A New Route to Sila- and Phosphaheterocycles: Nucleophilic Aminomethylation

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The aminals tetramethylmethylenediamine (TMMDA) **1a**, dicyclohexyldimethylmethylenediamine (CMMDA) **1b**, and diisopropyldimethylmethylenediamine (IMMDA) **1c** are doubly metalated by Li*t*Bu to give $LiCH_2N(R)CH_2N(R)CH_2Li$ [**2a**: R = Me, **2b**: R = Cy (Cy = cyclohexyl), **2c**: R = *i*Pr], which precipitate out of pentane as highly pyrophoric substances. Deuteration confirms *N*-methyl metalation exclusively. A series of aminomethylation reactions were performed by means of the doubly lithiated aminals **2a–c**. The reactions of **2a–c** with monochlorosilanes yield the silylated species $R'_3SiCH_2N(R)CH_2N(R)CH_2SiR'_3$ (**3a**: R' = Me, R = Me; **3b**: R' = Me, R = Cy; **3c**: R' = Me, R = *i*Pr; **4**: R' = Ph, R = Me, see Scheme 2). The use of dichlorosilanes lead to six-membered heterocycles **6a–6d**. **6a** is transferred into a mono quarternary ammonium salt **7** by methylation with MeI. The spirocycle **8** is obtained from $SiCl_4$ and two equivalents of **2a**. Similarly, several substituted 1,3-diaza-5-phosphacyclohexanes **9a–e** (R^1 = Me, Ph, NPh_2, NCy_2, see Scheme 3) are synthesized by the reaction of dichlorophosphanes R^1PCl_2 with **2a** and **2b**, respectively. Oxidation of **9d** with sulfur yields **12a**, which is characterized by X-ray structure determination.

Introduction

Aminomethylation reactions are of major interest in organoelement and organic chemistry. Normally these reactions are restricted to electrophilic aminomethylations. This is due to the fact, that in contrast to positively polarized carbon centers[1], carbanionic centers are not noticeably stabilized by an α-amino functionality.[2] Therefore, deprotonation of methylamines even with strong bases is normally unsuccessful. Since nucleophilic alkylation reactions rank among the most versatile tools in synthetic organic chemistry, a suitable method for nucleophilic aminomethylation reactions seems highly desirable.

In principle, this aim can be reached by using lithiated alkyl species with an "activated" α-nitrogen atom. This route has been successfully used in a vast variety of systems[3], the "activated" nitrogen can be transformed to an amino nitrogen in further synthetic steps. Nevertheless, the application of lithiated α-aminomethyl species seems advantageous, and in fact, these species have been synthesized via stannyl intermediates and used successfully for nucleophilic aminomethylations.[4] Unfortunately, the method has some disadvantages, in part due to the involvement and final waste of the organotin species. A further synthetical but also indirect route to lithiated methylamines is represented in a reductive cleavage of the C–S bond in (phenylthiomethyl)amines.[5] Consequently, a more direct route to the desired lithiated methylamines was established in the reaction of methylamines with very strong organolithium bases. In many cases, the yield is low[6] or the metalation proceeds unselectively.[7] In the case of $Me_2NCH_2NMe_2$, the lithiated product has not been investigated further.[8] In a previous short communication, we reported preliminary results on an easy double lithiation of $Me_2NCH_2NMe_2$ with an acceptable yield and its use for nucleophilic aminomethylation reactions with chlorosilanes.[9] We now report in full on this new method and on an extension for a more general application in organoelement synthesis.

Results and Discussion

Synthesis of the Doubly Lithiated Aminals 2a, 2b, and 2c

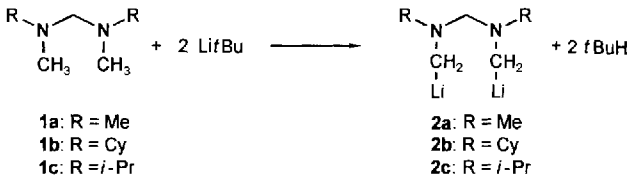
The starting compounds used for nucleophilic aminomethylation were synthesized in varying yields by treating tetramethylmethylenediamine (TMMDA), $Me_2NCH_2NMe_2$, **1a**, or the newly synthesized *N,N'*-dicyclohexyl- and *N,N'*-diisopropyl-substituted 1,3-diaminomethanes (CMMDA), (Cy)N(Me)CH_2N(Me)(Cy) (Cy = cyclohexyl), **1b**, and (IMMDA), MeN(*i*Pr)CH_2N(*i*Pr)Me, **1c**, with two equivalents of Li*t*Bu at −78°C in pentane solution (Scheme 1).

In the case of **1a** and **1b** precipitation of a white solid is observed after 3 h at 25°C, but is not finished even after two days. In contrast, for the lithiation of **1c**, precipitation of the white solid is only observed after 24 h. Products **2a**, **2b**, and **2c** are isolated as white, highly pyrophoric substances which were identified as the doubly lithiated species by elemental analysis and subsequent reactions.

Compound **2a**, which is only slightly soluble in toluene or THF at −78°C, was formed as the only product, if less than the necessary two equivalents of Li*t*Bu were used: a monolithiated species was not found. The overall yield of

  0009–2940/97/1212–1777 $ 17.50+.50/0

Scheme 1



2a or **2b** after prolonged reaction times amounts to 90%, but some impurities probably due to N–C cleavage were also formed in these cases. Therefore it is advisable to stop the reactions after 3 d, where 60% yield of pure product are isolated in the case of **2a** and 50% of **2b**. The overall yield of **2c** is lower (20%) after 5 d reaction time, probably for sterical reasons.

In marked contrast to $Me_2PCH_2PMe_2$, which by organolithium reagents is deprotonated exclusively at the methylene carbon atom[6], **1a**, **1b**, and **1c** are exclusively deprotonated at the methyl groups. Whereas double phosphane substitution markedly stabilizes carbanions[2], double amine substitution obviously destabilizes carbanions. Furthermore, methyl metalation is more favorable sterically. The monolithiated species might be envisaged, but the concentration of the monolithiated species is very low under all circumstances: it is not detected spectroscopically and in subsequent reactions no monosubstitution product is found even in the presence of excess aminal. Thus it appears, that a kinetically favorable second metalation step due to complexation of the lithium atom should rather be taken into account.

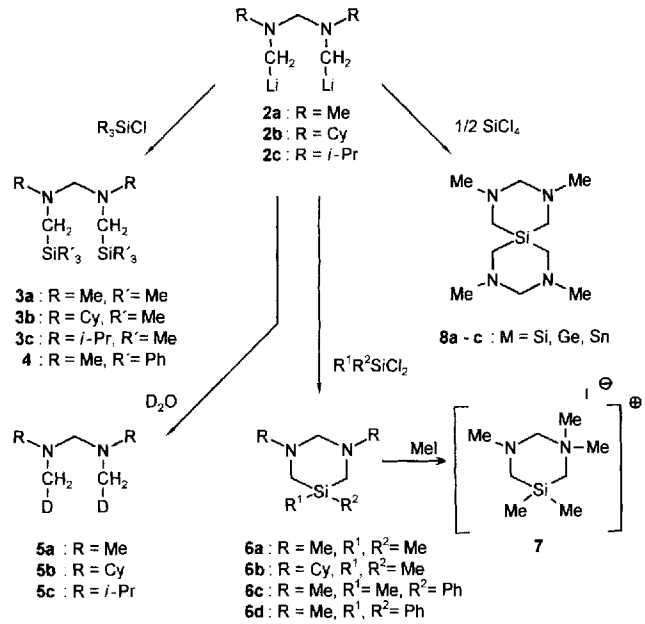
The actual structures for **2a**, **2b**, and **2c** could not be established. Crystalline samples were unobtainable in all cases, and it was not possible to obtain reasonable solution NMR spectra of these compounds, mainly due to their low soubility.

Reactions of 2a, 2b, and 2c and Synthesis of Diazasilaheterocycles

In order to clarify the kind of metalation of **1a**, **1b**, and **1c**, reactions with two equivalents of Me_3SiCl were performed in all cases and the bis-silylated products **3a**, **3b**, and **3c** were obtained as colourless liquids (Scheme 2). Their constitution as double silylated aminals is unambiguously demonstrated by their NMR spectra (^1H, ^{13}C, $\{^1H\}^{13}C$, $\{^1H\}^{29}Si$, see Experimental Section), which compare well with the data of known aminomethylsilanes.[5] Likewise, with two equivalents of Ph_3SiCl, **1a** gives the double silylated product **4**.

Double lithiation of the methyl functionality in **2a–c** is also demonstrated in the reaction with D_2O (Scheme 2). In the ^1H-NMR spectra of **5a** and **5c** a 1:1:1 triplet is found with a chemical shift corresponding to the *N*-methyl groups of compounds **1a** and **1c**. The geminal H-D coupling amounts to 1.7 (**5a**) and 2.0 Hz (**5c**), respectively. Due to superposition of the cyclohexyl CH_2 signals and the CH_2D signals in the ^1H-NMR of **5b**, convincing data are only available from the ^{13}C NMR. The 1:1:1 triplet for both CH_2D groups are found at δ (^{13}C) = 35.35 [^1J(CD) = 20.0 Hz].

Scheme 2



Reactions of **2a** and **2b** with Me_2SiCl_2, $Me(Ph)SiCl_2$, and Ph_2SiCl_2, led to the formation of *N*-methyl- or *N*-cyclohexyl-substituted 1,3-diaza-5-silacyclohexanes **6a–6d** (Scheme 2), which all are isolated as colourless liquids. The methyl-substituted compound **6a** is purified by distillation. The compounds are identified by NMR spectroscopy and MS or GC-MS. No splitting of the individual N-CH_3, Si-CH_3, NCH_2Si, and NCH_2N signals in the ^1H-NMR spectra of **6a**, even at −100°C, indicate that ring inversion is fast on the NMR time scale. NMR studies and conformational analyses on various 1,3-diazacyclohexanes[10] are consistent with slowly inverting rings at low temperatures (−70°C). A reason for this discrepancy most probably lies in the different C–C and Si–C bond lengths, with the consequence of more flexibility of the silacycles and a more planar ring conformation, as it is also observed for analogous phosphaheterocycles (see below). On the other hand, if more bulky substituents are introduced, as in the case of **6d**, the NMR signals of the diastereotopic methylene protons indicate a much higher inversion barrier even at room temperature.

Compound **6a** was used for further reactions. The mono-quarternary ammonium salt **7** is obtained by using MeI as a methylating agent.[11] A bis-quarternary ammonium salt was not formed, in either slightly polar (Et_2O) or polar solvents (MeCN). **7** is obtained as a colourless microcristalline product. Elemental analysis and NMR spectroscopy confirm the considered structure.

Symmetrical silicon containing spiranes have already been prepared directly from alkyldilithium reagents and silicon tetrachloride.[12] Using the dilithiated 1,3-diamine **2a** as alkylating agent, a new spirocycle **8**, with nitrogen atoms in β-positions to the silicon is obtained (Scheme 2) as a colourless liquid and purified by fractional distillation. The structure is confirmed by NMR and mass spectroscopy.

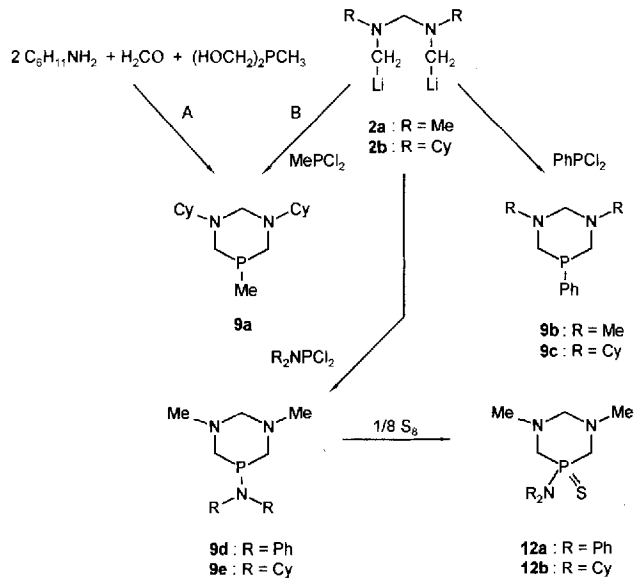
The syntheses of some of these 1,3-diaza-5-silacyclohexanes, which are performed in toluene solution, are accompanied by unwanted and yield reducing side reactions such as oligomerization or monoalkylation of the dichlorosilanes. Side products are not detected by NMR spectroscopy, but GC-MS studies definitely show peaks at higher masses.

Similar results are obtained if the reactions are performed in ether or THF solutions, but the amount of undesirable impurities rises considerably.

Syntheses of Phosphadiazaheterocycles

Similarly to nucleophilic aminomethylation of dichlorosilanes, dichlorophosphanes are also converted to six-membered heterocycles by means of **2b**. Again the reactions are carried out in toluene solution. The 1,3-diaza-5-phosphorinane derivative **9a** is identified in the viscous liquid obtained from the reaction according to Scheme 3 (route B) by NMR and mass spectroscopy.

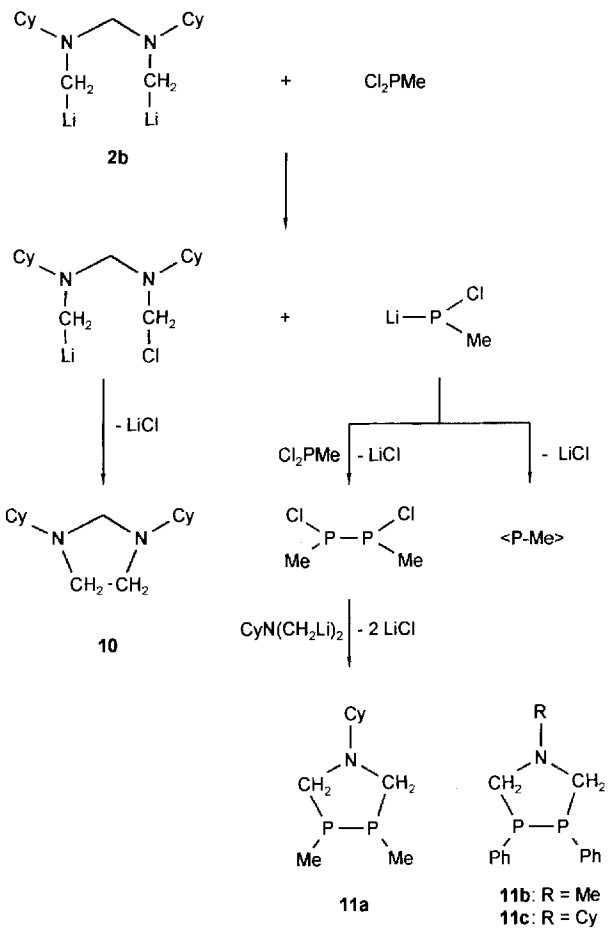
Scheme 3



Considerable amounts of byproducts, i. e. **10** and **11a** (see Scheme 4) are also present in the substance, which could not be separated. Therefore, an alternative condensation reaction[13] for the synthesis of **9a** was successfully tested (Scheme 3, route A). **9a** thus obtained pure is a colourless solid ($\delta^{31}P = -68.26$). Its spectroscopic data is consistent with the data for product **9a** from route B.

For the observed side-products, it seems reasonable to assume a Li/Cl exchange reaction between **2b** and $MePCl_2$, a process which has often been observed in organophosphorus chemistry.[14] As depicted in Scheme 4, this would account for the formation of **10** and **11a** by LiCl abstraction. [A phosphinidene formation step would likewise be feasible and account for the observed products, but oligomerisation products, e.g. $(PMe)_5$, could not be detected]. At this stage, the origin of the $(CH_2)_2NCy$ moiety in **11a** is not yet clear. It may well be, that this fragment is derived from

Scheme 4



2b during the substitution process. Alternatively, it may be due to an impurity in **2b**, which is formed from **1b** with Li*t*Bu under N–C cleavage similar to the process observed in the system TMEDA/Li*t*Bu.[7] A $(LiCH_2)_2NR$ species has been prepared previously,[4] but not by direct metalation of dimethylamines. It seems an attractive goal to optimize its formation in the metalation reaction.

Both **10** and **11a** are identified in the product by NMR spectroscopy (**11a**: $\delta^{31}P = -13.43$) and by GC-MS. As far as we know, 1-aza-3,4-diphosphacyclopentanes have not to date been described in the literature. Comparable saturated heterocyclic systems containing a P–P single bond within a five-membered ring system, i. e. 1-*n*-butyl-, 1-trimethylsilyl-, 1,2-di-*n*-butyl-, 1,2-trimethylene-1,2-diphospholane, and 1,2-di-phospholane are reported in the literature.[15] ^{31}P-NMR data reported are in good agreement with δ-values of our five-membered ring systems. We observed only one isomer of **11a** (probably the *trans* isomer) in the obtained products.

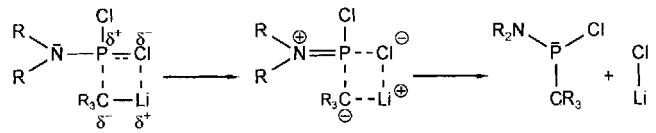
Likewise, with $PhPCl_2$, Ph_2NPCl_2, and Cy_2NPCl_2, the analogous 1,3-diaza-5-phosphorinanes **9b–9e** are obtained in the reaction with **2a** and **2b** as yellow (**9b**, **9c**, **9e**) or orange liquids (**9d**) from pentane or toluene (Scheme 3). In the case of both **9b** and **9c**, in addition to ^{31}P-NMR signals at $\delta = -57.63$ and $\delta = -62.92$ (which compares to $\delta =$

−60.0 for 1,3,5-triphenyl-1,3-diaza-5-phosphorinane[13]), a second signal in approximately 1:1 ratio is present at δ = −13.43 and δ = −17.84, respectively, which by comparison with **11a** and GC-MS results is attributed to the phospholanes **11b**, **11c** (see Scheme 4). Again, *cis/trans* isomers are not observed. The $(CH_2)_2NR$ moiety (**11b**: R = Me, **11c**: R = Cy) may be derived from an analogous substitution process as postulated for the formation of **11a** (Scheme 4).

In the case of **9b**, examination of the ^{31}P-NMR spectrum of the raw product reveals, in addition to the signals for **9b** and **11b**, the presence of an A_2B spin system [δP_A = 10.42, δP_B = −0.97, $J(P_AP_B)$ = 292.2 Hz] with low intensity (ca 5%). The observed pattern is indicative for a compound with a $P^{III}-P^{III}-P^{III}$ moiety. The ^{31}P-NMR spectra of open chain, triphosphines with alkyl or aryl substituents (i. e. 1,2,3-triphenyltriphosphane)[16] usually exhibit P-P coupling constants of about 195−225 Hz, which is significantly lower as in the present case. Therefore, the presence of a cyclic molecule seems most likely. No hints are provided from the NMR or GC-MS spectra about the nature of this byproduct. Again, a Li/Cl exchange reaction between **2a** and $PhPCl_2$ would account for the formation of a P−P−P moiety.

Quite remarkably, in the synthesis of **9d** and **9e**, side-products are observed only to a small extent. No P−P coupling is observed, probably due to a stabilization of the phosphenium form by the adjacent nitrogen as an intermediate in the substitution reaction (Scheme 5).

Scheme 5. Stabilization of the phosphenium form by the adjacent nitrogen atom avoids a P−P bond formation



The NMR spectroscopic data of **9d** and **9e** are in good accordance with those of **9a−c** and of comparable compounds[17], but $\delta^{31}P$ (**9d**: −18.50; **9e**: −10.55) differ from the respective data for **9a−c**. A low field shift is typical for the replacement of an organo by an amino group (cf.: δPMe_3 = −63.3[18]; $\delta(Me_2N)PMe_2$ = 39.0[19]), but it is less in the present case (ΔδP = ca. +50 ppm) than usual.

Only slow inversion of the six-membered rings **9d** as well as **9e**, in contrast to the cases of **9a−c**, is indicated by diastereotopic methylene protons in the ^1H-NMR spectra.

For the NCH_2N fragment, ΔδH for the geminal protons is most pronounced and amounts to 0.58 ppm [^2J(HH) = 11.2 Hz] in the case of **9d** and to 0.28 ppm [^2J(HH) = 10.4 Hz] in the case of **9e**, probably due to the influence of two parallel orientations of the N-lone pairs and *N*-methyl groups, respectively.[10][20]

Both **9d, e** are converted to the respective phosphorinane sulfides **12a, b** (Scheme 3) with elemental sulfur, which both are obtained from toluene as colourless crystals. Their $\delta^{31}P$ values (**12a**: 43.90, **12b**: 43.81) are within the expected range and indicate the presence of only one isomer in solution. According to the ^1H-NMR spectra, this is rigid at room temperature in both cases, because all signals of methylene protons are split by geminal couplings.

Figure 1. Molecular structure of **12a**

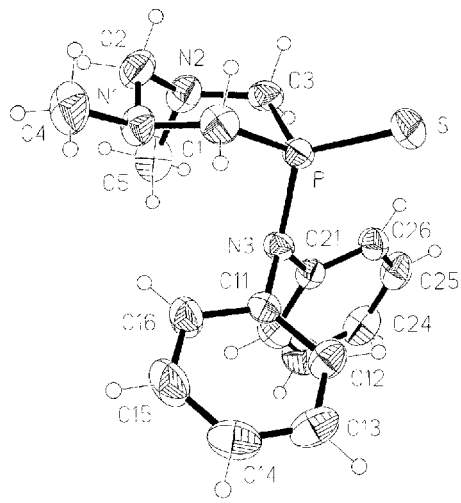


Table 1. Crystal data and details of the X-ray structural analysis of compound **12a**

	12a
Empirical formula	$C_{17}H_{22}N_3PS$
Molecular mass	331.41
Crystal size [mm]	0.60 × 0.40 × 0.30
Temperature [K]	205(2)
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a [Å]	9.449(1)
b [Å]; β [°]	16.014(2); 91.82(1)
c [Å]	11.442(1)
V [Å^3]; *Z*	1730.5(3); 4
Diffractometer	Enraf Nonius CAD4-Turbo
Radiation	Mo-K_α (λ = 0.71073 Å)
Density (calculated) [Mg/m^3]	1.272
Absorption coefficient [mm^{-1}]	0.280
F(000)	704
θ range for data collection [°]	3 to 26
Limiting indices	$-11 \le h \le 11, 0 \le k \le 19, 0 \le l \le 14$
Reflexions collected	3527
Independent reflexions	3363 (R_{int} = 0.0136)
Absorption correction	DIFABS
Max./min. transmission	1.000/0.552
Data/restraints/parameters	3362/0/201
Goodness-of-fit on F^2	1.049
Final *R* indices [$F_o > 4\sigma(F_o)$]	*R1* = 0.0353, *wR2* = 0.0876
R indices (all data)	*R1* = 0.0553, *wR2* = 0.0964
Largest diff. peak and hole	0.223 and −0.312 e × Å^{-3}

12a has been characterized by X-ray structure determination (Figure 1, Tables 1 and 2). The phosphorus atom is four coordinated, P−C as well as P−N bond distances are in the typical range of single bonds. In comparison to other phosphane sulfides with P−N or P−O single bonds[21], the P−S bond in **12a** [1.950(8) Å] is slightly elongated. The diazaphosphacyclohexane shows the expected chair conformation. The interplanar angles between the planes

C(1)PC(3), N(1)N(2)C(3)C(1), and N(1)C(2)N(2) amount to 38.3° and 60.4°, thus demonstrating the ring "flattening" effect of heavier tetracoordinated heteroclements.

One of the *N*-methyl groups is oriented axial, the other equatorial, thus minimizing their mutual influence. The Ph_2N group at the phosphorus atom is oriented axial, the sulfur equatorial. In phosphorinane chalcogens the chalcogen atom will normally occupy the axial position unless steric factors elsewhere on the ring dictate otherwise.[22] Electronegative groups (Ph_2N) on phosphorus may alter this preference.[23]

Conclusion

These results demonstrate that the *N*-methyl-substituted aminals TMMDA, CMMDA, and IMMDA can be doubly lithiated and used for nucleophilic aminomethylation at silicon and phosphorus centers, but side reactions often lower the yields considerably. Nevertheless, a new route in the synthesis of nitrogen containing heterocycles is at hand, which can be superior to other methods in certain cases. Further work in this field has proven the utility of **2a–c** as ligands in transition metal chemistry.[24] Their subsequent use as novel building blocks in organic synthesis is under current investigation.

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Experimental Section

General: All operations were performed under dry nitrogen atmosphere and with thoroughly dried solvents and glassware. Standard high-vacuum-line techniques were used. – Elemental analyses were obtained on a vario EL CHN elemental analyzer of the microanalytical laboratory of the TU Muenchen. – MS: Varian MAT 311A, EI, 70 eV, CI, FI. – GC-MS: Hewlett-Packard 5890 series II including a mass selective detector 5971A, EI, 70 eV. – NMR: FT NMR spectrometer JEOL GX 270 and 400 (270.05 MHz/399.65 MHz and 67.94 MHz/100.40 MHz for ^1H and ^{13}C NMR, respectively; 53.67 MHz/79.50 MHz for ^{29}Si NMR; for referencing the ^1H-, ^{13}C-, and ^{29}Si-NMR spectra, TMS ($\delta = 0$) was used as internal standard; 109.40 MHz/161.70 MHz for ^{31}P NMR, and 80% H_3PO_4 as external standard ($\delta = 0$); 40.52 MHz for ^{15}N NMR and CH_3NO_2 as external standard ($\delta = 0$), all measurements were carried out at 25°C in C_6D_6 as solvent with exception of compound **7**. All chemical shifts are reported in parts per million (ppm) and coupling constants *J* in Hz. In cases of high-order spin systems, the distance "*N*" [Hz] between the two outermost lines of the multiplet is given. In cases of ambiguity, the $\{^1H\}^{13}C$-NMR measurements were completed by DEPT-135 measurements (cf.: **9a–9e**) and the ^1H-NMR measurements with ^{31}P coupled HH COSY (cf.: **9a**, **9b**, **9e**). Temperature dependent NMR spectra were recorded with [D_8]toluene as solvent.

The syntheses of the phosphorus containing heterocycles **9a–9e** have been repeated twice in order to obtain NMR spectra (^1H, $\{^1H\}^{13}C$, ^{31}P) indicating a slightly different composition of product mixtures and therefore an additional simplification of interpreting the spectra of the product mixtures.

Li*t*Bu (pentane solution 15%) was a donation of the Metallgesellschaft and was not further purified prior to use. $MePCl_2$, $PhPCl_2$, TMMDA (**1a**) and all chlorosilanes were obtained from commercial sources. The latter and the chlorophosphines were dried over K_2CO_3 and were distilled immediately prior to use. Ph_2NPCl_2 and Cy_2NPCl_2 were synthesized according to literature procedures.[25]

Synthesis of **1b**: To 5.00 ml (66.91 mmol) of an aqueous solution of formaldehyde (37%), 17.46 ml (133.82 mmol) of cyclohexylmethylamin was added in two portions while stirring at room temp. Subsequently ca. 10 g of K_2CO_3 was added to the slurry which was stirred for further 3 d. The aqueous layer was extracted twice with 30 ml of Et_2O. The organic layer was separated from the solid residue by filtration through a sinter disk and dried over Na_2SO_4. 10.95 g (67%) of a colourless liquid product was obtained after fractional distillation (bp. 170–172°C, 9.5 mbar) and stored over molecular sieves. – ^1H NMR (C_6D_6): $\delta = 1.00 - 1.63$ (m br, 20 H, Cy: CH_2), 2.20 (s, 6 H, NCH_3), 2.45 (m, 2 H, NCH), 3.03 (s, 2 H, NCH_2N). – ^{13}C NMR (C_6D_6): $\delta = 26.62$ (s, Cy: CH_2), 26.93 (s, Cy: CH_2), 29.13 (s, Cy: CH_2), 35.57 (s, NCH_3), 60.40 (s, NCH), 74.85 (s, NCH_2N). – FI-MS; *m/z*: 238 [M^+]. – GC-MS (70 eV); *m/z*: 141 [$C_6H_{11}N(H)CH_2NCH_3^+$], 127 [$C_6H_{11}N(CH_3)_2^+$], 113 [$C_6H_{11}NH(CH_3)^+$], 43 [$CH_3NCH_2^+$]. – $C_{15}H_{30}N_2$ (238.4): calcd. C 75.57, H 12.68, N 11.75; found C 75.48, H 12.80, N 12.59.

Synthesis of **1c**: The same procedure as described in the synthsis of **1b** was applied. 7.18 ml (95.98 mmol) of formaldehyde solution and 20 ml (191.96 mmol) of isopropylmethylamine were used. Yield: 8.00 g (53%) of a colourless liquid after fractional distillation (bp. 70–73°C, 9.5 mbar) which was stored over molecular sieves. – ^1H NMR (C_6D_6): $\delta = 0.93$ [d, $^3J(HH) = 7$ Hz, 12 H, $(CH_3)_2CH$], 2.19 (s, 6 H, NCH_3), 2.96 (s, 2 H, NCH_2N), 2.98 [sept, $^3J(HH) = 7$ Hz, 2 H, $(CH_3)_2CH$]. – ^{13}C NMR (C_6D_6): $\delta = 17.96$ [s, $(CH_3)_2CH$], 34.04 (s, NCH_3), 50.68 [s, $(CH_3)_2CH$], 74.73 (s, NCH_2N). – Cl-MS; *m/z* (%): 158(9) [M^+], 157 (100) [$M^+ - H$], 100 (67) [$M^+ - (CH_3)_2CHN$]. – $C_9H_{20}N_2$ (158.29): calcd. C 68.29, H 14.01, N 17.70; found C 67.27, H 13.79, N 17.97.

Synthesis of **2a**: 100.00 ml (169.0 mmol) of an 1.69 M solution of Li*t*Bu in pentane was added to a solution of 8.63 g (84.5 mmol) of **1a** in 50 ml of pentane at –78°C. The mixture was allowed to warm up to room temp. The white precipitate formed during 5 d was isolated by filtration through a sinter disk and washed three times with 50 ml of pentane. Drying in vacuo gives 6.46 g (67%) of a white solid. The solid is highly pyrophoric. Due to its low solubility, it was characterized by elemental analysis and subsequent reactions. Addition of TMEDA, DME, or THF did not decisively improve the solubility nor were crystals obtained. From the mother liquor, on storage at room temp. for 14 d, an additional amount [2.70 g (28%)] of a slightly yellowish precipitate was obtained, which likewise could be used for subsequent reactions, but more unidentified impurities were observed in the reactions. – $C_5H_{12}Li_2N_2$ (114.03): calcd. C 52.65, H 10.61, Li 12.17, N 24.56; found C 52.41, H 10.54, Li 11.81, N 23.22.

Synthesis of **2b**: A procedure analogous to the preparation of **2a** was used. 20.15 g (84.5 mmol) of **1b** in 60 ml of pentane and 100.0 ml (169.0 mmol) of Li*t*Bu was used. After filtration and washing three times with 40 ml of pentane, drying of the solid residue in vacuo gave 10.38 g (49%). – $C_{15}H_{28}Li_2N_2$ (238.4): calcd. C 71.98, H 11.28, N 11.19; found C 69.81, H 11.51, N 10.65.

Synthesis of **2c**: The analogous procedure described in the synthesis of **2a** was used. 13.61 g (85.98 mmol) of **1c**, dissolved in 60 ml of pentane was used. 112.61 ml (171.96 mmol) of an 1.53 M solution of Li*t*Bu in pentane was added to the solution at –78°C. 2.90 g (20%) of a white, pyrophoric solid was obtained after 5 d. – $C_9H_{20}Li_2N_2$ (170.2): calcd. C 63.53, H 11.85, Li 8.16, N 16.46; found C 61.09, H 12.00, Li 10.10, N 10.93.

General Procedure for Synthsis of Sila- and Phospha-Heterocycles: The following general procedure was used to synthesize the sila- or phospha-heterocycles: equimolar amounts (ca. 5–10 mmol) of chlorosilanes or chlorophosphanes dissolved in toluene were added to a suspension of **2a–c** in 50 ml of toluene at −78°C with stirring. The solution was slowly warmed up to room temp. (3 h) and stirred for another 10 h. Subsequently the solvent was replaced by 50 ml of pentane and the resulting suspension filtered through a sinter disk. On removing the solvent from the pentane solution, an oily residue or crystalline product was obtained. If necessary, an extraction of the solid residue on the sinter disk was performed with toluene.

Synthesis of **3a**: See ref.[9]

Synthesis of **3b**: The general procedure was used. To a suspension of 0.85 g (3.40 mmol) of **2b** in 40 ml of toluene, 0.78 ml (6.12 mmol) of Me_3SiCl, dissolved in 20 ml of toluene, was added slowly with stirring at −78°C. yield: 0.31 g (44%) of a yellow oil. – ^{1}H NMR (C_6D_6): δ = 3.08 (s, 2 H, NCH_2N), 2.71 (s, br, 2 H, Cy: NCH, 2.29 (s, 4 H, NCH_2SiMe_3), 1.50 – 1.80 (m, 10 H, Cy: CH_2), 1.00 – 1.35 (m, 10 H, Cy: CH_2). – ^{29}Si NMR (C_6D_6): δ = −0.82.

Synthesis of **3c**: The general procedure was used. To a suspension of 0.64 g (3.76 mmol) of **2c** in 40 ml of toluene, 0.95 ml (7.52 mmol) of Mc_3SiCl, dissolved in 20 ml of toluene was added slowly with stirring at −78°C. 0.20 g (18%) of a yellow liquid was obtained. – ^{1}H NMR (C_6D_6): δ = 2.02 (s, 4 H, CH_2SiMe_3), 2.89 (s, 2 H, NCH_2N), 3.30 [sept, ^3J(HH) = 7.0 Hz, 2 H, $CH(CH_3)_2$], 0.95 [d, ^3J(HH) = 7.0 Hz, 12 H, $CH(CH_3)_2$], 0.11 [s, 18 H, $Si(CH_3)_3$]. – ^{13}C NMR (C_6D_6): δ = −1.06 [s, $Si(CH_3)_3$], 17.18 [s, $CH(CH_3)_2$], 38.09 (s, NCH_2Si), 48.49 [s, $CH(CH_3)_2$], 69.94 (s, NCH_2N). – ^{29}Si NMR (C_6D_6): δ = −0.63 (s, $SiMe_3$).

Synthesis of **4**: The general procedure was used. 0.73 g (6.30 mmol) of **2a** and 3.34 g (11.30 mmol) of Ph_3SiCl was used in the reaction. Yield: 1.38 g (57%) of an oily residue was obtained after the extraction. – ^{1}H NMR (C_6D_6): δ = 2.12 (s, 6 H, NCH_3), 2.89 (s, 2 H, NCH_2N), 2.26 (s, 4 H, NCH_2Si), 6.95 – 7.75 [m, 36 H, $(C_6H_5)_3Si$]. – ^{13}C NMR (C_6D_6): δ = 82.53 (s, NCH_2N), 44.50 (s, NCH_3), 48.53 [s, ^{29}Si satellites: ^1J(CSi) = 54.0 Hz, NCH_2SiPh_3], 136.30 (s, Ph: *i*-C), 135.51 (s, Ph: *o*-C), 128.44 (Ph: *m*-C_3), 130.98 (Ph: *p*-C). – ^{29}Si NMR (C_6D_6): δ = −11.72 (s, $SiPh_3$).

Synthesis of **5a**: See ref.[9]

Synthesis of **5b**: The analogous NMR tube experiment as described in the synthesis of **5a** was carried out with compound **2b**. – ^{13}C NMR (C_6D_6, 399.78 MHz): δ = 74.83 (s, NCH_2N), 60.40 (s, Cy: C_1), 35.35 [1:1:1 triplet, ^1J(CD) = 20.0 Hz, NCH_2D], 29.13 (s, Cy: C_2), 26.89 (s, Cy: C_4), 26.58 (s, Cy: C_3).

Synthesis of **5c**: The analogous NMR tube experiment as described in the synthesis of **5a** was carried out with compound **2c**. – ^{1}H NMR (C_6D_6): δ = 2.94 (s, 2 H, NCH_2N), 2.96 [sept, ^3J(HH) = 9.0 Hz, 2 H, $CH(CH_3)_2$], 0.91 [d, ^3J(HH) = 9.0 Hz, 12 H, $CH(CH_3)_2$], 2.15 [1:1:1 triplet, ^2J(HD) = 2.0 Hz, 4 H, NCH_2D]. – ^{13}C NMR (C_6D_6): δ = 17.95 [s, $(CH_3)_2CH$], 33.94 [1:1:1 triplet, ^1J(CD) = 20.3 Hz, NCH_2D], 50.74 [s, $(CH_3)_2CH$], 74.69 (s, NCH_2N).

Synthesis of **6a**: See ref.[9]; ^{15}N NMR (C_6D_6): δ = −357.32.

Synthesis of **6b**: The general procedure was used. To a suspension of 2.21 g (8.83 mmol) of **2b** in 30 ml of toluene, 1.07 ml (8.83 mmol) of Me_2SiCl_2, dissolved in 20 ml of toluene, was added. 0.88 g (63%) of a colourless liquid was obtained. – ^{1}H NMR (C_6D_6): δ = 0.09 [s, 6 H, $Si(CH_3)_2$], 1.53 (m br, 8 H, Cy: CH_2), 1.70 (m br, 12 H, Cy: CH_2), 2.09 (s, 4 H, NCH_2Si), 2.35 (m, 2 H, Cy: NCH), 3.31 (s, 2 H, NCH_2N). – ^{13}C NMR (C_6D_6): δ = 75.33 (s, NCH_2N), 64.85 (s, Cy: C_1), 38.89 (s, NCH_2Si), 29.41 (s, Cy: C_2), 26.92 (s, Cy: C_4), 26.40 (s, Cy: C_3). – GC-MS (70 eV); *m/z*: 294 [M^+], 251 [M^+ − CH_2NCH_3], 279 [M^+ − CH_3], 211 [M^+ − Cy], 168 [211 − CH_2NCH_3].

Synthesis of **6c**: A procedure analogous to the preparation of **6a** was used. 0.82 g (7.20 mmol) of **2a** and 1.25 g (6.50 mmol) of $MePhSiCl_2$ were employed in 65 ml of toluene. 1.20 g (84%) of a yellow viscous liquid was obtained after drying in vacuo. – ^{1}H NMR (C_6D_6): δ = 7.06 – 7.14 (m br, 5 H, *aromatic* H), 2.82 [d, 1 H, ^2J(HH) = 9.8 Hz, NCH_2N], 2.77 [d, 1 H, ^2J(HH) = 9.8 Hz, NCH_2N], 2.13 (d, 6 H, NCH_3), 1.91 (m, 4 H, NCH_2Si), 0.28 (s, 3 H, $SiCH_3$). – ^{13}C NMR (C_6D_6): δ = 82.58 (s, NCH_2N), 48.51 (s, NCH_3), 45.51 [s, ^{29}Si satellites: ^1J(CSi) = 55.1 Hz, NCH_2Si], −5.41 [s, ^{29}Si satellites: ^1J(CSi) = 55.8 Hz, $SiCH_3$], 136.82 [s, *i*-C, ^{29}Si-satellites ^1J(CSi) = 64.6 Hz], 134.65 (s, *o*-C), 127.98 (s, *m*-C), 129.61 (s, *p*-C). – ^{29}Si NMR (C_6D_6): δ = −18.86 (s). – GC-MS (70 eV); *m/z*: 221 [M^+], 220 [M^+ − H], 219 [M^+ − 2 H], 191 [219 − Si], 176 [219 − CH_2NCH_3], 205 [220 − CH_3], 135 [178 − CH_2NCH_3], 58 [$(CH_3)_2NCH_2^+$].

Synthesis of **6d**: The general procedure was used. To a suspension of 1.07 g (9.40 mmol) of **2a** in 40 ml of toluene, 1.76 ml (8.50 mmol) of Ph_2SiCl_2, dissolved in 20 ml of toluene was added. 1.97 g (82%) of a pale yellow oil was obtained. – ^{1}H NMR (C_6D_6): δ = 2.13 (s, 6 H, NCH_3), 2.23 (s, 4 H, NCH_2Si), 2.87 (s, 2 H, NCH_2N), 7.13 (m, 6 H, *o*-H, *p*-H), 7.68 (m, 4 H, *m*-H). – ^{13}C NMR (C_6D_6): δ = 44.45 [s, ^{29}Si satellites: ^1J(CSi) = 56.7 Hz, NCH_2Si], 48.44 (s, NCH_3), 82.53 (s, NCH_2N), 128.09 (s, *m*-C), 129.84 (s, *p*-C), 135.15 (s, *i*-C), 135.57 (s, *o*-C). – GC-MS (70 eV); *m/z*: 282 [M^+], 238 [M^+ − CH_2NCH_3], 253 [M^+ − SiH].

Synthesis of **7**: 0.34 ml (5.40 mmol) of MeI, dissolved in 5 ml of CH_2Cl_2, was added to a solution of 0.57 g (3.60 mmol) of **6a**, dissolved in 10 ml of CH_2Cl_2, at −10°C. The solution was warmed up to room temp. and stirred for further 16 h in the dark. After storage at −30°C, colourless crystals were obtained. – ^{1}H NMR ($CDCl_3$): δ = 0.19 (s, 6 H, CH_3Si), 2.26 (s, 2 H, $SiCH_2N$), 2.54 (s, 3 H, NCH_3), 3.09 (s, 2 H, $SiCH_2N$), 3.27 (s, 6 H, NCH_3), 4.21 (s, 2 H, NCH_2N). – ^{13}C NMR ($CDCl_3$): δ = −2.99 (s, $SiCH_3$), 44.84 [s, $CH_2(Me)NCH_2Si$], 47.83 (s, NCH_3), 52.94 [s br, $(CH_3)_2N(CH_2)_2$], 55.17 [s, $(Me)_2NCH_2Si$], 85.24 (s, NCH_2N). – $C_8H_{21}IN_2Si$, (272.2): calcd. C 32.00, H 7.05, N 9.33, Si 9.35; found C 32.27, H 7.30, N 9.16, Si 10.3.

Synthesis of **8**: See ref.[9]

Synthesis of **9a**: *Route A:* At room temp., 3.33 ml (29.06 mmol) of cyclohexylamine, dissolved in 10 ml of toluene, was added to a solution of 1.57 g (14.53 mmol) of bis(hydroxymethyl)methylphosphane and 0.47 g (15.65 mmol) of paraformaldehyde in 15 ml of toluene. The mixture was refluxed for 24 h and then dried over Mg_2SO_4. The toluene was evaporated to afford a solid crude product which was recristallized from pentane. 3.02 g (73%) of colourless crystals were obtained. – ^{1}H NMR (C_6D_6): δ = 2.35 (m, 2 H, Cy: NCH), 2.50 [d, 2 H, ^2J(HH) = 13.2 Hz, NCH_2P], 2.88 [t, 2 H, ^2J(HH) = 13.7 Hz, NCH_2P], 3.39 (m, 2 H, NCH_2N), 1.65 (m, 10 H, Cy: CH_2), 1.45 (m, 2 H, Cy: CH_2), 1.07 [d, 3 H, ^2J(HP) = 2.9 Hz, PCH_3], 1.05 (m, 8 H, Cy: CH_2). – ^{13}C NMR (C_6D_6): δ = 72.60 (s, NCH_2N), 63.04 (s, Cy: C_1), 49.60 [d, ^1J(CP) = 11.0 Hz, NCH_2P], 30.11, 29.30 (s, Cy: C_2), 26.63 (s, Cy: C_4), 26.20, 26.10 (s, Cy: C_3), 7.25 [d, PCH_3, ^1J(CP) = 14.7 Hz]. – ^{31}P NMR (C_6D_6): δ = −68.33 (s, PCH_3). – CI-MS; *m/z* (%): 283 (100) [M^+], 171 (95) [M^+ − $CH_2NC_6H_{11}$], 156 (8) [M^+ − $CH_2(CH_3)NC_6H_{11}$], 124 (46) [M^+ − $CH_2(CH_3)NC_6H_{11}$, PH]. – EI MS (70 eV); *m/z* (%): 282 (8) [M^+], 171 (100) [M^+ − $C_6H_{11}NCH_2$], 156 (20) [M^+ −

$C_6H_{11}N(CH_3)CH_2$]. – $C_{16}H_{31}N_2P$ (283.4): calcd. C 68.05, H 11.06, N 9.92; found C 67.88, H 11.07, N 10.06.

Route B: A procedure analogous to the preparation of the diazasilacyclohexanes was used, the solvent was toluene. 1.59 g (6.35 mmol) of **2b**, 20 ml of toluene, and 0.57 ml (6.33 mmol) of dichloromethylphosphane were used. After evaporation, the pentane and toluene extracts afforded 1.45 g of a yellowish viscous liquid. GC MS analyses showed that both extracts contained a mixture of three components **9a**, **10**, and **11a** in a ratio of 1:2:2. Separation by fractional distillation was unsuccessful. – ^{1}H NMR (HH–COSY, C_6D_6): δ = 2.34 (m, 2 H, Cy: NCH), 2.49 [d, 2 H, ^2J(HH) = 13.2 Hz, NCH_2P], 2.85 [t, 2 H, ^2J(HH) = 13.7 Hz, NCH_2P], 3.37 [dd, 2 H, ^2J(HH) = 10.7 Hz, ^4J(HP) = 2.9 Hz, NCH_2N], 1.65 (m, 10 H, Cy: CH_2), 1.44 (m, 2 H, Cy: CH_2), 1.05 (m, 8 H, Cy: CH_2), 1.07 (d, ^1J(CP) = 2.9 Hz, PCH_3). – ^{13}C NMR (DEPT–135, C_6D_6): δ = 72.60 (s, NCH_2N), 63.07 [d, ^3J(CP) = 3.3 Hz, Cy: C_1], 49.59 [d, ^1J(CP) = 11.6 Hz, NCH_2P], 30.14, 29.31 (s, Cy: C_2), 26.67 (s, Cy: C_4), 26.23, 26.17 (s, Cy: C_3), 7.26 [d, ^1J(CP) = 14.9 Hz, PCH_3]. – ^{31}P NMR (C_6D_6): δ = –68.26 (s br, PCH_3). – GC-MS (70 eV); *m/z*: 283 [M^+], 282 [M^+ – H], 267 [282 – CH_3], 235 [282 – CH_3PH], 171 [M^+ – $CH_2NC_6H_{11}$], 156 [171 – CH_3], 124 [156 – PH].

Byproduct **10**: The existence of **10** was confirmed by GC MS analysis, NMR data were extracted from the spectrum of a sample of the product mixture. – ^{1}H NMR (C_6D_6): δ = 3.47 (s, NCH_2N), 2.63 (s, NCH_2), 2.90 (m, Cy: NCH). – ^{13}C NMR (DEPT–135, C_6D_6): δ = 72.84 (s, NCH_2N), 50.18 (s, NCH_2); the C_6H_{11} signals were not identified due to superposition of signals with those of **9** and **11a**. – GC-MS (70 eV); *m/z*: 236 [M^+], 235 [M^+ – H], 221 [235 – CH_2], 153 [M^+ – Cy], 125 [153 – NCH_2].

Byproduct **11a**: The existence of **11a** was confirmed by GC-MS analysis, NMR data were extracted from the spectrum of the product mixture. A separation from other products by fractional distillation was unsuccessful. – ^{13}C NMR (C_6D_6): δ = 53.05 ("t", *N* = 22.3 Hz, NCH_2P), 62.10 (m, *N* = 8.5 Hz, NCH_2P), 10.12 ("t", *N* = 1.7 Hz, PCH_3); the cy-C_6H_{11} signals were not identified due to superposition of signals with those of **9a** and **10**. – ^{31}P NMR (C_6D_6): δ = –44.80 (s). – GC-MS (70 eV); *m/z*: 217 [M^+], 202 [M^+ – CH_3], 170 [M^+ – CH_3PH], 125 [170 – CH_2P].

Synthesis of **9b**: The general procedure was used. To a suspension of 0.91 g (7.98 mmol) of **2a** in 40 ml of toluene was added 0.97 ml of $PhPCl_2$, dissolved in 20 ml of toluene. After evaporation, the pentane and toluene extracts afforded 0.56 g (37%) and 0.92 g (61%) of pale brown oils. Two components **9b** and **11b** in a ratio of 10:1 were identified in both extracts by GC-MS and NMR spectroscopy. A further compound in the pentane extract revealed an A_2B spin system in the ^{31}P-NMR spectra [δP_A = 10.42, δP_B = –0.97 $J(P_AP_B)$ = 292.2 Hz, RP(Ph)-P(Ph)-P(Ph)R]. No further hints are given from the ^{1}H or ^{13}C NMR or GC-MS analyses, in which way this P–P–P system is integrated into a molecule. NMR spectroscopic data of **9b** was extracted from the spectrum of the product mixture. – ^{1}H NMR (HH–COSY, C_6D_6, 399.65 MHz): δ = 1.88 [d, ^2J(HH) = 2.4 Hz, 1 H, NCH_2N], 2.11 (s, 6 H, NCH_3), 2.86 [m, ^4J(HH) = 2.9 Hz, ^2J(HP) = 3.4 Hz, 4 H, NCH_2P], 3.11 [m, 1 H, ^4J(HH) = 2.9 Hz, ^2J(HH) = 2.4 Hz, NCH_2N], 7.14 – 7.62 (m, 5 H, *aromatic* H). – ^{13}C NMR (DEPT–135, C_6D_6, 100.40 MHz): δ = 44.98 (d, ^3J(CP) = 6.1 Hz, NCH_3), 53.70 [d, ^1J(CP) = 13.8 Hz, NCH_2P], 79.60 [d, ^3J(CP) = 1.1 Hz, NCH_2N], 128.27 [d, ^3J(CP) = 6.1 Hz, *m*-C], 132.28 [d, ^4J(CP) = 8.3 Hz, *p*-C], 132.73 [d, ^2J(CP) = 13.8 Hz, *o*-C], 139.15 [d, ^1J(CP) = 17.1 Hz, *i*-C]. – ^{31}P NMR (C_6D_6, 161.70 MHz): δ = –57.63 (s br, PhP). – GC-MS (70 eV); *m/z*: 208 [M^+], 165 [M^+ – (CH_2NCH_3)], 122 [M^+ – 2 (CH_2NCH_3)], 78 [$C_6H_6^+$].

Byproduct **11b**: A separation from the main product by fractional distillation was unsuccessful. NMR data was extracted from the spectra of the sample of the product mixture. – ^{13}C NMR (C_6D_6, 100.40 MHz): δ = 45.05 (s, NCH_3), 53.75 ("d", *N* = 13.8 Hz, NCH_2P), 62.46 ("t", *N* = 27.6 Hz, NCH_2P), 128.18 (s, *p*-C), 128.58 [t, ^2J(PC) = 2.8 Hz, *o*-C], 132.90 [t, ^3J(PC) = 13.8 Hz, *m*-C], 139.25 [t, ^1J(PC) = 4.1 Hz, *i*-C]. – ^{31}P NMR (C_6D_6, 161.70 MHz): δ = –13.43 (s). – GC-MS (70 eV); *m/z*: 273 [M^+], 230 [M^+ – CH_2NCH_3], 185 [M^+ – $PCH_2N(CH_3)CH_2$], 152 [230 – C_6H_6], 108 [$C_6H_5P^+$], 57 [$(CH_2)_2N(CH_3)^+$].

Synthesis of **9c**: The general procedure was used. To a suspension of 2.75 g (10.99 mmol) of **2b** in 40 ml of toluene, 1.49 ml (10.99 mmol) of $PhPCl_2$, dissolved in 20 ml of toluene, was added dropwise, while stirring at –78°C. After the solvent was evaporated the pentane and toluene extracts afforded 1.18 g (31%) and 2.36 g (62%) of yellow oils. Both extracts contained a product mixture of **9c** and **11c** in a ratio of ca. 1:1, (^{31}P NMR). – ^{1}H NMR (HH-COSY, C_6D_6): δ = 6.90 – 7.70 (m, 6 H, *aromatic* H), 3.70 [d, ^2J(HH) = 11.7 Hz, 1 H, NCH_2N], 3.45 [dd, ^2J(HH) = 11.7 Hz, ^4J(HP) = 10.3 Hz, NCH_2N], 2.55 (m, 2 H, NCH), 2.04 (s, 6 H, NCH_3), 1.38 – 1.82 (m, 12 H, Cy: CH_2), 0.80 – 1.25 (m, 8 H, Cy: CH_2). – ^{13}C NMR (DEPT–135, C_6D_6): δ = 71.20 [d, ^3J(CP) = 1.7 Hz, NCH_2N], 61.65 [d, ^3J(CP) = 5.5 Hz, Cy: C_1], 50.22 [d, ^1J(CP) = 12.1 Hz, NCH_2P], 29.88, 30.13 (s, Cy: C_2), 26.23, 26.37 (s, Cy: C_3), 26.54 (s, Cy: C_4), 140.21 [d, ^1J(CP) = 19.8 Hz, *i*-C], 132.52 (s, *o*-C), 132.27 (s, *m*-C), 128.27 (s, *p*-C). – ^{31}P NMR (C_6D_6): δ = –62,92 (s, PPh). – CI-MS; *m/z* (%): = 345 (15) [M^+ + H], 237 (93) [345 – PPh].

Byproduct **11c**: A separation from the main product **9c** was unsuccessful by fractional distillation. The ^{13}C-NMR resonance signals were extracted from the spectrum of the sample of the product mixture. ^{13}C NMR (C_6D_6): δ = 133.41 ("t", *N* = 27.0 Hz, *o*-C), 139.47 [d, ^1J(CP) = 4.4 Hz, *i*-C], 128.45 (s, *p*-C), 128.19 (s, *m*-C), 62.03 ("t", *N* = 8.8 Hz, NCH), 54.62 ("t", *N* = 23.1 Hz, NCH_2P), 25.98 (s, Cy: C_3), 34.39 [t, ^4J(CP) = 7.7 Hz, Cy: C_2], 26.62 (s, Cy: C_4). – ^{31}P NMR (C_6D_6): δ = –17,84 (s).

Synthesis of **9d**: The general procedure was used. 0.38 g (3.33 mmol) of **2a** was suspended in 20 ml of toluene. 0.81g (3.00 mmol) of Ph_2NPCl_2 dissolved in 20 ml of toluene was added to the suspension at –78°C while stirring. The mixture was warmed up slowly to room temp. Subsequently the solvent was replaced by pentane. The extraction yielded 0.81 g (90%) of a yellowish oil. – ^{1}H NMR (C_6D_6): δ = 2.27 (s, 6 H, NCH_3), 3.08 [m, 3 H, ^2J(HH) = 11.2 Hz, NCH_2N, NCH_2P], 2.50 [dd, 1 H, ^2J(HH) = 11.2 Hz, ^4J(HP) = 3.9 Hz, NCH_2N], 2.35 [dd, 2 H, ^2J(HH) = 11.7 Hz, ^2J(HP) = 12.2 Hz, NCH_2P], 6.80 – 7.20 (m, 10 H, *aromatic* H). – ^{13}C NMR (DEPT-135, C_6D_6): δ = 78.71 [d, ^3J(CP) = 1.7 Hz, NCH_2N], 56.30 [d, ^1J(CP) = 14.3 Hz, NCH_2P], 44.17 [d, ^3J(CP) = 10.5 Hz, NCH_3], 147.04 (s, *i*-C), 146.93 (s, *i*-C), 129.27 (s, *m*-C), 124.69 (s, *o*-C), 124.56 (s, *o*-C), 123.33 (s, *p*-C). – ^{31}P NMR (C_6D_6): δ = –18.50 (s).

Synthesis of **9e**: To a suspension of 0.60 g (5.26 mmol) of **2a** in 50 ml of toluene was added 1.34 g (4.74 mmol) of Cy_2NPCl_2, dissolved in 20 ml of toluene, at –78°C while stirring. The mixture was warmed up to room temp. and subsequently the solvent was replaced with pentane. The extraction yielded 1.30 g (88%) of a yellowish oil. – ^{1}H NMR (C_6D_6): δ = 2.98 (m br, 2 H, Cy: NCH), 2.88 [m, 3 H, ^2J(HH) = 10.4 Hz, ^4J(HP) = 3.1 Hz, NCH_2N, NCH_2P], 2.63 [m, 3 H, ^2J(HH) = 10.4 Hz, ^2J(HP) = 12.2 Hz, NCH_2N, NCH_2P], 2.19 (s, 6 H, NCH_3), 1.61 (m, 16 H, Cy: CH_2), 0.90 – 1.20 (m br, 4 H, Cy: CH_2). – ^{13}C NMR (DEPT–135,

C_6D_6): δ = 79.86 [d, ^3J(CP) = 1.1 Hz, NCH_2N], 56.60 [d, ^1J(CP) = 14.7 Hz, NCH_2P], 56.14 [d, ^3J(CP) = 5.5 Hz, Cy: C_1], 45.21 [d, ^3J(CP) = 7.4 Hz, NCH_3], 35.33 und 35.40 (s, Cy: C_2), 26.85 (s, Cy: C_3), 26.05 (s, Cy: C_4). – ^{31}P NMR (C_6D_6): δ = −10.55. – GC-MS (70 eV); *m/z*: 311 [M^+], 268 [$M^+ - CH_2NCH_3$], 225 [268 − CH_2NCH_3], 143 [226 − C_6H_{11}].

Synthesis of **12a**: A solution of 0.05 g (1.60 mmol) of sulfur in 20 ml of toluene was added to a solution of 0.42 g (1.40 mmol) of **9d** in 20 ml of toluene while stirring at room temp. The mixture was maintained at 40°C for 17 h. The yellow colour of the solution intenisified during the reaction period. Subsequently, the solvent was replaced by 20 ml of pentane and filtered through a sinter disk in order to separate from excess sulfur and other precipitates. After the solvent was removed, 0.13 g (28%) of yellow crystals were obtained. – ^{1}H NMR (HH−COSY, C_6D_6): δ = 3.05 (d, 1 H, ^2J(HH) = 11.7 Hz, NCH_2N], 2.78 [d, 1 H, ^2J(HH) = 11.7 Hz], 3.42 ("t", 2 H, *N* = 28.4 Hz, NCH_2P), 2.79 [m, 2 H, ^2J(HH) = 14.2 Hz, ^2J(HP) = 14.2 Hz, NCH_2P], 1.96 [d, 6 H, ^4J(HP) = 2.9 Hz, NCH_3], 6.85 − 7.15 (m, 6 H, *aromatic* H), 7.70 [d, 4 H, ^2J(HH) = 8.3 Hz, *aromatic* H]. – ^{13}C NMR (DEPT-135, C_6D_6): δ = 77.37 [d, ^3J(CP) = 3.7 Hz, NCH_2N], 60.00 [d, ^2J(CP) = 65.3 Hz, NCH_2P], 42.77 [d, ^3J(CP) = 7.4 Hz, NCH_3], 145.13 (s, *i*-C), 118.13 (s, *p*-C), 129.25 (s, *m*-C), 129.49 (s, *o*-C). – ^{31}P NMR (C_6D_6): δ = 43,90 (s). – CI-MS (70 eV); *m/z* (%): 332 (54) [M^- + H], 331 (24) [M^+], 288 (40) [M^- − CH_2NCH_3], 256 (2) [288 − S], 222 (39) [M^+ − C_6H_5S], 177 (21) [M^+ − 2 C_6H_5], 169 (100) [$(C_6H_5)_2N^+$].

Crystal Structure Determination: A suitable single crystal of **12a** was sealed into a glass capillary and used for measurement of precise cell constants and for intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Diffraction intensities were corrected for Lp and absorption effects. The structure was solved by direct methods and refined by full matrix least-squares calculations against F^2 [SHELXL-93].[26] An absorption correction was applied with program DIFABS.[27] The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were calculated in idealized positions and their isotropic thermal parameters were tied to that of the adjacent carbon atom by a factor of 1.5 at the methyl groups and by 1.2 at methylene and phenyl groups. Interatomic distances and angles are given in Table 2. Further information may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-406391, the names of the authors, and the full journal citation.

Table 2. Interatomic distances [Å] and angles [°] of **12a**

S−P	1.950(8)	N(3)−P−S	116.93(6)
P−N(3)	1.686(2)	C(1)−P−S	111.04(7)
P−C(1)	1.810(2)	C(3)−P−S	116.26(7)
P−C(3)	1.830(2)	C(1)−N(1)−C(4)	111.2(2)
N(1)−C(1)	1.460(3)	C(1)−N(1)−C(2)	109.8(2)
N(1)−C(4)	1.462(2)	C(4)−N(1)−C(2)	111.2(2)
N(1)−C(2)	1.464(3)	C(2)−N(2)−C(3)	113.2(2)
N(2)−C(2)	1.442(3)	C(2)−N(2)−C(5)	113.0(2)
N(2)−C(3)	1.453(3)	C(3)−N(2)−C(5)	115.8(2)
N(2)−C(5)	1.461(3)	C(21)−N(3)−C(11)	114.8(1)
N(3)−C(21)	1.439(2)	C(21)−N(3)−P	120.7(1)
N(3)−C(11)	1.449(2)	C(11)−N(3)−P	118.1(1)
N(3)−P−C(1)	106.26(8)	N(1)−C(1)−P	113.2(1)
N(3)−P−C(3)	104.94(9)	N(2)−C(3)−P	115.2(1)
C(1)−P−C(3)	99.63(9)	N(2)−C(2)−N(1)	113.8(2)

Synthesis of **12b**: A procedure analogous to the preparation of **12a** was used. 0.10g (3.20 mmol) of sulfur was dissolved in toluene and added to a toluene solution of 1.01g (3.20 mmol) of **17** at room temp. Subsequently the mixture was maintained at 40°C while stirring for further 10 h. A slight increase of the yellow colour was observed. Toluene was replaced with pentane. The extraction afforded 0.66 g (60%) of yellow crystals. – ^{1}H NMR (HH−COSY, C_6D_6): δ = 1.11 − 1.91 (m, 20 H, Cy: CH_2), 1.98 [d, 6 H, ^4J(HP) = 2.4 Hz, CH_3N], 2.43 [dd, 1 H, ^2J(HH) = 10.3 Hz, ^4J(HP) = 2.0 Hz, NCH_2N], 2.72 [d, 2 H, ^2J(HH) = 14.2 Hz, PCH_2N] 3.04 [d, 1 H, ^2J(HH) = 10.3 Hz, NCH_2N], 3.22 [t, 2 H, ^2J(HH) = 13.7 Hz, PCH_2N], 3.54 (m, 2 H, Cy: NCH). – ^{13}C NMR (DEPT-135, C_6D_6): δ = 25.97 (s, Cy: C_4), 27.22 (s, Cy: C_3), 34.40 [d, ^3J(CP) = 2.2 Hz, Cy: C_2], 44.24 [d, ^3J(CP) = 12.8 Hz, NCH_3], 57.88 [d, ^2J(CP) = 2.2 Hz, Cy: C_1], 63.60 [d, ^1J(CP) = 69.4 Hz, PCH_2N], 78.83 [d, ^3J(CP) = 2.2 Hz, NCH_2N]. – ^{31}P NMR (C_6D_6): δ = 43.81 (s).

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