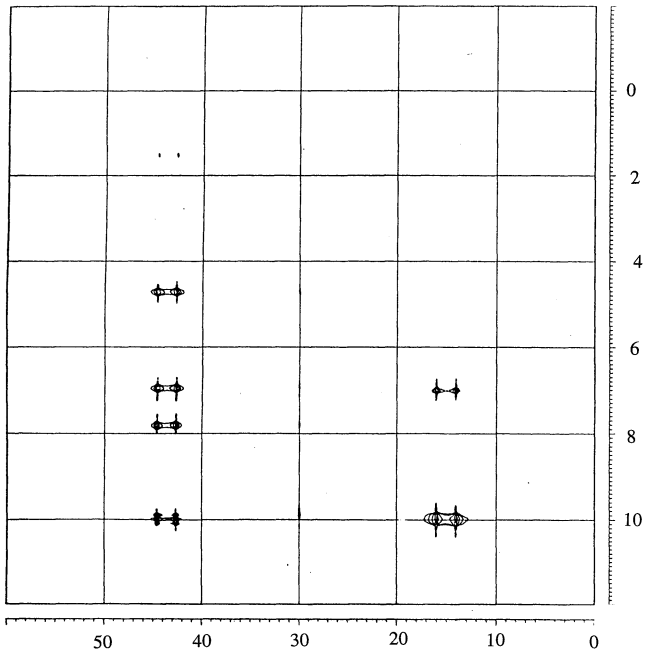
Table 1. Selected NMR-spectroscopic data of cyclic phosphonium salts



No.	R	R′	A	δ ^{31}P (λ^3P)	δ ^{31}P (λ^4P)	$^1J_{P\text{-}P}$	δ ^{1}H (CH)	δ ^{13}C (CH)	δ ^{13}C (CN)
1a	$SiMe_3$	Cl	Cl	69.2	54.9	227.9	10.26	[a]	191.0
1b	$SiMe_3$	Cl	OSO_2CF_3	73.0	61.7	233.5	8.77	78.2	191.5
1c	$SiMe_3$	Cl	BPh_4	69.5	63.1	241.0	6.15	–	–
2a	$SiMe_3$	NEt_2	Cl	74.4	29.4	269.1	10.08	–	–
2b	$SiMe_3$	NMe_2	Cl	74.9	30.1	263.5	9.90	69.0	190.6
2c	$SiMe_3$	NEt_2	OSO_2CF_3	84.5	31.2	190.4	8.23	[a]	188.8
2d	$SiMe_3$	NEt_2	BPh_4	86.5	33.2	279.5	6.11	72.5	188.5
4	H	NEt_2	OSO_2CF_3	82.3	10.6	304.9	8.19	65.0	184.0
10a	H	Ph	Cl	15.0	43.8	238.5	10.09	64.8	186.4
10b	H	Et	Cl	28.6	39.6	245.4	9.44	63.7	185.8

[a] Not identified.

Figure 1. 2D-^{31}P{^{1}H} ^{1}H-NMR correlation spectrum of $Ph_2P^aP(Ph)N(H)C(t\text{Bu})=C^bH(P^a-C^b)Cl$ (**10a**)



of the two isomers between −45 and +60°C, while prolonged heating (12 h at 60°C) led to complete decomposition of the sample. No signals attributable to the formation of a *cis* isomer were observed.

In solutions of the metal complexes **5a** or **5b**, the ^{31}P-NMR spectral signal for the metal-coordinated ring phosphorus atoms was shifted by ca. 50 ppm to lower frequency, whereas the influence on the chemical shifts of the PPh_2 groups was only small. Probably due to the quadrupolar moment of the coordinated copper centre, the lines were, particularly for **5a**, so broad that any coupling information was obscured. Slightly sharper lines were observed for **5b**, so that $J_{P(A)P(X)}$ = 297 Hz was determined, being ca. 100 Hz larger than in the free ligand **3a**. The unusual magnitude of these coupling constants in **3** and **5**, being in the lower range of reported directly bonded P-P coupling constants[11], is attributed to a through-space coupling rather than a $^4J(^{31}P\text{-}^{31}P)$. This is supported by the close P···P contacts between phosphane and ring phosphorus atoms in the crystal structures of **3a** [3.262(1) Å] and **5a** [3.252(3) and 3.319(3) Å]. A similar effect had been observed for **6**, where the closeness of the ring phosphorus atom and the trimethylsilyl group gave rise to a coupling ($J_{P\text{-}H}$ = 1.3 Hz[1]) between these two groups.

There has been much interest in the *cis*/*trans* isomerism in 1,3,2,4-diazadiphosphetidines, with the *cis* generally the thermodynamically and the *trans* the kinetically favoured isomer (refs.[14][15][16][17][18][19][20][21][22][23], and literature cited therein). For bulky ligands at N and P, the *trans* isomer is usually thermodynamically favoured. Studies into the relationship between isomer and the chemical shift δ(^{31}P) showed the signals of the *cis* isomer to be ca. 50−90 ppm at higher frequency than in the *trans* isomer[14][18][19][20][21][22][23]. Each of the diazadiphosphetidines having the bulky C(*t*Bu)=C(H)R′ (R′ = $SiMe_3$ and PPh_2) substituent at N, which we have so far characterised, has invariably adopted the *trans* conformation.

The ^{31}P-NMR spectroscopic shifts previously reported for *trans*-diazadiphosphetidines coordinated to metals were for most part in the same region (δ ≈ 130−170[2]) as observed for **5a** and **5b**. Only for Pd or Pt complexes, values of 40 or 80 ppm to lower frequency have been observed. The direction of the shift change, as between the free ligand and the complex upon coordination, seems largely to depend on the metal[2]. Since **5a** and **5b** are, to our knowledge, the first compexes of diazadiphosphetidines with copper, no comparative data are available.

The structures of **8** and **9** were determined with the help of multinuclear NMR spectra and MS. The assignments of the ^{13}C-NMR spectroscopic shifts were made on the basis of (i) their chemical shift values and (ii) the information derived from $J_{P\text{-}C}$ coupling constants (when compared with literature data[24]). The interpretation of the ^{1}H-NMR spectroscopic shift data required NOE-difference NMR-spectroscopic studies. Irradiation of an individual *t*Bu group gave a 6.4% enhancement for the olefinic CH signal, while irradiation of the CNMe group gave enhancements of 3.9 and 2.0% for the CH and the *exo*-H at the neighbouring CH_2 group, respectively. The hydrogen atoms of the remaining CH_2 groups were not unambiguously identified, as any NOE enhancement was obscured due to the closeness of these signals to the centre of irradiation.

The spectra of **9** were very similar to those of **8**, the major difference being a higher frequency shift of the CH proton in the ^{1}H-NMR spectrum and a similar effect in the ^{13}C-NMR spectrum for the carbon atom directly bonded to the phosphorus atom (**8**: C*H*: δ = 5.83; *C*P: δ = 183.2; **9**: C*H*: δ = 5.26; *C*P: δ = 166). A further difference was the magnitude of the coupling constants of the nuclei close to the phosphorus atom, being much larger for **9** [$^{3}J(^{1}H\text{-}^{31}P)$ = 30.0; $^{1}J(^{13}C\text{-}^{31}P)$ = 94.4; $^{2}J(^{13}C\text{-}^{31}P)$ = 46.4 Hz] than for **8** [$^{3}J(^{1}H\text{-}^{31}P)$ = 17.1; $^{1}J(^{13}C\text{-}^{31}P)$ = 4.1; $^{2}J(^{13}C\text{-}^{31}P)$ = 36.0 Hz].

X-ray Structural Analysis of 3a and 5a

The X-ray molecular structures of **3a** and **5a** are illustrated in Figures 2 and 3, with the atom-numbering scheme and selected bond lengths and angles being shown in Tables 2 and 3.

The crystalline compound **3a** is centrosymmetric and adopts a *trans* configuration with the substituents at N(1) being *anti* to one another. The $P^{a}NPN^{a}(P^{a}-N^{b})$ ring is planar, with the *N*-ligating sp^2-carbon atoms also coplanar, the sum of angles at nitrogen (Σ N) being 360°. The endocyclic ring angle at nitrogen, 100.8(1)°, is much larger than that at phosphorus, 79.2(1)°. The N(2)−P(2)−N(1) and N(2)−P(2)−N(1′) bond angles are significantly narrower than tetrahedral, indicating the presence of a stereochemically active lone pair at P(2). The alkenyl groups have the (*E*) configuration, so as to minimise steric effects, the *tert*-butyl group being *trans* to PPh_2. As a consequence, there are close contacts between the phosphorus atom of one diphenylphosphane group [P(1)] and one ring phosphorus atom [P(1)−P(2): 3.262(1) Å] which may account for the large coupling constant between P(1) and P(2) (J_{PP} = 190 Hz) observed in the solid-state ^{31}P-NMR spectrum. The *exo* P−N distances [P(2)−N(2): 1.671(3) Å] are much shorter than the *endo* ones [P(2)−N(1): 1.751(1); P(2)−N(1′): 1.730(2) Å].

In general, the skeletal geometry of **3b** closely resembles that of other known *trans*-1,3,2,4-diazadiphosphetidines, such as $[(MeO)PN(Ph)]_2$[25], $\{[F_3C(F_2C)_2H_2C]PN(tBu)\}_2$[21], $[(F_3CH_2CO)PN(Ph)]_2$[14], $[(Ph_2N)PN(Ph)]_2$[17], $[(C_6H_4Me\text{-}4)OPN(Ph)]_2$[20], $[Me_2C^{a}(CH_2)_3(Me)_2C^{b}NPN(SiMe_3)(C^{a}-C^{b})]_2$[26] and $\{[Me_3Si)_2N]PN(SiMe_3)\}_2$[27].

In the CuI complex **5a**, the copper centre is surrounded in a distorted tetrahedral fashion by the iodine, the ring phosphorus P(1) and the two phosphorus atoms P(3) and P(4) of the *exo*-diphenylphosphane groups, Figure 4. The coordination to the metal atom leads to a *syn* conformation in the diazadiphosphetidine and a slight puckering

Figure 2. Molecular structure of **3a**

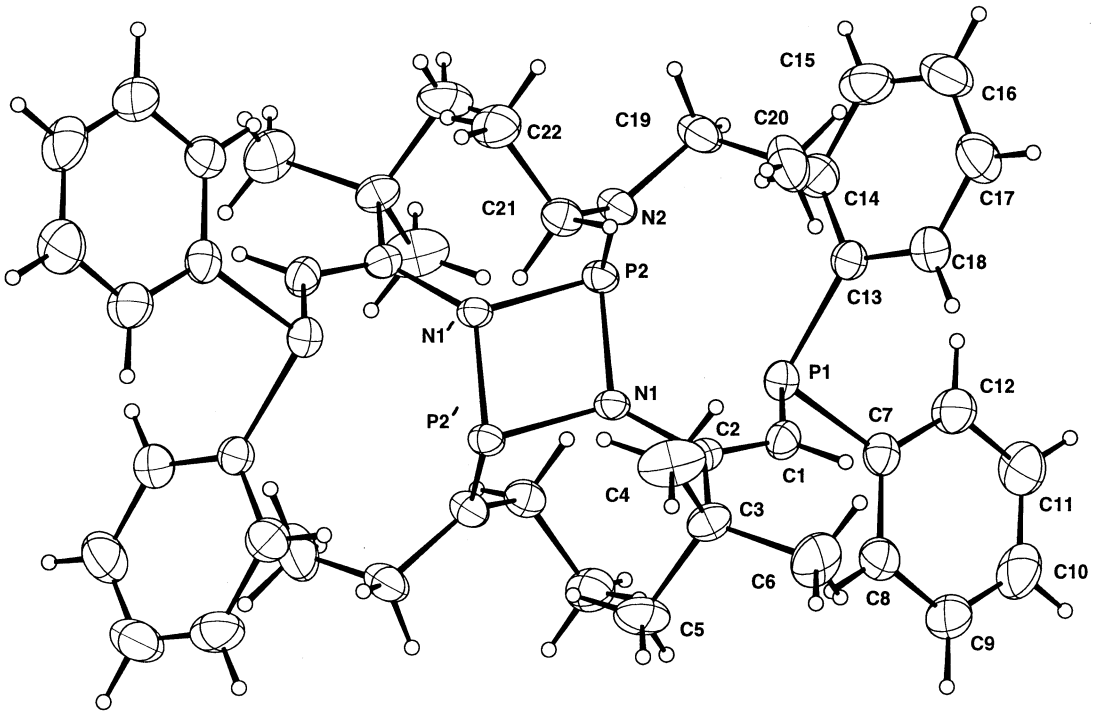


Figure 3. Molecular structure of **5a**

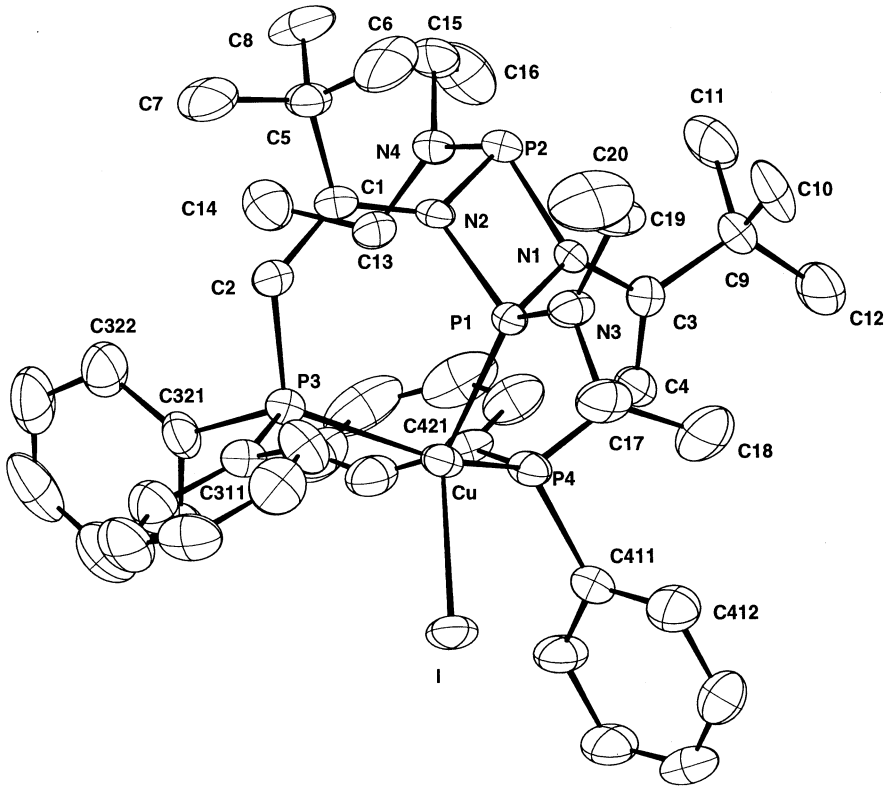


Table 2. Selected bond lengths [Å] and angles [°] for **3a**

P(1)−C(1)	1.805(3)	P(1)−C(13)	1.831(3)
P(1)−C(7)	1.846(3)	P(2)−N(2)	1.671(3)
P(2)−N(1)′	1.730(2)	P(2)−N(1)	1.751(2)
N(1)−C(2)	1.405(3)	N(2)−C(19)	1.458(4)
N(2)−C(21)	1.462(4)	C(1)−C(2)	1.340(4)
C(2)−C(3)	1.535(4)	C(3)−C(6)	1.527(5)
C(3)−C(4)	1.532(5)	C(3)−C(5)	1.536(4)
C(7)−C(12)	1.380(4)	C(7)−C(8)	1.384(4)
C(8)−C(9)	1.390(5)	C(9)−C(10)	1.355(5)
C(10)−C(11)	1.362(5)	C(11)−C(12)	1.382(5)
C(13)−C(18)	1.378(4)	C(13)−C(14)	1.381(4)
C(14)−C(15)	1.387(5)	C(15)−C(16)	1.360(6)
C(16)−C(17)	1.372(6)	C(17)−C(18)	1.373(5)
C(19)−C(20)	1.503(5)	C(21)−C(22)	1.518(4)
C(1)−P(1)−C(13)	104.60(14)	C(1)−P(1)−C(7)	98.9(2)
C(13)−P(1)−C(7)	99.80(14)	N(2)−P(2)−N(1)′	104.12(12)
N(2)−P(2)−N(1)	108.06(12)	N(1)−P(2)−N(1)′	79.18(12)
C(2)−N(1)−P(2)	125.3(2)	C(2)−N(1)−P(2)′	133.9(2)
P(2)−N(1)−P(2)′	100.82(12)	C(19)−N(2)−C(21)	116.6(2)
C(19)−N(2)−P(2)	117.1(2)	C(21)−N(2)−P(2)	126.1(2)
C(2)−C(1)−P(1)	126.7(2)	C(1)−C(2)−N(1)	120.3(3)
C(1)−C(2)−C(3)	122.8(3)	N(1)−C(2)−C(3)	116.8(2)
C(6)−C(3)−C(4)	108.9(3)	C(6)−C(3)−C(2)	112.1(3)
C(4)−C(3)−C(2)	109.7(3)	C(6)−C(3)−C(5)	107.4(3)
C(4)−C(3)−C(5)	109.1(3)	C(2)−C(3)−C(5)	109.6(3)
C(12)−C(7)−C(8)	117.7(3)	C(12)−C(7)−P(1)	122.3(3)
C(8)−C(7)−P(1)	119.7(2)	C(7)−C(8)−C(9)	120.5(3)
C(10)−C(9)−C(8)	120.5(4)	C(9)−C(10)−C(11)	120.1(4)
C(10)−C(11)−C(12)	119.9(4)	C(7)−C(12)−C(11)	121.4(4)
C(18)−C(13)−C(14)	117.9(3)	C(18)−C(13)−P(1)	123.6(3)
C(14)−C(13)−P(1)	118.5(3)	C(13)−C(14)−C(15)	120.5(4)
C(16)−C(15)−C(14)	120.5(4)	C(15)−C(16)−C(17)	119.6(4)
C(18)−C(17)−C(16)	120.0(4)	C(17)−C(18)−C(13)	121.5(4)
N(2)−C(19)−C(20)	114.0(3)	N(2)−C(21)−C(22)	112.6(3)

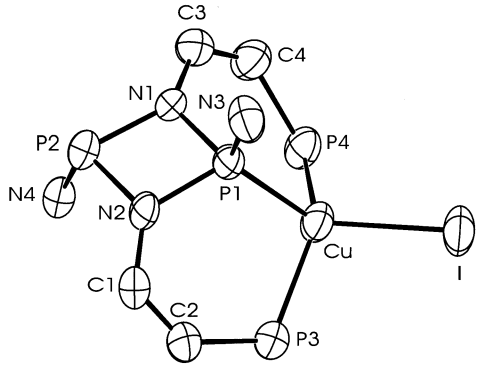
Table 3. Selected bond lengths [Å] and angles [°] for **5a**

I−Cu	2.574(1)	Cu−P(1)	2.223(2)
Cu−P(4)	2.292(3)	Cu−P(3)	2.306(3)
P(1)−N(3)	1.643(7)	P(1)−N(1)	1.723(7)
P(1)−N(2)	1.736(6)	P(2)−N(4)	1.649(8)
P(2)−N(1)	1.754(6)	P(2)−N(2)	1.755(7)
P(3)−C(2)	1.788(8)	P(3)−C(321)	1.813(10)
P(3)−C(311)	1.837(10)	P(4)−C(4)	1.812(9)
P(4)−C(411)	1.819(9)	P(4)−C(421)	1.839(10)
P(1)−Cu−P(4)	94.61(9)	P(1)−Cu−P(3)	91.77(9)
P(4)−Cu−P(3)	133.87(10)	P(1)−Cu−I	129.32(8)
P(4)−Cu−I	107.15(7)	P(3)−Cu−I	103.49(7)
N(3)−P(1)−N(1)	110.1(4)	N(3)−P(1)−N(2)	106.2(3)
N(1)−P(1)−N(2)	80.9(3)	N(3)−P(1)−Cu	121.9(3)
N(1)−P(1)−Cu	113.8(2)	N(2)−P(1)−Cu	116.5(2)
N(4)−P(2)−N(1)	108.3(3)	N(4)−P(2)−N(2)	105.9(3)
N(1)−P(2)−N(2)	79.5(3)	C(2)−P(3)−C(321)	106.5(5)
C(2)−P(3)−C(311)	96.9(4)	C(321)−P(3)−C(311)	102.0(5)
C(2)−P(3)−Cu	117.2(3)	C(321)−P(3)−Cu	119.5(3)
C(311)−P(3)−Cu	111.6(3)	C(4)−P(4)−C(411)	99.3(4)
C(4)−P(4)−C(421)	103.8(5)	C(411)−P(4)−C(421)	102.8(4)
C(4)−P(4)−Cu	113.2(3)	C(411)−P(4)−Cu	114.2(3)
C(421)−P(4)−Cu	120.8(3)	C(3)−N(1)−P(1)	125.9(5)
C(3)−N(1)−P(2)	133.4(6)	P(1)−N(1)−P(2)	100.0(3)
C(1)−N(2)−P(1)	127.5(5)	C(1)−N(2)−P(2)	130.6(5)
P(1)−N(2)−P(2)	99.4(4)	C(17)−N(3)−C(19)	114.6(7)
C(17)−N(3)−P(1)	117.9(6)	C(19)−N(3)−P(1)	126.0(6)
C(13)−N(4)−C(15)	116.4(7)	C(13)−N(4)−P(2)	126.0(6)
C(15)−N(4)−P(2)	117.6(6)		

of the PN heterocycle [angle between the planes P(1)N(2)P(2) and P(1)N(1)P(1): 5.7(7)°]. The *exo* P−N bond lengths [P(1)−N(3): 1.643(7); P(2)−N(4): 1.649(8) Å] are considerably shorter than the *endo* ones [P(1)−N(2):

1.736(6); P(2)−N(1): 1.754(6); P(1)−N(1): 1.723(7); P(2)−N(2): 1.755(7) Å], but the influence of metal coordination on the endocyclic P−N bonds is only small (Table 2). The Cu−I [2.574(1) Å] and Cu−P distances [Cu−P(1): 2.223(2); Cu−P(3): 2.306(3); Cu−P(4): 2.292(3) Å] are within the range of values reported for four- and three-coordinated phosphanecopper(I) complexes: $[CuI(PPh_3)_3]$ triclinic: $Cu-P_{av.}$ 2.34(1), Cu−I 2.686(1) Å[28]; $[CuI(PPh_3)_3]$ trigonal: $Cu-P_{av.}$ 2.355(8), Cu−I 2.67(1) Å[28]; $[(Cu\{\mu\text{-}I\}\{P(c\text{-}C_6H_{11})_3\})_2]$: Cu−P 2.23(1), $Cu-I_{av.}$ 2.58(1) Å[29]; $[(Cu\{\mu\text{-}I\}\{P(Ph)(CH_2CH_2PPh_2)_2\})_2]$: Cu−P 2.263(4)−2.325(5), Cu−I 2.614(2) Å[30]; $[Cu(PMe_3)(\mu\text{-}I)_2Cu(PMe_3)_2]$[31], $[\{Cu(\mu\text{-}I)(PPh_2Me)\}_2] \cdot SO_2$: $Cu-P_{av}$ 2.250(2), $Cu-I_{av}$ 2.719(1) Å[32]; $[(Cu\{\mu\text{-}I\}\{P(C_6H_4Me\text{-}4)_3\})_2](C_6H_5Me)_2$: Cu−P 2.238(4), $Cu-I_{av}$ 2.583(2) Å[33]. For two-coordinate phosphanecopper complexes, the observed Cu−P distances are usually slightly smaller: $[CuBr\{P(C_6H_2Me_3\text{-}2,4,6)_3\}]$ 2.193(2) Å[34]; $[CuX\{P(C_6H_2(OMe)_3\text{-}2,4,6\}_3]$ with X = Cl 2.177(1), X = Br 2.197(3), X = I, Cu−P 2.188(4) Å[35]; $[Cu\{N(SiMe_3)C(tBu)=C(H)SiMe_3\}(PPh_3)]$ 2.145(3) Å[36]. Apart from the already mentioned puckering of the ring, the nature of the backbone of the heterocycle in **5a** is similar to that of the free ligand **3a**.

Figure 4. Molecular structure of **5a** (core atoms only)



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Experimental Section

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 MHz; ^{11}B 80.3 MHz; ^{13}C 62.9 MHz; ^{31}P 101.2 MHz), DPX 300 (^{1}H 300.1 MHz; ^{13}C 75.5 MHz; ^{31}P 121.5 MHz), and AMX 500 (^{1}H 500.1MHz; ^{13}C 125.7 MHz) and referenced internally to residual solvent resonances in the case of ^{1}H and ^{13}C spectra. The ^{31}P and ^{11}B spectra were referenced externally to H_3PO_4 and $BF_3(OEt_2)$, respectively. Unless otherwise stated, all NMR spectra, other then ^{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. Elemental analyses were determined by Medac Ltd., Brunel University. Due to incorporation of solvent, some of the phoshonium salts and the copper complexes **5** gave unsatisfactory elemental analyses.

Preparation of the Phosphonium Chlorides $[Ph_2P^aP(NR'_2)N(SiMe_3)C(tBu)=C^bH(P^a-C^b)]A$ (**2a**: R′ = Et, A = Cl; **2b**: R′ = Me, A = Cl; **2c**: R′ = Et, A = OSO_2CF_3; **2d**: R′ = Et, A = BPh_4): Me_3SiNEt_2[2] (0.34 ml, 1.82 mmol) was added to a solution of $[Ph_2P^aP(Cl)N(SiMe_3)C(tBu)=C^bH(P^a-C^b)]Cl$ (**1**)[1] (0.83 g, 1.82 mmol) in CH_2Cl_2 (15 ml) at −50°C. The yellow solution was slowly warmed to room temperature and stirred for 1 h. Removal of volatiles in vacuo gave crude **2a** (0.90 g, 100%). − ^{1}H NMR ($CDCl_3$): δ = 0.15 [s, $SiMe_3$], 0.84 [s, broad, Me], 1.61 [s, *t*Bu], 2.2−3.1 [m, very broad, CH_2], 7.52−7.69 [Ph, 10 H], 10.08 [dd, CH, $J(^1H\text{-}^{31}P)$ 27.5 and 27.6 Hz]. − ^{31}P NMR ($CDCl_3$): δ = 74.4 [d, λ^3P, $^1J(^{31}P\text{-}^{31}P)$ = 269.1 Hz], 29.0 [d, λ^4P, $^1J(^{31}P\text{-}^{31}P)$ = 269.1 Hz].

Crude compound **2b** (1.45 g, 100%) was prepared in an identical fashion, from **1** (1.40 g, 3.07 mmol) and Me_3SiNMe_2 (0.49 ml, 3.07 mmol). − ^{1}H NMR ($CDCl_3$): δ = 0.13 [s, $SiMe_3$], 1.59 [s, *t*Bu], 2.60 [s, very broad, CH_3], 5.26 [s, CH_2Cl_2], 7.46−7.73 [Ph, 10 H], 9.90 [s, broad, CH]. − ^{31}P NMR ($CDCl_3$): δ = 74.9 [d, λ^3P, $^1J(^{31}P\text{-}^{31}P)$ = 263.5 Hz], 30.1 [s, broad, λ^4P^+]. − ^{13}C NMR ($CDCl_3$): δ = 5.2 [s, $SiMe_3$], 30.9 [s, $C(CH_3)_3$], 41.3 [d, $C(CH_3)_3$, $^3J(^{13}C\text{-}^{31}P)$ = 13.8 Hz], NMe_2 signal not observed, 53.4 [s, CH_2Cl_2], 69.0 [d, CH, $^1J(^{13}C\text{-}^{31}P)$ = 20.2 Hz], 120.1 [d, *ipso* C, $^1J(^{13}C\text{-}^{31}P)$ = 66.3 Hz], 127.3−133.7 [Ph], 190.6 [s, broad, CN].

Compound **2c** or **2d** was obtained by adding $Ag(OSO_2CF_3)$ (0.21 g, 0.81 mmol) or $Na[BPh_4]$ (0.46 g , 1.36 mmol) at −40°C to a solution of **2a** (0.4 g, 0.81 mmol; or 0.67 g, 1.36 mmol, respectively) in CH_2Cl_2 (15 ml). The mixture was allowed to warm to room temperature and was stirred for another 4 h or 2.5 h, then filtered and all volatiles were removed from the filtrate in vacuo. The crude product was recrystallised from a mixture of CH_2Cl_2 and pentane to give colourless crystals of **2c** (0.36 g, 75%) or **2d** (0.59 g, 68%).

2c: ^{1}H NMR ($CDCl_3$): δ = 0.13 [s, $SiMe_3$], 0.74 [m, broad, Me], 1.56 [s, *t*Bu], 2.50 [m, very broad, CH_2], 3.09 [m, very broad CH_2], 7.60−7.84 [Ph, 10 H], 7.97−8.04 [d, 2 H], 8.23 [dd, CH, $^3J(^1H\text{-}^{31}P)$ 27.7 Hz, $^2J(^1H\text{-}^{31}P)$ 19.7 Hz]. − ^{31}P NMR ($CDCl_3$): δ = 84.5 [d, λ^3P, $^1J(^{31}P\text{-}^{31}P)$ = 190.4 Hz], 31.2 [s, very broad, λ^4P^+]. − ^{13}C NMR ($CDCl_3$): δ = 5.0 [s, $SiMe_3$], 13.1 [s, Me], 30.3 [s, $C(CH_3)_3$], 41.4 [d, $C(CH_3)_3$, $^3J(^{13}C\text{-}^{31}P)$ = 13.0 Hz], 45 [s, very broad CH_2], CH and OSO_2CF_3 signals not identified, 116.9 [d, *ipso* C, $^1J(^{13}C\text{-}^{31}P)$ = 71.2 Hz], 118.7 [d, *ipso* C, $^1J(^{13}C\text{-}^{31}P)$ = 50.6 Hz], 130.1 [d, Ph, $J(^{13}C\text{-}^{31}P)$ = 12.4 Hz], 130.5 [d, Ph, $J(^{13}C\text{-}^{31}P)$ = 13.1 Hz], 132.7 [d, Ph, $J(^{13}C\text{-}^{31}P)$ = 9.9 Hz], 133.8 [s, Ph], 134.3 [s, Ph], 135.1 [d, Ph, $J(^{13}C\text{-}^{31}P)$ = 9.4 Hz], 188.8 [d, CN, $^2J(^{13}C\text{-}^{31}P)$ = 11.8 Hz].

2d · $(CH_2Cl_2)_{0.5}$: Mp 105°C (dec.). − $C_{49.5}H_{60}BClN_2P_2Si_2$ (819.41): calcd. C 72.6, H 7.38, N 3.42; found C 70.7, H 7.30, N 3.39. − ^{1}H NMR ($CDCl_3$): δ = 0.22 [s, $SiMe_3$], 0.69 and 0.80 [s, broad, Me], 1.40 [s, *t*Bu], 2.24−2.93 [m, very broad, CH_2], 5.28 [s, CH_2Cl_2], 6.11 overlapping dd, CH, $J(^1H\text{-}^{31}P)$ = 29.5 Hz], 6.94 [t, 4 H, $J(^1H\text{-}^{31}P)$ = 7.1 Hz], 7.07 [t, 8 H, $J(^1H\text{-}^{31}P)$ = 7.3 Hz], 7.48−7.69 [m, 16 H]. − ^{31}P NMR ($CDCl_3$): δ = 86.5 [d, λ^3P, $^1J(^{31}P\text{-}^{31}P)$ = 279.5 Hz], 33.2 [d, λ^4P^+, $^1J(^{31}P\text{-}^{31}P)$ = 279.5 Hz]. − ^{11}B NMR ($CDCl_3$): δ = −9.1. − ^{13}C NMR ($CDCl_3$): δ = 5.0 [s, $SiMe_3$], 14.8 [s, Me], 30.3 [s, $C(CH_3)_3$], 40.6 [d, $C(CH_3)_3$, $^3J(^{13}C\text{-}^{31}P)$ = 14.1 Hz], 41.5 [s, CH_2], δ 43.7 [d, CH_2 $^1J(^{13}C\text{-}^{31}P)$ = 37.0 Hz], δ 53.4 [s, CH_2Cl_2], δ 72.5 [d, CH, $^1J(^{13}C\text{-}^{31}P)$ = 16.9 Hz], 118.3 [d, *ipso* C, $^1J(^{13}C\text{-}^{31}P)$ = 68.0 Hz], 121.5 [s, BPh], 122.5 [d, *ipso*-C, $^1J(^{13}C\text{-}^{31}P)$ = 24.7 Hz], 125.4 [s, BPh], 130.1 [t, Ph], 132.0 [d, Ph, $J(^{13}C\text{-}^{31}P)$ = 6.4 Hz], 133.5 [d, Ph, $J(^{13}C\text{-}^{31}P)$ = 9.7 Hz],

134.1 [d, Ph, $J(^{13}C\text{-}^{31}P)$ = 19.9 Hz], 136.3 [s, BPh], 164.2 [q, *ipso* C, $^{1}J(^{13}C\text{-}^{11}B)$ = 49.4 Hz], 188.5 [d, CN, $^{2}J(^{13}C\text{-}^{31}P)$ = 9.4 Hz].

Preparation of cis/trans-[$Et_2NP^{a}N(R)P(NEt_2)N^{d}R(P^{a}-N^{d})$] [**3a**: R = C(*t*Bu)=C(H)PPh_2]: Crude **2a** (0.90 g, 1.82 mmol) was heated in toluene (15 ml) under reflux until a clear yellow solution had formed and was then allowed to cool to room temperature. After 1 d, colourless crystals of **3a** (0.6 g, 85%) had formed. A second crop of crystals (0.1 g, 14%) was obtained after removing part of the solvent from the mother liquor; mp 192°C (dec.). − $C_{44}H_{60}N_4P_4$ (768.89): calcd. C 68.7, H 7.86, N 7.29; found C 68.4, H 7.88, N 7.53. − MS; *m/z* (%): 768 (2) $[M_2]^+$, 696 (2) $[M_2 - NEt_2]^+$, 384 (43) $[M]^+$. − ^{1}H NMR ($CDCl_3$): δ = 0.68 [s, very broad, CH_3, *cis/trans*], 1.29 [s, *t*Bu, *cis/trans*], 2.72 [s, broad, CH_2, *trans*], 4.05 [s, broad, CH_2, *cis*], 5.38 [s, broad, CH, *cis*], 5.50 [t, CH, $^{2}J(^{1}H\text{-}^{31}P)$ = 4.2 Hz, *trans*], 7.15−7.30 [Ph, 8 H], 7.50−7.60 [*o*-Ph, 2 H]. − ^{31}P NMR ($CDCl_3$): *trans* isomer (AA′XX′ system): δ = −29.4 [t, PPh_2 $_J(^{31}P\text{-}^{31}P)_{AX}$ = 202.6 Hz], 186.6 [t, PN, $^{2}J(^{31}P\text{-}^{31}P)_{AA'}$ = 20.4 Hz]; *cis* isomer: δ = −30.1 [d, PPh_2, $J(^{31}P\text{-}^{31}P)$ = 198.0 Hz], 176.8 [s, PN uncoord., $^{2}J(^{31}P\text{-}^{31}P)$ = 20.7 Hz], 193.9 [dt, PN coord., $J(^{31}P\text{-}^{31}P)$ = 198.0 Hz, $^{2}J(^{31}P\text{-}^{31}P)$ = 20.7 Hz]. − ^{13}C NMR ($CDCl_3$): isomeric mixture: δ = 13.8 [s, broad, CH_3], 30.4 [s, $C(CH_3)_3$,], $C(CH_3)_3$ signal not identified, 39.8 [s, broad, CH_2], 103.8 [s, CH,], 126.5 and 127.8 [s, Ph], 131.2 and 134.3 [d, Ph, $J(^{13}C\text{-}^{31}P)$ = 15.9 and 19.0 Hz], 141.0 and 141.1 [s, Ph], 145.3 and 145.4 [s, Ph], 162.3 and 162.6 [s, CN]. − CP-MAS ^{31}P NMR: δ = −27.7 [d, PPh_2 $_J(^{31}P\text{-}^{31}P)$ = 191.6 Hz], 186.6 [s, broad, PN].

Preparation of trans-[$Me_2NP^{a}N(R)P(NMe_2)N^{c}R(P^{a}-N^{c})$] [**3b**: R = C(*t*Bu)=C(H)PPh_2]: Colourless crystals of **3b** (1.04 g, 95%) were obtained similarly to **3a**, from **2b** (1.45 g, 3.07 mmol) in hot toluene (20 ml); mp 185°C (dec.). − $C_{40}H_{52}N_4P_4$ (712.78): calcd. C 67.4, H 7.35, N 7.86; found C 67.0, H 7.43, N 7.70. − MS; *m/z* (%): 712 (3) $[M_2]^+$, 668 (22) $[M_2 - NMe_2]^+$, 357 (100) $[M + H]^+$, 356 (54) $[M]^+$, 342 (50) $[M - Me]^+$, 312 (97) $[M - NMe_2]^+$. − ^{1}H NMR ($CDCl_3$): δ = 1.23 [s, *t*Bu], 2.52 [s, broad, NCH_3], 5.24 [d, CH, $^{2}J(^{1}H\text{-}^{31}P)$ = 2.5 Hz], 7.19−7.29 [Ph, 8 H], 7.41−7.47 [*o*-Ph, 2 H]. − ^{31}P NMR ($CDCl_3$): δ = −28.7 [t, PPh_2 $_J(^{31}P\text{-}^{31}P)$ = 101.8 Hz], 184.9 [t, PN, $^{1}J(^{31}P\text{-}^{31}P)$ = 101.8 Hz]. − ^{13}C NMR ($CDCl_3$): δ = 30.2 [s, $C(CH_3)_3$,], 36.8 [s, broad, NCH_3], 38.7 [s, CH_2], 39.5 [s, $C(CH_3)_3$,], 102.8 [d, CH, $^{3}J(^{13}C\text{-}^{31}P)$ = 8.1 Hz], 127.3 [d, Ph, $J(^{13}C\text{-}^{31}P)$ = 26.4 Hz], 127.9 [s, Ph], 132.0 [d, Ph, $J(^{13}C\text{-}^{31}P)$ = 18.6 Hz], 132.6 [d, Ph, $J(^{13}C\text{-}^{31}P)$ = 18.5 Hz], 141.1 [d, Ph, $J(^{13}C\text{-}^{31}P)$ = 9.7 Hz], 161.7 [d, CN, $^{2}J(^{13}C\text{-}^{31}P)$ = 20.3 Hz].

*Preparation of the Phosphonium Salt [$Ph_2P^{a}P(NEt_2)$]*N(H)-C(tBu)=C^{b}*H*$(P^{a}-C^{b})$*][*OSO_2CF_3*]·*$^{1}/_{2}$ C_6H_6 (**4**): Compound **3a** (0.35 g, 0.46 mmol) and $CF_3SO_3SiMe_3$ (0.36 ml, 9.1 mmol) were stirred in toluene (20 ml) for 96 h at 80°C. After removing the volatiles, a colourless solid remained. Attempts to recrystallise it from toluene or a mixture of CH_2Cl_2/Et_2O or THF/pentane failed, but dissolving in hot benzene gave, on cooling to room temperature, colourless crystals of **4** (0.31 g, 59%); mp > 105°C (dec.). − $C_{26}H_{34}F_3N_2O_3P_2S$ (573.58): calcd. C 54.4, H 5.97, N 4.88; found C 56.5, H 6.03, N 4.53. − ^{1}H NMR ($CDCl_3$): δ = 0.82 [t, Me, $^{4}J(^{1}H\text{-}^{31}P)$ ′ = 7.1 Hz], 1.39 [s, *t*Bu], 2.92 [s, very broad, CH_2], 5.04 [d, NH, $^{4}J(^{1}H\text{-}^{31}P)$ = 10.5 Hz], 7.35 [s, C_6H_6], 7.54−7.66 [Ph, 10 H], 8.19 overlapping dd, CH, $J(^{1}H\text{-}^{31}P)$ = 29.0 Hz]. − ^{31}P NMR ($CDCl_3$): δ = 82.3 [d, λ^3P, $^{1}J(^{31}P\text{-}^{31}P)$ = 304.9 Hz], 10.6 [d, λ^4P, $^{1}J(^{31}P\text{-}^{31}P)$ = 304.9 Hz. − ^{13}C NMR ($CDCl_3$): δ = 14.5 [s, Me], 28.6 [s, $C(CH_3)_3$], 37.8 [d, $C(CH_3)_3$, $^{3}J(^{13}C\text{-}^{31}P)$ = 10.7 Hz], 43 [s, broad CH_2], 65.0 [d, CH $^{2}J(^{13}C\text{-}^{31}P)$ = 68.0 Hz], CF_3SO_3 signal not identified, 120.1 [d, *ipso* C, $^{2}J(^{13}C\text{-}^{31}P)$ = 70.8 Hz], 124.3 [d, *ipso* C, $^{2}J(^{13}C\text{-}^{31}P)$ = 76.6 Hz], 128.3 [s, C_6H_6], 130.0 [dd, *o*-C, $J(^{13}C\text{-}^{31}P)$ = 12.0 and 4.6 Hz], 132.2 [dd, *o*-C, $J(^{13}C\text{-}^{31}P)$ = 8.0 and 4.5 Hz], 133.1 [s, Ph], 133.2 [s, Ph], 133.5 [s, Ph], 133.9 [s, Ph], 184.0 [t, CN, $J(^{13}C\text{-}^{31}P)$ = 15.0 Hz].

*Preparation of trans-***5a**: The diazadiphosphetidine **3a** (0.47 g, 0.61 mmol) was suspended in toluene (20 ml) and Cu_2I_2 (0.12 g, 0.31 mmol) was added. The reaction mixture was heated until **3a** had completely dissolved, then stirred for 12 h at room temperature, whereafter a very fine precipitate had formed. Further toluene (15 ml) was added. The mixture was heated under reflux until most of the precipitate had dissolved. Hot filtration and cooling the filtrate to room temperature gave colourless crystals of **5b** (0.1 g, 14%). Removing ca. 2/3 of the solvent from the mother liquor and cooling at −20°C gave colourless crystals of **5a** (0.31 g, 53%); mp 175°C (dec.). − $C_{51}H_{68}CuIN_4P_4$ (1051.48): calcd. (**5a** + 1 molecule of toluene) C 58.3, H 6.52, N 5.33; found C 57.2, H 6.09, N 5.17. − MS; *m/z* (%): 958 (0.1) $[M]^+$, 831 (0.3) $[M - I]^+$, 574 (0.6) $[M - Et_2NPNC(tBu)=CHPPh_2]^+$, 511 (2.5) $[M - Et_2NPNC(tBu)=CHPPh_2 - Cu]^+$, 384 (35) $[Et_2NPNC(tBu)=CHPPh_2]^+$. − ^{1}H NMR ($CDCl_3$): δ = 0.04 [s, CH_3 coord., 3 H], 0.82 [s, CH_3 coord., 3 H], 1.20 [t, CH_3 coord., 6 H, $^{4}J(^{1}H\text{-}^{31}P)$ = 7.0 Hz], 1.25 [s, *t*Bu, 18 H], 2.45 [s, broad, CH_2 coord. 3 H], 2.95 [s, broad, CH_2 coord., 3 H], 3.69 [m, CH_2 uncoord., 3 H], 5.73 [s, broad, CH], 7.17−7.43 [mult. multiplets, Ph, 8 H, PhMe], 7.69 [t, *o*-Ph, 2 H, $^{2}J(^{1}H\text{-}^{31}P)$ = 8.3 Hz]. − ^{31}P NMR ($CDCl_3$): δ = − 24.9 [s, very broad, PPh_2], 142.6 [s, very broad, ring P coord.], 172.2 [s, ring P uncoord.]. − ^{13}C NMR ($CDCl_3$): δ = 11.3 and 12.5 [s, CH_3 coord.], 14.8 [s, CH_3 uncoord.], 30.6 [d, $C(CH_3)_3$, $^{4}J(^{13}C\text{-}^{31}P)$ = 8.4 Hz], 35.6 [s, CH_2], 38.7 [s, CH_2], 40.6 [s, $C(CH_3)_3$,], 105.9 [d, CH, $^{3}J(^{13}C\text{-}^{31}P)$ = 33.0 Hz], 128.0 [d, Ph, $J(^{13}C\text{-}^{31}P)$ = 36.2 Hz], 128.2 [s, Ph], 129.3 [d, Ph, $J(^{13}C\text{-}^{31}P)$ = 41.3 Hz], 131.8 [s, Ph], 133.3 [d, Ph, $J(^{13}C\text{-}^{31}P)$ = 17.0 Hz], 135.5 [dd, Ph, overlayed], 139.7 [d, Ph, $J(^{13}C\text{-}^{31}P)$ = 39.2 Hz], 163.1 [s, CN].

Preparation of **5b**: Cu_2I_2 (0.25 g, 0.65 mmol) was added to a solution of **3a** (0.5 g, 0.325 mmol) in hot (105°C) toluene (100 ml). The mixture was stirred for 15 h, whereafter the greyish Cu_2I_2 had disappeared and a white precipitate had formed. After 12 h at room temperature, the supernatant liquor was filtered off and the residue dried in vacuo to give **5b** (0.7 g, 94%), as a colourless, extremely insoluble, white powder; mp 260°C (dec.). − $C_{47.5}H_{64}Cu_2I_2N_4P_4$ (1195.85): calcd. C 56.8, H 6.42, N 5.57; found C 42.4, H 5.32, N 4.46. − MS (300°C); *m/z* (%): 831 (5) $[M - 2\,I - Cu]^+$, 574 (13) $[M - Et_2NPNC(tBu)=CHPPh_2]^+$; (250°C); *m/z* (%): 559 (22) $[M_{1/2} - Me]^+$, 480 (3) $[M_{1/2} - Et - Cu]^+$. − ^{1}H NMR ($CDCl_3$): δ = 0.46 [s, broad, CH_3], 0.69 [s, broad, CH_3], 1.53 [s, *t*Bu], 2.45 and 3.72 [m, very broad, NCH_2], 5.91 [t, CH, $^{2}J(^{1}H\text{-}^{31}P)$ = 3.82 Hz], 7.34−7.37 [m, Ph, 3 H], 7.40−7.42 [m, Ph, 3 H], 7.57−7.7.64 [m, Ph, 2 H], 7.75−7.82 [m, Ph, 2 H]. − ^{31}P NMR ($CDCl_3$): δ = −38.0 [d, PPh_2, $J(^{31}P\text{-}^{31}P)$ = 292.8 Hz], 131.3 [d, PN, $J(^{31}P\text{-}^{31}P)$ = 292.8 Hz]. − ^{13}C NMR ($CDCl_3$): δ = 11.2 [s, CH_3], 31.0 [d, $C(CH_3)_3$, $^{4}J(^{13}C\text{-}^{31}P)$ = 8.7 Hz], 39.3 [s, CH_2], $C(CH_3)_3$ signal not identified, 106.6 [d, CH, $^{3}J(^{13}C\text{-}^{31}P)$ = 33.2 Hz], 126.3−133.9 [phenyl C], 163.0 [s, CN].

Preparation of [$Me_2NP^{a}N(R)P(NMe_2)N^{c}R$]$(P^{a}-N^{c})$ [**7**: R = C(*t*Bu)=C(H)$SiMe_3$]: Me_3SnNMe_2 (0.13 g, 0.64 mmol) was added to a solution of [ClP^{a}N(R)P(Cl)N^{b}R$(P^{a}-N^{b})$][1] (0.15 g, 0.32 mmol) in CH_2Cl_2 (5 ml). The reaction mixture was stirred for 12 h at room temperature, whereafter a white solid had crystallised. All volatiles were removed and the resulting residue was extracted with hot toluene (10 ml). The hot mixture was filtered. Cooling the filtrate to −15°C gave colourless crystals of **7** (0.11 g, 70%); mp 170°C (dec.). − MS; *m/z* (%): 488 (5) $[M_2]^+$, 473 (1) $[M_2 - Me]^+$, 444 (9) $[M_2 - NMe_2]^+$, 415 (2.5) $[M_2 - SiMe_3]^+$, 244 (75) $[M]^+$, 229 (11) $[M - Me]^+$, 187 (72) $[M - tBu]^+$. − ^{1}H NMR (C_6D_6): δ = 0.16 [s,

Table 4. Crystallographic data for compounds **3a** and **5a**

Compounds	**3a**	**5a**
Empirical formula	$C_{44}H_{60}N_4P_4$	$C_{51}H_{68}CuIN_4P_4$
Formula weight	768.84	1051.41
Temperature [K]	293(2)	293(2)
Radiation, λ [Å]	Mo-K_α, 0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a [Å]	8.568(2)	11.021(2)
b [Å]	10.504(3)	12.114(2).
c [Å]	13.324(5)	21.816(3).
α [°]	110.59(3)	74.28(1)
β [°]	92.54(2)	76.15(1)
γ [°]	98.30(2)	72.86(1)
V [Å^3]	1104.9(6)	2638.6(7)
Z	1	2
$D_{calcd.}$ [g cm^{-3}]	1.16	1.323
μ [mm^{-1}]	0.21	1.16
F[000]	412	1088
Crystal size [mm]	0.4 × 0.2 × 0.1	0.3 × 0.2 × 0.2
θ min and max [°]	2 to 25	2 to 25
Dataset	0/10; −12/12; −15/15	0/13; −13/14; −24/25
Tot., uniq. data	3880, 3880	9249, 9249
Reflections with $I > 2\sigma(I)$	2609	4685
Structure solution	Direct methods	Direct methods
Refinement method	Full-matrix least squares on all F^2	Full-matrix least squares on all F^2
Parameters	235	520
Final R indices $I > 2\sigma(I)$	$R1$ = 0.051, $wR2$ = 0.099	$R1$ = 0.073, $wR2$ = 0.150
R indices (all data)	$R1$ = 0.091, $wR2$ = 0.115	$R1$ = 0.160, $wR2$ = 0.192
Largest diff. peak and hole [e/Å^3]	0.23 and −0.20	1.05 and −0.53
Abs.correction from ψ scans	not applied	T_{max} = 1.00, T_{min} = 0.91
Max. shift/error	0.005	0.002

$SiMe_3$], 1.19 [s, *t*Bu], 2.75 [d/t, NMe_2], 4.36 [s, CH]. − ^{31}P NMR (C_6D_6): δ = 187. − ^{13}C NMR (C_6D_6): δ = 2.0 [s, $SiMe_3$], 30.6 [s, $C(CH_3)_3$], 37.7 [t, NMe_2, $^2J(^{13}C\text{-}^1H)$ = 9.1 Hz], 39.8 [s, $C(CH_3)_3$], 100.4 [s, CH], 160.8 [s, CN].

Preparation of $N^aC(tBu)C(H)C^eP^aN(Me)(CH_2)_2N^cMe(N^a{-}P^a)(C^c{-}N^c)$ (**8**): A mixture of [$ClP^aN(R)P(Cl)N^bR(P^a{-}N^b)$] (**6**)[1] (0.71 g, 1.5 mmol) and [$=C^aN(Me)(CH_2)_2N^aMe(C^a{-}N^a)]_2$[3] (0.30 g, 1.5 mmol) in toluene (15 ml) was stirred for 60 h at 50°C. Removal of the solvent and distillation (130°C, 10^{-2} Torr) of the residue in vacuo gave the yellow oil **8** (0.22 g, 32%), which slowly crystallised; mp 58−60°C. − MS; *m*/*z* (%): 225 (80) $[M]^+$, 210 (67) $[M - Me]^+$, 197 (10) $[M - CH_2CH_2]^+$, 182 (90) $[M - MeNCH_2]^+$. −^{1}H NMR ($CDCl_3$): δ = 1.36 [s, *t*Bu], 2.08 [m, CH_2], δ 2.30 [m, CH_2], 2.37 [m, CH_2], 2.41 [d, NMe $^4J(^1H\text{-}^{31}P)$ = 2.7 Hz], 2.58 [d, NCH_3 $^3J(^1H\text{-}^{31}P)$ = 12.9 Hz], 3.06 [ddd, CH_2], 5.83 [d, CH, $^3J(^1H\text{-}^{31}P)$ = 17.1 Hz]. − ^{31}P NMR ($CDCl_3$): δ = 98.9 [s]. − ^{13}C NMR ($CDCl_3$): δ = 29.2 [d, $C(CH_3)_3$, $^4J(^{13}C\text{-}^{31}P)$ = 2.3 Hz], 38.4 [d, $C(CH_3)_3$, $^3J(^{13}C\text{-}^{31}P)$ = 7.5 Hz], 40.6 [s, NCH_3], 42.9 [d, NCH_3 $^2J(^{13}C\text{-}^{31}P)$ = 38.5 Hz], 51.5 [d, NCH_2, $^2J(^{13}C\text{-}^{31}P)$ = 3.1 Hz], 53.7 [s, NCH_2], 98.5 [d, CH, $^2J(^{13}C\text{-}^{31}P)$ = 36.0 Hz], 183.2 [d, CP, $^1J(^{13}C\text{-}^{31}P)$ = 4.1 Hz], 185.8 [s, CN].

Preparation of $N^aC(tBu)C(H)C^eP^a(S)N(Me)(CH_2)_2N^cMe(N^a{-}P^a)(C^c{-}N^c)$ (**9**): Sulfur (0.02 g, 0.63 mmol) was added to a solution of **8** (0.1 g, 0.44 mmol) in toluene (5 ml) and the mixture was stirred for 15 h, then filtered and the solvent removed from the filtrate in vacuo. Recrystallisation of the residue from Et_2O gave yellow crystals of **9** (0.07 g, 70%); mp 126°C (dec.). − HR-MS: calcd. for $C_{11}H_{20}N_3PS$ 257.1116; found 257.1118. − MS; *m*/*z* (%): 257 (100) $[M]^+$, 242 (15) $[M - Me]^+$, 224 (27) $[M - HS]^+$, 214 (65) $[M - MeNCH_2]^+$, 201 (15) $[M - Me_2C{=}CH_2]^+$. − ^{1}H NMR ($CDCl_3$): δ = 1.21 [s, *t*Bu], 2.05 [m, CH_2], 2.15 [s, NMe], 2.27 and 2.35 [m, CH_2], 2.56 [d, NMe, $^3J(^1H\text{-}^{31}P)$ = 12.0 Hz], 4.33 [ddd, CH_2], 5.26 [d, CH, $^3J(^1H\text{-}^{31}P)$ = 30.0 Hz]. − ^{31}P NMR ($CDCl_3$): δ = 83.6 [s]. − ^{13}C NMR ($CDCl_3$): δ = 28.2 [d, $C(CH_3)_3$], 35.3 [s, NCH_3], 35.3 [d, $C(CH_3)_3$, $^4J(^{13}C\text{-}^{31}P)$ = 25.0 Hz], 39.1 [d, NCH_3, $^2J(^{13}C\text{-}^{31}P)$ = 5.7 Hz], 46.8 [s, NCH_2], 50.9 [d, NCH_2, $^2J(^{13}C\text{-}^{31}P)$ = 12.4 Hz], 94.1 [d, CH, $^2J(^{13}C\text{-}^{31}P)$ = 46.4 Hz], 166.9 [d, CP, $^1J(^{13}C\text{-}^{31}P)$ = 94.4 Hz], 193.8 [d, CN, $^2J(^{13}C\text{-}^{31}P)$ = 7.5 Hz].

X-ray Structure Determination of the Diazadiphosphetidines **3a** *and* **5a**[37]: Data were collected with an Enraf-Nonius CAD4 diffractometer using monochromatic Mo-K_α radiation and single crystals sealed under argon in Lindemann capillaries. Cell dimensions were calculated from the setting angles for 25 reflections with 9° < θ < 13°. Intensities were measured by an ω-2θ scan. Corrections were made for Lorentz and polarisation effects and in the case of **5a** for absorption. There was no crystal decay as measured by two standard reflections. Positions of non-hydrogen atoms were derived by direct methods using SHELXS-86[38] and refined on F^2 with anisotropic thermal parameters by full-matrix least squares using SHELXL-93[39]. Further details are in Table 4.

☆ Dedicated to Prof. Dr. Dr. h. c. mult. *Heinrich Nöth* on the occasion of his 70th birthday as a mark of respect and (by M. F. L.) of friendship.

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[37] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101392. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax (internat.): +44(0)1223/336033; e-mail: deposit@ccdc.cam.ac.uk].
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