Supporting Information

Hydrogen abstraction from organotin di- and trihydrides by *N*-heterocyclic carbenes: a new method for the preparation of NHC adducts to tin(II) species and observation of an isomer of a hexastannabenzene derivative [R₆Sn₆]."

Christian P. Sindlinger and Lars Wesemann* Institut für Anorganische Chemie, Auf der Morgenstelle 18, 72076 Tübingen, Germany

Table of Contents

Experimental Details	
General Information	S2
NMR spectroscopy	S2
Synthetic Details	
General procedure for tin hydrides	S2
$Trip_2SnH_2$ (1)	S2
Reaction of $(trip)_2$ SnH ₂ with TMEDA	S3
Reaction of distannane $\{(trip)_2 Sn(H)\}_2$ with TMEDA	S3
Reaction of $(trip)_2$ SnH ₂ with Pyridine	S3
Crystallographic Details	
Refinement Details	S3
X-Ray Structure of (Trip)SnH ₃ (6)	S4
Tale 1: Selected crystallographic data for 6, 7, and 9.	S4
NMR Spectra	
Compound 1 trip ₂ SnH ₂ [¹ H, 13 C, 119 Sn]	S5-S6
Compound 3 (trip) ₂ Sn=NHC [1 H, 13 C, 119 Sn]	S6-S7
Compound 4 (trip) ₂ SnH-SnH(trip) ₂ [¹ H, ¹³ C, ¹¹⁹ Sn]	S8-S9
Compound 5 Ph ₂ SN=NHC [¹ H, ¹³ C, ¹¹⁹ Sn]	S9-S10
Compound 7 Ar*SnH(NHC) [¹ H, ¹³ C, ¹¹⁹ Sn]	S11-S12
Compound 8 RXN Mixtures of tripSnH ₃ 6 and 2 carbene 2 [¹ H, ¹³ C, ¹¹⁹ Sn]	S12-S13
RXN Mixtures of tripSnH ₃ 6 and 1.5 carbene 2 [¹ H]	S14
Literature	
	S14

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-triisopropylphenyltin trichloride was prepared according to literature procedures.¹ The bis-2,6-(2',4',6'-triisopropylphenyl)phenyl iodide (Ar*I) and its lithiated derivative [Ar*Li(OEt₂)] were prepared according to literature procedures.^{2, 3} Bis-2,6-(2',4',6'-triisopropylphenyl)phenyl tin trichloride⁴ was synthesized 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 AvancelI+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 ²H resonance frequency. The proton and carbon signals were assigned where possible via a detailed analysis of ¹H, ¹³C, ¹³C-UDEFT, ¹H-¹H COSY, ¹H-¹³C HSQC, ¹H-¹³C 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 solvent was removed in vacuo to yield the organotin hydride in almost quantitative yield as colorless oils or solids.

(trip)₂SnH₂ (1): To a solution of (trip)SnCl₃ (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. ¹¹⁹Sn NMR control revealed complete educt conversion and formation of three products assigned to (trip)₂SnCl₂ (approx. 35%), (trip)₂SnClBr (approx. 45%) and (trip)₂SnBr₂ (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 LiAlH₄ (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 to yield 1(1.79 g, 3.39 mmol, 97%) as a colorless oil, that slowly solidifies. Analytical data: ¹H (250.13 MHz, C₆D₆) δ 7.25 (s, 4H, ⁴J_{117/1195n-H} = 20.1 Hz, *m*-H_{ar}), 6.33 (s, 2H, ¹J_{1195n-H} = 1819.5 Hz, ¹J_{1175n-H} = 1737.7 Hz, Sn-H), 3.46 (sept., 4H, ³J_{H-H} = 6.72 Hz, *o*-CHMe₂); 2.90 (sept., 2H, ³J_{H-H} = 6.92 Hz, *p*-CHMe₂), 1.34 (d, 24H, ³J_{H-H} = 6.72 Hz, *o*-CHMe₂), 1.33 (d, 12H, ³J_{H-H} = 6.93 Hz, *p*-CHMe₂); ¹³Cl¹H (62.90 MHz, C₆D₆) δ 155.4 (s, ²J_{5n-C} = 35.5 Hz, *o*-C_{ar}), 150.1 (s, *ipso*-C_{ar}), 135.7 (s, *p*-C_{ar}), 121.3 (s, ³J_{5n-C} = 45.2 Hz, *m*-C_{ar}), 38.0 (s, ³J_{5n-C} = 41.1 Hz, *o*-CHMe₂), 34.5(s, *p*-CHMe₂), 24.5 (s, *o*-CHMe₂), 24.0 (s, *p*-CHMe₂); ¹¹⁹Sn¹H (93.28 MHz, C₆D₆) δ -352.1. Anal. Calcd for C₃₀H₄₈Sn: C 68.32, H 9.17 Found: C 68.36, H 8.50.

Reaction of (trip)₂SnH₂ with TMEDA

To a solution of $(trip)_2SnH_2$ (0.042 g, 0.08 mmol) in THF-d₈ (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 cylcotristannane 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-d₈ (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)₂SnH₂ 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. ¹¹⁹Sn 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 K α radiation. X-ray data for **9** were collected with a Bruker Smart APEXIIduo diffractometer with graphite- monochromated Mo K α 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.⁵⁻⁸ 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- $2(C_7H_8)$ 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)



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).

Compound	$7 \cdot (C_7 H_8)$	$9 \cdot 2(C_7H_8)$	(trip)SnH ₃ (6)
CCDC number			
Empirical formula	C ₅₂ H ₇₄ N ₂ Sn	C ₁₀₄ H ₁₅₄ Sn ₆	C ₁₅ H ₂₆ Sn
Formula weight	845.82	2116.41	325.05
T[K]	100(2)	100(2)	100(2)
Λ[Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	P2 ₁ /c	$P2_1/c$
a [Å]	13.7423(3)	15.8297(6)	12.1651(4)
b [Å]	19.1733(5)	14.7507(6)	11.0065(3)
<i>c</i> [Å]	18.7204(5)	43.5163(17)	11.8112(3)
α[°]	90	90	90
β[°]	105.7610(10)	97.259(2)	99.3510(10)
γ [°]	90	90	90
$V[Å^3]$	4747.1(2)	10079.6(7)	1560.45(8)
Ζ	4	4	4
ρ [Mg m ⁻³]	1.183	1.395	1.384
μ [mm ⁻¹]	0.572	1.506	1.615
F(000)	1800	4312	664
Crystal size [mm ³]	0.15×0.20×0.20	0.03×0.06×0.26	0.10×0.11×0.34
Theta range [°]	1.87 to 27.18	1.30 to 27.53	2.51 to 28.73
Index ranges	$-17 \le h \le 17$	$-20 \le h \le 20$	$-16 \le h \le 16$
	$-23 \le k \le 24$	$-19 \le k \le 19$	$-14 \le h \le 14$
	$-24 \le l \le 24$	$-56 \le l \le 56$	$-15 \le h \le 15$
Refl. collected	10545	23195	4029
Indep. refl. / [R(int)]	9398 / 0.0240	18111 / 0.0624	3789/0.0168
Completeness to theta max	99.7%	99.8%	99.6%
Data/restraints/parameter	10545/0/517	23195/69/1053	4029/0/163
GooF	1.046	1.027	1.044
Final <i>R</i> indices [<i>I</i> >2sigma(<i>I</i>)]			
R1 / wR2	0.0256/ 0.0578	0.0388/ 0.0728	0.0132 / 0.0350
<i>R</i> indices (all data)			
R1 / wR2	0.0312/ 0.0605	0.0594 / 0.0801	0.0147 / 0.0360
Largest diff. peak and hole [eA ⁻³]	1.227 and -0.972	1.495 and -1.076	0.366 and -0.248

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

NMR Spectra





Compound 3 (trip)₂Sn=NHC













121.020







S13



S14

RXN Mixtures of tripSnH₃ and 1.5 carbene 2



Literature

- 1. P. G. Hayes, C. W. Gribble, R. Waterman and T. D. Tilley, *J. Am. Chem. Soc.*, 2009, **131**, 4606-4607.
- 2. B. Schiemenz and P. P. Power, *Organometallics*, 1996, **15**, 958-964.
- 3. R. S. Simons, S. T. Haubrich, B. V. Mork, M. Niemeyer and P. P. Power, *Main Group Chemistry*, 1998, **2**, 275-283.
- 4. Brian P. Johnson, S. Almstätter, F. Dielmann, M. Bodensteiner and M. Scheer, Z. Anorg. Allg. Chem., 2010, 636, 1275-1285.
- 5. SAINT, APEX2; Bruker AXS Inc.: Madison, WI, 2007.
- 6. G. M. Sheldrick, SADABS; University of Göttingen, Göttingen, Germany, 2008.
- 7. L. J. Farrugia, J. Appl. Crystallogr. **1999**, 32, 837 838.
- 8. G. M. Sheldrick, SHELXS 97; University of Göttingen, Göttingen, Germany, 1997.