

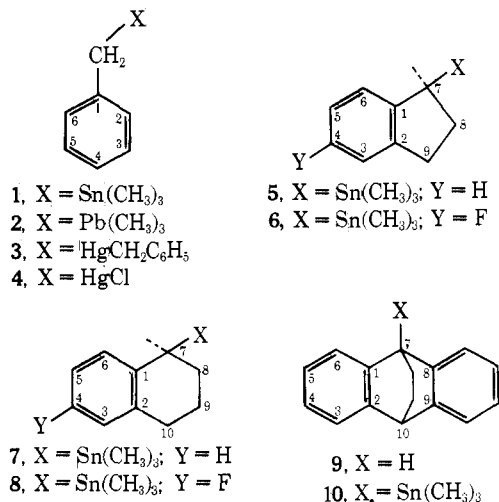
### Conformational Consequences of Metallo-Methyl Interactions. A $^{13}\text{C}$ Nuclear Magnetic Resonance Study

Sir:

Recently we conjectured that the relatively large five-bond carbon-tin coupling ( $^5J_{^{13}\text{C}-^{119}\text{Sn}}$ ) observed in benzyltrimethylstannane may be a manifestation of hyperconjugation involving the carbon-tin bond.<sup>1</sup> This proposal was based essentially on the observation that, whereas the relative magnitude of the coupling from  $^{119}\text{Sn}$  to aryl carbons in the phenyl system is  $J_{\text{meta}} > J_{\text{para}}$ , the order is reversed in the benzyl case. Further, in *p*-tolyltrimethylstannane where hyperconjugative effects (but not in principle *p*-*d* interactions) are inoperative,  $^5J_{^{13}\text{C}-^{119}\text{Sn}}$  was not observed.<sup>2</sup>

If our suggestion is correct then  $^5J_{^{13}\text{C}-^{119}\text{Sn}}$  should show a strong conformational dependence. Consequently, we have synthesized<sup>3</sup> and measured the  $^{13}\text{C}$  nmr spectra of a number of model benzylic tin compounds (5–10) in which the geometrical relationship of the C–Sn bond with respect to the adjacent aromatic system has been considerably varied.<sup>4</sup> Further, in order to test for the generality of the phenomenon, we have also examined three benzylic derivatives of lead and mercury (2–4).<sup>5</sup> Our data are assembled in Tables I and II. The assignments listed in Table I were based on methods recently outlined and thus require little comment.<sup>6–9</sup> However, it is worth noting that the  $^{13}\text{C}$  spectra of compounds 6 and 8, readily assigned on the basis of  $^{13}\text{C}$ – $^{19}\text{F}$  couplings,<sup>7</sup> were crucial for assigning the spectra of 5 and 7. In addition, Gunther and coworkers' "fingerprint"

method<sup>8</sup> was essential for distinguishing between  $\text{C}_3$ ,  $\text{C}_6$  and  $\text{C}_4$ ,  $\text{C}_5$  in compound 9.



Several conclusions follow from the results set out in the tables. In the first place, the pronounced increased shielding of the para shifts ( $\text{C}_4$ ) and the essential constancy of the meta shifts ( $\text{C}_3$ ,  $\text{C}_5$ ) for compounds 1–5 relative to the corresponding positions in the appropriate parent systems (ethylbenzene,<sup>6</sup> indan<sup>7</sup>), plus the fact that the para ( $\text{C}_4$ ) SCS for 10 ( $\theta = 0^\circ$ )<sup>4</sup> is zero (Table II), are completely in line with the established stereoelectronic requirements of a hy-

Table I.  $^{13}\text{C}$  Nmr Parameters<sup>a, b</sup>

Compound	X	Y	$\text{C}_1$	$\text{C}_2$	$\text{C}_3$	$\text{C}_4$	$\text{C}_5$	$\text{C}_6$	$\text{C}_7$	$\text{C}_8$	$\text{C}_9$	$\text{C}_{10}$
Chemical Shifts												
1	$\text{Sn}(\text{CH}_3)_3^c$		142.8	126.8	128.4	123.3						
2	$\text{Pb}(\text{CH}_3)_3^c$		143.5	126.2	127.7	122.8						
3	$\text{HgCH}_2\text{C}_6\text{H}_5$		145.3	128.0	128.4	123.1						
4	$\text{HgCl}^c$		141.2	128.5	128.3	124.7						
5	$\text{Sn}(\text{CH}_3)_3$	H	149.1	141.6	124.5	124.4	126.5	122.1	33.4	30.6	33.4	
6	$\text{Sn}(\text{CH}_3)_3$	F	144.5	143.8	111.6	160.7	113.1	122.5	32.2	31.1	33.6	
7	$\text{Sn}(\text{CH}_3)_3$	H	142.2	134.3	129.6	123.8	125.9	127.0	31.1	29.7	24.1	31.1
8	$\text{Sn}(\text{CH}_3)_3$	F	137.7	136.1	115.6	160.2	112.9	127.9	30.1	29.7	23.3	30.1
9	H		143.8	143.8	123.2	125.5	125.5	123.2	44.1	26.7	26.7	44.1
10	$\text{Sn}(\text{CH}_3)_3$		146.9	146.6	123.9	125.5 <sup>d</sup>	125.4 <sup>d</sup>	125.1	43.0	30.7	29.1	44.8
Coupling Constants ( $J_{^{13}\text{C}-\text{X}}$ )												
1	$^{117,119}\text{Sn}^e$		36.6	22.6	12.0	14.8						
2	$^{207}\text{Pb}$		64.6	44.2	26.4	32.4						
3	$^{199}\text{Hg}$			55.0	23.2	30.0						
4	$^{199}\text{Hg}$		151.2	110.0	50.6	62.4						
5	$^{117,119}\text{Sn}^e$		32.0	22.0	12.3	15.4	13.0	20.0	<i>f</i>	14	~8	
6	$^{117,119}\text{Sn}^e$		<i>f</i>	<i>f</i>	11.0	<i>f</i>	12.8	21.4	~340	<i>f</i>	<i>f</i>	
6	F		2.4	8.5	22.0	239.7	23.2	7.3	<i>f</i>	<i>f</i>	<i>f</i>	
7	$^{117,119}\text{Sn}^e$		34.5	24.6	13.2	15.7	14.0	22.4	~340	6.6	19.2	<i>f</i>
8	$^{117,119}\text{Sn}^e$		<i>f</i>	<i>f</i>	12.7	<i>f</i>	13.4	23.0	~340	<i>f</i>	19.6	<i>f</i>
8	F		2.8	6.20	20.8	241.7	20.8	7.3	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>
10	$^{117,119}\text{Sn}^e$		5.9	34.1	7.1	≥5	≥5	34.5	<i>f</i>	<i>f</i>	41.3	<i>f</i>

<sup>a</sup> Carbon-13 nmr spectra were obtained for 1–4 at 15.18 MHz and for 5–10 at 22.625 MHz, the latter in the Fourier transform mode. Samples were either neat or concentrated solutions in cyclohexane or chloroform-*d*. Chemical shifts referenced to TMS ( $\pm 0.1$  ppm). Positive values indicate decreased shielding relative to TMS. Coupling constants in Hertz ( $\pm 1.0$  Hz or better). <sup>b</sup> The carbon-numbering system is as shown on the structural formulas. <sup>c</sup> Assignments confirmed by examination of ortho-deuterated compounds. <sup>d</sup> Assignments could be reversed. <sup>e</sup>  $^{119}\text{Sn}$ ,  $^{117}\text{Sn}$  couplings not resolved. The  $\delta$  and  $J$  values for some of the nonring carbons will be reported in full later. <sup>f</sup> Not observed.

Table II.  $^{13}\text{C}$  Substituent Chemical Shifts (SCS)

Position	Compound						
	1	2	3	4	5	7	10
Meta ( $\text{C}_3$ , $\text{C}_5$ )	-0.2 <sup>a</sup>	+0.5 <sup>a</sup>	-0.2 <sup>a</sup>	-0.1 <sup>a</sup>	-0.1 <sup>b</sup>	-0.4 <sup>c</sup>	-0.7 <sup>d</sup>
Para ( $\text{C}_4$ )	+2.2 <sup>a</sup>	+2.7 <sup>a</sup>	+2.4 <sup>a</sup>	+0.8 <sup>a</sup>	+1.8 <sup>b</sup>	+1.4 <sup>c</sup>	0.0 <sup>d</sup>

<sup>a</sup> Relative to  $\text{C}_3$  and  $\text{C}_4$  in ethylbenzene. <sup>b</sup> Relative to  $\text{C}_3$ ,  $\text{C}_4$ , and  $\text{C}_5$  in indan. <sup>c</sup> Relative to  $\text{C}_3$ ,  $\text{C}_4$ , and  $\text{C}_5$  in tetralin. <sup>d</sup> Relative to  $\text{C}_3$ ,  $\text{C}_4$ , and  $\text{C}_5$  in compound 9.

perconjugative mechanism for the electron-releasing metal-methyl substituents.<sup>10,11</sup> This conclusion is based on good experimental evidence that for structurally similar compounds the chemical shift of C<sub>4</sub> is not influenced by steric, compressional, and related factors but reflects changes in local  $\pi$ -charge density.<sup>12</sup> The para (C<sub>4</sub>) <sup>13</sup>C SCS for **1**, **5**, and **7** (Table II) parallels the <sup>19</sup>F SCS (ppm) for *p*-fluorobenzyltrimethylstannane (2.60), **6** (2.14), and **8** (2.15).<sup>13</sup>

Secondly, the coupling constant data in Table I for entries **1-4** demonstrate the generality that <sup>5</sup>J<sub>C<sub>4</sub>-X is uniformly larger than <sup>4</sup>J<sub>C<sub>3</sub>-X for benzyl-metallic systems. That this phenomenon has its origin in carbon-metal ( $\sigma$ - $\pi$ ) hyperconjugation, and is a ground state property of some significance, is clearly exemplified by a comparison of the coupling data for compound **10** with the data for compound **5**. Note that in **10** where the dihedral angle ( $\theta$ ) is zero, <sup>5</sup>J<sub>C<sub>4</sub>-Sn is less than 5 Hz, whereas in **5** where  $\theta \approx 60^\circ$ , <sup>5</sup>J<sub>C<sub>4</sub>-Sn is 15.4 Hz! This striking result suggests that the long-range coupling is being determined predominantly by a  $\pi$ -electron contribution to the coupling mechanism which is enhanced when direct access to the tin s orbitals is possible via  $\sigma$ - $\pi$  interactions. Interestingly, the similar value of <sup>5</sup>J<sub>C<sub>4</sub>-Sn for **1** and **5** implies that the average or effective dihedral angle ( $\theta$ ) in the mobile monocyclic species ArCH<sub>2</sub>Sn(CH<sub>3</sub>)<sub>3</sub> must approach 60°. This was expected, for if C-Sn hyperconjugation is important, it must tend to increase this angle in order to maximize the resulting stabilization.<sup>14</sup></sub></sub></sub></sub></sub>

Finally, the similar values of <sup>5</sup>J<sub>C<sub>4</sub>-Sn for **7** (15.7 Hz) and **5** (15.4 Hz) indicate that the effective dihedral angle ( $\theta$ ) for the conformationally mobile tetralin system must also be  $\approx 60^\circ$ . This can only be achieved if the predominant conformation has the Sn(CH<sub>3</sub>)<sub>3</sub> group axially orientated.<sup>4</sup> The magnitude of the vicinal coupling constant <sup>3</sup>J<sub>C<sub>3</sub>-Sn (19.2 Hz) unambiguously confirms this conclusion.<sup>15</sup> These conclusions are strongly supported by the appropriate relative chemical shifts (<sup>13</sup>C and <sup>19</sup>F).</sub></sub>

Further studies on other model systems are in progress and these will be reported on shortly.

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- The conclusion is equivocal since a comparison of relative coupling constants in different systems through a different number of intervening bonds is highly questionable. Further, relative magnitudes can be complicated by the sign of the  $\sigma$  and  $\pi$  contributions to the coupling mechanism.
- All new compounds (**5-8**) gave satisfactory analyses, and their other properties (including their proton nmr spectra) were in accordance with the assigned structures.
- Model systems **5** and **9** have been successfully employed in other studies concerning the origin of the electronic effect of metallomethyl substituents (see ref 10a and 10b). An examination of Dreiding models indicates that the angle between the CCSn plane and the aromatic ring (dihedral angle  $\theta$ ) in the rigid systems **5** or **6** and **10** is approximately 60 and 0°, respectively. However, in **7** or **8** the alicyclic ring is potentially mobile, there being two possible conformations in which the Sn(CH<sub>3</sub>)<sub>3</sub> group can occupy either an equatorial ( $\theta \approx 30^\circ$ ) or an axial ( $\theta \approx 70^\circ$ ) position. A consideration of nonbonding interactions and hyperconjugative stabilizing interactions suggests the axial conformer should be favored.
- Sn, Pb, and Hg have magnetically active isotopes ( $I = \frac{1}{2}$ ) in natural abundance sufficient to give rise to easily detectable long-range spin coupling with <sup>13</sup>C.
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- Utilizing the correlation line generated between para <sup>13</sup>C SCS and  $\sigma^+$  (see ref 12e) the following approximate values of  $\sigma^+$  can be obtained: -CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub> (-0.4, ref 6), -CH<sub>2</sub>Sn(CH<sub>3</sub>)<sub>3</sub> (-0.45), -CH<sub>2</sub>Pb(CH<sub>3</sub>)<sub>3</sub> (-0.52), -CH<sub>2</sub>HgCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> (-0.50). On this correlation  $\sigma^+_{\text{OC}_6\text{H}_5} = -0.65$ . However, these  $\sigma^+$  values are significantly less than those derived from reactivity and charge transfer measurements. See W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, 92, 829 (1970).
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- The fluorine nmr spectra of **6** and **8** were measured in benzene with a Varian A56/60 operating at 56.4 MHz. The value for p-FC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Sn(CH<sub>3</sub>)<sub>3</sub> in cyclohexane was taken from a previous report; A. J. Smith, W. Adcock, and W. Kitching, *J. Amer. Chem. Soc.*, 92, 6140 (1970). The SCS quoted are upfield relative to *p*-fluoroethylbenzene, 5-fluorindan (ref 10c), and 6-fluorotetralin (ref 10c), respectively.
- The effective dihedral angle ( $\theta$ ) for mobile electron-deficient species, where presumably electronic demands on the C-Sn  $\sigma$ -bond are much larger than the neutral ground state (see ref 10b and 11), must therefore approach 90° (the most favored orientation for maximum  $\sigma$ - $\pi$  interactions).
- A Karplus relation has been established between <sup>3</sup>J<sub>C<sub>3</sub>-C<sub>3</sub>Sn and the dihedral angles ( $\phi$ ) about the C-C bond (see ref 9). When Sn(CH<sub>3</sub>)<sub>3</sub> is equatorial  $\phi$  is 180°, when Sn(CH<sub>3</sub>)<sub>3</sub> is axial  $\phi \approx 70^\circ$ . Note that in **10**, where  $\phi$  is 180°, <sup>3</sup>J<sub>C<sub>3</sub>-Sn is 41.3 Hz.</sub></sub>

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## Hot 1,4-Biradicals from the Photodecomposition of 3-Ethyl-2-propylthietane Vapor<sup>1</sup>

Sir:

Biradicals are important intermediates in the photochemical and thermal decompositions of many classes of compounds, including the cyclic ketones,<sup>2</sup> the cyclic azo compounds,<sup>3</sup> those alkanones with  $\gamma$ -hydrogen atoms,<sup>4</sup> and the cyclic ethers and thioethers.<sup>5</sup> In many of the photochemical studies of these systems it has been suggested that "hot" biradicals may be involved and the consequences of the vibrational and rotational disequilibrium which exists in such species has been a subject of great interest and some controversy.<sup>4c,d,e</sup>

3-Ethyl-2-propylthietane (EPT), prepared according to Searles, *et al.*,<sup>6</sup> was purified and separated into *cis* and *trans* isomers by preparative gas chromatography. Samples of pure *cis*-EPT or pure *trans*-EPT at pressures of 0.5 Torr were allowed to come to thermal equilibrium with mercury vapor at  $25.0 \pm 0.1^\circ$  and were illuminated with 253.7-nm