Solid-State and High-Resolution Liquid $^{119}$Sn NMR Spectroscopy of Some Monomeric, Two-Coordinate Low-Valent Tin Compounds: Very Large Chemical Shift Anisotropies

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Received May 12, 2000

High-resolution liquid- and solid-state $^{119}$Sn NMR spectroscopy was used to study the bonding environment in the series of monomeric, two-coordinate Sn(II) compounds of formula Sn(X)C$_6$H$_3$-2,6-Trip$_2$ (X = Cl, Cr(η$_5$-C$_5$H$_5$)(CO)$_3$, t-Bu, Sn(Me)$_2$C$_6$H$_3$-2,6-Trip$_2$; Trip = C$_6$H$_2$-2,4,6-i-Pr$_3$). The trends in the principal components of the chemical shift tensor extracted from the solid-state NMR data were consistent with the structures determined by X-ray crystallography. Furthermore, the spectra for the first three compounds displayed the largest $^{119}$Sn NMR chemical shift anisotropies (up to 3798 ppm) of any tin compound for which data are currently available. Relaxation time based calculations for the dimetallic compound 2,6-Trip$_2$H$_3$C$_6$Sn–Sn(Me)$_2$C$_6$H$_3$-2,6-Trip$_2$ suggests that the chemical shift anisotropy for the two-coordinate tin center may be as much as ca. 7098 ppm, which is as broad as the 1 MHz bandwidth of the NMR spectrometer.

Introduction

The use of $^{119}$Sn NMR spectroscopy has proven to be an invaluable structural probe in all areas of tin chemistry. A large body of data is now available which demonstrates that $^{119}$Sn NMR studies provide accurate, relatively easily obtainable information on the bonding to the tin atom. In many cases the most important spectroscopic parameter available from these studies is the value of the chemical shift ($\delta$). While much of the chemical shift data concern isotropic $^{119}$Sn shift values measured in solution, solid-state $^{119}$Sn NMR measurements usually afford more detailed information involving the $\delta_{11}$, $\delta_{22}$, and $\delta_{33}$ components of the nuclear shielding tensor, information that can provide considerably more insight into the bonding at tin. Monomeric, two-coordinate tin(II) compounds (e.g., SnR$_2$; R = alkyl,$^4$ aryl,$^5$ amide,$^6$ or alkoxide$^7$ groups) whose bonding is often more complex than that in tin(IV) compounds owing to the presence of a formally empty, nonbonding p-orbital and a stereochemically active lone pair (in an orbital that is mostly 5s in character) at the tin centers, are particularly amenable to solid-state $^{119}$Sn NMR investigation. Unfortunately, there are no such studies available for this important compound class. This may be due to the fact that monomeric compounds of this kind are not numerous and that they usually require careful handling owing to their extreme air and moisture sensitivity. Nonetheless, studies$^8$ on the related compounds such as R$_2$-

Results and Discussion

To better understand bonding and electronic structure in the series of compounds of formula SnX(C₆H₅)₂,2,6-Trip; illustrated schematically in Figure 1 where X = Cl, t-Bu, Cr(η⁵-C₅H₅)(CO)₃, and Sn(Me)₂(C₆H₃-2,6-Trip₂), ¹¹⁹Sn NMR data in both the liquid phase and the solid state were recorded. It is well-known that the isotropic liquid state ¹¹⁹Sn chemical shift δliq is sensitive to both valence and electronic structure. ¹,² For example, Sn(IV) compounds tend to be more shielded and resonate further to what is observed. Other explanations for the order of chemical shifts of the series with X = Cl, t-Bu, Cr(η⁵-C₅H₅)(CO)₃, and Sn(Me)₂(C₆H₃-2,6-Trip₂) and Ar – Sn – X bond angle θ determined by X-ray crystallography are summarized in Table 2.

Table 1. Summary of ¹¹⁹Sn Liquid State Chemical Shifts of 2,6-Trip₂H₃C₆H₃SnX (Trip = C₆H₃-2,4,6-i-Pr₃, X = Cl, Cr(η⁵-C₅H₅)(CO)₃, t-Bu, Sn(Me)₂C₆H₃-2,6-Trip₂)

<table>
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<th>X</th>
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<th>Reference</th>
</tr>
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<tr>
<td>Cl</td>
<td>793.4</td>
<td>10</td>
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<tr>
<td>Cr(η⁵-C₅H₅)(CO)₃</td>
<td>2,297.9</td>
<td>11b</td>
</tr>
<tr>
<td>t-Bu</td>
<td>1,904.4</td>
<td>11a</td>
</tr>
<tr>
<td>Sn(Me)₂C₆H₃-2,6-Trip₂</td>
<td>2856.9</td>
<td>11a</td>
</tr>
<tr>
<td>(Sn(µ-Cl)C₆H₅-2,6-Mes₂)₂</td>
<td>257.4</td>
<td>9</td>
</tr>
</tbody>
</table>

a Chemical shift of the tetravalent tin atom.

Since the HOMO–LUMO gap in group 14 carbene analogues increases with more electronegative substituents, a smaller contribution to the paramagnetic shielding is expected to produce a more upfield resonance (since paramagnetic effects augment the applied field). This consideration has been used to account for the higher field shifts for tin(II) amides and alkoxides.²,¹⁴,¹⁵ However, the observed isotropic chemical shift is not only a sum of paramagnetic and diamagnetic terms, but also a function of directionally dependent components.

In the absence of unusual averaging effects, the liquid-state shift is equal to the isotropic chemical shift, the average δiso = (δ₁₁ + δ₂₂ + δ₃₃)/3 of the three principal components δ₁₁, δ₂₂, and δ₃₃ of the chemical shift tensor. Here δ₁₁ and δ₃₃ label the downfield and upfield edges of the observed NMR spectrum in the solid state whereas δ₂₂ represents the frequency that corresponds to a singularity in the powder pattern where the spectral amplitude tends to infinity. Physically, these δiso values describe the shape of an ellipsoid in three dimensions in the principal axis system of the chemical shift tensor. This shape is related to the topology of the electronic wave function at the site of the nucleus and can therefore lead to details about chemical bonding. The size of and difference between δiso values for a particular site is a strong function of the symmetry and structure of the bonding environment. This structural dependence is illustrated by a comparison of shift tensor values for tetraphenyl tin, SnPh₄, and the already mentioned R₂SnSnR₂ (R = CH(SiMe₃)₂) dimer (which is dissociated to SnR₂ monomers in dilute solution) which have the values δiso = −117 ppm and +700 ppm, respectively. The relaxed tetrahedral environment at tin in SnPh₄ yields an axially symmetric powder pattern with δ₁₁ = −90 ppm and δ₂₂ = δ₃₃ = −130 ppm whereas the less symmetric environment in R₂SnSnR₂ generates δ₁₁ = +1600 ppm, δ₂₂ = +400 ppm, and δ₃₃ = +100 ppm, thereby affording an asymmetric powder pattern with record anisotropy γ = 3(δ₁₁ − δ₂₂)/2 = 1350 ppm.

Chemical Shift Trends in the Sn(X)C₆H₅-2,6-Trip₂ Compounds (X = Cl, Cr(η⁵-C₅H₅)(CO)₃, and t-Bu) and Related Species. The ¹¹⁹Sn solid-state NMR spectra shown in Figure 2a–c correspond to the mononuclear compounds in Figure 1 with X = Cl, Cr(η⁵-C₅H₅)(CO)₃, and t-Bu, respectively. The solid lines represent the actual experimental data while the dashed lines represent fits used to extract δiso values. The δiso values for these spectra and the spectra (not shown) for 2,6-Trip₂H₃C₆H₃Sn–Sn(Me)₂C₆H₃-2,6-Trip₂ and [Sn(µ-Cl)C₆H₅-2,6-Mes₂]₂ are included in Table 2 along with a calculation of the isotropic chemical shift and the Ar – Sn – X bond angle θ, C–Ar–Sn bond length rAr, and Sn–X bond length rX values obtained from X-ray data. It is important to note that the anisotropic chemical shift tensor values for the X = Sn(Me)₂C₆H₃-2,6-Trip₂ compound represent only the Sn(III) site with [δiso] = 257.4 ppm in Table 1. All attempts at obtaining solid-state data for the Sn(I) site failed, presumably, as discussed later, because the anisotropy γ is too large to measure by pulse-Fourier transform techniques at this field strength.

Although the trend in δiso values in Table 1 for the compounds in the series X = Cl, Cr(η⁵-C₅H₅)(CO)₃, and t-Bu is not obvious, the variation of each of the δiso components of the chemical

References

would expect appears to be consistent with back-bonding trends and X-ray measurements this assignment of the 11 and 33 directions shift tensor would be required. However, in the absence of such known dipolar coupling and the principal axis system of the shift tensor. With regard to the structure shown in Figure 1, orthogonality of the principal axis system of the chemical shielding or the minimum and maximum electron density along orthogonal directions in the principal axis system of the chemical shift tensor. Regarding the structure shown in Figure 1, which has both an empty p-orbital and lone electron pair, it is most likely that the 11 direction lies along the symmetry axis of the empty p-orbital whereas the 33 direction involves the hybrid orbital containing the lone electron pair. To be absolutely certain of the orientation of the principal axis system of the shift tensor in the molecular frame, either single crystal measurements or investigation of the relationship between a known dipolar coupling and the principal axis system of the shift tensor would be required. However, in the absence of such measurements this assignment of the 11 and 33 directions appears to be consistent with back-bonding trends and X-ray structural data. The structure in Figure 1 indicates essentially zero electron density along the 11 direction. Therefore, one would expect $\delta_{11}$ for these compounds to tend toward the bare nucleus value. The finite but large value for $\delta_{11}$, coupled with its variation in the order smallest to largest in the sequence $X = \text{Cl}, < \text{Cr}(\eta^3-C_5H_5)(CO)_3, < \text{t-Bu}$ can be explained by back-bonding. The filled nonbonding orbitals in the Cl ligand more efficiently overlap the p-orbital on tin than either the d-orbitals on the chromium in the $\text{Cr}(\eta^3-C_5H_5)(CO)_3$ moiety or any projection of C–C σ bond electron density from the t-Bu ligand. Of these three X ligands, Cl back-donates the most electron density to the tin, thus shielding the $^{119}\text{Sn}$ nucleus and causing the $\delta_{11}$ value to appear farther upfield. The same argument holds for the $\text{Cr}(\eta^3-C_5H_5)(CO)_3$ ligand in comparison to the t-Bu ligand since back-bonding orbital overlap is likely to be greater for the former moiety.\(^{2,18,15}\) The trend in $\delta_{33}$ values in order from largest to smallest as $X = \text{Cr}(\eta^3-C_5H_5)(CO)_3, > \text{t-Bu}, > \text{Cl}$, can be rationalized in terms of the variation of the Ar–Sn–X bond angle $\theta$. As $\theta$ decreases from 110.13° to 99.68° in Table 2, the hybrid orbital containing the lone pair gains more s character. This gain in s character at tin translates into increased shielding owing to the increased electron density at the $^{119}\text{Sn}$ nucleus. Thus the most shielded $\delta_{33}$ value of −165.1 ppm is observed for the most electronegative substituent $X = \text{Cl}$ since this compound has the narrowest interligand angle at tin. The narrowing of the angle is apparently caused by the tendency of the more electronegative ligands to attract the most p-character into the orbitals from the central element to which they are bound, thereby allowing the s-character of the lone pair to increase. Finally, the trend in $\delta_{33}$ values can be explained from the X-ray data and the structure in Figure 1. Since the direction of the $\delta_{33}$ components must be orthogonal to each other, $\delta_{32}$ must lie in the Ar–Sn–X plane and at an angle of 90° with respect to both $\delta_{11}$ and $\delta_{33}$. In other words, the $\delta_{32}$ component lies in the coordination plane of tin at a right angle to the $\delta_{33}$ component that is directed through the lone pair. From Table 2 it can be seen that both $\delta_{32}$ and $\chi$ decrease in the order $X = \text{Cr}(\eta^3-C_5H_5)(CO)_3, > \text{Cl}, > \text{t-Bu}$ which supports the suggestion that the direction of $\delta_{32}$ was at an angle of 90° to the 33 direction and close to the Sn–X bond direction in Figure 1. The correlation of $\delta_{32}$ with bond length is possibly easier to rationalize than the trends for $\delta_{11}$ and $\delta_{33}$. Here the increased bond length indicates that electron density will be depleted from around the metal center thus deshielding the $^{119}\text{Sn}$ nucleus and causing the $X = \text{Cr}(\eta^3-C_5H_5)(CO)_3$ compound to resonate farther downfield than the $X = \text{t-Bu}$ and Cl compounds. It is important to note that differing energy gaps corresponding to directionally dependent HOMO and LUMO’s as obtained from ab initio calculations, such as those performed on a family of singlet carbene molecules where similar trends are observed,\(^{17}\) would provide further insight into the observed trends in the $\delta_{33}$ components by carefully tracking both the paramagnetic and diamagnetic contributions to $\delta_{33}$.

Comparison of Liquid- and Solid-State Isotropic Shifts. It is interesting to compare $\delta_{\text{iso}}$ for each compound in Table 1 with $\delta_{\text{iso}}$ in Table 2 calculated from the $\delta_{\text{iso}}$ values and the magic angle centerband isotropic shift $\delta_{\text{mas}}$ in Table 2. The difference between $\delta_{\text{iso}}$ and $\delta_{\text{mas}}$ gives an estimate for the uncertainty of the powder pattern fitting routine due to linebroadening and noise in the spectral data. It is obvious from comparison that $\delta_{\text{iso}}$ is not equal to $\delta_{\text{mas}}$. Closer inspection of the data reveals that there is a ca. 5% difference between $\delta_{\text{iso}}$ and $\delta_{\text{mas}}$ values for both the $X = \text{Cr}(\eta^3-C_5H_5)(CO)_3$ and t-Bu compounds. In terms of the data sets shown in Figure 2, this 5% difference translates into a change in $\delta_{\text{iso}}$ values of less than four points. More bothersome, however, are the 17% and 35% difference between $\delta_{\text{iso}}$ and $\delta_{\text{mas}}$ for the Sn(II) sites in the {Sn(μ-Cl)C_6H_3-2,6-Mes}_2\^2 and X = Cl compounds respectively and the 19% difference for the Sn(III) site in the X = Sn(Me)\^2(C_6H_3-2,6-Trip)_2 compound. Barring incomplete averaging effects, chemical exchange, or unusual solvent effects, $\delta_{\text{iso}}$ should always equal $\delta_{\text{mas}}$. The 17% and 19% difference recognized in the dinuclear tin compounds could be due to any or all of these possibilities. These two dinuclear complexes also have two bulky aromatic ligands and are nearly twice the size of the other compounds, thus forcing the tumbling rate in solution to be slower. The decreased tumbling rate in the liquid could lead to incomplete averaging of the shift tensor components and yield a skewed

The 119 Sn solution NMR spectrum contains two peaks at ppm and

\[ ^{119}\text{Sn} \quad ^{117}\text{Sn} \]

Table 2. Summary of 119 Sn Solid-State NMR Data and X-ray Parameters in ArSnX Compounds (Ar = C₆H₄-2,6-Trip₂; X = Cl, Cr(n⁶-C₅H₅)(CO)₃, t-Bu, Sn(Me)₂C₆H₄-2,6-Trip₂)

<table>
<thead>
<tr>
<th>X</th>
<th>( \delta_{11} ) (ppm)</th>
<th>( \delta_{22} ) (ppm)</th>
<th>( \delta_{33} ) (ppm)</th>
<th>( \delta_{\text{iso}} ) (ppm)</th>
<th>( \delta_{\text{anis}} ) (ppm)</th>
<th>( \chi ) (deg)</th>
<th>( r_{1} ) (Å)</th>
<th>( r_{2} ) (Å)</th>
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<tr>
<td>Cl</td>
<td>3021</td>
<td>826</td>
<td>-165</td>
<td>1227</td>
<td>1176</td>
<td>99.68</td>
<td>2.409</td>
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<tr>
<td>Cr(n⁶-C₅H₅)(CO)₃</td>
<td>4426</td>
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<td>814</td>
<td>2187</td>
<td>3358</td>
<td>110.13</td>
<td>2.847</td>
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<tr>
<td>t-Bu</td>
<td>4994</td>
<td>697</td>
<td>697</td>
<td>1962</td>
<td>1829</td>
<td>101.79</td>
<td>2.228</td>
<td>2.211</td>
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<tr>
<td>Sn(Me)₂C₆H₄-2,6-Trip₂</td>
<td>781</td>
<td>111</td>
<td>58</td>
<td>317</td>
<td>263</td>
<td>119.3</td>
<td>2.891</td>
<td>2.201</td>
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<tr>
<td>{Sn(μ-C)C₆H₄-2,6-Mes₂}</td>
<td>1643</td>
<td>866</td>
<td>-259</td>
<td>750</td>
<td>-</td>
<td>-</td>
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</tr>
</tbody>
</table>

* Chemical shift tensor information for only the Sn(III) site.

Purcell technique gives \( T_{2} = 3.8 \) ms for the Sn(III) site at \( \delta_{\text{iso}} = +2856.9 \) ppm for the Sn(I) site at \( \delta_{\text{iso}} = +2856.9 \) ppm. An estimate of the size of the chemical shift anisotropy for the Sn(I) site can be made by assuming that \( T_{2} \) is governed by this anisotropy, a reasonable assumption for large, heavy molecules far from the extreme narrowing limit. This relaxation rate in terms of the 119 Sn gyromagnetic ratio \( \gamma \), magnetic field \( B_{0} \), correlation time \( \tau_{c} \), shift tensor elements \( \delta_{m} \), and the isotropic shift \( \delta_{\text{iso}} \) is given by

\[
\frac{1}{T_{2}} = \frac{2\gamma^{2}B_{0}^{2}r_{c}^{2}}{15}((\delta_{11} - \delta_{\text{iso}})^{2} + (\delta_{22} - \delta_{\text{iso}})^{2} + (\delta_{33} - \delta_{\text{iso}})^{2}) \times 10^{-12} \tag{1}
\]

where the \( 10^{-12} \) is a conversion factor between ppm and absolute shielding. Taking \( \delta_{\text{iso}} \approx \delta_{\text{iso}} \) from Table 1, \( T_{2} = 3.8 \) ms, and the \( \delta_{\text{iso}} \) values from Table 2 for the Sn(III) site gives \( \tau_{c} = 261 \) ns from eq (1). Using this \( \tau_{c} \) value along with \( T_{2} = 38 \) ms and \( \delta_{\text{iso}} = +2856.9 \) ppm for the Sn(II) site, the approximation of an axially symmetric shift tensor \( \delta_{22} = \delta_{33} \), and the definition of \( \delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3 \) allows calculation of \( \delta_{11} \) and \( \delta_{33} \) from eq (1) as +7589 ppm and +491 ppm, respectively. Although an axially symmetric tensor was assumed, these values are most likely accurate to within \( \pm 1000 \) ppm. Comparison of the anisotropy for these estimated components \( \chi = 7098 \) ppm with \( \chi = 3798 \) ppm for the X = C(CH₃)₃ compound, the widest powder pattern observed in this study, indicates that the Sn(I) pattern will be about two times wider or about 1.0 MHz, well beyond both the excitation bandwidth and detection limits of the pulsed NMR spectrometer. These limitations were seen by investigating the Sn(I) site in this compound using ¹H-¹¹⁹Sn cross polarization with the ¹¹⁹Sn rf carrier set to the isotropic +2856.9 ppm shift. The resulting spectrum was a 50 kHz wide Gaussian line, a width directly corresponding to the rf-excitation bandwidth of the NMR spectrometer. This result supports the existence of an extremely broad chemical shift powder pattern for the Sn(I) site in the 2,6-Trip₂H₆Sn-Sn(Me)₂C₆H₄-2,6-Trip₂ compound.

Conclusion

The \( \delta_{\text{anis}} \) components of the shift tensor in the series of compounds with \( X = \text{Cl, Cr}(n^{6-}\text{C}_{5}\text{H}_{5})(\text{CO})_{3} \) and t-Bu can be explained on the basis of chemical structure rather than electronegativity values of the substituents. It is this point which underscores the strength of solid-state NMR over liquid-state experiments where trends in chemical shift display no apparent correlation with structural data.

Acknowledgment.

We are grateful to the NSF for financial support. M.P.A. thanks The Packard Foundation for support.

IC000514Z