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Article

Benzimidazolin-2-stannylenes with *N*,*N*′-Alkyl (Me and Et) and Lewis Base Functional Groups

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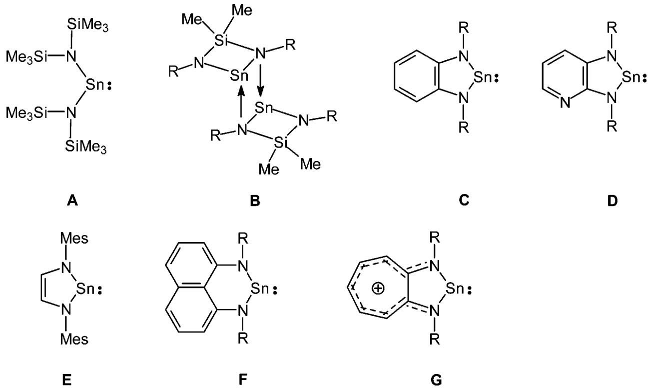
Symmetrically and unsymmetrically N,N′-substituted benzimidazolin-2-stannylenes with sterically nondemanding alkyl (Me and Et) and Lewis base functional groups ($-(CH_2)_nOMe$, $-(CH_2)_nNMe_2$; $n = 2, 3$) have been synthesized by the transamination reaction between suitably substituted *o*-phenylenediamines and $Sn[N(SiMe_3)_2]_2$. The *N*,*N*′-dimethyl-substituted stannylene **3** exists in the solid state as a bimolecular aggregate which is held together by strong intermolecular Sn•••N interactions leading to three-coordinated tin atoms. The benzimidazolin-2-stannylenes with *N*,*N*′-$(CH_2)_nOMe$ substituents (**5**, $n = 2$; **6**, $n = 3$) exhibit weak intramolecular Sn•••O interactions in solution. Benzannulated stannylenes with *N*,*N*′-$(CH_2)_nNMe_2$ substituents (**7**, $n = 2$; **8**, $n = 3$) are again dimers which exhibit both intramolecular Sn•••NMe_2 and intermolecular Sn•••N interactions, which leads to tri- or tetracoordinated tin atoms. Some unsymmetrically N,N′-substituted benzimidazolin-2-stannylenes have also been synthesized. The molecular structures of **3**, **5**, and **8** and the relation between the chemical shift recorded for the tin atoms and the solvent (C_6D_6 or THF-d_8) used for recording ^{119}Sn NMR spectra will be discussed.

Introduction

Stannylenes are diamagnetic derivatives of divalent tin which possess an unshared electron pair and a vacant p-orbital at the tin atom in the ground state.[1] Due to their electronic structure they are potential Lewis base ligands for transition metals[2] and can act in such complexes as σ-donor and weak π-acceptor ligands.[3] The longest known stable tin(II) organyl — bis(cyclopentadienyl)tin or stannocene — was synthesized by Fischer and Gruber in 1956.[4] The first stable dialkyl-[5] and diaminostannylenes **A**[6] (Scheme 1) were synthesized by Lappert et al. in 1973 and 1974, respectively. The reactive tin(II) atom in the monomeric diaminostannylene **A** is stabilized not only by the sterically demanding $N(SiMe_3)_2$ groups but also by the interaction of the vacant p-orbital at the tin atom with the free electron pairs of the trigonal-planar nitrogen atoms. The first N-heterocyclic

Scheme 1. Different Types of Diaminostannylenes



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stannylenes of type **B** were reported by Veith.[7] They are monomeric or dimeric, depending on the N-substituent R. Some years thereafter, the first representatives of a new type of cyclic diaminostannylenes **C**−**G**, which contain the tin atom as part of aromatic system, were described. The benzimidazolin-2-stannylene **C** was synthesized and characterized in 1995,[8] 4 years before its carbene analogue was reported.[9] The benzimidazolin-2-stannylenes of type **C** contain bulky N,N′-substituents (R = neopentyl or trimethylsilyl), which leads an efficient steric shielding of the tin(II) center. A different type of benzannulated stannylene **D** with a pyridoannulated five-membered ring was prepared by Heinecke et al.[10] The diaminostannylene **E** which is an analogue of Arduengo's carbene was isolated recently.[11] Finally, stannylenes derived from diaminonaphtalene **F**[12] and cationic stannylenes **G**[13] containing a 10-π-electron ring system have been prepared. We have previously described a benzannulated stannylene of type **C** with donor-functionalized N-substituents (R = $CH_2CH_2NMe_2$). This stannylene exists as a bimolecular aggregate in the solid state and exhibits strong intramolecular and intermolecular Sn···N interactions.[14] Here we describe a series of benzannulated stannylenes of type **C** (R = alkyl, donor-functionalized group). Their molecular structures and ^{119}Sn NMR spectra, which show a relation between the chemical shift observed for the tin atom and the solvent used for recording the spectra, are discussed.

Experimental Section

General Comments. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried over sodium/benzophenone under argon and were freshly distilled prior to use. ^{1}H and ^{13}C NMR spectra were measured on Bruker AC 200, AM 270, and AM 250 spectrometers. Tetramethylstannane (δ = 0) was used as an internal or external standard for ^{119}Sn NMR spectra. $Sn[N(SiMe_3)_2]_2$ was purchased from Aldrich. Spectroscopic data for the starting materials of types **1** and **2** can be found in the Supporting Information. Microanalytical data for the stannylenes were difficult to obtain. Multiple attempts gave different results due to the sensitivity of these compounds toward moisture and air. However, all stannylenes were characterized by mass spectroscopy (all molecular ions were detected) and ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy, and three derivatives, by X-ray diffraction.

Preparation of *N,N′*-Dialkylbenzimidazolin-2-stannylene Derivatives 3−12. A sample of $Sn[N(SiMe_3)_2]_2$ (1.66 mL, 4.3 mmol) was added to a solution of an *N,N*'-dialkyl-1,2-diaminobenzene (**2a**−**d**,**g**−**i**,**m**−**o**) (4 mmol) in toluene (40 mL). After stirring of the reaction mixture for 36 h at ambient remperature, the solvent and volatile products were removed in vacuo. The residue was recrystallized from toluene or THF. Stannylenes **4**, **6**, and **9**−**12** were isolated as brown or red oils.

***N,N′*-Dimethylbenzimidazolin-2-stannylene (3).** Recrystallization from toluene gave orange crystals (mp 169 °C). Yield: 98%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.07 (m, 2H, Ar-H), 6.79 (m, 2H, Ar-H), 3.28 (s, 6H, CH_3). ^{13}C NMR (100 MHz, C_6D_6): δ 147.6 (Ar-C_{ipso}), 117.9 (Ar-C_{meta}), 109.8 (Ar-C_{ortho}), 34.0 (CH_3). ^{119}Sn NMR (149 MHz, C_6D_6): δ 225.3. ^{119}Sn NMR (149 MHz, THF-d_8): δ 106.5. MS (EI, 70 eV) [*m/z* (%)]: 254 (21.3) $[M]^+$, 239 (4.3) $[M - CH_3]^+$, 224 (3.0) $[M - 2CH_3]^+$.

***N,N′*-Diethylbenzimidazolin-2-stannylene (4):** brown oil. Yield: 97%. ^{1}H NMR (400 MHz, C_6D_6): δ 6.99 (m, 2H, Ar-H), 6.83 (m, 2H, Ar-H), 3.76 (q, 4H, NCH_2), 1.36 (t, 6H, CH_3). ^{13}C NMR (100 MHz, C_6D_6): δ 147.1 (Ar-C_{ipso}), 117.9 (Ar-C_{meta}), 109.8 (Ar-C_{ortho}), 43.4 (NCH_2), 19.2 (CH_3). ^{119}Sn NMR (149 MHz, C_6D_6): δ 236.6. ^{119}Sn NMR (149 MHz, THF-d_8): δ 174.5. MS (EI, 70 eV) [*m/z* (%)]: 282 (19.4) $[M]^+$, 253 (6.8) $[M - CH_2CH_3]^+$.

***N,N′*-Bis(2-methoxyethyl)benzimidazolin-2-stannylene (5).** Compound **5** was recrystallized from THF to give yellow crystals (mp 156 °C). Yield: 99%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.02 (m, 2H, Ar-H), 6.76 (m, 2H, Ar-H), 3.69 (t, 4H, NCH_2), 3.32 (t, 4H, CH_2O), 2.96 (s, 6H, OCH_3). ^{13}C NMR (100 MHz, C_6D_6): δ 146.8 (Ar-C_{ipso}), 117.6 (Ar-C_{meta}), 110.4 (Ar-C_{ortho}), 72.2 (CH_2O), 57.6 (NCH_2), 48.0 (OCH_3). ^{119}Sn NMR (149 MHz, C_6D_6): δ 147.8. ^{119}Sn NMR (149 MHz, THF-d_8): δ 89.4. MS (EI, 70 eV) [*m/z* (%)]: 342 (4.1) $[M]^+$.

***N,N′*-Bis(3-methoxypropyl)benzimidazolin-2-stannylene (6):** brown oil. Yield: 95%. ^{1}H NMR (400 MHz, THF-d_8): δ 6.58 (m, 2H, Ar-H), 6.55 (m, 2H, Ar-H), 3.94 (t, 4H, NCH_2), 3.41 (t, 4H, CH_2O), 3.22 (s, 6H, OCH_3), 2.02 (quint, 4H, $CH_2CH_2CH_2$). ^{13}C NMR (100 MHz, THF-d_8): δ 147.3 (Ar-C_{ipso}), 116.9 (Ar-C_{meta}), 109.2 (Ar-C_{ortho}), 71.9 (CH_2O), 58.8 (NCH_2), 45.8 (OCH_3), 33.1 ($CH_2CH_2CH_2$). ^{119}Sn NMR (149 MHz, C_6D_6): δ 226.4. ^{119}Sn NMR (149 MHz, THF-d_8): δ 171.0. MS (EI, 70 eV) [*m/z* (%)]: 370 (3.6) $[M]^+$.

***N,N′*-Bis(2-(dimethylamino)ethyl)benzimidazolin-2-stannylene (7).** The spectroscopic data for stannylene **7** are identical with those previously reported by us.[14]

***N,N′*-Bis(3-(dimethylamino)propyl)benzimidazolin-2-stannylene (8).** Compound **8** was recrystallized from toluene as yellow crystals (mp 163 °C). Yield: 98%. ^{1}H NMR (400 MHz, C_6D_6): δ 6.92 (m, 2H, Ar-H), 6.75 (m, 2H, Ar-H), 3.75 (t, 4H, NCH_2), 2.12 (t, 4H, $CH_2N(CH_3)_2$), 1.79 (s, 12H, $N(CH_3)_2$), 1.62 (quint, 4H, $CH_2CH_2CH_2$). ^{13}C NMR (100 MHz, C_6D_6): δ 147.4 (Ar-C_{ipso}), 116.4 (Ar-C_{meta}), 109.2 (Ar-C_{ortho}), 59.2 (NCH_2), 46.2 ($CH_2N(CH_3)_2$), 45.3 (NCH_3), 27.6 ($CH_2CH_2CH_2$). ^{119}Sn NMR (149 MHz, C_6D_6): δ 51.7. ^{119}Sn NMR (149 MHz, THF-d_8): δ 51.4. MS (EI, 70 eV) [*m/z* (%)]: 396 (25.3) $[M]^+$, 338 (4.6) $[M - CH_2N(CH_3)_2]^+$, 58 (100) $[CH_2N(CH_3)_2]^+$.

***N*-(2-Methoxyethyl)-*N′*-ethylbenzimidazolin-2-stannylene (9):** brown oil. Yield: 98%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.05 (m, 2H, Ar-H), 6.84 (m, 1H, Ar-H), 6.78 (m, 1H, Ar-H), 3.75 (m, 4H, NCH_2), 3.29 (t, 2H, CH_2O), 2.94 (s, 3H, OCH_3), 1.32 (t, 3H, CH_3). ^{13}C NMR (100 MHz, C_6D_6): δ 147.3, 146.6 (Ar-C_{ipso}), 117.7, 117.6 (Ar-C_{meta}), 110.0, 109.9 (Ar-C_{ortho}), 72.3 (CH_2O), 57.4 (NCH_2CH_2), 48.1 (NCH_2CH_3), 43.1 (OCH_3); 16.0 (NCH_2CH_3). ^{119}Sn NMR (149 MHz, C_6D_6): δ 173.6. ^{119}Sn NMR (149 MHz, THF-d_8): δ 124.6. MS (EI, 70 eV) [*m/z* (%)]: 312 (2.38) $[M]^+$.

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Table 1. Crystallographic Data for **3**, **5**, and **8**

param	**3**	**5**	**8**
formula	$C_8H_{10}N_2Sn$	$C_{12}H_{18}N_2O_2Sn$	$C_{16}H_{28}N_4Sn$
M_r	252.87	340.97	395.11
a (Å)	6.8230(10)	7.4890(10)	8.5390(10)
b (Å)	7.8730(10)	17.5030(10)	11.1540(10)
c (Å)	15.404(2)	20.286(2)	11.097(2)
α (deg)	90.0	90.0	59.550(2)
β (deg)	96.0100(10)	90.0	78.7500(10)
γ (deg)	90.0	90.0	72.970(2)
V (Å^3)	821.4(2)	2659.1(5)	869.8(2)
Z	4	8	2
space group	$P2_1/c$	Pbca	$P\bar{1}$
ρ_{calcd} (g cm^{-3})	2.045	1.703	1.509
μ(Mo Kα) (mm^{-1})	3.042	3.048	1.469
2θ range (deg)	5.3−54.9	6.1−49.9	5.0−59.9
data collcd	1941	4039	5262
no. of unique data, R_{int}	1875, 0.0136	2322, 0.0365	5032, 0.0089
no. obsd data [$I \geq 2\sigma(I)$]	1622	1867	4934
R (all data)	0.0268	0.0415	0.0354
wR (all data)	0.0463	0.0742	0.0970
no. of variables	140	226	302
peak/hole (e Å^{-3})	0.541/−0.443	1.232/−0.911	2.459/−2.771

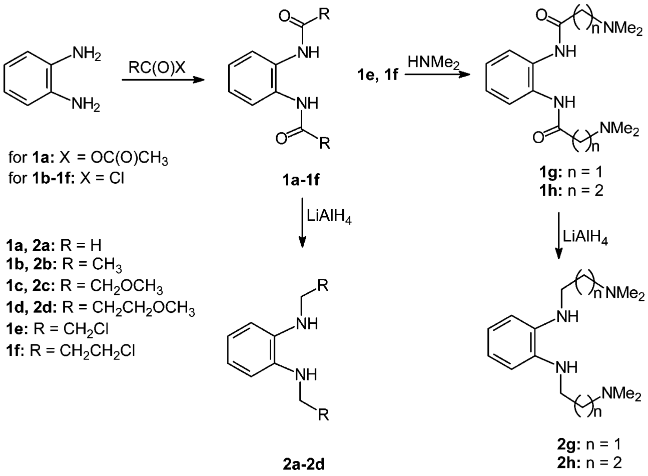
***N*-(2-(Dimethylamino)ethyl)-*N′*-ethylbenzimidazolin-2-stannylene (10):** red oil. Yield: 98%. ^{1}H NMR (400 MHz, C_6D_6): δ 6.96 (t, 1H, Ar-H), 6.88 (t, 1H, Ar-H), 6.75 (d, 1H, Ar-H), 6.69 (d, 1H, Ar-H), 3.73 (q, 2H, NCH_2CH_3), 3.40 (t, 2H, NCH_2CH_2), 2.07 (t, 2H, $CH_2N(CH_3)_2$), 1.69 (s, 6H, NCH_3), 1.44 (t, 3H, NCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6): δ 148.3, 146.2 (Ar-C$_{ipso}$), 118.7, 116.1 (Ar-C$_{meta}$), 111.9, 109.0 (Ar-C$_{ortho}$), 57.9 (NCH_2CH_2), 46.9 ($CH_2N(CH_3)_2$), 43.5 ($N(CH_3)_2$), 42.8 (NCH_2CH_3), 18.9 (NCH_2CH_3). ^{119}Sn NMR (149 MHz, C_6D_6): δ 95.9. ^{119}Sn NMR (149 MHz, THF-d_8): δ 102.4. MS (EI, 70 eV) [m/z (%)]: 325 (51.4) [M]$^+$, 267 (57.5) [M − $CH_2N(CH_3)_2$]$^+$, 58 (100) [$CH_2N(CH_3)_2$]$^+$.

***N*-(3-(Dimethylamino)propyl)-*N′*-ethylbenzimidazoline-2-stannylene (11):** red oil. Yield: 96%. ^{1}H NMR (400 MHz, C_6D_6): δ 6.93 (t, 1H, Ar-H), 6.89 (t, 1H, Ar-H), 6.63 (d, 1H, Ar-H), 6.61 (d, 1H, Ar-H), 3.65 (t, 2H, NCH_2CH_2), 3.52 (q, 2H, NCH_2CH_3), 1.93 (t, 2H, $CH_2N(CH_3)_2$), 1.48 (s, 6H, NCH_3), 1.36 (quint, 2H, $CH_2CH_2CH_2$), 1.34 (q, 3H, NCH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6): δ 149.2, 145.7 (Ar-C$_{ipso}$), 117.5, 116.0 (Ar-C$_{meta}$), 110.4, 108.8 (Ar-C$_{ortho}$), 59.7 (NCH_2CH_2), 46.3 ($CH_2N(CH_3)_2$), 45.0 ($N(CH_3)_2$), 43.0 (NCH_2CH_3), 24.8 ($CH_2CH_2CH_2$), 19.6 (NCH_2CH_3). ^{119}Sn NMR (149 MHz, C_6D_6): δ 41.7. ^{119}Sn NMR (149 MHz, THF-d_8): δ 51.1. MS (EI, 70 eV) [m/z (%)]: 339 (22.7) [M]$^+$, 281 (3.4) [M − $CH_2N(CH_3)_2$]$^+$, 266 (8.8) [M − CH_2CH_3 − $N(CH_3)_2$)]$^+$, 252 (5.7) [M − CH_2CH_3 − $CH_2N(CH_3)_2$]$^+$.

***N*-(3-(Dimethylamino)propyl)-*N′*-(2-(dimethylamino)ethyl)-benzimidazolin-2-stannylene (12):** red oil. Yield: 97%. ^{1}H NMR (400 MHz, C_6D_6): 6.96 (m, 2H, Ar-H), 6.62 (m, 2H, Ar-H), 3.84, 3.35 (t, 2H, NCH_2), 2.24, 2.10 (t, 2H, $CH_2N(CH_3)_2$), 1.86, 1.57 (s, 6H, $N(CH_3)_2$), 1.52 (quint, 2H, $CH_2CH_2CH_2$). ^{13}C NMR (100 MHz, C_6D_6): δ 148.8, 145.6 (Ar-C$_{ipso}$), 115.9, 115.8 (Ar-C$_{meta}$), 108.2, 107.9 (Ar-C$_{ortho}$), 60.8, 59.4 (NCH_2), 46.1, 45.8 ($CH_2N(CH_3)_2$), 44.9, 44.4 ($N(CH_3)_2$), 25.0 ($CH_2CH_2CH_2$). ^{119}Sn NMR (149 MHz, C_6D_6): δ −5.0. ^{119}Sn NMR (149 MHz, THF-d_8): δ −5.1. MS (EI, 70 eV) [m/z (%)]: 382 (5.4) [M]$^+$, 324 (7.2) [M − $CH_2N(CH_3)_2$)]$^+$.

X-ray Diffraction Studies. Diffraction data for **3**, **5**, and **8** were collected with a Enraf Nonius CAD-4 diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Diffraction data were collected at 143(2) K for **3** and at 293(2) K for **5** and **8** and were corrected for absorption. The data reduction was performed with the Bruker SMART[15] program package. For further crystal and data collection details, see Table 1. Structure solutions were found with the SHELXS-97[16] package using the heavy-atom method and were refined with SHELXL-97[17] against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atom positions were identified in subsequent Fourier maps and were added to the structure model. Their positional parameters were refined with isotropic thermal parameters.

Scheme 2. Preparation of Symmetric Amines **2a**−**d**,**g**,**h**



Results and Discussion

The symmetrically substituted *o*-phenylene diamines **2a**−**d** were obtained by $LiAlH_4$ reduction of the carbonyl groups of the amides **1a**−**d** (Scheme 2). The derivatives with amino-substituted side chains **2g**,**h** were synthesized by reaction of the chloro-substituted diamides **1e**,**f** with $HNMe_2$ and subsequent reduction of the carbonyl groups with $LiAlH_4$.

The preparation of the unsymmetric *o*-phenylene diamines **2i**,**m**−**o** was started from *o*-nitroaniline which was initially acylated. The remaining nitro group was subsequently reduced using Raney-Ni/N_2H_4 (Scheme 3). A second acy-

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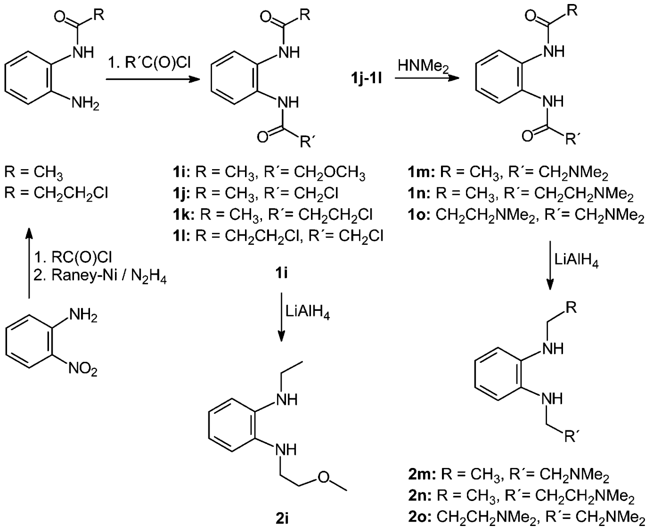
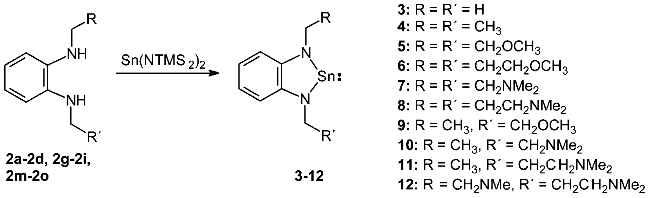
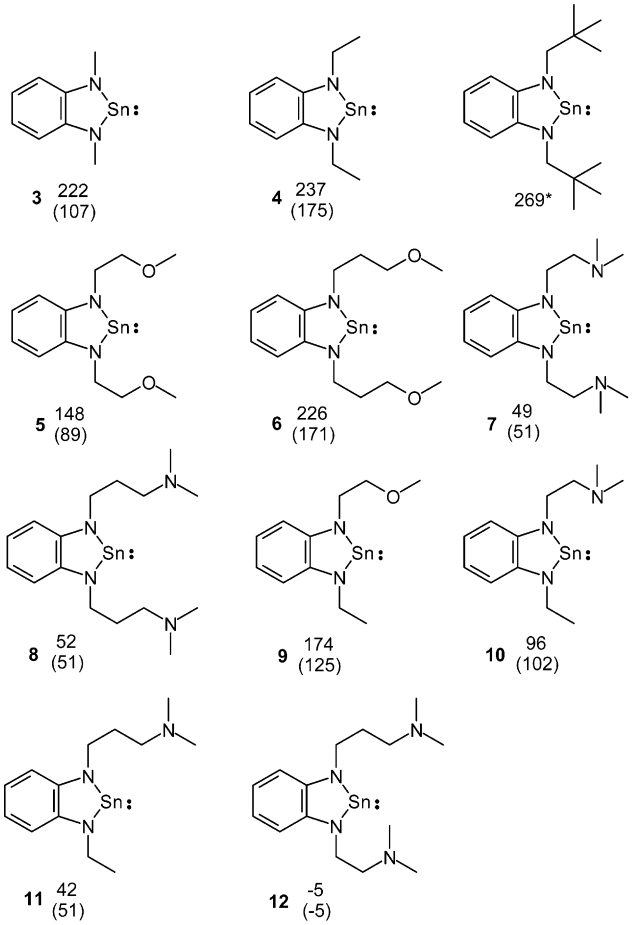
Scheme 3. Preparation of Unsymmetric Amines **2i**,**m−o**



Scheme 4. Preparation of Symmetric and Unsymmetric Stannylenes **3−12**



Scheme 5. ^{119}Sn Chemical Shifts for Stannylenes **3−12** in C_6D_6 and THF-d_8 (in Parentheses)[a]



[a] Asterisk indicates a value reported for a C_6D_6 solution reported in ref 8.

lation gave the unsymmetric diamides **1i−l**. One of these (**1i**) was directly converted by reduction of the carbonyl groups into the unsymmetric *o*-phenylene diamine **2i**. The *o*-phenylenediamides with chloro-substituted side chains **1j−l** were reacted with dimethylamine to give the unsymmetric diamides **1m−o** which upon reduction of the carbonyl function yielded the unsymmetric *o*-phenylene diamines **2m−o** (Scheme 3).

The reaction between the symmetric (**2a−d**,**g**,**h**) or unsymmetric (**2i**,**2m−o**) *o*-phenylenediamines and Sn[N(SiMe$_3$)$_2$]$_2$ gave the symmetric and unsymmetric stannylenes **3−12** as dark orange to brown solids or oils in good yield (95−99%) (Scheme 4). The stannylenes are sensitive to air and moisture. They are only sparingly soluble in hydrocarbons but dissolve well in ethers or aromatic solvents.

^{13}C NMR spectra of the stannylenes **3−12** show the characteristic downfield shift for the resonances of the *ipso*-carbon atoms of the aromatic ring ($\delta \approx 147$ ppm) compared to the corresponding *o*-phenylene diamines ($\delta \approx 137$ ppm). The ^{119}Sn NMR resonances fall in a broad range between $\delta = 237$ and $\delta = -5$ ppm (Scheme 5). A value comparable to these has been reported for *N*,*N*'-dineopentylbenzimidazolin-2-stannylene at 269 ppm.[8] It is obvious that chemical shift reflects the amount of electron density at the tin atom and a highfield shift would indicate a gain of electron density at the tin center.

The sterically least demanding substituted stannylene **3** shows a strong dependence of the ^{119}Sn NMR resonance for the stannylene tin atom from the solvent used (Scheme 5). The resonance in THF-d_8 ($\delta = 107$ ppm) is shifted highfield by 115 ppm compared to the resonance in nonpolar C_6D_6 ($\delta = 222$ ppm). Coordination of THF molecules to the electron deficient stannylene center explains the observed highfield shift for the tin resonance of **3** in THF compared to the lowfield value observed in benzene. The dependence of the chemical shift for the tin resonance from the solvent used can thus serve as a probe for the presence of additional donor interactions with the stannylene tin atom. For example, the dependence of the ^{119}Sn chemical shift from the solvent can be used to evaluate intramolecular interactions in stannylenes with donor-functionalized N,N′-substituents like **5−12**. The stronger the intramolecular or intermolecular Lewis-acid−Lewis-base interaction between the tin center and the donor groups of the N,N′-side chains is, the smaller will be the difference in the chemical shift of the ^{119}Sn resonance in THF and benzene. This effect is clearly visible with the stannylenes bearing amine-substituted side chains (**7**, **8**, **10−12**), which are strong donors.

The stannylenes with two amine-substituted side chains (**7**, **8**, **12**) exhibit almost identical ^{119}Sn chemical shifts in benzene and THF. The side-chain donors coordinate to the stannylene center in both solvents, and thus, no solvent dependence of the ^{119}Sn resonance was found. The presence of only one amine-substituted side chain like in **10** and **11** causes a slight dependence of the ^{119}Sn resonance from the solvent ($\Delta\delta = 6$ ppm for **10**; $\Delta\delta = 9$ ppm for **11**) indicating

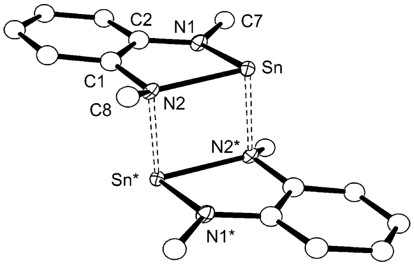


Figure 1. Molecular structure of stannylene **3**. Selected bond lengths (Å) and angles (deg): Sn−N1 2.092(2), Sn−N2 2.189(2), Sn···N2* 2.361(2), N1−C2 1.378(3), N1−C7 1.451(3), N2−C1 1.424(3), N2−C8 1.478(3), C1−C2 1.425(3); N1−Sn−N2 77.12(7), N1−Sn···N2* 90.69(7), N2−Sn···N2* 84.17(8), Sn−N1−C2 115.90(15), Sn−N1−C7 124.5(2), C2−N1−C7 118.3(2), Sn−N2−C1 110.67(14), Sn−N2−C8 118.83(15), C1−N2−C8 115.0(2).

that the tin center still acts as a Lewis acid in THF solution even after N-coordination of the amine group of the side chain.

The stannylenes **5**, **6**, and **9** with ether-functionalized side chains exhibit a strong dependence of the ^{119}Sn chemical shift from the solvent ($\Delta\delta = 59$ ppm for **5**; $\Delta\delta = 55$ ppm for **6**; $\Delta\delta = 49$ ppm for **9**) indicating a weak interaction of the tin center with the oxygen atoms of the side chain. In THF, the solvent molecules apparently displace the ether donors from the side chains. The stongest dependence of the ^{119}Sn chemical shift from the solvent used is, as expected, found for the *N,N′*-alkyl-substituted stannylenes **3** ($\Delta\delta = 115$ ppm) and **4** ($\Delta\delta = 62$ ppm).

The conclusions drawn from the NMR spectra have been confirmed by the molecular structures of the stannylenes **3**, **5**, and **8** which we determined by X-ray diffraction. In the solid state, stannylene **3** is a bimolecular aggregate with three-coordinated tin atoms (Figure 1). The centrosymmetric aggregate is held together by strong intermolecular Sn···N interactions (Sn···N2* 2.361(2) Å). This contrasts the dimerization behavior of the stannylene with the sterically demanding *N,N′*-CH_2*t*-Bu groups which exists in the solid state as a dimer with contacts between the tin atom of one stannylene and the phenyl ring of an adjacent stannylene molecule. The free electron pair of one of the ring nitrogen atoms (N2) interacts with the formally empty p-orbital of a tin atoms from an adjacent stannylene (Sn*). This leads to a significant pyramidalization of the nitrogen atoms involved in intermolecular coordination (sum of angles at N2 344.5°) compared to the other ring nitrogen atom (sum of angles at N1 358.7°). A similar but weaker interaction was observed in bridged benzannulated bisgermylenes.[18] As a consequence of the intermolecular interaction the Sn−N2 bond distance is significantly longer than the Sn−N1 distance due to the less effective π-bonding between N2 and Sn.

The *N,N′*-methyl groups in the crystal structure of **3** are nonequivalent. Only equivalent *N*-methyl groups have been detected in ^{1}H NMR and ^{13}C NMR spectra of **3**. This is obvious for a THF solution of **3**, as the dimer breaks up giving the monomer presumably of formula **3**·2THF with the THF donors coordinating into the empty p-orbital at the tin atom. The equivalence of the methyl groups of **3** in benzene solution could be the result of a fast intermolecular interchange of the nitrogen atoms coordinated to the tin atom. Alternatively, and more likely, the dimer simply breaks up in benzene solution into two monomers with two-coordinated tin atoms. Such a behavior is indicated by the significant highfield shift of the ^{119}Sn resonance of **3** in benzene compared to the same resonance in THF.

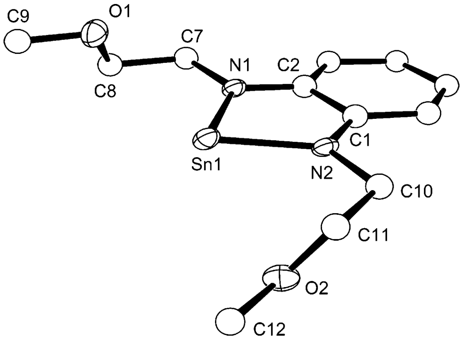


Figure 2. Molecular structure of stannylene **5**. Selected bond lengths (Å) and angles (deg): Sn−N1 2.079(3), Sn−N2 2.085(3), Sn···O1 3.060(3), Sn···O2 3.120(3), N1−C2 1.370(4), N1−C7 1.460(4), N2−C1 1.365(4), N2−C10 1.465(4), C1−C2 1.451(4); N1−Sn−N2 77.59(10), Sn−N1−C2 116.2(2), Sn−N1−C7 126.6(2), C2−N1−C7 117.2(3), Sn−N2−C1 116.1(2), Sn−N2−C10 126.8(2), C1−N2−C10 117.1(2).

Stannylene **5** exists in the solid state as a monomer (Figure 2). The heterocycle as well as the annulated ring are essentially planar. The nitrogen atoms are surrounded in a trigonal-planar fashion (sum of angles at N1 and N2 360°). The Sn−N bond lengths are identical within experimental error. Their values as well as the N−Sn−N bond angle compare well with with reported equivalent values for *N,N′*-dineopentylbenzimidazolin-2-stannylene.[8] The intramolecular Sn···O distances measure 3.060(3) and 3.120(3) Å and are only slightly shorter that the sum of the van der Waals radii for these atoms.[19] They are much longer than the Sn−O bonds on complex $SnCl_2$·1,4-dioxane, where the coordinative Sn−O bond lengths measures 2.527(5) Å.[20]

As predicted by the strong variation of the chemical shift for the stannylene tin atom in the ^{119}Sn NMR spectra ($\Delta\delta = 59$ ppm, Scheme 5), the molecular structure analysis confirmed the existence of only weak intramolecular Sn···O interactions in **5**. In THF solution this solvent will coordinate to the tin center substituting any other weak intramolecular Sn···O interaction and thereby causing the observed upfield shift of the ^{119}Sn resonance. While the chemical shift for the tin atoms is significantly different in **5** and **6**, the $\Delta\delta$ calculated for ^{119}Sn spectra recorded in C_6D_6 and THF-d_8 are almost identical, which we take as an indication that similar intramolecular interactions exist in those two stannylenes.

We have previosly described the molecular structure of the stannylene **7**, which is substituted at the nitrogen atoms with $CH_2CH_2NMe_2$ groups.[14] The structure analysis revealed the existence of both intermolecular Sn−N interactions like

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[19] (a) Bondi, A. *J. Chem. Phys.* **1964**, *68*, 441. (b) Batsanov, S. S. *Inorg. Mater.* **2001**, *37*, 871.

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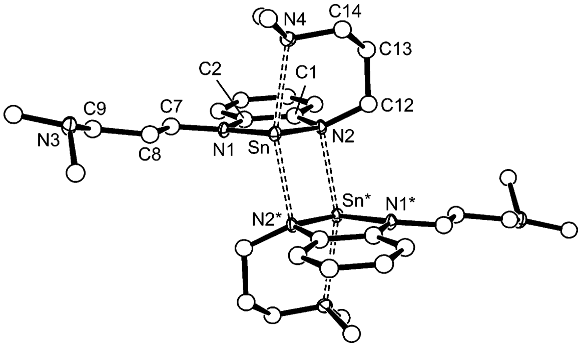

Figure 3. Molecular structure of stannylene **8**. Selected bond lengths (Å) and angles (deg): Sn−N1 2.111(2), Sn−N2 2.149(2), Sn−N2* 2.611(2), Sn−N4 2.612(2), N1−C2 1.380(2), N1−C7 1.456(2), N2−C1 1.411(2), N2−C12 1.468(2), C1−C2 1.427(3); N1−Sn−N2 77.90(6), N1−Sn−N2* 91.15(6), N1−Sn−N4 90.63(8), N2−Sn−N2* 80.36(6), Sn−N1−C2 114.82(12), Sn−N1−C7 126.81(13), C2−N1−C7 116.8(2), Sn−N2−C1 112.68(12), Sn−N2−C12 116.70(13), C1−N2−C12 117.5(2).

in **3** and intramolecular coordination of the Me_2N group of the side chains to the tin atoms. The intramolecular interaction appeared to be hampered by the topology of the ethylene side chain which is too short to allow for a strain-free interaction of the Me_2N donor with the p-orbital at the tin atom.

Stannylene **8** possesses longer $-CH_2CH_2CH_2NMe_2$ substituents at the ring nitrogen atoms, and this might allow for a strain-free intramolecular coordination of the Me_2N donor group. The molecular structure of **8** was established by X-ray diffraction (Figure 3). The unit cell of **8** contains a centrosymmetric bimolecular aggregate where each tin atom maintains four Sn−N contacts. Two Sn−N1(N2) bonds are formed within the stannylene heterocycle. In addition, one intermolecular Sn−N2* and one intramolecular Sn−N4 bonds are formed. As observed for **3**, the intramolecular Sn−N2 bond distance involving the nitrogen atoms engaged in intermolecular contacts is elongated (Sn−N2 2.149(2) Å) compared to the Sn−N1 bond distance of 2.111(3) Å. Consequently, atom N2 is pyramidalized (sum of angles 346.9°) while atoms N1 is surrounded in a trigonal-planar fashion (sum of angles 358.4°). The intermolecular distance Sn−N2* (2.611(2) Å) and the intramolecular Sn−N4 distance (2.612(2) Å) are about equally long. They are, however, much longer than the endocyclic Sn−N1(N2) distances. The Sn−N4 and Sn−N2* bonds are oriented almost perpendicular to the plane of the stannylene ring, indicating that the tin p-orbital interacts with these donor functions. The bimolecular aggregate appears to be stable in the solid state. However, since no dependence of the ^{119}Sn resonance from the solvent was observed, the dimer **8** appears to break up in solution as the NMR spectra indicate only one set of resonances for the NMe_2 donor groups.

Conclusions

Benzimidazolin-2-stannylenes with alkyl and donor-functionalized N,N′-substituents have been prepared and were characterized by ^{119}Sn NMR spectroscopy and X-ray analysis. Substitution of the ring nitrogen atoms with $-(CH_2)_nNMe_2$ ($n = 2, 3$) donor groups leads to stannylenes with tetracoordinated tin atoms by intermolecular or intramolecular nitrogen coordination showing the Lewis-acidic character of the tin atom in these derivatives. ^{119}Sn NMR spectroscopy indicates that these stannylenes are stabilized in solution by intramolecular coordination of donor-functionalized N-substituents and/or solvent molecules.

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Supporting Information Available: X-ray crystallographic files for compounds **3**, **5**, and **8** in CIF format and the spectroscopic data for the amides **1a**−**o** and amines **2a**−**d**,**g**−**i**,**m**−**o**. This material is available free of charge via the Internet at http://pubs.acs.org.

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