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Synthesis and Characterization of 2,6-Dipp$_2$-H$_3$C$_6$SnSnC$_6$H$_3$-2,6-Dipp$_2$ (Dipp = C$_6$H$_3$-2,6-Pr$^i_2$): A Tin Analogue of an Alkyne

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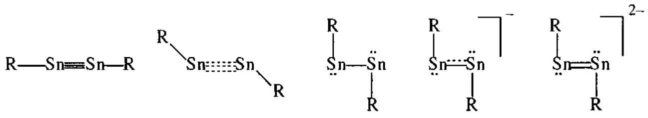
In 1997 it was reported that reduction of the aryltin(II) halide $Sn(Cl)C_6H_3\text{-}2,6\text{-}Trip_2$ (Trip = $C_6H_2\text{-}2,4,6\text{-}Pr^i_3$) by potassium afforded singly reduced valence isomers of distannynes in accordance with eq 1.[1]

$$2{:}Sn(Cl)Ar^* \xrightarrow{K} [K(THF)_6][Ar^*SnSnAr^*] \quad \text{or} \quad [K(18\text{-crown-6})(THF)_2][Ar^*SnSnAr^*]\cdot 2THF + 2KCl \qquad (1)$$

$$Ar^* = C_6H_3\text{-}2,6\text{-}Trip_2$$

Subsequently, it was shown that it was possible to induce further reduction by reaction with alkali metal for extended periods to obtain the doubly reduced species $K_2Ar^*SnSnAr^*$ as well as its germanium analogue $Na_2Ar^*GeGeAr^*$.[2] The main structural features of the singly and doubly reduced tin products[1-3] are a strongly trans-bent, planar skeleton and tin−tin bonds that are equal to, or slightly shorter than, the tin−tin distance (2.80 Å) in gray tin[4] or the 2.824 Å calculated for the Sn−Sn single bond in H_3SnSnH_3.[5] Due to the relatively narrow Sn−Sn−C angles in these compounds (See Table 1.),[1-3] they were viewed as singly (IV) or doubly (V) reduced forms of III which is a singly bonded valence isomer of the hypothetical triply bonded distannyne I. The double bonding in the twice reduced V is supported by analogy with the isoelectronic neutral group 15 species $R\dot{S}b{=}\dot{S}bR$.[6,7] Furthermore, EPR spectral data for IV supported the location of the unpaired electron spin density in a π-orbital which results from the overlap of a 5p orbital from each tin. The multiple Sn−Sn bonds in IV and V are not particularly short in comparison to a conventional Sn−Sn single bond,[4,5] but it could be argued that the multiple Sn−Sn bonding is partly masked by lengthening of the σ-bond which could have been weakened by the high p-character of the σ-bonding orbitals, and by Coulombic repulsion in the case of the dianion V. It is probable that IV and V are obtained through the reduction of neutral Ar*SnSnAr*; however, the structure and the degree of multiple bonding in this species has remained undefined experimentally. Such a molecule is of key importance in heavier group 14 element chemistry, where the only precedent is the compound Ar*PbPbAr*,[8] which has a long lead−lead bond of 3.188(1) Å and a Pb−Pb−C angle of 94.26(4)° consistent with metal−metal single bonding.[8,9] It is now reported that the use of a modified terphenyl substituent permits the synthesis and structure of a neutral diorganoditin species of formula Ar′SnSnAr′ (**1**; Ar′ = $C_6H_3\text{-}2,6\text{-}Dipp_2$; Dipp = $C_6H_3\text{-}2,6\text{-}Pr^i_2$), whose structural parameters support the presence of tin−tin multiple bonding.



I II III IV V

Table 1. Selected Bond Distances and Angles for Reduced Ar*SnSnAr* Species and **1**

cmpd	Sn–Sn(Å)	Sn–Sn–C (deg)	ref
$[K(THF)_6][Ar^*SnSnAr^*]^a$	2.8123(9)	95.20(13)	1
$[K(18\text{-crown-6})(THF)_2][Ar^*SnSnAr^*]$	2.7821(14) 2.8236(14)	93.6(4),95.0(4) 97.3(2)	1
$[(THF)_3Na\{Ar^*SnSnAr^*\}]$	2.8107(13)	97.9(3),98.0(4)	3
$[K_2Ar^*SnSnAr^*]$	2.7763(9)	107.50(14)	2
Ar′SnSnAr′ (**1**)^b	2.6675(4)	125.24(7)	this work

[a] Ar* = $C_6H_3\text{-}2,6\text{-}Trip_2$. [b] Ar′ = $C_6H_3\text{-}2,6\text{-}Dipp_2$.

The compound **1** was isolated by reaction of Sn(Cl)Ar′ with a stoichiometric quantity of potassium in benzene at room temperature.[10] The product was obtained as dark blue-green crystals which were spectroscopically and structurally characterized. The ^1H and ^{13}C NMR data were consistent with the presence of the Ar′ ligand. However, despite numerous attempts, a ^{119}Sn NMR signal could not be detected. It is probable that the signal is broadened to a sufficient extent to be undetectable directly owing to the large chemical shift anisotropies caused by the tin environment.[11] The UV−vis spectrum affords two moderately intense absorptions at 410 and 597 nm which may be due to $\pi\rightarrow\pi^*$ and $n-\pi^*$ transitions. An X-ray structure determination revealed a centrosymmetric molecule (Figure 1) that has trans-bent skeleton, as well as a planar C(1)Sn(1)Sn(1A)C(1A) array as required by symmetry.[12] The Sn−Sn distance is 2.6675(4) Å, and the Sn(1)−Sn(1A)-C(1A) angle is 125.24(7)°. The central aryl ring of the ligand is almost coplanar (torsion angle 3.2°) with the C(1)Sn(1)Sn(1A)C(1A) array. Furthermore, there is an angle of 4.9° between the Sn(1)−C(1) bond and the C(1)···C(4) vector. The flanking aryl rings are oriented at 82.8° with respect to the central aryl ring. A cyclic voltammogram of **1** in THF solution displayed a quasi-reversible reduction at ca. −1.22 V vs SCE.[12b] An irreversible oxidation was observed at ca. 0.0 V.

The compound **1** is a stable ditin analogue of an alkyne. The Sn−Sn distance is shorter, and the Sn−Sn−C angle is considerably wider, than those observed for the reduced compounds in Table 1. The Sn−Sn distance is shortened in comparison to that of a normal single bond[4,5] and close to the 2.659 Å calculated for the hypothetical compound TbtSnSnTbt (Tbt = $C_6H_2\text{-}2,4,6\text{-}\{CH(SiMe_3)_2\}_3$) which has a Sn−Sn−C angle of 122° and a torsion angle of 10.7° between the C−Sn−Sn planes.[5] Interestingly, calculations for the structurally uncharacterized compound Ar*SnSnAr* also yield a trans-bent structure (Sn−Sn−C = 111.0°).[5] However, the torsion angle of 54.7° is quite high, and there is a long Sn−Sn distance of 2.900 Å.[5,13] The calculated structure of Ar*SnSnAr* and the experimentally determined

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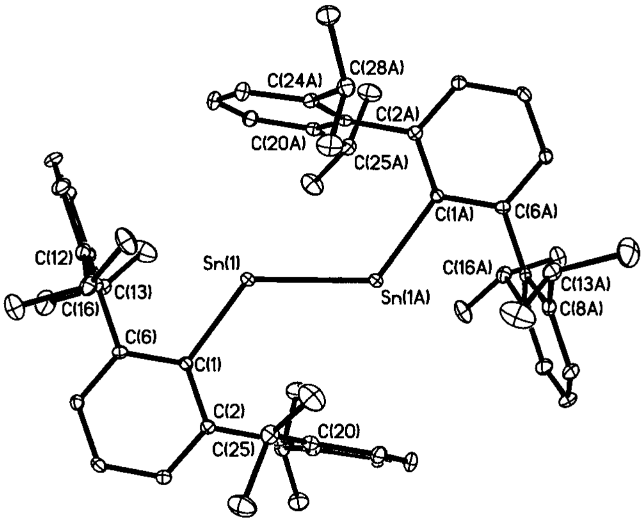

Figure 1. Selected bond lengths (Å) and angles (deg) for **1**. H atoms are not shown. Sn(1)−Sn(1A) = 2.6675(4), Sn(1)−C(1) = 2.191(3), C(1)−C(2) = 1.403(4), C(1)−C(6) = 1.405(4), Sn(1A)−Sn(1)−C(1) = 125.24(7), Sn(1)−C(1)−C(2) = 124.9(2), Sn(1)−C(1)−C(6) = 115.8(2), C(1)−C(2)−C(19) = 119.8(2), C(1)−C(6)−C(7) = 118.6(2), C(2)−C(1)−C(6) = 119.3(3).

structure of **1**, which differ only in the presence or absence of *p*-Pr^i groups on the flanking rings, illustrate the importance of these groups to the stability of the two configurations. It is becoming clear that the *p*-Pr^i groups play a key role in determining the overall structure of these compounds as well as other terphenyl derivatives. Previous calculations[14] have shown that they are important in stabilizing the controversial compound $Na_2Ar^*GaGaAr^*$.[15] In addition, the structures of the lithium derivatives of these ligands, $C_6H_6{\cdot}LiC_6H_3$-2,6-$Trip_2$ (i.e., $C_6H_6{\cdot}LiAr^*$) and (LiC_6H_3-2,6-$Dipp_2)_2$ (i.e., $(LiAr')_2$), show that the absence of the *p*-Pr^i groups decreases steric congestion sufficiently to allow dimerization to occur.[10c] The Sn−C(1) distance, 2.191(3) Å in **1**, is marginally shorter than the divalent tin carbon distance (2.227(2) Å) in $Ar^*(Me)_2SnSnAr^*$.[16] This, together with the near coplanarity of the central aryl ring and the C(1)−Sn(1)-Sn(1A) array, suggests the possibility of conjugation. However, the different C−Sn−Sn angles at tin, which may indicate changes in σ-bonding, makes it difficult to draw conclusions from the structural data.

Although the hypothetical species Ar*SnSnAr* and TbtSnSnTbt have been described as distannynes,[5] this name is misleading in respect of the bond order. The Sn−Sn distances calculated for TbtSnSnTbt, and observed in **1**, are clearly shorter than single bonds, but they are not as short[17] as the Sn−Sn double bond (2.59(1) Å) in the cyclotristannene $(Bu_3{}^tSi)_2\overline{SnSn(SiBu^t_3)Sn}(SiBu_3{}^t)$ where, possibly, the geometric constraints of the three-membered ring favor alignment of the tin p-orbitals to afford more efficient π-overlap.[18] They are similar to the Sn−Sn multiple bonds in the tristannaallene $Sn\{Sn(SiBu^t_3)_2\}_2$ (Sn−Sn = 2.68(1) Å)[17] and ca. 0.1 Å shorter than the Sn−Sn distance 2.768(1) Å in the compound R_2SnSnR_2 (R = $CH(SiMe_3)_2$) which is the shortest, currently known Sn−Sn bond in a "distannene".[19] Furthermore, the trans-bent geometry is indicative of lone pair character at each tin. The bonding in **1** thus approximates to II and lies between the extremes of the hypothetical linear triply bonded I and the singly bonded III.

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Supporting Information Available: Tables of data collection parameters, atom coordinates, bond distances, angles, anisotropic thermal parameters, and hydrogen coordinates (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) (a) Under strictly anaerobic and anhydrous conditions, a benzene solution (50 mL) of 2,6-$Dipp_2$-C_6H_3SnCl (1.10 g, 2 mmol, prepared by a method identical to that used for (2,6-$Dipp_2$-H_3C_6)SnI[10b] from LiC_6H_3-2,6-$Dipp_2$[10c] and $SnCl_2$), was added dropwise to finely divided potassium (0.086 g, 2.2 mmol) in 10 mL of benzene at room temperature. The reaction mixture was stirred for 2 days after which the precipitate was allowed to settle for 4 h. The intensely dark blue-green solution was decanted from the precipitated solid. The volume of the solution was reduced to incipient crystallization and stored in a ca. 6 °C refrigerator to give the product **1** as dark blue-green crystals. Yield: 0.31 g, 0.30 mmol, 32.2%; mp dec 208−210 °C. Anal. Calcd for $C_{60}H_{74}Sn_2$, **1**: C 70.31, H 7.22. Found: C 71.02, H 7.54. UV−vis (hexanes) λ_{max} ϵ (L mol^{-1} cm^{-1}) 410 nm, 4300; 597 nm, 1700. ^1H NMR (C_6D_6, 399.77 MHz, 25 °C) δ 1.13 (d, 24 H, ^3J = 6.0 Hz, *o*-$CH(CH_3)_2$), 1.39 (d, 24 H, ^3J = 6.0 Hz, *o*-$CH(CH_3)_2$), 2.87 (sept, 8 H, ^3J = 6.0 Hz, *o*-$CH(CH_3)_2$), 6.22 (t, 2 H, ^3J = 7.2 Hz, *p*-C_6H_3), 7.05 (d, 8 H, ^3J = 7.2 Hz, *m*-Dipp), 7.19 (t, 4 H, ^3J = 7.2 Hz, *p*-Dipp), 7.51 (d, 4 H, ^3J = 7.2 Hz, *m*-C_6H_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.53 MHz, 25 °C) δ 27.44 (*o*-$CH(CH_3)_2$), 32.67 (*o*-$CH(CH_3)_2$), 34.98 (*o*-$CH(CH_3)_2$), 124.55 (*p*-C_6H_3), 125.94 (*m*-Dipp), 130.65 (*m*-C_6H_3), 131.68 (*i*-Dipp), 141.72 (*p*-Dipp), 150.84 (*o*-Dipp), 153.98 (*i*-C_6H_3), 159.02 (*o*-C_6H_3). ^{119}Sn NMR (C_6D_6, 149.00 MHz, 25 °C) δ no signal observed. (b) Pu, L.; Olmstead, M. M.; Power, P. P.; Schiemenz, B. *Organometallics* **1998**, *17*, 5602−5606. (c) Schiemenz, B.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2150−2152.

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(12) (a) Crystal data for **1** at 90 K with Mo Kα (λ = 0.71073 Å) radiation: *a* = 20.4324(11) Å, *b* = 15.7584(9) Å, *c* = 16.2418(9) Å, orthorhombic, space group *Pccn*, *Z* = 4, R1 = 0.0317 for 4127 ($I > 2\sigma(I)$) data, wR2 = 0.0845 for all (7028) data. (b) Cyclic voltammetric data for **1** were obtained under anaerobic conditions using a PAR model 263 potentiostat/galvanostat with a Pt working electrode (against a SCE reference) scanning at 100 mV sec^{-1} in THF solution with 0.1 M $[NBu_4]PF_6$ as the electrolyte.

(13) This result suggests that a tin−tin single bond in this compound class is ca. 2.9 Å and is the distance to which the bond lengths in Table 1 should be compared. The Sn−Sn distance of 2.8909(2) Å in $Ar^*(Me)_2SnSnAr^*$[11] supports this argument.

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