

Polyhedron 20 (2001) 551-556



# The synthesis and structure of sterically encumbered terphenyl tin(II) halide derivatives: simultaneous existence of monomers and dimers in the crystalline phase

Barrett E. Eichler, Lihung Pu, Matthias Stender, Philip P. Power \*

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

Received 5 September 2000; accepted 4 December 2000

# Abstract

The reaction of  $Et_2O\cdot LiC_6H_3-2,6-Trip_2$  (Trip =  $C_6H^2-2,4,6-i-Pr_3$ ) with  $SnCl_2$  afforded the two coordinate monomer  $Sn(Cl)C_6H_3-2,6-Trip_2$  (1), and its dimer { $Sn(\mu-Cl)C_6H_3-2,6-Trip_2$ }\_2 (2), as orange and yellow crystals, respectively. Solution <sup>119</sup>Sn NMR spectroscopy of 2 in  $C_6D_6$  solution showed that it dissociated readily to give 1. The addition of pyridine (py) to a solution of 1 yielded the adduct py  $Sn(Cl)C_6H_3-2,6-Trip_2$  (3) which featured tin in a three coordinate pyramidal environment. The reaction of the closely related bulky terphenyl lithium reagent  $LiC_6H_3-2,6-Dipp_2$  (Dipp =  $C_6H_3-2,6-i-Pr_2$ ) with  $SnCl_2$  afforded the mixed halide species { $Sn(\mu-Cl)_{0.35}(\mu-I)_{0.65}C_6H_3-2,6-Dipp_2$ }\_2 (4). This arose from the preparation of the lithium aryl precursor in situ from  $IC_6H_3-2,6-Dipp_2$  and *n*-BuLi. The monomeric nature of 1, and the weak association of 2 and 4, were attributed to the large size of the terphenyl ligands. All compounds were characterized by X-ray crystallography, <sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn NMR spectroscopy, and IR and UV-Vis spectroscopy. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Terphenyl; Organotin(II) compounds; Bulky ligands; Stannanediyls

# 1. Introduction

The use of sterically crowding, meta-terphenyl substituents has enabled the synthesis and characterization of several new compound types throughout the periodic table which were previously unavailable as stable species [1]. In the case of the heavier Group 14 elements the employment of these ligands has led to the isolation of the first compounds with triple bonding to germanium [2], the first diplumbyne valence isomer of an alkyne [3], as well as the novel doubly bonded dianions of formula  $[ArMMAr]^{2-}$   $(Ar = C_6H_3 - 2, 6-Trip_2, M =$ Ge or Sn) [4]. The key starting materials for the synthesis of these compounds are the terphenyl element halide species M(X)Ar or M(X)Ar' (M = Ge, Sn or Pb; X = Cl, Br or I;  $Ar = C_6H_3 - 2,6$ -Trip<sub>2</sub>;  $Ar' = C_6H_3 - 2,6$ -Mes<sub>2</sub>; Trip =  $C_6H_2-2,4,6-i-Pr_3$ ; Mes =  $C_6H_2-2,4,6-i-Pr_3$ ;  $Me_3$  [5–7], which were synthesized by the reaction of

the lithium terphenyl and the metal dihalide. These precursors, however, are also of interest in their own right for several reasons; (i) well characterized compounds of the general formula M(X)R are relatively rare, especially when the organic group (R) is monodentate, (ii) M(X)R species display a variety of structures; e.g. halide bridged dimer [5,8], monomer [6,7] and metal-metal bonded dimer [5]. The latter two structural types have not been observed in the solid state with other monodentate ligands. In previous publications it has been shown that, when the less crowding  $-C_6H_3-2$ ,  $6-Mes_2$  (Ar') substitutent is used, the germanium species has the unique Ge-Ge bonded Ar'(Cl)GeGe(Cl)Ar' structure [5], whereas the tin analogue has the halide bridged arrangement Ar'Sn(µ-Cl)<sub>2</sub>SnAr' [5]. For the bulkier  $-C_6H_3-2,6$ -Trip<sub>2</sub> (Ar) substituent a V-shaped monomeric structure was observed for the orange germanium derivative Ge(Cl)Ar [6]. However, the structure of the corresponding tin species, Sn(Cl)Ar, which has been employed extensively as a starting material, was unknown. It is generally obtained as orange crystals from the reaction of SnCl<sub>2</sub>

<sup>\*</sup> Corresponding author. Tel.: +1-530-752-6913; fax: +1-530-752-8995.

E-mail address: pppower@ucdavis.edu (P.P. Power).

and Et<sub>2</sub>O·LiAr in diethyl ether and subsequent crystallization from hexane [9]. During the course of several recrystallizations it was observed that two different crystalline materials (one having an orange, the other a yellow color) were obtained. At first, it was assumed that the yellow crystals were an impurity (possibly the hydroxide Sn(OH)Ar), formed as a result of moisture contamination. However, further examination showed that solutions of the orange or yellow crystals had identical <sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn NMR spectra. In this paper the structural and spectroscopic characterization of these crystals are reported, together with their interaction with the Lewis bases THF and pyridine. The spectroscopic structural characterization of a related derivative involving the terphenyl ligand  $-C_6H_3-2,6-$ Dipp<sub>2</sub> (Dipp =  $-C_6H_3-2, 6-i-Pr_2$ ) is also given.

# 2. Experimental

#### 2.1. 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 twice immediately before use. The compounds  $Et_2O \cdot LiC_6H_3 - 2,6$ -Trip<sub>2</sub> [10] and LiC<sub>6</sub>H<sub>3</sub>-2,6-Dipp<sub>2</sub> [11] were prepared according to literature procedures. Anhydrous SnCl<sub>2</sub>, was purchased commercially and purified by sublimation under reduced pressure. Pyridine (py) was dried by distillation from CaH<sub>2</sub>. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>119</sup>Sn {<sup>1</sup>H} NMR spectra were recorded on a Bruker 300 MHz or Varian 400 Hz instrument and referenced to the deuterated solvent in the case of the <sup>1</sup>H and <sup>13</sup>C NMR spectra. The <sup>119</sup>Sn NMR spectra were referenced to SnMe<sub>4</sub>. Infrared and UV-Vis spectra were recorded on a Perkin PE-1430 and a Hitachi-1200 spectrometer.

# 2.2. $Sn(Cl) \{C_6H_3 - 2, 6-Trip_2\}$ (1) and $[Sn(\mu-Cl) \{C_6H_3 - 2, 6-Trip_2\}]_2$ (2)

(Et<sub>2</sub>O)LiC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (2.81 g, 5.0 mmol) in Et<sub>2</sub>O (30 ml) was added dropwise to a stirred suspension of SnCl<sub>2</sub> (0.95 g, 5.0 mmol) in Et<sub>2</sub>O (10 ml) with cooling in an ice bath. The orange solution was warmed to room temperature, and stirred for a further 15 h. The solvent was removed under reduced pressure, and the orange residue was extracted with hexane (70 ml) and filtered through Celite. Reduction in the volume to incipient crystallization under reduced pressure, and storage in a ca.  $-20^{\circ}$ C freezer afforded the products 1 and 2 as orange and yellow crystals, respectively. Yield 1.91 g, 60.6%. M.p.: 220–223°C. <sup>119</sup>Sn{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  793.4. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.08 (d, 12H, *p*-CH(*CH*<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 1.21 (d, 12H, *o*-

CH(CH<sub>3</sub>)<sub>2</sub>)  ${}^{3}J_{HH} = 6.6$  Hz, 1.39 (d, 12H, o-CH(CH<sub>3</sub>)<sub>2</sub>)  ${}^{3}J_{\text{HH}} = 6.9 \text{ Hz}, 2.81 \text{ (sept, 2H, } p-CH(\text{CH}_{3})_2) {}^{3}J_{\text{HH}} = 6.9$ Hz, 3.15 (sept, 4H,  $o-CH(CH_3)_2$ )  ${}^{3}J_{HH} = 6.9$  Hz, 7.19 (s, 4H, *m*-Trip) 7.22-7.31 (mult, 3H, o, p-C<sub>6</sub>H<sub>3</sub>), <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>H<sub>6</sub>):  $\delta$  23.12 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 24.26  $(p-CH(CH_3)_2),$ 26.43  $(o-CH(CH_3)_2),$ 31.07 (o-CH(CH<sub>3</sub>)<sub>2</sub>), 34.75 (p-CH(CH<sub>3</sub>)<sub>2</sub>), 121.68 (m-Trip), 130.68  $(m-C_6H_3)$ , 135.01  $(p-C_6H_3)$ , 145.38  $(o-C_6H_3)$ , 146.79 (*i*-Trip), 147.57 (*p*-Trip), 149.53 (*o*-Trip), 181.86 (*i*-C<sub>6</sub>H<sub>3</sub>). UV–Vis (hexane)  $\lambda_{\text{max}}$  (nm),  $\varepsilon = (\text{mol}^{-1})$  $cm^{-1}$ ): 284 (sh), 330; 395, 1040. IR (Nujol mull,  $cm^{-1}$ ) v: 1765(vw), 1730(w), 1600(m), 1550(m), 1310(w), 1175(vw), 1170(m), 1150(vw), 1110(w), 1090(vw), 1070(w), 1050(w), 1020(w), 1010(w), 955(w), 940(m), 920(vw), 880(s), 850(vw), 820(vw), 800(s), 770(m), 750(vw), 735(s), 720(vw), 695(vw), 650(m), 625(vw), 600(vw), 575(vw), 530(w), 465(vw), 395(vw), 300(s), 240(m).

#### 2.3. $py \cdot Sn(Cl)C_6H_3 - 2, 6-Trip_2$ (3)

Pyridine (0.37 ml, 4.6 mmol) was added to a rapidly stirred orange solution of Sn(Cl)C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (2.91 g, 4.58 mmol) in hexane (80 ml) at ca. 25°C. The reaction mixture became a yellow color and stirring was continued for a further 1 h. The yellow solution was separated from the small amount of white precipitate by decanting. The volume was reduced to incipient crystallization under reduced pressure and stored in a ca. 5°C refrigerator for 2 days to afford 3 as yellow crystals. Yield 2.67 g, 81%. M.p.: 140-142°C dec. <sup>119</sup>Sn{<sup>1</sup>H}(C<sub>6</sub>D<sub>6</sub>):  $\delta$  264. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.13 (12H, o-CH(CH<sub>3</sub>)<sub>2</sub>),  ${}^{3}J_{\rm HH} = 6.9$  Hz; 1.20 (d, 12H, o- $CH(CH_3)_2$ ),  ${}^{3}J_{HH} = 6.9$  Hz; 1.41 (d, 12H, *p*-CH(CH<sub>3</sub>)<sub>2</sub>),  ${}^{3}J_{\rm HH} = 6.9$  Hz; 2.74 (sept, 2H, *p*-CH(CH<sub>3</sub>)<sub>2</sub>),  ${}^{3}J_{\rm HH} = 6.9$ Hz; 3.34 (sept, 4H, o-CH(CH<sub>3</sub>)<sub>2</sub>),  ${}^{3}J_{HH} = 6.9$  Hz; 6.26 (d of d, 2H, m-C<sub>5</sub>H<sub>5</sub>N),  ${}^{3}J_{HH} = 6.0$  Hz; 6.59 (t of t, 1H,  $p-C_5H_5N$ ),  ${}^{3}J_{HH} = .75$  Hz,  ${}^{4}J_{HH} = 1.2$  Hz; 7.19 (s, 4H, *m*-Trip); 7.26 (tr, 1H, *p*-C<sub>6</sub>H<sub>3</sub>),  ${}^{3}J_{HH} = 7.6$  Hz; 7.93 (d of d, 2H, m-C<sub>6</sub>H<sub>3</sub>),  ${}^{3}J_{HH} = 6.0$  Hz;  ${}^{4}J_{HH} = 1.2$  Hz; 7.98 (br, 2H, o-C<sub>5</sub>H<sub>5</sub>N);  ${}^{13}C{}^{1}H{}$  NMR (C<sub>6</sub>H<sub>6</sub>):  $\delta$  23.18  $(o-CH(CH_3)_2);$  24.28  $(o-CH(CH_3)_2);$  26.22  $(p-CH(CH_3)_2);$  26.22 (p-CCH(CH<sub>3</sub>)<sub>2</sub>); 30.96 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>); 34.52 (*p*-CH(CH<sub>3</sub>)<sub>2</sub>); 120.85 (*m*-Trip); 124.15 (*m*-C<sub>5</sub>H<sub>5</sub>N); 126.45 (*p*-C<sub>6</sub>H<sub>3</sub>); 130.86  $(p-C_5H_5N)$ ; 137.43  $(m-C_6H_3)$ ; 138.60 (i-Trip); 146.34 (*p*-Trip); 147.69 (*o*-Trip); 148.50 (*o*- $C_6H_3$ ); 148.55 (*o*-C<sub>5</sub>H<sub>5</sub>N); 175.77 (*i*-C<sub>6</sub>H<sub>3</sub>). UV-Vis (hexane):  $\lambda_{\text{max}}$  (nm) 391; 750. IR (Nujol mull, cm<sup>-1</sup>) v: 1760(vw), 1640(vw), 1600(s), 1560(m), 1550(m) 1360(s), 1320(m), 1260(w), 1240(w), 1215(s), 1185(vw), 1170(m), 1150(m), 1100(s), 1070(s), 1035(s), 1010(s), 955(w), 940(m), 920(w), 880(s), 850(vw), 835(vw), 820(vw), 800(s), 775(m), 745(m), 740(m), 720(w), 690(s), 645(m), 625(s), 580(vw), 530(vw), 410(w), 270(s), 240(m).

LiC<sub>6</sub>H<sub>3</sub>-2,6-Dipp<sub>2</sub> (1.38 g, 3.40 mmol), generated in situ from 2,6–Dipp<sub>2</sub>H<sub>3</sub>C<sub>6</sub>I and *n*-BuLi, in Et<sub>2</sub>O (30 ml) was added dropwise to a stirred suspension of SnCl<sub>2</sub> (0.65 g, 3.43 mmol) in Et<sub>2</sub>O (10 ml) with cooling in an ice bath. The solution was stirred for ca. 15 h. The solvent was removed under reduced pressure, and the residue was extracted with hexane (70 ml). Filtration through Celite, and reduction in the volume to incipient crystallization, and storage in a  $-20^{\circ}$ C freezer afforded the product 4 as orange crystals. Yield 1.35 g, 72.2% mp: 185°C. <sup>119</sup>Sn {<sup>1</sup>H} NMR ( $C_6D_6$ ):  $\delta$  1042. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.02 (d, 12H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>), <sup>3</sup>J<sub>HH</sub> = 6.8, 1.33 (d, 12H, o-CH(CH<sub>3</sub>)<sub>2</sub>),  ${}^{3}J_{HH} = 6.8$  Hz, 3.09 (sept, 4H, o-CH(CH<sub>3</sub>)<sub>2</sub>)  ${}^{3}J_{HH} = 6.8$  Hz, 7.12–7.30(mult, 9H, aromatic region), <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>H<sub>6</sub>): δ 22.97  $(o-CH(CH_3)_2),$ 26.41  $(o-CH(CH_3)_2),$ 30.96 (o -CH(CH<sub>3</sub>)<sub>2</sub>), 124.04 (m-Trip), 129.59 (p-Trip), 130.56  $(m-C_6H_3)$ , 136.44  $(p-C_6H_3)$ , 144.76  $(o-C_6H_3)$ , 146.83 (*i*-Trip), 147.49 (*o*-Trip), 181.17 (*i*-C<sub>6</sub>H<sub>3</sub>). UV-Vis (hexane)  $\lambda_{\text{max}}$  (nm) = 391, 420. IR (Nujol mull, cm<sup>-1</sup>) v: 1590(vw), 1570(vw), 1550(vw), 1360(vw), 1320(vw), 1310(w), 1260(w), 1170(vw), 1090(m), 1060(w), 1010(vw), 970(vw), 955(vw), 930(vw), 815(w), 800(s), 790(m), 750(s), 740(s), 720(w), 685(vw), 670(vw), 580(w), 450(vw), 300(w), 240(m).

# 2.5. X-ray crystallographic studies

Crystals of 1, 2 and 4 were coated with hydrocarbon oil, mounted on a glass fiber and quickly placed in a  $N_2$  cold stream [12]. Data for 1, 2 and 4 were collected at

Table 1					
Crystal and	experimental	data	for	compounds	1-4

90 K using a Bruker SMART 1000 system (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å and a CCD area detector). The Bruker SHELXTL 5.11 program package was used for the structure solutions and refinement [13]. An absorption correction was applied using the program SADABS [14]. Data for **3** were obtained on Siemens R3 diffractometer at 140 K. An absorption correction was applied using program XABS2 [15]. All structures were solved by direct methods, and refined by full-matrix least square refinement. All non-hydrogen atoms were refined anisotropically. Anomalous electron densities were observed in the neighborhood of tin in both **1** and **2**, which were attributed to uncorrected absorption effects. Some details of the data collection and refinement are given in Tables 1 and 2.

# 3. Results and discussion

### 3.1. Synthesis and spectroscopy

The compounds 1 and 2 were obtained in moderate to good yields by the reaction of one equiv. of the lithium reagent ( $Et_2O$ )LiC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> [10] and SnCl<sub>2</sub> in diethyl ether. In several preparations it was found that 1 and 2 were always obtained but the formation of 2 was favored by slower cooling rates and lower temperatures. In hexane or benzene solutions an intense orange color was observed, which corresponded to the presence of the monomer 1. However, the orange color was bleached to a pale yellow in donor solvents such as THF (see below). The presence of monomeric 1 in solution was confirmed by <sup>119</sup>Sn NMR spectroscopy in

	1	2·hexane	3.0.5 methylcyclopenane 0.25 hexane	4	
Formula	$C_{36}H_{49}ClSn$	$C_{78}H_{112}Cl_2Sn_2$	C <sub>44.5</sub> H <sub>54</sub> ClNSn	$C_{30}H_{35}Cl_{0.35}I_{0.65}Sn$	
FW Calar habit	035.89	133/.90		393.43 	
Crystal system	orthorhombic	triclinic	monoclinic	monoclinic	
Space group	Pnma	$P\overline{1}$	$P2_1/c$	$P2_1/n$	
a (Å)	8.0503(3)	9.6955(12)	17.315(9)	13.3362(6)	
b (Å)	25.2002(10)	13.2479(16)	14.508(6)	14.1592(7)	
<i>c</i> (Å)	16.4070(6)	13.9837(17)	17.292(4)	14.4803(7)	
α (°)		93.306(2)			
$\beta$ (°)		93.801(2) 94.092(2)	97.83(3)	97.422(1)	
$V(Å^3)$	3328.5(2)	1784.1(4)	4303(3)	2711.4(2)	
Ζ	4	1	4	4	
$D_{\text{calc}} (\text{mg m}^{-3})$	1.269	1.264	1.200	1.459	
$\theta$ Range (°)	1.48-31.51	2.06-31.48	1.19-26.00	1.95-31.44	
$\mu  ({\rm mm}^{-1})$	0.869	0.815	0.684	1.576	
Observed data, $I > 2\sigma(I)$	4530	8218	6525	7185	
$R_1$	0.0368	0.0417	0.0554	0.0280	
$wR_2$	0.1001	0.0907	0.1621	0.0913	

Table 2 Selected bond lengths (Å) and bond angles (°) for compounds 1–4  $\!$ 

Compound 1		Compound 2		Compound 3		Compound 4	
Bond lengths							
Sn(1)-C(1)	2.180(2)	Sn(1)-C(1)	2.214(2)	Sn(1)-C(1)	2.229(4)	Sn(1)-C(1)	2.2303(18)
Sn(1)-Cl(1)	2.4088(8)	Sn(1)-Cl(1)	2.5768(6)	Sn(1)-Cl(1)	2.4478(19)	Sn(1)-Cl(1)	2.6061(13)
C(1)–C(2)	1.4013(17)	Sn(1)-Cl(1A)	2.5978(7)	N(1)–C(41)	1.337(6)	Sn(1)-Cl(1A)	2.8430(12)
., .,		C(1)-C(2)	1.408(3)	Sn(1)-N(1)	2.369(4)	Sn(1)-I(1A)	2.7700(5)
				N(1)–C(37)	1.331(6)	Sn(1)-I(1A)	3.1227(5)
Bond angles							
C(1) - Sn(1) - Cl(1)	99.67(6)	C(1)-Sn(1)-Cl(1)	92.61(6)	C(1)-Sn(1)-N(1)	104.02(14)	C(1)-Sn(1)-Cl(1)	92.42(6)
C(2)-C(1)-Sn(1)	119.67(9)	C(1)-Sn(1)-Cl(1A)	98.21(6)	N(1)-Sn(1)-Cl(1)	89.21(10)	C(1)-Sn(1)-I(1)	90.92(5)
C(2)-C(1)-C(2A)	120.03(18)	C(2)-C(1)-C(6)	118.9(2)	C(1)-Sn(1)-Cl(1)	93.14(11)	C(1)-Sn(1)-I(1)	90.92(5)
		Cl(1)-Sn(1)-Cl(1A)	81.21(2)	C(37)-N(1)-Sn(1)	127.9(3)	Cl(1)-Sn(1)-Cl(1A)	81.64(4)
		Sn(1)-Cl(1)-Sn(1A)	98.79(2)	C(41)-N(1)-Sn(1)	112.6(4)	I(1)-Sn(1)-I(1A)	91.309(12)
				Sn(1)-C(1)-C(2)	130.7(3)	Sn(1)-Cl(1)-Sn(1A)	98.36(4)
				Sn(1)–C(1)–C(6)	111.3(3)	Sn(1)-I(1)-Sn(1A)	88.69(12)

 $C_6D_6$  solution which displayed a single resonance at  $\delta = 793.4$ . It is notable that this value is close to the  $\delta = 777$  measured for the dimer {Sn(Cl)C(SiMe<sub>2</sub>Ph)<sub>3</sub>}<sub>2</sub> [8] in  $C_6D_6$  which supports the suggestion [8] that this compound is also dissociated in solution. Both values are upfield of the <sup>119</sup>Sn NMR shifts measured for  $Sn(I)C_6H_3-2,6-Trip_2$  ( $\delta = 1140$ ), or 4  $Sn(I)C_6H_3-2,6-$ Dipp<sub>2</sub> ( $\delta = 1042$ ). This is opposite to what is expected on the basis of inductive effects since the electronegativity of chlorine is significantly greater than that of iodine. This apparent anomaly can be explained on the basis that the paramagnetic shielding (a reflection of the mixing of the ground and excited states) is decreased by the more electronegative substituent leading (since paramagnetic effects augment the applied field) to an upfield shift [16].

The addition of pyridine to solutions of 1 afforded yellow crystals of the pyridine complex 3 in good yield. The <sup>1</sup>H NMR spectrum confirmed the presence of a 1:1 ratio of pyridine and the terphenyl ligand. The <sup>119</sup>Sn NMR spectrum displayed a single peak at  $\delta = 264$ . The > 500 ppm upfield shift in comparison to 1 is indicative of a higher coordination and increased shielding of the tin center. A ca. 300 ppm upfield shift was observed for solutions of 1 in THF ( $\delta = 456$ ) where it has a pale yellow color. Both the color and the upfield shift are consistent with the formation of a THF complex of 1 in this solvent. Attempts to isolate and characterize this complex have been unsuccessful so far. The upfield shift of **3** is also consistent with the  $\delta = 350.6$  observed for the chelated species  $Sn(Cl)C(SiMe_3)_2(2-NC_5H_4)$  [17] or the  $\delta = 155.6$  observed for the five-coordinate chelated complex  $Sn(Cl) \{C_6H_3 - 2, 6 - (CH_2NMe_2)_2\}$  [18].

The reaction of  $LiC_6H_3-2,6$ -Dipp<sub>2</sub> [11] with  $SnCl_2$  produced **4** which contains a major portion of

 $Sn(I)C_6H_3-2,6-Dipp_2$  rather than the expected product  $Sn(Cl)C_6H_3-2,6-Dipp_2$ . The presence of iodine arises from the synthetic method in which the lithium reagent was prepared in situ by the reaction of LiBu with  $IC_6H_3-2,6-Dipp_2$ .



Fig. 1. Thermal ellipsoid (30%) drawing of **1** (H atoms are not shown). Selected bond lengths and angles are given in Table 2.



Fig. 2. Thermal ellipsoid (30%) drawing of **2** (H atoms are not shown). Selected bond lengths and angles are given in Table 2.



Fig. 3. Thermal ellipsoid (30%) drawing of **3** (H atoms are not shown). Selected bond lengths and angles are given in Table 2.



Fig. 4. Thermal ellipsoid (30%) drawing of **4** (H atoms are not shown). Selected bond lengths and angles are given in Table 2.

#### 3.2. Structures

The structures of 1-4 are illustrated by the thermal ellipsoid plots in Figs. 1-4. It can be clearly seen that 1is a monomer with V-shaped geometry at tin. The monomeric structure is a consequence of the very large size of the terphenyl ligand [1]. It is a very rare example of an unassociated, two-coordinate organotin(II)halide structure in the solid state, and it is only preceded by the monomeric iodide species  $Sn(I)C_6H_3-2,6-Trip_2$  [6]. All other examples of such compounds are associated through halide bridging [5,8]. The geometry at tin is characterized by Sn(1)-C(1) and Sn(1)-Cl(1) distances of 2.180(2) and 2.4088(8) Å and an interligand angle of 99.67(6)°. The Sn-C distance and C(1)-Sn(1)-Cl(1)angle are very similar to the 2.213(13) Å and  $102.6(3)^{\circ}$ observed for Sn(I)C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> [6]. The Sn-Cl bond is slightly longer than the sum of the radii [19] of Sn (1.40 Å) and chlorine (0.99 Å). However, it is considerably shorter than 2.565(2) and 2.539(1) Å observed [20] for the terminal Sn-Cl distances in the SnCl<sub>2</sub> complexes SnCl<sub>2</sub>(2,2'-dipyridine) and SnCl<sub>2</sub>(1,10-phenanthroline). The shorter values in 1 can be attributed to the lower coordination of tin in comparison to the four and five coordination of the tins in these complexes. This view is supported by the Sn-Cl distance of 2.440(5) Å observed in Sn(Cl)C(SiMe<sub>3</sub>)<sub>2</sub>(2-NC<sub>6</sub>H<sub>4</sub>) [17] which has three coordinate tin and a slightly longer metal halogen bond.

The structure of 2, a dimer of 1, features chlorides bridging between the two tin atoms. The enthalpy of association cannot be very large, however, since 2 dissociates to 1 in hydrocarbon solvents. The molecule possesses a center of symmetry in the middle of the  $Sn_2Cl_2$  core which has a planar geometry. There are internal angles of 81.21(2)° at tin and 98.79(2)° at chloride. The Sn–C distance, 2.214(2) Å, is slightly longer than that in 1 which is probably due to the increase in the metal coordination number from two to three. The Sn-Cl distances are almost equal, and have an average value of 2.587(11) Å, which is comparable to the shorter of the two bridging Sn-Cl distances  $(2.596(3) \text{ and } 2.779(3) \text{ Å}) \text{ in } \{\text{Sn}(\text{Cl})\text{C}(\text{SiMe}_{2}\text{Ph})_{3}\}_{2} [8]$ and  $\{Sn(Cl)C_6H_3-2, 6-Mes_2\}_2$  [5] (2.600(2) and 2.685(2) A). The structural data for these three compounds are consistent with the fact that they are dissociated in solution as suggested previously by <sup>119</sup>Sn NMR data [8].

The addition of pyridine to 1 affords the monomeric 1:1 adduct 3 which has a three coordinate Sn(II) center. The tin has an extremely pyramidal coordination with  $\Sigma^{\circ}$ Sn = 286.37°. The coordination of the pyridine is almost perpendicular to the Cl(1)-C(1)-Sn(1) plane, although the plane of the pyridine ring deviates from the Sn(1)-N(1) line by 12° towards the less crowded side of the molecule. The Sn-C and Sn-Cl bond lengths, 2.229(4) and 2.4478(19) Å are both about 0.04 A longer than those observed in 1 as a result of the increase in the tin coordination number. The Sn-N distance, 2.364(4) Å, is slightly shorter than the calculated distance for H<sub>2</sub>SnNH<sub>3</sub> [21], or the average values (ca. 2.39 A) observed [20] for the complexes  $SnCl_2(2,2'$ bipyridine) and SnCl<sub>2</sub>(1,10-phenanthroline) which have higher metal coordination numbers. However, much shorter Sn–N distances were observed in the complexes  $Sn(Cl) \{C(SiMe_3)_2(2-NC_5H_4)\}$  (Sn-N = 2.37(2) A) [17] and  $(t-Bu)_2(py)SnCr(CO)_5$  (Sn-N = 2.29(1) Å [22]which have three and four coordinate tins, respectively. Perhaps, the chelating character of the former complex, and the less crowded nature of the latter species, account for the large differences in the Sn-N bond lengths.

The structure of **4** is dimeric, and is similar to **2**. However, the crystalline sample selected for measurement contains a mixture of chloride and iodide at the halide positions. The optimum refinement was obtained at an Cl:I ratio of 0.35:0.65. Like **2**, the structure is characterized by the presence of an inversion center. The Sn-C bond length 2.2303(18) Å is similar to that in 2. The structure features two Sn-Cl (2.6061(13) and 2.8430(12) Å) and two Sn-I (2.7700(5) and 3.1227(5) Å) distances. The former pair are very similar to the 2.596(3) and 2.779(3) Å reported for {Sn(Cl)C-(SiMe<sub>2</sub>Ph)<sub>3</sub>}<sub>2</sub> [17]. The iodine distances are 0.17-0.28 Å longer, although this is less than the almost 0.35 Å difference between the Sn-Cl bond in 1 and the corresponding Sn-I bond in Sn(I)C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>. The latter features on Sn-I bond length of 2.766(2)Å — very close to the shorter Sn-I bond length observed in 4.

#### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 149413–149416 for compounds 1–4. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

#### Acknowledgements

We are grateful to the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society for financial support and Cornel Stanciu and Dr Marilyn Olmstead for experimental assistance.

#### References

 (a) B. Twamley, S.T. Haubrich, P.P. Power Adv. Organomet. Chem. 41 (1999) 1. (b) For recent extensions to the lanthanide elements see: G.W. Rabe, C.S. Steissel, L.M. Liable-Sands, T.E. Concolino, A.L. Rheingold. Inorg. Chem. 38 (1999) 3445. (c) G. Heckmann, M. Niemeyer. J. Am. Chem. Soc. 122 (2000) 4227.

- [2] (a) R.S. Simons, P.P. Power J. Am. Chem. Soc. 118 (1996) 11966. (b) L. Pu, B. Twamley, S.T. Haubrich, M.M. Olmstead, B.V. Mork, R.S. Simons, P.P. Power J. Am. Chem. Soc. 122 (2000) 650.
- [3] L. Pu, B.T. Twamley, P.P. Power, J. Am. Chem. Soc. 122 (2000) 3524.
- [4] L. Pu, M.O. Senge, M.M. Olmstead, P.P. Power, J. Am. Chem. Soc. 120 (1998) 12682.
- [5] R.S. Simons, L. Pu, M.M. Olmstead, P.P. Power, Organometallics 16 (1997) 1920.
- [6] L. Pu, M.M. Olmstead, P.P. Power, B. Schiemenz, Organometallics 17 (1998) 5602.
- [7] L. Pu, B. Twamley, P.P. Power, Organometallics 19 (2000) 2874.
- [8] C. Eaborn, P.B. Hitchcock, J.D. Smith, S.E. Sözerli, Organometallics 16 (1997) 5653.
- [9] M.M. Olmstead, R.S. Simons, P.P. Power, J. Am. Chem. Soc. 119 (1997) 11705.
- [10] B. Schiemenz, P.P. Power, Organometallics 15 (1996) 964.
- [11] B. Schiemenz, P.P. Power, Angew. Chem. Int. Ed. Engl. 35 (1996) 2150.
- [12] H. Hope, Prog. Inorg. Chem. 41 (1995) 1.
- [13] SHELXTL version 5.1: Bruker AXS, Madison, WI, 1998.
- [14] SADABS an empirical absorption correction program part of the SAINT PLUS NT version 5.0 package Bruker AXS, Madison, WI, 1998.
- [15] S.R. Parkin, B. Moezzi, H. Hope, J. Appl. Crystallogr. 3 (1997) 1418.
- [16] B. Wrackmeyer, Annu. Rep. NMR Spectr. 38 (1999) 203.
- [17] L.M. Engelhardt, B.S. Jolly, M.F. Lappert, C.L. Raston, A.H. White. J. Chem. Soc., Chem. Commun. (1988) 336.
- [18] J.T.B.H. Jastrzebski, P.A. van der Schaaf, J. Boersma, G. van Koten, M.C. Zoutberg, D. Heijderijk, Organometallics 8 (1989) 1373.
- [19] A.F. Wells, Structural Inorganic Chemistry, 5th edn., Clarendon, Oxford, 1984, pp. 388 and 1279.
- [20] S.J. Archer, K.R. Koch, S. Schmidt, Inorg. Chim. Acta 126 (1987) 209.
- [21] W.W. Schoeller, R. Schneider, Chem. Ber./Receuil. 130 (1997) 1013.
- [22] M.D. Brice, F.A. Cotton, J. Am. Chem. Soc. 95 (1973) 4529.