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Higher Carbene Homologues: Naphtho[2,3-*d*]-1,3,2λ^2-diazagermole, -Diazastannole, and Attempted Reduction of 2,2-Dichloronaphtho[2,3-*d*]-1,3,2-diazasilole

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ABSTRACT: *N,N′-Dineopentyl-2,3-diaminonaphthalene* **1**, *obtained by reaction of 2,3-diaminonaphthalene with pivaloyl chloride and subsequent reduction, was dilithiated and cyclodisubstituted with* $SiCl_4$ *to give dichloro-dineopentyl-naphtho[2,3-d]-1,3,2-diazasilole* **2**. *Treatment of* **2** *with two equivalents of potassium in THF caused cleavage of the Si–N ring. A silylene could not be detected. The corresponding cyclic diaminogermylene* **3** *and diaminostannylene* **4** *were obtained by direct ring closure of* **1**–Li_2 *with* $GeCl_2$·*dioxane or* $SnCl_2$, *respectively. The compounds are structurally characterized by NMR and MS. The properties of* **3** *and* **4** *are compared with those of related germylenes and stannylenes.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:439–444, 1998

INTRODUCTION

Low-coordinate compounds of silicon, germanium, and tin are highly reactive species and valuable building blocks for syntheses [1–4]. Most representatives are short-lived intermediates that polymerize to chain or ring compounds or, with increasing metallic character of M^{II} and electronegativity of the substituents X, form μ-X bridging structures. The persistence of monomers increases with the relative stability of two- compared to four-valent species, with steric protection and stabilizing electronic factors such as intramolecular higher coordination [5] and $p\pi$-$p\pi$-bonding [6–8]. Thus, for silylenes with nucleophilic substituents, a considerable thermodynamic stabilization has been calculated increasing in the order halosilylenes < alkoxysilylenes ≈ mercaptosilylenes ≪ aminosilylenes [6] ≪ diaminosilylenes < cyclic delocalized diaminosilylenes [7,8]. While germanium and tin are known to form isolable acyclic and cyclic dicoordinate diaminocarbene homologues [2–4], the less-favored silylenes are sufficiently stabilized only in the case of five-membered diaminosilylenes [9–12]. The formation of cyclodelocalized Hückel-π-systems causes an additional gain in energy that is small [8c,e,9] but may be decisive for compounds at the border of persistence. Thus, 1,3-di-*t*-butyl-4,5-dihydro-1,3,2λ^2-diazasilole is unstable under ordinary conditions [8c,9] in contrast to 1,3,2λ^2-diazasiloles [9,10]. Annelated 1,3,2λ^2-diazasiloles exhibit a remarkable behavior; 1,3,2λ^2-benzodiazasiloles [11], -germoles [13], and -stannoles [14] **I** are thermally surprisingly stable and can be distilled or sublimed without decomposition. Pyr-

Dedicated to Prof. Dr. Heinrich Nöth on the occasion of his seventieth birthday.

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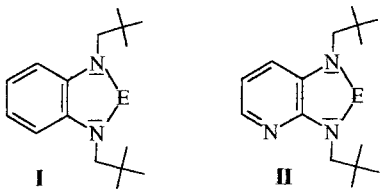
ido[2,3-*d*]-1,3,2λ^2-diazasiloles **II,** however, decompose to a large extent during sublimation, and even the corresponding germanium(II) and tin(II) homologues suffer from partial decomposition during sublimation. The pyrido[3,4] isomers could not be synthesized in an analogous manner. Because the calculated thermodynamic stabilizations of pyrido[2,3-*d*]- and pyrido[3,4-*d*]-1,3,2λ^2-diazasiloles are similar to those of benzo-1,3,2λ^2-diazasiloles, the different properties were attributed to the lower symmetry. Indeed, the isolable pyrido[2,3-*d*]-1,3,2λ^2-diazasilole possesses a nearly symmetrical π-charge distribution in the HOMO that has a nodal plane through the pyrido-nitrogen atom, whereas the pyrido[3,4] isomers exhibit an unsymmetrical charge distribution in the frontier orbitals [12]. The strong influence of annelation on the properties of the higher homologues of the Arduengo carbene [15] prompted us to carry out further studies on other annelated diazasiloles and related germanium and tin compounds. We report here on naphtho[2,3]-annelated systems.

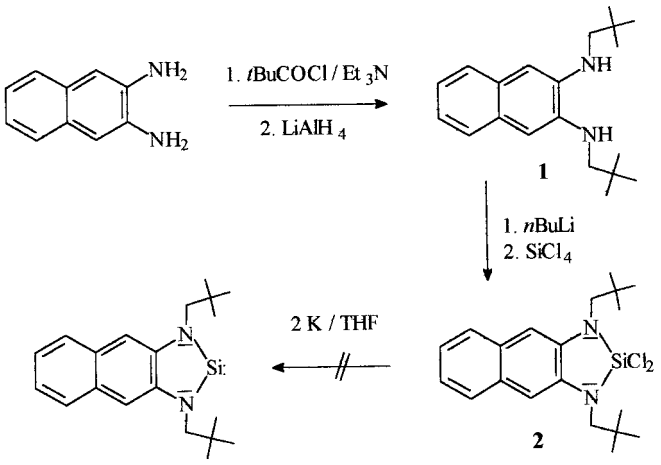


I **II**

(E = Si, Ge, Sn)

RESULTS

The investigations were carried out with *N,N′*-dineopentyl-2,3-diaminonaphthalene **1** that was synthesized by *N,N′*-dipivaloylation of 2,3-diaminonaphthalene and subsequent reduction with excess lithium aluminum hydride. The neopentyl substituents were selected because, even though the *t*-butyl groups are flexible, the neopentyl groups seem to enhance the electronic stabilization of *N,N′*-dineopentylbenzo-1,3,2λ^2-diazasilole and -stannole by their enhanced steric effects. On the other hand, the neopentyl groups did not hinder ring closure reactions with $E^{IV}Cl_4$ and can easily be introduced [11,14]. Dilithiation of **1** in benzene and subsequent reaction (Equation 1) with one equivalent of silicon tetrachloride provided a good yield of 2,2-dichloro-1,3-dineopentylnaphtho[2,3-**d**]-1,3,2-diazasilole **2** (δ^{29}Si-22.3), a viscous yellow orange oil that crystallized on prolonged standing.

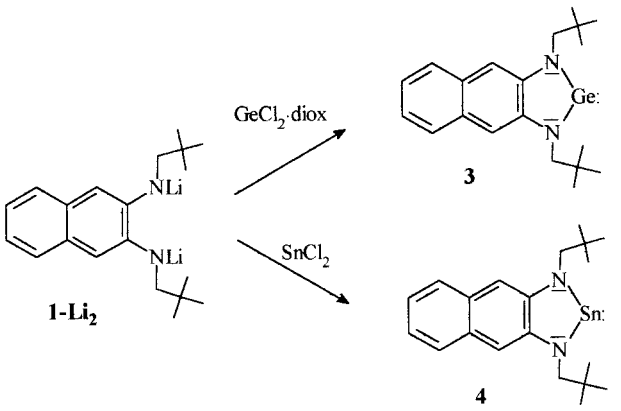


(1)

Attempts at different conditions to reduce this dichlorodiaminosilane by the action of two equivalents of potassium in THF led to dark red brown mixtures that did not exhibit a low-field δ^{29}Si signal typical of diaminosilylenes. A relatively broad resonance at δ^{29}Si-53 and a smaller signal at δ^{29}Si-82 lie in the region of $R\underline{Si}O_3$ and $\underline{Si}O_4$ absorptions, respectively. Therefore, we assume that THF was attacked and partly cleaved by intermediate silyl anions or silyl radical anions and that also the diazasilole ring was opened. The proton NMR spectrum revealed one main product with parameters consistent with **1** or a slightly modified structure. It should be mentioned that the proton NMR data of **1** and **2** are similar but differ noticeably for $\delta(NC\underline{H}_2)$ that is shifted downfield by about $\Delta\delta$ 0.3 in the ring. The reason for the cleavage is not clear just as the mechanisms of the reduction of the dichlorodiazasilole [9,10] or the annelated analogues [11,12] are not completely understood. Except as reported in Ref. [10], wherein K/Na in DME was used, all reductions were carried out with solid potassium in THF and are very sensitive to changes of the reducing agents or solvents. Thus, attempts to reduce 2,2-dichloro-1,3-dineopentylbenzodiazasilole with potassium in ether, in dioxane, in DME, or in benzene in the presence of two equivalents of dibenzo-18-crown[6] as well as use of potassium/sodium alloy, KC_8, or rubidium in THF did not give the anticipated silylene. In the naphthalene system, additional problems may arise from the lower LUMO and easier formation of radical anions that may cause different secondary reactions.

For an estimation of whether the putative silylene would be stable and the results similar in the behavior of the other compounds of types **I** and **II,** we investigated the higher analogs of the germanium and tin compounds and compared them with rep-

resentatives of types **I** and **II.** The synthesis of the naphtho[2,3-*d*]-annulated cyclic diaminogermylene and -stannylene was accomplished by dilithiation of the dineopentyl diaminonaphthalene **1** in THF or ether and reaction of the pale yellow solution of **1–Li$_2$** with $GeCl_2$·dioxane or with $SnCl_2$ (Equation 2). The yellow solid 1,3-dineopentyl-naphtho[2,3-*d*]-1,3,2λ^2-diazagermole **3** was obtained in good yield, and it was purified by sublimation at 125°C/10^{-5} Torr without substantial decomposition. The substance is easily soluble in THF, ether, and benzene and thus resembles the monomeric silylenes and germylenes of types **I** [9,10] and **II** [12]. The solubility in hexane, however, is much lower.



(2)

1,3-Dineopentylnaphtho[2,3-*d*]-1,3,2λ^2-diazastannole **4** was also formed in high yield. It precipitated from the red brown reaction mixture and was purified by extraction with boiling benzene. Small yellow needles deposited from the brown red solution. Compound **4** is slightly soluble in hexane, benzene, toluene, and ether. Use of Lewis basic solvents such as THF, pyridine, and benzene containing one or two equivalents of nBu$_3$P did not improve the solubility. This denotes a strong contrast to the behavior of the benzo- and pyrido[2,3-*d*]-annelated tin compounds of types **I** and **II.** Dineopentyl-benzo-1,3,2λ^2-diazastannole is a monomer in cyclohexane solution and presents uncommon π-bonded dimers in the unit cells of the crystals (average Sn C distance 323 pm, van der Waals radius 390 pm) [14]. The dineopentylpyrido[2,3-*d*]-1,3,2λ^2-diazastannole **II**(Sn) is slightly soluble in hexane, ether, and benzene but easily soluble in Lewis bases such as THF and even more so in pyridine. The strong difference of tin resonances in deuterobenzene (δ^{119}Sn 241.6) and in [d8]-THF (δ^{119}Sn 100.5), which has no parallel in the respective silylene, documents the inclination of tin to higher coordination by forming either π-bonded aggregates or solvent complexes. As can be seen from the solubilities, the strength of aggregation increases in the order **I**(Sn) < **II**(Sn) < **4.** The extension of the π-system in **4** lowers the effect of Lewis acid–Lewis base interactions. The noticeably better solubility in hot benzene or toluene (ca. 100 mg of **4** in 3 mL) may be due to competing π-interactions with these solvents. At a higher temperature (150°C/10^{-5} Torr), **4** can be sublimed and thus demonstrates either a monomeric nature or that monomers are formed in equilibrium. In the EI mass spectrum (60°C, 70 eV), the highest mass is that of the molecular ion (for ^{120}Sn m/z = 416.2, 20%) just as it was found in **3** (for ^{74}Ge m/z = 370.3, 65%). The fragmentation proceeds similarly with primary loss of a *t*-butyl group (**3:** m/z = 313.8, 100%; **4:** m/z = 359.5, 38%) or of the metal (m/z = 299, **3:** 23%; **4:** 38%) and subsequent cleavage of a *t*-butyl group (m/z = 242, **3:** 55%; **4:** 100%). Another effect that is connected with changes of the structure is the thermochromy of **4.** At 185–190°C (in a closed tube), the compound becomes black, and, on cooling, it reverts to yellow within seconds.

In the infrared spectra, we observed weak bands at 356 cm^{-1} (**3**) and 353 cm^{-1} (**4**) that are near the asymmetric Ge(II)N_2 and Sn(II)N_2 vibrations (375 and 385 cm^{-1}) reported in Ref. [16]. The structure elucidation of **1–4** was based on NMR data. The proton and carbon resonances confirm unambiguously the existence of the dineopentyl-diaminonaphthalene system. The proton chemical shifts depend markedly on the solvent (except for the *t*-Bu signals). Naphthyl protons are shifted downfield in C_6D_6 compared with $CDCl_3$ or CD_2Cl_2, whereas signals of $NC\underline{H}_2$ are shifted upfield. Characteristic of the germylene and stannylene structure is the strong deshielding of the NCH_2 protons compared with those of **1** ($\Delta\delta$ ca. 1.1) or of the silicon(IV) heterocyclus **2** ($\Delta\delta$ ca. 0.6) that was also observed in **I** [11,13,14] and **II** [12] and, to a smaller extent, for the *t*-butyl groups in di-*t*-butyl-1,3,2-λ^2-diazasilole [9]. This accounts for a ring current effect rather than for a local anisotropic influence because the different size and electronegativity of the group 14 heteroatoms with the respective changes of the E-N polarities are of minor importance. There is only a small additional downfield contribution in **I, II,** or **3** and **4** on going from Si or Ge to Sn. Aromaticity in the sense of a ring current effect shows the principal analogy with carbon systems with respect to delocalization and mobility of the electrons in the π levels that seem not to be interrupted by the polarity of the sp^2(N)–p(E^{IV}) σ-bonds. In the ^{13}C-NMR spectra, most of the ^{13}C nuclei of the element(II) heterocycles are not strongly shifted compared to the respective nuclei in **1.** A noticeable downfield shift is found for $N\underline{C}H_2$ (by $\Delta\delta$ 1.9

and 2.5) and, a smaller one, for CMe_3. It should be mentioned that the methyl signal exhibits a relatively large four-bond tin carbon coupling, indicating through interactions and thus the steric proximity and protection function of the neopentyl groups. An important deshielding is observed for the carbons within the five-membered ring. The strong relative increase of $\Delta\delta$ from the Ge(II) (4.7) to the Sn(II) (8.8) species suggests a core influence by the near heteroatom. π-Electrons are repelled to the naphthalene ring and induce there a shielding of the carbon atoms at δ 105 and of C-4a/C-8a ($\Delta\delta$ ca. 2).

From the high stability of **3** and **4** and the analogies with benzo- and pyrido[2,3-*d*]-annelated diazagermoles(II) and -stannoles(II), it may also be concluded that the naphtho[2,3-*d*]-diazasilole(II) could conceivably be isolable if a more suitable synthesis can be found. The trend in aggregation suggests formation of a monomer with no or nonsignificant intermolecular π-interactions between silicon(II) and the naphthalene ring of neighboring molecules.

EXPERIMENTAL

Materials and Spectroscopy

All operations were carried out under an argon atmosphere. Solvents were carefully dried and freshly distilled. $GeCl_2$·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, 111.9 MHz ^{119}Sn with $SnMe_4$ as reference. Assignment numbers of H and C atoms refer to the position in the ring. The carbon assignments were supported by DEPT-135 spectra. Mass spectra (EI, 70eV) were measured on a single-focusing sector-field mass spectrometer AMD40 (Intectra), UV spectra on Lambda19, and IR spectra on System2000 (Perkin Elmer).

2,3-Bis(2′,2′-dimethylpropionylamido)naphthalene. A 24.5 mL (24.0 g, 0.20 mol) amount of *t*-BuCOCl was added dropwise with cooling (ice water) and stirring to a mixture of 15.0 g (94.5 mmol) of 2,3-diaminonaphthalene and 27 mL (19.7 g, 0.21 mol) of triethylamine. The reaction mixture was refluxed for 4 hours, filtered, the precipitate washed with ether, and then treated with water to remove triethylamine hydrochloride. The residue was dried in a vacuum over P_4O_{10} to give 27.2 g (88%) of the diamide, mp 208–210°C, soluble in $CHCl_3$ and THF. IR (KBr): ν = 1659 (s), 3298 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.25 (s, 18H, C*Me*$_3$), 7.41 (m, 6,7-H), 7.72 (m, 5,8-H), 7.85 (s, 2H, 1,4-H), 8.3 (br s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ = 27.5 (C*Me*$_3$), 39.3 (*C*Me$_3$), 123.6 (C-1,4), 125.9 (C-5,8), 127.2 (C-6,7), 130.3, 131.3 (C-2,3, C-4a,8a), 178.8 (C=O). MS (EI, 70 eV): *m/z* = 326 (65%, M$^+$), 269 (24%, M$^+$-Bu), 228 (71%), 191 (89%), 57 (100%). Anal. calcd for $C_{20}H_{26}N_2O_2$ (326.44): C, 73.59; H, 8.03; N, 8.58%. Found: C, 72.49; H, 8.36; N, 7.99%.

N,N′-Dineopentyl-2,3-diaminonaphthalene **1.** A 15.0 g (46 mmol) amount of 2,3-bis(dimethylpropionylamido)naphthalene was added with stirring to 4.0 g (105 mmol) of $LiAlH_4$ in 200 mL of THF (ca. 10°C), and the mixture was stirred for 1 hour at room temperature and then refluxed for 6 hours. After hydrolysis, the precipitate of $Al(OH)_3$ was thoroughly washed with ether, the combined solution dried with sodium sulfate, and the solvents removed in vacuo. The product was extracted from the residue with ether and the solution concentrated to leave 12.7 g (93%) of colorless to pale brown crystals, mp 92–94°C, soluble in $CHCl_3$, THF, benzene. IR (nujol,Ar): (a) ν = 322 (m), 395 (m) 415 (m), 444 (s), 461 (s); (b) ν = 667 (m), 740 (s), 842 (s), 1184 (s), 1262 (s), 1293 (m), 1524 (s), 1630 (m), 3039 (w), 3337 (m), 3356 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.09 (s, 18H, CMe_3), 2.97 (d, $^3J_{H\text{-}H}$ = 6 Hz, 4H, NCH_2), 3.6 (br t, $^3J_{H\text{-}H}$ = 6 Hz, 2H, NH), 6.92 (s, 2H, 1,4-H), 7.20 (m, 2H, 6,7-H), 7.59 (m, 2H, 5,8-H). ^{13}C NMR ($CDCl_3$): δ 27.9 (CMe_3), 31.3 (CMe_3), 56.0 (NCH_2), 106.2, 122.7, 125.7 (C-1,4, C-5 to C-8), 129.2 (C-4a,8a), 139.2 (C-2,3). MS (EI, 70 eV): *m/z* = 298 (38%, M$^+$), 241 (100%, M$^+$-Bu), 171 [45%, $C_{10}H_6$-2,3$(NH)_2CH^+$]. Anal. calcd for $C_{20}H_{30}N_2$ (298.47): C, 80.48; H, 10.13; N, 9.39%. Found: C, 79.49; H, 10.39; N, 8.85%.

2,2-Dichloro-1,3-dineopentylnaphtho[2,3-d]-1,3,2-diazasilole **2.** A 12.25 g (41.1 mmol) amount of **1** was dissolved in 200 mL of benzene and 70 mL of a 1.22 M solution of *n*BuLi (85.4 mmol) in hexane were added dropwise with stirring and cooling (ca. 5–10°C) to give a yellow suspension of the diamide. After 30 minutes, 5.0 mL (7.15 g, 42 mmol) of $SiCl_4$ was dropped into the suspension. After having been stirred overnight, the mixture was refluxed for 6 hours, filtered, and the precipitate washed with benzene. The solvent was removed and the residual liquid distilled at 154–156°C/10^{-3} Torr. Yield: 10.0 g (62%) of yellow orange oil that crystallized after a month, mp 85–90°C, soluble in benzene, $CHCl_3$, THF. ^{1}H NMR (C_6D_6): δ = 0.99 (s, 18H, CMe_3), 3.25 (s, 4H, NCH_2), 7.09 (s, 2H, 4,9-H), 7.30 (m, 2H), 7.66 (m, 2H). ^{13}C NMR (C_6D_6): δ = 28.5 (C*Me*$_3$), 33.5 (*C*Me$_3$), 55.6 (NCH_2), 106.1, 123.6, 126.4 (C-4 to C-9), 129.1 (C-4a,8a), 139.6 (C-3a,9a). ^{29}Si NMR (C_6D_6): δ = −22.44. MS (EI, 70 eV, selected data for $^{35}Cl_2$):

m/z = 394 (21%, M^+), 337 (100%, M^+-*t*Bu). Anal. calcd for $C_{20}H_{28}Cl_2N_2Si$ (395.45): C, 60.75; H, 7.14; N, 7.08%. Found: C, 61.20; H, 7.80; N, 6.91%.

1,3-Dineopentylnaphtho[2,3-d]-1,3,2λ²-diazagermole **3.** A 0.65 g (2.2 mmol) amount of **1** was dissolved in THF (20 mL) and dilithiated with *n*BuLi (3.0 mL, 1.45 M in hexane, 4.4 mmol) at −78°C. A 9 mL amount of a solution of $GeCl_2$ dioxane (0.245 M, 2.2 mmol) in THF was added at −78°C and stirred for 2 days at room temperature, a brown suspension being formed. The solvent was removed in vacuo and the residue extracted with benzene (twice 5 mL). Benzene was evaporated (crude yield >60%) and the residue was sublimed at 125°C (bath)/10^{-5} Torr yielding 0.4 g (50%) of yellow solid **3,** mp 120–125°C. IR (nujol, Ar): (a) ν = 239 (w), 284 (m), 356 (wm); (b) ν = 670 (m), 737 (s), 844 (s), 1109 (m), 1190 (ms), 1266 (sh), 1283 (s), 1378 (s), 1524 (w), 3043 (w) cm^{-1}. UV (hexane): λ_{max} = 211 (sh), 216 (w), 230 (wm), 247 (sh), 252 (s), 375 (w) nm. ^1H NMR (C_6D_6): δ = 0.96 (s, 18H, CMe_3), 3.82 (s, 4H, NCH_2), 7.47 (s, 2H, 4,9-H), 7.41 (m, 2H), 7.94 (m, 2H); simulation with $^3J_{H\text{-}5,H\text{-}6}$ = 8.3, $^3J_{H\text{-}6,H\text{-}7}$ = 6.8, $^4J_{H\text{-}5,H\text{-}7}$ = 1.2 fits with experimental coupling pattern. ^{13}C NMR (C_6D_6): δ = 28.7 (CMe_3), 33.0 (CMe_3), 56.8 (NCH_2), 105.3, 123.2, 127.2 (C-4,C-9), 128.2 (C-4a,8a), 144.5 (C-3a,9a). MS (EI, 70 eV): *m/z* = 370.3 (65%, $[^{74}Ge]M^+$), 313.8 (100%), 299 (23%), 241.8 (55%). Anal. calcd for $C_{20}H_{28}N_2Ge$ (369.07): C, 65.09; H, 7.65; N, 7.59%. Found: C, 66.70; H, 8.06; N, 7.35%.

1,3-Dineopentyl-naphtho[2,3-d]-1,3,2λ²-diazastannole **4.** A 1,66 g (5.56 mmol) amount of **1** was dissolved in ether (50 mL) and reacted with *n*BuLi (8 mL, 1.4 M in hexane, 11.2 mmol) at 0–5°C to give a pale yellow precipitate. After 3 hours, THF (5 mL) was added to dissolve the dilithium reagent followed by 1.1 g (5.6 mmol) of $SnCl_2$ (ca. 0°C). The solution turned red brown, and, after some minutes, a yellow substance began to precipitate. Stirring was continued for 2 days (crude yield up to 75%), the solvent removed in vacuo, and the residue extracted with boiling benzene. Small yellow needles that precipitated from the dark red solution were collected by filtration and dried to give 1.25 g (54%) of **4,** mp >190°C (thermochrom). Compound **4** is slightly soluble in ether, THF, benzene, and hexane, and it is extremely sensitive to hydrolysis. The NMR samples were always contaminated by some **2.** IR (nujol, Ar): (a) ν = 218 (m), 242 (w), 353 (w) cm^{-1}. ^1H NMR (C_6D_6, TMS): δ = 0.92 (s, 18H, CMe_3), 3.88 (s, sat. $^3J_{SnH}$ = 15.8 Hz, 4H, NCH_2), 7.40 (s, 2H, 4,9-H), 7.37 (m, 2H), 7.92 (m, 2H). (CD_2Cl_2, TMS): δ = 1.06 (s, 18H, CMe_3), 4.08 (s, 4H, NCH_2), 6.90 (s, 2H, 4,9-H), 7.16 (m, 2H), 7.65 (m, 2H). ^{13}C NMR (C_6D_6, 60°C): δ = 28.9 (sat., $^4J_{SnC}$ = 18.8 Hz, CMe_3), 33.0 ($^3J_{SnC}$ = 6 Hz, CMe_3), 59.1 (NCH_2), 105.3, 122.8, 126.8 (C-4,C-9), 128.6 (C-4a,8a), 148.7 (C-3a,9a). ^{119}Sn NMR (C_6O_{65}60°C): S = 288, half width 408Hz. MS (EI 70 eV): *m/z* = 416.2 (20%, $[^{120}Sn]M^+$), 359.5 (38%, M^+-57); 299 (38%), 242 (100%). Anal. calcd for $C_{20}H_{28}N_2Sn$ (414.17): C, 57.86; H, 6.78; N, 6.73%. Found: C, 57.78; H, 6.79; N, 6.55%.

During sublimation of **4** at 150°C/10^{-5} Torr, partial decomposition occurred and nonvolatile material was formed.

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