Ln–dapda complexes do not exhibit this same property is not certain.

The four transition-metal ions Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} and the post-transition-metal ion Pb^{2+} all form strong complexes with dapda. Except for Pb^{2+}, which has a larger ionic radius, the other four all form dapda complexes that are stronger than dacda complexes. Inversion of the Irving–Williams series is also observed for the Ni^{2+} and Zn^{2+} complexes.[15] Both trends are consistent with the data obtained for the underivatized structural analogues 1,7-diaza-4,10,13-trioxacyclopentadecane (K21) and 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (K22). The compound K21 has a smaller size in which the two coordinating nitrogen atoms can relatively easily form a stable complex with any of the transition-metal ions without large compensation of the energy needed for conformational change for complexation.

The structures of Cu(II) complexes of 12-, 15-, and 18-membered diaza-crown-*N*,*N*′-diacetic acids have been discussed.[16] X-ray diffraction data are only reported for the 18-membered compound.[17] However, it is proposed that for the Cu^{II}–dapda complex the Cu(II) ion is contained inside the ring. This is consistent with very stable Cu^{II}–dapda complex formation.

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Registry No. dapda, 81963-61-3.

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Preparation of P–N–H and P–P Compounds from a Silylated Aminomethylenephosphine

Bei-Li Li and Robert H. Neilson*

Received April 29, 1985

Secondary amines react with the silylated aminomethylenephosphine $(Me_3Si)_2NP{=}CHSiMe_3$ (**1**) by a complex process involving Si–N bond cleavage as well as addition to the P=C bond. Thus, treatment of **1** with Et_2NH yields either the N–H phosphine $Me_3SiN(H)P(NEt_2)CH_2SiMe_3$ (**2**) or the unexpected P^V–P^{III} product $Me_3SiN{=}P(NEt_2)(CH_2SiMe_3)–P(CH_2SiMe_3)N(SiMe_3)_2$ (**3**), depending upon the reaction stoichiometry. In two separate experiments with mechanistic implications (a) **2** was prepared from the reaction of Et_2NH with $(Me_3Si)_2NP(NEt_2)CH_2SiMe_3$ (**1a**), the presumed intermediate in the Et_2NH/**1** reaction, and (b) **3** was prepared directly by addition of the N–H compound **2** to the methylenephosphine **1**. Compound **2** is smoothly oxidized by CCl_4 to the *P*-chlorophosphoranimine $Me_3SiN{=}P(Cl)(NEt_2)CH_2SiMe_3$ (**4**) or is deprotonated by *n*-BuLi. The ambident anion thus formed reacts with the chlorophosphines Ph_2PCl and $(Me_3Si)_2NP(Cl)CH_2SiMe_3$ to yield the P–P products $Me_3SiN{=}P(NEt_2)(CH_2SiMe_3)–PPh_2$ (**5**) and compound **3**, respectively.

Introduction

The chemistry of 2-coordinate, acyclic P^{III} compounds containing the P=C double bond, the methylenephosphines, is of considerable current interest.[1] Four major types of reactions of such compounds have been studied: (1) addition and cycloaddition reactions of the P=C bond, (2) complexation of transition metals to the phosphorus lone pair and/or the P–C π bond, (3) oxidation to the 3-coordinate P^V state, and (4) nucleophilic substitution at the 2-coordinate P^{III} center. Our recent studies,[2,3] in particular, have shown that methylenephosphines bearing the disilylamino group, e.g., $(Me_3Si)_2NP{=}CHSiMe_3$ (**1**),[4] actually exhibit all of these reaction pathways.

In addition, the Si–N bonds in compounds such as **1** are potentially reactive sites. The general lack of Si–N reactions in these 2-coordinate phosphines is rather surprising since many examples of silyl group rearrangement and/or elimination processes have been observed in 3- and 4-coordinate Si–N–P systems.[5] We report here, however, the observation of Si–N bond cleavage as part of a complex series of reactions between **1** and diethylamine. Some related preparative chemistry is also described.

Results and Discussion

The reactions of the 2-coordinate phosphines $(Me_3Si)_2NP{=}ESiMe_3$ (E = CH, N) with protic reagents generally occur either by simple 1,2-addition to the double bond[4] or by oxidative addition to the highly electrophilic phosphorus center.[6] Therefore, we expected to find one or both of these pathways operating in the reaction of **1** (E = CH) with secondary amines R_2NH (R = Et, *n*-Bu, *i*-Pr). A preliminary study of such reactions, however, in NMR-tube experiments, revealed an unexpected degree of complexity. The formation of the Si–N cleavage product Me_3SiNR_2 and mixtures of phosphorus-containing compounds was consistently observed. As a representative example, the reaction of **1** with Et_2NH was selected for more detailed study on a preparative scale.

In a typical experiment, Et_2NH was added to a CH_2Cl_2 solution of **1** at 0 °C with subsequent warming to room temperature. The

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(1) For example, see the following and references cited therein: (a) Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731. (b) van der Knaap, Th. A.; Klebach, Th. C.; Visser, F.; Bickelhaupt, F.; Ros, P.; Baerends, E. J.; Stam, C. H.; Konijn, M. *Tetrahedron* **1984**, *40*, 765. (c) Cowley, A. H.; Jones, R. A.; Lasch, J. G.; Norman, N. C.; Stewart, C. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Zhang, H.-M. *J. Am. Chem. Soc.* **1984**, *106*, 7015. (d) Xie, Z.-M.; Wisian-Neilson, P.; Neilson, R. H. *Organometallics* **1985**, *3*, 339.

(2) Li, B.-L.; Neilson, R. H. *Inorg. Chem.* **1984**, *23*, 3665.

(3) Ford, R. R.; Li, B.-L.; Neilson, R. H.; Thoma, R. J. *Inorg. Chem.* **1985**, *24*, 1993.

(4) Neilson, R. H. *Inorg. Chem.* **1981**, *20*, 1679.

(5) See, for example: (a) Ford, R. R.; Goodman, M. A.; Neilson, R. H.; Roy, A. K.; Wettermark, U. G.; Wisian-Neilson, P. *Inorg. Chem.* **1984**, *23*, 2063. (b) Morton, D. W.; Neilson, R. H. *Organometallics* **1982**, *1*, 289 and 623.

(6) Markovski, L. N.; Romanenko, V. D.; Ruban, A. V. *Phosphorus Sulfur* **1980**, *9*, 221.

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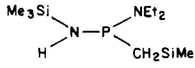
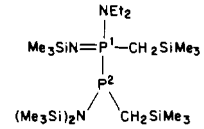
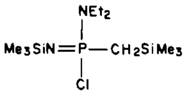
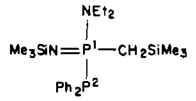
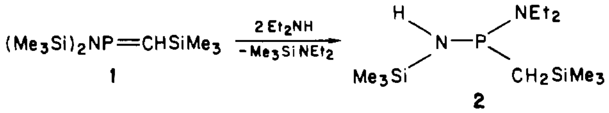
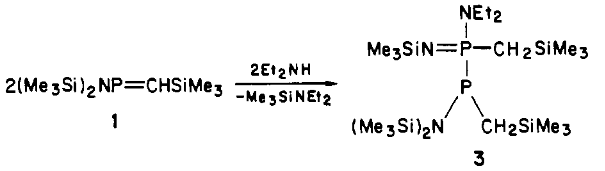
Table I. NMR Spectroscopic Data[a]

		^{1}H		^{13}C		^{31}P	
compd	signal	δ	J_{PH}[b]	δ	J_{PC}	δ	J_{PP}
 **2**	Me_3SiC	0.06	0.8	−0.06	5.5	68.5	
	Me_3SiN	0.11	0.8	1.32	5.5		
	PCH_2	0.88	1.8	24.69	25.6		
	$NCH_2\mathit{CH}_3$	1.03	(7.1)	15.41	5.5		
	$N\mathit{CH}_2CH_3$	2.90	8.6	41.16	16.5		
 **3**	$(Me_3Si)_2N$	0.07		4.63		26.9 (P^1)	
		0.18		5.85		38.0 (P^2)	
	Me_3SiN	0.15	2.4	3.86	3.6		290
	Me_3SiC	−0.03		0.00			
		0.03		0.53			
	PCH_2	0.9–1.3[c]		13–25[c]			
	$NCH_2\mathit{CH}_3$	0.93	(7.2)	14.80	1.8		
	$N\mathit{CH}_2CH_3$	2.7–3.1[c]		38.68	4.9, 6.0		
 **4**	Me_3SiC	0.09		−0.10	4.3	17.2	
	Me_3SiN	0.20		2.84	4.5		
	PCH_2	1.66	22.2	27.15	116.6		
		1.58	20.4				
	$NCH_2\mathit{CH}_3$	1.12	(7.2)	13.18	5.5		
	$N\mathit{CH}_2CH_3$	2.8–3.4[c]		38.97	3.1		
 **5**	Me_3SiC	−0.17	0.6	−0.19	3.9	17.1 (P^1)	
	Me_3SiN	0.06	0.6	2.76	4.9	−19.3 (P^2)	
	PCH_2	0.09–1.3[c]		27.13	116.2		209
	$NCH_2\mathit{CH}_3$	0.93	(7.2)	13.12	5.9		
	$N\mathit{CH}_2CH_3$	2.7–3.2[c]		38.95	2.9		
	Ph	7.2–7.9[c]		127–134[c]			

[a] Chemical shifts downfield from Me_4Si for ^{1}H and ^{13}C NMR spectra and from H_3PO_4 for ^{31}P NMR spectra; coupling constants in Hz. Solvents: ^{1}H and ^{31}P, CH_2Cl_2; ^{13}C, $CDCl_3$. [b] Values in parentheses are J_{HH}. [c] Complex multiplet.

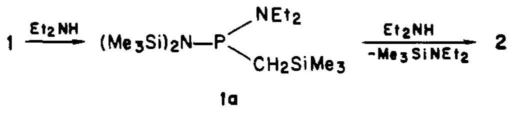
^{31}P NMR spectra of the reaction mixture showed that two major products (**2** and **3**) were formed in a ratio that depended upon the reaction stoichiometry (eq 1 and 2). Thus, from the reaction


(1)


(2)

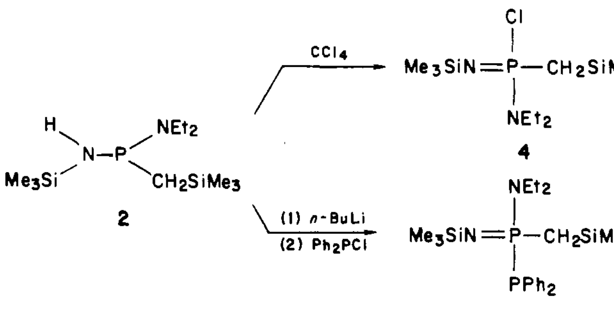
of **1** with 2 equiv of Et_2NH (eq 1), the N–H phosphine **2** was obtained in 59% yield by fractional distillation while the equimolar reaction (eq 2) afforded the unusual P^{III}–P^{V} product **3** in an isolated yield of 65%. In both cases, the byproduct Me_3SiNEt_2 was identified in the solvent fraction by NMR spectroscopy.

The structure of compound **2** was readily assigned on the basis of NMR (Table I), IR, and mass spectral data. Moreover, some reactions involving **2** provide chemical evidence for its structure as well as its mode of formation from **1**. Most likely, the production of **2** occurs via the intermediate formation of the 1,2-addition product **1a** (eq 3). Although **1a** was not detected by


(3)

^{31}P NMR among the reaction products, it is a stable compound (^{31}P NMR, δ 92) that has been prepared by an independent route.[7] Treatment of an authentic sample of **1a** with 1 equiv of Et_2NH in CH_2Cl_2 solution rapidly and cleanly gives the Si–N cleavage product **2** (81% isolated yield).

The P^{III}–N–H functional group in **2** was confirmed by the characteristic reaction with CCl_4,[8] which afforded the *P*-chlorophosphoranimine **4** (eq 4) in 83% yield. In addition, the ambident


(4)

(5)

anion, generated by depronation of **2** with *n*-BuLi, reacted with Ph_2PCl (eq 5) to give the P–P-bonded derivative **5**. The structure of **5**, a high-boiling liquid obtained in 61% yield, was confirmed by NMR spectral data. In particular, the ^{31}P NMR spectrum consists of an AB quartet with the J_{PP} value (209 Hz) and Ph_2P chemical shift (δ −19.3) being very similar to those of some close model compounds with the Ph_2P–P^V linkage.[9,10] The ^{13}C chemical shifts and J_{PC} values observed for the CH_2 and NEt_2 signals of **5** are also much more like those of the P^V analogue **4** than those of the P^{III} compound **2**. These NMR data, therefore, preclude the possibility of **5** having the isomeric P^{III}–N–P^{III} structure $Ph_2PN(SiMe_3)P(NEt_2)CH_2SiMe_3$. In fact, the Ph_2P group in that type of compound would be expected to have a ^{31}P chemical shift at much lower field (ca. 30–70 ppm).[10,11]

Compound **5**, in turn, is a good structural and synthetic model for the P–P-bonded product **3** obtained from the equimolar re-

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[7] Thoma, R. J. Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1984. Several other Si–N cleavage reactions, similar to the conversion of **1a** to **2**, have been observed in our laboratory.

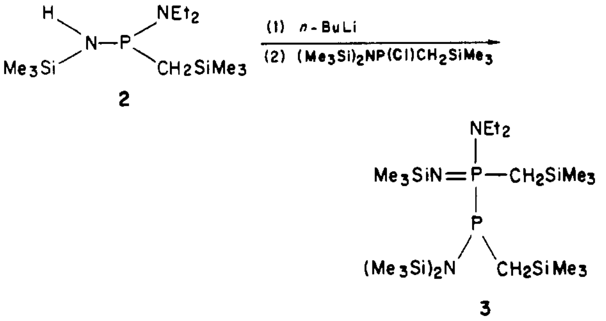
[8] For other examples see: (a) O'Neal, H. R.; Neilson, R. H. *Inorg. Chem.* **1984**, *23*, 1372. (b) Scherer, O. J.; Gick, W. *Chem. Ber.* **1970**, *103*, 71.

[9] Appel, R.; Milker, R. *Chem. Ber.* **1974**, *107*, 2650.

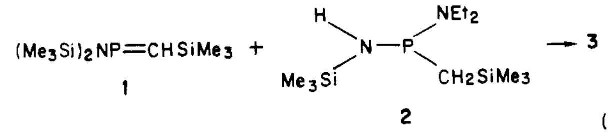
[10] Crutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van Wazer, J. R. *Top. Phosphorus Chem.* **1967**, *5*.

[11] For example, the ^{31}P shift of $Ph_2PN(SiMe_3)_2$ is δ 49. Nöth, H.; Meinel, L. *Z. Anorg. Allg. Chem.* **1967**, *349*, 225.

action of **1** with Et_2NH (eq 2). The large value of J_{PP} (290 Hz) found for **3** is especially indicative of the P–P bond. Also, it was possible to synthesize **3** from the N–H phosphine **2** (eq 6) by the same method used for the preparation of the Ph_2P derivative **5**. Moreover, compound **3** was produced quantitatively when the starting P=C reagent **1** was treated with the N—H derivative **2** (eq 7).



(6)



(7)

The latter finding accounts for how the P–P product **3** is formed in the reaction of **1** with an equimolar quantity of Et_2NH. It appears that **1** reacts first with 2 equiv of Et_2NH to produce the Si–N cleavage product **2**, probably via the 1,2-addition product **1a**. The unused **1** then reacts with **2**, as shown in eq 7, to afford the final product **3**.

Finally, it is interesting to note that compound **3** is the third different type of diphosphorus product to be derived from the methylenephosphine **1**. We have previously reported that the reactions of **1** with Ph_2PCl or $MeLi/Me_3SiCl$ yield the diphosphinomethanes $(Me_3Si)_2NP(Cl)CH(PPh_2)SiMe_3$[3] and $Me_2PCH(SiMe_3)P(Me)CH(SiMe_3)_2$[2], respectively. It seems clear, therefore, that aminomethylenephosphines such as **1** are useful reagents for the preparation of more complex types of organophosphorus compounds. This preparative chemistry is under continuing study in our laboratory.

Experimental Section

Materials and General Procedures. Chlorodiphenylphosphine, *n*-BuLi (hexane solution), and CCl_4 were obtained from commercial sources and used as received. Diethylamine was dried over KOH and distilled prior to use. Ether, hexane, and CH_2Cl_2 were distilled from CaH_2 and stored over molecular sieves. The starting materials $(Me_3Si)_2NP(X)CH_2SiMe_3$ ($X = Cl$,[4] NEt_2[7]) were prepared and purified according to published procedures. Proton NMR spectra were recorded on a Varian EM-390 spectrometer; ^{13}C and ^{31}P NMR spectra, both with ^1H decoupling, were obtained in the FT mode on a JEOL FX-60 instrument. Infrared spectra were recorded on a Beckman 4250 spectrophotometer using neat liquid samples. Mass spectra were obtained on a Finnigan OWA 1020 GC-MS system. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The procedures described herein are typical of those used for the preparation of the new compounds in this study.

(Diethylamino)[(trimethylsilyl)amino][(trimethylsilyl)methyl]phosphine (2). (a) From Methylenephosphine 1. Diethylamine (6.5 mL, 55 mmol) was added via syringe to a stirred solution of **1** (6.93 g, 25 mL) in CH_2Cl_2 (60 mL) at 0 °C. The mixture was allowed to warm to room temperature and then stirred overnight. Solvent removal under vacuum left a cloudy liquid residue. The byproduct Me_3SiNEt_2 was identified in the solvent fraction by comparing its ^1H NMR spectrum to that of an authentic sample. From the residue, **2** was obtained by fractional distillation through a 10-cm Vigreux column as a colorless liquid [4.1 g, 59% yield, bp 72–75 °C (0.9 mm)]. The NMR data are summarized in Table I. On standing at room temperature for a few days, compound **2** deposited some unidentified white solids, presumably P–N–P condensation products, and evolved Me_3SiNEt_2. Due to this thermal instability it was not submitted for elemental analysis. Its derivatives **4** and **5**, however, did give satisfactory analyses (see below). The IR spectrum of **2** contained the characteristic N–H stretching band at 3320 cm^{-1}. Mass spectrum, *m/e* (relative intensity): 278 (7.8) (M^+), 263 (8.2), 192 (76.2), 146 (45.7), 130 (35.4), 118 (45.7), 74 (93.6), 59 (41.2), 45 (100).

(b) From $(Me_3Si)_2NP(NEt_2)CH_2SiMe_3$ (1a). In a similar manner, compound **1a** (7.0 g, 20 mmol) in CH_2Cl_2 (50 mL) was treated with Et_2NH (4.5 mL, 40 mmol) at 0 °C. After the mixture was stirred overnight at room temperature, workup as described above gave **2** as a colorless liquid [4.5 g, 81% yield, bp 71–74 °C (1.0 mm)] having the same NMR spectral data as the sample prepared above.

***P*-(Diethylamino)-*P*-[(trimethylsilyl)methyl]-*P*-([bis(trimethylsilyl)amino][(trimethylsilyl)methyl]phosphino)-*N*-(trimethylsilyl)phosphoranimine (3). (a) From 1 and Et_2NH.** Diethylamine (3.1 mL, 30 mmol) was added via syringe to a stirred solution of **1** (8.3 g, 30 mmol) in CH_2Cl_2 (30 mL) at 0 °C. After the mixture was warmed to room temperature and stirred overnight, solvent removal left a while solid/liquid residue. Fractional distillation gave a major fraction with a boiling point of 70–75 °C (0.01 mm) that solidified in the receiving flask and the condenser. The solids were combined by washing the condenser and flask with CH_2Cl_2. Solvent removal left **3** as a waxlike solid (5.4 g, 65% yield). Anal. Calcd C, 45.36; H, 10.70. Found: C, 45.56; H, 10.77.

(b) From 1 and 2. Equimolar quantities (3.5 mmol) of compounds **1** and **2** were combined at 0 °C in CH_2Cl_2 (6 mL). After the mixture was stirred for 4 h at 0 °C, ^{31}P NMR indicated that no reaction had occurred. The mixture was then allowed to warm to room temperature and was stirred overnight. At this point, the quantitative formation of product **3** was confirmed by the AB quartet pattern in the ^{31}P NMR spectrum (Table I).

(c) From 2 and *n*-BuLi, etc. *n*-Butyllithium (3.2 mL, 2.6 M, 8.3 mmol) was added via syringe to a stirred solution of **2** (2.2 g, 7.9 mmol) in Et_2O (12 mL) at −78 °C. The mixture was allowed to warm to room temperature and was stirred for ca. 10 min. After the mixture was cooled to 0 °C, $(Me_3Si)_2NP(Cl)CH_2SiMe_3$ (2.8 mL, 8 mmol) was added via syringe. A white precipitate formed immediately. The mixture was then stirred overnight at room temperature, filtered under nitrogen, and freed of solvent. Hexane (ca. 20 mL) was added in order to extract the product from additional solids that had formed. Following another filtration and solvent removal, distillation through a short-path apparatus gave **3** as a colorless liquid (2.2 g, 50% yield), bp 90–92 °C (0.05 mm), that solidified on standing.

***P*-Chloro-*P*-(diethylamino)-*P*-[(trimethylsilyl)methyl]-*N*-(trimethylsilyl)phosphoranimine (4).** Carbon tetrachloride (2 mL, ca. 20 mmol) was added to a stirred solution of **2** (2.8 g, 10.0 mmol) in CH_2Cl_2 (10 mL) at 0 °C. After the mixture was warmed to room temperature and stirred overnight, fractional distillation gave **4** as a colorless liquid [2.6 g, 83% yield, bp 66–67 °C (0.05 mm)]. Anal. Calcd C, 42.28, H, 9.69. Found: C, 42.50; H, 9.93.

***P*-(Diethylamino)-*P*-[(trimethylsilyl)methyl]-*P*-(diphenylphosphino)-*N*-(trimethylsilyl)phosphoranimine (5).** The same procedure (12-mmol scale) as that described above for the preparation of **3** (method c) gave **5** as a colorless, viscous liquid [3.4 g, 61% yield, bp 142–148 °C (0.05 mm)]. Anal. Calcd C, 59.70; H, 8.72. Found: C, 59.30; H, 8.90.

Acknowledgment. We thank the U.S. Office of Naval Research and the Robert A. Welch Foundation for generous financial support.

Registry No. 1, 76173-65-4; 1a, 99642-69-0; 2, 99642-66-7; 3, 99642-67-8; 4, 99655-29-5; 5, 99642-68-9; $(Me_3Si)_2NP(Cl)CH_2SiMe_3$, 76946-89-9; Ph_2PCl, 1079-66-9; diethylamine, 109-89-7; carbon tetrachloride, 56-23-5.