



Homologues of *N*-heterocyclic carbenes: Detection and electronic structure of *N*-bridgehead pyrido[*a*]-annelated 1,3,2-diazagermol-2-ylidenes

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ARTICLE INFO

Article history:

Received 2 September 2008

Received in revised form 27 October 2008

Accepted 7 November 2008

Available online 13 November 2008

Keywords:

Dilithium reagent

Germylene

Germanium

Silicon heterocycle

Pyridine

Quantum chemical calculation

Carbene

ABSTRACT

Novel *N*-bridgehead pyrido[*a*]-annelated 1,3,2-diazagermol-2-ylidenes **1a,b** were obtained from $\text{GeCl}_2 \cdot \text{dioxane}$ and dilithium reagents formed from *N*-*tert*-butyl pyridine-2-aldimines and excess lithium in THF whereas attempts to generate the analogous silylene by reduction of the dichloro-pyrido[*a*]-1,3,2-diazasilole **4a**, synthesized from SiCl_4 and the new dilithium reagent, failed. Characteristic chemical shifts of the pyrido ¹H and ¹³C nuclei between those of pyridine compounds and the not fully cyclodelocalized electron-rich **4a** with dihydropyridine substructure hint to a cyclodelocalized 10π electron system in **1a,b**. Quantum chemical investigations of a series of pyrido[*a*]- and benzo-annelated imidazol-2-ylidenes and their silylene and germylene homologues show for all compounds cyclodelocalized 10π-systems but for pyrido[*a*]-anellation an increase of the energy of the π-MO's relative to those of element(II) lone electron pairs which leads to destabilization compared to the benzo-annelated isomers.

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1. Introduction

The first heterocyclic diaminogermynes (NHGe) and diaminostannylenes (NHSn) [1,2] were discovered some years before stable monomer *N*-heterocyclic carbenes (NHC) [3], but the unexpected high stability of imidazol-2-ylidenes and the powerful development of the chemistry of NHCs and their use in transition metal catalysis [4] has increased the interest in their higher homologues and led soon to new NHGe [5,6], NHSn [7,8], the previously unknown *N*-heterocyclic silylenes (NHSi) [9,10], and recently also to charged systems such as cationic diaminogermynes [11]. Comparing investigations of related benzo-, pyrido[*b*]- and pyrido[*c*]-annelated NHSi, NHGe and NHSn [12] and NHC [13] of the imidazol-2-ylidene type, each with equal *N,N'*-substituents, show that the properties of the heavier homologues are distinct from those of the homologous *N*-heterocyclic carbenes, and that pyrido-annellation amplifies these differences. Pyrido[*b*]- and pyrido[*c*]-annelated dineopentyl-imidazol-2-ylidenes are stable and distillable in vacuum [13a] like the corresponding benzimidazol-2-ylidene [14]. Pyrido[*b*]-annelated 1,3-dineopentyl-1,3,2-diazasilol-2-ylidene and its homologous germylene and stannylene, however, are much more sensitive to heating than related benzoannelated

compounds and suffer from partial decomposition during high vacuum distillation (increasingly in the order $\text{NHSn} < \text{NHGe} \ll \text{NHSi}$). Pyrido[*c*]-annelated NHSi, NHGe or NHSn of this type could not even be detected using the same synthetic approach and reaction conditions despite according to calculations of isodesmic reactions the thermodynamic stability is the same as for the benzo- or pyrido[*b*]-annelated compounds [12a]. We therefore wondered if *N*-bridgehead pyrido[*a*]-annelated imidazol-2-ylidene homologues, isomers of the benzoannelated compounds, would be accessible and which properties they would display [15]. Recently reported pyrido[*a*]-annelated imidazol-2-ylidenes [16] are stable at ordinary temperature if sterically protected and display the ¹³C(II) nuclei upfield from non-annelated imidazol-2-ylidenes [3] whereas benzo- [14] and pyrido[*b*]- or pyrido[*c*]-annellation [13a] cause downfield shifts. Thus pyrido[*a*]-annellation should lead to heterocycles with increased electron density at the two-valent heteroelement.

2. Results and discussion

2.1. Synthesis

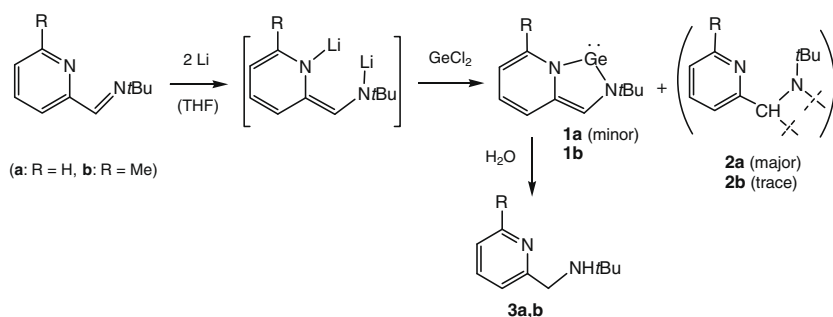
N-Heterocyclic germynes are conveniently synthesized from dilithium diamides by reaction with $\text{GeCl}_2 \cdot \text{dioxane}$ [5,6,12]. The dilithium reagents required to obtain the target germynes **1** were hitherto unknown. Since α,α'-dipyridyl as well as 1,2-diimines are

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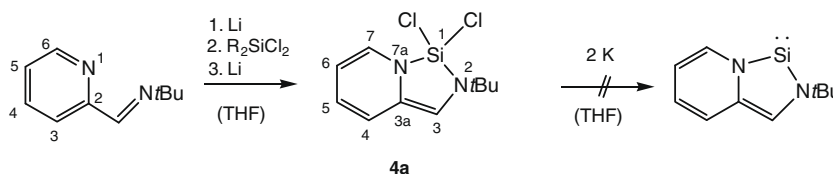
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known to form silicon heterocycles when treated with excess lithium in THF and then with SiCl_4 [17,18], it was anticipated that pyridine-2-aldimines, despite the lack of symmetry and different electronic nature might also form dilithium reagents. A defined lithium compound could so far not be isolated from the solution formed from 2-(*N*-*tert*-butyl)pyridalimine and excess lithium in THF, but reaction of the solution with $\text{GeCl}_2 \cdot \text{dioxane}$ as well as with SiCl_4 provided the expected heterocycles (Scheme 1). The pyrido[*a*]-annelated 1,3,2-diazagermol-ylidene **1a** was detected in the crude product in varying amounts, usually 20–30 mol%, besides compound **2a** (30–40%), formed by decomposition of **1a**, and unconverted aldimine (up to 40%). Compound **2a** is a highly symmetric 2-pyridylCHN*t*Bu compound and at least formally derived from **1a** by extrusion of germanium. The germylene **1a** was found to be unstable and decomposed in C_6D_6 solution at room temperature, the major part within about one day. If the reaction time was kept short (0.5–1 h) and thus decomposition of **1a** remained low, the compound could be separated by vacuum distillation at 75–80 °C/10⁻² Torr as a slightly brownish oil, weakly contaminated (content of **1a** ca. 85 mol%) by pyridinealdimine, but free of **2a**. After one day at room temperature, this distilled fraction again displayed the signals of **2a** indicating decomposition of **1a** to **2a**. Only storage below 4 °C prevented the decay. Traces of **3a** in NMR samples of distilled **1a** in C_6D_6 indicate very high moisture sensitivity of the germylene.

As the recently reported pyrido[*a*]-imidazol-2-ylidene homologue of **1a**, equally unstable without additional steric protection, gives stable derivatives by introduction of either a methyl group in 6-position or a fused benzene ring (quinoline-annelation) [16], 6-methyl-2-*tert*-butylaldiminopyridine and 2-*tert*-butylaldiminopyridine was subjected to reductive dilithiation in THF and subsequent conversion with $\text{GeCl}_2 \cdot \text{dioxane}$ in THF at -78 °C. The iminoquinoline failed to give a germylene, but the 6-methyl-2-iminopyridine provided **1b** in good yield (60–70 mol% in the crude product). Compound **2b** was detected only as a minor component and **3b** as a trace. Compound **1b** was stable in C_6D_6 for more than a week at room temperature, can be distilled, but similar to **1a** is highly sensitive to moisture and air as indicated by immediate disappearance of the intense orange-red color and formation of **3b**.



Scheme 1. Pyrido[*a*]-annelated *N*-heterocyclic germylenes **1a,b** and side products.



Scheme 2. Synthesis of 1,1-dichloro-2-*tert*-butyl-1,3,2-diazasilolo[1,5-*a*]pyridine **4a**.

Attempts to synthesize related tin(II) heterocycles from the dilithium reagents and SnCl_2 in THF led to a black precipitate of elemental tin even at low temperature, either by direct reduction of SnCl_2 by the dilithiated dihydropyridine species or by reductive decomposition of the product. Reaction of 2-*tert*-butylaldiminopyridine with lithium and SiCl_4 in THF gave the expected pyrido[*a*]-annelated dichloro-1,3,2-diazasilole **4a** (Scheme 2) in moderate yield as a highly moisture and air sensitive red oil, which formed compact dark red crystals after distillation. So far, only non-functional, bulky organosubstituted pyrido[*a*]-1,3,2-diazasiloles are known, obtained by Weidenbruch et al. by trapping reactions of photochemically generated di-*tert*-butyl- or dimethylsilylene with *N*-*tert*-butyl pyridine-2-alimine [19]. Attempts to transform **4a** to the respective silylene by reduction with potassium-sodium alloy or with potassium in THF, so far the only known route to convert dichlorosilicon(IV) precursors to the corresponding diaminosilylenes [9,10,12a], failed under various conditions including low temperature. No downfield silicon(II) signals could be detected by ²⁹Si NMR in the crude products. Possibly potassium is unsuitable in this case, but since **1a** proved to be labile and silylenes are usually less stable than the homologous germylens, the expected low stability of the envisaged silylene is thought to be the main reason.

2.2. Structure elucidation

The structure elucidation of the dihydropyridine-type annelated diazasilole **4a** is based on conclusive NMR and mass spectrometric data and satisfying elemental analyses. HH- and CH-COSY experiments (Fig. 1) along with typical values of ³J_{HH} and long range couplings allowed an unambiguous assignment of all proton and ¹³C NMR signals. The strong upfield shifts of the proton and carbon resonances except of C-4 and the *tert*-butyl group display the loss of aromaticity of the pyridine system and formation of a very electron-rich conjugated triene system containing two π -donor nitrogen atoms in a terminal and a terminal/cross (*N*-bridging atom) position. The stronger upfield shifts concern C-7, C-5 and C-3a in conjugated positions ($\Delta\delta = -21.5, -16.9, -29.5$ ppm) and in particular C-3 ($\Delta\delta = -53.4$ ppm), showing that the five-membered ring profits the most from the high electron density gained in the

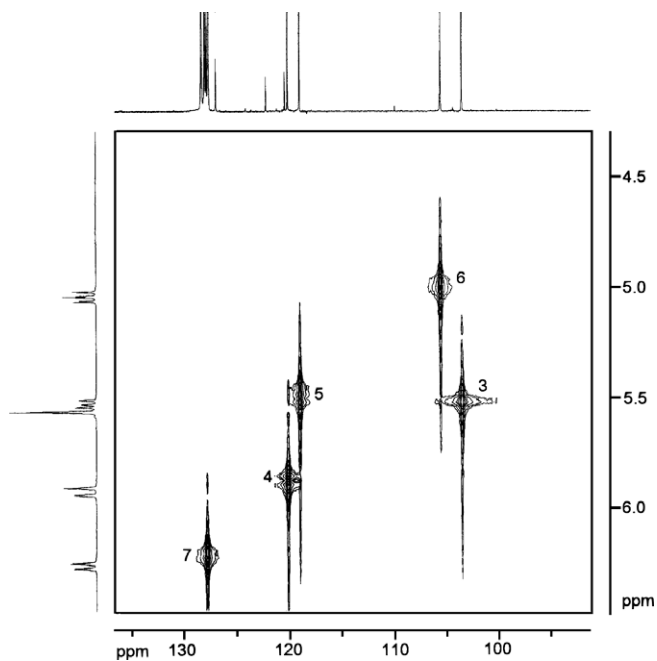


Fig. 1. CH-COSY presentation of **4a**.

reduction. Likewise, the ^{29}Si resonance ($\delta = -39.5$ ppm) is strongly upfield shifted compared to that of the benzoannelated isomer ($\Delta\delta = -15.4$ [9a]) and pyrido[b]- and pyrido[c]-annelated dichlorodiazasiloles ($\Delta\delta = -15.5$ and -18.8 ppm [12a]).

The pyrido[a]-annelated *N*-heterocyclic germylene **1a**, which slowly decomposes at room temperature, can be easily observed by ^1H and ^{13}C NMR spectroscopy alongside unconverted pyridine-2-alimine and the 2-pyridyl-CH-*Nt*Bu compound **2a** by characteristic chemical shifts. Conclusive evidence is given by NMR data of the distilled samples of **1a** and **1b**. The assignment of the ^{13}C NMR resonances of **1a,b** is based on similarities with those of the dihydropyridine ring-carbon nuclei C-3 to C-6 of **4a**. The proton signals of **1a,b**, however, are strongly downfield shifted as compared to those of **4a**. For CH-7 and CH-3, adjacent to the nitrogen atoms coordinating to Ge(II), the differences are largest with $\Delta\delta = 1.75$ and ca. 1.6 ppm; for CH-4,5 and 6 the differences amount to $\Delta\delta = 1.11$, 0.73 and 0.57 ppm, respectively and for the *tert*-butyl group $\Delta\delta = 0.3$ ppm. These differences suggest ring current effects in **1a,b** and thus a cyclodelocalized 10π -electron system like the one in benzo- and pyrido[b]-diazagermoles [12a,25] while cyclodelocalization is lacking in **4a**. The particular strong downfield shifts for those carbon atoms close to germanium(II) may be accomplished by core electrons, an effect known for carbon atoms adjacent to the heteroatom in heavier group15 heterobenzenes [21]. The monomeric nature of the novel germylenes is evident from the rather low boiling point and the elemental composition from the molecular ions in the mass spectrum of **1a** and HRMS of **1b**, each with its characteristic germanium isotopic patterns (Fig. 2). Strong fragment peaks are formed by loss of C_4H_8 and C_4H_9 which lead to cations were the principal NHGe structure is unchanged. The 2-pyridyl-CH-*Nt*Bu fragment of **2a,b** is evident from typical ^1H and ^{13}C chemical shifts and proton couplings, while the singlets for CH at $\delta^1\text{H}$ 4.65 and $\delta^{13}\text{C}$ 73.3 and only one set of cross-peaks in the HH-COSY spectrum hint to a highly symmetric *t*BuN-CH(pyr) compound as is the case in a four-membered 1,3-diazetidone ring with symmetrically arranged substituents (by steric reasons probably all-*trans*). The ^{13}C satellites show a rather large one-bond coupling ($d, {}^1J_{\text{CH}} = 141$ Hz) for the sp^3 -carbon atoms which is known for α -C in azetidines while this coupling is smaller in the six-mem-

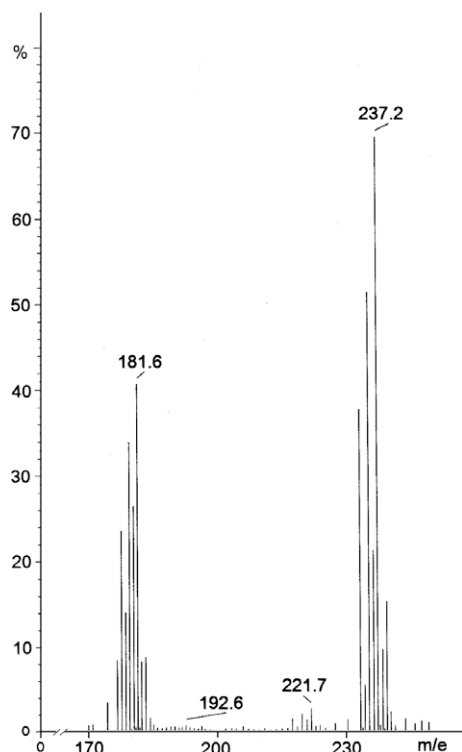


Fig. 2. Germanium-isotope pattern of the molecular and $\text{M}^+ - \text{C}_4\text{H}_6/\text{M}^+ - \text{C}_4\text{H}_7$ ions of **1a**.

bered piperidine ring [22]. Therefore, a four-membered cyclodimeric structure of **2** is suggested despite the appearance of averaged singlets may be due also to a symmetric six-membered triazacyclohexane structure at room temperature [23].

2.3. Electronic structure

The proton and carbon chemical shifts of the pyridine nuclei of **1a,b** are in the majority found between those of the pyridine-2-aldimines or **2a,b** and **4a** indicating a strong delocalization and a π -density distribution between that in pyridine and in electron-rich dihydropyridine π -systems. The upfield shift compared to pyridines is observed also for the carbene homologues of **1a,b**, pyrido[a]-annelated NHCs (p_{ya}NHC) [16], where in particular the $^{13}\text{C}(\text{II})$ resonance is strongly upfield shifted compared to the values found in related pyrido[b]- and pyrido[c]-annelated NHCs or isomeric benzimidazol-2-ylidenes [14]. High basicity of the two-valent heteroelement would be desirable for use in catalysis, but as the respective p_{ya}NHC transition metal complexes show ordinary properties and NMR data [16], the effect may be due rather to a high π -density at C(II) of the ligand. To obtain more insight into the electronic structure and relative stabilities of isomeric benzo- and pyrido[a]-NHE heterocycles (E = two-valent C, Si, Ge) and the higher-shell influence of the two-valent group 14 element, quantum chemical calculations with NH-model compounds were carried out. Geometry optimization was performed on the B3LYP/cc-pVTZ level of theory [24]. Calculated total and relative energies of the model compounds as well as energies of the four highest occupied molecular orbitals are depicted in Table 1.

It can be seen that the pyrido[a]-annelated NHE heterocycles are generally much less stable than the isomeric benzo-annelated compounds. The destabilization is highest for the silylene and lowest for the carbene. An isomeric three-membered pyridyl germylene, that might form formally by addition of lithium at the C=N bond and subsequent reaction with germanium dichloride, was also in-

Table 1
Calculated total and orbital energies of isomeric benzo- and pyrido[*a*]-annellated NHC, NHSi and NHGe model compounds.

Model compound (a.u.)	$E_{\text{tot.}}$ (B3LYP/cc-pVTZ)	$E_{\text{rel.}}$ (kcal/mol)	E_{MO} (eV) (B3LYP/cc-pVTZ)
	-379.9610901	0.00	-6.11 (n_{C}) -6.54 (π) -6.75 (π) -9.02 (π)
	-379.9312108	18.75	-5.50 (π) -6.06 (n_{C}) -7.58 (π) -8.68 (π)
	-631.450017132	0.00	-5.77 (π) -6.39 (π) -6.87 (n_{Si}) -8.79 (π)
	-631.4119276	23.90	-4.73 (π) -6.80 (n_{Si}) -7.31 (π) -8.28 (π)
	-2419.01986274	0.00	-5.54 (π) -6.24 (π) -7.34 (n_{Ge}) -8.64 (π)
	-2418.9849921	21.88	-4.52 (π) -7.20 (π) -7.23 (n_{Ge}) -8.15 (π)
	-2418.9308649	55.85	-

cluded into the calculations but found to be highly unstable despite the aromaticity of the pyridine ring preserved in the germylene. This shows the strong effect of the second Ge–N bond on the stabilization. Another aspect which is of interest with respect to the reactivity is the energy of the HOMOs. These are considerably higher for the pyrido[*a*]- than for the isomeric benzo-annellated NHC and suggest high reduction potential explaining the sensitivity to oxidation. The orbital energies of the E(II) electron lone pairs in the respective isomers are almost the same, they are only slightly lower in the pyrido compared to the benzo-compounds. On the other hand, the first π -orbitals in the benzo-compounds are strongly stabilized compared to those of the pyrido derivatives. This indicates that the stability difference between the two types is caused by different aromatic structures. It is remarkable that the HOMO of the pyrido[*a*]-annellated NHC is a π -state while that of the benzimidazol-2-ylidene is the carbon(II) electron lone pair, as is the case in the pyrido[*b*]- and pyrido[*c*]-annellated NHCs [13a]. The high π -density explains the high shielding of the ^{13}C (II) NMR signals of p π aNHCs relative to other annellated imidazol-2-ylidenes where repulsion of π -density by the electron lone pair localized at the sp^2 -hybridized C(II) is more efficient. The energies of the E(II) electron lone pairs decrease considerably for the higher homologues, which predicts decreasing donor strengths in the order NHC > NHSi > NHGe which is in agreement with the re-

ported properties [4–6,10] and was recently also confirmed for complexes with benzo-annellated NHGe and NHSn [25,26]. The opposite trend for the orbital energies of the electron lone pairs and the highest π -states, which reflects the lower (p–p) π bonding strength for the heavier elements, is illustrated by the correlation of the ionization potentials calculated by using the ROVGF/cc-pVDZ level of theory on the optimized geometries of the pyrido[*a*]-annellated NHCs (Table 2, Fig. 3). The validity of this method was shown earlier [13a]. Applied to *N,N'*-dineopentyl substituted

Table 2
Calculated IPs (eV) of pyrido[*a*]-annellated NHC, NHSi and NHGe model compounds using ROVGF/cc-pVTZ and B3LYP/cc-pVTZ [24] optimized geometries.

7.52	6.61	6.38
8.44	9.08	9.18
9.61	9.29	9.40
10.83	10.35	10.22
12.35	11.88	11.73
12.69	12.05	11.81
13.28	12.79	12.70

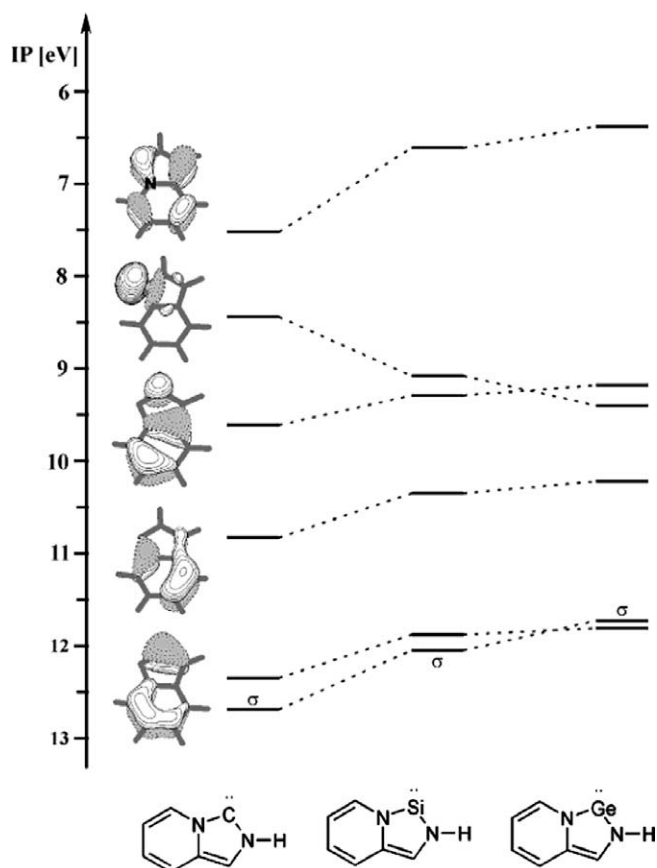


Fig. 3. IP correlation scheme and orbital presentation of pyrido[a]-annelated NHC, NHSi and NHGe model compounds (position of the bridgehead N-atom indicated in the HOMO).

benzo- and pyrido[b]-annelated NHEs it provided good correlation of calculated IPs and experimental vertical ionization energies, determined by photoelectron spectroscopy [12a,13a,20b], and it demonstrated the same trends as shown in Fig. 3, with the only difference that for benzo-, pyrido[b]- and pyrido[c]-NHCs, the C(II) electron lone pair is the HOMO and determines the reactivity.

3. Conclusions

N-Bridgehead pyrido[a]-annelated 1,3,2-diazagermol-2-ylidenes are accessible from $\text{GeCl}_2 \cdot \text{dioxane}$ and dilithium reagents formed from *N*-*tert*-butyl pyridine-2-aldimines and excess lithium in THF. Without steric protection they are thermally labile at room temperature and decompose with (formal) extrusion of germanium to form pyridyl substituted nitrogen heterocycles $(\text{pyrNtBu})_2$, but with substituents at both sides of Ge(II), a 6-methyl and *N*-*tert*-butyl group, they become storable.

The extreme sensitivity to air, moisture and any OH groups is not diminished by the second substituent and complicates purification and application studies. Theoretical studies within series of pyrido[a]- and benzo-annelated imidazol-2-ylidene model compounds and their silylene and germylene counterparts show lower stability of the pyrido[a]-annelated heterocycles but similar delocalized 10π -systems and trends for the orbital energies of the E(II) electron lone pairs and π -MOs. The kinetic (thermal) stability of the pyrido[a]-annelated germylenes **1** is also lower than that of the symmetric benzo-annelated *N,N'*-dineopentyl-diazagermol-2-ylidene [12], but is comparable to that of the pyrido[b]- and higher than that of the pyrido[c]-annelated *N,N'*-dineopentyl-diazagermol-

2-ylidene. The quantum chemical calculations of the pyrido[a]-annelated NHE model compounds show for the reactivity controlling HOMO a nodal plane through the pyridine nitrogen (see Fig. 3), similarly as found for a pyrido[b]-annelated NHSi model compound. This explains the similar kinetic stability whereas the pyrido[c]-annelated NHSi possesses a strongly unsymmetric π -density distribution which lowers the activation energy for decomposition reactions.

4. Experimental

4.1. General

All reactions were carried out under an atmosphere of dry argon using Schlenk techniques. Glassware was heat-dried in vacuum; solvents were dried with sodium/benzophenone and freshly distilled before use. The pyridine-2-aldimines were prepared in analogy to a known procedure [27], $\text{GeCl}_2 \cdot \text{dioxane}$ was initially synthesized according to Ref. [28], later purchased from ABCR GmbH. NMR spectra were recorded on a multinuclear FT-NMR spectrometer ARX300 (Bruker) at 300.1 (^1H), 75.5 (^{13}C), and 59.6 (^{29}Si) MHz. Shift references are benzene ($\delta = 7.16$ and 128.0 ppm) for ^1H and ^{13}C and tetramethylsilane for ^{29}Si NMR. Assignment numbers follow the nomenclature and are given in Scheme 2. Coupling constants refer to J_{HH} unless stated otherwise. Assignments are based on HH- and CH-COSY NMR experiments with **4a** and DEPT ^{13}C NMR spectra for selected compounds. Melting points (uncorrected) were determined with a Sanyo Gallenkamp melting point apparatus, elemental analysis with a CHNS-932 analyzer from LECO using standard conditions.

4.2. *N*-*tert*-Butyl-2-pyridyl-aldimine

This compound was prepared from pyridine-2-aldehyde and *tert*-butylamine in toluene in the presence of *p*-toluenesulfonic acid [27], yield 90%, bp. 52–58 °C/0.15 Torr, yellow liquid. IR (cap.): $\bar{\nu} = 1678$ m, 1645 s, 1588 s, 1568 s, 1467 s, 1436 s, 1364 m, 1388 s, 1292 m, 1227 s, 1210 vs, 1146 m, 1090 m, 994 m, 972 m, 910 s, 861 m, 775 s, 744 cm^{-1} . ^1H NMR (C_6D_6): δ 1.19 (s, 9H, CMe_3), 6.68 (ddd, $^3J_{45} = 7.4$, $^3J_{56} = 4.8$, $^4J_{35} = 1.2$ Hz, 1H, H-5), 7.10 (tdd, $^3J_{34} = 8.0$, $^3J_{45} = 7.4$, $^4J_{46} = 1.7$ Hz, 1H, H-4), 8.20 (dt, $^3J_{34} = 7.9$, $^4J_{35} = 1.2$, $^5J_{36} = 1.1$ Hz, 1H, H-3), 8.50 (ddd, $^3J_{56} = 4.8$, $^4J_{46} = 1.7$, $^5J_{36} = 1.0$ Hz, 1H, H-6), 8.57 (s, 1H, CH=N) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 28.4 (CMe_3), 57.5 (CMe_3), 120.4 (C-3) 124.1 (C-5), 135.8 (C-4), 149.4 (C-6), 156.4 (C_q -2), 156.7 (C=N) ppm. Anal. Calc. for $\text{C}_{10}\text{H}_{14}\text{N}_2$ (162.23): C, 74.03; H, 8.70; N, 17.27. Found: C, 73.76; H, 8.53; N, 17.31%.

4.3. *N*-*tert*-Butyl-6-methyl-2-pyridyl-aldimine

This compound was obtained by reaction of 6-methyl-pyridine-2-aldehyde (5.0 g, 41.3 mmol) with *tert*-butylamine (13.0 mL, 123.8 mmol) in toluene (100 mL) in the presence of a small amount of *p*-toluenesulfonic acid for 2 d at room temperature. It was purified by high vacuum distillation of the crude product at 75 °C/ 10^{-4} Torr yielding 6.4 g (88%) of colorless oil. ^1H NMR (C_6D_6): δ 1.21 (s, 9H, CMe_3), 2.42 (s, 3H, Me), 6.62 (d, $^3J = 7.7$ Hz, 1H, H-5), 7.08 (t, $^3J = 7.8$ Hz, 1H, H-4), 8.10 (d, $^3J = 7.8$ Hz, 1H, H-3), 8.57 (s, 1H, CH=N) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 24.96 (Me), 30.3 (CMe_3), 58.22 (CMe_3), 118.31 (CH-3), 124.27 (CH-5), 136.97 (CH-4), 156.66 (C_q -2), 157.91 (CH=N), 158.60 (C_q -6) ppm. MS (EI, 70 eV, 20 °C): m/z (%) = 176 (5), $[\text{M}^+]$, 162 (4), 161 (39), $[\text{M}^+ - \text{Me}]$, 149 (8), 144 (10), 121 (21), 120 (55), 119 (12) $[\text{M}^+ - \text{C}_4\text{H}_9]$, 107 (5), 94 (12), 93 (100), 92 (14), 65 (13), 57 (39). Anal. Calc. for $\text{C}_{11}\text{H}_{16}\text{N}_2$ (176.26): C, 74.96; H, 9.15; N, 15.89. Found: C, 74.58; H, 9.09; N, 13.72%.

4.4. 2-*tert*-Butyl-1,2-dihydro-1,3,2-diazagermolol[1,5-*a*]pyridine-1-ylidene (**1a**)

Lithium suspension (0.15 g, 21.6 mmol) was reacted with *N*-*tert*-butyl-2-pyridyl-aldimine (1.2 g, 7.5 mmol) in THF (50 mL) for 2 h at room temperature. The red-brown solution was added through glass wool slowly at 0 °C to a solution of $\text{GeCl}_2 \cdot \text{dioxane}$ (1.75 g, 7.6 mmol) in THF (100 mL). The mixture was stirred for 2 h, THF was evaporated in vacuum, and the residue was extracted with benzene. The solvent was removed and the residue distilled in vacuum. The second fraction, a red-brown oil (0.52 g) with bp. 75–80 °C/10⁻² Torr, was identified by characteristic ¹H and ¹³C NMR and mass spectrometric data as slightly contaminated **1a**. Impurities were small amounts of the pyridine-2-alidime and **2a** (by ¹H integration in sum ca. 5 mol%) and a trace of **3a** when C_6D_6 was used without drying by LiAlH_4 . Germylene **1a**: ¹H (and HH-COSY) NMR (C_6D_6): δ 1.39 (s, 9H, CMe_3), 5.46 (ddd, ³ $J_{67} = 7.0$, ³ $J_{56} = 6.1$, ⁴ $J_{46} = 1.2$ Hz, 1H, H-6), 6.15 (ddd, ³ $J_{45} = 9.0$, ³ $J_{56} = 6.0$, ⁴ $J_{57} = 1.1$ Hz, 1H, H-5), 6.91 (ddd, ³ $J_{45} = 9.0$, ⁴ $J_{46} = 1.2$, ⁵ $J_{47} = 1.1$ Hz, 1H, H-4), 7.06 (s, 1H, H-3), 7.87 (ddd, ³ $J_{67} = 7.0$, ⁴ $J_{57} = 1.1$, ⁵ $J_{47} = 1.1$ Hz, 1H, H-7) ppm. ¹³C{¹H} (and DEPT) NMR (C_6D_6): δ 33.81 (CMe_3), 57.30 (CMe_3), 106.74 (CH-6), 116.24 (CH-5), 120.75 (CH-4), 122.77 (CH-3), 123.64 (CH-7) ppm; C_q -3a uncertain. MS (EI, 70 eV, 260 °C): 240 (2), 239 (15) [MH^+ (⁷⁶Ge)], 237 (70) [MH^+ (⁷⁴Ge)], 235 (51) [MH^+ (⁷²Ge)], 233 (38) [MH^+ (⁷⁰Ge)], 183 (8) [MH_2^+ -tBu (⁷⁶Ge)], 181 (40) [MH_2^+ -tBu (⁷⁴Ge)], 179 (34) [MH_2^+ -tBu (⁷²Ge)], 177 (23) [MH_2^+ -tBu (⁷⁰Ge)], 165 (57), 147 (37), 107 (100), 179 (49), 57 (39) [tBu]. Compound **2a**. ¹H NMR (C_6D_6): δ 0.95 (s, CMe_3), 4.65 (s, NCH), 6.60 (superimposed t, H-5), 7.10 (superimposed t, H-4), 7.59 (d br, ³ $J = 7.8$ Hz, H-3), 8.34 (d, ³ $J = 4.8$ Hz, H-6). ¹³C{¹H} and DEPT NMR (C_6D_6): δ 32.59 (CMe_3), 54.34 (CMe_3), 73.27 (CH), 121.38 (CH-3), 122.77 (CH-5), 136.51 (CH-4), 147.36 (CH-6), 166.69 (C_q -2). Hydrolysis product **3a**: ¹H NMR (C_6D_6): δ 1.05 (s, CMe_3), 1.39 (br, NH), 3.85 (d, ³ $J = 7.4$ Hz, NCH_2), 6.63 (superimposed t, H-5), 7.11 (superimposed t, H-4), 7.19 (d br, ³ $J = 7.8$ Hz, H-3), 8.20 (superimposed d, H-6).

4.5. 2-*tert*-Butyl-7-methyl-1,2-dihydro-1,3,2-diazagermolol [1,5-*a*]pyridine-1-ylidene (**1b**)

Li (40 mg, 5.68 mmol) was added to a solution of *N*-*tert*-butyl-6-methyl-2-pyridyl-aldimine (250 mg, 1.42 mmol) in THF (15 mL) at room temperature and activated by sonification. After stirring overnight excess lithium was removed by filtration. The red-brown solution was cooled to -78 °C, and $\text{GeCl}_2 \cdot \text{dioxane}$ (362 mg, 1.56 mmol) was added as a solid. The mixture was stirred for 6 h at room temperature, the solvent was evaporated in vacuum, and the residue was extracted with *n*-hexane to give 116 mg orange-red viscous oil. NMR-analysis indicated impure **1b** (ca. 70 mol% by ¹H integration of tBu). Minor impurities detected by NMR were **2b** (15 mol%), the pyridine-2-alidimine and **3b** (each 7 mol%). Distillation at 78–85 °C/10⁻² Torr (bath temperature) furnished **1b** slightly contaminated by the aldimine. Compound **1b** was stable in C_6D_6 for more than 6 d at room temperature but is highly sensitive to air, moisture and silica gel, which prevented further purification by chromatography. Germylene **1b**: ¹H NMR (C_6D_6 , ref. C_6H_6 δ 7.16): δ 1.46 (s, 9H, CMe_3), 2.26 (s, 3H, Me), 5.48 (d, ³ $J = 6.2$ Hz, 1H, H-6), 6.38 (dd, ³ $J = 9.0$, 6.2 Hz, 1H, H-5), 7.07 (d, ³ $J = 9.2$ Hz, 1H, H-4), 7.34 (s, 1H, H-3). ¹³C{¹H} NMR (C_6D_6 , ref. C_6H_6 δ 128.7): δ 23.87 (Me), 33.90 (CMe_3), 57.34 (CMe_3), 105.93 (CH-6), 118.07 (CH-5), 121.22, 121.88 (CH-3, CH-4), 137.38, 144.92 (C_q -7, C_q -3a). HRMS (EI, 70 eV): Calc. for $\text{C}_{11}\text{H}_{16}\text{N}_2\text{Ge}$ 250.0527 (100%), found 250.0504; the isotopic pattern of the molecular cation observed is in accordance with the calculated intensity ratios. Impurity **2b**: ¹H NMR (C_6D_6): δ 0.98 (s, CMe_3), 2.47 (s, 3H, Me), 4.61 (s, NCH), 6.56 (d, ³ $J = 7.7$ Hz, H-5), 7.13 (superimposed t, H-4), 7.48 (d,

³ $J = 7.7$ Hz, H-3). Hydrolysis product **3b**: ¹H NMR (C_6D_6 , ref. C_6H_6 δ 7.16): δ 1.07 (s, CMe_3), 2.43 (s, 3H, Me), 3.89 (d, ³ $J = 7.2$ Hz, NCH_2), 6.62 (d, ³ $J = 7.1$ Hz, H-5), H-4 and H-3 superimposed. ¹³C{¹H} NMR (C_6D_6 , ref. C_6H_6 δ 128.7): δ 25.18 (Me), 29.92 (CMe_3), 49.86 (NCH_2), 50.98 (CMe_3), 119.85 (CH-3), 121.88 (CH-5), 136.88 (CH-4); C_q in noise.

4.6. 2-*tert*-Butyl-1,1-dichloro-1,2-dihydro-1,3,2-diazasilolol[1,5-*a*]pyridine (**4a**)

A lithium suspension (0.45 g, 64.8 mmol) was added to a solution of *N*-*tert*-butyl-2-pyridyl-aldimine (10.0 g, 61.7 mmol) in THF (150 mL) and stirred at room temperature until the metal was dissolved (ca. 2 h, slightly exothermic reaction). The red-brown solution was cooled to 0–5 °C, and SiCl_4 (7.5 mL, 65.5 mmol) was added dropwise. At first the mixture became colorless, then an orange brown solid precipitated. After stirring for 2 h at 20 °C, a further portion of Li suspension (0.45 g, 64.8 mmol) was added and the brown mixture stirred overnight at 20 °C. THF was removed in vacuum, and the residue was extracted with benzene. Vacuum distillation provided **4a** along with small amounts of 2- $\text{C}_5\text{H}_4\text{NCH}_2\text{N}(\text{tBu})\text{SiCl}_3$. Rectification at 73–74 °C/0.05 Torr furnished 6.2 g (38%) of pure deeply orange **4a**, crystallizing on cooling, mp. 39–43 °C (dec.). IR (cap.): $\bar{\nu} = 1624$ m, 1589 s, 1470 m, 1436 m, 1397 m, 1369 s, 1315 s, 1265 m, 1242 vs, 1207 s, 1150 vs, 1135 s, 1103 s, 1075 vs, 852 m, 727 vs, 698 m, 675 m cm^{-1} . ¹H (and HH-COSY) NMR (C_6D_6): δ 1.16 (s, 9H, CMe_3), 4.99 (ddd, ³ $J_{67} = 7.1$, ³ $J_{56} = 5.9$, ⁴ $J_{46} = 1.1$ Hz, 1H, H-6), 5.49 (ddd, ³ $J_{45} = 9.7$, ³ $J_{56} = 5.9$, ⁴ $J_{57} = 1.1$ Hz, 1H, H-5), 5.51 (s, 1H, H-3) 5.88 (ddd, ³ $J_{45} = 9.7$, ⁴ $J_{46} = 1.1$, ⁵ $J_{47} = 1.1$ Hz, 1H, H-4), 6.23 (ddd, ³ $J_{67} = 7.2$, ⁴ $J_{57} = 1.1$, ⁵ $J_{47} = 1.1$ Hz, 1H, H-7) ppm. ¹³C{¹H} (and CH-COSY) NMR (C_6D_6): δ 30.4 (CMe_3), 52.9 (CMe_3), 103.4 (CH-3), 105.5 (CH-6), 118.9 (CH-5), 120.0 (CH-4), 126.9 (C_q -3a), 127.8 (CH-7) ppm. ²⁹Si NMR (C_6D_6): δ -39.5 ppm. MS (EI, 70 eV, 25 °C): selected data for ³⁵Cl, m/z (%) = 261 (20), 260 (28) [M^+], 245 (15) [M^+ -Me], 203 (100) [M^+ -tBu], 176 (18), 149 (26), 106 (13), 78 (32), 57 (19) [tBu], 32 (56). Anal. Calc. for $\text{C}_{10}\text{H}_{14}\text{Cl}_2\text{N}_2\text{Si}$ (261.22): C, 45.98; H, 5.40; N, 10.73; Cl, 27.14. Found: C, 45.64; H, 5.64; N, 10.84; Cl, 27.25%. 2- $\text{C}_5\text{H}_4\text{NCH}_2\text{N}(\text{tBu})\text{SiCl}_3$: ¹H NMR (C_6D_6): δ 1.33 (s, 9H, CMe_3), 4.23 (s, 2H, NCH_2), 6.56 (t br, ³ $J = 7.5$, 5.3 Hz, 1H, H-5), 6.80 (d br, ³ $J_{34} = 7.9$ Hz, 1H, H-3), 6.98 (td, ³ $J = 7.9$, 7.5, ⁴ $J_{46} = 1.7$ Hz, 1H, H-4), 8.41 (ddd, ³ $J_{65} = 5.3$, ⁴ $J_{64} = 1.5$, ⁴ $J_{63} = 1.1$ Hz, 1H, H-6) ppm. ¹³C{¹H} NMR (C_6D_6): δ 30.86 (CMe_3), 49.84 (NCH_2), 56.53, (CMe_3), 120.31 (C-3), 122.15 (C-5), 137.38 (C-4), 146.18 (C-6), 158.37 (C_q -2) ppm.

5. Quantum chemical studies

Quantum chemical calculations were performed for all investigated molecules by the GAUSSIAN 03 program package [24]. All of the structures were optimized at the B3LYP/cc-pVTZ level of theory. The stationary points were characterized by second-derivative calculations using the same models. For comparison with the PE spectra of 1,3-dineopentyl-benzimidazol-2-ylidene [13a], the corresponding silylene [12a,20b] and germylene [25a], and for the IP correlation scheme (Fig. 3) the ionization potentials were calculated at the ROVGF/cc-pVDZ level of theory using the optimized geometries.

Acknowledgements

Support of this work by the Deutsche Forschungsgemeinschaft and a grant for A.I.O. is gratefully acknowledged. We thank the Fonds der Chemischen Industrie for gifts of chemicals, B. Witt for NMR, W. Heiden for MS and Dr. G. Fischer (Ludwig-Maximilians-

Universität München) for HRMS measurements. T.V. also thanks OTKA T048796 for financial support.

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