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Bonding and Metal-Atom Dynamics in Two Unique Sn(I)–Sn(III) Complexes

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Two recently reported tin complexes, which incorporate both Sn(I) and Sn(III) sites in their structure, have been examined by temperature-dependent ^{119}Sn Mössbauer effect (ME) spectroscopy. The distinct hyperfine parameters of the two sites make it possible to assign relative occupancies of the two sites (at 90 K) on the basis of the recoil-free fraction data extracted from the ME spectra. The temperature dependencies of the recoil-free fractions, elucidated from the ME spectra, show that the metal-atom dynamics are very similar for the two sites in the temperature range $90 < T < 150$ K.

Introduction

It has been shown recently that the reaction of LiMe or LiPh with Sn(Cl)Ar* (Ar* = C_6H_3-2,6(C_6H_2-2,4,6-Pr^i_3)$_2$) leads to the unsymmetric products **I**[1] and **II**[2] (eqs 1 and 2)

$$2\text{LiMe} + 2\text{Sn(Cl)Ar*} \rightarrow \underset{\textbf{I}}{\text{Ar*SnSnMe}_2\text{Ar*}} + 2\text{LiCl} \quad (1)$$

$$2\text{LiPh} + 2\text{Sn(Cl)Ar*} \rightarrow \underset{\textbf{II}}{\text{Ar*SnSnPh}_2\text{Ar*}} \leftrightarrows 2\text{Ar*SnPh*} + 2\text{LiCl} \quad (2)$$

in which there is a bond between divalent (formally Sn(I)) and tetravalent (formally Sn(III)) tin centers. Compounds of this type are quite scarce, and are limited to a handful of examples. At present, compounds **I**[1] and **II**[2] as well as Sn($SnPh_2$Ar*)$_2$[3] and Sn[Sn{C_6H_3-2,6(OEt)$_2$}$_3$][4] are the only structurally characterized species of this class that contain a tin that is both divalent and two-coordinate.[5] ^{119}Sn NMR spectroscopy [1,2,6] has shown that the signals of the divalent and tetravalent tin nuclei in compounds **I** and **II** occur at widely different (by more than 2600 ppm) chemical shifts because of their different magnetic environments. ^{119}Sn Mössbauer and NMR data provide complementary information on the structure of tin compounds in the solid state. However, the amount of Mössbauer data available for divalent, two-coordinate tin species is quite small.[7−9] We now report Mössbauer studies of **I** and **II**, and show that the tin sites are quite clearly distinguished by their isomer shift (IS) and quadrupole splitting (QS) parameters.

Experimental Section

Sample Preparation. Samples of the two organotin compounds examined in the present study, $C_{74}H_{104}Sn_2$ (**I**) and $C_{84}H_{104}Sn_2$ (**II**), were prepared as described in the literature, and their compositions were verified by NMR spectroscopy.[1,2]

^{119}Sn Mössbauer Effect (ME) Spectroscopy. The samples were received as powders in sealed ampules; they were transferred in an inert-atmosphere glovebox to standard O-ring-sealed plastic sample holders, and were immediately cooled to 78 K in liquid nitrogen. Samples for spectral analysis were transferred cold to a precooled cryostat, and subjected to ME spectroscopy as previously

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10.1021/ic050916c CCC: $30.25

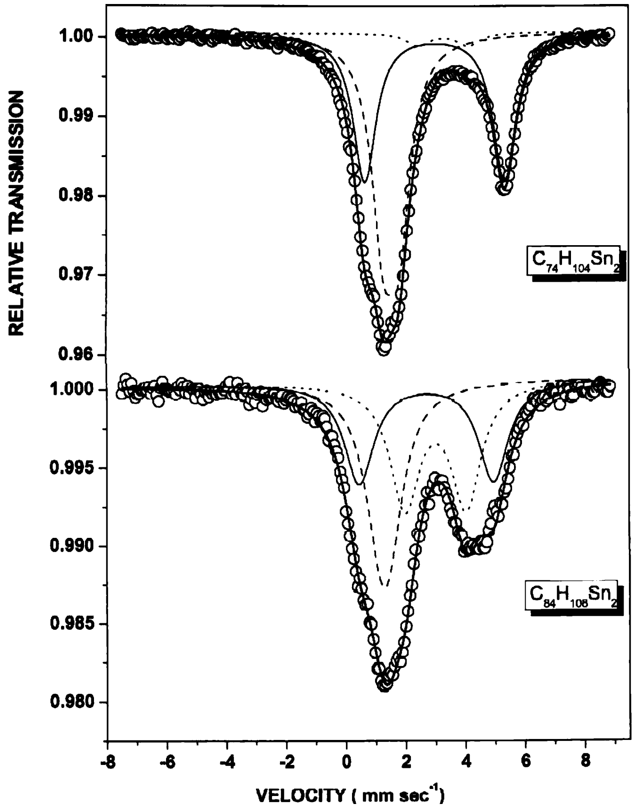

Figure 1. ^{119}Sn Mössbauer spectra of **I** ($C_{74}H_{104}Sn_2$) and **II** ($C_{84}H_{104}Sn_2$) at 92 K. The velocity scale is with reference to the centroid of a $BaSnO_3$ absorber spectrum at room temperature. The solid and dotted lines correspond to the two Sn(II) sites, whereas the dashed line traces the absorbance due to the Sn(IV) site.

Table 1. ^{119}Sn Mössbauer Parameters at 90 K of Compounds **I** and **II**

parameter	Sn oxidation number	parameter value[a] (mm s^{-1}) $C_{74}H_{104}Sn_2$ **I**	parameter value[a] (mm s^{-1}) $C_{84}H_{108}Sn_2$ **II**
IS (a)	II	2.70	2.70
QS (a)	II	4.50	4.50
IS (b)	IV	1.29	1.29
QS (b)	IV	0.32	0.32
IS (c)	II	3.00	3.00
QS (c)	II	2.05	2.05

	fractional area (%) $C_{74}H_{104}Sn_2$ **I**	fractional area (%) $C_{84}H_{108}Sn_2$ **II**
site a	44	30
site b	52	36
site c	3.8	34

[a] The fractional area assigned to each tin site at 90 K. The experimental standard deviations are +0.01 mm s^{-1} for compound **I** and +0.02 mm s^{-1} for **II**.

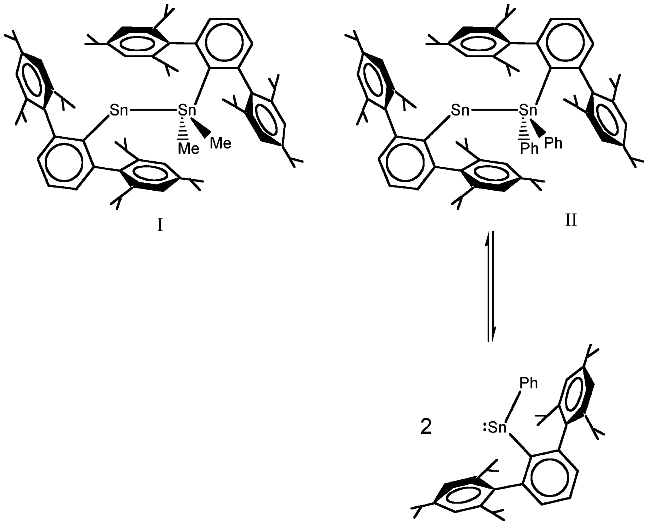

Figure 2. Schematic Drawings of **I** and **II**, and the equilibrium of **II** with its monomeric form.

described.[10] The rest of the samples were stored under liquid nitrogen until they were ready for examination.

ME spectroscopy was carried out in transmission geometry, using an ~5 mCi source of ^{119m}Sn in a $BaSnO_3$ matrix. Spectrometer calibration was effected using an α-Fe absorber at room temperature (^{57}Co in Rh source). All tin isomer shifts are reported with respect to the centroid of a $BaSnO_3$ absorber spectrum at room temperature. Data at each temperature point required 8−16 h to acquire (in excess of 10 × 10^6 counts per velocity channel), and temperature stability over this time interval is judged to be good to ±0.2°.

Results and Discussion

The ME spectra of both **I** and **II** clearly indicate the presence of three tin sites, with typical spectra summarized graphically in Figure 1, and 90 K values and parameters derived therefrom summarized in Table 1. The 92.6 K spectrum of **I** consists of two major tin resonances corresponding to a divalent site a and a tetravalent site b. In addition, there is a small second divalent site c, observable as shown in the figure. The a and b sites at 92.6 K constitute 44 and 52%, respectively, of the area under the resonance curve. Extrapolation of the recoil-free fraction data (vide infra) to 0 K yields a ratio in the low-temperature limit of approximately 1:1, in consonance with the molecular structure such as that shown in Figure 1 in ref 2 (see illustration in Figure 2), in which the Sn(1) atom corresponds to the divalent site a and Sn(2) to the tetravalent site b. The hyperfine parameters of the third (minor) site are indicative of divalent tin, but because of its small contribution to the total absorbance this site is not otherwise identified. Nonetheless, it is notable that the isomer shift (IS) and quadrupole splitting (QS) parameters for site c, 3.29 ± 0.01 and 1.69 ± 0.01 mm ss^{-1}, respectively, bear a resemblance to the 3.28 ± 0.06 and 1.90 ± 0.06 mm s^{-1} values reported[8] at 77 K for the Sn(II) diaryl Sn(C_6H_2-2,4,6-Bu^t_3)$_2$,[11] and to the 3.37 ± 0.03 and 1.90 ± 0.06 mm s^{-1} values reported for Sn{C_6H_3-2,6-(CF_3)$_2$}$_2$, respectively.[12] The similarity of the spectroscopic parameters suggests that site c involves a two-coordinate Sn(II) diaryl—possibly SnAr*$_2$.

Neither the IS value of the divalent a site nor that of the tetravalent b site is significantly temperature-dependent over the accessible range (92 < T < 170 K), and the shifts have average values of 3.00 ± 0.01 and 1.54 ± 0.01 mm s^{-1} K^{-1} for sites a and b, respectively; thus the second-order Doppler shift is not experimentally accessible. Clearly, the a site is

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identified with the Ar*−Sn− moieties of the molecule, whereas the b site resonance arises from the $-\mathrm{Sn(CH_3)_2}-$Ar* fragment.

The QS parameters of the two major tin sites are widely different, as expected, but they are not sensitive as a function of the temperature over the above range. That of the a site at 90 K corresponds to 4.68 ± 0.01 mm s^{-1}, whereas that of the b site is 0.53 ± 0.01 mm s^{-1}. As the extensive compilations of Zuckerman et al.[13] have shown, major contribution to the QS of the a site arises from the lone pair of electrons in the proximity of the Sn(II) atom. The QS of the b site is surprisingly small in terms of known tri-organo ligand structures, but there is little in the literature[14] here to serve as a guide to compounds in which such a fragment is ligated to a Sn(II) atom.

Turning next to the temperature dependence of the recoil-free fraction (f), which, for an optically thin absorber, scales directly with the area (A) under the resonance curve d/dT $\{\ln[A(T)/A(90)]\}$, it is interesting to note that the slope of the parameter $\ln[A(T)/A(90)]$ is only slightly different for the a and b sites, corresponding to $-(3.01 \pm 0.01) \times 10^{-2}$ and $-(2.76 \pm 0.01) \times 10^{-2}$ K^{-1}, respectively. The tetravalent tin atom, ligated to two methyl groups, is only slightly more firmly bound to the lattice than is the corresponding tin atom in the divalent site. Moreover, from this parameter, it is possible to calculate the mean-square-amplitude-of-vibration (msav) of the ME active atom, as $-k^2\langle x_{\mathrm{ave}}^2\rangle = \ln f$, where k is the wave vector of the ^{119}Sn gamma ray (23.88 keV) and has a value of 1.210×10^9 cm and $\langle x_{\mathrm{ave}}^2\rangle$ is the msav of the tin atom. This parameter will be discussed more fully below.

Although the ME parameters of **II** are very similar to those of **I**, there is a major difference in the spectra arising from the fact that the third site contributes nearly one-third of the total area under the resonance curve at 90 K. Again, the third site is clearly attributable to Sn(II), and its presence is readily understood in terms of the demonstrated monomer ↔ dimer equilibrium (eq 2 and Figure 2) discussed by Phillips, Hino, and Power[2] in connection with an NMR and crystallographic study of such complexes. In this context, one of the divalent tin sites can confidently be ascribed to the monomer Ar*SnPh, whereas the remaining two sites correspond to the divalent and tetravalent sites of the diphenyl-tin-containing dimer. As before, the ME hyperfine parameters are summarized in Table 1. In this context, it is interesting to note that the IS at 90 K of the Sn(IV) site in **I** and that in **II** are significantly different, compared to the reported isomer shifts of $\mathrm{Sn(CH_3)_4}$[15] and $\mathrm{Sn(Ph)_4}$,[16] which are identical within experimental error. It is plausible to assume that steric crowding due to the presence of the bulky Ar* ligand in **II** reduces the electron density in the Sn−ligand bonds, compared to their tetra-organo homologues in **I**. This reduction, because of the fact[17] that $\delta R/R$ is positive for ^{119}Sn, is reflected in the smaller IS of the tetravalent site in **II** compared to that of **I**.

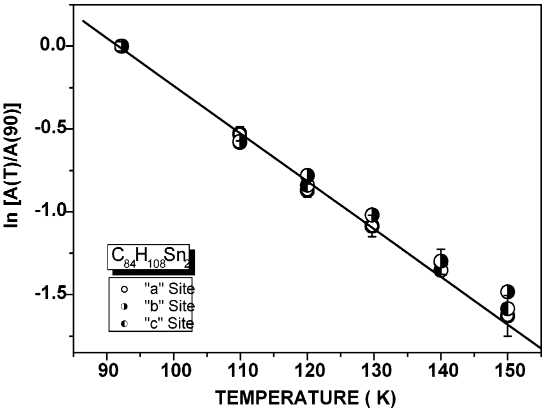

Figure 3. Temperature dependence of the recoil-free fraction of the three Sn atoms in **II**. This temperature dependence is identical (within experimental error) for the three tin sites over the indicated temperature range.

As noted above for **I**, the temperature dependence of the area under the resonance curve can be related to the temperature dependence of the vibrational amplitudes of the three tin sites. As shown in Figure 3, these are surprisingly similar, as indicated by the data there summarized, in which the slope of ln A versus T is identical for the three data sets within experimental error over the indicated temperature range ($92 \le T \le 170$ K). As noted above, this implies that the msav of the tin atoms in the three sites must be very nearly identical over the indicated temperature range. That this should be so in the presence of two phenyl groups around the Sn(IV) atom in the dimer compared to the Sn(II) site in the monomer, in which the metal atom is ligated to only one phenyl group, was unexpected. The limited temperature range over which the ME data could be acquired leaves open the question of whether this identity in the temperature dependencies holds true at higher temperatures.

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(12) The structural details of $\mathrm{Sn\{C_6H_3\text{-}2,6\text{-}(CF_3)_2\}_2}$ are unknown. However, crystal structures of the closely related $\mathrm{Sn\{C_6H_2\text{-}2,4,6\text{-}(CF_3)_3\}_2}$ showed that it could exist as a two-coordinate monomer with weak Sn−F interactions or as a weakly dimerized species having a very long Sn−Sn distance of 3.639(1) Å. See: Grützmacher, H.; Pritzkow, H.; Edelman, F. T. *Organometallics* **1991**, *10*, 23. Lay, U.; Pritzkow, H.; Grützmacher, H. *Chem. Commun.* **1992**, 260.

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