Characterization of the Sterically Encumbered Terphenyl-Substituted Species 2,6-$Trip_2H_3C_6\ddot{S}n-Sn(Me)_2C_6H_3$-2,6-$Trip_2$, an Unsymmetric, Group 14 Element, Methylmethylene, Valence Isomer of an Alkene, Its Related Lithium Derivative 2,6-$Trip_2H_3C_6(Me)_2Sn-Sn(Li)(Me)C_6H_3$-2,6-$Trip_2$, and the Monomer Sn(*t*-Bu)C_6H_3-2,6-$Trip_2$ (Trip = C_6H_2-2,4,6-*i*-Pr_3)

Barrett E. Eichler and Philip P. Power*

Department of Chemistry, University of California, Davis, One Shields Avenue, Davis, California 95616

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The reaction of the recently reported sterically encumbered terphenyl tin(II) halide species Sn(Cl)C_6H_3-2,6-$Trip_2$ (Trip = C_6H_2-2,4,6-*i*-Pr_3), **1**, with 1 equiv of MeLi or MeMgBr afforded 2,6-$Trip_2H_3C_6\ddot{S}n-Sn(Me)_2C_6H_3$-2,6-$Trip_2$, **2**, which is the first stable group 14 element methylmethylene (i.e., CH_3CH) analogue of ethylene (H_2CCH_2). Reaction of **1** with 1.5 equiv of MeLi yielded the stannylstannate species 2,6-$Trip_2H_3C_6(Me)_2Sn-Sn(Li)(Me)$-$C_6H_3$-2,6-$Trip_2$, **3**, whereas reaction of **1** with 1 equiv of t-BuLi gave the heteroleptic stannanediyl monomer Sn(*t*-Bu)C_6H_3-2,6-$Trip_2$ (**4**). The compounds **2**−**4** were characterized by ^{1}H, ^{13}C (^{7}Li, **3** only), and ^{119}Sn NMR spectroscopy in solution and by UV−vis spectroscopy. The X-ray crystal structures of **2**−**4** were also determined. The formation of the stannylstannanediyl **2** instead of the expected symmetrical, valence isomer "distannene" form {Sn(Me)C_6H_3-2,6-$Trip_2$}$_2$, **6**, is explained through the ready formation of $LiSn(Me)_2C_6H_3$-2,6-$Trip_2$, **5**, which reacts rapidly with **1** to produce **2** which can then react with a further equivalent of MeLi to give **3**. The stability of singly bonded **2** in relation to the formally doubly bonded **6** was rationalized on the basis of the difference in the strength of their tin−tin bonds. In contrast to the methyl derivatives, the reaction of **1** with t-BuLi proceeded smoothly to give the monomeric compound **4**. Apparently, the formation of a t-Bu analogue of **5** was prevented by the more crowding t-Bu group. Compound **2** is also the first example of a stable molecule with bonding between a two-coordinate, bivalent tin and four-coordinate tetravalent tin. Both compounds **2** and **3** display large J ^{119}Sn−^{119}Sn couplings between their tin nuclei and the tin−tin bond lengths in **2** (2.8909(2) Å) and **3** (2.8508(4) Å) are relatively normal despite the presence of the sterically crowding terphenyl substituents.

Introduction

Recent studies of the reactivity of Pb(Br)C_6H_3-2,6-$Trip_2$ (Trip = C_6H_2-2,4,6-*i*-Pr_3) with MeMgBr, Li(t-Bu), and LiPh showed that the first two-coordinate lead(II) derivatives of simple organic ligands such as CH_3, t-Bu, or Ph could be stabilized by the use of the sterically encumbering terphenyl group C_6H_3-2,6-$Trip_2$ as coligand.[1] It was expected that the corresponding reactions of the related tin halide Sn(Cl)C_6H_3-2,6-$Trip_2$ (**1**)[2] with these reagents would lead to products with similar stoichiometries in which tin is bound to these simple groups. In general, stable, two-coordinate dialkyls or diaryls of tin(II) can be synthesized by the reaction of an Sn(II) halide with lithium alkyls or aryls, and, provided that the ligands are of sufficient size, the diorganotin(II) products are isolated either as monomers[3] or as "distannene" dimers[4] that feature tin−tin bonds with varying degrees of multiple character. With less crowded organic ligands, for example, a Trip or a phenyl group, oligomers such as the three- or six-membered ring compounds c-{$SnTrip_2$}$_3$[5] or c-$(SnPh_2)_6$[6] are obtained. All of these species are related in that they feature two organic groups at each tin and have the metal in the formal oxidation state +2. Unlike these findings, it is now shown that the reaction between MeLi or MeMgBr with Sn(Cl)C_6H_3-2,6-$Trip_2$ does not lead to the isolation of the expected alkene-like symmetric product {Sn(Me)C_6H_3-2,6-$Trip_2$}$_2$ (**6**) but to the first instance of a stable group 14 element valence isomer of an alkene 2,6-$Trip_2H_3C_6\ddot{S}n-Sn(Me)_2C_6H_3$-2,6-$Trip_2$, **2**, and the lithium salt 2,6-$Trip_2H_3C_6(Me)_2Sn-Sn(Li)C_6H_3$-2,6-$Trip_2$, **3** (Scheme 1), in which the tin atoms have different substituents and different formal oxidation states. In contrast, the reaction with t-BuLi gives the monomeric stannanediyl Sn(*t*-Bu)C_6H_3-2,6-$Trip_2$. The reasons for this unexpected result involve the unique steric properties of the bulky terphenyl group, the small size of the methyl substituents, and the relative weakness of the putative multiple Sn−Sn bond in **6**.

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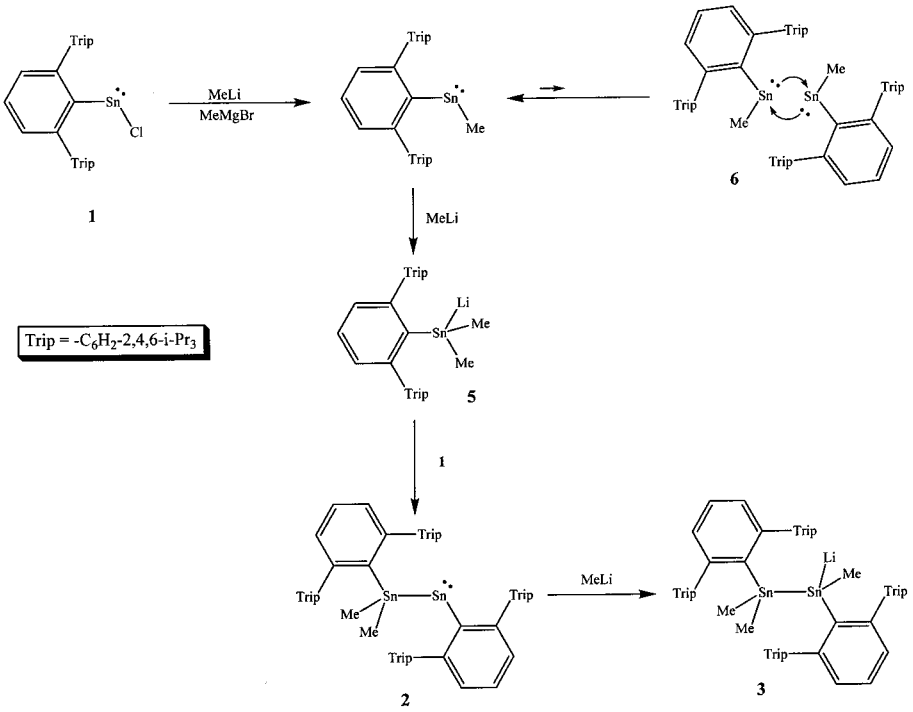
Scheme 1. Illustration of the Possible Relationships between the Compounds **1**−**3**, **5**, and **6**



Experimental Section

General Procedures. All manipulations were carried out by using modified Schlenk techniques under an atmosphere of N_2 or in a Vacuum Atmospheres HE-43 drybox. All solvents were distilled from Na/K alloy and degassed three times before use. The compound $Sn(Cl)C_6H_3$-2,6-$Trip_2$ (**1**) was prepared according to literature procedures.[2] Solutions of MeLi, MeMgBr, and t-BuLi were purchased commerically and used as received. ^{1}H, ^{7}Li, ^{13}C, and ^{119}Sn NMR spectroscopic data were recorded on a Varian INOVA 400 MHz spectrometer. ^{1}H and ^{13}C spectra were referenced to the deuterated solvent. The ^{7}Li spectrum of **3** was referenced externally to $LiCl/D_2O$ and the ^{119}Sn spectra were referenced externally to $SnMe_4/C_6D_6$. UV−vis data were recorded on a Hitachi-1200 spectrometer.

2,6-$Trip_2H_3C_6$Sn−Sn(Me)$_2C_6H_3$-2,6-$Trip_2$ (2). Method A: MeMgBr (0.77 mL, 2.30 mmol, 1.0 equiv) was added dropwise to a pale yellow solution of **1** (1.47 g, 2.31 mmol) in pentane (80 mL) at ca. −78 °C. Slow warming to ca. 0 °C caused the solution to turn bright green with a concomitant formation of a colorless precipitate (magnesium halide). The solution was further stirred at ca. 25 °C for 1 h and the solvents were removed under reduced pressure. The green solid was extracted with hexanes (100 mL) and the solution was filtered through a Celite pad. The volume of the solution was then reduced to ca. 10 mL and the flask was stored in a ca. −20 °C freezer overnight to afford green crystals of **2** (1.25 g, 0.98 mmol, 85%).

Method B: MeLi (1.45 mL, 2.32 mmol, 1.1 equiv) was added dropwise to a pale yellow solution of **1** (1.34 g, 2.11 mmol) in hexanes (60 mL) at −78 °C, to afford a bright green solution. The solution was stirred at −78 °C for 30 min and was allowed to warm to ca. 25 °C. A workup procedure similar to method A afforded green crystals of **2** (0.25 g, 0.20 mmol, 9%). Mp = 210−213 °C (dec to red). Anal. Calcd for $C_{37}H_{52}Sn$: C, 72.20; H, 8.52. Found: C, 72.88; H, 8.96. UV−vis (hexanes) λ_{max}, ϵ(mol^{-1} cm^{-1}): 689 nm, 271. ^{1}H NMR (C_6D_6, 399.77 MHz, 25 °C): δ −0.34 (s, 6H, $Sn(CH_3)_2$), 1.07 (br d, 24 H, ^3J = 6.6 Hz, *o*-CH(CH_3)$_2$), 1.31 (d, 12 H, ^3J = 7.0 Hz, *p*-CH(CH_3)$_2$), 2.85 (sept, 2 H, ^3J = 7.0 Hz, *p*-C*H*(CH_3)$_2$), 2.99 (br s, 2H, *o*-C*H*(CH_3)$_2$), 3.21 (br s, 2 H, *o*-C*H*(CH_3)$_2$), 7.10 (s, 4 H, *m*-Trip), 7.07−7.22 (br m, 3 H, *p*- and *m*-C_6H_3). ^{13}C {^{1}H} NMR (C_6D_6, 100.53 MHz): δ 0.34 ($Sn(CH_3)_2$), 24.12 (*o*-CH(CH_3)$_2$), 26.22 (*p*-CH(CH_3)$_2$), 30.85 (*o*-*C*H(CH_3)$_2$), 34.59 (*p*-*C*H(CH_3)$_2$), 121.90(*m*-Trip), 126.10 (*m*-Trip), 127.70 (*i*-Trip) 131.11 (br, *o*-Trip), 146.45 (*p*-Trip), 146.94 (*o*-C_6H_3), 147.19 (*m*-C_6H_3), 148.58 (*p*-C_6H_3), 165.23 (*i*-C_6H_3). ^{119}Sn {^{1}H} NMR (C_6D_6, 149.24 MHz): δ 257.4 (Sn (four-coordinate), $^1J(^{119}Sn-^{119/117}Sn)$ = 8332 Hz), 2856.9 (Sn (two-coordinate), $^1J(^{119}Sn-^{119/117}Sn)$ = 8332 Hz).

2,6-$Trip_2H_3C_6$(Me)$_2$Sn−Sn(Li)(Me)C_6H_3-2,6-$Trip_2$ (3). MeLi (2.40 mL, 3.84 mmol, 1.5 equiv) was added dropwise to an orange solution of **1** (1.63 g, 2.56 mmol) in diethyl ether (40 mL) at ca. −10 °C. The solution initially became a green color, but it had changed to yellow-orange after the addition of the MeLi was completed. The solution was warmed to ca. 10 °C and stirred for 5 min, after which the solvent was removed under reduced pressure. The orange solid was extracted with hexanes (40 mL) and filtered through a Celite pad. The volume of the solution was reduced to ca. 3 mL under reduced pressure, and the flask was stored at ca. −20 °C for 2 days to afford orange-yellow crystals of **3** (1.51 g, 1.17 mmol, 91%). Mp = 166 °C (dec to brown). Anal. Calcd for $C_{75}H_{107}LiSn$: C, 71.89; H, 8.61. Found: C, 72.10; H, 9.05. UV−vis (hexanes) λ_{max}, ϵ($mol^{-1}cm^{-1}$): 305 nm, 16050 (tails to 528 nm). ^{1}H NMR (C_6D_6, 399.77 MHz, 25 °C): δ −0.05 (s, 3 H, Sn-(CH_3)$_2$), −0.01 (s, 3 H, Sn(CH_3)$_2$), 1.04−1.37 (m, 36 H, *o*- and *p*-CH-(CH_3)$_2$), 2.77−3.00 (m, 8 H, *o*-C*H*(CH_3)$_2$), 3.10 (sept., 2 H, ^3J = 6.8 Hz, *p*-C*H*(CH_3)$_2$), 3.54 (sept, 2 H, ^3J = 7.0 Hz, *p*-C*H*(CH_3)$_2$), 6.92−7.40 (br m, 14 H, aromatic H's). ^{7}Li {^{1}H} NMR (C_6D_6, 155.36 MHz): δ −3.35 ($^1J(^7Li-^{119}Sn)$ = 736 Hz, $^1J(^7Li-^{117}Sn)$ = 702 Hz, $^2J(^7Li-^{119}Sn)$ = 47 Hz). ^{13}C {^{1}H} NMR (C_6D_6, 100.53 MHz): δ −3.82 (Sn−(CH_3)$_2$), −1.61 (Sn−(*C*H$_3$)$_2$), 23.01−24.12 (multiple peaks, *o*-CH-(CH_3)$_2$), 25.58−26.18 (multiple peaks, *p*-CH(*C*H$_3$)$_2$), 29.95 (*o*-*C*H(CH_3)$_2$), 30.29 (*o*-*C*H(CH_3)$_2$), 30.94 (*o*-*C*H(CH_3)$_2$), 31.93 (*o*-*C*H(CH_3)$_2$), 34.27 (*p*-*C*H(CH_3)$_2$), 34.45 (*p*-*C*H(CH_3)$_2$), 120.08 (*m*-Trip), 120.20 (*m*-Trip), 120.65 (*m*-Trip), 120.83 (*m*-Trip), 121.01 (*m*-Trip), 121.19 (*m*-Trip), 121.25 (*m*-Trip), 121.32 (*m*-Trip), 130.00 (*m*-C_6H_3), 130.24 (*m*-C_6H_3), 125.47 (*p*-C_6H_3), 142.65 (*i*-Trip), 146.65 (*p*-Trip), 147.86 (*o*-Trip), 147.90 (*o*-Trip), 147.92 (*o*-Trip), 148.10 (*o*-Trip), 148.58 (*o*-C_6H_3), 148.72 (*o*-C_6H_3), 161.20 (*i*-C_6H_3). ^{119}Sn {^{1}H} NMR (C_6D_6, 149.24 MHz): δ −431 (q, $^1J(^{119}Sn-^7Li)$ = 736 Hz, ^{1}J (^{119}Sn−^{119}Sn) = 4437 Hz, ^{1}J (^{119}Sn−^{117}Sn) = 4046 Hz)), +151 (s, $^1J(^{119}Sn-^{119}Sn$ = 4464 Hz, $^1J(^{119}Sn-^{117}Sn)$ = 4088 Hz) ($^2J(^{119}Sn-^7Li)$ = 47 Hz)).

Sn(t-Bu)(C_6H_3-2,6-$Trip_2$) (4). *t*-BuLi (1.53 mL, 2.30 mmol, 1.1 equiv) was added dropwise to a pale yellow solution of **1** (1.33 g, 2.09 mmol) in hexanes (50 mL) at −78 °C. Slow warming to ca. −40 °C caused the solution to turn deep red, and by ca. −5 °C, the solution had turned dark purple. The solution was stirred at 25 °C for 1 h, and the solution was filtered through a Celite pad. The volume of the

Table 1. Selected Crystallographic Data for Compounds **2**·0.5 Hexane, **3**·0.5 Hexane, and **4**

	2·0.5 hexane	**3**·0.5 hexane	**4**
formula	$C_{77}H_{111}Sn_2$	$C_{78}H_{114}LiSn_2$	$C_{40}H_{58}Sn$
fw	1274.16	1296.13	657.55
crystal color/habit	green block	yellow block	purple-red shard
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
a (Å)	16.8704(5)	14.4163(6)	32.1821(13)
b (Å)	19.2696(6)	15.9717(7)	9.5744(4)
c (Å)	21.4850(6)	19.0328(8)	24.7577(10)
α (deg)		67.083(1)	
β (deg)	99.600(1)	74.633(1)	106.900(1)
γ (deg)		72.654(1)	
V (Å^3)	6886.7(4)	3797.2(3)	7299.0(5)
Z	4	2	8
ρ_{calcd} (mg/m^3)	1.229	1.134	1.197
μ (mm^{-1})	0.765	0.695	0.724
R1[a] (obsd)	0.0383	0.0509	0.0385
wR2 (all data)	0.0957	0.1337	0.0865

[a] $R1 = \Sigma||F_o| - |F_c||/|F_o|$. $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o)^2]]^{1/2}$.

solution was reduced to ca. 2 mL, and the flask was stored at ca. −20 °C overnight, providing large, red-purple crystals of **4** (0.45 g, 0.68 mmol, 33%). Mp = 112−115 °C. Anal. Calcd for $C_{40}H_{58}Sn_2$: C, 73.06; H, 8.87. Found: C, 73.31; H, 8.73. UV−vis (hexanes) λ_{max}, ϵ(mol^{-1} cm^{-1}): 485 nm, 655. ^{1}H NMR (C_6D_6, 399.77 MHz, 25 °C): 1.13 (d, 12 H, ^3J = 7.2 Hz, *o*-CH(CH_3)$_2$), 1.17 (d, 12 H, ^3J = 7.2 Hz, *o*-CH(CH_3)$_2$), 1.41 (d, 12 H, ^3J = 7.2 Hz, *p*-CH(CH_3)$_2$), 135 (C(CH_3)$_3$), 2.75 (sept., 2 H, ^3J = 7.2 Hz, *p*-C*H*(CH$_3$)$_2$), 3.29 (sept, 4 H, ^3J = 7.2 Hz, *o*-C*H*(CH$_3$)$_2$), 7.05−7.25 (br m, 3 H, *p*- and *m*-C_6H_3), 7.34 (s, 4 H, *m*-Trip). ^{13}C {^{1}H} NMR (C_6D_6, 100.53 MHz): δ 23.08 (*o*-CH(*C*H$_3$)$_2$), 24.21 (*p*-CH(*C*H$_3$)$_2$), 26.76 (*o*-CH(*C*H$_3$)$_2$), 27.55 (C(*C*H$_3$)$_3$), 31.02 (*o*-*C*H(CH$_3$)$_2$), 34.74 (*p*-*C*H(CH$_3$)$_2$), 70.07 (*C*(CH$_3$)$_3$, ^1J(^{13}C−$^{119/117}$Sn) = 160 Hz), 121. 51 (*m*-Trip), 126.72 (*p*-C_6H_3), 129.60 (*m*-C_6H_3), 135.18 (*i*-Trip), 144.62 (*p*-Trip), 147.02 (*o*-Trip), 149.08 (*o*-C_6H_3), 179.94 (*i*-C_6H_3), ^1J(^{13}C−$^{119/117}$Sn) = 286/274 Hz. ^{119}Sn {^{1}H} NMR (C_6D_6, 149.20 MHz): δ 1904.

X-ray Crystallographic Studies. The crystals were removed from the Schlenk tube under a stream of N_2 and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in a low-temperature nitrogen stream.[7] All data were collected near 130 K using Bruker SMART 1000 (Mo Kα radiation and a CCD area detector). The SHELXTL version 5.03 program package was used for the structure solutions and refinements.[8] Absorption corrections were applied using the SADABS program.[9] The crystal structures were solved by direct methods and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement at calculated positions using a riding model included in the SHELXTL program. Compounds **2** and **3** were crystallized from hexanes as the solvates **2**·0.5 hexane and **3**·0.5 hexane. The structure of **4** displays a partial occupancy by two species, the stannanediyl Sn(t-Bu)C_6H_3-2,6-Trip$_2$ (**4**, 83% occupancy) and the isomeric stannanediyl Sn(i-Bu)C_6H_3-2,6-Trip$_2$ (17% occupancy) as a result of contamination of commercial t-BuLi solutions with i-BuLi. An anomalous electron density of 2.86 electrons/Å^3 was observed within the covalent radius of Sn(2) in which is attributed to uncorrected absorption effects. Some details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

Results and Discussion

Synthesis. The generation of compounds **2** and **3** can be accounted for in accordance with Scheme 1. Although the reaction of **1** with 1 equiv of MeLi, or preferably MeMgBr, affords **2** in up to 85% yield, it is likely that Sn(Me)C_6H_3-2,6-Trip$_2$ is generated initially. However, this molecule apparently reacts rapidly with another 1 equiv of MeLi or MeMgBr to give **5** or its equivalent magnesium halide derivative. This species may then react further with **1** to afford the product **2**. In addition, compound **2** may be converted to **3** by its reaction with a further 1 equiv of LiMe. Alternatively, **3** can be generated directly from the reaction of **1** with 1.5 equiv of MeLi. In contrast to this reaction sequence, treatment of **1** with t-BuLi generates neutral Sn(t-Bu)C_6H_3-2,6-Trip$_2$, **4**, directly which, probably for steric reasons, does not react further with t-BuLi to generate a t-Bu-substituted analogue of **5**. Attempts to convert **2** into its symmetrical isomer **6** by a thermal rearrangement resulted in decomposition.

Since the overall steric congestion in **2** and the putative **6** should be similar, the preference for the symmetric structure **2** over its unsymmetric isomer **6** is unlikely to be due to steric effects. It is more probable that the instability of **6** is a result of the difference in the Sn−Sn bond strengths of the two compounds. Tetraorganoditin species such as **6** are often referred to as "distannenes" owing to their stoichiometric resemblance to their carbon analogues, the alkenes. But this name can be a misleading[10] one since the currently known examples dissociate in solution owing to the weakness of the Sn−Sn bond. For example the Sn−Sn bond enthalpy[11] of {(Me$_3$Si)$_2$CH}$_2$SnSn{CH(SiMe$_3$)$_2$}$_2$, which has the shortest Sn−Sn bond, 2.768(1) Å,[4b] in "distannenes", is 12.6 kcal mol^{-1}. This is much less than typical[12] Sn−Sn single bond enthalpies which are ca. 40 kcal mol^{-1}. Thus, it can be argued that, if **6** has a comparable (ca. 10 kcal mol^{-1}) Sn−Sn bond energy and it is to be energetically preferred over **2**, ca. 30 kcal mol^{-1} would have to be found from the differences in tin carbon bond strengths in **2** and **6** to compensate for this difference. It seems doubtful that such differences in energy between tetravalent and divalent tin−carbon bonds would be sufficient to overcome this obstacle.[13] In addition, it is notable that calculations[14] on model hydrogen compounds of formula Sn_2H_4 indicate that the doubly bridged *trans*-HSn(μ-H)$_2$SnH is more stable than the unsymmetric stannylstannanediyl H$_3$Sn-S̈nH but that the latter is more stable than the "distannene" form H_2SnSnH_2. The lower bridging tendency of the methyl group suggests that the bridging structure in MeSn(μ-Me)$_2$SnMe may not be the most stable, and that the Me$_3$S̈n-SnMe isomer may be the preferred one for the hypothetical species Sn_2Me_4 although this has not been substantiated by calculations. The high sensitivity[10] of the "soft double bond"[15] in distannenes to steric effects also suggests that dissociation to monomers would be preferred over rearrangement to the unsymmetrical isomer. In the previously known "distannenes" such a rearrangement would have resulted in three bulky groups at one tin atom which would be disfavored sterically. In **2**, however, such a configuration is feasible since two of these substituents are relatively small methyl groups.

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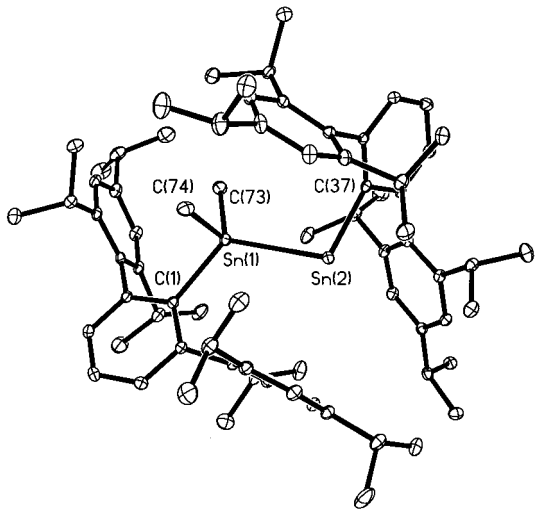

Figure 1. Thermal ellipsoid (30%) plot of **2**. H atoms are not shown. Selected bond distances and angles are given in Table 2.

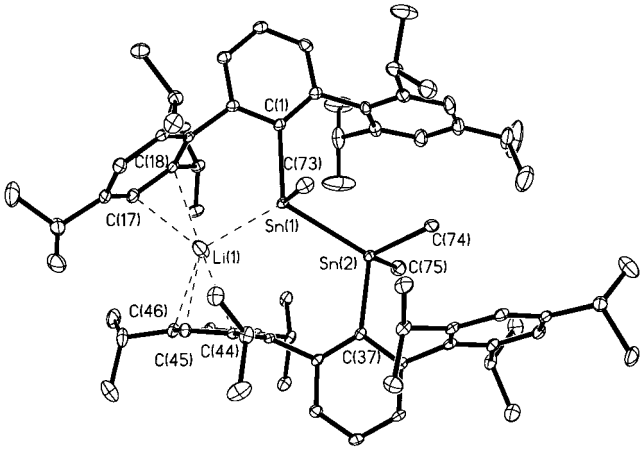

Figure 2. Thermal ellipsoid (30%) plot of **3**. H atoms are not shown. Selected bond distances and angles are given in Table 2.

Structural Data and Bonding. The structure of **2** is illustrated in Figure 1. It consists of well-separated molecules that crystallize along with 2.0 equiv of hexane per unit cell or 0.5 hexane per asymmetric unit. No strong interactions are apparent between the molecules themselves or with the co-crystallized hexane. It can be seen that the two tin centers are quite distinct since Sn(1) is bound to three carbons as well as Sn(2), whereas Sn(2) is two coordinate with bonds to Sn(1) and C(37). The geometry at Sn(1), whose interligand angles vary from 93.56(9) to 119.30(6)°, is grossly distorted from idealized tetrahedral. This can be attributed to the large variation in size and electronic properties of the substituent groups. The widest angle Sn(2)−Sn(1)−C(1) = 119.30(6)° involves the bulky aryl substituent. The Sn(1)−C bond lengths are in the range 2.164(2) to 2.201(2) Å with the latter value associated with the bulky aryl group. The two coordinate Sn(2) center has an interligand angle of 101.17(5) ° as well as Sn(2)−C(37) and Sn(2)−Sn(1) bond lengths of 2.227(2) Å and 2.8909(2) Å. Previous results[16] have shown that tin−carbon and tin−tin distances in catenated tin compounds are significantly affected by the steric properties of the organo groups. Comparison of the Sn−C and Sn−Sn bond lengths in **2** with those observed in other sterically crowded molecules shows that they display some, but not an excessive, elongation. For instance, comparison of the Sn−C distances for the tin methyl groups in $Me_3SnSnPh_3$ (Sn−C(Me) = 2.138(5) Å),[17] shows that they are ca. 0.03 Å shorter than the Sn−C(Me) bonds (ca. 2.17 Å) in **2**. However, in the more crowded molecule $(t\text{-Bu})_2$TripSnSnTrip$(t\text{-Bu})_2$[18] the Sn−C(t-Bu) bonds are significantly longer at ca. 2.26 Å. Similarly, the Sn(1)−C(1) distance, 2.201(2) Å, to the bulky terphenyl group is 0.06 Å longer than the Sn−C(Ph) distances in $Ph_3SnSnPh_3$,[19] but is shorter than the Sn−C(Trip) bond of ca. 2.22 Å in $(t\text{-Bu})_2$TripSnSnTrip$(t\text{-Bu})_2$. The two-coordinate Sn(II) features a slightly longer Sn−C bond distance of 2.227-(2) Å, but this is within the previously known range (2.21−2.23 Å) for two-coordinate Sn(II)-aryl derivatives.[3]

The most interesting structural parameters in **2** are the Sn-(1)−Sn(2) bond distance, 2.8909(2) Å, and the interligand angle of 101.17(5) ° at Sn(2). The only known structure with a bond between a divalent and tetravalent tin concerns Sn(2-{$(Me_3$-$Si)_2$CH}C_5H_4N){$Sn(SiMe_3)_3$},[20] which has an Sn−Sn bond 2.8689(5) Å long between four-coordinate and three-coordinate tin centers. The Sn−Sn distance in **2** is slightly longer despite the lower (two) coordination at one of its tin atoms. The slightly increased Sn−Sn distance is probably due to the large size of the terphenyl substituents. Nonetheless, the tin−tin bond cannot be regarded as being unduly lengthened since Sn−Sn bonds as long as 3.034(1) Å have been observed in previously mentioned $(t\text{-Bu})_2$TripSnSnTrip$(t\text{-Bu})_2$ compound.[18] The interligand angle at Sn(2) is in the middle of the known range (87−118°)[4,21] for divalent diorganotin(II) compounds, which also suggests a moderate degree of crowding in **2**.

The structure of **3** (Figure 2) has many similarities to that of **2**. In **3** both tins are four-coordinate, but Sn(1) has the same formal oxidation state (i.e., Sn(I)) as the two-coordinate tin center (i.e., Sn(2)) in **2**. Accordingly, the Sn−Sn bond length in **3**, 2.8508(4) Å, is similar to that in **2** although it displays some shortening. Possibly, the four-coordination in both tins leads to an increase s−p orbital mixing in the Sn−Sn bond which leads to the shorter Sn−Sn distance. However, the Sn-(1)−C bond lengths, 2.202(4) Å (Me) and 2.259(4) Å (terphenyl), are slightly longer than those to Sn(2), perhaps as a result of the negative charge density at Sn(1) which reduces the ionic contribution to the Sn−C bond strengths. The Li−Sn(1) distance, 2.685(8) Å, is extremely short in comparison to the 2.871(7) Å observed in the complex [Li(PMDETA)$SnPh_3$],[22] or the 2.89(4) Å in $(THF)_3LiSn\{N(SiMe_3)CH_2\}_3CCH_3$.[23] It is possible that the simultaneous binding of the Li^+ ion by the ortho-Trip groups of the terphenyls plays a role in the shortening of the distance. The Li−Sn bond is maintained in solution as shown by the observation of large $^7Li-^{119/117}Sn$ couplings. The

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Table 2. Selected Bond Lengths (Å) and Angles (°) for **2**−**4**

2

Sn(1)−Sn(2)	2.8909(2)
Sn(1)−C(1)	2.201(2)
Sn(1)−C(73)	2.164(2)
Sn(1)−C(74)	2.182(3)
Sn(2)−C(37)	2.227(2)
Sn(2)−Sn(1)−C(1)	119.30(6)
Sn(1)−Sn(2)−C(37)	101.17(5)
C(1)−Sn(1)−C(73)	112.74(9)
C(1)−Sn(1)−C(74)	93.56(9)
C(73)−Sn(1)−C(74)	109.37(10)
C(73)−Sn(1)−Sn(2)	115.67(7)
C(74)−Sn(1)−Sn(2)	102.58(6)
C(6)−C(1)−Sn(1)	118.3(2)
C(2)−C(1)−Sn(1)	122.02(15)
C(38)−C(37)−Sn(2)	117.06(15)
C(42)−C(37)−Sn(2)	123.32(15)

3

Sn(1)−Sn(2)	2.8508(4)	Li−C(17)	2.538(9)
Sn(1)−C(1)	2.259(4)	Li−C(18)	2.601(9)
Sn(1)−C(73)	2.202(4)	Li−C(44)	2.707(9)
Sn(1)−Li	2.685(8)	Li−C(45)	2.367(9)
Sn(2)−C(37)	2.229(4)	Li−C(46)	2.513(9)
Sn(2)−C(74)	2.159(4)	Li-centroid (C13−C18)	2.746
Sn(2)−C(75)	2.172(4)	Li-centroid (C43−C48)	2.424
C(1)−Sn(1)−Sn(2)	120.06(9)		
C(37)−Sn(2)−Sn(1)	110.81(9)		
C(1)−Sn(1)−C(73)	95.02(14)		
C(1)−Sn(1)−Li	110.9(2)		
C(73)−Sn(1)−Sn(2)	90.05(12)		
C(73)−Sn(1)−Li	121.1(2)		
C(37)−Sn(2)−C(74)	108.14(14)		
C(37)−Sn(2)−C(75)	96.71(15)		
C(74)−Sn(2)−C(75)	102.78(18)		
C(2)−C(1)−Sn(1)	112.8(2)		
C(6)−C(1)−Sn(1)	130.5(3)		
C(38)−C(37)−Sn(2)	121.3(3)		
C(42)−C(37)−Sn(2)	121.8(2)		
Li−Sn(1)−Sn(2)	116.7(2)		
C(74)−Sn(2)−Sn(1)	111.33(12)		
C(75)−Sn(2)−Sn(1)	125.33(12)		

4

Sn(1)−C(1)	2.2114(18)
Sn(1)−C(37)	2.227(2)
C(1)−Sn-C(37)	101.61(8)
C(2)−C(1)−Sn	121.03(13)
C(6)−C(1)−Sn	118.76(13)

Sn(2)−C bond lengths are slightly longer than the corresponding distances in **2**.

The monomeric, two-coordinate tin(II) alkyl/aryl **4** (Figure 3) has the expected V-shaped coordination at tin and is isomorphous with its lead analogue.[1] The Sn−C(t-Bu) distance 2.227(2) Å is marginally longer than the 2.211(2) Å Sn−C(terphenyl) bond length. The latter is virtually identical to the 2.213(13) Å Sn−C bond previously reported for the iodide Sn(I)C_6H_3-2,6-$Trip_2$.[24] The C−Sn−C angle, 101.61(6)°, is slightly wider than the 100.5(5) ° in its lead analogue, and it is very similar to the 102.6(3)° observed for the C−Sn−I angle in Sn(I)C_6H_3-2,6-$Trip_2$ and the 101.17(5)° angle at Sn(2) in **2**. As already discussed for **2**, these angles are near the middle of the range for two-coordinate diorganotin species.

NMR Spectroscopy. The solution ^{119}Sn NMR spectra for compounds **2**−**4** provide considerable information on the structural and electronic environment at tin. The ^{119}Sn NMR spectra of compounds **2** and **4** were also studied in more detail by CP MAS ^{119}Sn NMR spectroscopy, but this information will be discussed elsewhere.[25] In general, the ^{119}Sn NMR chemical shifts of divalent tin species (>+200 ppm) lie considerably downfield of their tetravalent (<+200 ppm) counterparts.[26] The ^{119}Sn NMR chemical shift of compound **4** (δ 1904) is consistent with this generalization and is indicative of the deshielded environment at the tin atom as a result of its lower coordination number. The chemical shift of the divalent tin in **2** is 2856.9 ppm which is further downfield than the shifts observed for **4**, Sn[C_6H_2-2,4,6-{$CH(SiMe_3)_2$}$_3$] (δ = 2208),[3b] SnC$(SiMe_3)_2(CH_2)_2$C$(SiMe_3)_2$ (δ = 2323)[3a] or Sn{$CH(SiMe_3)_2$}$_2$ (δ = 2315).[10] The downfield shift is probably due to an increase in paramagnetic effects as a result of the substitution of an organic group by the more electropositive -Sn$(Me)_2C_6H_3$-2,6-$Trip_2$ moiety. The ^{119}Sn NMR chemical shift of the tetravalent site in **2** is +257.4 ppm, which is at the lower end of the range normally found for four-coordinate tin compounds.[26] The value of the coupling constant ($^{119/117}$Sn−$^{119/117}$Sn) between the tin atoms in compound **2** is 8330 Hz, which is larger than is normally observed for hexaorganoditin species such as Ph_3SnSnPh_3 ($^1J(^{117}Sn-^{119}Sn)$ = 4470 Hz).[26] It is also greater than the coupling in the four-coordinate tin/three-coordinate tin species reported by Cardin and co-workers[16] by ca. 2000 Hz. The tin−tin coupling constants observed in **3** ($^1J(^{117/119}Sn-^{117/119}Sn)$ = ca. 4050 Hz) is very close to the value in **2**. In **3** the coordination number of the Sn(I) center is increased from 2 to 4, and this results in a dramatic upfield change in the ^{119}Sn chemical shift by ca. 3300 ppm to −431 ppm. The shift of the four-coordinate tin atom is moved by only ca. 100 ppm downfield. The assignment of the two resonances in the ^{119}Sn NMR spectrum of **3** is also facilitated by the observation of coupling to ^{7}Li (I = 3/2). The resonance at −431 ppm is split into a quartet with large $^1J(^{119}Sn-^7Li)$ coupling of ca. 740 Hz. The other tin resonance at +151 ppm has a much smaller coupling of 47 Hz (^2J = ^{119}Sn−^{7}Li). The coupling of 740 Hz is the largest one bond ^{119}Sn−^{7}Li coupling observed to date,[27] which is consistent with the short Sn−Li distance observed in the X-ray crystal structure.

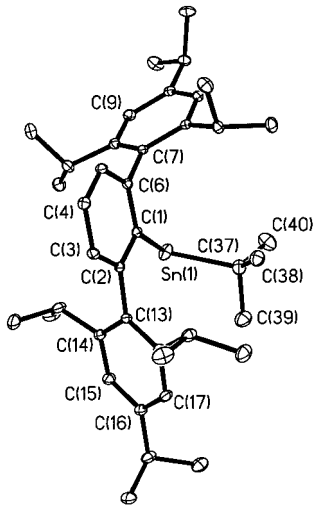

Figure 3. Thermal ellipsoid (30%) plot of **4**. H atoms are not shown. Selected bond distances and angles are given in Table 2.

The ^{1}H and ^{13}C NMR spectra of **2** indicate that the Trip groups are rotationally hindered. Broad singlets in the ^{1}H NMR

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spectrum at ca. 3 ppm appear in the region of the methine hydrogens ($CH(CH_3)_2$) of the isopropyl groups. The ^{13}C NMR spectrum of the *o*-isopropyl groups also displays two sets of resonances. The two tin methyl groups are assignable to a singlet at −0.34 ppm in the ^1H spectrum and a broad singlet at +0.34 ppm in the ^{13}C spectrum. The ^1H and ^{13}C NMR spectra of **3** are more complex than those of **2**. Not only are the two 2,6-$Trip_2C_6H_3$- groups inequivalent owing to the different ligand sets at the tins (i.e., $-Me_2Sn-SnMeLi-$), in addition, one Trip group on each terphenyl ligand is coordinated to a lithium ion (see Figure 2). Thus, all four Trip groups in the molecule are inequivalent. Two singlets are observable for the methyl groups on tin in both the ^1H and ^{13}C NMR spectra of **3**. The methyl group bound to the same tin as the lithium atom may couple to ^7Li, thereby reducing the height of the peaks and possibly rendering it unobservable above the baseline.

Conclusion. The unsymmetric stannanestannanediyl **2** is preferred over the symmetric isomer **6** owing to the weakness of the Sn−Sn polar dative bonds in **6** relative to the covalent Sn−Sn single bond in **2**. The isolation of **2** is made possible by the unique steric combination of the large terphenyl ligands and the small methyl groups which, unlike other large substituents, stabilize the bonding between two and four coordinate tins.

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Supporting Information Available: Three X-ray files, in CIF format, are available.. This material is available free of charge via the Internet at http://pubs.acs.org.

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