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- [10] The MP4 energy for the first reaction is  $-18.3 \text{ kcal mol}^{-1}$ , that for the second  $+90.0 \text{ kcal mol}^{-1}$ , when corrected for zero-point vibrational energy and for atomic spin-orbit coupling of  $\text{Pb}(^3\text{P})$  (cf. ref. [11b]). See ref. [2b] for QCISD(T) results on the lead hydrides and fluorides.
- [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  $s \rightarrow p$  excitation energies (ref. [11b]) for  $\text{Pb}^{+1}$  ( $176 \text{ kcal mol}^{-1}$ ),  $\text{Pb}^{+2}$  ( $206 \text{ kcal mol}^{-1}$ ), and  $\text{Pb}^{+3}$  ( $258 \text{ kcal mol}^{-1}$ ). b) C. E. Moore, *Atomic Energy Levels*, Circular Nat. Bur. Standards 467, Washington, 1958.

## $[(\eta^5\text{-Cp})_2\text{Sn}(\mu\text{-}\eta^5\text{-Cp})\text{Na} \cdot \text{PMDETA}]$ , 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>11, 21</sup> The monomeric complex  $[\text{Ph}_3\text{SnLi} \cdot \text{PMDETA}]$  (PMDETA =  $(\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{-NMe}$ ) was shown to be the first compound to contain such a bond in the solid state,<sup>11</sup> and the retention of such bonding in solutions of this complex was proved by the first observation of direct  $^{119, 117}\text{Sn}-^7\text{Li}$  NMR coupling.<sup>11</sup> More recently our efforts have concerned the development of synthetic routes to complexes with M–E bonds (including  $\text{M} = \text{Sn}$ ).<sup>12</sup>

Here we report the synthesis of the title compound **1** by the addition of sodium cyclopentadienide ( $\text{CpNa}$ ) to bis(cyclopentadienyl)tin(II)<sup>31</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>14</sup>

$[(\eta^5\text{-Cp})_2\text{Sn}(\mu\text{-}\eta^5\text{-Cp})\text{Na} \cdot \text{PMDETA}]$  **1**

Compound **1** is monomeric in solid state (Fig. 1 top). The structure contains an  $(\eta^5\text{-Cp})_3\text{Sn}$  unit, a “paddle wheel” triorganostannate anion in which one Cp ligand is additionally involved in a  $\text{Sn}(\mu\text{-}\eta^5\text{-Cp})\text{Na}$  bridge. The Sn center is nearly trigonal-planar (average angle  $\text{Cp}_c\text{-Sn-Cp}_c$ ,  $119.7(1)^\circ$ ,

$\text{Cp}_c = \text{Cp}$  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  $\text{Cp}_3\text{Sn}$  unit, can be rationalized in terms of the competition by the Sn and Na centers for the electron density on the  $\mu\text{-}\eta^5\text{-Cp}$  ligand, through the slightly bent  $\text{Sn}(\mu\text{-}\eta^5\text{-Cp})\text{Na}$  bridge ( $\text{Sn}(1)\text{-Cp(A)-Na}(1)$   $172.3(1)^\circ$ ). This competition weakens the interaction of the  $\mu\text{-}\eta^5\text{-Cp}$  contact with the Sn center ( $\text{Cp(A)-Sn}(1)$   $2.733(1)$  Å) compared to that between Sn and terminally attached Cp ligands (average value  $\text{Cp(B,C)-Sn}(1)$ ,  $2.538(1)$  Å; cf.  $\text{Sn-Cp}$ , ca.  $2.42$  Å in  $[\text{Cp}_2\text{Sn}]^{13}$ ).

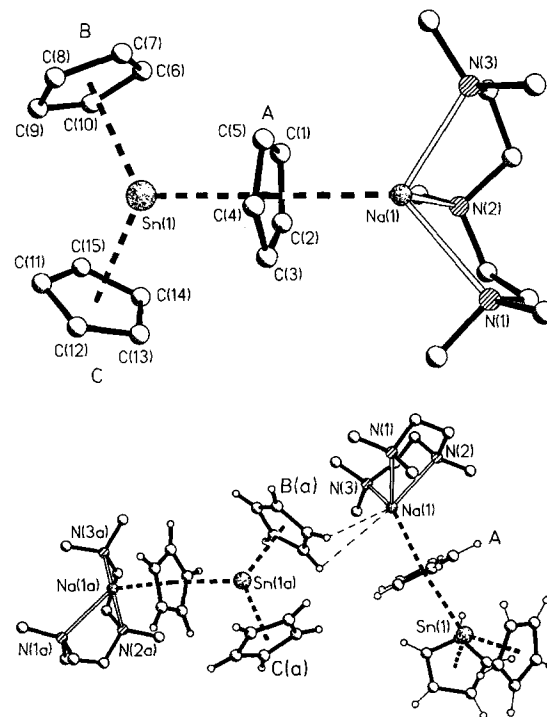


Fig. 1. Top: Crystal structure of **1**. Hydrogen atoms have been omitted for clarity. Selected distances [Å] and angles [°]:  $\text{Cp(A)-Sn}(1)$   $2.733(1)$ ,  $\text{Cp(B)-Sn}(1)$   $2.551(1)$ ,  $\text{Cp(C)-Sn}(1)$   $2.526(1)$ ,  $\text{Cp(A)-Na}(1)$   $2.550(1)$ ,  $\text{Cp(A)-Sn}(1)\text{-Cp(B)}$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

The deviation from linearity of the  $\text{Sn}(\mu\text{-}\eta^5\text{-Cp})\text{Na}$  bridge ( $172.3(1)^\circ$ ) appears to be almost entirely a consequence of crystal packing. The  $\text{Na-Cp}_c$  vector is almost perpendicular ( $88.30(1)^\circ$ ) to the plane of the Cp ligand ( $\text{Cp(A)-Na}(1)$   $2.550(1)$  Å; cf.  $(\mu\text{-}\eta^5\text{-Cp})\text{-Na}$  in the polymer  $[(\mu\text{-}\eta^5\text{-Cp})\text{Na} \cdot \text{TMEDA}]_\infty$  (TMEDA =  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ ) ca.  $2.65$  Å,<sup>15</sup> and  $\text{Cp}^*\text{-Na}$  ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ) in molecular  $[\text{Cp}^*\text{Na}(\text{py})_3]$  ( $\text{py} = \text{pyridine}$ )  $2.40$  Å<sup>16</sup>). This bending of the  $\text{Sn}(\mu\text{-}\eta^5\text{-Cp})\text{Na}$  bridge is caused by two long-range intermolecular  $\text{C(H)} \cdots \text{Na}$  interactions ( $\text{H} \cdots \text{Na}(1)$   $3.148(2)$  and  $3.490(2)$  Å) with the  $\text{Na} \cdot \text{PMDETA}^+$  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  $[\text{Ph}_3\text{SnLi} \cdot \text{PMDETA}]$  contains a metal–Sn contact.<sup>11</sup> The role of the  $\mu\text{-}\eta^5\text{-Cp}$  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  $[\text{Li}(\mu_2\text{-Ph}_2\text{C}_6\text{H}_3\text{O})_3\text{Sn}]$ .<sup>17</sup> The planar geometry of the Sn center in **1** is unprecedented in the structures of triorganostannates.

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