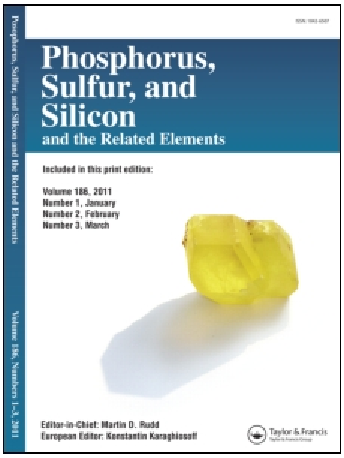

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SYNTHESIS OF CYCLIC SECONDARY AMINOPHOSPHANES

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SYNTHESIS OF CYCLIC SECONDARY AMINOPHOSPHANES

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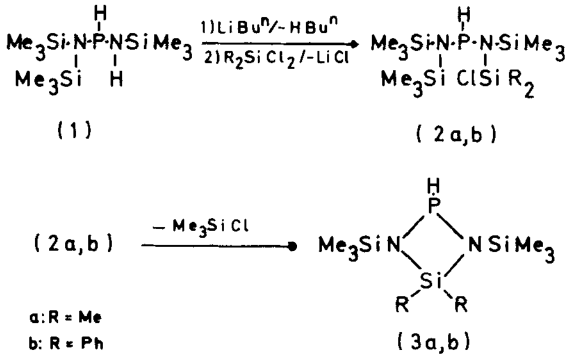
The first cyclic secondary aminophosphanes are synthesized by δ-elimination of trimethylchlorosilane from acyclic precursors. Contrary to acyclic phosphanes, these cyclic derivatives show abnormal low ir absorptions for the PH-stretching mode and the lowest PH-coupling constant ever reported.

Previously, we have demonstrated that the N-silylated secondary bisaminophosphane[1] **1** is a key molecule for the synthesis of three-membered phosphorus-nitrogen ring compounds by β- or γ-eliminations.[2,3] Now we report an efficient route to novel cyclic secondary bisaminophosphanes **3a**, **b** by thermal δ-elimination[4] of trimethylchlorosilane from the acyclic precursors **2a**, **b**. The composition and constitution of compounds **2a**, **b** and **3a**, **b** are determined by elemental analysis and by mass-, ir-, and nmr-spectra.



The mass-spectra of **2a**, **b** and **3a**, **b** show the molecular ion peaks with high intensity (60–80%). The loss of hydrogen from these ions give the base peaks.

In the ir-spectra, the presence of secondary phosphanes is proved by characteristic absorptions at 2260–2280 cm^{-1} in the case of **2a**, **b**.[5] Ring closure to **3a**, **b** leads to a significant lowering of these P-H-modes with strong absorptions at 2080–2090 cm^{-1}, reflecting an abnormal weak phosphorus-hydrogen bond.

In the ^{31}P nmr spectra (Table), **2a**, **b** show low field dubletts at about 60 ppm ($^1J_{HP} = 205$ Hz), typical for N-silylated acyclic bisaminophosphanes.[6] The formation of the four-membered ring compounds **3a, b** leads to a further low field shift of about 70 ppm. However, the most remarkable feature is the extreme low $^1J_{HP}$ of about 125 Hz which is even smaller than that of phosphiranes[7] and of the phosphide ion.[7] This may be explained by pure *p*-character of the phosphorus orbital bonding to hydrogen. The very low frequency of ν(PH) and the intensity of its ir-absorptions, indicating high polarity, favor this argument.[8] The ^1H-, $^{13}C\{^1H\}$-, and

TABLE

Chemical shifts, ppm, in the ^{31}P, ^{1}H, ^{13}C and, ^{29}Si spectra and coupling constants, Hz, of compounds **2a**, **b** and **3a**, **b**[a]

compound	**2a**		**2b**		**3a**		**3b**	
$\delta(^{31}P)$ (J_{PH})	58.7	(206)	60.5	(206)	128.9	(125)	132.7	(127)
$\delta(^{1}H)$ (J_{HP})								
PH	6.72	(205.7)	7.02	(205.7)	7.75	(125.4)	7.91	(127.1)
$PN(SiMe_3)_2$	0.25	(1.0)	0.20	(1.2)	—		—	
$PNSiMe_3$	0.31	(1.1)	0.21	(1.2)	0.06	(0.8)	−0.04	(0.6)
$PNSiR_2$	0.61	(1.7)	7.5–7.8		0.23	(0.8)	7.3–7.6	
$\delta(^{13}C)$ (J_{CP})								
$PN(SiC_3)_2$	4.1	(5.4)	3.7	(5.9)	—		—	
$PNSiC_3$	3.8	(5.2)	3.9	(5.2)	1.3	(3.8)	1.5	(3.2)
$PNSiR_2$	7.4	(7.8)	127–135		2.6	(3.0)	128–137	
	7.1	(5.3)			3.2	(9.1)		
$\delta(^{29}Si)$ (J_{SiP})								
$PNSi_2$	8.0	(9.2)	9.3	(11.8)	—		—	
PNSi	9.2	(9.3)	10.4	(8.6)	−1.5	(11.3)	0.6	(11.4)
$PNSi(R_2)$	14.9	(12.2)	−7.1	(3.5)	24.2	(10.5)	−0.9	(11.0)

[a] 40% solution in CD_2Cl_2, 85% H_3PO_4 as external standard for ^{31}P and Me_4Si as internal standard for ^{1}H, ^{13}C, ^{29}Si, 300 K.

$^{29}Si\{^{1}H\}$-nmr spectra of **2a**, **b** and **3a**, **b** are in accord with the configuration of the molecules, all resonances splitted to dubletts by coupling with phosphorus.

The cyclic secondary aminophosphanes **3a**, **b** are highly reactive species showing reactions typical for secondary phosphanes. In addition to that, ring opening by phosphorus-nitrogen bond cleavage represents a further functionality of these diazaphosphasilacyclobutanes. At −10°C, pure **3a**, **b** are stable for several month, but even at room temperature, they slowly disproportionate with formation of a phosphorus-phosphorus bond in an $>N-P_{\alpha}(H)-P_{\beta}=\dot{N}-$arrangement. The constitution of this molecular skeleton is obvious from its phosphorus nmr-spectrum.[9] Further studies on the mechanism of this new reaction pathway are in progress.

EXPERIMENTAL

1. Spectra: ^{13}C-, ^{29}Si-, ^{31}P-NMR: Varian FT 80 A; ^{1}H-NMR: Varian EM 360 L; mass spectra: Varian MAT 311 A, source 200°C, 70 eV, direct insertion; IR: Perkin Elmer 598 Infrared Spectrometer, kapillary films on KBr.

2. Materials and preparations: The solvents were purified and dried by column chromatography over Al_2O_3 super I. Oxygen and moisture must be completely excluded for successful preparation of **3a**, **b** at any time. Heating the glass distillation apparatus to 200°C for one day and cooling under inert gas before doing the pyrolysis experiments is recommended.

N,N',N',-Tris(trimethylsilyl)-N-chloro(dimethyl)silyl-diaminophosphan **2a** and N,N',N',-Tris(trimethylsilyl)-N,-chloro(diphenyl)silyl-diaminophosphan **2b** are obtained in quantitative yields by metallation of 20 mmol of **1**, dissolved in 50 ml hexane, with the equimolar amount of *n*-butyllithium (7.5% in hexane) at −80°C and subsequent addition of stoichiometric quantities of dimethyldichlorosilane or diphenyldichlorosilane, respectively. After filtration, for separation of the precipitated LiCl, the reaction mixture is evaporated in vacuo (0.5 Torr) at room temperature to give the pure products **2a**, **b** (2% impurity by nmr-control) as slightly brown oily residues. **2a** can be distilled in vacuo to give a colorless liquid, boiling point 85°C, 0.5 Torr.

Analysis: calculated (found):
2a: C 35.41% (35.1), H 9.18% (9.4), N 7.51% (7.4)
2b: C 50.72% (50.2), H 7.70% (8.1), N 5.63% (5.6)

1,3-Bis(trimethylsilyl)-4,4-dimethyl-1,3-diaza-2-phospha-4-silacylclobutane **3a**

In a micro distillation apparatus, 20 mmol (5.3 g) of **2a** are heated to 200°C under a pressure of about 400 Torr (argon atmosphere). **3a** is distilling from the reaction mixture, giving a colorless liquid, which can be purified by further distillation, boiling point 32°C, 0.5 Torr; yield 1.85 g (7 mmol, 35%)

Analysis: calculated (found): C 36.32% (36.0), H 9,53% (9.7), N 10.59% (10.2)

1,3-Bis(trimethylsilyl)-4,4-diphenyl-1,3-diaza-2-phospha-4-silacyclobutane **3b**

In a micro distillation apparatus, 20 mmol (7.8 g) of **2b** are pyrolyzed under a pressure of 0.5 Torr at a temperature of 150°C. Pure **3b** is obtained as pale yellow distillate; boiling point 120–125°C, 0.5 Torr; yield 5.85 g (15.1 mmol, 75%).

Analysis: calculated (found): C 55.63% (55.2), H 7.52% (7.6), N 7.21% (7.0)

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