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Heptacoordinate Structures of Organotin Halides with Three Phosphine Donors: Halogen-Substituent Effect on Geometry

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Abstract: Structural studies were performed on heptacoordinate compounds of triorganotin halides {(o-Ph₂P)C₆H₄}₃SnX (X = F (1), Cl (3), Br (4), I (5)) with three phosphine donors. The fluorostannane (1) has an unusual heptacoordinate geometry, in which the three phosphine donors interact with the Sn center around the opposite coordination site of the Sn-F bond (a form). In contrast, the chloro (3) and bromo (4) analogues have highly distorted pentagonalbipyramidal geometries (b form), while the iodo analogue (5) has a tricapped tetrahedral geometry (c form). Although both b and c forms have two phosphine donors coordinating to the Sn center around the opposite site of the C_{ipso} atoms and one phosphine donor coordinating to the Sn atom trans to the halogen atom, the geometry around the Sn center is much more distorted from tetrahedral geometry in **b** form than in **c** form. Density functional theory (DFT) calculations indicate that the presence of the halogen atom on the Sn center facilitates access from the opposite side of the halogen due to the strong electrostatic and intramolecular donor-acceptor transfer interactions. The difference in electronegativity of the halogen atoms also appear to contribute to structural modification by altering the halogen substituent, because a strongly electronegative halogen facilitates the formation of a structure that is highly distorted from the tetrahedral geometry (Bent's rule).

Introduction

The chemistry of hypercoordinate compounds of group 14 elements has been developed due to their interesting geometries (similar to transition states or intermediates of S_N2 -type reactions) and their essential roles in molecular transformation and catalytic functions.^[1] An ER₄ molecule of a heavier group 14 element (E) can interact with

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Lewis bases using the $\sigma^*(E-R)$ orbital to form a hypercoordinate geometry. The characteristics of the heavier group 14 elements results in several and curious geometries involving not only pentaand hexacoordination but also higher coordination.^[2-6] These geometries and bonding interactions would be useful for discussing the reaction mechanisms and/or reasons for stereoselectivity. Corriu's group provided several pioneering examples of neutral hepta-coordinate species (Figure 1).^[2] They used a bidentate ligand having a 2-electron donor moiety (L) at one end and a 1-electron donor moiety (X) at the other. This type of ligand has been denoted as an LX-type ligand hereafter. Corriu's group reported that silane compounds adopted a heptacoordinate geometry by forming three $LP(N) \rightarrow \sigma^*(Si-X)$ interactions (LP = lone pair) (type I in Figure 1).^[2a] Other types of heptacoordinate silane, germane, and stannane compounds were also investigated by other groups using an L₃Xtype ligand (type II).^[4] Both types I and II form a tricapped tetrahedral geometry around the central atom. A different type of heptacoordinate geometry was reported for stannane systems. The O, N, N, N, O-pentadentate^[5a] and cupferronato (N-nitroso-Nphenylhydroxylaminato)^[5b] ligands as well as the combination of N, N, O-tridentate and N, O-bidentate ligands^[5c] allowed the formation of a pentagonal bipyramidal geometry (type III).

We have been interested in the use of a phosphine-based LXtype ligand for the synthesis of novel hypercoordinate compounds because of its strong multiple LP(P) \rightarrow E donor-acceptor interactions induced by the effective overlap between the larger lone pair orbital of phosphine relative to a nitrogen donor and the $\sigma^*(E-X)$ orbital.^[6-8] Previously, we reported that fluorosilane and fluorogermane {o- $(Ph_2P)C_6H_4$ ₃E(F) (E = Si, Ge) adopted a different type of heptacoordinate geometry, whereby one of the three phosphine donors was coordinated to E at the coordination site trans to the E-F bond owing to the significant LP(P) $\rightarrow \sigma^*(E-X)$ interaction (type IV in Figure 1).^[6b] Furthermore, we found that tin fluorostannane {o-(Ph₂P)C₆H₄}₃SnF (1) adopted an unusual heptacoordinate structure, in which the three phosphine donors equivalently interacted with one $\sigma^*(Sn-F)$ orbital.^[6a] FSnC₃ core in **1** strongly distorted from a tetrahedral geometry and its structure adopted a trigonal pyramidal geometry with the axial fluoride atom (\sum (CSnC) = 358.23(7), Σ (CSnF) = 282.96(15)) (type V in Figure 1). In contrast, the hydride analogue $\{o-(Ph_2P)C_6H_4\}_3SnH$ (2) of 1 has a different heptacoordinate geometry in which each phosphine donor coordinates via the LP(P) $\rightarrow \sigma^*(Sn-C)$ interactions in a way similar to type I in Figure 1.^[9] Note that the HSnC₃ core adopts a less-distorted tetrahedral geometry despite the presence of $P \rightarrow \sigma^*(Sn-C)$ interactions (Σ (CSnC) = 314.86(12), Σ (CSnF) = 341.1(15)).

Such structural changes in heptacoordinate tin compounds motivated us to investigate further on different halogen analogues of 1 to determine the different hypercoordinate structures and elucidate the substituent effect on the heptacoordinate geometry. In this contribution, we performed systematic studies on chloro, bromo, and

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Figure 1. Representative examples of neutral heptacoordinate species featuring the heavier group 14 elements and a schematic representation of the associated coordination patterns

iodo analogues {o-(Ph₂P)C₆H₄}₃SnX (**3**: X = Cl, **4**: X = Br, **5**: X = I) of **1** and demonstrated that these compounds adopted heptacoordinate geometries different from those of **1** and **2**. In addition, the origin of these structural modifications was investigated by density functional theory (DFT) calculation.

Results and Discussion

Since the ortho-phenylene framework has been reported to be useful for inducing an intramolecular P \rightarrow Sn interaction,^[8n] we used this framework to fabricate three intramolecular P \rightarrow Sn interactions. The chloro analogue of **1**, o-{(Ph₂P)C₆H₄)₃SnCl (**3**), was isolated by

modifying the procedure previously reported.^[80] The reaction of {o-(Ph₂P)C₆H₄}Li with one-third equivalents of SnCl₄ provided **3** as a white powder (Scheme 1). The bromo analogue {o-(Ph₂P)C₆H₄}_3SnBr (**4**) was successfully synthesized in a way similar to **3** using SnBr₄ instead of SnCl₄. Br/l exchange of **4** using excess amount of KI provided the iodo analogue {o-(Ph₂P)C₆H₄}₃SnI (**5**).

X-ray diffraction studies of $3^{(10)}$ and 4 were carried out using single crystals obtained from the slow diffusion of *n*-hexane into dichloromethane solution (Figure 2, Table 1). Structural analysis showed that 3 and 4 have a similar structure but their geometries were different from those of the fluoro and hydrido analogues (1 and 2). In 3 and 4, one phosphine donor (P_{ax}) occupies the position *trans* to the halogen X atom, and two phosphine donors (P_{eq}) are



located around the opposite coordination site of ipso-carbons, where the subscripts "ax" and "eq" represent the axial and equatorial positions, respectively. All the Sn-P distances (3.3039(7), 3.4119(7), 3.5087(7) Å for 3; and 3.2688(7), 3.4236(7), 3.5048(7) Å for 4) are longer than the sum of the covalent radii (2.46 Å)^[11] but significantly shorter than the sum of the van der Waals radii (4.20 Å),^[12] suggesting the presence of P→Sn interaction. The relatively short distance of the Sn-P bond trans to the Sn-X bond (X = Cl, Br) would be attributed to the strong LP(P_{ax})- $\sigma^*(Sn-X)$ CT interaction. The other two Sn-P bonding interactions could be formed by LP(P_{ea})- σ^* (Sn-C) CT, but one Sn-P_{ea} distance for ca. 3.41 Å is significantly shorter than that for ca. 3.51 Å. This is probably because two phosphine donors around the opposite coordination site to ipso-carbons (Peg) are differently oriented; one slightly tilts downward and the other tilts upward as shown in Figures 2a and 2c. Accordingly, the lone pairs on the phosphorus atoms tilting upward are directed toward the regions of the $\sigma^*(Sn-C)$ orbitals of the Sn center, while that on the phosphorus tilting downward strays somewhat from the regions of the $\sigma^*(Sn-C)$ orbitals. Consequently, a smaller overlap would be found between this LP(P) and the $\sigma^*(Sn-C)$ orbitals, leading to the longer Sn-P distance.

Two Sn–C bonds (2.148(2) and 2.159(2) Å for **3**; 2.154(2) and 2.157(3) Å for **4**) participating in LP(P)– σ^* (Sn–C) interactions are longer than the other (2.134(2) Å for **3**; 2.136(3) Å for **4**), and the Sn–X (X = Br, Cl) bonds are slightly longer in **3** and **4** (2.3732(7) Å for **3**; 2.5255(3) Å for **4**) than the corresponding halogenotriphenylstannanes Ph₃SnX (2.360 Å for X = Cl^[13a,13b]; 2.495 Å for X = Br^[13c]), suggesting that the LP(P)– σ^* (Sn–C) and LP(P)– σ^* (Sn–X) interactions weaken the corresponding Sn–C and Sn–X bonds. The sum of C–Sn–C angles in **3** and **4** are 346.58(15) and 347.19(17), respectively, and the C–Sn–X angles in **3** and **4** range from 96.47(7) to 108.56(6)°. Also, P_{eq}–Sn–X angles range from 74.8 to 107.7°, and two P_{eq} atoms as well as three *ipso*-carbons are roughly situated on one plane. Further, the P_{ax}–Sn–X angle is considerably large (157.9 for **3**; 158.6° for **4**), indicating



Figure 2. XRD structures of 3 and 4 with thermal ellipsoids set at 40% probability. H atoms and phenyl groups except the *ipso*-carbons are omitted for clarity. a) side view of 3. b) top view of 3. c) side view of 4. d) top view of 4.

Table 1. Selected Distances (Å) and Angles (°) of 3, 4 and 5.					
V	3 (X = Cl)	4 (X = Br)	5 (X = I)		
Sn1-C1 (Å)	2.134(2)	2.136(3)	2.176(6)		
Sn1-C19 (Å)	2.148(2)	2.154(2)	2.148(6)		
Sn1-C37 (Å)	2.159(2)	2.157(3)	2.181(5)		
Sn1-P1 (Å)	3.3039(7)	3.2688(7)	3.265(2)		
Sn1-P2 (Å)	3.4119(7)	3.4236(7)	3.416(2)		
Sn1-P3 (Å)	3.5087(7)	3.5048(7)	3.4979(18)		
Sn1-X (Å)	2.3732(7)	2.5255(3)	2.7166(9)		
C1-Sn1-C19 (°)	112.55(8)	112.94(9)	117.5(2)		
C1-Sn1-C37 (°)	128.53(9)	128.59(10)	111.3(2)		
C19-Sn1-C37 (°)	105.50(9)	105.66(10)	110.9(2)		
X−Sn−P1 (°)	157.89(2)	158.570(16)	157.53(4)		
X-Sn-P2 (°)	74.75(2)	75.484(16)	80.19(4)		
X-Sn-P3 (°)	107.73(2)	107.727(14)	78.06(4)		

that ${\bf 3}$ and ${\bf 4}$ adopt a pentagonal bipyramidal geometry with a $P_{ax}\text{-}Sn\text{-}X$ axis.

Single crystals of the iodo analogue **5** were prepared from the slow diffusion of *n*-hexane into the dichloromethane solution (Figure 3). The crystal lattice includes the solvent molecules CH_2Cl_2 , which weakly interact with H atom in Ph group through one of Cl atoms (Figure S5). The structure of **5** is different from those of fluoro (1), chloro (3) and bromo (4) analogues. One of the phosphine donors is located at the position *trans* to the iodo atom, and two of the phosphine donors are situated at the position *trans* to the *ipso*-carbons. Although these geometrical features are similar to those of

3 and 4, both phosphine donors trans to the ipso-carbons tilt downward unlike in 3 and 4 (Figure 3a). Accordingly, both lone pairs on the phosphorus atoms are directed toward the regions of the $\sigma^*(Sn-C)$ orbitals, presumably giving rise to a substantially large orbital overlap between LP(P) and $\sigma^*(Sn-C)$ orbitals. The three Sn-P distances (3.265(2), 3.416(2), and 3.4979(18) Å) are significantly shorter than the sum of the van der Waals radii (4.20 Å),^[12] suggesting the presence of $P \rightarrow Sn$ interactions. Similar to 3 and 4, the Sn-P distance trans to the Sn-I bond is the shortest among the three Sn-P distances, which would be attributed to the strong LP(P) $\rightarrow \sigma^*(Sn-I)$ CT interaction. The two Sn-C bonds (2.176(6) and 2.181(5) Å) in 5 trans to the phosphine donors are longer than the other Sn-C bond (2.148(6) Å), and the Sn-I bond (2.7166(19) Å) is somewhat elongated in comparison with that in Ph₃SnI (2.704 Å).^[14] These results support the presence of $P \rightarrow \sigma^*(Sn-I)$ and $P \rightarrow \sigma^*(Sn-C)$ interactions. The sum of the three C-Sn-C angles (339.7(3)°) in 5 is significantly less than those of fluoro (1), chloro (3), and bromo (4) analogues (358.32(5)° for 1: 346.58(15)° for 3; 347.19(17)° for 4), indicating that the SnC₃I core in 5 adopts a less-distorted tetrahedral geometry despite the presence of LP(P) $\rightarrow \sigma^*(Sn-I)$ and LP(P) $\rightarrow \sigma^*(Sn-C)$ interactions.





Recently, Wagler and Bhargava reported that heptacoordinate tin chloride {(o-Ph₂P)C₆F₄}₃SnCl, in which the o-(Ph₂P)C₆H₄ in **3** was replaced with o-(Ph₂P)C₆F₄, adopted a similar geometry to the iodo analogue **5** but not to that of **3**.^[3e] Possibly, the acceptor ability of (Ph₂P)C₆F₄ which is better than that of o-(Ph₂P)C₆H₄ may be responsible for the formation of the geometry due to the large orbital overlaps between LP(P) and $\sigma^*(Sn-C)$ orbitals.

The signal in the ¹¹⁹Sn{¹H} NMR spectrum of **3** appears at δ = -121 ppm, which is at somewhat lower frequency than those of Ar₃SnCl derivatives (Ar = Ph (δ = -44.8 ppm), Ar = o-MeO-C₆H₄ (δ = -56.7 ppm), and Ar = 2,4,6-Me₃C₆H₂: (δ = -84.4 ppm)).^[13,15] On one hand, the ¹¹⁹Sn{¹H} NMR chemical shifts of **4** (δ = -126.6 ppm) and **5** (δ = -177.2 ppm) are within the ranges observed in those of Ar₃SnBr (Ar = Ph (δ = -60.0 ppm), Ar = o-MeO-C₆H₄ (δ = -74.3 ppm), Ar = 2,4,6-Me₃C₆H₂: (δ = -121.0 ppm))^[13c,15] and Ar₃SnI (Ar = Ph (δ = -113.4 ppm), Ar = o-MeO-C₆H₄ (δ = -135.7 ppm), Ar = 2,4,6-Me₃C₆H₂: (δ = -217.1 ppm)),^[13c,14,15] respectively.^[16] These results are contrast with the ¹¹⁹Sn{¹H} NMR signal of **1** (δ = -164.5 ppm), which is at significantly lower frequency than those of Ar₃SnF

 $(\delta = -65 \text{ to } -85 \text{ ppm})$.^[13c, 17] The ³¹P{¹H} NMR spectrum showed one singlet around 0 ppm (δ = -1.2 ppm ($w_{1/2}$ = 15.6 Hz) for 3; δ = -2.2 ppm ($w_{1/2}$ = 10.6 Hz) for 4; δ = -3.1 ppm ($w_{1/2}$ = 11.9 Hz) for 5 in a 4/1 mixture of THF- d_8 and toluene- d_8) (Figure S1 in ESI). At a low temperature (-80 °C), one broad singlet was observed around 0 ppm (δ = -1.5 ppm (w_{1/2} = 109.7 Hz) for **3**; δ = -3.7 ppm (w_{1/2} = 80.3 Hz) for 4; $\delta = -5.3$ ppm (w_{1/2} = 67.5 Hz) for 5), indicating the presence of fast site exchange due to the rotation of orthodiphenylphosphinophenyl groups. Previously, the similar site exchange was reported to take place more smoothly in {o-(Ph₂P)C₆H₄}₃GeF than in the Si analogue because the longer Ge-C bonds than the Si-C bonds facilitate the rotation of orthodiphenylphosphinophenyl groups.[6b] Similarly, the longer Sn-C bonds may be responsible for the faster site exchange in 3 to 5 over NMR time scale. Further, the presence of an equilibrium including other isomers may contribute to the broadening of the signals.

To understand deeply the effect of the halogen substituent in $\{o-(Ph_2P)C_6H_4\}_3SnX$ (X = F, Cl, Br, I, H) on their geometries, DFT calculations were carried out in a series of heptacoordinate species 1 to 5 and for their possible isomers, namely four types of geometrical arrangements around the central Sn, **a**, **b**, **c**, and **d** forms (see Tables S4-S5 and Figures S6-S10 in the ESI);

a form: Three phosphine donors interact with the tin center through the same coordination site involving antibonding orbital of the Sn-X bond (type V in Figure 1).

b and **c** forms: One phosphine coordinates at the position *trans* to the Sn–X bond and two phosphines coordinate around the opposite coordination site to the Sn–C_{*ipso*} bond. SnC₃ fragment in **b** form builds parts of pentagonal planar (type III), while the SnC₃ fragment in **c** form adopts the tetrahedral geometry with a very small deviation (type IV).

d form: Three phosphine donors coordinate to the tin center at different position *trans* to the Sn–C_{*i*pso} bond (type I)).

For example, with 1, although the **a** form was observed in a solid phase, we obtained the optimized structures of **1a-1d** to investigate the relative stability and understand its origin. We herein employed PBE-D3 level of theory (SDD for Sn and I; 6-311G* for C and P; 6-31G* for H (except for Hydride); 6-311+G* for F, Cl, Br, Hydride), which well reproduced the key geometries such as Sn-P distances in the X-ray structures of **3b**, **4b**, and **5c** (Table S4 in the ESI).

Gibbs energies relative to **d** (in CH_2CI_2) form are displayed in Table 2 (the data in other solvents and in gas phase are shown in Table S6 in the SPI), and data for (LP(P)- $\sigma^*(Sn-X)$ (X = F, CI, Br, I, H) and LP(P)- $\sigma^*(Sn-C)$) donor-acceptor interactions are listed in Table 3. In H analogues, the rotation of phosphine arms in **2d** provides little stabilization; the stability of **2d** is comparable to other isomers **2a-2c**. This is consistent with the absence of significant donor-acceptor interactions in **2a-2c**. In contrast, the phosphine rotation starting from **d** form provides significant stabilization in halogen systems, and **a-c** forms are significantly more stable than the **d** form. This is attributed to the presence of significant donoracceptor interactions between the lone pair of phosphine and the anti-bonding orbital of the Sn-X bond.^[18] Forms **b** and **c** resulting from one phosphine arm are energetically comparable in all systems, which is consistent with comparable CT interactions

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Table 2. Relative stabilities for four forms. Gibbs energies relative to that of d form are given (in CH_2CI_2 (PCM); kcal/mol).					
Ar ₃ SnX ^[a]	a form	b form	c form	d form	
1 (X = F)	−10.6 (1a)	−4.5 (1b)	-4.0 (1c)	0.0 (1d)	
3 (X = CI)	-8.4 (3a)	-4.7 (3b)	-3.6 (3c)	0.0 (3d)	
4 (X = Br)	−7.7 (4a)	-4.2 (4b)	-4.0 (4d)	0.0 (4d)	
5 (X = I)	−7.5 (5a)	-4.9 (5b)	-4.7 (5c)	0.0 (5d)	
2 (X = H)	1.2 (2a)	3.6 (2b)	2.1 (2c)	0.0 (2d)	

[a] $Ar = o - (Ph_2P)C_6H_4$.

Table 3. Intramolecular donor-acceptor interactions of the lone pair of the
phosphine with the σ^* antibonding MOs of Sn–X and Sn–C bonds (kcal/mol),
which were calculated by NBO analyses (second-order perturbation) $[a]$



1 (X = F)	<i>P</i> = P2	7.7	2.6	3.2	2.6
	<i>P</i> = P3	7.5	0.5	2.7	2.5
	<i>P</i> = P1	9.8	21.2	20.8	4.7
3 (X = CI)	<i>P</i> = P2	9.9	3.7	3.5	3.7
	<i>P</i> = P3	9.2	0.7	3.4	1.7
	<i>P</i> = P1	10.2	14.2	12.5	4.9
4 (X = Br)	<i>P</i> = P2	10.4	4.3	4.9	3.4
	<i>P</i> = P3	9.7	0.6	3.8	1.7
	<i>P</i> = P1	8.2	17.5	17.3	4.1
5 (X = I)	<i>P</i> = P2	8.3	4.6	4.4	3.6
	<i>P</i> = P3	7.9	0.5	3.9	3.8
	<i>P</i> = P1	2.0	3.9	3.6	3.6
2 (X = H)	<i>P</i> = P2	2.0	3.7	3.6	3.7
	<i>P</i> = P3	1.9	_[c]	3.6	3.7

[a] Although each $P \rightarrow Sn$ interaction includes several $LP(P) - \sigma^*(Sn-C)$ interactions in a similar way to the previously reported analysis on 1 and $\mathbf{2}_1^{[6a]}$ trans $P \rightarrow \sigma^*(Sn-X)$ and $P \rightarrow \sigma^*(Sn-C)$ interactions play key roles for the geometry changes. Therefore, only this donor-acceptor interaction per $P \rightarrow Sn$ interaction is mentioned here. [b] Ar = σ -(Ph₂P)C₆H₄. [c] Not detected.

observed in **b** and **c** forms. Although the **a** form resulting from the rotation of the three phosphine arms is the most stable in all halogen systems, the stability of **a** form may be overestimated if the solid-state structures of **3b**, **4b**, and **5c** are considered. In addition, we could not rule out the possibility that the packing effects reflected the form observed in the solid-state.

×	d (Å)	X = F	X = CI	X = Br	X = I	X = H
Sn	2.0	+0.102	+0.103	+0.097	+0.095	+0.070
d T	2.5	+0.059	+0.060	+0.056	+0.054	+0.036
	3.0	+0.039	+0.040	+0.038	+0.036	+0.023
		10-			-	

Figure 4. Electrostatic potential of $\{(o-H)C_6H_4\}_3Sn(X)$ (X = F, Cl, Br, I, H) at the position *trans* to the Sn-X bond.

Secondly, we investigated the electrostatic potential at the position *trans* to the Sn-X bond (Figure 4). In the regions *trans* to the Sn-X bond, the electronic potential is more positive in the halogen systems (1, 3-5) than in the hydrogen system (2). Hence, the electrostatic effect would also be an important factor for stabilizing **a-c** forms containing the LP(P)- $\sigma^*(Sn-X)$ interaction (X = F, Cl, Br, I).

Next, we investigated the effect of the electronegative character of a halogen atom^[19] on the sp hybridization of the central Sn. According to Bent's rule, the highly electronegative X atom enhances the p character of Sn in the Sn–X bond and increases the s character of the Sn in the Sn–C bond,^[20] accordingly causing large C–Sn–C angles. Wharf et al. reported that the s character of Sn in the Sn–C bond in Ph₃SnX (X = F, Cl, Br, I) increases in the order (H) < I < Br < Cl < F through the ¹J_{Sn–C} coupling constant and the geometrical features such as the sum of the three C–Sn–C angles.^[136,21] These results indicate that a higher electronegative halogen is expected to facilitate the formation of a more distorted geometry from a tetrahedral one around the tin center.

As shown in Table 4, the sum of C-Sn-C angles increases in the order **d** form < **c** form < **b** form < **a** form, and the average of C-Sn-X angles (X = F, Cl, Br, I, H) decreases in the order **d** form > **c** form > **b** form > **a** form for all systems. These calculations may indicate that the relative stabilities of these forms are mainly explained by the hybridization of tin, which is caused by X, rather than CT interaction and electrostatic effect. The potential energy of Ph₃SnX (X = F, Cl, Br, I, H) was found to strongly depend on the geometric environment around the tin center (Figure 5). For

Table 4. Sum of three C-Sn-C angles and average of three C-Sn-F angles in $\{o-(Ph_2P)C_6H_4\}_3SnX$ (X = F (1), Cl (3), Br (4), I (5), H (2)) and their isomers.

А	r₃SnX ^[a]	a form	b form	c form	d form
1 (X = F)	∑(CSnC)	358.4	350.0	342.5	334.5
	ave. (CSnF)	94.3	100.7	104.1	107.4
3 (X = Cl)	∑(CSnC)	357.3	349.1	341.2	316.6
	ave. (CSnCl)	95.4	101.0	104.6	113.3
4 (X = Br)	∑(CSnC)	357.9	348.7	340.2	315.1
	ave. (CSnBr)	95.9	101.3	105.0	113.8
5 (X = I)	∑(CSnC)	356.2	347.4	339.2	315.8
	ave. (CSnI)	96.5	101.8	105.4	113.4
2 (X = H)	∑(CSnC)	351.5	337.3	327.6	322.1
	ave. (CSnH)	99.8	106.2	109.7	112.4

[a] $Ar = o-(Ph_2P)C_6H_4$.

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Figure 5. Potential energy of Ph_3SnX (X = F, Cl, Br, I, H) for which the average C-Sn-X angle in the optimized structure of Ph_3SnX has been progressively diminished to 90°.

example, the potential energy of Ph₃SnF increases when the average of the three C-Sn-F angles (104.7° in optimized geometry of Ph₃SnF) decreases in the order 1.0 kcal/mol (av. 100.7°) > 3.7 kcal/mol (av. 96.7°) > 8.3 kcal/mol (av, 92.7°) > 12.6 kcal/mol (av. 90°). Similarly, the potential energy of Ph₃SnX (X = CI, Br, I, H) increases with decreasing C-Sn-X angles, and the destabilizations increase in the order Ph₃SnF << Ph₃SnCl < Ph₃SnBr ≈ Ph₃Snl < Ph₃SnH. Accordingly, the highly electronegative halogen alleviates the destabilization induced by the distortion around the tin atom. This factor is, at least partially, responsible for the structural modification by changing the halogen substituent.

Conclusions

We demonstrate the preparation of heptacoordinate bromo- (4) and iodostannane (5) compounds featuring three $P \rightarrow Sn$ interactions. Introduction of a different halogen at the tin center significantly influences the heptacoordinate geometry in solid state. As previously reported, fluorostannane (1) adopts a C_3 symmetric geometry, in which three phosphine donors interact with one $\sigma^*(Sn-F)$ orbital, while the other halogeno analogues adopt a C_1 symmetric geometry. The chloro (3) and bromo (4) analogues have a distorted pentagonal bipyramidal geometry, and the iodo analogue (5) adopts a tri-capped tetrahedral geometry. The intramolecular donor-acceptor interaction, the electrostatic interaction, and the hybridization of the tin center (Bent's rule) would be important factors for changes in geometry.

Experimental Section

General procedures. All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Benzene- d_6 , toluene- d_6 , tetrahydrofuran- d_8 , and diethylether were dried over sodium benzophenone ketyl and distilled under a dinitrogen atmosphere. Tetrahydrofuran, and *n*-hexane were purified using a two-column solid-state purification system. Chloroform-d and dichloromethane were dried

over P_2O_5 and stored over 4-Å molecular sieves. The other reagents used in this study were purchased from commercial sources and used without further purification. ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra were recorded with a JEOL JNM-AL 400 spectrometer. The ¹H and ¹³C{¹H} NMR data were analyzed with reference to the residual peaks of the solvent, and ³¹P{¹H} NMR chemical shifts were referenced to an external 85% H₃PO4 (0 ppm) sample. Elemental analyses were conducted using a J-Science Lab JM-10 or FISONS Instrument EA108 elemental analyzer. {o-(Ph₂P)C₆H₄)Li-Et₂O^[8o] was prepared as described in the literature.

Preparation of {o-(Ph2P)C6H4}3Sn(CI) (3). A Schlenk tube was charged with 45.1 µL of SnCl4 (0.386 mmol) and 5 mL of toluene, and the solution was cooled to -78 °C. 8 mL toluene solution of {o-(Ph2P)C6H4}Li·Et2O (413 mg, 1.21 mmol) was added slowly to the prepared reaction solution, and the mixture was then allowed to warm to room temperature. The reaction mixture was stirred at ambient temperature for 15 h. After the resulting solution was filtered through a Celite pad, the volatile materials were then removed under reduced pressure to give a white solid. The residue was washed with hexane (5 mL × 2) and toluene (3 mL × 2) and dried under vacuum to afford 3 (49.1 mg, 0.0523 mmol) in 14% yield as a white powder. ¹H NMR (400 MHz, C_6D_6): δ 6.86–7.13 (m, 30H), 7.36–7.43 (m, 9H), 8.21–8.24 (m, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 128.1 (s), 129.7 (s), 133.2 (d, $J_{P-C} = 5.8 \text{ Hz}$, 133.3 (d, $J_{P-C} = 5.0 \text{ Hz}$), 133.4 (m), 135.2 (s), 137.4 (m), 137.6 (m), 143.5 (s), 157.0 (m). $^{119}\text{Sn}\{^{1}\text{H}\}$ NMR (149 MHz, CDCl_3): δ -121.4 (q, J_{P-}^{119} sn = 42.7 Hz). ³¹P{¹H} NMR (163 MHz, C₆D₆): δ -1.4 (s, J_{P-119Sn} = 42.7 Hz). Anal. Calc. for C₅₄H₄₂ClP₃Sn: C, 69.15; H, 4.51. Found: C, 68.87; H, 4.53.

Preparation of {o-(Ph2P)C6H4}3Sn(Br) (4). A Schlenk tube was charged with 920 mg of {o-(Ph2P)C6H4}Li·Et2O (2.69 mmol) and 10 mL of toluene, and the solution was cooled to -78 °C. SnBr₄ (115 μ L, 0.0876 mmol) was added slowly to the prepared reaction solution, and the mixture was then allowed to warm to room temperature. The reaction mixture was stirred at ambient temperature for 15 h. After the resulting solution was filtered through a Celite pad, the volatile materials were then removed under reduced pressure to give a white solid. The residue was washed with hexane (5 mL × 2), Et₂O (3 mL), and toluene (2 mL) and dried under vacuum to afford 4 (298 mg, 0.303 mmol) in 34% yield as a white powder. ¹H NMR (400 MHz, CDCl₃): δ 6.92-6.96 (m, 12H, Harom), 7.03-7.09 (m, 12H, Harom), 7.14-7.22 (m, 9H, Harom), 7.30-7.34 (m, 6H, Harom), 7.91-7.94 (m, 3H, Harom). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 128.2 (s), 128.2 (m), 129.0 (m), 129.7 (s), 133.3 (m), 135.2 (2), 137.5 (m), 138.0 (m), 143.5 (s), 156.1 (m). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ -1.3 (s, J_{P-}¹¹⁹Sn = 46.9 Hz). ¹¹⁹Sn{¹H} NMR (149 MHz, CDCl₃): δ -126.6 (q, J_{P-}^{119} sn = 46.9 Hz). Anal. Calc. for C₅₄H₄₂BrP₃Sn: C, 66.02; H, 4.31. Found: C, 66.18; H, 4.49.

Preparation of {o-(Ph₂P)C₆H₄}₃Sn(I) (5). A Schlenk tube was charged with 152 mg of {o-(Ph₂P)C₆H₄}₃SnBr (4) (0.155 mmol), 924 mg of Kl (5.57 mmol), and 15 mL of THF, and the reaction mixture was stirred at 80° C for 72 h. The volatile materials were then removed under reduced pressure, and the residue was extracted with benzene. After the solution was filtered through a Celite pad, the volatile materials were then removed under reduced pressure to give a white solid. The residue was washed with hexane (5 mL × 2) and dried under vacuum to afford **5** (121 mg, 0.118 mmol) in 76% yield as a white powder. ¹H NMR (400 MHz, CDCl₃): δ 6.92-6.98 (m, 12H, H_{arom}), 7.07-7.11 (m, 12H, H_{arom}), 7.14-7.22 (m, 9H, H_{arom}), 7.25-7.29 (m, 6H, H_{arom}), 7.91-7.94 (m, 3H, H_{arom}). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ -1.7 (s, J_{P-1}¹¹⁹Sn = 64.6 Hz). ¹¹⁹Sn{¹H} NMR (100 MHz, CDCl₃): δ 128.1 (s), 128.3 (t, J_{P-C} = 13.2 Hz), 129.4 (m), 129.7 (d, J_{P-C} = 5.8 Hz), 133.4 (m), 135.2 (s), 137.4 (m),

138.5 (m), 143.4 (s), 154.2 (m). Anal. Calc. for $C_{54}H_{42}IP_3Sn:$ C, 63.00; H, 4.11. Found: C, 62.74; H, 4.30.

Structure Determination by X-ray Diffraction. Single crystals suitable for X-ray diffraction analysis were obtained as described above. Diffraction intensity data were collected with a Rigaku/MSC Mercury CCD diffractometer at 200 K(2), and a semiempirical multi-scan absorption $^{\left[22\right] }$ correction was performed. The space groups were chosen based on the systematic absences in the diffraction data. The structures were solved using SIR97^[23] by subsequent difference Fourier synthesis, and refined by full matrix least-squares procedures on F². All nonhydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms were treated as idealized contributions and refined in rigid group model. All software and sources of scattering factors are contained in the SHELXL97 program package.[24] CCDC 1425640, 1425641, and 1425642 contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Density Functional Theory Calculations. Gaussian09 was employed for all calculations here.^[25] The geometry was optimized by the DFT method with the PBE-D3 functional in *C*₁ symmetry. For Sn and I atom, the Stuttgart–Dresden–Bonn (SDD) basis set attaching two additional d polarization functions^[26] was used with the corresponding effective core potentials (ECPs). Usual 6-311G(d,p) basis sets were employed for C, H, P, and usual 6-311+G(d,p) basis sets were employed for F, Cl, Br. Key geometric data for **3b**, **4b**, and **5c** agreed with the experimental values in the solid state (see Table S4 in the SPI). The polarizable continuum model (PCM)^[27] was used to calculate solvation free energies, where the gas-phase optimized geometries were employed. Thermal correction and entropy contributions to the Gibbs energy at 298.15 K were taken from the frequency calculation. Donor-acceptor interactions were analyzed by second-order perturbation theory in Natural Bond Orbital (NBO) method.^[28]

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Keywords: tin • heptacoordination • phosphorus • DFT calculation • X-ray analysis

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Entry for the Table of Contents

FULL PAPER



Structural studies were performed on heptacoordinate compounds of organotin halides $\{(o-Ph_2P)C_6H_4\}_3SnX \ (X = F (1), Cl (3), Br (4), I (5)) with three phosphine donors. Introduction of a different halogen at the tin center significantly influences the heptacoordinate geometry in solid state. The origin of these structural modifications was investigated by density functional theory (DFT) calculation.$

Heptacoordination

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Heptacoordinate Structures of Organotin Halides with Three Phosphine Donors: Halogen-Substituent Effect on Geometry