DALTON

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

N. Dastagiri Reddy,[a] **Anil J. Elias** *,[a] **and Ashwani Vij**[b]

[a] *Department of Chemistry, Indian Institute of Technology, Kanpur, 208 016, UP, India*
[b] *Single Crystal Diffraction Laboratory, University of Idaho, Moscow, Idaho 83843, USA*

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

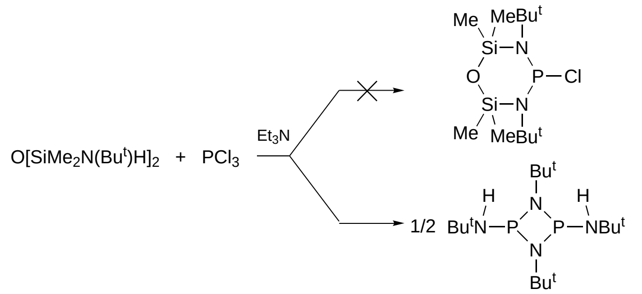
All manipulations were carried out using standard Schlenk techniques using a vacuum line in an atmosphere of dry nitrogen. The compound $O[SiMe_2N(Bu^t)H]_2$ **1** was prepared according to the reported procedure,[7] PCl_3 (Aldrich) was distilled prior to use and hexane and triethylamine were distilled 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 $-12 \le h \le 12$, $-6 \le k \le 7$, $-25 \le l \le 24$, 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^{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.

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 $^2J_{PNH}$ 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.

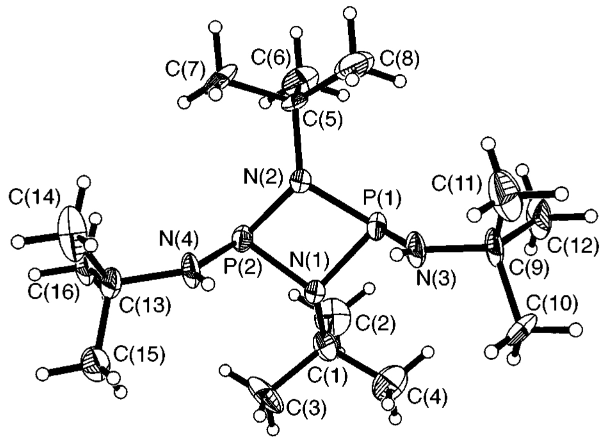
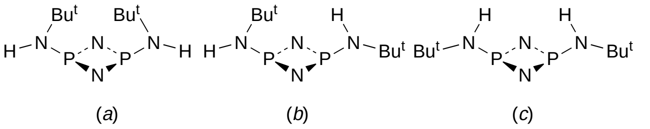


Fig. 1 Molecular structure of *cis*-[(Bu^{t}NH)PNBu^t]$_2$ **2** showing the atom numbering scheme



(*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)

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.

Acknowledgements

A. J. E. thanks the Department of Science and Technology, India, (DST) for financial assistance for this work under the SERC young scientist scheme (SR/OY/C-03/94). N. D. R. thanks University Grants Commission (UGC), India for a research fellowship.

References

1 U. Wannagat, K. Giesen and F. Rabet, *Z. Anorg. Allg. Chem.*, 1971, **382**, 195.

2 U. Wannagat, K.-P. Giesen and H.-H. Falius, *Monatsh. Chem.*, 1973, **104**, 1444.

3 U. Wannagat and F. Rabet, *Inorg. Nucl. Chem. Lett.*, 1970, **6**, 155.

4 D. J. Brauer, H. Bürger, H. H. Moretto, U. Wannagat and K. Wiegel, *J. Organomet. Chem.*, 1979, **170**, 161.

5 H. Bürger and K. Wiegel, *Z. Anorg. Allg. Chem.*, 1976, **419**, 157; *J. Organomet. Chem.*, 1977, **124**, 279; *Z. Anorg. Allg. Chem.*, 1976, **426**, 301.

6 A. J. Elias, H. W. Roesky, W. T. Robinson and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1993, 495.

7 A. J. Elias, H.-G. Schmidt, M. Noltemeyer and H. W. Roesky, *Eur. J. Solid State Inorg. Chem.*, 1992, **29**, 23.

8 U. Engelhardt and T. Bünger, *Z. Naturforsch, Teil B*, 1979, **34**, 1107; *Inorg. Nucl. Chem. Lett.*, 1978, **14**, 21; U. Engelhardt, T. Bünger and B. Stromburg, *Acta Crystallogr., Sect B*, 1982, **38**, 1173.

9 T. G. Hill, R. C. Haltiwanger, M. L. Thompson, S. A. Katz and A. D. Norman, *Inorg. Chem.*, 1994, **33**, 1770.

10 L. N. Markovskii, V. D. Romanenko, A. V. Ruba and L. A. Robenko, *Zh. Obshch. Khim.*, 1980, **50**, 337.

11 R. R. Holmes and J. A. Forstner, *Inorg. Chem.*, 1963, **2**, 380.

12 G. M. Sheldrick, SADABS, Siemens Analytical Instruments Division, Madison, WI, 1996.

13 SMART V 4.043 and SAINT V 4.035 softwares for CCD detector system, Siemens Analytical Instruments Division, Madison, WI, 1995.

14 G. M. Sheldrick, *Acta Crystallogr., Sect A*, 1990, **46**, 467.

15 (*a*) G. M. Sheldrick, SHELXL 93, Program for the refinement of crystal structure, University of Göttingen, 1993; (*b*) SHELXTL 5.03 (PC Version), Program library for structure solution and molecular graphics, Siemens Analytical Instruments Division, Madison, WI, 1995.

16 K. W. Muir, *J. Chem Soc., Dalton Trans.*, 1975, 259.

17 G. Bulloch and R. Keat, *J. Chem Soc., Dalton Trans.*, 1974, 2010.

18 R. Jefferson, J. F. Nixon, T. M. Painter, R. Keat and L. Stobbs, *J. Chem. Soc., Dalton Trans.*, 1973, 1414.

19 R. H. Nielson, in *Encyclopedia of Inorganic Chemistry*, ed. R. B. King, Wiley, Chichester, 1994, vol. 6, pp. 3181–3198; M. Shakir and H. W. Roesky, *Phosphorus Sulfur Silicon Relat. Elem.*, 1994, **93**, 13; R. A. Shaw, *Phosphorus Sulfur Relat. Elem.*, 1978, **4**, 101.

20 J. E. Huheey, E. A. Keiter and L. R. Keiter, *Inorganic Chemistry*, Harper Collins, New York, 4th edn., 1993, p. A 30.

21 M. L. Thompson, A. Tarassoli, R. C. Haltiwanger and A. D. Norman, *Inorg. Chem.*, 1987, **26**, 684.

22 D. A. Harvey, R. Keat, A. N. Keith, K. W. Muir and D. S. Rycroft, *Inorg. Chim. Acta*, 1979, **34**, L201.

23 W. A. Kamil, M. R. Bond, R. D. Willet and J. M. Shreeve, *Inorg. Chem.*, 1987, **26**, 2879.

24 S. S. Kumaravel, S. S. Krishnamurthy, T. S. Cameron and A. Liden, *Inorg. Chem.*, 1988, **27**, 4546.

25 K. W. Muir, *Acta Crystallogr., Sect B*, 1977, **33**, 3586.

26 A. Tarassoli, M. L. Thompson and A. D. Norman, *Inorg. Chem.*, 1988, **27**, 3382.

27 C.-C. Chang, R. C. Haltiwanger, M. L. Thompson, H.-J. Chen and A. D. Norman, *Inorg. Chem.*, 1979, **18**, 1899.

Received 27*th January* 1997; *Paper* 7/00604G