DE GRUYTER DOI 10.1515/mgmc-2012-0051 — Main Group Met. Chem. 2012; 35(5-6): 179–182

Short Communication

Jens Beckmann*, Andrew Duthie and Michal Wiecko

Synthesis and structure of pentamethylcyclopentadienyltin(II) tetraphenylborate

Abstract: The title compound (Cp*Sn)BPh_4 was obtained by the metathesis reaction of Cp*SnCl with $NaBPh_4$ and characterized by single crystal X-ray diffraction as well as solution and solid-state ^{119}Sn nuclear magnetic resonance (NMR) spectroscopy. The coordination modes are best described as $(\eta^5\text{-}C_5Me_5)Sn(\mu\text{-}\eta^6\text{-}Ph)_2BPh_2$.

Keywords: Cp compounds; solid-state NMR spectroscopy; tin cation; X-ray crystallography.

***Corresponding author: Jens Beckmann,** Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstraße 34/36, 14195 Berlin, Deutschland, e-mail: j.beckmann@uni-bremen.de
Jens Beckmann: Institute of Inorganic & Physical Chemistry, Bremen University, Leobener Straße, 28359 Bremen, Germany
Andrew Duthie: School of Life and Environmental Sciences, Deakin University, Pigdons Road, Waurn Ponds 3217, Australia
Michal Wiecko: Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstraße 34/36, 14195 Berlin, Deutschland

---

Cyclopentadienyl complexes of the main group elements have received considerable attention in recent years (Jutzi and Burford, 1999). The first fully characterized cyclopentadienyltin(II) complex, namely, (Cp*Sn)BF_4, was prepared by Jutzi more than 30 years ago (Jutzi et al., 1979, 1980). More recently, Rhodes et al. (1998) reported the preparation of (Cp*Sn)$B(C_6F_5)_4$ and described its use as co-catalyst for the polymerization of α-olefins and Jones et al. (2005) determined its X-ray structure.

In both complexes, the Cp*Sn cations are associated with the anions via electrostatic Sn···F interactions [2.97–2.99 Å in (Cp*Sn)BF_4 (Jutzi et al., 1979) and 3.172 (2)–3.294 (1) Å in (Cp*Sn)$B(C_6F_5)_4$ (Jones et al., 2005)] that are shorter than the sum of the van der Waals radii (3.54 Å) (Martina et al., 2009). We were interested in the preparation of a pentamethylcyclopentadienyltin(II) cation in which the anion lacks potential donor atoms such as fluorine. Such a complex, namely, (Cp*Sn)BPh_4, was obtained as colourless crystals in 78% yield by the metathesis reaction of Cp*SnCl with $NaBPh_4$. The molecular structure of (Cp*Sn)BPh_4 determined by single crystal X-ray diffraction is shown in Figure 1.

Similar to (Cp*Sn)BF_4 and (Cp*Sn)$B(C_6F_5)_4$, the Sn atom is situated face-on to the Cp* ring. The $C_{Cp\text{-}ring}$-$C_{Cp\text{-}ring}$ bond distances of 1.414 (4), 1.435 (4), 1.419 (4), 1.434 (4), and 1.423 (4) Å account for the η^5-coordination.

The Sn-$C_{Cp\text{-}ring}$ bond lengths range from 2.488 (3) to 2.535 (3) Å. The centroid (C1-C5)-Sn1 distance of 2.1963 (8) Å is slightly longer than in (Cp*Sn)$B(C_6F_5)_4$ [2.114 (3) Å] (Jones et al., 2005). Despite the lack of donor atoms, there are significant cation-anion interactions in (Cp*Sn)BPh_4, most prominently between the Sn atom and the π-electrons of two phenyl rings. The Sn-$C_{Ph\text{-}ring}$ distances range from 3.2693 (2) to 3.6145 (2) Å. The centroid (C10-C15)-Sn1 and centroid (C20-C25)-Sn1 distances are 3.168 (2) and 3.110 (2) Å, respectively. The latter values are longer than the arene Sn interactions of the dicationic tin(II) arene complex $[Sn(toluene)_3][B(C_6F_5)_4]_2$ [2.5591 (3), 2.5735 (3), and 3.0515 (3) Å] (Schäfer et al., 2011) and the aryltin(II) monocation $[2,6\text{-}(Ph_2CH)_2\text{-}4\text{-}Me\text{-}N(SiMe_3)Sn]Al[OC(CF_3)_3]_4$ (2.82 Å) (Li et al., 2012). For more reference compounds featuring arene *p*-block element interactions, refer to a recent review (Schmidbaur and Schier, 2008). Taking into account all π-interactions, the spatial arrangement of the Sn atom is somewhat pyramidal, which suggests that the lone pair is stereochemically active. Overall, the coordination modes of the title compound (Cp*Sn)BPh_4 might be best described as $(\eta^5\text{-}C_5Me_5)Sn(\mu\text{-}\eta^6\text{-}Ph)_2BPh_2$. The nonbonding Sn···B distance is 4.202 (2) Å. The title compound Cp*SnBPh_4 was further characterized by ^{119}Sn solid-state nuclear magnetic resonance (NMR) spectroscopy. A representative ^{119}Sn magic angle spinning (MAS) NMR spectrum acquired at a spinning frequency of 9.86 kHz is depicted in Figure 2. The spinning frequency independent centre band was observed at δ_{iso}=-2236 ppm, which is consistent with the ^{119}Sn NMR chemical shift measured in the solution (see below). The large ^{119}Sn NMR chemical shift anisotropy gave rise to a spinning sideband manifold that was used to determine the principal components δ_{11} (-1991 ppm), δ_{22} (-2328 ppm), and δ_{33} (-2389 ppm) of the chemical shielding tensor, which were converted into the Haeberlen convention featuring

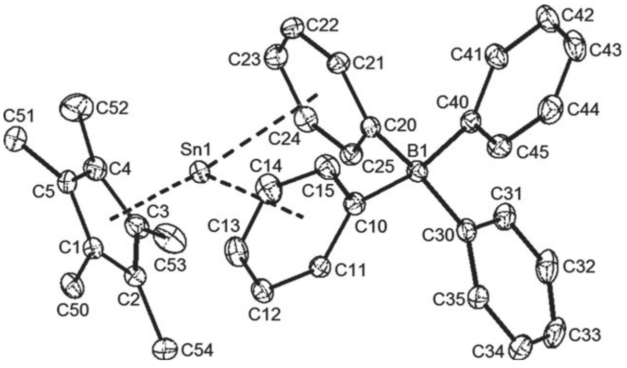

Figure 1 Molecular structure $(Cp^*Sn)BPh_4$ showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters are as follows (Å): Sn1-C1 2.510 (2), Sn1-C2 2.496 (2), Sn1-C3 2.488 (3), Sn1-C4 2.512 (3), Sn1-C5 2.535 (3), centroid (C1-C5)-Sn1 2.1963 (8), centroid (C10-C15)-Sn1 3.168 (2), centroid (C20-C25)-Sn1 3.110 (2), B1-C10 1.656 (4), B1-C20 1.647 (4), B1-C30 1.632 (4), and B1-C40 1.640 (4).

the parameters anisotropy Δδ (367.6 ppm), reduced anisotropy δ (245 ppm), and asymmetry η (0.25) as well as the Herzfeld-Berger convention featuring the parameters span Ω (398 ppm) and skew κ (-0.693).

Group theory requires the asymmetry η to be zero when the local symmetry of the NMR active nucleus contains a threefold or higher symmetry axis. This criterion is fulfilled in the isolated η^5-Cp^*Sn^+ cation having fivefold symmetry axis perpendicular to the Cp* ring; however, the cation-anion contact of $(Cp^*Sn)BPh_4$ seems to break down the local symmetry, thus explaining why the asymmetry is not zero. In the solid state, protected from ambient light and stored under argon, $(Cp^*Sn)BPh_4$ showed no signs of decomposition for several weeks. However, in inert solvents, rapid decay was observed, with Ph_4Sn being identified amongst the decomposition products by its ^{119}Sn NMR chemical shift (δ=-128.1).

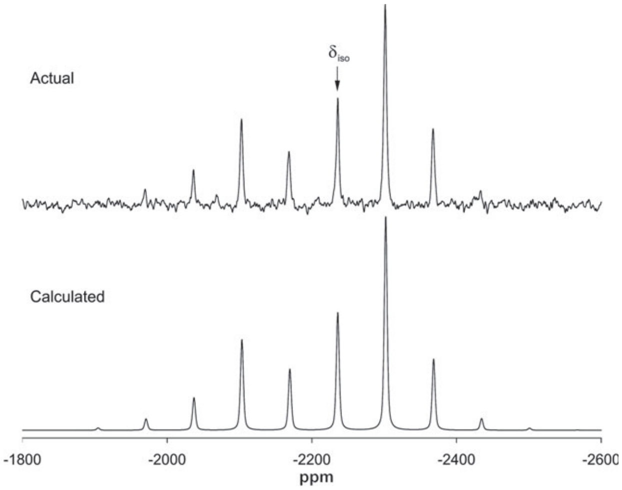

Figure 2 Experimental and iteratively fitted ^{119}Sn MAS NMR spectrum (spinning frequency, 9.86 kHz) of $(Cp^*Sn)BPh_4$. The centre peak δ_{iso}=-2236 is indicated with an arrow.

Nonetheless, a complete set of NMR data (^{119}Sn, ^{13}C, and ^{1}H) of $(Cp^*Sn)BPh_4$ was obtained. The ^{119}Sn NMR spectrum ($CDCl_3$) shows a signal at δ=-2246 ppm that closely resembles the ^{119}Sn NMR chemical shift of $(Cp^*Sn)BF_4$ (δ=-2247 ppm) (Jutzi, 1990), whereas that of $(Cp^*Sn)B(C_6F_5)_4$ (δ=-2219 ppm) (Rhodes et al., 1998) somewhat deviates. Substantial differences were also observed in the ^{1}H and ^{13}C NMR spectra of $(Cp^*Sn)B(C_6F_5)_4$ and $(Cp^*Sn)BPh_4$. Thus, the methyl groups give rise to ^{1}H and ^{13}C NMR resonances at δ=1.86 and 9.41 for $(Cp^*Sn)BPh_4$ and at δ=2.25 and 9.07 for $(Cp^*Sn)B(C_6F_5)_4$, respectively (Rhodes et al., 1998). The C atoms of the Cp* ring resonate at δ=127.37 for $(Cp^*Sn)BPh_4$ and at δ=122.97 for $(Cp^*Sn)B(C_6F_5)_4$ (Rhodes et al., 1998). The BPh_4^- anion gave rise to four signals in the ^{13}C NMR spectrum, indicating the magnetic equivalence of all four phenyl rings, which suggests that electrolytic dissociation takes place in solution.

Experimental

General

Cp*SnCl was prepared according to literature procedure (Constantine et al., 1997), and $NaBPh_4$ (Aldrich, Germany) was obtained from a commercial source and used as received. Solution NMR spectra were recorded on Varian 300 Unity Plus (^{1}H, ^{13}C) and JEOL GX 270 (^{119}Sn) spectrometers and were referenced against Me_4Si and Me_4Sn. The solid state, ^{119}Sn NMR spectra were acquired using a Jeol Eclipse Plus 400 spectrometer equipped with a 6-mm MAS probe and spinning frequencies between 7 and 10 kHz. A relaxation delay of 100 s was used and 800–1200 transients were collected. The isotropic chemical shift δ_{iso} was determined by comparison of two acquisitions measured at sufficiently different spinning frequencies. Crystalline *c*-Hex_4Sn (δ=-97.35) was used as a secondary reference. The tensor analysis was performed using the method of Herzfeld and Berger (Herzfeld and Berger, 1980; Herzfeld and Chen, 1996) implemented in DmFit 2002 (Massiot et al., 2002). The microanalysis was obtained from a Vario EL elemental analyser.

Synthesis of $(Cp^*Sn)BPh_4$

Cp*SnCl (500 mg, 1.72 mmol) and $NaBPh_4$ (589 mg, 1.72 mmol) were suspended in CH_2Cl_2 (25 ml) and stirred for 16 h at room temperature. The colourless solution was filtered and concentrated to 10 ml at about 35°C. Colourless single crystals furnished after several hours. Further concentration of the mother liquor provided another crop of crystals. Combined yield was 769 mg (78%). ^{1}H NMR (299.96 MHz, $CDCl_3$): δ=1.86 (s, 15H; Me), 6.92 (t, 4H; Ph_p), 7.11 (t, 8H; Ph_o), 7.66

Formula	$C_{34}H_{35}BSn$
Formula weight, g/mol	528.84
Crystal system	Monoclinic
Crystal size, mm	0.40×0.25×0.20
Space group	$P\,2_1/c$
a, Å	15.107 (6)
b, Å	10.101 (6)
c, Å	19.06 (1)
α, º	90
β, º	107.63 (4)
γ, º	90
V, Å^3	2772 (3)
Z	4
ρ_{calcd}, Mg m^{-3}	1.374
T, K	150
μ (Mo $K\alpha$), mm^{-1}	0.942
F(000)	1176
θ range, degrees	2.24–29.19
Index ranges	$-20 \leq h \leq 19$
	$0 \leq k \leq 13$
	$0 \leq l \leq 26$
No. of reflections collected	7405
Completeness to θ_{max}	98.7%
No. of independent reflections	7405
No. of observed reflections with ($I>2\sigma(I)$)	4994
No. of refined parameters	325
GooF (F^2)	0.882
R_1 (F) ($I>2\sigma(I)$)	0.0351
wR_2 (F^2) (all data)	0.0716
$(\Delta/\sigma)_{max}$	<0.001
Largest difference peak/hole, e Å^{-3}	0.485/-0.498

Table 1 Crystal data and structure refinement of (Cp*Sn)BPh_4.

(br, 8H; Ph_m); $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$): $\delta = 9.41$ (Me), 122.11 (Ph_p), 126.62 (Ph_m), 127.37 (C_5Me_5), 128.33 [$^1J(^{13}C\text{-}^{11}B)=30$, Ph_i], 136.29 (Ph_o); $^{119}Sn\{^1H\}$ NMR (100.75 MHz, $CDCl_3$): $\delta=-2246$ ppm; ^{119}Sn MAS NMR (149.08 MHz): $\delta_{iso}=-2236$ ppm, $\delta_{11}=-1991$ ppm, $\delta_{22}=-2328$ ppm, $\delta_{33}=-2389$ ppm, $\Delta\delta=367.6$ ppm, $\delta=245$ ppm, $\eta=0.25$, $\Omega=398$ ppm, $\kappa=-0.693$; anal. calcd. for $C_{34}H_{35}BSn$ (573.16): C, 71.25; H, 6.15. Found C, 70.81; H, 5.79%.

X-ray crystallography

Intensity data of (Cp*Sn)BPh_4 were collected on a STOE IPDS 2T area detector with graphite-monochromated Mo-Kα (0.7107 Å) radiation. Data were reduced and corrected for absorption. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WinGX 2002 (Farrugia, 1999). Full-matrix least-squares refinements on F^2, using all data, were carried out with anisotropic displacement parameters applied to all nonhydrogen atoms. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model and were refined isotropically. Crystal and refinement data are collected in Table 1. Figures were created using DIAMOND (Brandenburg and Putz, 2006). Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC number 901652. Copies of this information may 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 http://www.ccdc.cam.ac.uk).

Acknowledgements: The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support.

Received September 28, 2012; accepted November 5, 2012

References

Brandenburg, K.; Putz, H. DIAMOND V3.1d. Crystal Impact GbR: Bonn, Germany, 2006.

Constantine, S. P.; De Lima, G. M.; Hitchcock, P. B.; Keates, J. M.; Lawless, G. A.; Marziano, I. Synthesis and characterization of Sn(η^5-C_5Me_5)Cl and Sn[η^5-C_5Me_4($SiMe_2Bu^t$)]Cl. *Organometallics* **1997**, *16*, 793–795.

Farrugia, L. J. WinGX suite for small-molecule single-crystal crystallography *J. Appl. Crystal*. **1999**, *32*, 837–838.

Herzfeld, J.; Berger, A. E. Sideband intensities in NMR spectra of sample spinning at the magic angle. *J. Chem. Phys*. **1980**, *73*, 6021–6030.

Herzfeld, J.; Chen, X. Sideband analysis in magic angle spinning NMR of solids. In *Encyclopedia of Nuclear Magnetic Resonance*; Vol. 7. Grant, D. M.; Harris R. K., Eds. John Wiley & Sons: Chichester, 1996; pp. 4362–4369.

Jones, J. N.; Moore, J. A.; Cowley, A. H.; Macdonald, C. L. B. Group 14 triple-decker cations. *Dalton Trans*. **2005**, 3846–2851.

Jutzi, P. Cyclopentadienyl complexes with main-group elements as central atoms – a decade of research. *J. Organomet. Chem*. **1990**, *400*, 1–17.

Jutzi, P.; Burford, N. Structurally diverse π-cyclopentadienyl complexes of the main group elements. *Chem. Rev*. **1999**, *99*, 969–990.

Jutzi, P.; Kohl, F.; Krüger, C. Synthesis and structure of the *nido*-cluster $(CH_3)_5C_5Sn^+$. *Angew. Chem. Int. Ed*. **1979**, *18*, 59–60.

Jutzi, P.; Kohl, F.; Hofmann, P.; Krüger, C.; Tsuy, Y.-H. Bis(pentamethyl cyclopentadieny1)germanium und -zinn sowie (pentamethylcyclopentadieny1)germanium- und -zinn-kationen: Synthese, struktur und bindungsverhältnisse. *Chem. Ber*. **1980**, *113*, 757–769.

Li, J.; Schenk, C.; Winter, F.; Scherer, H.; Trapp, N.; Higelin, A.; Keller, S.; Pöttgen, R.; Krossing, I.; Jones, C. Weak arene stabilization of bulky amido-germanium(II) and Tin(II) monocations. *Angew. Chem. Int. Ed*. **2012**, *51*, 9557–9561.

Martina, M.; Chamberlin, A. C.; Valerop, R.; Cramer, C. J.; Truhlar, D. G. Consistent van der Waals radii for the whole main group. *J. Phys. Chem. A*. **2009**, *113*, 5806–5812.

Massiot, D.; Fayon, F.; Capron, M.; King, I.; Le Calvé, S.; Alonso, B.; Durand, J.-O.; Bujoli, B.; Gan, Z.; Hoatson, G. Modelling one- and two-dimensional solid-state NMR spectra. *Mag. Res. Chem*. **2002**, *40*, 70–76.

Rhodes, B.; Chien, J. C. W.; Rausch, M. D. (η^5-Pentamethylcyclopentadienyl)tin(II) tetrakis(pentafluorophenyl)borate: a new cocatalyst for the polymerization of α-olefins. *Organometallics* **1998**, *17*, 1931–1933.

Schäfer, A.; Winter, F.; Saak, W.; Haase, D.; Pöttgen, R.; Müller, T. Stannylium ions, a tin(II) arene complex, and a tin dication stabilized by weakly coordinating anions. *Chem. Eur. J*. **2011**, *17*, 10979–10984.

Schmidbaur, H.; Schier, A. π-Complexation of post-transition metals by neutral aromatic hydrocarbons: the road from observations in the 19th century to new aspects of supramolecular chemistry. *Organometallics* **2008**, *27*, 2361–2395.