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Reactivity of C,N-Chelated Stannylene with Azobenzene

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The reactivity of a C,N-chelated stannylene L_2Sn [L = 2-$(Me_2NCH_2)C_6H_4$] with azobenzene yielded two different products. In the case of reaction in diethyl ether at room temperature, the cyclic complex $L_2Sn–N(Ph)–N(Ph)–SnL_2$ was isolated. The second compound, isolated from the reaction in boiling THF, is the product of C–H activation and *ortho*-metallation of azobenzene, the cyclic [2-(SnL_2)-C_6H_4]–N–N–[C_6H_4-2-(SnL_2)]. Byproducts in the second reaction are the free ligand (LH) and the cyclic complex $L_2Sn–(L)Sn–Sn(L)_2–O(H)$.

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Introduction

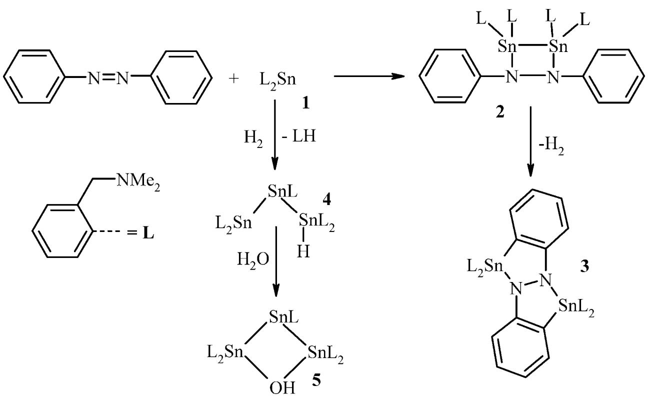
Although the heavier low-valent group 14 organometallic compounds attracted much attention in recent years,[1] there is only a limited number of articles dealing with the reactivity of such compounds, carbene and/or alkyne analogues, with unsaturated systems such as azobenzene, alkynes or nitriles.[2]

In our recent papers, we reported on the reactivity of C,N-chelated stannylene[3] towards oxidizing agents[4] and group 4 metallocenes.[5]

In this paper we would like to communicate on the reactivity of C,N-chelated stannylene towards azobenzene.

Results and Discussion

C,N-Chelated stannylene L_2Sn {L = 2-[(dimethylamino)-methyl]phenyl} (**1**) reacts with azobenzene in diethyl ether to form compound **2** (Scheme 1, Figure 1) in 14% yield under argon at room temperature after 2 d. Compound **2** is the product of reduction of azobenzene and formation of a symmetrical planar four-membered 1,2-diaza-distannacycle. According to the interatomic distances found, this cycle contains only single bonds [Sn1–N3 2.160(2), Sn1–Sn1a 2.8584(3), N3–N3a 1.440(4) Å].



Scheme 1. Reactivity of stannylene **1** towards azobenzene.

The distance Sn1–Sn1a is comparable to distances usually found in triorganotin(IV) distannanes.[6] One of each two nitrogen donor atoms of the ligands is coordinated to the tin atom by a medium strong interaction [2.622(3) Å], comparable to those found in diorganotin(IV) dihalides having the same ligand.[7] On the other hand, the only known comparable structures of azobenzene derivatives described by Power et al.[2e] (Sn and Ge) reveal no cyclic structures without bonding contacts between heavy atoms [Sn–Sn 3.2257(6) Å].

The second complex (**3**) was isolated from the same reaction in THF in a sealed ampoule under vacuum at elevated temperature (70 °C). The cyclic complex **3** is the product of C–H activation and *ortho*-metallation of azobenzene, and one can predict that it was formed from **2** by rearrangement of the cycles and rupture of the Sn–Sn bond in connection with H_2 elimination. The core structure (Figure 2) of **3** is

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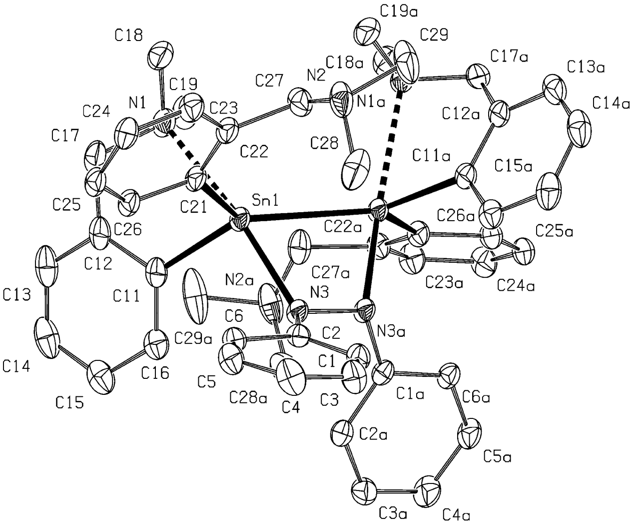

Figure 1. Molecular structure of **2**, ORTEP diagram, 50% probability level; hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1–C11 2.155(3), Sn1–N3 2.160(2), Sn1–C21 2.170(3), Sn1–Sn1a 2.8584(3), N3–C1 1.387(3), N3–N3a 1.440(4), Sn1–N1 2.622(3), Sn1–N2 4.745(3), C11–Sn1 N3 96.89(10); C11–Sn1–C21 106.29(11), N3–Sn1–C21 105.57(10), C11–Sn1–Sn1 122.97(7), N3–Sn1–Sn1 70.73(5), C21–Sn1–Sn1a 130.73(8), C1–N3–N3a 114.6(2), C1–N3–Sn1 121.83(17), N3a–N3–Sn1 108.96(6), N1–Sn1–N3 167.62(9), Sn1a–Sn1–N1 108.21(6).

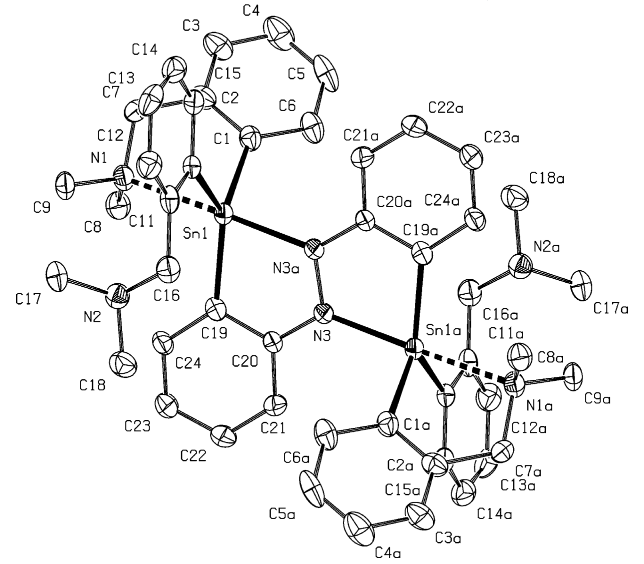

Figure 2. Molecular structure of **3**, ORTEP diagram, 50% probability level; hydrogen atoms are omitted for clarity. One of two independent molecules is shown only. Selected interatomic distances [Å] and angles [°] (values for the second molecule are given in brackets): Sn1–C19 2.101(9) [2.110(8)], Sn1–C10 2.146(9) [2.138(9)], Sn1–C1 2.156(9) [2.159(9)], Sn1–N3a 2.160(7) [2.157(7)], Sn1–N1 2.568(7), [2.670(8)], Sn1–N2 3.597(8) [4.411(11)], N3–N3a 1.424(13) [1.435(12)]; C19–Sn1–C10 128.6(3) [124.1(3)], C19–Sn1–C1 126.6(3) [127.8(3)], C10–Sn1–C1 104.0(3) [106.9(3)], C19–Sn1–N3a 78.4(3) [78.9(3)], C10–Sn1–N3 102.7(3) [103.1(3)], C1–Sn1–N3 100.9(3) [101.3(3)], N3–Sn1–N1 167.8(3) [170.5(3)].

planar with two SnC_2N_2 cycles connected by the N–N bond of the rings. All distances within the rings are single bonds. Organotin(IV) derivatives of azobenzene were prepared from organomercury complexes and tin(IV) compounds previously, but there is significant double-bond character between both nitrogen atoms and only a medium strong intramolecular interaction between the Sn and N atoms.[7]

The C–H activation, a phenomenon known mainly in s- and d-block elements, is very rare for tin compounds.[8] In order to explain difficulties during ^{119}Sn NMR spectra measurements, we prepared complex **3** enriched in one of the azobenzene nitrogen atoms by ^{15}N (100%); but it was only possible to find ^{15}N resonances split exclusively by tin atoms (see Supporting Information). This is probably due to low solubility and fast dynamic exchange processes.

Minor byproducts in this reaction are the free ligand (LH) and complex **5**, most probably the product of reduction of the parent stannylene **1** by hydrogen abstracted from azobenzene and subsequent oxidation by traces of water. We propose here an intermediate **4** as a product of the reduction of **1**. The formation of a low-valent hydridotin species is supported by the reaction of **1** with H_2 under pressure – monitored by HP NMR spectroscopy to give LH and an insoluble material (30 bar of H_2, 2 h, yield 6%).

A similar RSnH complex was very recently published by Roesky et al.[9] The structure of **5** consists of a planar four-membered ring (Figure 3) of three tin atoms, where Sn1 and Sn3 can be described as tetravalent and Sn2 as divalent, respectively. This is clearly seen in the Sn–C distances and the almost rectangular arrangement between the plane defined by the four-membered ring and the Sn2–C19 bond [89.7(1)]°. The bridge between Sn1 and Sn3 is made up by an OH group connected intramolecularly to N4. The only proposed complex of such a type where a bond between Sn^{IV} and Sn^{II} is present is a triply chelated Sn^{IV}–Sn^{II}–Cl unit.[10]

These results were further rationalized by theoretical methods (see Supporting Information). Oxidation of stannylene **1** by O_2, S_8, Se, and Te leads to the formation of cyclic compounds bearing Sn–X bonds only (no Sn–Sn or X–X interactions).[4] Since the reactivity of stannylene **1** towards azobenzene is strikingly different, it was of interest to model the reaction pathway at the DFT level (for details see Supporting Information). The first step of interaction of **1** with N_2Ph_2 (Figure 4) is the formation of the three-membered ring compound **A** (E^0 = 7.5 kcal/mol) via transition state **TS A** (E^0 = 16.6 kcal/mol). Further insertion of a second stannylene **1** into the Sn–N bond in **A** leads to the formation of **2** (E^0 = –11.4 kcal/mol) via transition state **TS B** (E^0 = 19.3 kcal/mol). Thus, the formation of **2** is exothermic, and the total reaction barrier of 19.3 kcal/mol corresponds to a room-temperature reaction.

An alternative path of the reaction is stannylene attack at the nitrogen atom, **TS C** (E^0 = 34.9 kcal/mol), leading to stannaimine complex **C** (E^0 = 2.6 kcal/mol). Formation of two isolated imines **D** is energetically unfavorable (ΔE^0 = 11.8 kcal/mol). Formation of the (Sn–N–Sn–N) four-membered ring in **E** (E^0 = –31.2 kcal/mol) proceeds via transition state **TS E** (E^0 = 6.7 kcal/mol), which is the isomer of

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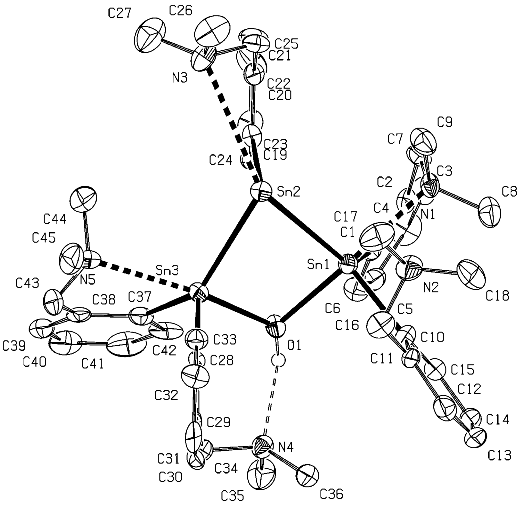

Figure 3. Molecular structure of **5**, ORTEP diagram, 50% probability level; hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1–C10 2.152(8), Sn1–C1 2.155(7), Sn1–O1 2.207(4), Sn1–N1 2.542(6), Sn1–Sn2 2.9074(8), Sn2–C19 2.228(8), Sn2–Sn3 2.8514(7), Sn1–Sn3 3.431(1), Sn3–O1 2.110(4), Sn3–C28 2.164(8), Sn3–C37 2.170(8), Sn1–N2 3.583(6), Sn2–N3 3.296(7), Sn3–N5 2.638(6); C10–Sn1–C1 102.0(3), C10–Sn1–O1 91.6(2), C1–Sn1–O1 91.5(2), C10–Sn1–N1 95.5(3), C1–Sn1–N1 73.7(2), O1–Sn1–N1 164.66(19), C10–Sn1–Sn2 133.7(2), C1–Sn1–Sn2 124.3(2), O1–Sn1–Sn2 89.01(12), N1–Sn1–Sn2 95.78(14), C19–Sn2–Sn3 95.71(18), C19–Sn2–Sn1 88.09(18), Sn3–Sn2–Sn1 73.14(2), O1–Sn3–C28 95.1(2), O1–Sn3–C37 93.0(2), C28–Sn3–C37 111.6(3), O1–Sn3–Sn2 92.48(12), C28–Sn3–Sn2 107.87(19), C37–Sn3–Sn2 139.4(2), Sn3–O1–Sn1 105.25(18), C37–Sn3–Sn2 165.45(17), N1–Sn1–O1 164.67(18), N4–H1···O1 2.732(8) 119.0.

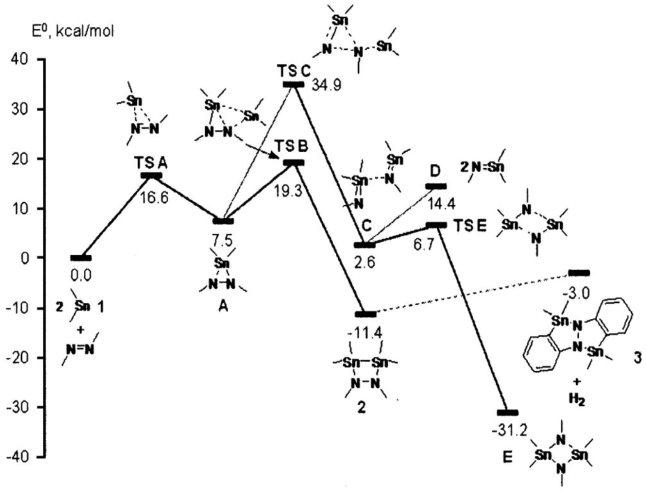

Figure 4. Potential-energy surface for the interaction of stannylene **1** with azobenzene (relative energies in kcal/mol; aryl groups at Sn and Ph groups are denoted by sticks).

2, bearing only Sn–N bonds in the cycle. Although **E** lies significantly lower in energy than **2**, the energy barrier leading to its formation (**TS C**) is prohibitively high.

Finally, the formation of **3** from **2** was found to be endothermic (ΔE^0 = 8.4 kcal/mol). We suppose that this reaction is entropy-driven, since the release of hydrogen gas proceeds at elevated temperature and reduced pressure. We are currently working on a theoretical model of unusual double C–H activation leading to **3**.

Conclusions

We demonstrated the different reactivity of a C,N-chelated stannylene with azobenzene giving unusual products of dimerization and C–H bond activation. A trinuclear tin complex containing a bridging OH group is also described.

Experimental Section

Preparation of compound 2: Stannylene **1** (0.5 g, 1.3 mmol) was mixed with azobenzene (0.236 g, 1.3 mmol) in diethyl ether (100 mL) at room temperature and stirred for 2 d. The amount of solvent was reduced to about 25 mL and the mixture filtered. The filtrate was stored in the freezer at –28 °C. Yellow crystals of **2** were obtained after one week in 14% yield (based on **1**). M.p. 172–176 °C. $C_{48}H_{58}N_6Sn_2$ (956.38): calcd. C 60.28, H 6.11, N 8.79; found C 60.3, H 6.2, N 8.7. ^1H NMR (500 MHz, [D$_6$]benzene, 295 K): δ = 1.65 (br. s, 24 H, NCH_3), 2.09 and 3.72 (AX spin system, 8 H, NCH_2), 6.61 [d, J = 7.0 Hz, 4 H, H(2′)], 6.78 [dd, J = 7.1 Hz, J = 7.0 Hz, 4 H, H(3′)], 6.93 [t, J = 6.9 Hz, 2 H, H(4′)], 7.05 [d, J = 7.1 Hz, 4 H, H(3)], 7.10 [m, 8 H, H(4,5)], 8.43 [d, J = 6.9 Hz, 4 H, H(6)] ppm. Crystallographic data: $C_{48}H_{58}N_6Sn_2$, M = 956.38, monoclinic, $C2/c$, a = 21.7109(6), b = 10.2532(2), c = 19.7708(5) Å, β = 97.2938(15)°, Z = 4, V = 4365.47(18) Å^3, $D_{\text{calcd.}}$ = 1.455 g cm^{-3}, μ = 1.184 mm^{-1}, $T_{\min}$ = 0.773, $T_{\max}$ = 0.920, 72539 reflections measured ($\theta_{\max}$ = 27.52°), 5021 independent (R_{int} = 0.0443), 4051 with $I > 2\sigma(I)$, 257 parameters, S = 1.054, R_1(obsd. data) = 0.0315, wR_2(all data) = 0.0722; max./min. residual electron density = 1.214/–1.050 e Å^{-3}.

Preparation of Compounds 3 and 5: Stannylene **1** (0.5 g, 1.3 mmol) was mixed with azobenzene (0.236 g, 1.3 mmol) in THF (100 mL) and refluxed an ampoule (sealed in vacuum) for 2 weeks. During this time, red crystals were obtained in 23% (based on **1**). The filtrate was stored in a Schlenk tube in a freezer at –28 °C for about 1 month to yield additional 19% of **3** (based on **1**) and 2% of yellow crystals of **5** (based on **1**). **3:** M.p. 216–220 °C. $C_{48}H_{56}N_6Sn_2$ (954.37): calcd. C 60.41, H 5.91, N 8.81; found C 60.4, H 6.0, N 8.7. ^1H NMR (500 MHz, [D$_8$]toluene, 295 K): δ = 1.97 (br. s, 24 H, NCH_3), 3.36 (br. s, 8 H, NCH_2), 6.06 [t, J = 7.0 Hz, 2 H, H(5′)], 6.31 [d, J = 6.9 Hz, 2 H, H(6′)], 6.48 [t, J = 6.9 Hz, 2 H, H(4′)], 7.01 [d, J = 7.2 Hz, 4 H, H(3)], 7.18 [dd, J = 7.0 Hz, 4 H, H(5)], 7.39 [dd, J = 7.3 Hz, 4 H, H(4)], 7.32 [d, J = 6.8 Hz, 2 H, H(4′)], 7.65 [d, J = 7.0 Hz, 4 H, H(6)] ppm. Crystallographic data: $C_{48}H_{56}N_6Sn_2$, M = 954.37, monoclinic, $P2_1/c$, a = 12.6902(14), b = 16.683(3), c = 20.911(4) Å, β = 107.822(11)° Z = 4, V = 4214.6(11) Å^3, $D_{\text{calcd.}}$ = 1.504 g cm^{-3}, μ = 1.227 mm^{-1}, $T_{\min}$ = 0.854, $T_{\max}$ = 0.929, 41788 reflections measured ($\theta_{\max}$ = 27°), 9516 independent (R_{int} = 0.0888), 6425 with $I > 2\sigma(I)$, 505 parameters, S = 1.148, R_1(obsd. data) = 0.0787, wR_2(all data) = 0.1636, max./min. residual electron density = 1.184/–1.228 e Å^{-3}. **5:** M.p. 130–134 °C (dec.). $C_{45}H_{61}N_5OSn_3$ (1044.06): calcd. C 51.77, H 5.89, N 6.71; found C 51.8, H 6.0, N 6.7. ^1H NMR (500 MHz, [D$_8$]THF, 295 K): δ = 1.72 and 1.79 (br. s, 30 H, NCH_3), 2.46 (s, 1 H, OH), 3.24 and 3.33 (br. s, 10 H, NCH_2), 6.98 [br., 1 H, H(3′)], 7.03 [d, J = 7.2 Hz, 4 H, H(3)], 7.28 [m, 5 H, H(4,4′)], 7.43 [m, 5 H, H(5,5′)], 8.19 [d, J = 7.3 Hz, 4 H, H(6)], 8.38 [br., 1 H, H(6′)] ppm. Crystallographic data: $C_{45}H_{61}N_5OSn_3$, M = 1044.06, monoclinic, $P2_1/c$, a =

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9.8949(7), b = 20.4812(10), c = 22.589(2) Å, β = 97.338(9)° Z = 4, V = 4540.4(6) Å^3, $D_{\text{calcd.}}$ = 1.526 g cm^{-3}, μ = 1.675 mm^{-1}, T_{min} = 0.721, T_{max} = 0.880, 10057 reflections measured (θ_{max} = 27.5°), 10057 independent (R_{int} = 0.2481), 4348 with $I > 2\sigma(I)$, 487 parameters, S = 1.003, R_1(obsd. data) = 0.0691, wR_2(all data) = 0.070, max./min. residual electron density = 0.870/–1.814 e Å^{-3}.

CCDC-711629 (for **2**), -711630 (for **3**), and -711631 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Spectroscopic data (NMR, UV/Vis, Raman), parameters of refinement and measurement of X-ray diffraction studies and method of calculation including calculated structures.

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