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A zwitterionic carbene–stannylene adduct via cleavage of a dibenzotetraazafulvalene by a stannylene

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Abstract

Reaction of the tetraamine 1,2-C_6H_4-$[NHCH_2CH_2N(CH_3)_2]_2$ (**8**) with bis(bis(trimethylsilyl)amido)tin(II) yields the *N*-heterocyclic stannylene 1,2-C_6H_4-$[NCH_2CH_2N(CH_3)_2]_2Sn$ (**9**) which contains additional 2-(dimethylamino)ethyl groups at the nitrogen atoms of the five-membered ring. These additional donor groups provide for an intramolecular stabilization of the electron deficient tin center. The X-ray structure analysis with crystals of **9** shows two three-coordinated tin atoms with different coordination environments in a dinuclear complex. Reaction of the stannylene **9** with the *N,N′N″N‴*-tetramethyldibenzotetraazafulvalene **4** leads via C=C bond cleavage in the dibenzotetraazafulvalene to the yellow carbene–stannylene adduct **10**. The X-ray structure analysis of **10** reveals bond parameters consistent with a zwitterionic species made up from a partially cationic carbene subunit and a partially anionic stannylene unit. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Dibenzotetraazafulvalene; C–C cleavage; Carbene; Stannylene; Adduct

1. Introduction

Some years after the synthesis of the first stable carbene of the imidazolin-2-ylidene type **1** [1] the preparation of saturated imidazolidin-2-ylidenes **2** [2] and of *N,N′*-bis(2,2-dimethylpropyl)benzimidazolin-2-ylidene **3** [3,4] as well as triazol derived [5] and acyclic *N,N′*-stabilized carbenes [6] were reported [7]. The *N*-heterocyclic carbene **3** exhibits, with respect to the five-membered ring, the topology of an unsaturated carbene of type **1**. However, spectroscopic and structural properties of **3** are similar to those observed for saturated derivatives of type **2** [4].

Not only spectroscopically, but also chemically *N,N′*-dialkylated benzimidazolin-2-ylidenes are similar to saturated carbenes of type **2** [2]. During their preparation from the corresponding thiones according to Kuhns method [8], different products are obtained depending on the *N*-substituents. Larger substituents, like neopentyl, stabilize the free carbene **3** [3,4], while the *N*-methyl substituted thione yields upon reduction the dibenzotetraazafulvalene **4** [4,9] with a N_2C=CN_2 double bond.

Dimerization and C=C–bond formation was never observed with unsaturated carbenes of type **1** but can be enforced by bridging the carbenes together over the ring nitrogen atoms [10]. On the other hand, enetetraamine formation is not untypical for derivatives of type **2**, which depending on the steric bulk of the *N*-substituents can exist as monomeric carbenes or as enetetraamines [2b].

We have shown recently, that an equilibrium between the carbene and the enetetraamine exists at room temperature in the presence of KH for the *i*-butyl substituted derivative **5** [11]. This behavior was proposed almost 40 years ago [12] but was never demonstrated conclusively [13–15] for carbenes of type **2**. For the sterically less demanding methyl substituted dibenzotetraazafulvalene **4**, the carbene–enetetraamine equilibrium can only be established in the presence of a catalyst, presumably a trace of electrophile, and it becomes impracticably slow in the presence of KH [16] (see Scheme 1).

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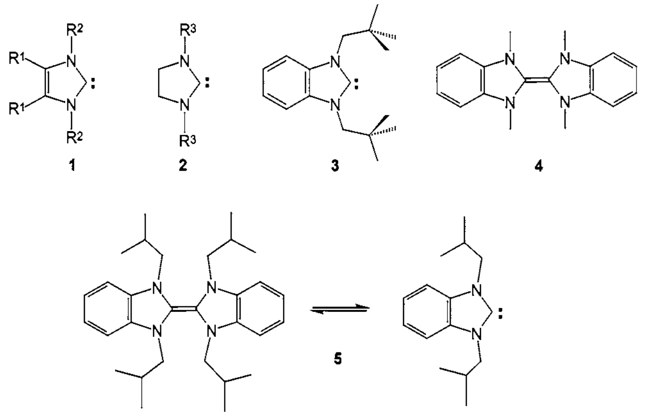
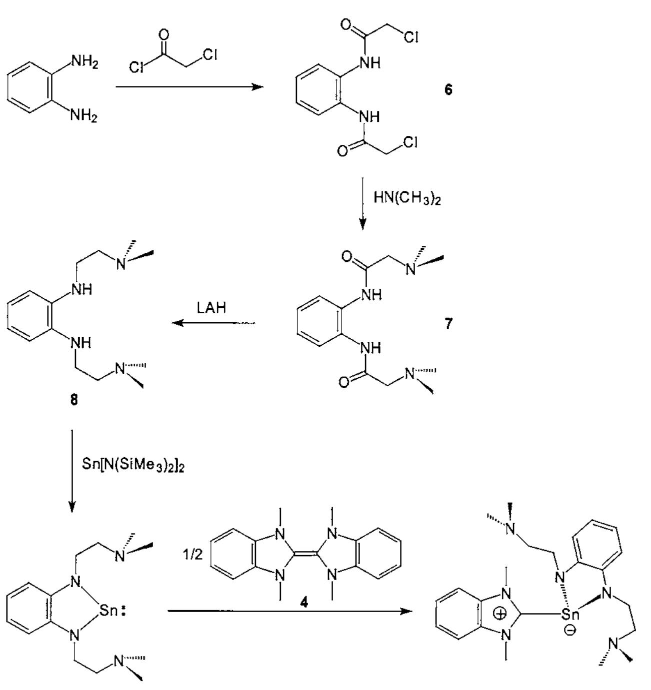
While the carbene–enetetraamine equilibrium observed for **5** at room temperature is unique [11], the cleavage of enetetraamines including **4** under catalysis by an electrophile is not. In fact, reaction of an enetetraamine with a coordinatively unsaturated metal complex is a standard method for the preparation of complexes with *N*-heterocyclic carbene ligands and Lappert and coworkers have reported numerous examples for such carbene complexes [17]. In the light of these results, we became interested in searching for the weakest Lewis acids which would still be able to induce cleavage of dibenzotetraazafulvalene **4** and to form a carbene complex. Cyclic diazastannylenes were selected as promising weak Lewis acids for such a study (see Scheme 2).



Scheme 1.



Scheme 2. Preparation of stannylene **9** and of the carbene–stannylene adduct **10**.

In contrast to heteroatom stabilized carbenes, which react normally as strong nucleophiles [7], the isoelectronic diazastannylenes show both nucleophilic and electrophilic properties [18]. The nucleophilic character of stannylenes is apparent from the multitude of metal complexes with stannylene ligands [18]. Braunschweig et al. reported the molecular structures of *N*,*N*′-disubstituted *o*-phenylenediamido tin(II) compounds [19]. These stannylenes possess an electrophilic p-orbital, which lead to the formation of stable adducts with a tertiary amine.

Free stable carbenes like **2** or **3** react with bivalent Group 14 compounds like plumbylenes [20] or silylenes [3] to yield zwitterionic carbene adducts in which carbene coordination occurs in the empty p-orbital of the Group 14 atom. We report here the reaction of the dibenzotetraazafulvalene **4** with the diazastannylene **9** which leads to C=C–bond cleavage and formation of a zwitterionic carbene–stannylene adduct.

2. Results and discussion

The tetraamine **8** (Scheme 2) was obtained according to methods described previously [4] by double acylation of *o*-phenylenediamine followed by substitution of the chloro groups for tertiary amines and finally reduction with lithium aluminum hydride. The tetraamine **8** reacts with $Sn[N(SiMe_3)_2]_2$ in THF to yield the orange, air sensitive diazastannylene **9**, which can be recrystallized from toluene.

The resonance of the tin atom in the ^{119}Sn-NMR spectrum of **9** is strongly shifted upfield from that observed for similar *N*-heterocyclic diazastannylenes (e.g. $1,2\text{-}C_6H_4[N(CH_2^tBu)]_2Sn$ in C_6D_6 $\delta = 269.03$ ppm [19]). In addition, the ^{119}Sn resonance of **9** does not depend on the solvent used (in C_6D_6 $\delta = 49.0$ ppm, in THF-d_8 $\delta = 50.6$ ppm). We take the upfield shift and the independence of the ^{119}Sn resonance from the solvent as an indication of either intermolecular or intramolecular donor stabilization. An intermolecular stabilization can, for example, result from an interaction of the ring amido groups of one stannylene with the tin atom of another stannylene molecule, leading to a dimer with three-coordinated tin atoms. Such dimerization has been reported by Veith [21]. Alternatively, the ethylamine arms at the ring nitrogen atoms allow an intermolecular or intramolecular donor stabilization of the tin atom. A similar stabilization of a cyclic diazastannylene with free tmeda has been reported by Lappert [19]. The ^{1}H- and ^{13}C-NMR spectroscopic data in solution indicate, that **9** is a highly symmetric and probably monomeric. The N-bonded residues are found to be equivalent by NMR spectroscopy and only three ^{13}C resonances are observed in the aromatic region. However, solid state NMR measurements of **9** shows

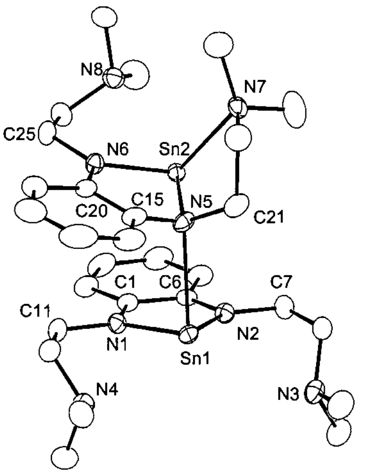


Fig. 1. Molecular structure of **9**. Selected bond lengths [Å] and bond angles [°]: Sn1–N1 2.101(2), Sn1–N2 2.131(2), Sn1–N5 2.541(2), N1–C1 1.386(3), N1–C11 1.454(3), N2–C6 1.378(3), N2–C7 1.448(3), Sn2–N5 2.202(2), Sn2–N6 2.105(2), Sn2–N7 2.497(2), N5–C15 1.420(4), N5–C21 1.471(4), N6–C20 1.386(3), N6–C25 1.443(3); N1–Sn1–N2 76.75(8), N1–Sn1–N5 89.69(8), N2–Sn1–N5 90.78(8), Sn1–N1–C1 116.2(2), Sn1–N1–C11 127.4(2), C1–N1–C11 116.2(2), Sn1–N2–C6 115.5(2), Sn1–N2–C7 126.8(2), C6–N2–C7 117.4(2), N5–Sn2–N6 76.74(8), N5–Sn2–N7 74.82(8), N6–Sn2–N7 104.31(8), Sn1–N5–Sn2 106.00(8), Sn2–N5–C15 112.5(2), Sn2–N5–C21 111.2(2), C15–N5–C21 114.0(2), Sn2–N6–C20 117.5(2), Sn2–N6–C25 125.5(2), C20–N6–C25 117.0(2).

three to four different signals for some atoms, indicating a more complex structure of **9** in the solid state.

The molecular structure of **9** (Fig. 1) was established by single crystal X-ray diffraction and shows, that both an intermolecular and an intramolecular mode of nitrogen donor coordination is operative in **9**. The asymmetric unit contains a dinuclear complex made up from two molecules of **9**. The tin atoms in the distannylene are both three-coordinated. Atom Sn1 is coordinated by two amido nitrogen atoms from its *N*-heterocyclic ring (N1, N2) and one amido group (N5) from the second stannylene of the dinuclear complex. As expected, nitrogen atoms N1 and N2 are planar (sum of angles are 359.8 and 359.7°, respectively) as is the whole five-membered ring. The bond distances Sn1–N1 (2.101(2) Å) and Sn1–N2 (2.131(2) Å) are similar and are much shorter than the Sn1–N5 bond (2.541(2) Å). The bond angle N1–Sn1–N2 76.75(8)° is typical for cyclic diazastannylenes and corresponds well with the values reported for similar molecules [19]. Atom Sn2 is also coordinated by two ring amido atoms. However, atoms N5 and N6 show different geometries. While atom N6 is planar (sum of angles 360°) like atoms N1 and N2, this does not hold for N5 which deviates significantly from planarity (sum of angles 337.7°) owing to its simultaneous intramolecular coordination to Sn2 and intermolecular coordination to Sn1. The sp^3-character and the reduced electronegativity of atom N5 are also expressed in an elongation of the Sn2–N5 bond length (2.202(2) Å) compared to the Sn2–N6 distance (2.105(2) Å), where the Sn2–N6 distance is in the range observed for the Sn1–$N(sp^2)$ distances. Atom Sn2 completes its coordination sphere by interaction with nitrogen atoms N7 (Sn2–N7 2.497(2) Å). It is interesting to note, that the intermolecular Sn1–N5 bond is almost of the same length as the intramolecular Sn2–N7 bond although different donors (amido N5 or amine N7) are involved.

The coordination geometry at the tin atoms differs significantly. The Sn1–N5 vector resides almost perpendicular on the N1–Sn1–N2 plane (angles N1–Sn1–N5 89.69(8)°, N2–Sn1–N5 90.78(8)°), as would be expected for a donor atom coordination into the p-orbital at Sn1. The Sn2–N7 bond, on the other hand, is strongly tilted towards N5 (N5–Sn2–N7 74.82(8)°, N6–Sn2–N7 104.31(8)°) which is due to the steric limitations of the short ethylamine ligand arm (see Fig. 1).

The yellow, crystalline stannylene–carbene adduct **10** was obtained by slow evaporation of the toluene solvent from a solution of **9** and dibenzotetraazafulvalene **4**. The yield of crystalline **10** was about 67%. However, the product is extremely unstable. A very likely reason for the rapid decomposition is the interaction with visible light during purification attempts. Therefore all experiments to isolate a pure sample from the solution failed. Similar behavior has been reported for a carbene–plumbylene adduct [20], while a carbene–silylene adduct which is very similar to **10** appears to be more stable [3]. NMR investigations with **10** could not be carried out. However, it was possible to isolate and prepare for X-ray analysis a crystal from the reaction mixture.

Compound **10** crystallizes with two independent molecules in the asymmetric unit. The results of the X-ray structure analysis of **10** are presented in Fig. 2. Only one of the two essentially identical molecules is shown. Complex **10** possesses a long $Sn–C_{carbene}$ bond (Sn–C30 2.399(4) for molecule A, 2.382(4) Å for molecule B). The essentially planar carbene is oriented in a perpendicular fashion to the planar stannylene unit. The bond lengths found for the $N(sp^2)$–Sn contacts (Sn–N1 2.142(3), Sn–N2 2.162(4) Å for molecule A; 2.160(4) and 2.133(4) Å for molecule B) are slightly longer than those found in the dinuclear stannylene **9** (range 2.101(2)–2.131(2) Å), indicating a partial negative charge at the tin atom. Compared to the free benzimidazolin-2-ylidene **3** [4], the coordinated carbene in **10** experiences a widening of the N–C–N angle (N31–C30–N32 106.1(3) and 105.4(3)° vs. 103.5(1) and 104.3(1)° in **3**) and a shortening of the $N–C_{carbene}$ bond lengths (N31–C30 1.346(5) and 1.356(5) Å, N32–C30 1.347(5) and 1.348(5) vs. average 1.365 Å in **3**). The bond parameters observed for the carbene subunit in **10** are comparable to those of the dication of **4** (N–C–N 109.0(7), 111.5(7)° and N–C 1.333(7), 1.328(7) Å) [9], indicating that the carbene subunit in **10** possesses a partial positive charge.

The tertiary amine groups (N13, N23) which were at least partially coordinated to the tin atom in **9** are no longer in the vicinity of the tin atom in **10**. One of them (N23) is now positioned over the empty p-orbital of the partially positive charged carbene carbon atom C30 at a distance of 3.208(6) (molecule A) or 3.230(6) Å (molecule B) which is slightly shorter than the sum of the corresponding van der Waals radii (N–C 3.25 Å [22]). This might be due to packing effects but could also result from a weak interaction between the partial positive carbene carbon atom C30 and the electron rich tertiary amine nitrogen atom N23. The direction of the C30–N23 vector is not exactly perpendicular to the carbene plane, apparently due to the limited lengths of the ethylamine arm (see Fig. 2).

The bond parameters determined for **10** allow the conclusion that the labile carbene–stannylene adduct has zwitterionic character and is made up from a partially cationic carbene and a partially anionic stannylene subunit. The molecular structure of **10** is similar to those of the carbene–silylene adduct reported by Lappert [3] or the carbene–plumbylene adduct described by Weidenbruch [20]. All three molecules contain a nucleophilic carbene coordinated to a subvalent Group 14 atom where the carbene plane and the ER_2 plane ($E =$ subvalent Group 14 element) are oriented in an almost perpendicular fashion. This differs, obviously due to the different size of the involved orbitals, from the bonding situation in dimers of benzimidazolin-2-ylides, where the two singlet carbenes combine to form a non-planar double bond [9,11].

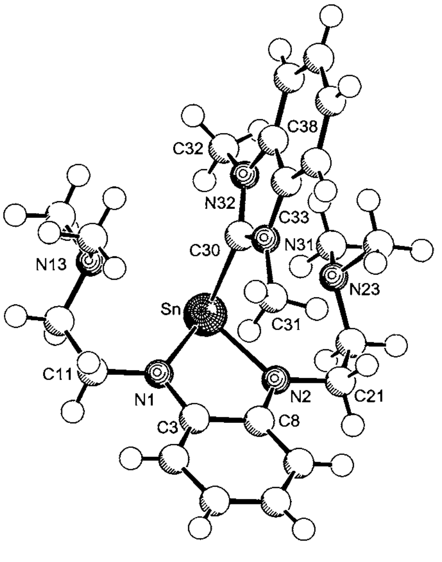


Fig. 2. Molecular structure of **10**. Only one of the two molecules in the asymmetric unit is shown. Selected bond lengths [Å] and angles [°] for molecule A [molecule B]: Sn–N1 2.142(3) [2.160(4)], Sn–N2 2.162(4) [2.133(3)], Sn–C30 2.399(4) [2.382(4)], N1–C3 1.381(5) [1.383(6)], N1–C11 1.447(5) [1.422(7)], N2–C8 1.382(6) [1.379(6)], N2–C21 1.441(6) [1.444(7)], N31–C30 1.346(5) [1.356(5)], N31–C31 1.457(5) [1.460(6)], N31–C33 1.393(5) [1.392(5)], N32–C30 1.347(5) [1.348(5)], N32–C32 1.456(6) [1.464(5)], N32–C38 1.392(5) [1.398(5)], N23···C30 3.208(6) [3.230(6)]; N1–Sn–N2 74.85(14) [75.10(15)], N1–Sn–C30 98.93(13) [93.69(14)], N2–Sn–C30 92.87(14) [97.94(15)], Sn–C30–N31 130.9(3) [122.0(3)], Sn–C30–N32 122.5(3) [132.5(3)], N31–C30–N32 106.1(3) [105.4(3)].

Meanwhile carbene–stannylene adducts have been reported for cyclopropenylidene [23], imidazolin-2-ylidene [24], and benzimidazolin-2-ylidene [25], where the latter two *N*-heterocyclic carbenes, in contrast to the benzimidazolin-2-ylidenen in **10**, can also be isolated in the free state. None of these adducts exhibits properties consistent with a Sn=C double bond. However, the Sn–C distances vary in the carbene–stannylene adducts from 2.472(5) [25] to 2.303(9) Å [23] which appears to be caused by the steric demand of the carbene or stannylene, respectively.

The carbene–stannylene adduct **10** is part of a wider study to explore the reactivity of nucleophilic *N*-heterocyclic carbenes with main group compounds. The carbenes used for this will be either of type **3**, as in carbene–stannylene adduct reported by Lappert [25] or can be generated in situ by cleavage of suitably substituted dibenzotetraazafulvalenes by quite weak Lewis acids like stannylene **9**.

3. Experimental

3.1. General procedures

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AC 200 or Bruker AM 250 spectrometer. Elemental analyses were obtained with a Vario EL elemental analyzer at the Freie Universität Berlin. Mass spectra (EI, 70 eV) were taken on a Finnigan MAT 112 spectrometer. Air sensitive compounds were prepared and handled under argon by Schlenk techniques. All solvents used were dried rigorously (typically over Na or Na/K and benzophenone) and freshly distilled prior to use. X-ray data sets were collected on a CAD-4 counter diffractometer for **9** or on a Nonius KappaCCD diffractometer for **10**. $Sn[N(SiMe_3)_2]_2$ was purchased from Aldrich.

*3.2. N,N′-Bis(2-chloroethyl)-1,2-diamidobenzene (**6**)*

Yield 90% of a red solid. ^{1}H-NMR (250 MHz, DMSO-d_6): 9.61 (s, 2H, NHC(O)), 7.50 (m, 2H, ArH), 7.18 (m, 2H, ArH), 4.42 (s, 4H, $CH_2C(O)$). ^{13}C-NMR (62.9 MHz, DMSO-d_6): 165.2 (NHC(O)), 130.2, (*i*-ArC*)*, 125.7 (*m*-ArC), 125.1 (*o*-ArC), 43.3 (CH_2Cl).

3.3. N,N′-Bis(2-dimethylaminoethyl)-1,2-diamidobenzene (***7***)

Yield 84% of a brown oil. ^{1}H-NMR (250 MHz, DMSO-d_6): 9.2 (s, br, 2H, NHC(O)), 7.43 (m, 2H, ArH), 6.71 (m, 2H, ArH), 2.96 (s, 4H, $\mathrm{CH_2C(O)}$), 2.06 (s, 12H, $\mathrm{CH_3}$). ^{13}C-NMR (62.9 MHz, DMSO-d_6): 168.6 (NHC(O)), 129.2 (*i*-ArC*)*, 125.2 (*m*-ArC), 123.9 (*o*-ArC), 62.2 ($\mathrm{CH_2N}$), 45.1 ($\mathrm{CH_3}$).

3.4. N,N′-Bis(2-dimethylaminoethyl)-1,2-diaminobenzene (***8***)

Yield 85% of an air-sensitive brown oil. ^{1}H-NMR (250 MHz, $\mathrm{C_6D_6}$): 6.98 (m, 2H, ArH), 6.76 (m, 2H, ArH), 4.20 (s, br, 2H, $\mathrm{N}H\mathrm{CH_2}$), 2.96 (t, 4H, $\mathrm{NHC}H_2$), 2.38 (t, 4H, $\mathrm{C}H_2\mathrm{N(CH_3)_2}$), 1.97 (s, 12H, $\mathrm{CH_3}$). ^{13}C-NMR (62.9 MHz, $\mathrm{C_6D_6}$): 138.2 (*i*-ArC), 119.3 (*m*-ArC), 111.6 (*o*-ArC), 58.2 ($\mathrm{NHCH_2}$), 45.1 ($\mathrm{CH_3}$), 41.9 ($C\mathrm{H_2N(CH_3)_2}$).

3.5. Synthesis of N,N′-bis(2-dimethylaminoethyl)-1,2-diamidobenzene tin(II) (***9***)

To a stirred solution of **8** (0.30 g, 1.2 mmol) in 30 ml of THF was added 0.53 g (1.2 mmol) of $\mathrm{Sn[N(SiMe_3)_2]_2}$. The solution was stirred for 36 h at room temperature (r.t.) and then evaporated to dryness. The orange residue was recrystallized from toluene to yield 0.37 g (83%) of orange, air-sensitive crystals of **9**. M.p. 163°C. ^{1}H-NMR (400 MHz, THF-d_8): 6.48 (m, 2H, ArH), 6.41 (m, 2H, ArH), 3.51 (t, 4H, $\mathrm{HNC}H_2$), 2.43 (t, 4H, $\mathrm{C}H_2\mathrm{N(CH_3)_2}$), 2.12 (s, 12H, $\mathrm{CH_3}$). ^{13}C-NMR (100 MHz, THF-d_8): 147.8 (*i*-ArC), 116.6 (*m*-ArC), 109.3 (*o*-ArC), 59.6 ($\mathrm{SnNCH_2}$), 47.1 ($C\mathrm{H_2N(CH_3)_2}$), 44.7 ($\mathrm{CH_3}$). ^{13}C-NMR (75.5 MHz, MAS, solid state): 150.9 (*i*-ArC), 147.4 (*i*-ArC), 146.3 (*i*-ArC), 143.4 (*i*-ArC), 120.1 (*m*-ArC), 115.5 (*m*-ArC), 115.1 (*m*-ArC), 114.6 (*m*-ArC), 108.4 (*o*-ArC), 106.9 (*o*-ArC), 60.7 ($\mathrm{SnNCH_2}$), 58.7 ($\mathrm{SnNCH_2}$), 55.4 ($\mathrm{SnNCH_2}$), 50.3 ($C\mathrm{H_2N(CH_3)_2}$), 46.8 ($C\mathrm{H_2N(CH_3)_2}$), 45.2 ($C\mathrm{H_2N(CH_3)_2}$), 43.3 ($\mathrm{CH_3}$). ^{119}Sn-NMR (149 MHz, $\mathrm{C_6D_6}$): 49.0. ^{119}Sn-NMR (149 MHz, THF-d_8): 50.6. MS (EI, relative intensity %) *m*/*e*: 368 (3.8, $\mathrm{M^+}$), 310 (8.6, $\mathrm{M^+ - CH_2N(CH_3)_2}$), 58 (100, $\mathrm{(CH_2N(CH_3)_2)^+}$).

3.6. Synthesis of N,N′,N″,N‴-tetramethyl-dibenzotetraazafulvalene (***4***)

We have synthesized compound **4** according to the method described in Ref. [4]. An alternative synthesis is described by Lappert et al. in Ref. [9]. ^{1}H-NMR (400 MHz, $\mathrm{C_6D_6}$): 6.82 (m, 4H, ArH), 6.40 (m, 4H, ArH), 2.69 (s, 12H, $\mathrm{CH_3}$). ^{13}C-NMR (100 MHz, $\mathrm{C_6D_6}$): 136.4 (*i*-Ar*C*), 124.4 ($\mathrm{N_2C=CN_2}$), 120.8 (*m*-ArC), 110.8 (*o*-ArC), 36.0 ($\mathrm{CH_3}$).

3.7. Synthesis of the (N,N′-dimethyl-benzimidazolin-2-ylidene)-[N,N′-bis(2-dimethylamino-ethyl)-1,2-diamidobenzene tin(II)] adduct (***10***)

Stannylene **9** (0.22 g, 0.6 mmol) was dissolved in 20 ml of toluene. To this solution was added a solution of dibenzotetraazafulvalene **4** (0.09 g, 0.3 mmol) in 10 ml of toluene. The resulting solution was stirred for 24 h. Slow evaporation of the toluene solvent yielded yellow, air sensitive crystals of **10**. Yield 0.21 g (0.4 mmol, 66.7%). Upon isolation the crystals decompose rapidly. NMR spectroscopic investigations showed only the resonances for the starting materials **4** and **9**. The crystals can be stored under toluene for some weeks without decomposition.

3.8. Selected crystallographic details for ***9***

Orange crystals of **9** were obtained from a toluene solution at r.t. Selected crystallographic details for **9**: size of data crystal $0.15 \times 0.5 \times 0.8$ mm, formula $\mathrm{C_{28}H_{48}N_8Sn_2}$, $M = 734.12$ amu, monoclinic, space group $P2_1/n$ (no. 14), $a = 12.2857(12)$, $b = 16.8231(8)$, $c = 15.5989(14)$ Å, $\beta = 97.828(8)°$, $V = 3194.0(5)$ Å^3, $Z = 4$, $\rho_{\mathrm{calc}} = 1.527$ g cm^{-3}, Mo–K$_\alpha$ radiation, ($\lambda = 0.71073$ Å, graphite monochromator), $\mu(\mathrm{Mo-K_\alpha}) = 1.594$ mm^{-1}. 9265 symmetry independent diffraction data were measured at $-120(2)$°C in the 2Θ-range 5–60°. Structure solution with Patterson and refinement with Fourier methods, refinement (on F^2) of positional parameters of all non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms on calculated positions (d(C–H) = 0.95 Å) with $U_{\mathrm{eq(H)}} = 1.3U_{\mathrm{eq(C)}}$. $R = 0.034$, $wR^2 = 0.092$ for 8310 structure factors $I \geq 2\sigma(I)$ and 343 refined parameters. Neutral atomic scattering factors were used and all scattering factors were corrected for anomalous dispersion. All calculations were carried out with the SHELX program package [26,27].

3.9. Selected crystallographic details for ***10***

Air sensitive crystals of **10** were obtained at r.t. Formula $\mathrm{C_{23}H_{34}N_6Sn{*}C_7H_8}$, $M = 605.39$ amu, yellow crystal $0.35 \times 0.20 \times 0.05$ mm, $a = 11.112(1)$, $b = 16.302(1)$, $c = 16.631(1)$ Å, $\alpha = 68.97(1)$, $\beta = 77.91(1)$, $\gamma = 84.43(1)°$, $V = 2748.8(3)$ Å^3, $\rho_{\mathrm{calc}} = 1.463$ g·cm^{-3}, $\mu(\mathrm{Mo-K_\alpha}) = 0.960$ mm^{-1}, empirical absorption correction via SORTAV ($0.730 \leq T \leq 0.954$), $Z = 4$, triclinic, space group $P\bar{1}$ (no. 2), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 36 786 reflections collected ($\pm h$, $\pm k$, $\pm l$) in the 2Θ-range 3.8–55.0°, 12 594 independent ($R_{\mathrm{int}} = 0.039$) and 10 062 observed reflections [$I \geq 2\sigma(I)$], 575 refined parameters, $R = 0.050$, $wR^2 = 0.161$, max residual electron density 1.39 (-1.62) e Å^{-3} in the region of the disordered solvate molecules toluene (refined with geometrical constrains), two almost identical independent molecules in the asymmetric unit, hydrogen atoms reside on calculated positions and were refined as riding atoms. Data set was collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection [28], data reduction [29], absorption correction [30], structure solution [26], structure refinement [27], graphics [31].

4. Supplementary material available

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 149333 for compound **9** and CCDC no. 149 334 for compound **10**. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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