Supporting Information

Hydrogen abstraction from organotin di- and trihydrides by \(N\)-heterocyclic carbenes: a new method for the preparation of NHC adducts to \(\text{tin(II)}\) species and observation of an isomer of a hexastannabenzene derivative \([R_6\text{Sn}_6]\).”

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Experimental Details

General Information

All manipulations were carried out under argon atmosphere using standard Schlenk techniques or an MBraun Glovebox. THF, diethylether and benzene were distilled from sodium/benzophenone, toluene from sodium and hexane from potassium. Pentane was obtained from an MBRAUN solvent purification system. Benzene-d$_6$ was distilled from sodium and stored over potassium.

2,4,6-triisopropylphenyl bromide (>98%), diphenyltin dichloride were purchased from Aldrich chemical company and used without further purification. 2,4,6-trisopropylphenylphenyl tin trichloride was prepared according to literature procedures. The bis-2,6-(2',4',6'-triisopropylphenyl)phenyl iodide (Ar*I) and its lithiated derivative [Ar*Li(OEt)]$_2$(trip) were prepared according to literature procedures. Bis-2,6-(2',4',6'-triisopropylphenyl)phenyl phenyl trichloride was prepared along slightly modified procedures known to the literature. Elemental analysis was performed by the Institut für Anorganische Chemie, Universität Tübingen using a Vario MICRO EL analyzer.

NMR spectroscopy

NMR spectra were recorded with either a Bruker DRX-250 NMR spectrometer equipped with a 5 mm ATM probe head and operating at 250.13 (1H), 62.90 (13C) 93.3 MHz (119Sn), a Bruker AvanceII+400 NMR spectrometer equipped with a 5 mm QNP (quad nucleus probe) head and operating at 400.13 (1H), 100.62 (13C) or a Bruker AvII+ 500 NMR spectrometer with a 5 mm ATM probe head and operating at 500.13 (1H), 125.76 (13C), 186.5 MHz (119Sn) and a low-temperature set-up. Chemical shifts are reported in δ values in ppm referenced on the solvent $^1$H resonance frequency. The proton and carbon signals were assigned where possible via a detailed analysis of $^1$H, $^1$C, $^1$H-UDEFT, $^1$H-$^1$H COSY, $^1$H-$^1$C HSQC, $^1$H-$^1$C HMBC spectra.

Synthetic Details

A general procedure known to the literature for the hydrides was performed as follows:

A solution of the respective pure organotin chloride in diethylether (approx. 7 mL/mmol) was added dropwise to a cooled (−30°C for dichlorides/ −78°C for trichlorides) suspension of lithium aluminiumhydride (1.1 eq per chloride) in diethylether (approx 4 mL/mmol) under exclusion of light and oxygen. The suspension was stirred for 20 min at the respective cooling bath temperature and then allowed to warm to room temperature within 2h. The solvent was completely removed under reduced pressure and the grey residue was dried thoroughly. The residue was extracted with hexane (2 × 15 mL/mmol) and the colorless solid residue was extracted twice with diethylether (25 mL, 10 mL). The extracts were reduced pressure and the grey residue was dried thoroughly and extracted with hexanes (3 × 20 mL). Solvents were removed in vacuo to yield the organotin hydride in almost quantitative yield as colorless oils or solids.

$(trip)_2$SnH$_2$ (1): To a solution of $(trip)$SnCl$_3$ (1.499 g, 3.50 mmol, 1 eq) in THF (15 mL) a stock solution of $(trip)$MgBr (5 mL, 0.77M in THF, 3.85 mmol, 1.1 eq) was added dropwise at room temperature and the mixture was subsequently heated to the reflux for 6h. $^{119}$Sn NMR control revealed complete educt conversion and formation of three products assigned to $(trip)_2$SnCl$_2$ (approx. 35%), $(trip)_2$SnClBr (approx. 45%) and $(trip)_2$SnBr$_2$ (approx. 20%). Solvents were removed under reduced pressure and the colorless solid residue was extracted twice with diethylether (25 mL, 10 mL). The extracts were concentrated in vacuo to approx. 20 mL and, under the total exclusion of light, added dropwise to a cooled (−78°C) suspension of LiAlH$_4$ (0.246 g, 7.35 mmol, 2.1 eq) in diethylether (15 mL). The mixture was stirred for 30 min before the cooling bath was removed and the mixture was allowed to warm to approx. room temperature for 2.5h. Ether was removed in vacuo and the grey residue was dried thoroughly and extracted with hexanes (3 × 20 mL). Solvents were removed in vacuo to yield 1(1.79 g, 3.39 mmol, 97%) as a colorless oil, that slowly solidifies. Analytical data: $^1$H (250.13 MHz, C$_6$D$_6$) δ 7.25 (s, 4H), $^1$H$_{17}$/$^1$H$_{19}$Sn-n = 20.1 Hz, m-H$_{ar}$, 6.33 (s, 2H) $^1$H$_{195}$Sn-n = 1819.5 Hz, $^1$H$_{17}$Sn-n = 1737.7 Hz, Sn-$^1$H, 3.46 (sept., 4H, $^1$H$_{2}$-C$_{2}$-H$_{sm}$), 2.90 (sept., 2H, $^1$H$_{2}$-C$_{ar}$-H$_{ar}$) 6.49 Hz, $^1$H$_{i}$-C$_{2}$-H$_{sm}$) 6.72 Hz, o- CMe$_2$, 2.90 (sept., 2H, $^1$H$_{2}$-C$_{ar}$-H$_{ar}$) 6.92 Hz, p-CMe$_2$, 1.34 (d, 24H, $^1$H$_{2}$-C$_{2}$-H$_{sm}$) 6.72 Hz, o-CMe$_2$, 1.33 (d, 12H, $^1$H$_{2}$-C$_{ar}$-H$_{ar}$) 6.93 Hz, p-CMe$_2$, $^{13}$C(1H) (62.90 MHz, C$_6$D$_6$) δ 155.4 (s, $^1$C$_{2}$-C$_{ar}$) 35.5 Hz, o-C$_{Cu}$, 150.1 (s, ipso-C$_{Cu}$), 135.7 (s, p-C$_{Cu}$), 121.3 (s, $^1$C$_{2}$-C$_{ar}$) 45.2 Hz, m-C$_{Cu}$, 38.0 (s, $^1$C$_{2}$-C$_{ar}$) 41.1 Hz, o-CMe$_2$, 34.5 (s, p-CMe$_2$), 24.5 (s, o-CMe$_2$), 24.0 (s, p-CMe$_2$); $^{119}$Sn(1H) (93.28 MHz, C$_6$D$_6$) δ −352.1. Anal. Calcd for C$_{32}$H$_{68}$Sn: C 68.32, H 9.17 Found: C 68.36, H 8.50.
Reaction of (trip)_2SnH_2 with TMEDA

To a solution of (trip)_2SnH_2 (0.042 g, 0.08 mmol) in THF-d_8 (0.5 mL) two drops of TMEDA were added and the mixture was kept under the exclusion of light for 24h. The reaction progress is indicated by evolution of hydrogen and a characteristic bright pink-orange discoloration. Quantitative conversion to the known cyclotristannane was [(trip)_2Sn]_3 indicated by means of NMR spectroscopy. Spectral data and thermochromic behaviour on heating to 60°C (rationalized by changes in the equilibrium 2[(trip)_2Sn]_3 <-> 3[(trip)_2Sn]_2) are equal to the properties reported. Though most obviously [(trip)_2Sn]_3 is slowly formed no formation of distannane 4 by insertion into residual dihydride was observed. This contrasts assumptions for the formation of the distannane by means of the reported carbene approach. No hydrogen abstraction from distannane 4 by means of TMEDA was observed (vide infra). Therefore the absence of distannane in the TMEDA mediated reaction can only be explained by a TMEDA mediated suppression of the stannylene to insert the Sn–H bond.

Reaction of distannane [(trip)_2Sn(H)]_2 with TMEDA

To a solution of distannane 4 (30 mg, 0.028 mmol) in THF-d_8 (0.4 mL) TMEDA (0.1 mL) was added at room temperature and the pale yellow mixture was kept at room temperature. After three days at room temperature and daylight no change in colour was observed.

Reaction of (trip)_2SnH_2 with Pyridine

In order to test a different amine base already reported to be capable to promote hydrogen release from tin dihydrides, a sample of (trip)_2SnH_2 (0.030 g, 0.057 mmol) was dissolved in pyridine-d_5 (0.5 mL). After several hours at room temperature no change of the sample was observed. After 6h with gentle heating to approx. 60°C a pale yellow color was observed. ^{119}Sn NMR revealed >90% educt along with approx. <10% distannane. On further heating (above 80°C) the sample decomposed indicated by dark brown colour and formation of a tin mirror.

Crystallographic Details

Refinement Details

X-ray data for 6 and 7 were collected with a Bruker Smart APEX II diffractometer with graphite- monochromated Mo Ka radiation. X-ray data for 9 were collected with a Bruker Smart APEXIIduo diffractometer with graphite- monochromated Mo Ka radiation from a fine-focussed microsource. The programs used were Bruker’s APEX2 v2011.8-0, including SADABS for absorption correction and SAINT for structure solution, as well as the WinGX suite of programs version 1.70.01, including SHELXS for structure solution and SHELXL for structure refinement. For refinement details see the attached .cif-files.

Hydrogen atoms attached to tin atoms in 6 and 7 were located in the difference Fourier map and Sn–H bond length may be underestimated.

In 9- 2(C_6H_5) one of the toluene molecules was disordered and treated with a split model. The thermal ellipsoids of one p-isopropyl group of one trip-moiety attached to Sn(4) was found to be oblate and treated with the EADP command included in ShelXL.
X-ray structure of (trip)SnH₃ (6)

\[ \text{Scheme 1SI. ORTEP plot of the molecular structure of (trip)SnH₃ (6). Thermal ellipsoids are shown at 50\% probability level. Hydrogen atoms (except H100-102) have been omitted for clarity. Hydrogen atoms H100-102 were located in the Fourier map. Selected bond lengths [Å] and angles are given: C(1)−Sn(1) 2.1547(11) Sn(1)−H(100) 1.638(19), Sn(1)−H(101) 1.611(18), Sn(1)−H(102) 1.629(19).} \]

Table 1. Selected crystallographic data for compounds 6, 7 and 9.

<table>
<thead>
<tr>
<th>Compound</th>
<th>7 · (C₇H₈)</th>
<th>9 · 2(C₇H₈)</th>
<th>(trip)SnH₃ (6)</th>
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<tbody>
<tr>
<td>CCDC number</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C₅₂H₇₄N₂Sn</td>
<td>C₁₀₄H₁₅₄Sn</td>
<td>C₁₅H₂₆Sn</td>
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<td>Formula weight</td>
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<td>2116.41</td>
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<td>( T ) [K]</td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
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<td>( \Lambda ) [Å]</td>
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<td>0.71073</td>
<td>0.71073</td>
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<td>Space group</td>
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<td>( P_2_1/c )</td>
<td>( P_2_1/c )</td>
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<td>( a ) [Å]</td>
<td>13.7423(3)</td>
<td>15.8297(6)</td>
<td>12.1651(4)</td>
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<td>( b ) [Å]</td>
<td>19.1733(5)</td>
<td>14.7507(6)</td>
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<td>( c ) [Å]</td>
<td>18.7204(5)</td>
<td>43.5163(17)</td>
<td>11.8112(3)</td>
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<td>( \alpha ) [°]</td>
<td>90</td>
<td>90</td>
<td>90</td>
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<tr>
<td>( \beta ) [°]</td>
<td>105.7610(10)</td>
<td>97.259(2)</td>
<td>99.3510(10)</td>
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<td>( \gamma ) [°]</td>
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<td>90</td>
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<tr>
<td>( V ) [Å³]</td>
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<td>10079.6(7)</td>
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<td>( Z )</td>
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<td>( \rho ) [Mg m⁻³]</td>
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<td>1.395</td>
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<td>( \mu ) [mm⁻¹]</td>
<td>0.572</td>
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<td>( F(000) )</td>
<td>1800</td>
<td>4312</td>
<td>664</td>
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<td>Crystal size [mm³]</td>
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<td>0.03×0.06×0.26</td>
<td>0.10×0.11×0.34</td>
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<td>Theta range [°]</td>
<td>1.87 to 27.18</td>
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<td>-16≤h≤16</td>
</tr>
<tr>
<td></td>
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<td>-19≤k≤19</td>
<td>-14≤h≤14</td>
</tr>
<tr>
<td></td>
<td>-24≤l≤24</td>
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<td>-15≤h≤15</td>
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<tr>
<td>Refl. collected</td>
<td>10545</td>
<td>23195</td>
<td>4029</td>
</tr>
<tr>
<td>Indep. refl. / [R(int)]</td>
<td>9398 / 0.0240</td>
<td>18111 / 0.0624</td>
<td>3789 / 0.0168</td>
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<td>Completeness to theta max</td>
<td>99.7%</td>
<td>99.8%</td>
<td>99.6%</td>
</tr>
<tr>
<td>Data/restraints/parameter</td>
<td>10545/0/517</td>
<td>23195/69/1053</td>
<td>4029/0/163</td>
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<tr>
<td>( GooF )</td>
<td>1.046</td>
<td>1.027</td>
<td>1.044</td>
</tr>
<tr>
<td>Final ( R ) indices [( I &gt; 2\sigma(I) )]</td>
<td>( R_1 / wR_2 )</td>
<td>0.0256/ 0.0578</td>
<td>0.0388/ 0.0728</td>
</tr>
<tr>
<td>( R ) indices (all data)</td>
<td>( R_1 / wR_2 )</td>
<td>0.0312/ 0.0605</td>
<td>0.0594 / 0.0801</td>
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<tr>
<td>Largest diff. peak and hole [eÅ⁻³]</td>
<td>1.227 and -0.972</td>
<td>1.495 and -1.076</td>
<td>0.366 and -0.248</td>
</tr>
</tbody>
</table>
NMR Spectra

Compound 1 (trip)$_2$SnH$_2$
Compound 3 (trip)\text{Sn=NHC}
IH NMR
Trip2Sh-NHC in toluene-d8

Trace impurities of NHCH3 are indicated by asterisks.
Compound 4 (trip)₂SnH-SnH(trip)₂

The Sn-H coupling pattern for 1H NMR and 13C NMR is shown in zoom.
119Sn 1H-coupled NMR
Trip2Sn{(H)2}4Trip2 in C6D6

ABX Spectrum

Compound 5 Ph2SN=NHC

1H NMR
Ph2Sn=NHC in C6D6
13C NMR
Ph2Sn=NHC in toluene-

Solvent signals have not been picked.
Zoom from 150 - 150 ppm is from a
sample of the crude Ph2Sn=NHC
and NHC-E2 mixture which was taken
with more scans. The broad Sn-carbene
carbon resonance can be found.
Compound 7 TripTpSnH(NHC)

SnH resonance and satellites, in the low-field shifted region overlap with aromatic signals

13C NMR
TripTpSnH-NHC in C6D6

weak Sn satellites for Sn--Carbone
119Sn NMR
TripTpSnE-NHC, in C606

Compound 8 RXN Mixtures of tripSnH₃ and 2 carbene 2

1H NMR
RXN tripSnH₃ + 2 NHC
1:1 mixture of TripSnH(NHC) and NHC-H₂
-40°C in toluene-d₈

zoom: Sn-H and satellites
13C NMR
RXN TriSbH3 + 2 NHC
1:1 mixture of TriSbH3 (NHC) + NHC-H2
-40°C in toluene-d8
* indicates hexane

Proton-coupled 119Sn NMR
RXN (TriSbH3 + 2 eq NHC)
1:1 mixture of (TriSbH3) (NHC) and NHC-H2
in toluene-d8 at -40°C
RXN Mixtures of tripSnH$_3$ and 1.5 carbene 2

Literature

5. SAINT, APEX2; Bruker AXS Inc.: Madison, WI, 2007.