

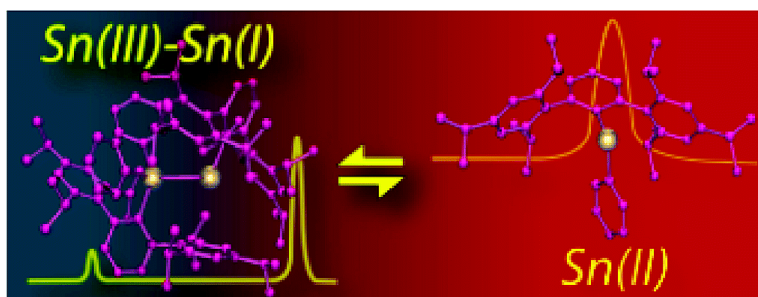
Communication

## A Reversible Valence Equilibrium in a Heavier Main Group Compound

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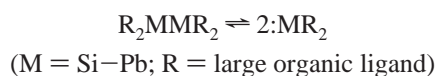
## A Reversible Valence Equilibrium in a Heavier Main Group Compound

Andrew D. Phillips, Shirley Hino, and Philip P. Power\*

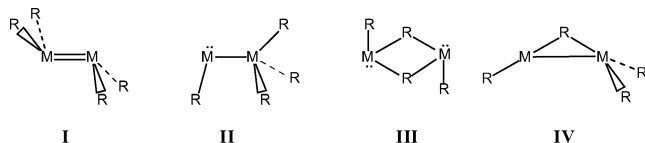
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A characteristic feature of the heavier group 14 element analogues of alkenes is their adoption of increasingly transpyramidal geometries as the group is descended.<sup>1</sup> This is accompanied by a tendency to dissociate into v-shaped monomers that are analogous to singlet carbenes. The dissociation is especially marked for derivatives of tin and lead. In solution, a dimer–monomer equilibrium given by

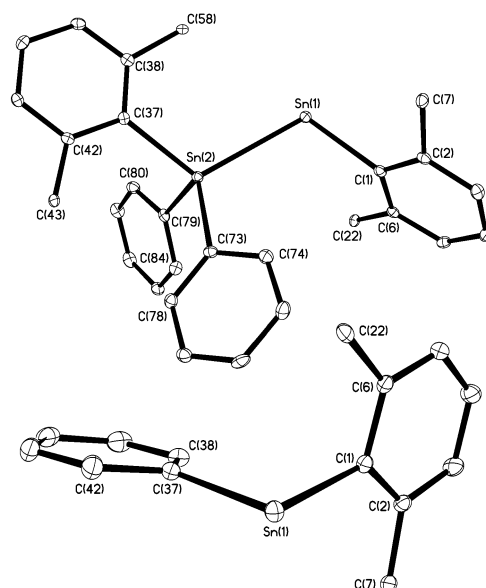


can exist, and NMR spectroscopy has shown that the structure of the dimers is symmetric; that is, each M center is spectroscopically equivalent.<sup>2–5</sup> No other type of structure has been reported for M<sub>2</sub>R<sub>4</sub> species in solution.<sup>6</sup> Nonetheless, computational studies of the model hydrides M<sub>2</sub>H<sub>4</sub> (M = Sn or Pb) showed that the H bridged trans-HM(μ-H)<sub>2</sub>MH and the unsymmetric HMMH<sub>3</sub> are both lower in energy than the trans-pyramidal H<sub>2</sub>MMH<sub>2</sub>.<sup>7</sup> Furthermore, the energy differences between the unsymmetric and trans-pyramidal forms were predicted to be less than 10 kcal mol<sup>-1</sup>. Unfortunately, there exist no high level computational studies on the corresponding organically substituted group 14 element model species indicated by I–IV (R = Me or Ph).



It seems likely that the bridged isomers III and IV would be less favored due to the weaker bridging characteristics of Me or Ph groups in comparison to H.<sup>8</sup> Nonetheless, the stability pattern for small, unbridged, organically substituted, symmetric, and unsymmetric isomers I and II could resemble that of the corresponding hydrides. Because large substituents are required for the stability of such dimers, structure II is disfavored because it places three large substituents at one M atom. Yet, it can be seen that if one of the two organic substituents at each M atom in I is relatively small, movement of that substituent to the other M atom to generate isomer II would cause no undue increase in crowding. In such circumstances, an equilibrium of a new type between an unsymmetric isomer and a monomer could be observed. We now show that the use of this approach has enabled the isolation of two tin compounds that undergo the first instance of such an equilibrium in solution.

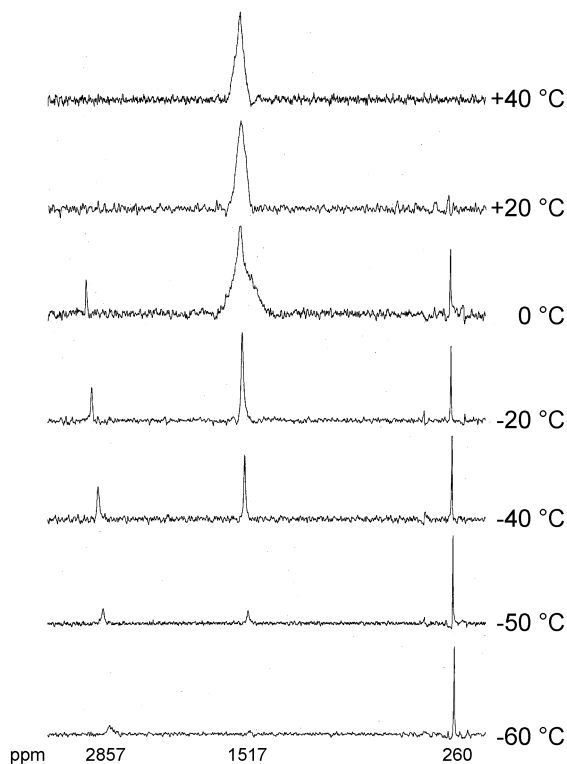
The reaction<sup>9</sup> of 1 equiv of LiPh with Ar\*SnCl<sup>10</sup> (Ar\* = C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>; Trip = C<sub>6</sub>H<sub>2</sub>-2,4,6-<sup>i</sup>Pr<sub>3</sub>) in Et<sub>2</sub>O, at ca. –78 °C, afforded a dark green solution which became purple-red upon warming to ca. 25 °C. Standard workup and crystallization from hexanes at ca. –30 °C afforded Ar\*SnSnPh<sub>2</sub>Ar\* (Figure 1) as dark blue-green crystals. In contrast, crystallization at ca. 25 °C yielded dark red crystals of the monomer Ar\*SnPh (Figure 1). Some structural



**Figure 1.** Thermal ellipsoid (30%) plots of Ar\*SnSnPh<sub>2</sub>Ar\* (top) and Ar\*SnPh (bottom). Only ipso-carbons of Trip groups are shown. Selected bond lengths (Å) and angles (deg): Ar\*SnSnPh<sub>2</sub>Ar\*, Sn(1)–Sn(2) = 2.9688(5), Sn(1)–C(1) = 2.261(2), Sn(2)–C(37) = 2.176(2), Sn(2)–C(73) = 2.176(2), Sn(2)–C(79) = 2.184(2) Å, C(1)–Sn(1)–Sn(2) = 108.48(6)°, Sn(1)–Sn(2)–C(37) = 113.01(6)°, Sn(1)–Sn(2)–C(73) = 109.47(7)°, Sn(1)–Sn(2)–C(79) = 116.11(6)°; Ar\*SnPh, Sn(1)–C(1) = 2.220(3), Sn(1)–C(37) = 2.187(3) Å, C(1)–Sn(1)–C(37) = 96.87(10)°.

details<sup>11</sup> of the two compounds Ar\*SnSnPh<sub>2</sub>Ar\* and Ar\*SnPh are provided in the figure caption. The most notable features are the long Sn(1)–Sn(2) bond (2.9688(5) Å) and wide Sn(2)–Sn(1)–C(1) angle of 108.48(6)° in the dimer (cf., 2.8909(2) Å and 101.17(5)° in Ar\*SnSnMe<sub>2</sub>Ar\*)<sup>12</sup> as well as the much narrower C(1)–Sn(1)–C(37) angle of 96.87(10)° in Ar\*SnPh. These findings may be contrasted with those for germanium and lead where the symmetric dimer Ar\*PhGeGePhAr\*<sup>13</sup> and monomer Ar\*PbPh<sup>14</sup> were obtained exclusively upon reaction of Ar\*GeCl or Ar\*PbBr with LiPh. The reaction of LiMe with Ar\*SnCl yielded Ar\*SnSnMe<sub>2</sub>Ar\* as the only product. That result is thought to be due to the rapid reaction of initially formed Ar\*SnMe with LiMe to give LiSnMe<sub>2</sub>Ar\*, followed by immediate reaction with Ar\*SnCl to give Ar\*SnSnMe<sub>2</sub>Ar\*.<sup>12</sup> No solution equilibrium was observed, and an attempted thermal rearrangement resulted in decomposition.

Deuterated toluene solutions of either Ar\*SnSnPh<sub>2</sub>Ar\* or Ar\*SnPh have a red-purple color and identical NMR spectra above 25 °C. The <sup>119</sup>Sn NMR spectrum (Figure 2) displays a broad resonance near δ = 1517 consistent with two-coordinate Sn(II) geometry (cf., δ = 1401 and 1506 for Sn(C<sub>6</sub>H-2-<sup>i</sup>Bu-4,5,6-Me<sub>3</sub>)-{Si(SiMe<sub>3</sub>)<sub>3</sub>}<sup>15</sup> and Sn(C<sub>6</sub>H-2-<sup>i</sup>Bu-4,5,6-Me<sub>3</sub>)<sub>2</sub>).<sup>6b</sup> Upon cooling, two further signals appear – upfield near δ = 245 and downfield near δ = 2800. By –60 °C, the central signal has essentially disappeared, while signals at δ = 246 and 2857, which display a



**Figure 2.** Variable temperature  $^{119}\text{Sn}$  NMR spectra in  $\text{C}_7\text{D}_8$  illustrating the  $\text{Ar}^*\text{SnSnPh}_2\text{Ar}^* \rightleftharpoons 2\text{Ar}^*\text{SnPh}$  equilibrium.

$^1J$  ( $^{119}\text{Sn}$ – $^{119/117}\text{Sn}$ ) coupling of 7237 Hz, remain. These parameters are comparable to  $\delta = 257$  and 2857, and  $^1J = 8330$  Hz observed for  $\text{Ar}^*\text{SnSnMe}_2\text{Ar}^*$ , and establish the presence of  $\text{Ar}^*\text{SnSnPh}_2\text{Ar}^*$  in solution. Rewarming the sample resulted in a color change from green to red and the reappearance of the signal at  $\delta = 1517$ . The spectral behavior is thus consistent with an equilibrium given by



It is noticeable that the downfield peaks in the spectrum are broader than the upfield peak. This is due to the greater anisotropy of the chemical shift tensors for the divalent tins which shorten the relaxation times of these nuclei.<sup>12</sup>

The rearrangement and dissociative process of  $\text{Ar}^*\text{SnSnPh}_2\text{Ar}^*$  probably occurs through a Ph bridged intermediate species analogous to IV. This is supported by calculations on  $\text{Sn}_2\text{H}_4$  which showed that monobridged  $\text{HSn}(\mu\text{-H})\text{SnH}_2$  is a minimum on the potential surface and is close in energy to the doubly bridged and unsymmetric isomers.<sup>7</sup> Some further experimental support for the incipient transfer of a Ph group from Sn(2) to Sn(1) can be discerned in the structure of  $\text{Ar}^*\text{SnSnPh}_2\text{Ar}^*$  where the C(79) ring is oriented correctly for a face-on interaction with the unoccupied Sn(1) 5p orbital. Furthermore, the Sn(1)–Sn(2)–C(79) angle is almost 7° wider than the Sn(1)–Sn(2)–C(73) angle, and the Sn(2)–C(79) bond is slightly, 0.01 Å, longer than Sn(2)–C(73).

In summary, a new type of reversible equilibrium, which probably operates through an aryl bridged intermediate, has been established for heavier group 14 element alkene analogues. Work is in progress to isolate examples of such intermediates.

**Acknowledgment.** We thank the NSF (CHE-0096913) for financial support.

**Supporting Information Available:** CIF data for  $\text{Ar}^*\text{SnSnPh}_2\text{Ar}^*$  and  $\text{Ar}^*\text{SnPh}$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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