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- [11] a) For a given principal quantum number, orbitals with higher angular momentum quantum number generally are affected less strongly by an increase of the nuclear charge. This is obvious from the spin-orbit-averaged experimental s→p excitation energies (ref. [11b]) for Pb<sup>+1</sup> (176 kcalmol<sup>-1</sup>), Pb<sup>+2</sup> (206 kcalmol<sup>-1</sup>), and Pb<sup>+3</sup> (258 kcalmol<sup>-1</sup>).
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### ${(\eta^{5}-Cp)_{2}Sn(\mu-\eta^{5}-Cp)Na \cdot PMDETA],}$ a Compound with a Trigonal-Planar "Paddle Wheel" Triorganostannate Ion\*\*

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Recently we have explored the bonding between early main group metals M (alkali or alkaline earth metals) and heavy p-block metals E such as In, Tl (group 3), Sn, Pb (group 4), and Sb, Bi (group 5).<sup>[1, 2]</sup> The monomeric complex [Ph<sub>3</sub>SnLi · PMDETA] (PMDETA = (Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-NMe) was shown to be the first compound to contain such a bond in the solid state,<sup>[1]</sup> and the retention of such bonding in solutions of this complex was proved by the first observation of direct <sup>119, 117</sup>Sn<sup>-7</sup>Li NMR coupling.<sup>[1]</sup> More recently our efforts have concerned the development of synthetic routes to complexes with M–E bonds (including M = Sn).<sup>[2]</sup>

Here we report the synthesis of the title compound 1 by the addition of sodium cyclopentadienide (CpNa) to bis(cyclopentadienyl)tin(II)<sup>[3]</sup> and PMDETA (mol ratio 1:1:1) in THF. Recrystallization of the crude product from toluene gives yellow crystals of 1 (see *Experimental Procedure*), which were investigated by X-ray diffraction.<sup>[4]</sup>

 $[(\eta^5-Cp)_2Sn(\mu-\eta^5-Cp)Na \cdot PMDETA] = 1$ 

Compound 1 is monomeric in solid state (Fig. 1 top). The structure contains an  $(\eta^5$ -Cp)<sub>3</sub>Sn unit, a "paddle wheel" triorganostannate anion in which one Cp ligand is additionally involved in a Sn( $\mu$ - $\eta^5$ -Cp)Na bridge. The Sn center is nearly trigonal-planar (average angle Cp<sub>e</sub>-Sn-Cp<sub>e</sub>, 119.7(1)°,

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 $Cp_e = Cp$  centroid); Sn deviates approximately 0.14 Å from the plane of the three Cp centroids. The overall structure of 1, and in particular the geometry of its Cp<sub>3</sub>Sn unit, can be rationalized in terms of the competition by the Sn and Na centers for the electron density on the  $\mu$ - $\eta^5$ -Cp ligand, through the slightly bent Sn( $\mu$ - $\eta^5$ -Cp)Na bridge (Sn(1)-Cp(A)-Na(1) 172.3(1)°). This competition weakens the interaction of the  $\mu$ - $\eta^5$ -Cp contact with the Sn center (Cp(A)-Sn(1) 2.733(1) Å) compared to that between Sn and terminally attached Cp ligands (average value Cp(B,C)-Sn(1), 2.538(1) Å; cf. Sn-Cp, ca. 2.42 Å in [Cp<sub>2</sub>Sn]<sup>[3]</sup>).



Fig. 1. Top: Crystal structure of 1. Hydrogen atoms have been omitted for clarity. Selected distances [Å] and angles [°]: Cp(A)-Sn(1) 2.733(1), Cp(B)-Sn(1) 2.551(1), Cp(C)-Sn(1) 2.526(1), Cp(A)-Na(1) 2.550(1); Cp(A)-Sn(1)-Cp(B) 116.3(1), Cp(A)-Sn(1)-Cp(C) 118.9(1), Cp(B)-Sn(1)-Cp(C) 124.0(1), Sn(1)-Cp(A)-Na(1) 172.3(1). Bottom: Crystal packing of 1 determined by intermolecular C-H $\cdots$  Na interactions. Selected distances [Å]: H $\cdots$ Na 3.148(2), 3.490(2).

The deviation from linearity of the Sn( $\mu$ - $\eta^5$ -Cp)Na bridge (172.3(1)°) appears to be almost entirely a consequence of crystal packing. The Na–Cp<sub>c</sub> vector is almost perpendicular (88.30(1)°) to the plane of the Cp ligand (Cp(A)–Na(1) 2.550(1) Å; cf. ( $\mu$ - $\eta^5$ -Cp)–Na in the polymer [( $\mu$ - $\eta^5$ -Cp)Na · TMEDA]<sub>∞</sub> (TMEDA = Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>) ca. 2.65 Å,<sup>[5]</sup> and Cp\*–Na (Cp\* = C<sub>5</sub>Me<sub>5</sub>) in molecular [Cp\*Na(py)<sub>3</sub>] (py = pyridine) 2.40 Å<sup>[6]</sup>). This bending of the Sn( $\mu$ - $\eta^5$ -Cp)Na bridge is caused by two long-range intermolecular C(H) ··· Na interactions (H ··· Na(1) 3.148(2) and 3.490(2) Å) with the Na · PMDETA<sup>+</sup> unit. Thus, the apparently "naked" Na face is further coordinated and, as a result, units of **1** are linked into a polymeric array (Fig. 1 bottom).

Although a number of early main group metal stannates have been structurally characterized, only [Ph<sub>3</sub>SnLi · PMDETA] contains a metal–Sn contact.<sup>[11]</sup> The role of the  $\mu$ - $\eta$ <sup>5</sup>-Cp ligand in 1 in holding the Sn and Na centers together is comparable with that of bridging heteroatoms (e.g., O, P, Cl) in other stannate complexes, for example O in [Li( $\mu_2$ -Ph<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O)<sub>3</sub>Sn].<sup>[7]</sup> The planar geometry of the Sn center in 1 is unprecedented in the structures of triorganostannates.

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All other such complexes, whether separated ions<sup>[8]</sup> or contact ion pairs are present,<sup>[1]</sup> have nearly pyramidal stannate ions as a result of the construction of  $\sigma$  bonds with substantial Sn p character and the lone pair on Sn having mainly s character. The geometry of the Sn center in 1 implies a very different use of orbitals than in other stannates.<sup>[9]</sup>

The title compound 1 is rare among organotin(II) compounds in containing three aromatic ligands  $\pi$ -bonded to Sn. Polymerically linked  $(\mu - \eta^5 - Cp)_3 SnX$  units  $(X = \mu - F - BF_3^$ and THF) have been seen in the structure of  $\{[(\eta^5 - Cp)_2 Sn(\mu - \eta^5 - Cp)Sn(thf)]^+ BF_4^-\}_{\infty}$ , produced by the reaction of BF<sub>3</sub> with  $[Cp_2Sn]$  in THF (Cp–Sn, ca. 2.29–3.67 Å).<sup>[10]</sup> In orthorhombic  $[Cp_2Pb]$ ,  $(\mu - \eta^5 - Cp)_2(\eta^5 - Cp)Pb$  units are present within its polymeric zigzag structure<sup>[11]</sup> (cf. the well-known bent structure of  $[Cp_2Sn]^{[3]}$ ). Interestingly  $[Cp_2Pb]$  forms a 1:1 electrolyte in THF.<sup>[12]</sup> On the basis of our current work, it seems most likely that  $[CpPb(thf)_x]^+[Cp_3Pb]^-$  is present in solution, rather than the suggested  $[CpPb]^+$  and discrete  $Cp^-$  ions.<sup>[12, 13]</sup>

Finally, cryoscopic molecular mass determinations combined with variable-temperature <sup>1</sup>H NMR spectroscopy show that 1 is involved in a dissociative equilibrium in aromatic solvents.<sup>[14]</sup> At room temperature 1 is completely dissociated into  $[(\eta^5-Cp)_3Sn]^-$  and  $[Na \cdot PMDETA]^+$  ions. As the temperature is reduced (finally to ca. -80 °C) these ions pair up to give intact 1. These results illustrate that the paddle wheel  $[(\eta^5-Cp)_3Sn]^-$  ion has a separate existence.

Previous work has concentrated on the reactions of electrophiles such as MeI with  $[Cp_2Sn]$ .<sup>[13, 15]</sup> We are currently investigating the addition reactions (which produce mixed-ligand triorganostannates  $[Cp_2RSn]^-$ ) and the substitution reactions (which produce mixed ligand organotin compounds [CpSnR]) of various nucleophiles, such as organo-lithium compounds, with  $[Cp_2Sn]$ . To our knowledge, these are new approaches to triorganostannate complexes and organotin(II) compounds. We are also investigating the use of  $[Cp_3Sn]^-$  as a new ligand to other main group metals.

#### **Experimental** Procedure

1: CpNa (1.25 mL, 2.0 mol L<sup>-1</sup> in THF, 2.5 mmol) was added to a solution of [Cp<sub>2</sub>Sn] (0.623 g, 2.5 mmol) (preparation ref. [3]) and PMDETA (0.53 mL, 2.5 mmol) in THF (5 mL) at 20 °C under nitrogen. Stirring the reaction mixture (0.5 h) at 20 °C gave an orange-red solution. The THF was removed under vacuum, replaced with toluene (5 mL), and the solution was filtered to remove a faint precipitate. Storage of the orange-red filtrate at 20 °C (48 h) gave air-sensitive, yellow crystals, identified as 1. First-batch yield 20%, m.p. 93–98 °C to a yellow oil. IR (solid):  $\tilde{\nu} = 3079$ , 3061 cm<sup>-1</sup> (s,  $\nu$ , C-H,  $\eta^{5}$ -Cp), disappears upon exposure to air. <sup>1</sup>H NMR (25 °C, C<sub>6</sub>D<sub>6</sub>):  $\delta = 6.00$  (s, 15H;  $\eta^{5}$ - and  $\mu$ - $\eta^{5}$ -CpH; cf.  $\delta = 5.78$  (<sup>2</sup>/(Sn,H) = 15.7 Hz) in [Cp<sub>2</sub>Sn]), 1.80 (s, 15H;  $\eta^{5}$ . Man di (CH<sub>3</sub>)<sub>2</sub>N), 1.65 (s, 8H; (CH<sub>2</sub>)<sub>2</sub>). Correct C, H, N analysis.

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solved by direct methods (SHELXS 92) and refined by full least squares  $\sigma_n F^2$  with all data to  $R_1$  and  $wR_2$  values of 0.026 and 0.050, respectively (SHELXL 92); largest difference peak and hole 0.39 and -0.33 eÅ<sup>-3</sup>, respectively. All hydrogen atoms were located in the difference Fourier map and their positions were refined freely with common refined U values for chemically equivalent atoms. Further details of the crystal structure investigations are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, GB-Cambridge CB2 1EW (UK), by quoting the full journal citation.

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# **Opening of an Aza-***closo***-dodecaborane to an Aza-***nido***-dodecaborate**\*\*

### By Franc Meyer, Jens Müller, Peter Paetzold,\* and Roland Boese

Aza-closo-dodecaborane  $NB_{11}H_{12}$  is isoelectronic with dicarba-closo-dodecaborane  $C_2B_{10}H_{12}$ .<sup>[1]</sup> Upon attack by base the icosahedral framework of  $C_2B_{10}H_{12}$  is broken down into the open frame of dicarba-nido-undecaborate  $C_2B_9H_{12}^{-}$ .<sup>[2]</sup> We wanted to apply this reaction to  $NB_{11}H_{12}$ . Its N-bound proton is so acidic, however, that it is removed even by a weak base like  $NEt_3$  forming  $[HNEt_3][NB_{11}H_{11}]$ 1.<sup>[1]</sup> Thus, before the examination of the attack of a base on the  $NB_{11}$  framework, it was imperative to protect the N atom by alkylation. The salt 1 was treated with the strong methylating agent methyltriflate, and  $MeNB_{11}H_{11}$  2 was obtained [Eq. (a)]. The three <sup>11</sup>B NMR signals of 2, their inten-

$$[HNEt_3][NB_{11}H_{11}] \xrightarrow{+MeO_3SCF_3} -[HNEt_3][O_3SCF_3] + MeNB_{11}H_{11} \qquad (a)$$

$$1 \qquad \qquad 2$$

sity ratio of 5:5:1, and the characteristic B–H coupling constant leave no doubt that  $NB_{11}H_{12}$  and its methyl derivative are structurally analogous.

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