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Reactions of Phenyllithium with the Stannylene Ar*SnPh (Ar* = C_6H_3-2,6-$Trip_2$; Trip = C_6H_2-2,4,6-Pr^i_3) and the Synthesis of the Distannylstannylene $Sn(SnPh_2Ar^*)_2$: Contrasting Behavior in Methyl and Phenyl Derivatives

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The reaction of LiPh with Ar*SnPh (Ar* = C_6H_3-2,6-$Trip_2$; Trip = C_6H_2-2,4,6-Pr^i_3) afforded either the monomeric etherate $(Et_2O)LiSnPh_2Ar^*$ (**1**) or the dimer $(LiSnPh_2Ar^*)_2$ (**2**). The reaction of **2** with $SnCl_2$ in a 1:1 ratio in Et_2O yielded the monomeric distannylstannylene $Sn(SnPh_2Ar^*)_2$ (**3**). The compounds **1**−**3** were characterized by ^1H, ^7Li, ^{13}C, and ^{119}Sn NMR and UV−vis spectroscopy. Complete single-crystal X-ray crystal structures of **2** and **3** were determined as well as a partial structure for **1**. The structure of **1** showed that the tin was pyramidally coordinated by the three organic groups as well as by lithium. The lithium was found to be ligated by ether and η^6-coordinated by one of the phenyl rings. The structure of **2** showed that it was dimerized through η^6-interactions of a tin-coordinated lithium with a phenyl group of a partner monomer rather than through tin−tin bonding. The structure of **3** featured a central, two-coordinate tin(II) bound to two $SnPh_2Ar^*$ groups with long Sn−Sn distances near 2.96 Å and a very wide Sn−Sn−Sn angle of 115.19(2)°. The ^{119}Sn NMR chemical shift of the central tin is 3752 ppm, which is the furthest downfield ^{119}Sn NMR chemical shift recorded for a stannylene.

Introduction

Recently described reactions of the terphenyltin(II) halide Ar*SnCl (Ar* = C_6H_3-2,6-$Trip_2$; Trip = C_6H_2-2,4,6-Pr^i_3)[1] with the organolithium reagents LiMe[2] or LiPh[3] have led to unexpected products. In the former case the unsymmetric species $Ar^*SnSnMe_2Ar^*$, which featured a rare instance of bonding between divalent and tetravalent tin, was isolated as the sole product in preference to the symmetric distannylene Ar*MeSnSnMeAr* as shown in eq 1.[2]

$$2Ar^*SnCl + 2LiMe \rightarrow Ar^*SnSnMe_2Ar^* + 2LiCl \quad (1)$$

$$2Ar^*SnCl + 2LiPh \rightarrow Ar^*SnSnPh_2Ar^* \rightleftharpoons 2Ar^*SnPh + LiCl \quad (2)$$

For the reaction of Ar*SnCl with LiPh, the monomeric Ar*SnPh was obtained at room temperature, whereas the unsymmetric dimer $Ar^*SnSnPh_2Ar^*$ was isolated at ca. −20 °C. A temperature-dependent equilibrium between these two compounds could be observed in solution (eq 2).[3] The further reaction of $Ar^*SnSnMe_2Ar^*$ with LiMe afforded the lithium salt $LiAr^*MeSnSnMe_2Ar^*$ in which the LiMe is added to the Sn(II) center while the Sn−Sn bond is preserved and even shortened in comparison to that in $Ar^*SnSnMe_2Ar^*$.[3] We were therefore interested in the corresponding reaction of LiPh with the $Ar^*SnPh/Ar^*SnSnPh_2Ar^*$ system. We also wished to explore the use of the lithium aryl tin salts expected from such reactions in the synthesis of other classes of tin−tin bonded compounds. It is now shown that LiPh reacts with Ar*SnPh to form the monomeric, ether-solvated species $(Et_2O)LiSnPh_2Ar^*$ (**1**) or the dimeric $(LiSnPh_2Ar^*)_2$ (**2**), which has no Sn−Sn bond, and is associated mainly through Li- -Ph interactions. The reaction between these lithium salts and $SnCl_2$ affords the distannylstannylene species $Sn(SnPh_2Ar^*)_2$ (**3**), which is a rare example of tin(II) coordinated by two stannyl groups and which possesses the furthest downfield ^{119}Sn NMR chemical shift for monomeric stannylenes.

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 immediately before use. The compounds Ar*SnPh[3] and LiPh[4] were synthesized according to literature procedures. ^1H, ^7Li, ^{13}C, and ^{119}Sn NMR spectra were recorded on a Bruker 300 MHz instrument and referenced to the deuterated solvent.

$(Et_2O)LiSnPhAr^*$ (1). A solution of Ar*SnPh (1.36 g, 2 mmol) in diethyl ether (50 mL) was added dropwise to a cooled

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(ca. −78 °C) solution of LiPh (0.168 g, 2 mmol) in diethyl ether (20 mL) with rapid stirring. The solution was stirred for 18 h, after which the solution was allowed to warm to room temperature overnight and filtered. The volume of the filtrate was reduced to incipient crystallization. After several days of storage at −25 °C, the product was obtained as pale yellow blocks. Yield: 74%, 1.24 g, 1.47 mmol, 74%. Mp: 175−9 °C dec. ^{1}H NMR (399.7 MHz, 25 °C, C_6D_6): δ(ppm) 0.63 (t, $^3J_{HH}$ = 6.93 Hz, $(CH_3CH_2)_2O$)), 1.06 (d, 12H, $^3J_{HH}$ = 6.59 Hz, *o*-CH-$(CH_3)_2$), 1.14 (d, 12H, $^3J_{HH}$ = 6.59 Hz, *p*-CH$(CH_3)_2$), 1.21 (d, 12H, $^3J_{HH}$ = 6.59 Hz, *o*-CH$(CH_3)_2$), 2.72 (sept., 2H, $^3J_{HH}$ = 6.59 Hz, *p*-C*H*$(CH_3)_2$), 2.72 (q, $^3J_{HH}$ = 6.93 Hz, $CH_3CH_2)_2O$)), 3.40 (sept, 4H, $^3J_{HH}$ = 6.59 Hz, *o*-C*H*$(CH_3)_2$), 6.98 (s, 4H, *m*-Trip), 7.05−7.60 (m, 13H, *m*-C_6H_3, *p*-C_6H_3 and all Ph). ^{7}Li{^{1}H} NMR (155.36 MHz, 25 °C, C_6D_6): δ −2.79 ppm. ^{13}C{^{1}H} NMR (100.53 MHz, 25 °C, C_6D_6): δ(ppm) 14.45 $(CH_3CH_2)_2O$), 23.06 (*o*-CH$(CH_3)_2$), 24.02 (*p*-CH$(CH_3)_2$), 25.85 (*o*-CH$(CH_3)_2$), 30.99 (*p*-CH$(CH_3)_2$), 34.27 (*o*-CH$(CH_3)_2$), 65.69 $(CH_3CH_2)_2O$), 120.40 (*m*-Trip), 125.06 (*p*-Ph), 125.44 (*p*-C_6H_3), 127.09 (*m*-Ph), 129.16 (*m*-C_6H_3), 139.05 (*o*-Ph), 144.24 (*i*-Trip), 147.06 (*p*-Trip), 147.62 (*o*-Trip), 149.15 (*o*-C_6H_3), 156.80 (*i*-Ph, $^1J(^{13}C-^{117/119}Sn)$ = 110 Hz), 159.64 (*i*-C_6H_3). ^{119}Sn{^{1}H} NMR (149.07 MHz, 25 °C, C_6D_6): δ(ppm) −112 (q, $^1J(^7Li-^{119}Sn)$ = 580 Hz).

$(LiSnPh_2Ar^*)_2$ (2). A solution of Ar*SnPh (1.36 g, 2 mmol) in toluene (65 mL) was added to a cooled (ca. −78 °C) suspension of LiPh (2 mmol, 0.168 g) in toluene (30 mL) with rapid stirring. The solution was stirred for 2 days and filtered. The volume of the filtrate was reduced to incipient crystallization. After several days of storage at −25 °C, the product **2** was obtained as pale yellow blocks. Yield: 1.23 g, 1.61 mmol, 81%. Mp: 180 °C dec. ^{1}H NMR (399.8 MHz, 25 °C, C_6D_6): δ-(ppm) 0.96 to 1.32 (multiple d, 36H, *o*- and *p*-CH$(CH_3)_2$), 2.65−3.45 (multiple septs., 6H, *o*- and *p*-C*H*$(CH_3)_2$), 6.95 (s, 4H, *m*-Trip), 7.02−7.55 (multiple br s, 13H, *m*-C_6H_3, *p*-C_6H_3 and all Ph). ^{13}C{^{1}H} NMR (100.53 MHz, 25 °C, C_6D_6): δ(ppm) 23.06−25.86 (multiple, s, *o*-CH$(CH_3)_2$), 29.53−31.20 (multiple s, *p*-CH$(CH_3)_2$), 34.45−35.24 (multiple s, *p*- and *o*-CH$(CH_3)_2$), 120.02 (*m*-Trip), 120.72 (*m*-Trip), 124.72 (*p*-Ph), 125.45 (*p*-Ph), 126.76 (*p*-C_6H_3), 127.42 (*m*-Ph), 138.22 (*o*-Ph), 138.78 (*o*-Ph), 146.85 (*p*-Trip), 147.01 (*p*-Trip), 147.54 (*o*-Trip), 149.08 (*o*-C_6H_3), 157.34 (*i*-Ph). ^{119}Sn{^{1}H} NMR (149.07 MHz, 25 °C, C_6D_6): δ(ppm) −117.

$Sn(SnPh_2Ar^*)_2$ (3). A solution of $(LiSnPh_2Ar^*)_2$ (1.54 g, 1 mmol) in diethyl ether (50 mL) was added dropwise to a rapidly stirred suspension of $SnCl_2$ (0.18 g, 1 mmol) in diethyl ether (20 mL) with cooling in an ice bath. Upon addition, the resulting mixture became a dark orange color. After stirring overnight, the solvent was removed under reduced pressure and the dark orange residue was extracted with benzene (60 mL). After filtration, the volume of the solution was reduced to incipient crystallization. Storage of the solution at ca. 5 °C for 1 week resulted in the deposition of the product as pale orange blocks. Yield: 0.40 g, 0.24 mmol, 24%. Mp: 175−182 °C dec. UV−vis λ_{max} (ϵ L mol^{-1} cm^{-1}): 311 nm (7300). ^{1}H (399.8 MHz, 25 °C, C_6D_6): δ(ppm) 1.07 (d, $^3J_{HH}$ = 6.34 Hz, 24H, *o*-CH-$(CH_3)_2$), 1.18 (d, $^3J_{HH}$ = 6.34 Hz, 24H, *o*-CH$(CH_3)_2$), 1.38 (d, $^3J_{HH}$ = 6.34 Hz, 12H, *p*-CH$(CH_3)_2$), 2.99 (sept, $^3J_{HH}$ = 6.34 Hz, 4H, *p*-CH$(CH_3)_2$), 3.13 (sept, $^3J_{HH}$ = 6.34 Hz, 8H, *o*-CH$(CH_3)_2$), 7.10 (s, 8H, *m*-Trip), 7.06−7.20 (m, 26H, *m*-C_6H_3, *p*-C_6H_3 and all Ph). ^{13}C{^{1}H} NMR (100.53 MHz, 25 °C, C_6D_6): δ(ppm) 24.19 (*o*-CH$(CH_3)_2$), 25.09 (*p*-CH$(CH_3)_2$), 27.02 (*o*-CH$(CH_3)_2$), 31.63 (*o*-CH$(CH_3)_2$), 35.29 (*p*-CH$(CH_3)_2$), 122.06 (*m*-Ph), 127.26 (*m*-Trip), 128.27 (*p*-Ph), 131.26 (*m*-C_6H_3), 138.54 (*p*-C_6H_3), 141.92 (*i*-Trip), 146.45 (*p*-Trip). ^{119}Sn{^{1}H} NMR (147.07. MHz, 25 °C, C_6D_6): δ(ppm) 398 (s, Sn(*Sn*$Ph_2Ar^*)_2$), 3752 (s, *Sn*$(SnPh_2Ar^*)_2$).

Crystallographic Studies. Crystals of **2** and **3** were coated with hydrocarbon oil under a rapid flow of argon, mounted on a glass fiber attached to a copper pin, and placed in a N_2 cold stream on the diffractometer. X-ray data for **2**·$2C_6H_6$ and **3**·$3.5C_6H_6$ were collected on a Bruker SMART 1000 diffractometer at 90(2)K with use of Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were applied using XABS[5] or SADABS.[6] The structures were solved with use of direct methods or the Patterson option in SHELXS[6] and refined by the full matrix least-squares procedure in SHELXL.[7] All non-hydrogen atoms were refined anisotropically, while hydrogens were placed at calculated positions and included in the refinement using a riding model. Some details of the data collection and refinement are given in Table 1. Further details are in the Supporting Information.

Table 1. Selected Details of Data Collection and Refinement for Compounds 2 and 3

	2·$2C_6H_6$	**3**·$3.5C_6H_6$
formula	$C_{108}H_{130}Li_2Sn_2$	$C_{117}H_{139}Sn_3$
fw	1679.38	1901.35
color, habit	pale yellow, block	yellow, block
cryst dmns, mm	0.11 × 0.08 × 0.06	0.23 × 0.18 × 0.10
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	12.7537(5)	15.9150(5)
b (Å)	19.0983(7)	15.9963(5)
c (Å)	18.8735(6)	21.5430(7)
α (deg)		71.370(1)
β (deg)	98.913(1)	74.912(1)
γ (deg)		80.575(1)
V (Å^3)	4541.6(3)	4998.4(3)
Z	2	2
d_{calc} (Mg/m^3)	1.228	1.263
μ (mm^{-1})	0.597	0.791
θ range	1.53−30.00	1.71−31.53
no. of obsd data ($I > 2\sigma(I)$)	5872	17 047
R_1	0.0491	0.050
wR_2	0.0883	0.1237

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2 and 3

2		**3**	
Li(1A)−Sn(1)	2.809(6)	Sn(1)−C(1)	2.204(3)
Li(1)−C(43)	2.561(8)	Sn(1)−C(85)	2.160(4)
Li(1)−C(44)	2.504(7)	Sn(1)−C(91)	2.174(4)
Li(1)−C(45)	2.524(7)	Sn(1)−Sn(3)	2.9644(3)
Li(1)−C(46)	2.571(7)	Sn(2)−Sn(3)	2.9630(3)
Li(1)−C(47)	2.582(8)	Sn(2)−C(37)	2.210(3)
Li(1)−C(48)	2.551(8)	Sn(2)−C(73)	2.166(3)
Sn(1)−C(37)	2.210(4)	Sn(2)−C(79)	2.178(4)
Sn(1)−C(43)	2.206(4)		
Sn(1)−C(1)	2.236(3)	Sn(1)−Sn(3)−Sn(2)	115.19(1)
		C(1)−Sn(1)−C(85)	113.94(1)
Li(1A)−Sn(1)−C(37)	106.6(1)	C(1)−Sn(1)−C(91)	96.80(1)
Li(1A)−Sn(1)−C(43)	131.7(2)	C(85)−Sn(1)−C(91)	103.7(2)
Li(1A)−Sn(1)−C(1)	112.4(2)	Sn(3)−Sn(1)−C(1)	114.1(1)
C(1)−Sn(1)−C(37)	95.0(1)	Sn(3)−Sn(1)−C(85)	121.27(9)
C(1)−Sn(1)−C(43)	106.6(1)	Sn(3)−Sn(1)−C(91)	102.1(3)
C(37)−Sn(1)−C(43)	96.9(1)		

Results and Discussion

Synthesis. The reaction between Ar*SnPh and LiPh in Et_2O at −78 °C proceeded as shown in eq 3. Variable-

$$\mathrm{LiPh} + \mathrm{Ar^*SnPh} \xrightarrow[\text{ca. } -78\ ^\circ\mathrm{C}]{\mathrm{Et_2O}} \underset{\mathbf{1}}{\mathrm{Et_2OLiSnPh_2Ar^*}} \qquad (3)$$

temperature ^{119}Sn NMR spectroscopic studies have shown that Ar*SnPh exists in equilibrium with its unsymmetric dimer Ar*SnSnPh$_2$Ar*. At low temperature (ca. −60 °C) the latter predominates.[3] To maximize

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(5) XABS: Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.

(6) *SADABS*: Area-Detection Absorption Connections; Bruker AXS Inc.: Madison, WI, 1996.

(7) *SHELXL* PC version 5.03; Bruker AXS Inc.: Madison, WI, 1994.

the probability of obtaining a dimeric LiPh derivative product (i.e., LiAr*PhSnSnPh$_2$Ar*) similar to the methyl species LiMeAr*SnSnMe$_2$Ar*,[3] we carried out the addition with cooling in a dry ice/acetone bath at ca. −78 °C. However, only the monomeric product **1** was obtained from diethyl ether irrespective of whether 0.5 or 1 equiv of LiPh was used per tin. Similarly, the reaction of LiPh with Ar*SnPh in toluene solution at ca. −78 °C did not afford LiPhAr*SnSnPh$_2$Ar* but, instead, yielded the dimer **2** in accordance with

$$2\text{LiPh} + 2\text{Ar*SnPh} \xrightarrow[-78\ ^\circ\text{C}]{\text{PhMe}} \underset{\mathbf{2}}{(\text{LiSnPh}_2\text{Ar*})_2} \qquad (4)$$

As will be shown below, this dimer has a symmetric structure without a tin−tin bond and is associated through Li−aryl interactions.

The tritin compound **3** was first isolated as a byproduct from the attempted preparation of LiSnPh$_2$Ar* from the in situ reaction of 2 equiv of LiPh with Ar*SnCl, also generated in situ. The latter may have been contaminated with SnCl$_2$, which reacted with LiSnPh$_2$Ar* to afford **3**. However, **3** may be prepared in a more rational manner by the stoichiometric reaction of **1** or **2** with SnCl$_2$ in Et$_2$O as in eq 5.

$$(\text{LiSnPh}_2\text{Ar*})_2 + \text{SnCl}_2 \xrightarrow[0\ ^\circ\text{C}]{\text{Et}_2\text{O}} \underset{\mathbf{3}}{\text{Sn(SnPh}_2\text{Ar*})_2} + 2\text{LiCl} \qquad (5)$$

Spectroscopy and Structures. Compound **1** is characterized by a monomeric structure in the solid state. A partial X-ray crystal structure,[8] which was marred by severe disorder problems in the LiSnPh$_2$Ar* moiety and the solvating ether, showed that lithium was coordinated to tin, to an aryl ring in an η^6-fashion, and to an ether oxygen. The Li−Sn contact is approximately 2.78 Å long, which may be compared to the longer distances of 2.871(7) Å in Li(PMDETA)SnPh$_3$,[9] 2.89(4) Å in (THF)$_3$LiSn{N(SiMe$_3$)$_2$CH$_2$}$_3$CH$_3$,[10] 2.93(5) Å in (THF)$_3$Li{N(p-Tol)SiMe$_2$}$_3$CH,[10] and 3.06(2) Å in (THF)$_3$LiSn{N(1-naphthyl)SiMe$_2$}$_3$CH.[11] It seems likely that the Li−Sn distance in **1** is shorter than those in the Lewis base-complexed molecules because the complexation of lithium by three Lewis base atoms is probably a more effective coordination array than the single Lewis base and an η^6-aryl coordination in **1**. In contrast there is an extremely short Li−Sn distance of 2.685(8) Å in the methyl-substituted species LiAr*MeSnSnMe$_2$Ar*$_2$, which is probably due to the chelating action of a flanking aryl ring of the Ar* ligand The latter also possesses a large ^{7}Li−^{119}Sn coupling of 736 Hz, whereas **1** has a corresponding value of 580 Hz. The lower value of the coupling is consistent with the longer Li−Sn bond in **1**.

Removal of the diethyl ether solvent and crystallization of the lithium salt from benzene results in dimerization of the LiSnPh$_2$Ar* units to afford the centrosymmetric molecule **2**. The dimerization occurs through interaction of the lithium in each unit with a phenyl ring (Li−Ph centroid = 2.137 Å) from its partner. In addition, the lithium is weakly solvated (Li−C = 3.034−3.170 Å) by a Trip ring within the same unit as shown in Figure 1. These Li−C distances may be compared to the Li−C interactions (ca. 2.40 Å) in [Li$_2${N(Mes)}$_2$SiMe$_2$]$_2$,[13] in which lithium is sandwiched between six-membered aryl rings. The Sn(1)−C(1)−C(2) angle is also ca. 16° narrower than the Sn(1)−C(1)−C(6) angle, which tends to corroborate the existence of the weak solvation of lithium by the Trip group. There is no Sn−Sn bonding, as indicated by the Sn−Sn distance of 4.690(1) Å, which is in excess of the sum of the van der Waal's radii, 4.4 Å.[14] The Li(1)−Sn(1A) bond length is 2.809(6) Å, which is slightly longer than that in **1**. Apparently, the replacement of the ether in the ligand sphere of **1** with a chelating η^6-Trip ring in **2** creates a more tightly bound lithium, which is reflected in a slightly weaker Li−Sn interaction.

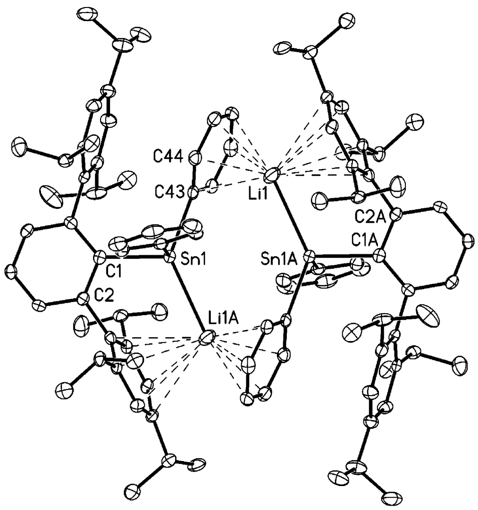

Figure 1. Thermal ellipsoid plot (30%) of **2**. H atoms are not shown.

Owing to the low solubility of **2** in benzene, we were unable to detect ^{7}Li−^{119}Sn coupling and the ^{119}Sn NMR signal was detected only with difficulty at −117 ppm. This shift is quite close to the −112 ppm observed for **1**. Both these shifts are in a region similar to the −431 ppm reported for LiAr*MeSnSnMe$_2$Ar*, but are further downfield, probably as a result of the poorer electron-releasing properties of Ph in comparison to Me.

The tritin species Sn(SnPh$_2$Ar*)$_2$, **3**, was obtained as orange-yellow crystals in moderate yield from the reaction of (LiSnPh$_2$Ar*)$_2$ with SnCl$_2$. Its structure is illustrated in Figure 2. It is a rare example of a structurally characterized distannylstannylene and is precedented only by the recently described Sn{Sn(C$_6$H$_3$-2,6-OPr$^i{}_2$)$_3$]$_2$, **4**.[15] In **3** the central two-coordinate tin is bound to two SnPh$_2$Ar* units to afford a V-shaped geometry. The interligand angle at the central tin is 115.19(1)°, which is the widest such angle observed in monomeric stannylenes.[16] The average Sn−Sn bond

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(8) Eichler, B. E.; Power, P. P. Unpublished results.

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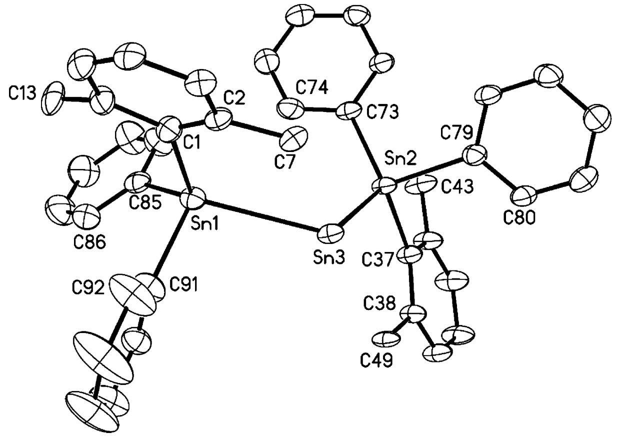

Figure 2. Thermal ellipsoid plot (30%) of **3**. H atoms are not shown and only ipso carbons of the Trip rings of the terphenyl groups are shown.

distance, ca. 2.964 Å, is close to that observed (2.9688(5) Å) in the recently reported species Ar*SnSnPh$_2$Ar* but is ca. 0.1 Å longer than the 2.866(1) Å in **4**, which has less bulky substituents.[2] A relatively long Sn−Sn distance of 2.8909(2) Å was also observed in Ar*SnSnMe$_2$Ar*, and it may be noted that all these Sn−Sn distances are longer than the 2.81 Å in elemental tin.[17] The Sn−C distances to the Ar* ligand are slightly (ca. 0.04 Å) longer than those to the Ph groups probably as a result of the greater crowding produced by this ligand.

The ^{119}Sn NMR spectrum of **3** is characterized by two signals at 398 and 3752 ppm (cf. −14.6 and 1302 ppm in **4**). The former signal can be assigned to the four-coordinate tins and lies in the same region (but further upfield) as the ca. 260 ppm signals found for the four-coordinate tins in Ar*SnSnMe$_2$Ar* and Ar*SnSnPh$_2$Ar*. The signal at 3752 ppm is due to the central tin and lies further downfield[18,19] than any currently known ^{119}Sn NMR signal for a monomeric stannylene (cf. ca. 2858 ppm for the two-coordinate tins in Ar*SnSnMe$_2$Ar* and Ar*SnSnPh$_2$Ar*).[3] The shift approaches that of the reduced species [Sn{Cr(CO)$_5$}$_3$]$^{2-}$, $\delta = 3924$, which has the furthest downfield chemical shift of any tin compound.[20] The very low chemical shift in **3** is due in part to the two-coordination of tin but is further enhanced by the presence of two electropositive stannyl substituents, which decreases the energy difference between the ground and excited states. This has the effect of increasing the deshielding paramagnetic contribution of the excited state to the chemical shift and moves it in the opposite direction (i.e., downfield) from what is expected on the basis of σ-inductive effects.[18,21]

The UV−visible spectrum of **3** displays a fairly intense (ϵ, 7300) absorption at 311 nm and possibly a very weak shoulder feature at ca. 367 nm. This is consistent with the yellow color of the solution. Previous spectroscopic data for a range of two-coordinate divalent germanium, tin, and lead species have shown that the absorption due to the n−p transition falls in the range 345−1056 nm.[22] Moreover the n−p absorptions for compounds with electropositive substituents such as silyl groups lie at longer wavelength, e.g., 838 nm for Sn{Si(SiMe$_3$)$_3$}$_2$[23] and 643 nm for Sn{Si(SiMe$_3$)$_3$}(C$_6$H-2-Bu^t-4,5,6-Me$_3$),[24] whereas electron-withdrawing groups induce absorption at shorter wavelengths as shown by Sn{Si(SiMe$_3$)$_3$}{C$_6$H$_2$-2,4,6-(CF$_3$)$_3$}[25] (540 nm) and Sn{C$_6$H$_2$-2,4,6-(CF$_3$)$_3$}$_2$ (345 nm).[26] We conclude therefore that the absorption at 311 nm observed for **2** is not due to an n−p transition. We believe that the n−p transition occurs at a wavelength in the near infrared region and that the shorter wavelength absorption may be due to a σ−σ* transition associated with the weaker Sn−Sn bonds.

Conclusion

The reactivity of Ar*SnPh/Ar*SnSnPh$_2$Ar* toward LiPh underlines the weakness of the Sn−Sn bond in the unsymmetric dimer Ar*SnSnPh$_2$Ar*. The reaction produces a LiSnPh$_2$Ar* salt that is either monomeric in ether or a dimer in benzene that is associated through Li−Ar interactions. It can be used as a transfer agent for the very bulky SnPh$_2$Ar* stannyl group to generate the distannylstannylene Sn(SnPh$_2$Ar*)$_2$.

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Supporting Information Available: CIF data for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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