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Very Large Changes in Bond Length and Bond Angle in a Heavy Group 14 Element Alkyne Analogue by Modification of a Remote Ligand Substituent

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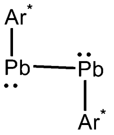
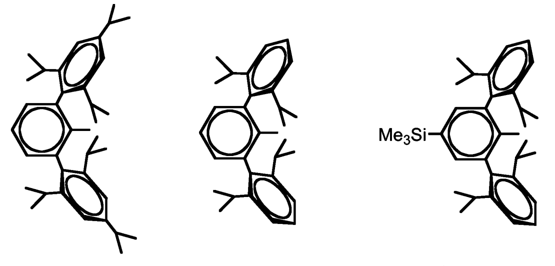
Recent experimental work[1−8] has resulted in the syntheses and structural characterization of several examples of stable heavier group 14 element alkyne analogues of formula RMMR (R = large aryl or silyl substituent, M = Si, Ge, Sn, Pb). X-ray crystallographic studies have shown that they have a *trans*-bent, planar,[1−3,7] or almost planar[8] core arrangement with angles at M that range from 137.44(4)° (M = Si)[7] to 94.26(4)° (M = Pb).[1] With the exception of the lead derivative, the M−M distances fall in the range expected for an M−M bond order between 2 and 3. For the lead species Ar*PbPbAr* (Ar* = C_6H_3-2,6-(C_6H_2-2,4,6-*i*-Pr_3)$_2$, Scheme 1), the Pb−Pb bond length is 3.1881(1) Å and there is a strongly bent (Pb−Pb−C = 94.26(4)°) core structure consistent with the representation



in which there is single-bonding and a nonbonding pairs of electrons at each lead. Calculations by Frenking and co-workers have shown that the Ar* ligand plays a crucial role in stabilizing the observed molecular configuration in comparison to others that would be more stable (by <10 kcal mol^{-1}) with less crowding ligands.[9] Calculations by Nagase and Takagi[10] for the Ge and Sn species RMMR (R = Ar* or Tbt (Tbt = C_6H_2-2,4,6-{CH($SiMe_3$)$_2$}$_3$) predicted structures for Ar*GeGeAr* (Ge−Ge = 2.277 Å, Ge−Ge−C = 123.2°)[11] and TbtGeGeTbt (Ge−Ge = 2.231 Å, Ge−Ge−C = 121.8°) that were quite similar to those experimentally measured for Ar′GeGeAr′ (Ar′ = C_6H_3-2,6-(C_6H_3-2,6-*i*-Pr_2)$_2$[3], Ge−Ge = 2.2850(6) Å, Ge−Ge−C = 128.27(8)°) and more recently by Tokitoh and co-workers for BbtGeGeBbt (Bbt = C_6H_2-2,6-{CH($SiMe_3$)$_2$}$_2$-4-C($SiMe_3$)$_3$, Ge−Ge = 2.22 Å avg, Ge−Ge−C = 131° avg).[8] These bond distances were in the range observed for the Ge−Ge double bonds in digermenes.[12] The stronger bonding in BbtGeGeBbt was rationalized on the basis of a lower Δ_{D-Q} for the GeBbt fragment, which leads to a stronger Ge−Ge interaction.[8] In contrast, the calculations predicted that a "multiple-bonded" Ar*SnSnAr* should have a more *trans*-bent structure (Sn−Sn−C = 111.0°, a C−Sn−Sn−C torsion angle of 125.3°) and a relatively long Sn−Sn bond of 2.900 Å. These values differed considerably from those experimentally measured for Ar′SnSnAr′ (Sn−Sn = 2.6675(4) Å, Sn−Sn−C = 125.249(2)°). The calculations also predicted that the singly-bonded Ar*SnSnAr* isomer (analogous to the Ar*PbPbAr* structure above) with Sn−Sn = 3.087 Å and Sn−Sn−C = 99.0° differed in energy by only 4.8 kcal mol^{-1} from "multiple-bonded" Ar*SnSnAr*. Seemingly, these large structural changes carry only a small energy penalty, and this unusual result has been confirmed by calculations on simpler RMMR (M = Si−Pb; R = H[13] or Me[14]) models.

Scheme 1. Schematic Drawing of Ar*, Ar′, and Ar′-4-$SiMe_3$

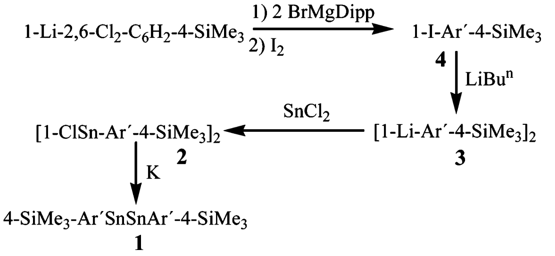


Ar* = C_6H_3-2,6-(C_6H_2-2,4,6-Pr^i_3)$_2$

Ar′ = C_6H_3-2,6-(C_6H_3-2,6-Pr^i_2)$_2$

Ar′-4-$SiMe_3$ = C_6H_2-2,6-(C_6H_3-2,6-Pr^i_2)$_2$-4-$SiMe_3$

Scheme 2. Synthetic Routes to **1**−**4**



We now supply experimental evidence to support this prediction by the synthesis and characterization of the alkyne analogue 4-Me_3-Si−Ar′SnSnAr′-4-$SiMe_3$ (**1**). This compound employs the modified terphenyl ligand C_6H_2-2,6-(C_6H_3-2,6-*i*-Pr_2)$_2$-4-$SiMe_3$ (Ar′-4-$SiMe_3$, Scheme 1) in place of Ar′. This results in a species that has a much longer Sn−Sn distance and a narrower Sn−Sn−C angle than those found in Ar′SnSnAr′.

The ligand precursor 1-I-C_6H_2-2,6-(C_6H_3-2,6-*i*-Pr_2)$_2$-4-$SiMe_3$ (**4**) was isolated by the addition of 2 equiv of $BrMgC_6H_3$-2,6-*i*-Pr_2 (BrMgDipp) to 1-Li-2,6-Cl_2-C_6H_2-4-$SiMe_3$, with subsequent quenching with I_2 by a standard route[15] (Scheme 2). In a manner similar to the preparation of [Ar′Li]$_2$,[16] **3** was synthesized by reaction of **4** with *n*-BuLi.

Subsequent reaction of **3** with excess $SnCl_2$ in diethyl ether and crystallization from the same solvent at −20 °C yielded [1-ClSnC_6H_2-2,6-(C_6H_3-2,6-*i*-Pr_2)$_2$-4-$SiMe_3$]$_2$ (**2**). Reduction of **2** with potassium in diethyl ether and subsequent crystallization afforded **1** as dark green, air- and moisture-sensitive crystals.[17] X-ray crystallography showed that **1** has a *trans*-bent structure in the solid state[18] with geometric (Figure 1) parameters that differ dramatically (Figure 2) from those previously reported for Ar′SnSnAr′.

In **1**, the Sn−Sn bond length is 3.066(1) Å, which is about 0.4 Å longer than the 2.6675(4) Å in Ar′SnSnAr′. In addition, the Sn−

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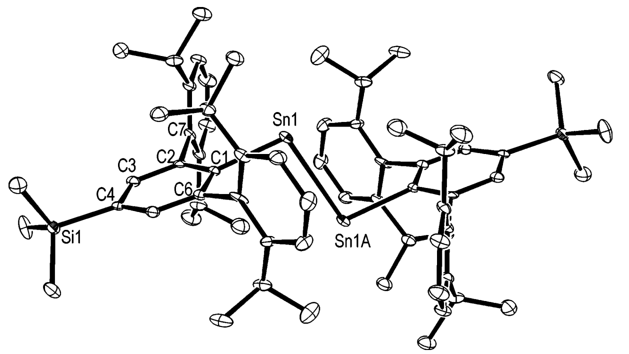

Figure 1. Thermal ellipsoidal plot of **1** (30% probability) without H atoms. Selected bond distances (Å) and angles (°): Sn(1)−Sn(1a), 3.066(1); Sn(1)−C(1), 2.208(5); Si(1)−C(4), 1.878(6); C(1)−Sn(1)−Sn(1a), 99.25(14); C(2)−C(1)−Sn(1), 125.6(4); C(6)−C(1)−Sn(1), 115.0(4); C(2)−C(1)−C(6), 118.3(5); C(1)−C(2)−C(7), 121.6(5); C(3)−C(2)−C(7), 118.5(5).

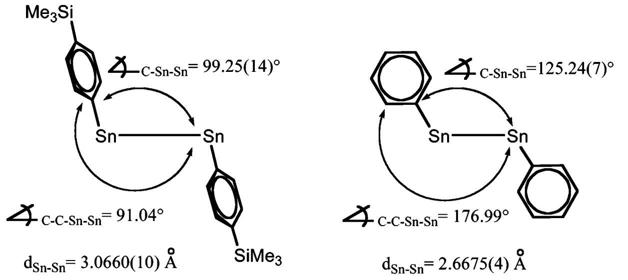

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Figure 2. Comparison of core geometries for 4-$SiMe_3$Ar′SnSnAr′-4-$SiMe_3$ **1** and Ar′SnSnAr′, flanking aryl groups are not shown for clarity.

Sn−C bond angle is 99.25(14)°, a decrease of about 26° in comparison to the 125.24(7)° in Ar′SnSnAr′. Hence, the structural parameters resemble those of Ar*PbPbAr* (Pb−Pb = 3.1881(1) Å, Pb−Pb−C = 94.26(4)°) more than those of Ar′SnSnAr′ and are consistent with Sn−Sn single bonding. Another striking difference between the solid-state structures of **1** and Ar′SnSnAr′ is the perpendicular arrangement of the ligand's central aryl rings relative to the C−Sn−Sn−C in contrast to the parallel orientation in Ar′SnSnAr′, where the central aryl rings lie in the plane with the central structural unit. The dihedral angles Sn−Sn−C−C in **1** are 91.04 and −101.08°, but are 176.99° and 3.09° in Ar′SnSnAr′, whereas the lead derivative Ar*PbPbAr* exhibits torsional angles of 95.16° and −88.98°.

The UV−vis spectrum of **1** in hexanes displays two strong absorptions at 416 ($\epsilon = 4700$ L mol^{-1} cm^{-1}) and 608 ($\epsilon = 1200$ L mol^{-1} cm^{-1}) nm and are slightly bathochromically shifted in comparison to those of Ar′SnSnAr′ (410 and 597 nm) and Ar*SnSnAr* (409 and 593 nm), suggesting similar, strongly bent structures of the three compounds in solution.

Our results vindicate the theoretical prediction[10,13,14] that relatively small amounts of energy separate two different bonding modes of the tin analogues of alkynes. Modification of the known terphenyl ligand Ar′ by the introduction of $SiMe_3$ instead of H at the *para*-position of the central aryl ring induces a single-bonded structure without alteration of the steric crowding near the tin center. Preliminary theoretical data on model moieties MC_6H_4-4-$SiMe_3$ and MC_6H_5 (M = Ge, Sn) indicate about a 2 kcal mol^{-1} difference in their Δ_{D-Q} energies that, when added together in the dimerized product, results in a 4 kcal mol^{-1} difference.[19] However it should be borne in mind that these energy differences are sufficiently small to be in the range of packing forces.

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Supporting Information Available: X-ray data (CIF) for **1**. This material is available free of charge via the Internet at http:\\www.pubs.acs.org.

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(17) At room temperature and under strictly anhydrous and anaerobic conditions, a solution of 0.850 g (1.36 mmol) [1-ClSn-C_6H_2-2,6-(C_6H_3-2,6-*i*-Pr_2)$_2$-4-$SiMe_3$]$_2$ (prepared in a fashion similar to previously reported procedures)[5] in diethyl ether (25 mL) was added to a diethyl ether suspension of 0.059 g (1.51 mmol) of finely dispersed potassium with rapid stirring. The reaction mixture quickly adopted a deep green color, and stirring was continued for 24 h, after which the precipitated material and unreacted potassium were allowed to settle. The solution was filtered through a filter-tipped cannula and concentrated in vacuo to incipient crystallization (ca. 10 mL). Storage at −20 °C yielded 0.41 g (0.328 mmol, 48% yield) of dichroic green-dark orange crystals of **1**·Et_2O. Anal. Calcd for **1**·Et_2O $C_{70}H_{100}OSi_2Sn_2$: C, 67.20; H, 8.06. Found: C, 66.79; H, 8.22. Mp 183−185 dec. UV−vis λ_{max} (nm, ϵ [L $mol^{-1}cm^{-1}$]): 416 (4700), 608 (1200). ^1H NMR (C_6D_6, 599.814 MHz, 25 °C): −0.28 (s, 18H, (CH_3)$_3$Si), 1.12 (t, 6H, (CH_3CH_2)$_2$O), 1.16 (d, 24H, $^3J_{HH} = 6.8$ Hz, *o*-CH(CH_3)(CH_3)), 1.38 (d, 24H, $^3J_{HH} = 6.8$ Hz, *o*-CH(CH_3)(CH_3)), 2.94 (septet, 8H, $^3J_{HH} = 6.8$ Hz, *o*-CH(CH_3)(CH_3)), 3.27 (q, 4H, (CH_3CH_2)$_2$O), 7.07 (d, 8H, $^3J_{HH} = 6.7$ Hz, *m*-Dipp), 7.17 (t, 4H, $^3J_{HH} = 6.7$ Hz, *p*-Dipp), 7.98 (s, 4H, *m*-$C_6H_2Si(CH_3)_3$). $^{13}C\{1H\}$ (C_6D_6, 150.823 MHz, 25 °C): −0.6 ((H_3C)$_3$Si), 15.5 ((CH_3CH_2)$_2$O), 26.9 (CH(CH_3)(CH_3)), 32.5 (CH(CH_3)(CH_3)), 35.9 (CH(CH_3)(CH_3)), 65.9 ((CH_3CH_2)$_2$O), 125.2 (*p*-Dipp), 127.9 (*m*-Dipp), 138.0 (*m*-C_6H_2), 141.2 (*o*-Dipp), 143.2 (*p*-C_6H_2), 151.1 (*i*-Dipp), 161.4 (*o*-C_6H_2), 174.6 (*i*-C_6H_2). $^{29}Si\{^1H\}$ (C_6D_6, 119.165 MHz, 25 °C): −4.2. $^{119}Sn\{^1H\}$ (C_6D_6, 223.671 MHz, 25 °C): no signal observed.

(18) Crystal data for **1**·Et_2O at 90 K with Mo Kα ($\lambda = 0.71073$ Å): $a = 11.605(3)$ Å, $b = 24.573(5)$ Å, $c = 12.733(3)$ Å, $\beta = 114.407(4)°$, $V = 3306.5(12)$ Å^3, $M = 1251.06$ g mol^{-1}, $\beta_{calcd} = 1.257$ Mg m^{-3}, F(000) = 1312, monoclinic, space group $P2(1)/c$, $Z = 2$, $R1 = 0.0557$ for 3272 ($I > 2(I)$) data, $wR2 = 0.1246$ for all 5975 data. Equipment: Bruker SMART1000 CCD system. Absorption correction was performed using SADABS.[18a] The structure was solved by direct methods (SHELXS-97),[18b] and nonhydrogen atoms were refined anisotropically (full-matrix least-squares on F^2, SHELXL-97).[18c] (a) Sheldrick G. M. *SADABS*, version 2.10; Universität Göttingen: Göttingen, Germany, 2003. (b) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. (c) Sheldrick, G. M. *SHELXS-97* and *SHELXL-97*; Universität Göttingen: Göttingen, Germany, 1997.

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