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Formation of a diazadiphosphetidine from the reactions of a bis(aminosilyl) ether with PCl_3: crystal structure of *cis*-$[(Bu^tNH)PNBu^t]_2$

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Reaction of $O[SiMe_2N(Bu^t)H]_2$ **1** with PCl_3 in 1 : 1 molar ratio in hexane in presence of NEt_3 gave the cyclic four-membered diazadiphosphetidine *cis*-$[(Bu^tNH)PNBu^t]_2$ **2** instead of the expected six-membered silazoxyphosphine indicating cleavage of the Si–N bond. A crystal structure analysis of **2** showed that the NH hydrogens of the Bu^tNH groups are in an *endo-endo* orientation above the $(PN)_2$ ring which is in contrast to the *exo-endo* orientation for the known structure of its disulfide.

Bis(aminosilyl) ethers of the type $O[SiMe_2N(R)H]_2$ (R = Me, Et or Bu^t) are excellent starting materials for the synthesis of novel inorganic heterocycles as well as metallacycles having Si, N, O and another heteroelement as part of the ring framework. Wannagat and co-workers carried out detailed reactions of $O[SiMe_2N(R)H]_2$ (R = Me or Et) with a variety of main-group halides such as $PPhCl_2$, $PEtCl_2$,[1] $PMeCl_2$,[2] $SnCl_4$, $GeCl_4$, $AsCl_3$, $SiMe(CH_2{=}CH)Cl_2$, $SiCl_4$, $SiBr_4$,[3] and $BeCl_2$[4] in the presence of NEt_3 as HCl scavenger or after dilithiation using *n*-butyllithium. The reactions invariably led to the formation of six-membered heterocycles of the type $L_nMSi_2N_2O$ [L_nM = PhP, EtP, MeP, Cl_2Sn, Cl_2Ge, ClAs, $Me(CH_2{=}CH)Si$, Cl_2Si, Br_2Si or Be]. Reactions with $TiCl_4$ and $ZrCl_4$ also gave similar metallacycles which were spirocyclic in nature.[5] Recently Roesky and co-workers carried out reactions of $O[SiMe_2N(Bu^t)H]_2$ **1** after dilithiation with main-group and transition metal halides in low oxidation states to synthesize novel six-membered silazoxy metallacycles with Te^{II}, Sn^{II} and Ge^{II}[6] as the heteroelement as well as twelve-membered silazoxy metallacycles with Zn^{II}, Co^{II},[7] Fe^{II}, Mn^{II}, Ni^{II} or Cr^{II}[6] wherein the metals, were stabilized in low co-ordination and oxidation states. A variety of reactions have also been carried out on $P^{III}Si_2N_2O$ ring compounds (Me and Ph substituents on P, Me on N) leading to oxidation of the phosphorus(III) site to P^V while retaining the six-membered ring structure.[2] Similar silazoxy heterocycles with P^V as part of the ring framework were also prepared by reactions of phenoxy thiophosphoryl dihydrazide and phenoxy phosphoryl dihydrazide with tetraalkyl-1,3- dichlorodisiloxanes and structurally characterized.[8]

Reactions of $O[SiMe_2N(R)H]_2$ with PCl_3 have been reported briefly as leading to only polymeric products which were not properly identified.[1] In our attempts to make silazoxyphosphines with varying ring sizes and substituents on silicon, nitrogen and phosphorus, we observed for the first time that instead of cyclization to form a six-membered silazoxyphosphine, $O[SiMe_2N(Bu^t)H]_2$ cleaves at the Si–N bonds and forms the diazadiphosphetidine *cis*-$[(Bu^tNH)PNBu^t]_2$ **2**. We report herein the details of this unusual reaction as well as the crystal structure of **2**.

Experimental

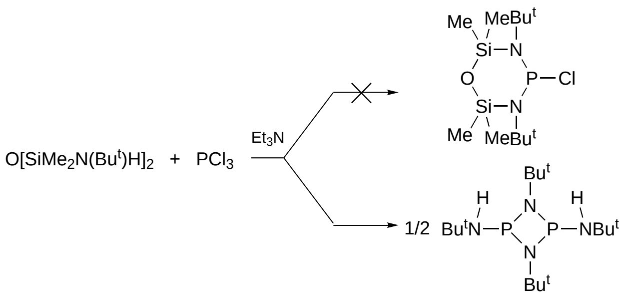
All manipulations were carried out using standard Schlenk techniques using a vacuum line in an atmosphere of dry nitrogen. The compound $O[SiMe_2N(Bu^t)H]_2$ **1** was prepared according to the reported procedure,[7] PCl_3 (Aldrich) was distilled prior to use and hexane and triethylamine were distilled and dried by standard procedures. In a typical reaction **1** (1.22 g, 4.4 mmol) was first dissolved in hexane (30 cm^3), the solution cooled to 0 °C and with vigorous stirring, PCl_3 (0.62 g, 4.5 mmol) added slowly using a syringe. After adding triethylamine (1.50 cm^3), the mixture was brought to room temperature over a period of 15 min and then refluxed for 36 h whereupon a white solid (identified as $NEt_3{\cdot}HCl$) was observed. This was filtered off using a frit under nitrogen and the filtrate concentrated *in vacuo* to yield a semisolid mass which was sensitive to air and moisture. On redissolving this in hexane and keeping it at 0 °C for 24 h, colourless crystals of *cis*-$[(Bu^tNH)PNBu^t]_2$ **2** were obtained (0.43 g, 56%), m.p. 143 °C (from hexane) (Found: C, 55.1; H, 11.2. $C_{16}H_{38}N_4P_2$ requires C, 55.2; H, 10.9%); $\tilde{\nu}_{max}/cm^{-1}$ 3320w, 2915s, 1460s, 1362s, 1220s, 1040m, 1030m, 998s, 915w, 870s, 820m, 790m and 735m (Nujol); $\delta_H(C_6D_6)$ 1.28 (18 H, s, CH_3), 1.53 (18 H, s, CH_3) and 2.60 (2 H, br s, NH); $\delta_P(C_6D_6)$ 89.1 (s). These data were found to agree with the reported values for **2**.[9–11]

Crystallography

Single crystals of *cis*-$[(Bu^tNH)PNBu^t]_2$ **2** suitable for X-ray studies were obtained by slow crystallization under nitrogen from hexane at 0 °C.

Crystal data and data collection parameters. $C_{16}H_{38}N_4P_2$, $M = 348.44$, monoclinic, space group Pc, $a = 9.6654(5)$, $b = 5.9212(3)$, $c = 18.9757(9)$ Å, $\beta = 100.68(10)°$, $U = 1067.18(9)$ Å^3, $T = 213$ K, graphite-monochromated Mo-Kα radiation, $\lambda = 0.710\,73$ Å, $Z = 2$, $D_c = 1.084$ Mg m^{-3}, $F(000) = 384$, colourless crystals with dimensions 0.35 × 0.20 × 0.15 mm, μ(Mo-Kα) = 0.207 mm^{-1}, SADABS absorption correction,[12] maximum and minimum transmission 0.962 and 0.783, Siemens SMART diffractometer with a CCD detector at −54 °C, θ range for data collection 2.14–25.00°, limiting indices $-12 \leqslant h \leqslant 12$, $-6 \leqslant k \leqslant 7$, $-25 \leqslant l \leqslant 24$, reflections collected 10 309, independent reflections 3102 ($R_{int} = 0.0297$). The data were acquired using Siemens SMART software and processed on a SGI-Indy/Indigo 2 workstation by using the SAINT software.[13]

Structure solution and refinement. The structure was solved by direct methods using the SHELXS 90[14] program and refined by full-matrix least squares on F^2 using SHELXL 93, incorporated in SHELXTL-PC V 5.03.[15] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference electron-density maps and included in the refinement process in an isotropic manner. The final R indices were



Scheme 1

[$I > 2\sigma(I)$]; $R(F) = 0.047$ and $wR(F^2) = 0.113$, parameters refined = 188, goodness of fit = 1.06.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/494.

Results and Discussion

In our attempts to make P$^{\text{III}}$-containing silazoxy heterocycles by the reactions of compound **1** with $PPhCl_2$ in presence of a tertiary amine or after lithiation we observed a general hesitancy for the reaction to proceed. A similar trend in reactivity was observed when transamination was attempted using $P(NR_2)_3$ (R = Me or Et) with **1**. However, a reaction of PCl_3 with **1** in the presence of NEt_3 was found to proceed slowly on refluxing in hexane. Instead of the expected silazoxy phosphine, the reaction gave exclusively a diazadiphosphetidine **2** (Scheme 1).

All reactions reported so far of O[SiMe$_2$N(R)H]$_2$ and MeN-[SiMe$_2$N(R)H]$_2$ as such or after metallation, with main-group and transition-metal halides, have resulted in the formation of six- or twelve-membered heterocycles indicating the stability of the Si–N bond during such reactions. Reactions of phosphorus(III) dihalides like $PRCl_2$ (R = Me, Et or Ph) with O[SiMe$_2$N(R)H]$_2$ and MeN[SiMe$_2$N(R)H]$_2$ (R = Me or Et) are reported to give silazoxy and silaza phosphines which have been characterized by spectral and analytical techniques.[1,2] The fact that O[SiMe$_2$N(Bu^t)H]$_2$ **1** behaves differently may be related to a variety of factors. The bulkiness of the tertiary butyl group possibly prevents attack of the PCl_2 moiety of the HN(Bu^t)-SiMe$_2$OMe$_2$Si(Bu^t)NPCl$_2$ unit formed in the first step of the reaction on the other amino hydrogen. This may lead to the formation of ClSiMe$_2$OMe$_2$Si(Bu^t)NP(Cl)N(Bu^t)H which may further cleave at the Si–N bond leading to Bu^{t}N=PNHBu^t. Dimerization of the latter can lead to the diazadiphosphetidine **2**. It is noteworthy that isolation of mono- and di-chloro analogues of the diazadiphosphetidines[16–18] were not observed in this reaction.

Reactions leading to cleavage of Si–N bonds with phosphorus chlorides are well documented.[19] This being the first step followed by N–H cleavage to precipitate amine hydrochloride may also bring about the formation of **2**. This is further assisted by the fact that the P–Cl bonds in PCl_3 are comparatively weaker (326 kJ mol^{-1}) than a standard Si–Cl bond (381 kJ mol^{-1}).[20] In addition, the inherent stability of the diazadiphosphetidine **2** over the sterically crowded silazoxy phosphine also might contribute to the reaction proceeding in this way, similar to the observation of Markovskii *et al.*[10] where **2** is also formed in the reaction of (2,2,6,6-tetramethylpiperidino)-phosphorus dichloride with *tert*-butylamine.

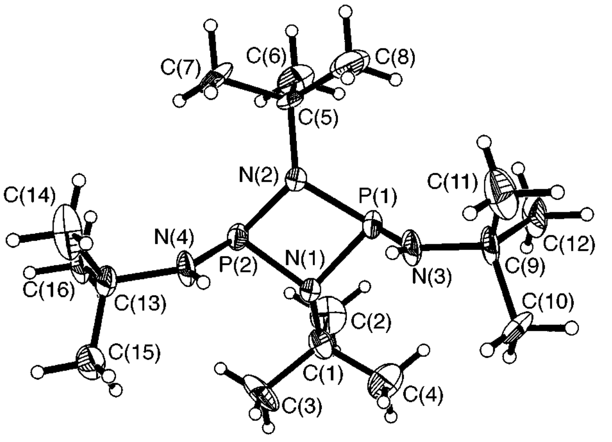
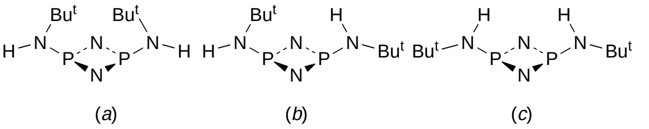


Fig. 1 Molecular structure of *cis*-[(Bu^{t}NH)PNBu^t]$_2$ **2** showing the atom numbering scheme



(*a*) (*b*) (*c*)

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

P(1)–N(3)	1.619(6)	P(2)–N(1)	1.725(5)
P(1)–N(2)	1.743(5)	N(1)–C(1)	1.463(9)
P(1)–N(1)	1.763(6)	N(2)–C(5)	1.495(8)
P(1)–P(2)	2.616(7)	N(3)–C(9)	1.493(8)
P(2)–N(2)	1.702(6)	N(4)–C(13)	1.489(8)
P(2)–N(4)	1.710(5)		
N(3)–P(1)–N(2)	105.3(3)	N(4)–P(2)–P(1)	118.2(2)
N(3)–P(1)–N(1)	104.7(3)	N(1)–P(2)–P(1)	42.0(2)
N(2)–P(1)–N(1)	79.6(2)	C(1)–N(1)–P(2)	126.9(5)
N(3)–P(1)–P(2)	117.5(2)	C(1)–N(1)–P(1)	124.1(4)
N(2)–P(1)–P(2)	40.0(2)	P(2)–N(1)–P(1)	97.2(3)
N(1)–P(1)–P(2)	40.8(2)	C(5)–N(2)–P(2)	125.8(5)
N(2)–P(2)–N(4)	105.0(3)	C(5)–N(2)–P(1)	122.4(4)
N(2)–P(2)–N(1)	81.8(2)	P(2)–N(2)–P(1)	98.8(3)
N(4)–P(2)–N(1)	105.0(3)	C(9)–N(3)–P(1)	129.7(5)
N(2)–P(2)–P(1)	41.2(2)	C(13)–N(4)–P(2)	131.1(5)

Structure of *cis*-[(Bu^{t}NH)PNBu^t]$_2$

The compound *cis*-[(Bu^{t}NH)PNBu^t]$_2$ **2** was first prepared in 1963 by Holmes and Forstner[11] by the reaction of *tert*-butylamine with PCl_3. Although initially the molecule was thought to be Bu^{t}N=PNHBu^t, subsequent reports on the compound with a molecular weight determination and a single signal in the ^{31}P NMR spectrum confirmed the molecule as a diazadiphosphetidine existing as a pure configurational isomer.[9,10] While three different structural isomers are possible with respect to the orientation of the Bu^{t}NH groups on the $(PN)_2$ ring, namely the NH hydrogens in the *exo-exo* (*a*), *exo-endo* (*b*) and *endo-endo* (*c*) orientations, the crystal structure shows that the orientation (*c*) is preferred. It is noteworthy that this was the structure predicted by Norman and co-workers[9] in the solution phase based on $^2J_{\mathrm{PNH}}$ values from ^{31}P NMR data measured at various temperatures. Fig. 1 shows the molecular structure of compound **2** with the atom numbering scheme. Selected bond distances and angles are given in Table 1.

In contrast, the crystal structure of the disulfide of the diazadiphosphetidine *cis*-[(Bu^{t}NH)P(S)NBu^t]$_2$[9] shows the *exo-endo* orientation (*b*). A similar orientation was observed for the phosphorus(III) diazadiphosphetidine [(PhNH)P$_2$(NPh)$_2$]$_2$-NPh.[21] The *endo-endo* orientation is similar to the orientation of the N(Me) groups observed in the case of *cis*-[(Ph$_2$P)N(Me)PNBu^t]$_2$.[22] The crystal structure of **2** also provides data for an interesting comparison of the P–N ring bond distances of phosphorus-(III) and -(V) 1,3,2,4-diazadiphosphetidines. It is generally observed that these distances in phosphorous(III) diazadiphosphetidines are comparatively longer than those of phosphorous(V) diazadiphosphetidines.[23–25] Muir[16] while comparing the structures of $(Bu^tNPCl)_2$ (average ring P–N distance 1.689 Å) and $[Bu^tNP(O)Cl]_2$ (average ring P–N distance 1.661 Å) have proposed that a possible reason for this can be due to a lesser delocalization of the nitrogen lone pairs on to the phosphorus atoms in the phosphorous(III) heterocycles. On comparing the structure of **2** with that of *cis*-$[(Bu^tNH)P(S)NBu^t]_2$[9] we observe that the average ring P–N distance in the former is 1.733 Å while that of latter is 1.685 Å. A similar variation is observed in the cases of $[(PhNH)PNPh]_3$[26] (average ring P–N distance 1.722 Å) and $[(PhNH)P(S)NPh]_2$[27] (average ring P–N distance 1.698 Å).

In conclusion, cleavage of $O[SiMe_2N(Bu^t)H]_2$ at the Si–N bond on reaction with PCl_3 is observed instead of substitution of the NH hydrogen. The diazadiphosphetidine **2** formed is characterized by X-ray structural analysis to have the NH groups of the Bu^tNH moiety in an *endo-endo* orientation above the $(PN)_2$ ring as predicted from solution studies. The method offers a new synthetic route to a variety of diazadiphosphetidines and indicates the need for a relook into the reactions of silazoxy and silaza diamines with transition- and main-group metal halides. Further work in this regard is currently underway.

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