Unsymmetrical Carbene Homologues: Isolable Pyrido[*b*]-1,3,2λ^2-diazasilole, -germole and -stannole and Quantum-Chemical Comparison with Unstable Pyrido[*c*] Isomers

Joachim Heinicke,* Anca Oprea, Markus K. Kindermann, Tamás Karpati, Laszlo Nyulászi, and Tamás Veszprémi

This work is dedicated to Professor Dr. Manfred Weidenbruch on the occasion of his 60th birthday.

Abstract: Reaction of the dilithium pyridine-2,3-diamide **1a**-Li_2 with $SiCl_4$ and subsequent reduction of the resulting **2a** with potassium or direct ring closure with $GeCl_2 \cdot$dioxane or $SnCl_2$ gave the stable carbene homologues 1,3-dineopentylpyrido[*b*]-1,3,2λ^2-diazasilole (**3a**), -germole (**4a**) and -stannole (**5a**). Similarly, the dilithium pyridine-3,4-diamide **1b**-Li_2 and $SiCl_4$ furnished the pyrido[*c*]-1,3,2λ^4-diazasilole (**2b**). However, attempts to obtain the silylene **3b** as well as the analogous germylene and stannylene failed. Ab initio quantum chemical studies of model compounds **III a**, **III b** and benzo-1,3,2λ^2-diazasilole (**III c**) reveal a comparable thermodynamic stabilization. Unexpected similarities of benzo and pyrido[*b*] derivatives and lower kinetic stability of carbene homologues of the pyrido[*c*]-type (**b**) correlate with high symmetry of the HOMO π charge densities in the former (**III a** has a nodal plane through the N-atom) and with unsymmetrical charge distribution in **III b**. All compounds are structurally characterized by NMR and MS, the carbene homologues also by UV and **3a** by photoelectron spectroscopy.

Keywords: ab initio calculations · carbene homologues · heterocycles · photoelectron spectroscopy · silanediyl

Introduction

Like carbenes,[1] most silylenes (silanediyls) are highly reactive, short-lived intermediates which are detected by spectroscopic methods or trapping reactions.[2] A few isolable representatives with higher coordination number were described recently.[3] Furthermore, silylenes can be considerably stabilized by (p – p)π bonding in amino-, alkoxy-, or mercaptosilylenes and especially in diaminosilylenes.[4] Nevertheless, noncyclic derivatives are very reactive and have not yet been isolated under normal conditions, but have been detected by either matrix techniques or trapping reactions.[5] A much more effective stabilization occurs in cyclic and, substantially stronger, in cyclodelocalized Hückel-aromatic diaminocarbenes and their heavier homologues. The first isolated compound of the latter type, a benzo-1,3,2λ^2-diazagermole,[6] was described in 1989, followed by the Arduengo carbene,[7] an analogous diazagermole,[8] and the first dicoordinate stable silylenes 1,3-di-*tert*butyl-1,3,2λ^2-diazasilole[9] and 1,3-di-neopentyl-1,3,2λ^2-benzodiazasilole.[10] Stabilization by π bonding is largest for carbon,[7b] whereas the higher carbene homologues benefit increasingly from the growing s character of the lone pair of electrons of the Group-14 element, thus giving rise to stable acyclic diaminostannylenes.[11] Silylenes seem to be the least favored species of this group and stabilizing factors such as the symmetry in the known derivatives might be crucial. Stable unsymmetric nucleophilic carbenes were reported recently.[12] In this work we describe the first isolable silylene with an unsymmetrical basis structure,[13] the analogous germylene, and the stannylene. Quantum-chemical investigations comparing the stable pyrido[*b*]- with unstable pyrido[*c*]-1,3,2-diazasilole illuminate the importance of a symmetrical charge density in the frontier orbitals (FOs) for the persistence of molecules at the border of stability.

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Results

Reaction of *N*,*N*′-dineopentyl-2,3-diaminopyridine (**1a**) with two equivalents of butyllithium and subsequently with $SiCl_4$ gave the cyclic diaminodichlorosilane (**2a**), which under mild conditions in THF was reduced with two equivalents of

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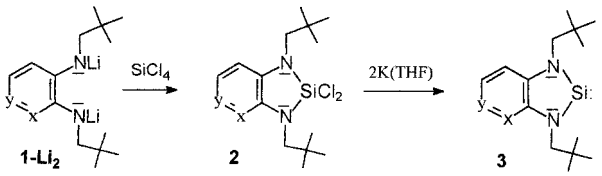
potassium to give 1,3-dineopentylpyrido[*b*]-1,3,2λ^2-diazasilole (**3a**) (Scheme 1). Crude yields of about 50% (NMR) were reproducible. However, work-up by sublimation at 100–115 °C/10^{-5} Torr caused formation of polymer products and lowered the yield of **3a** to about 4–6%.

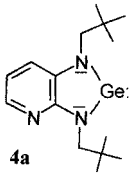


a: (x = N, y = CH)
b: (x = CH, y = N)

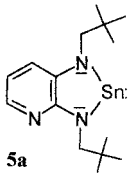
Scheme 1. The formation of **2** and **3**.

Purification by extraction or chromatography was not successful. Despite the reduced electrophilicity (see below) **3a** is very sensitive towards OH groups. Traces of water or alcohols underwent immediate oxidative addition yielding the corresponding hydridosilicon(IV) compounds. Excess hydroxy compounds caused cleavage of the Si–N bonds and recovery of **1a**. However, in absence of air and moisture the pure silylene may be stored for months. Also a solution of **3a** in C_6D_6 remained nearly unchanged during two months at room temperature and exposure to sunlight.

Repeated attempts to synthesize the isomeric silylene 1,3-dineopentylpyrido[*c*]-1,3,2λ^2-diazasilole (**3b**) in an analogous manner failed. Dilithiation of *N,N'*-dineopentyl-3,4-diaminopyridine (**1b**) with two equivalents of *n*BuLi and cyclization with $SiCl_4$ gave 2,2-dichloro-1,3-dineopentylpyrido[*c*]-1,3,2-diazasilole (**2b**) in moderate yield, but the subsequent reduction with potassium in THF provided a mixture in which no silylene could be detected by means of NMR. To see whether this is a consequence of a preferred reduction of the diaminopyridine ring system or of a lower stability of **3b**, we investigated the reactions of **1a** and **1b** with $GeCl_2 \cdot$ dioxane and with $SnCl_2$. The higher homologues of **3a**, the yellow germylene **4a** and the orange stannylene **5a**, could be synthesized in good yields (80% in crude products) in this way. Again sublimation caused, but to a lesser extent, formation of nonvolatile components and decreased the yields of **4a** (23%) and **5a** (50%). Analogous reactions of **1b** with $GeCl_2 \cdot$ dioxane and with $SnCl_2$, however, did not give the pyrido[*c*]-1,3,2λ^2-germole or -stannole derivatives. This indicates a much lower tendency of formation or stability compared with the pyrido[*b*] isomers.



4a



5a

3a and **4a** are easily soluble in C_6D_6, ether, and even saturated hydrocarbons. ^{29}Si NMR chemical shifts of **3a** in C_6D_6 and [D_8]THF are similar. This and the monomeric nature of the Lewis-basic carbene homologues **3a** and **4a** indicate a strongly reduced electrophilicity of the divalent elements and a lower tendency to form Lewis-base complexes. The stannylene **5a** is only slightly soluble in benzene, but soluble in THF and in pyridine. The very different ^{119}Sn chemical shifts in C_6D_6 ($\delta = 242$) and in [D_8]THF ($\delta = 100.5$) indicate that the stannylene has a much higher tendency to form complexes with Lewis bases and, thus, differs considerably from the silylene and germylene. It should be mentioned that benzo-1,3,2λ^2-diazastannole[14] exhibits similar properties although it does not contain the third Lewis-basic nitrogen atom. An X-ray structural investigation reveals a distance between Sn^{II} and the aryl plane that is significantly shorter than the van der Waals distance which accounts for intermolecular π complexation and thus the low solubility. Nevertheless, monomers are formed in equilibrium, as indicated by the residual solubility and the possibility of subliming **5a**.

The structures of all the compounds were elucidated by NMR (Table 1) and MS investigations. A typical feature of the carbene homologues **3a–5a** is the strongly deshielded NCH_2 protons compared with **2a** ($\Delta\delta > 0.4$); this is consistent with a ring current effect and a cyclodelocalized electronic system. The slight low-field shift with increasing size of the group-14 heteroatom indicates an additional core influence. The inclusion in the delocalized π-system of the lone pairs of electrons on nitrogen in the five-membered rings is shown for **4a** by a strong ^{14}N downfield shift of $\Delta\delta \approx 100$ compared with the signals of **1a** and **2a**. The ^{29}Si and ^{119}Sn nuclei of **3a** and **5a** (in C_6D_6 $\delta(^{29}Si) = 95.1$ and $\delta(^{119}Sn) = 242$) are also strongly but much less deshielded than the nonaromatic five-membered cyclic diaminosilylene of West and Denk ($\delta(^{29}Si) = 119$)[9b] and nonaromatic diaminostannylenes ($\delta(^{119}Sn)$ in the range 700–800).[11] This accounts for markedly increased π charge densities at Si^{II} and Sn^{II} by delocalized π systems in **3a–5a**.

Despite the π-deficient character of the pyridine compared with the benzene ring, the ^{29}Si or ^{119}Sn chemical shifts of **3a** or **5a** are close to those of benzo-1,3,2λ^2-diazasilole and the

Abstract in German: *Die Umsetzung des Dilithium-pyridin-2,3-diamids **1a**-Li_2 mit $SiCl_4$ und Reduktion des entstehenden **2a** mit Kalium oder der direkte Ringschluß mit $GeCl_2 \cdot$ Dioxan oder $SnCl_2$ führte zu den stabilen Carbenhomologen 1,3-Dineopentylpyrido[b]-1,3,2λ^2-diazasilol (**3a**), -germol (**4a**) bzw. -stannol (**5a**). Dilithium-pyridin-3,4-diamid **1b**-Li_2 und $SiCl_4$ reagierten zu Pyrido[c]-1,3,2λ^4-diazasilol (**2b**). Die Reduktion zum Pyrido[c]–annellierten 1,3,2λ^2-Diazasilol **3b** sowie Versuche zur Darstellung analoger Germylene und Stannylene gelangen dagegen nicht. Ab-initio-Studien der Modellverbindungen **III a**, **III b** und des Benzo-1,3,2λ^2-diazasilols (**III c**) zeigten eine vergleichbare thermodynamische Stabilisierung. Unerwartete Ähnlichkeiten der Benzo- und Pyrido[b]-derivate und die geringere kinetische Stabilität der Carbenhomologen des Pyrido[c]-typs **b** korrelieren mit höherer Symmetrie der HOMO-π-Ladungsdichteverteilung ersterer (in **III a** Knotenebene durch das N-Atom) und mit einer unsymmetrischen π-Ladungsdichte im HOMO von **III b**. Alle Verbindungen wurden durch NMR- und Massenspektroskopie, die Carbenhomologen auch durch UV- und **3a** durch PE-Spektroskopie charakterisiert.*

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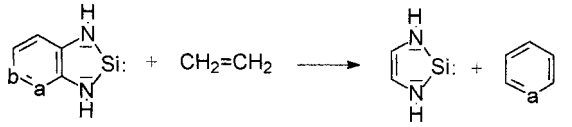
Table 1. ^{1}H and ^{13}C NMR data of **1a**, **2a** and the carbene homologues **3a**, **4a**, **5a**.

	1a (C_6D_6)	**1a** ([D_8]THF)	**2a** (C_6D_6)	**3a** (C_6D_6)	**4a** (C_6D_6)	**5a** (C_6D_6)[a]	**5a** ([D_8]THF)
CC*H*$_3$	0.83, 0.93 (2s)	0.92, 1.01 (2s)	0.86, 1.10 (2s)	0.81, 1.03 (2s)	0.80, 1.01 (2s)	0.81, 1.01 (2s)	0.95, 0.99 (2s)
NC*H*$_2$	2.48 (d), 3.48 (d) (J_{HH} = 6.5, 6.2 Hz) NH: 4.29 (brt)	2.83 (d), 3.4[b] (J_{HH} = 6.5 Hz) NH: 4.8 (brt)	3.02, 3.71 (2s)	3.40, 4.15 (2s)	3.57, 4.36 (2s)	3.69, 4.52 (2s, br)	3.70, 4.08 (2s, satellite[c])
*H*6	8.08 (dd) (J = 4.7, 1.9 Hz)	7.53 (d) ($J \approx 5$ Hz)	7.81 (dd) (J = 5.1, 1.5 Hz)	8.15 (dd) (J = 4.8, 1.5 Hz)	8.21 (dd) (J = 4.7, 1.5 Hz)	8.16 (br.)	7.37 (dd) (J = 4.8, 1.4 Hz)
*H*5	6.56 (dd) (J ca. 7.5, 4.7 Hz)	6.37 (dd) ($J \approx 8$, 5 Hz)	6.47 (dd) (J = 7.7, 5.1 Hz)	6.65 (dd) (J = 7.8, 4.8 Hz)	6.69 (dd) (J = 7.9, 4.7 Hz)	6.68 (br.)	6.29 (dd) (J = 4.8, 7.8 Hz)
*H*4	6.58 (dd) ($J \approx 7.5$, 1.9 Hz)	6.73 (d) ($J \approx 8$ Hz)	6.58 (dd) (J = 7.7, 1.5 Hz)	6.87 (dd) (J = 7.8, 1.5 Hz)	6.94 (dd) (J = 7.9, 1.5 Hz)	6.93 (brd) (J = 7.8 Hz)	6.72 (dd) (J = 7.8, 1.4 Hz)
C*Me*$_3$	27.6, 27.7		29.3, 29.5	28.5 (q), 28.6 (q)[d]	28.4, 28.5	28.59, 28.63	28.90, 28.96
*C*Me$_3$	31.3, 31.8		33.9, 34.2	32.9 (m), 33.2 (m)	32.6, 32.9	32.5, 32.9	33.4, 34.2
NC*H*$_2$	52.9, 56.3		54.0, 56.1	52.9 (t), 55.3 (t)[e]	54.4, 57.0	55.9, 58.8	55.7, 59.1
C_q2	151.9		151.4	152.7 (–)	153.9	157.4	158.7
*C*6	138.8		137.6	137.8 (ddd, 177, 7.0, 3.0 Hz)	137.3	135.8	133.4
*C*5	113.5		115.6	113.7 (ddd, 163, 9.2, 1.7 Hz)	113.0	111.9	110.5
*C*4	118.6		115.6	115.3 (dd, 160, 7.5 Hz)	114.8	114.6	112.2
C_q3	131.8		134.6	134.4 (d, 7 Hz)	136.1	140.0	140.9

[a] Signals are broadened. [b] Superimposed on solvent signal. [c] $^{3}J(^{119/117}Sn^{1}H)$ = 16.4 (br), 17.7 Hz (br). [d] $^{1}J(CH)$ = 123 Hz. [e] $^{1}J(CH)$ = 136, 135 Hz.

analogous stannylene $\delta(^{29}Si) = 96.9$[10] and $\delta(^{119}Sn) = 269$ (C_6D_6),[14] respectively. Also the UV/Vis spectra of pyrido[*b*] and benzo analogues are very similar. To understand the similarities between the unsymmetrical pyrido[*b*]- and symmetrical benzo-derivatives and why the isomeric pyrido[*c*]-1,3,2λ^2-diazasilole, -germole and -stannole could not be prepared by analogous procedures, ab initio quantum chemical calculations with model compounds pyrido[*b*]- (**IIIa**), pyrido[*c*]- (**IIIb**) and benzo-1,3,2λ^2-diazasilole (**IIIc**) were carried out with the isodesmic equation shown in Scheme 2.



IIIa: a = N, b = CH
IIIb: a = CH, b = N
IIIc: a = b = CH

IIId (a = CH, N)

Scheme 2. Reaction scheme used in the ab initio calculations.

The differences in energy were < 1 kcal mol^{-1} for **IIIa** and **IIIc** and 4.86 kcal mol^{-1} for **IIIb** and **IIIc** (MP2/6-31G* level of theory); **IIIa** is thermodynamically more stable than **IIIb** by 3.8 kcal mol^{-1}. This value is small, mainly due to the different relative position of the nitrogen atoms (2,3-$(H_2N)_2C_5H_3N$ is more stable by 3.76 kcal mol^{-1} than 3,4-$(H_2N)_2C_5H_3N$), and does not explain the large difference in the reactivity.

These results suggest that pyrido[*c*] isomers could not be isolated for kinetic reasons. This is supported by the calculated charge-density distribution in the highest occupied MOs (Figure 1). The HOMO of **IIIa** is very similar to that of **IIIc** and exhibits an almost symmetrical π charge distribution around a nodal plane through the pyrido nitrogen atom, whereas the HOMO of **IIIb** is a very unsymmetrical π orbital and results in a much higher reactivity. The lower charge symmetry in the HOMO-1 of **IIIb** with respect to **IIIa** reinforces this trend. Only the HOMO-2, representing the lone pair of electrons on silicon, is similar to the respective MOs of **IIIa** and **IIIc**. Taking into account the effects of N-alkylation, the calculated orbital energies correlate well with the ionization potentials determined by photoelectron spectroscopy of **3a** (Figure 2). The assignments are based on Koopman's theorem[15] and are in good accordance with the previous results on 1,3-dineopentylbenzo-1,3,2λ^2-diazasilole.[16]

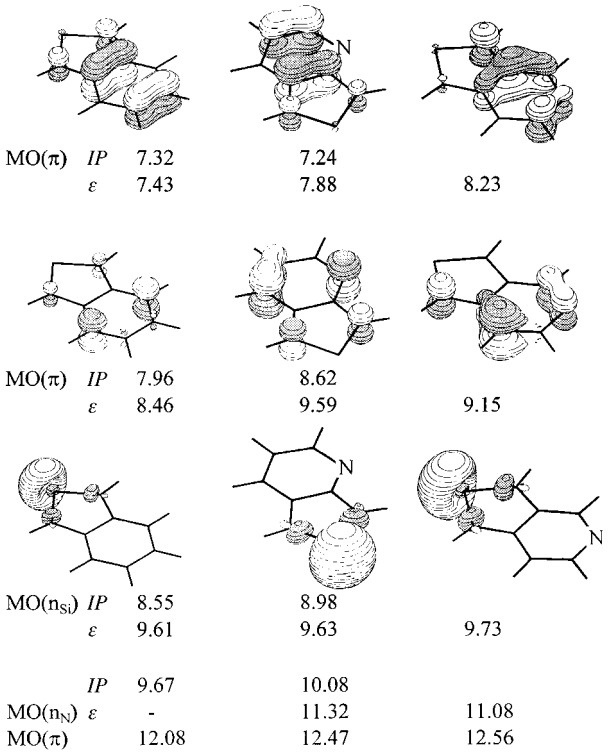


Figure 1. Charge density distribution in the three highest occupied MOs of benzo-, pyrido[*b*]- and pyrido[*c*]-1,3,2λ^2-diazasilole, calculated orbital energies (ε) and and experimental ionization potentials (in [eV]).

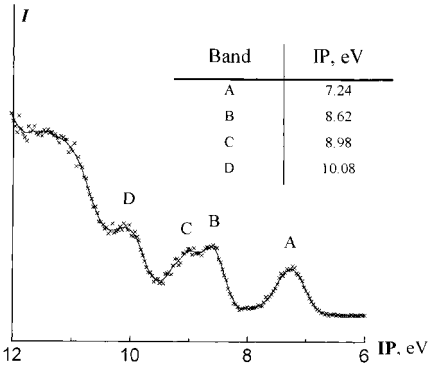


Figure 2. Photoelectron spectrum of **3a**.

Conclusions

The preparation and some features of an unsymmetrical isolable silylene, pyrido[*b*]-1,3,2λ^2-diazasilole (**3a**), and the corresponding germylene and stannylene are described. Analogous syntheses of the pyrido[*c*] isomers were unsuccessful although ab initio quantum-chemical calculations show similar thermodynamic stabilization of model compounds of both isomers. The difference may be explained by the high symmetry of the π-charge density in the HOMO of **3a** around a nodal plane through the nitrogen atom and a low π-charge symmetry in the HOMO of **3b**. This strongly diminishes the reactivity of **3a** which has similarities with benzo-1,3,2λ^2-diazasilole. Thus, it may be concluded that electronically unsymmetrical silylenes, even those fitting the Hückel rule, are usually highly reactive species which can hardly be isolated. Less reactive, isolable unsymmetrical silylenes will be restricted to compounds in which the highest occupied MOs possess a highly symmetrical charge-density distribution. Unsymmetrical carbenes or stannylenes have a better chance of stability as a result of stronger (p–p)π bonds in the former and the higher s character and tendency to form complexes of the latter. Nevertheless, the symmetry of charge distribution in the frontier orbitals may remain a critical point.

Experimental Section

General Procedures: All operations were carried out under an argon atmosphere and in carefully dried and freshly distilled solvents. $GeCl_2$·dioxane was prepared according to ref. [17]. NMR data were recorded on a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.1 (^{1}H), 75.5 (^{13}C) and 59.6 MHz (^{29}Si) with tetramethylsilane as reference. $^{14/15}$N chemical shifts were referenced to CH_3NO_2 (external, capillary). The assignments were ascertained by 135-DEPT spectra and proton-coupled spectra of **4a**; assignment numbers of H and C atoms refer to the position in the pyridine ring. Mass spectra (EI, 70 eV) were measured on a single focussing sector-field mass spectrometer AMD 40 (Intectra), UV spectra on Lambda 19 (Perkin–Elmer) and photoelectron spectra of **3a** with an instrument described earlier[18] at He^I resonance lines. For calibration nitrogen, methyl iodide, and the He peak were used as internal standards.

The quantum chemical calculations were performed with the GAUSSIAN 94 package;[19] for further details see ref. [16]. The geometries of the model compounds **IIIa–d** included in the isodesmic Scheme 2 were optimized by means of the MP2/6-31G* level of theory. All the stationary points were checked by second derivative calculations. The calculated bond lengths (Å) and angles (°) are given in Table 2. The calculated orbital energies and experimental ionization potentials (in eV) are given in Figure 1.

Table 2. Calculated bond lengths and angles for **IIIa–d**.

	C(N)–C(N) (Å)	C–N (Å)	N–Si (Å)	N-Si-N (°)
IIIa	1.414	1.381/1.385	1.777/1.766	86.2
IIIb	1.409	1.385/1.387	1.774/1.768	86.1
IIIc	1.412	1.389	1.768	85.8
IIId	1.364	1.385	1.775	84.7

***N,N′*-dineopentyl-2,3-diaminopyridine (1a)**:

a) C_5H_3N-2,3-$(NHCOCMe_3)_2$: *t*BuCOCl (58.8 g, 60 mL, 0.488 mol) was added dropwise with stirring to a cooled (ca. 10 °C) mixture of 2,3-diaminopyridine (25 g, 0.229 mol) and NEt_3 (48.9 g, 67 mL, 0.483 mol) in dry ether (150 mL). After 3 days the ether was evaporated; the residue was treated with water, filtered, and thoroughly washed with water. The brown solid was dried in vacuum over P_4O_{10} to yield slightly contaminated diamide (58.2 g, 0.210 mol, 91.7%). Recrystallization from ether gave colorless crystals soluble in $CHCl_3$ and CH_3OH. M.p.: 131–133 °C; ^{1}H NMR ($CDCl_3$): $\delta = 1.28$ (s, 9H, CH_3), 1.37 (s, 9H, CH_3), 8.38 (br s, 1H, NH), 9.21 (br s, 1H, NH), 7.23 (dd, $^3J_{45} = 8.1$ Hz, $^3J_{56} = 4.7$ Hz, 1H, H5), 8.13 (dd, $^3J_{56} = 4.7$ Hz, $^4J_{46} = 1.6$ Hz, 1H, H6), 8.26 (dd, $^3J_{45} = 8.1$ Hz, $^4J_{46} = 1.6$ Hz, 1H, H4); MS (70 eV): *m/z* (%) = 277 (14) [M^+], 220 (100) [$M^+ - t$Bu], 136 (98) [$M^+ - 2\,t$Bu – CO], 57 (97) [tBu$^+$]; $C_{15}H_{23}N_3O_2$ (277.4): calcd C 64.96, H 8.36, N 15.15; found C 64.21, H 8.46, N 15.09.

b) C_5H_3N-2,3-$(NHCH_2CMe_3)_2$ (**1a**): C_5H_3N-2,3-$(NHCOCMe_3)_2$ (8.8 g, 31.8 mmol) was added in small portions to a stirred suspension of $LiAlH_4$ (3.0 g, 79 mmol) in ether (100 mL). The mixture was allowed to react at room temperature for 1 week. Then it was cooled (0–10 °C) and cautiously hydrolyzed. $Al(OH)_3$ was filtered off, the solution dried with Na_2SO_4, and the solvent slowly evaporated. Solid, slightly yellow diamine **1a** (7.0 g, 28.1 mmol, 88%) was obtained. For further purification this was distilled (b.p.: 102–103 °C/0.05 Torr) or sublimed at 90 °C/0.01 Torr, m.p. 96–98 °C. (**1a** becomes brown upon contact with air.) ^{1}H NMR ($CDCl_3$): $\delta = 1.02$ (s, 9H, CH_3), 1.04 (s, 9H, CH_3), 2.79 (d, $J = 4.1$ Hz, 2H, 3-NCH_2), 2.87 (br t, 1H, NH), 3.25 (d, $J = 5.9$ Hz, 2H, 2-NCH_2), 4.27 (br t, 1H, NH), 6.56 (dd, $J = 7.5$, 5.1 Hz, 1H, H5), 6.80 (dd, $^3J_{45} = 7.5$ Hz, $^4J_{46} = 1.5$ Hz, 1H, H4), 7.71 (dd, $^3J_{5,6} = 5.1$ Hz, $^4J_{46} = 1.5$ Hz, 1H, H6); ^{13}C NMR ($CDCl_3$): $\delta = 27.6$, 27.7 (CMe_3), 31.3, 31.4 (CMe_3), 52.9, 56.2 (NCH_2), 113.2 (CH5), 117.8 (CH4), 131.9 (C_q3), 137.6 (CH6), 151.2 (C_q2); ^{1}H and ^{13}C NMR data in C_6D_6 see Table 1; ^{15}N NMR (C_6D_6, CH_3NO_2 cap.): $\delta = -330.7$ (NCH_2), -312.8 (NCH_2), -116.8 (pyrido-N); MS (70 eV); *m/z* (%) = 249.6 (16) [M^+], 192.4 (100) [$M^+ - t$Bu], 122.2 (33) [C_5H_3N-2,3-$(NH)_2CH^+$]; $C_{15}H_{27}N_3$ (249.4): calcd C 72.24, H 10.91, N 16.85; found C 72.04, H 11.13, N 16.50.

***N,N′*-dineopentyl-3,4-diaminopyridine (1b)**:

a) C_5H_3N-3,4-$(NHCOCMe_3)_2$: 3,4-Diaminopyridine (10.0 g, 91.6 mmol) was suspended in dry ether (100 mL) and NEt_3 (19.7 g, 27 mL, 195 mmol) and *t*BuCOCl (23.5 g, 24 mL, 195 mmol) were added dropwise at about 10 °C. After stirring for 5 d, the suspension was filtered, and the precipitate washed with ether and then with water. The residue was dried in vacuum over P_4O_{10} yielding the diamide (21.8 g, 78.6 mmol, 85.8%), m.p. 165–168 °C. It was soluble in $CHCl_3$ and MeOH, moderately soluble in THF and insoluble in ether or water. ^{1}H NMR ($CDCl_3$): $\delta = 1.28$ (s, 9H, CH_3), 1.35 (s, 9H, CH_3), 8.16 (br s, 1H, NH), 8.7 (br s, 1H, NH), 7.70 (d, $^3J_{56} = 5.6$ Hz, 1H, H5), 8.34 (s, 1H, H2), 8.35 (d, $^3J_{56} = 5.6$ Hz, 1H, H6); ^{13}C NMR ($CDCl_3$): $\delta = 27.4$, 27.6 (CMe_3), 39.5, 39.8 (CMe_3), 118.5 (CH5), 125.7 (C_q3), 139.6 (C_q4), 147.3, 147.4 (CH2/CH6), 178.3, 179.5 (C=O); MS (70 eV): *m/z* (%) = 277 (18) [M^+], 220 (29) [$M^+ - t$Bu], 86 (99), 57 (100) [tBu$^+$]; $C_{15}H_{23}N_3O_2$ (277.37): calcd C 64.91, H 8.36, N 15.15; found C 64.83, H 8.33, N 15.18.

b) C_5H_3N-3,4-$(NHCH_2CMe_3)_2$ (**1b**): C_5H_3N-3,4-$(NHCOCMe_3)_2$ (8.75 g, 31.5 mmol) was added in small portions to a stirred and cooled (10 °C) suspension of $LiAlH_4$ (3.0 g, 79 mmol) in THF (150 mL). After stirring overnight it was refluxed for 8 h, hydrolyzed, and washed with ether. The solution was dried over Na_2SO_4, the solvent evaporated, and the remaining solid sublimed at 123 °C/0.01 Torr to give colorless crystals of **1b** (4.0 g, 16.0 mmol, 51%), m.p. 125–127 °C, soluble in $CHCl_3$. ^{1}H NMR ($CDCl_3$): $\delta = 1.02$ (s, 9H, CH_3), 1.04 (s, 9H, CH_3), 2.78 (d, $J = 6.9$ Hz, 2H, 3-NCH_2), 2.66 (br t, $J = 6.9$ Hz, 1H, NH), 2.91 (d, $J = 5.9$ Hz, 2H, 4-NCH_2), 4.55 (br t, 1H, NH), 6.46 (d, $^3J_{56} = 5.4$ Hz, 1H, H5), 7.89 (s, 1H, H1), 7.98 (d, $^3J_{5,6} = 5.4$, 1H, H6); ^{13}C NMR ($CDCl_3$): $\delta = 27.6$, 27.7 (CMe_3), 31.6, 31.9 (CMe_3), 54.4, 58.0 (NCH_2), 104.3 (CH5), 131.4 (C_q3), 137.3 (CH2), 144.4 (CH6), 146.9

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(C_q4); MS (70 eV): *m/z* (%) = 249.5 (55) [M^+], 193.1 (92) [$M^+ - t$Bu], 122.9 (100) [C_5H_3N-3,4-$(NH)_2CH^+$]; $C_{15}H_{27}N_3$ (249.40): calcd C 72.24, H 10.91; found C 72.17, H 10.88.

2,2-Dichloro-1,3-dineopentylpyrido[*b*]-1,2-dihydro-1,3,2-diazasilole (**2a**): **1a** (12.5 g, 48.7 mmol) was dissolved in benzene (200 mL) and metalated at 15 °C with two equivalents of *n*BuLi (69.0 mL 1.45 M, 100 mmol) to give a red-brown solution. After 30 min, $SiCl_4$ (6.0 mL, 8.9 g, 52.4 mmol) was added dropwise. The color changed to green and after about 2 h back to brown. The suspension was stirred for 5 days, filtered, the solvent removed, and the residue distilled to give a yellow-orange viscous oil of **2a** (10.0 g, 28.9 mmol, 59 %), b.p. 97–104 °C/0.01 Torr, soluble in C_6H_6, $CHCl_3$. ^{1}H and ^{13}C NMR see Table 1; ^{15}N NMR (C_6D_6, CH_3NO_2 cap.): $\delta = -309.2$ (NCH_2), -294.5 (NCH_2), -116.4 (pyrido-N); ^{29}Si NMR (C_6D_6): $\delta = -24.0$; MS (EI 70 eV, selected data for $^{35}Cl_2$): *m/z* (%) = 345 (24) [M^+], 288 (100) [$M^+ - t$Bu], 232 (22) [$M^+ - 57 - 56$], 218 (41) [C_5H_3N-2,3-$N_2CHSiCl_2^+$], 36 (55) [HCl^+]; (no peak for $M^+ - Cl_2$); $C_{15}H_{25}Cl_2N_3Si$ (346.4): calcd C 52.01, H 7.27, N 12.13; found C 52.93, H 7.82, N 12.62.

2,2-Dichloro-1,3-dineopentyl-pyrido[*c*]-1,2-dihydro-1,3,2-diazasilole (**2b**): **1b** (6.5 g, 26.1 mmol) was dilithiated in benzene (100 mL) with *n*BuLi (40 mL 1.35 M in *n*-hexane, 54 mmol). After 30 min, $SiCl_4$ (3.5 mL, 5.2 g, 30.5 mmol) was added dropwise to the yellow suspension. The diamide dissolved, but after about 15 min a new precipitate was formed. The mixture was refluxed for 3 h, filtered after 2 d at RT and washed, the solvent was removed, and the remainder distilled at 120–125 °C/0.01 Torr to give a pale-yellow oil of **2b** (2.0 g, 5.8 mmol, 22 %), soluble in $CHCl_3$, THF, slightly soluble in benzene, which then slowly solidified. ^{1}H NMR ($CDCl_3$): $\delta = 1.09$ (s, 9H, CH_3), 1.10 (s, 9H, CH_3), 3.34 (s, 2H, NCH_2), 3.42 (s, 2H, NCH_2), 6.98 (d, $^3J_{56} = 6.1$ Hz, 1H, H5), 7.96 (s, 1H, H2), 8.08 (d, $^3J_{56} = 6{,}1$ Hz, 1H, H6); ^{13}C NMR ($CDCl_3$): $\delta = 28.6$, 28.8 (CMe_3), 33.8, 33.9 (CMe_3), 56.0, 56.3 (NCH_2), 106.1 (CH5), 119.9 (CH2), 134.0 (CH6), 137.3 (C_q3), 151.8 (C_q4); ^{29}Si NMR ($CDCl_3$): $\delta = -20.7$; ^{15}N NMR (C_6D_6, CH_3NO_2 cap. ext.): $\delta = -116.8$, -294.5, -309.2; MS (70 eV): *m/z* (%) = 345 (21) [M^+], 288 (100) [M^+-tBu], 220 (20) [C_5H_3N-3,4-$CHSiCl_2^+$], 36 (99) [HCl^+]; $C_{15}H_{25}Cl_2N_3Si$ (346.4): calcd C 52.01, H 7.27, N 12.13; found C 51.50, H 7.70, N 11.13.

1,3-Dineopentylpyrido[*b*]-1,3,2λ^2-diazasilole (**3a**): **2a** (2.0 g, 5.8 mmol) was dissolved in THF (30 mL) and stirred for 3 d at 15–20 °C with a piece of potassium (0.45 g, 11.5 mmol) to give a yellow, later red-brown, suspension. This was filtered, the solvent removed in vacuum, and the residue (crude yield ≈ 50 %) sublimed at 105 °C/10^{-5} Torr yielding pale yellow crystals of **3a** (100 mg, 0.36 mmol, 6 %), m.p. 64–65 °C, easily soluble in pentane, benzene, THF. (The crude yield was estimated according to mass of the residue and integral ratio of NCH_2 in ^{1}H NMR.) UV/Vis (*n*-hexane): λ_{max} (ε) = 302 (3300), 249 nm (5800); ^{1}H and ^{13}C NMR see Table 1; ^{29}Si NMR (C_6D_6): $\delta = +95.1$; MS (70 eV): *m/z* (%) = 275 (64) [M^+], 260 (13) [M^+ – Me], 218 (100) [$M^+ - t$Bu], 150 (26), 148 (26), 57 (11), 32 (56); $C_{15}H_{25}N_3Si$ (275.5): calcd C 65.40, H 9.15, N 15.25; found C 64.94, H 9.60, N 15.11.

1,3-Dineopentylpyrido[*b*]-1,3,2λ^2-diazagermole (**4a**): **1a** (0.87 g, 3.5 mmol) was dissolved in THF (20 mL) and dilithiated at -78 °C with *n*BuLi in hexane (5.0 mL, 1.45 M, 7.25 mmol). After 1 h a solution of $GeCl_2 \cdot$dioxane (0.88 g, 3.8 mmol) in THF was added dropwise at -78 °C and the mixture allowed to warm up to RT. THF was evaporated in vacuo and crude **4a** extracted with benzene. The solvent was removed and the residue (crude yield 80 %) sublimed at 100 °C/10^{-5} Torr to give pale yellow needles of **4a** (0.25 g, 0.8 mmol, 23 %), m.p. 118–120 °C, solubility as for **3a**. UV/Vis (*n*-hexane): λ_{max} (ε) = 360 (14000), 307 (5600), 241 nm (18000); ^{1}H and ^{13}C NMR see Table 1; ^{15}N NMR (C_6D_6, CH_3NO_2 cap. ext.): $\delta = -101$ (pyrido-N), $^{15}NCH_2$ within noise; ^{14}N NMR ($^{14}NCH_2$) $\delta = -203$ (br); MS (EI, 70 eV): *m/z* (%) = 324 (5) [M^+_{76Ge}], 322 (23) [M^+_{74Ge}], 320 (19) [M^+_{72Ge}], 318 (13) [M^+_{70Ge}], 267 (22) [$M^+_{76Ge} - t$Bu], 265 (100) [$M^+_{74Ge} - t$Bu], 263 (73) [$M^+_{72Ge} - t$Bu], 261 (54) [$M^+_{70Ge} - t$Bu], 196 (10), 194 (19), 192 (26), 190 (10); $C_{15}H_{25}N_3Ge$ (320.0): calcd C 56.30, H 7.87, N 13.13; found C 56.90, H 8.06, N 12.97.

1,3-Dineopentylpyrido[*b*]-1,3,2λ^2-diazastannole (**5a**): Compound **1a** (2.0 g, 8.02 mmol), dissolved in ether (100 mL), was dilithiated at -30 °C with *n*BuLi in hexane (13 mL, 1.3 M, 16.9 mmol). After 2 h, $SnCl_2$ (2.5 g, 13.2 mmol) was added. The color of the solution turned to dark red and within 10 min a slow precipitation of a solid began. The mixture was stirred for 3 d at room temperature, the solvent was evaporated and the remainder was sublimed at 160 °C (bath)/10^{-5} Torr. Compound **5a** was obtained as an orange solid (1.5 g, 4.1 mmol, 50 %), which was soluble in THF and slightly soluble in pentane, benzene, and ether. ^{1}H and ^{13}C NMR in Table 1; ^{119}Sn NMR (C_6D_6): $\delta = 241.6$ (br); ([D_8]THF): $\delta = 100.5$; $C_{15}H_{25}N_3Sn$ (366.09): calcd C 49.21, H 6.88, N 11.48; found C 47.70, H 7.17, N 11.00.

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