

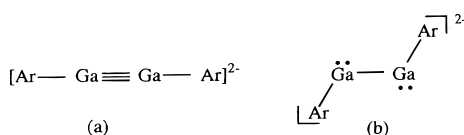
## Synthesis and Characterization of $[\text{Sn}_2\{\text{C}_6\text{H}_3\text{-}2,6(2,4,6\text{-i-Pr}_3\text{C}_6\text{H}_2)_2\}_2]^{2-}$ : A Singly Reduced Valence Isomer of a "Distannyne"<sup>†</sup>

Marilyn M. Olmstead, Richard S. Simons, and Philip P. Power\*

Department of Chemistry  
University of California  
Davis, California 95695

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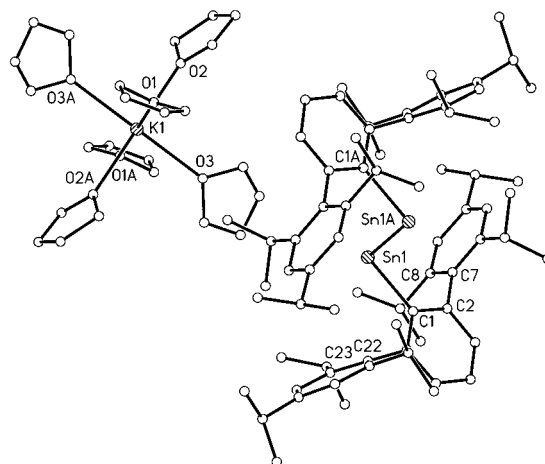
The recently reported species  $\text{Na}_2[\text{ArGaGaAr}]$  ( $\text{Ar} = \text{-C}_6\text{H}_3\text{-}2,6(2,4,6\text{-i-Pr}_3\text{C}_6\text{H}_2)_2 = \text{-C}_6\text{H}_3\text{-}2,6\text{-Trip}_2$ ) has a nonlinear, *trans*-geometry with C–Ga–Ga angles of 128.5(4) and 133.5(4)° and a Ga–Ga distance of 2.319(3) Å. It was described as the first example of a compound with a Ga–Ga triple bond.<sup>1</sup> Its *trans*-configuration and Ga–Ga distance (which is marginally shorter than some less sterically crowded Ga–Ga singly bonded compounds<sup>2</sup>) suggest a more complex view of the bonding, however. Thus, in simplistic valence bond terms, the dianion  $[\text{ArGaGaAr}]^{2-}$  may be written in the two extreme forms (a) and (b). In (a) the Ga–Ga bond conforms to the normal three-



electron-pair triple bond model commonly associated with the isoelectronic alkynes. In (b) two of the original three bonding pairs become a lone pair at each Ga, which are now connected by a formal single bond leaving an empty p-orbital at each metal perpendicular to the molecular plane. Their bonding should be similar to the unknown isoelectronic neutral neighboring group 14 element derivatives  $\text{ArMMAr}$  ( $\text{M} = \text{Si, Ge, Sn, or Pb}$ ). Previous work has shown that Ge can triple bond to a transition element in  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{MoGeC}_6\text{H}_3\text{-}2,6\text{-Mes}_2$  ( $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{-}$ ) where the Ge atom has almost linear ( $\text{Mo-Ge-C} = 172.2(2)^\circ$ ) geometry and there is a short Mo–Ge bond length of 2.271(1) Å.<sup>3</sup> Nonetheless, there are no stable heavier group 14 compounds analogous to either structure (a) or (b). Here, the first example of a related species, in which the neutral tin analog of (a) or (b),  $\text{ArSnSnAr}$ , is singly reduced to the anion  $[\text{ArSnSnAr}]^{2-}$ , is now described.

The anion  $[\text{ArSnSnAr}]^{2-}$  was synthesized<sup>4</sup> by the reduction of  $\text{Sn}(\text{Cl})\text{Ar}$  in THF solution. It may be crystallized as either of the salts  $[\text{K}(\text{THF})_6][\text{ArSnSnAr}]$  (**1**) or  $[\text{K}(\text{dibenzo-18-crown-6})(\text{THF})_3][[\text{ArSnSnAr}]\cdot 2\text{THF}]$  (**2**·2THF). In THF solution at room temperature, their EPR spectra are essentially identical and exhibit an EPR signal near  $g = 2.0069$  with hyperfine coupling to the  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  nuclei which may be simulated to afford the values  $a(^{117}\text{Sn}) = 8.3$  G and  $a(^{119}\text{Sn}) = 8.5$  G.

The X-ray crystal structures of **1** and **2** have also been determined.<sup>5</sup> For **1**, each asymmetric unit contains a half cation and a half anion, the remainder is generated by a crystallographically required inversion center at  $\text{K}^+$  and at the center of the Sn–Sn bond (Figure 1). The  $\text{K}^+$  ion is octahedrally coordinated to six THF molecules with an average K–O distance of 2.67(3) Å. The Sn–Sn and Sn–C distances are



**Figure 1.** Computer-generated drawing of **1**. Hydrogen atoms are not shown. Important bond distances (Å) and angles (deg): Sn(1)–Sn(1A) 2.8123(9), Sn(1)–C(1) 2.236(5), K(1)–O(1) 2.684(7), K(1)–O(2) 2.703(6), K(1)–O(3) 2.610(9), C(1)–Sn(1)–Sn(1A) 95.20(13).

2.8123(9) and 2.236(5) Å, and the Sn–Sn–C angle is 95.20(13)°. In the asymmetric unit of **2**, there are two half anions as well as a whole cation in which  $\text{K}^+$  is coordinated by dibenzo-18-crown-6 and three THF molecules. The remaining half of each anion is generated by an inversion center. For the Sn(1) moiety, there is disorder of the organic substituent over two sites of almost equal occupancy. The Sn(1)–Sn(1A) distance, 2.7821(14) Å, remains unaffected, but there are two, slightly different Sn(1)–C(1) distances of 2.293(13) and 2.269(14) Å and two C(1)–Sn(1)–Sn(1A) angles (93.6(4) and 95.0(4)°). In the other half anion, the Sn(2)–Sn(2a) and Sn(2)–C(37) distances are 2.8236(14) and 2.226(7) Å and the C(37)–Sn(2)–Sn(2a) angle is 97.3(2)°.

The structural and spectroscopic data for the anions of **1** and **2** are consistent with a *trans-bent* structure for the  $[\text{ArSnSnAr}]^{2-}$  anion, as represented by structure (d) in which the lone pairs are located on the tins and the unpaired electron is in a  $\pi$ -orbital formed by overlap of the tin p-orbitals. This species has a formal Sn–Sn bond order of 1.5, and the narrow, *ca.* 95° bond angle at the tins suggests little hybridization at these atoms.

(4) All manipulations were carried out under anaerobic and anhydrous conditions. (a) For  $\text{Sn}(\text{Cl})\text{Ar}$ :  $(\text{Et}_2\text{O})\text{LiAr}^{\text{db}}$  (5.50 g, 9.77 mmol) in toluene (50 mL) was added dropwise to a stirred suspension of  $\text{SnCl}_2$  (2.24 g, 11.81 mmol) (20% excess) in toluene (10 mL) with cooling in an ice-bath. The mixture was allowed to warm to room temperature and was stirred for 6 h. The resultant green solution (red in transmitted light) was filtered through Celite and was concentrated to incipient crystallization (*ca.* 30 mL) under reduced pressure. Storage in *ca.*  $-20^\circ\text{C}$  freezer for 3 days afforded the product  $\text{Sn}(\text{Cl})\text{C}_6\text{H}_3\text{-}2,6\text{-Trip}_2$  (**1**) as orange crystals: yield 1.82 g, 2.86 mmol, 29.3%; mp 205–210 °C;  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  1.08 (d,  $J = 6.6$  Hz, 12 H, *p*- $\text{CH}(\text{CH}_3)_2$ ), 1.21 (d,  $J = 6.6$  Hz, 24H, *o*- $\text{CH}(\text{CH}_3)_2$ ), 2.79 (sept,  $J = 6.9$  Hz, 4H, *o*- $\text{CH}(\text{CH}_3)_2$ ), 3.14 (sept,  $J = 6.9$  Hz, 2H, *p*- $\text{CH}(\text{CH}_3)_2$ ), 7.24 (s, 4H, *m*- $\text{Trip}$ ), 7.22 (t, 1H,  $J = 7.2$  Hz, *p*- $\text{C}_6\text{H}_3$ ), 7.31 (d, 2H,  $J = 7.9$  Hz, *m*- $\text{C}_6\text{H}_3$ ); UV ( $\lambda_{\text{max}}$ ,  $\epsilon$ ) 710 nm, 340; 522 nm, 1180; 480 nm, 1120. Anal. Calcd  $\text{C}_{36}\text{H}_{49}\text{ClSn}$ : C, 67.99; H, 7.77. Found: C, 67.32; H, 7.51. For  $[\text{K}(\text{THF})_6][\text{ArSnSnAr}]$  (**1**): 2,6-Trip<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SnCl (**1**) (1.00 g, 1.57 mmol) and  $\text{KC}_8$  (0.21 g, 1.54 mmol) in THF (20 mL) were stirred rapidly at room temperature for 2 h. All volatile materials were removed under reduced pressure, and the residue was extracted with THF/toluene, 3:1 mixture (30 mL), and rapidly filtered through Celite. The dark red solution was concentrated to incipient crystallization and stored in a *ca.*  $-20^\circ\text{C}$  freezer for 2 days to afford the product **1** as orange-green dichroic crystals: yield 0.36 g, 0.22 mmol, 27%; mp 120 °C (dec.). Anal. Calcd for  $\text{C}_{96}\text{H}_{146}\text{K}_2\text{O}_6\text{Sn}_2$ : C, 68.92; H, 8.80. Found C, 68.13; H, 8.97. The compound **2**·2THF was obtained similarly except that dibenzo-18-crown-6 was included in the reaction mixture. The product **2**·2THF was obtained in 22% yield, mp 125 °C (dec.). (b) Schiemenz, B.; Power, P. P. *Organometallics* **1996**, *15*, 958.

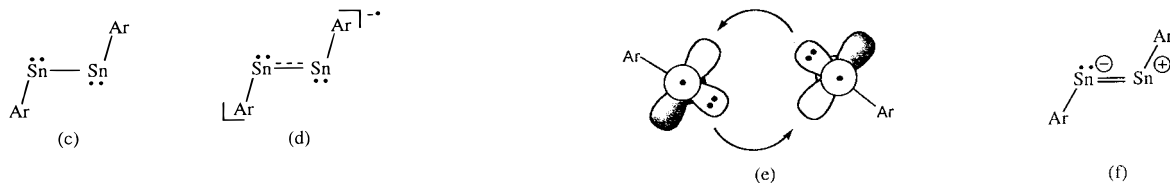
(5) Crystal data at 130 K with  $\text{Mo K}\alpha$  (**1**,  $\lambda = 0.71073$  Å) or  $\text{Cu K}\alpha$  (**2**·2THF,  $\lambda = 1.54178$  Å). For **1**:  $a = 13.036(3)$  Å,  $b = 21.742(4)$  Å,  $c = 17.034(3)$  Å,  $\beta = 105.91(3)^\circ$ , monoclinic, space group  $\text{P}2_1/c$ ,  $R_1 = 0.061$  for 5599 ( $I > 2\sigma(I)$ ) data. For **2**·2THF:  $a = 15.111(3)$  Å,  $b = 15.812(3)$  Å,  $c = 23.189(5)$  Å,  $\alpha = 81.16(3)^\circ$ ,  $\beta = 84.07(3)^\circ$ ,  $\gamma = 87.92(3)^\circ$ , triclinic, space group  $\text{P}1$ ,  $R_1 = 0.088$ , with 114 29 ( $I > 2\sigma(I)$ ) data.

<sup>†</sup> Preliminary data for **1** were reported at the 213th National Meeting of the American Chemical Society, San Francisco, CA, April 1997.

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The Sn–Sn distances in **1** and **2** (av 2.806(16) Å) are close to the Sn–Sn single bond distance in gray tin (2.80 Å)<sup>6</sup> and the quasi-double Sn–Sn bond length (2.764(2) Å) in Sn<sub>2</sub>[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>4</sub>.<sup>7</sup> The structures of **1** and **2** appear to imply that the p–p  $\pi$ -bond overlap is quite weak, although a comparison with the Sn–Sn distance in the neutral precursors (**c**) is necessary to confirm this.

We have attempted to isolate the neutral species (**c**) without success by the use of exactly 1 equiv of KC<sub>8</sub> per Sn(Cl)C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>. Apparently, (**c**) is very susceptible to reduction and (**d**) is always produced during the reaction. In the current absence of structural data for the neutral (**c**), the expected structure can be imagined by removing the  $\pi$ -electron. This should result in a slight increase in the Sn–Sn bond distance (since the formal bond order is lowered) and the angle at tin may also change slightly, but a *trans-bent* structure should be retained. The preference for the *trans-bent* configuration rather than the linear distannyne structure (**a**) is supported by preliminary 3-21G basis set calculations<sup>8</sup> on the hypothetical molecule MeSnSnMe (**3**), which show that the *trans-bent* form, with a Sn–Sn–C angle of 125.0° and an Sn–Sn distance of 2.673 Å, is 141.0 kJ mol<sup>-1</sup> more stable than the linear, formally triply bonded (Sn–Sn distance = 2.432 Å) form. The Sn–Sn distance for *trans-bent* MeSnSnMe<sup>8</sup> affords a Pauling bond order (PBO) value of 1.46.<sup>9</sup> One explanation for the multiple character comes from the molecular orbital representation of the MeSn: units which possess doublet ground states which may interact in a donor–acceptor fashion (represented by (**e**)) with the unpaired electrons in the p-orbitals also interacting to afford further bonding. The implied multiple bonding can be

represented in valence bond terms by a resonance form (**f**). The *ca.* 95° Sn–Sn–C angles in **1** and **2**, however, suggest that the lone pair donor–acceptor interaction is weak and that the single bond represented by (**c**) is a reasonable bonding approximation. Calculations on some Si congeners<sup>10</sup> show that the linear triply bonded form is as little as 20–25 kJ mol<sup>-1</sup> (Si substituents = Si(*t*-Bu)<sub>3</sub> or Si(C<sub>6</sub>H<sub>3</sub>-2,6-Et<sub>2</sub>)<sub>3</sub>)<sup>10a</sup> or as much as 75 kJ mol<sup>-1</sup> (Si substituent = Me)<sup>10a,b</sup> less stable than the *trans-bent* structures which have Si–Si bonds in the range of 2.068–2.072 Å, consistent with a PBO of 2.17 Å.<sup>11</sup>

Unfortunately, in the absence of theoretical data on the hypothetical, triply bonded, linear [MeGaGaMe]<sup>2-</sup>, it is not possible to calculate the PBO of the GaGa bond in Na<sub>2</sub>[ArGaGaAr]. However, we note that the Ga–Ga distance (2.319(2) Å) observed<sup>1</sup> in Na<sub>2</sub>[ArGaGaAr] is quite close to the 2.343(2) Å seen<sup>12</sup> in the anion [Trip<sub>2</sub>GaGaTrip<sub>2</sub>]<sup>-</sup> (**3**), which has a formal bond order of 1.5. Attempted reduction to doubly reduced [Trip<sub>2</sub>Ga=GaTrip<sub>2</sub>]<sup>2-</sup> (**4**) with a formal Ga–Ga bond order of 2 has not yet been successful. However, the singly and doubly reduced boron analogs of **3** and **4** have similar B–B distances.<sup>13</sup> It is thus probable that a putative Ga–Ga double bond in [Trip<sub>2</sub>GaGaTrip<sub>2</sub>]<sup>2-</sup> would be similar in length (i.e., *ca.* 2.34 Å) to the Ga–Ga distance in [Trip<sub>2</sub>GaGaTrip<sub>2</sub>]<sup>-</sup>. It is therefore concluded that the Ga–Ga bond order in doubly reduced Na<sub>2</sub>[ArGaGaAr] is close to 2, since it has a very similar Ga–Ga bond length as well as a *trans-bent*, rather than linear, structure.

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**Supporting Information Available:** Tables of data collection parameters, atom coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (37 pages). See any current masthead page for ordering and Internet access instructions.

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(11) For the PBO of an Si–Si bond of 2.07 Å long in the *trans-bent* structure, the Si–Si single bond distance of 2.34 Å and a calculated<sup>10b</sup> Si–Si triple bond length of 1.938 Å in linear MeSiSiMe were used in accordance with the method described in ref 9.

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(8) Allen, T. L. Unpublished results. The corresponding data for the germanium analog are Ge–Ge = 2.168 Å and Ge–Ge–C = 130.5° for the *trans-bent* form which is 63.4 kJ mol<sup>-1</sup> more stable than the linear form in which the Ge–Ge bond length is 2.014 Å. The PBO<sup>9</sup> for the *trans-bent* form assuming a Ge–Ge single bond length of 2.44 Å (ref 6) is 2.02. See also: Grev, R. S.; Deleuw, B. J.; Schaefer, H. F., III. *Chem. Phys. Lett.* **1990**, *165*, 257.

(9) Pauling, L. *Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960; p 239: The relationship of bond order to length is given by  $D(n') = D(1) - C \log(n')$  ( $n'$  = bond order,  $D(1)$  = single bond length, and  $C$  is a constant). If the length of a single bond (from gray tin, i.e., 2.80 Å<sup>6</sup>) and a triple bond (2.432 Å for the linear form<sup>8</sup>) are plotted on a graph whose ordinates are Sn–Sn distance and  $\log n'$  and connected by a straight line, the PBO for any Sn–Sn distance can be estimated. The Sn–Sn distance (2.673 Å) in *trans-bent* MeSnSnMe gives a  $\log n' = 0.164$  giving a PBO of 1.46.