Stereochemical Nonrigidity and Ligand Dynamics in Hypervalent Tin(IV) Compounds. Heteronuclear NMR and Crystallographic Studies of Triorganoyltin(IV) and Diorganoyltin(IV) Complexes with Dithiolate Ligands

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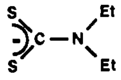
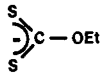
Tin-119, phosphorus-31, and carbon-13 NMR data have been used to examine the effective coordination spheres in dichloromethane solution of a series of triorganoyl- and diorganoyltin(IV) dithiolate compounds $R_3Sn(S–S)$ (where R = Ph, Me) and $R_2Sn(S–S)_2$ (where R = Ph, Me, ^{n}Bu, ^{t}Bu) for S–S = S_2CNEt_2, S_2COEt, and $S_2P(OEt)_2$ as well as diorganoyltin(IV) dithiolate halide complexes $R_2SnX(S–S)$ (R = Ph; X = Cl, Br; and R = Me, ^{n}Bu, ^{t}Bu; X = Cl). For $R_3Sn(S–S)$ compounds only dithiocarbamate (S–S = S_2CNEt_2) seems to behave as an actual bidentate sulfur ligand whereas for other systems intramolecular monodentate–bidentate dithiolate exchange is rapid at room temperature, with the equilibrium favoring bidentate sulfur coordination at low temperature for some systems. The effectiveness of dithiolates as chelate ligands becomes more evident in $R_2Sn(S–S)_2$ and in $R_2SnCl(S–S)$ derivatives. There is evidence that the dithiocarbamate ligand in $Ph_2SnCl(S_2CNEt_2)$ is bidentate and that the compound is five coordinate and stereochemically rigid in solution at −100 °C. A comparison of solid-state and solution NMR data indicates that in solution the dithiocarbamate ligand acts as a bidentate sulfur donor in $Me_2Sn(S_2CNEt_2)_2$ but only as a monodentate donor in $^{t}Bu_2Sn(S_2CNEt_2)_2$. The crystal structure of $^{t}Bu_2Sn(S_2CNEt_2)_2$ has been determined and is almost identical to the known structure of $Me_2Sn(S_2CNEt_2)_2$. In the structure of $^{t}Bu_2Sn(S_2CNEt_2)_2$ the Sn–S bond lengths are asymmetric (2.5 and 2.9 Å), but the overall stereochemistry suggests that the role of the two sulfur atoms of each chelate may be easily interchanged, possibly through a pseudooctahedral intermediate having the chelates symmetrically displaced. There is no evidence for any steric stress resulting from the ^{t}Bu groups, and consequently electronic influences are invoked to explain observed differences in stereochemical nonrigidity for various hypervalent tin(IV) systems in solution. The crystal structures of $^{t}Bu_2SnCl(S_2CNEt_2)$ and $Ph_2SnCl(S_2CNEt_2)$ have also been determined, and in each case there is asymmetric coordination by the sulfur atoms of the dithiolate ligand to tin.

Introduction

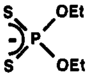
Each halide in R_3SnCl and R_2SnCl_2 can be simply replaced by ligands such as dithiolate anions S–S [where S–S = S_2CNEt_2 (Et_2dtc), S_2COEt (Et(xan)), $S_2P(OEt)_2$ (Et_2dtp)]. Effective coordination numbers between four and six can be contemplated for such series of complexes in the solid state, depending on whether the dithiolate ligands behave as monodentate or bidentate donors toward the tin atom. In solution the tin complexes may undergo dynamic processes such as intermolecular ligand exchange and intramolecular monodentate–bidentate dithiolate ligand exchange as well as molecular fluxionality. Furthermore, steric and electronic effects of the organoyl R group substituent at tin may also influence the stereochemistry of the hypervalent tin(IV) complex in solution.



Et_2dtc^-



$Etxan^-$



Et_2dtp^-

The solid-state structures of a number of triorganoyl-[3,4] and diorganoyltin(IV) dithiolate complexes[5-10] have been described. These structures are generally characterized by asymmetric coordination of the dithiolate to the tin atom (with a Sn–S distance spanning the range 2.5–3.2 Å) so that the coordination number of the tin atom may appear ambiguous, depending on the significance given to Sn–S distances which are longer than normal covalent bonds but shorter than the sum of the respective van der Waals radii. Accordingly, even within the fairly simple series derived from R_3SnCl, the structure of the resultant tin complex in the solid state may be either five-coordinate as in $Me_3Sn(Me_2dtc)$[3] or four-coordinate as in $Ph_3Sn(Et_2dtp)$.[4] In the diorganoyl series $Ph_2SnCl(^{i}Pr(xan))$[7] the tin atom is effectively five coordinate whereas in $Ph_2Sn(Et_2dtc)_2$,[5] $Ph_2Sn(Et_2dtp)_2$,[6] $Me_2Sn(Et_2dtc)_2$,[8] $Me_2Sn(Me_2dtp)_2$,[9] and $Me_2Sn(Et(xan))_2$[10] the tin atoms appear to be six coordinate in the solid state.

There is a paucity of data describing the stereochemistry of such hypervalent tin(IV) complexes in solution. Tin-119 NMR spectroscopy is a particularly sensitive probe for determination of the coordination environment of the tin atom in many of its complexes. In general tin-119 chemical shifts move to lower frequency with increasing coordination number. Although the shift ranges are somewhat dependent on the nature of the substituents at the tin atom, the following ranges have been proposed for some tin(IV) dithiocarbamato complexes: −150 to −250 ppm for five-coordinate compounds, −300 to −500 ppm for six-

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coordinate compounds, and −700 to −800 ppm for seven-coordinate compounds.[11-16] Furthermore, NMR spectroscopy is well-suited for studying dynamic processes such as inter- and intramolecular ligand exchange as well as stereochemical nonrigidity arising from fluxionality. As part of an ongoing study of dithiolate complexes of main group elements[17,18] and of the coordination chemistry of tin(IV) compounds,[19] we now report the results of a tin-119 NMR investigation of the formation in dichloromethane solution of three series of tin(IV) dithiolate complexes, $R_3Sn(S–S)$, $R_2SnX(S–S)$ (X = Cl, Br), and $R_2Sn(S–S)_2$. Solid-state ^{119}Sn NMR shifts are reported for selected cases. We also report the crystal structure determinations for $^tBu_2Sn(Et_2dtc)_2$, $^tBu_2SnCl(Et_2dtc)$, and $Ph_2SnCl(Et_2dtc)$.

Experimental Section

Preparations and Instrumentation. Tin-119 NMR spectra were recorded at 100.75 MHz with broad-band proton decoupling using a JEOL GX 270-MHz spectrometer and referenced against exernal Me_4Sn. Phosphorus-31 spectra were recorded at 109.38 MHz and referenced against external 85% phosphoric acid. Carbon-13 spectra were recorded at 67.94 MHz and referenced against internal TMS. Temperatures were maintained using a JEOL GTV3 control system. Solid-state ^{119}Sn NMR spectra were recorded by Dr. T. J. Bastow (CSIRO, Division of Materials Science and Technology) using a Bruker MSL 400 at 149.21 MHz. The pulse width was 2.5 μs, and spinning frequencies for magic angle spinning (MAS) ranged between 4.1 and 4.8 kHz. NMR investigations were generally on solutions of the complex prepared in situ by reaction of the organoyltin(IV) halide with appropriate mole ratios of the dithiolate ligands as the KEt_2dtc, NaEt(xan) or $NaEt_2dtp$ salts in dichloromethane solution. Tin-119 chemical shifts were not affected by changes in concentration over the range 0.05–0.25 M. Addition of excess dithiolate ligand had no effect on the tin-119 spectra. NMR spectra of pure isolated samples which were subsequently redissolved in dichloromethane were identical to spectra obtained on samples prepared in situ. Complexes were isolated by evaporation of the filtered dichloromethane solution, and the solid material was dissolved in dichloromethane followed by addition of ethanol to induce crystallization. Data for $Ph_2SnCl(Et_2dtc)$: mp 142–144 °C. Anal. Calcd for $C_{17}H_{20}ClS_2NSn$ C, 44.72; H, 4.41; N, 3.07. Found: C, 44.51; H, 4.40; N, 3.01. Data for $^tBu_2SnCl(Et_2dtc)$: mp 110–112 °C. Anal. Calcd for $C_{13}H_{28}ClNS_2Sn$: C, 37.48; H, 6.77; N, 3.36. Found: C, 37.10; H, 6.99, N 2.90. Data for $^tBu_2Sn(Et_2dtc)_2$: mp 105–106 °C. Anal. Calcd for $C_{18}H_{38}N_2S_4Sn$: C, 40.75; H, 7.23; N, 5.28. Found: C, 40.87; H, 7.34; N, 5.11.

X-ray Diffraction Studies. Summaries of crystal and intensity data for compounds $^tBu_2Sn(Et_2dtc)_2$, $^tBu_2SnCl(Et_2dtc)$, and $Ph_2SnCl(Et_2dtc)$ are reported in Table I.

All X-ray measurements were performed at room temperature on a Enraf-Nonius CAD4 diffractometer using Mo Kα radiation monochromatized with a graphite crystal. The cell parameters were determined by least-squares refinement of the setting angles of 25 randomly selected reflections. As a general procedure, three standard reflections were collected every 2 h (no decay of intensities was observed). Intensity data were corrected for Lorentz-polarization effects. Absorption corrections were determined by the azimuthal-scan method.[20] Atomic scattering factors are those reported[21] with anomalous dispersion corrections taken from ref 22. All structures were solved by the heavy atom technique. Refinement was by full-matrix least-squares calculations, initially with isotropic thermal parameters and in the final cycles with anisotropic parameters for all the non-hydrogen atoms. The nonaromatic hydrogen atoms were found from difference Fourier maps, and their positional and isotropic parameters were successfully refined. In the refinement of $Ph_2SnCl(Et_2dtc)$ each phenyl ring was treated as a rigid body (C–C distances 1.39 Å) and all hydrogen atoms were introduced at calculated positions (C–H = 0.95 Å). The final refinement cycles were performed using the weighting scheme $w = k/(\sigma^2(F) + \rho F^2)$ (ρ values of 0.001 gave the smallest variations of the mean value of $w(F_o - F_c)^2$ for all structures). Final Fourier maps were featureless in all cases.

Table I. Summary of Crystal Data for $^tBu_2Sn(Et_2dtc)_2$ (**1**), $^tBu_2SnCl(Et_2dtc)$ (**2**), and $Ph_2SnCl(Et_2dtc)$ (**3**)[a]

	1	2	3
formula	$C_{18}H_{38}S_4N_2Sn$	$C_{13}H_{28}S_2NClSn$	$C_{17}H_{20}S_2NClSn$
fw	529.46	416.65	456.63
space group	*P*2/*n* (No. 13)	*P*2/*c* (No. 13)	$P\bar{1}$ (No. 2)
a/Å	10.033 (1)	18.629 (2)	9.272 (1)
b/Å	6.920 (2)	6.864 (3)	12.415 (1)
c/Å	18.301 (1)	31.614 (3)	9.234 (1)
α/deg			92.30 (1)
β/deg	98.53 (1)	106.14 (1)	116.85 (1)
γ/deg			91.14 (1)
V/Å^3	1256.55	3833.13	946.72
Z	2	8	2
T/K	296	296	296
d_{calc}/(g cm^{-3})	1.40	1.42	1.60
μ/cm^{-1}	13.44	16.54	17.04
λ/Å	0.710 69	0.710 69	0.710 69
R	0.021	0.045	0.025
R_w	0.023	0.051	0.028

[a] The agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum(w|F_o| - |F_c|)^2/\sum|F_o|^2)^{1/2}$.

Table II. Tin-119 Chemical Shifts for Some Triorganoyltin(IV) Dithiolate Complexes in Dichloromethane Solution at 25 °C

species	δ(^{119}Sn)	species	δ(^{119}Sn)
Ph_3SnCl	−46	Me_3SnCl	172
$Ph_3Sn(Et_2dtc)$[a]	−192	$Me_3Sn(Et_2dtc)$	21
$Ph_3Sn(Et(xan))$	−103	$Me_3Sn(Et(xan))$	80
$Ph_3Sn(Et_2dtp)$[b]	−82	$Me_3Sn(Et_2dtp)$[c]	114 ($w_{1/2}$ = 2000 Hz)

[a] Reference 11 quotes a value of −191 ppm in $CDCl_3$. [b] δ(^{31}P) = 92.4 ppm, *J*(Sn–P) = 40 Hz. [c] δ(^{31}P) = 96.1 ppm. At −100 °C δ(^{119}Sn) = 118 ppm, *J*(Sn–P) = 31 Hz.

Results and Discussion

NMR Spectroscopy of Triorganoyltin(IV) Dithiolate Complexes. Triorganoyltin(IV) chlorides R_3SnCl (R = alkyl, aryl) react in dichloromethane solution with each of the dithiolate salts KEt_2dtc, NaEt(xan), and $NaEt_2dtp$ to give compounds $R_3Sn(S–S)$ in which the dithiolate, S–S, replaces the chloride according to $R_3SnCl + M(S–S) \rightarrow R_3Sn(S–S) + MCl$. In each case the tin-119 spectrum in dichloromethane solution indicates the formation of a single species, with the tin-119 resonance appearing at lower frequency than that of its R_3SnCl precursor.

NMR data in Table II show tin-119 shift values for $R_3Sn(Et(xan))$ and $R_3Sn(Et_2dtp)$ which suggest that these complexes have similar geometries in solution. The monodentate nature of the dithiophosphate ligand has been confirmed in the solid state for $Ph_3Sn(Et_2dtp)$[4] (the two Sn–S distances are 2.458 and 5.326 Å), and on the basis of the solution tin-119 NMR data, it appears reasonable to assume that $R_3Sn(Et(xan))$ and $R_3Sn(Et_2dtp)$ are all four coordinate in solution, with each dithiolate ligand effectively behaving as a monodentate sulfur donor. Interestingly, the tin-119 resonance for $Me_3Sn(Et_2dtp)$ has a $w_{1/2}$ of 2000 Hz

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at room temperature, but on cooling to −60° the resonance narrows, and at −100 °C a doublet resonance (31 Hz) due to *J*(Sn–P) coupling is clearly observed. Significantly the tin-119 chemical shift moves only 4 ppm to lower frequency when the solution is cooled to −100 °C. These observations are consistent with rapid intermolecular dithiolate exchange in $Me_3Sn(Et_2dtp)$ at room temperature which slows at low temperature but does not lead to a change in the overall effective coordination number of the tin atom. There is no appreciable change in the chemical shift position of $\delta(^{31}P)$ between room and low temperature. The carbon-13 spectrum of $Me_3Sn(Et_2dtp)$ indicates a single resonance for the three methyl substituents at tin in the temperature range of +25 to −100 °C.

The tin-119 chemical shifts of the dithiocarbamate complexes $R_3Sn(Et_2dtc)$ are at significantly lower frequency than their dithiophosphate and xanthate analogues which implies a higher effective electron density at tin in $R_3Sn(Et_2dtc)$. This observation is consistent with the higher effective coordination number observed in the solid state for $Me_3Sn(Me_2dtc)$[3] where the tin atom shows a higher tendency to accept a second sulfur donor of the dithiocarbamate ligand (the two Sn–S distances are 2.47 and 3.16 Å, respectively[3]). This type of differing monodentate–bidentate behavior has been observed for dithiolate complexes involving other main-group elements[17,18] and is generally attributed to a stronger Lewis basicity of sulfur in the dithiocarbamate anion as compared to the dithiophosphate and xanthate anions. The carbon-13 spectrum of $Me_3Sn(Et_2dtc)$ shows that the methyl substituents at tin are equivalent (as are the ethyl groups of the dithiocarbamate ligand) in the temperature range +25 to −100 °C. This indicates that the five-coordinate molecule is not stereochemically rigid under these conditions but may be undergoing fluxional behavior such as Berry pseudorotation.

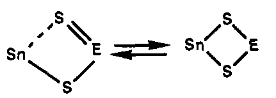
NMR Spectroscopy on Diorganoyltin(IV) Dithiolate Complexes. Stepwise replacement of halide in R_2SnCl_2 by dithiolate ligands leads to two series of compounds, $R_2SnCl(S{-}S)$ and $R_2Sn(S{-}S)_2$, according to

$$R_2SnCl_2 + M(S{-}S) \rightarrow R_2SnCl(S{-}S) + MCl$$

$$R_2SnCl(S{-}S) + M(S{-}S) \rightarrow R_2Sn(S{-}S)_2 + MCl$$

Tin-119 chemical shifts accompanying substitution of halide in Ph_2SnCl_2 by dithiolate are consistent with formation of complexes $Ph_2SnCl(S{-}S)$ and $Ph_2Sn(S{-}S)_2$. However, the differences between the chemical shift positions for $Ph_2SnCl(S{-}S)$ and $Ph_2Sn(S{-}S)_2$ (Table III) decrease on going from Et_2dtc to Et(xan) to Et_2dtp, and the associated geometrical changes are not immediately obvious.

Variable-temperature experiments are instructive and show that the tin-119 chemical shifts for $Ph_2SnCl(S{-}S)$ move to lower frequency as the temperature is decreased. The magnitude of tin-119 chemical shift changes with temperature is dependent on the dithiolate. For the series $Ph_2SnCl(S{-}S)$, the change in the tin-119 chemical shift between room temperature and −100 °C is 3 ppm for Et_2dtc, 11 ppm for Et(xan), and 31 ppm for Et_2dtp. These changes indicate that the tin coordination environment is essentially constant in $Ph_2SnCl(Et_2dtc)$ and that the dithiocarbamate ligand is effectively bidentate at both room and low temperature. On the other hand, the dithiophosphate ligand $Ph_2SnCl(Et_2dtp)$ is undergoing monodentate–bidentate equilibrium which favors the bidentate form at low temperature.



This results in shorter average Sn–S interactions and consequently a higher effective coordination number for tin for the dithiophosphate compound at low temperature. It is likely that in solution at low temperature all three $Ph_2SnCl(S{-}S)$ compounds contain the bidentate dithiolate ligand and are effectively five coordinate.

Table III. Tin-119 NMR Data for Diorganoyltin(IV) Dithiolate Complexes in Dichloromethane Solution at 25 °C (Values in Parentheses Are $\delta(^{119}Sn)$ Shift Values at −100 °C)

species	$\delta(^{119}Sn)$	species	$\delta(^{119}Sn)$
$^{n}Bu_2SnCl_2$	122	Me_2SnCl_2	141
$^{n}Bu_2SnCl(Et_2dtc)$	−200	$Me_2SnCl(Et_2dtc)$	−201 (−213)
$^{n}Bu_2Sn(Et_2dtc)_2$	−336	$Me_2Sn(Et_2dtc)_2$[a]	−336 (−359)
$^{n}Bu_2SnCl(Et(xan))$	−142	$Me_2SnCl(Et(xan))$[b]	−119 (−140)
$^{n}Bu_2Sn(Et(xan))_2$	−239	$Me_2Sn(Et(xan))_2$[b]	−221 (−273)
$^{n}Bu_2SnCl(Et_2dtp)$[i]	−83	$Me_2SnCl(Et_2dtp)$[h]	−71 (−108)
$^{n}Bu_2Sn(Et_2dtp)_2$[j]	−169	$Me_2Sn(Et_2dtp)_2$[k]	−154 (−218)
Ph_2SnCl_2	−27	$^{t}Bu_2SnCl_2$	56
Ph_2SnBr_2	−75		
$Ph_2SnCl(Et_2dtc)$	−327 (−330)	$^{t}Bu_2SnCl(Et_2dtc)$	−217 (−223)
$Ph_2SnBr(Et_2dtc)$	−343 (−345)		
$Ph_2Sn(Et_2dtc)_2$	−499 (−507)	$^{t}Bu_2Sn(Et_2dtc)_2$[c]	−239 (−227)
$Ph_2SnCl(Et(xan))$[b]	−275 (−286)	$^{t}Bu_2SnCl(Et(xan))$	−166 (−174)
$Ph_2SnBr(Et(xan))$	−285 (−295)		
$Ph_2Sn(Et(xan))_2$[b]	−312 (−393)	$^{t}Bu_2Sn(Et(xan))_2$	−90 (−148)
$Ph_2SnCl(Et_2dtp)$[e]	−248 (−279)	$^{t}Bu_2SnCl(Et_2dtp)$[m]	−131 (−154)
$Ph_2SnBr(Et_2dtp)$[l]	−250 (−282)		
$Ph_2Sn(Et_2dtp)_2$[f]	−265 (−332)	$^{t}Bu_2Sn(Et_2dtp)_2$[n]	−90 (−122)

[a] The same value as reported in ref 17. [b] Previously reported in ref 8. [c] Reference 18 gives $\delta(^{119}Sn) = -262$ ppm in CCl_4 solution. [d] $\delta(^{119}Sn) = -501$ ppm in ref 11. [e] $\delta(^{31}P) = 89.0$ ppm, *J*(Sn–P) = 35 Hz. [f] $\delta(^{31}P) = 92.2$ ppm, *J*(Sn–P) = 30 Hz. [g] $\delta(^{31}P) = 95.3$ ppm, *J*(Sn–P) = 32 Hz. [h] $\delta(^{31}P) = 90.4$ ppm, *J*(Sn–P) = 35 Hz. [i] $\delta(^{31}P) = 90.9$ ppm, *J*(Sn–P) = 60 Hz. [j] $\delta(^{31}P) = 96.0$ ppm, *J*(Sn–P) = 45 Hz. [k] $\delta(^{31}P) = 94.7$ ppm, *J*(Sn–P) = 27 Hz. [l] $\delta(^{31}P) = 89.9$ ppm, *J*(Sn–P) = 42 Hz. [m] $\delta(^{31}P) = 92.7$ ppm, *J*(Sn–P) = 95 Hz. [n] $\delta(^{31}P) = 95.3$ ppm, *J*(Sn–P) = 32 Hz.

Additional evidence that at least $Ph_2SnCl(Et_2dtc)$ is five coordinate is provided by carbon-13 spectra for that compound. The carbon-13 resonances for the ethyl carbons in $Ph_2SnCl(Et_2dtc)$ broaden at −60 °C and begin to split at −70 °C. At −100 °C there are clearly two nonequivalent ethyl groups in the carbon-13 spectrum ($\delta = 10.21$ and 10.68 ppm for CH_3, and $\delta = 49.78$ and 50.09 ppm for CH_2), indicating that each ethyl group on the dithiocarbamate ligand is in a different environment at this temperature. This nonequivalence of the ethyl groups can only arise if the dithiocarbamate ligand is effectively bidentate in solution and the resulting five coordinate tin complex is not fluxional; i.e., the stereochemistry in solution at −100 °C approximates that observed in the solid state (Figure 3). The rate of rotation about the $S_2C{-}N$ bond is likely to be slow at room temperature[25,26] and therefore not a cause for the different ethyl carbon resonances.

Interchange of sulfur atom positions effectively permits interconversion of the ethyl groups of the dithiocarbamate ligand. An intramolecular mechanism is most likely. The long and short Sn–S bonds can be interchanged by a twist mechanism, invoking a square-pyramidal geometry with the chloride in the apical position (Scheme I) or by several successive Berry pseudorotations.

The temperature dependence of tin-119 chemical shifts for the $Ph_2Sn(S{-}S)_2$ series are greater than those observed for $Ph_2SnCl(S{-}S)$. The tin-119 chemical shift changes for $Ph_2Sn(S{-}S)_2$ between room temperature and −100 °C are 8 ppm for Et_2dtc, 67 ppm for Et_2dtp, and 81 ppm for Et(xan). These data imply that the coordination environment about tin in $Ph_2Sn(Et_2dtc)_2$ is the same at both temperatures and that the tin is six coordinated with a geometry similar to that found in the solid state.[5] However, for $Ph_2Sn(Et_2dtp)_2$ and $Ph_2Sn(Et(xan))_2$ intramolecular monodentate–bidentate dithiolate exchange is facile, with the equilibrium favoring bidentate ligand coordination at low temperature. Thus, $Ph_2Sn(Et(xan))_2$ and $Ph_2Sn(Et_2dtp)_2$ are six coordinate at low

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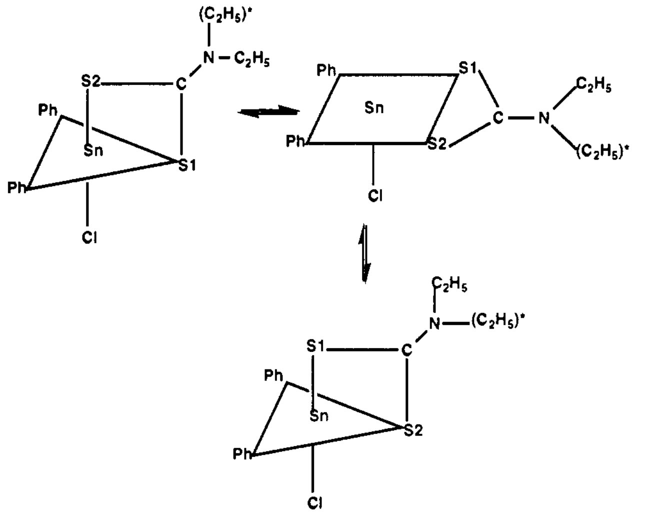
(25) Weir, J. R.; Fay, R. C. *Inorg. Chem.* **1986**, *25*, 2969.
(26) Fackler, J. P.; Lin, I. J. B.; Andrews, J. *Inorg. Chem.* **1977**, *16*, 450.

Scheme I



temperature but at room temperature have effective coordination numbers intermediate between five and six because of the effective lengthening of the average Sn–S distance brought about from the monodentate–bidentate dithiolate exchange equilibrium.

Evidence that the exchange process described above is actually intramolecular rather than intermolecular in nature is provided by the observation of J(Sn–P) coupling for $Ph_2SnCl(Et_2dtp)$ and $Ph_2Sn(Et_2dtp)_2$ (Table III). Evidence that the halide in Ph_2SnX (dithiolate) remains directly coordinated to tin is provided by the tin-119 shift values for the Ph_2SnBr(dithiolate) series (Table III) where a normal halogen dependence of the tin-119 shift is observed; i.e., the resonances of the bromo complexes lie at lower frequency than those of their corresponding chloro analogue.

For R = Me and R = ^{n}Bu the tin-119 chemical shifts for R_2SnCl(S–S) and $R_2Sn(S–S)_2$ (Table III) move progressively to lower frequency relative to R_2SnCl_2, with the chemical shifts for $R_2Sn(S–S)_2$ being at significantly lower frequency than those of R_2SnCl(S–S). These data are consistent with formation of five-coordinate R_2SnCl(S–S) and six-coordinate $R_2Sn(S–S)_2$ complexes, respectively. A six-coordinate structure for $R_2Sn(S–S)_2$ in solution is supported (at least for R = Me derivatives) by successful correlation of $^2J(^{119}Sn–H)$ values with the Me–Sn–Me angle determined in the solid state.[23] However, these NMR data themselves do not distinguish whether in solution the dithiolate ligands are symmetrically or asymmetrically coordinated to tin.

Significant changes become apparent when ^{n}Bu is replaced by ^{t}Bu. The ^{119}Sn chemical shift values for $^tBu_2SnCl(Et_2dtc)$ and $^tBu_2Sn(Et_2dtc)_2$ at 25 °C are similar, –217 and –239 ppm, respectively (Table III), and suggest similar effective coordination geometries about the tin atoms. There is only little change in tin-119 chemical shift positions as solutions of $^tBu_2SnCl(Et_2dtc)$ and $^tBu_2Sn(Et_2dtc)_2$ are cooled to –100 °C (Table III). A comparison of $\delta(^{119}Sn)$ values with those for the ^{n}Bu analogues (Table III) implies that both $^tBu_2SnCl(Et_2dtc)$ and $^tBu_2Sn(Et_2dtc)_2$ could be effectively five coordinate. The tin-119 spectrum at 25 °C of a dichloromethane solution containing a mixture of $^tBu_2SnCl(Et_2dtc)$ and $^tBu_2Sn(Et_2dtc)_2$ comprises sharp resonances due to each of these species, thus indicating the rate of intermolecular dithiolate ligand exchange is slow on the NMR time scale. Five-coordination for these two compounds would require a bidentate coordination of the dithiocarbamate ligand in $^tBu_2SnCl(Et_2dtc)$ whereas $^tBu_2Sn(Et_2dtc)_2$ requires both monodentate and bidentate dithiocarbamate ligands. Only one $-CS_2$ carbon-13 resonance is observed for $^tBu_2Sn(Et_2dtc)_2$ in the temperature range +25 to –100 °C, indicating that both dithiocarbamate ligands are equivalent. The carbon-13 spectra indicate a single ethyl group in $^tBu_2Sn(Et_2dtc)_2$ in the temperature range +25 to –100 °C. However, the carbon-13 resonances for the ethyl carbons in $^tBu_2SnCl(Et_2dtc)$ broaden at –20 °C and at –30 °C are clearly split (δ = 11.70 and 12.17 ppm for CH_3, and δ = 50.30 and 50.79 ppm for CH_2) indicating that each ethyl group on the dithiocarbamate ligand is in a different environment. These data imply the existence of an intramolecular exchange mechanism for $^tBu_2SnCl(Et_2dtc)$ similar to that described above for $Ph_2SnCl(Et_2dtc)$.

The effect of the ^{t}Bu group is even more pronounced in the dithiophosphate and xanthate series where the tin-119 chemical shifts move to higher frequency on going from $^tBu_2SnCl(Et(xan))$ and $^tBu_2SnCl(Et_2dtp)$ to $^tBu_2Sn(Et(xan))_2$ and $^tBu_2Sn(Et_2dtp)_2$, respectively (Table III), and imply a decrease in the effective coordination number on addition of the second dithiolate ligand. Observation of J(Sn–P) for $^tBu_2SnCl(Et_2dtp)$ demonstrates that the rate of intermolecular dithiolate exchange is slow at 25 °C. Somewhat curiously, the resonance for $^tBu_2Sn(Et_2dtp)_2$ remains a singlet down to –100 °C which implies that intermolecular dithiolate ligand exchange is more labile than in $^nBu_2Sn(Et_2dtp)_2$.

One plausible interpretation of these NMR data is that the steric pressure of the ^{t}Bu groups in $^tBu_2SnCl$(S–S) and $^tBu_2Sn(S–S)_2$ is such that only monodentate coordination of the dithiolate ligand is possible. However, this is not supported by the solid-state structures for $^tBu_2SnCl(Et_2dtc)$ and $^tBu_2Sn(Et_2dtc)_2$ (see below).

The tin-119 chemical shift value for $^tBu_2Sn(Et_2dtc)_2$ in the solid state (–392 ppm) is at much lower frequency than observed in dichloromethane solution (–239 ppm at 25 °C) and is consistent with a higher effective coordination number about tin in the solid state than in solution. In fact the solid state tin-119 chemical shift for $^tBu_2Sn(Et_2dtc)_2$ is at lower frequency than the values in solution for either $^nBu_2Sn(Et_2dtc)_2$ or $Me_2Sn(Et_2dtc)_2$ and is in line with the stronger electron-releasing capability of ^{t}Bu compared to ^{n}Bu and Me groups. These observations indicate that the dithiocarbamate ligand remains a monodentate sulfur donor in solution, even at low temperature. The tin-119 chemical shift for $Me_2Sn(Et_2dtc)_2$ in the solid state shows two resonances at –364 and –375 ppm (in accord with the monoclinic modification which contains two crystallographic independent molecules[8]) which are reasonably close to the value for the compound in dichloromethane solution (–336 ppm at 25 °C). Noteworthy is that the tin-119 chemical shift value for $^tBu_2SnCl(Et_2dtc)$ in the solid state (–216 ppm) is essentially the same as the value found for the compound in dichloromethane solution (–217 ppm at 25 °C).

Description of the Structure of $^tBu_2Sn(Et_2dtc)_2$. Relevant bond lengths and angles are given in Table IV. A PLUTO diagram of the molecule showing the numbering scheme is shown in Figure 1.

The geometry of $^tBu_2Sn(Et_2dtc)_2$ is almost identical to that observed for $Me_2Sn(Et_2dtc)_2$,[6] and there is no evidence for steric crowding by the ^{t}Bu groups. The structure has a pseudo-C_{2v} symmetry, with the two mirror planes defined by the atoms C(6)SnC(6′) and S(1)S(2)S(1′)S(2′)Sn, respectively. The molecule fits on a crystallographic 2-fold (orthogonal) axis. The dithiocarbamate ligands are coordinated asymmetrically with short Sn–S(1) (2.554 (1) Å) and long Sn–S(2) (2.953 (1) Å) distances. Accordingly, the coordination at the tin atom is intermediate between tetrahedral and octahedral geometries. If a pseudotetrahedral geometry is considered, this is evidently strained in order to allow the approach to the two less interacting sulfur atoms. When the angle C(6)–Sn–C(6)′ is opened from a tetrahedral value toward 180° (146.17 (9)°, the actual value), some room is created in the ideal cis coordination sites of an octahedron. The S–C–S groups that in the monodentate mode are likely able to rotate freely about the Sn–S(1) bonds are forced to stay in a unique plane with the tin atom (the equatorial octahedral plane). To favor the bidentate mode of the chelates, the S(1)–Sn–S(1)′ angle closes to 84.12 (2)°. The above

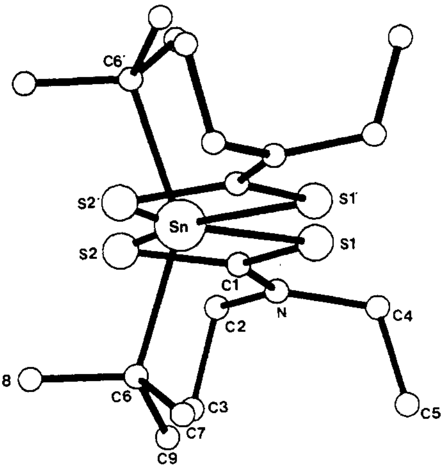


Figure 1. PLUTO diagram of ^{t}Bu$_2$Sn(S$_2$CNEt$_2$)$_2$.

Table IV. Selected Bond Distances (Å) and Angles (deg) for ^{t}Bu$_2$Sn(Et$_2$dtc)$_2$

Sn–S(1)	2.554 (1)	S(2)–C(1)	1.699 (2)
Sn–S(2)	2.953 (1)	N–C(1)	1.332 (3)
Sn–C(6)	2.246 (2)	N–C(2)	1.476 (3)
S(1)–C(1)	1.739 (2)	N–C(4)	1.468 (3)
S(1)–Sn–S(1′)	84.12 (2)	S(1)–C(1)–N	118.2 (2)
S(1)–Sn–S(2)	64.70 (1)	S(1)–C(1)–S(2)	119.2 (1)
S(1′)–Sn–S(2)	148.66 (4)	S(2)–C(2)–N	122.6 (2)
S(2)–Sn–S(2′)	146.60 (3)	C(6)–Sn–C(6′)	146.17 (9)
Sn–S(2)–C(1)	93.8 (1)	S(1′)–Sn–C(6)	104.16 (7)
Sn–S(1)–C(1)	81.5 (1)	S(2)–Sn–C(6)	85.67 (6)
S(1)–Sn–C(6)	100.8 (1)	S(2′)–Sn–C(6)	84.73 (6)

Table V. Selected Bond Distances (Å) and Angles (deg) for ^{t}Bu$_2$SnCl(Et$_2$dtc)

	molecule A	molecule B
Sn–S(1)	2.479 (2)	2.482 (2)
Sn–S(2)	2.732 (2)	2.734 (2)
Sn–Cl	2.498 (2)	2.505 (2)
Sn–C(6)	2.191 (8)	2.195 (8)
Sn–C(10)	2.201 (9)	2.20 (1)
S(1)–C(1)	1.731 (6)	1.738 (6)
S(2)–C(1)	1.701 (6)	1.699 (7)
N–C(1)	1.326 (7)	1.325 (8)
S(1)–Sn–S(2)	68.54 (5)	68.54 (5)
S(1)–Sn–Cl	84.65 (6)	85.63 (6)
S(1)–Sn–C(6)	115.1 (2)	114.5 (2)
S(1)–Sn–C(10)	115.0 (2)	115.6 (2)
S(2)–Sn–Cl	153.19 (6)	154.15 (6)
S(2)–Sn–C(6)	93.5 (1)	93.0 (2)
S(2)–Sn–C(10)	95.3 (2)	95.5 (2)
Cl–Sn–C(6)	97.6 (2)	97.0 (2)
C(6)–Sn–C(10)	128.8 (3)	128.7 (3)
Cl–Sn–C(10)	96.5 (2)	97.1 (2)

interpretation of the solid structural data also contains a hint for the possible mechanism of the sulfur donor exchange. In solution the attainment of a regular octahedron with a C(6)–Sn–C(6)′ angle of 180° and symmetric coordination of the chelate may not be out of reach.

The pseudooctahedral geometry of ^{t}Bu$_2$Sn(Et$_2$dtc)$_2$ is confirmed by the near coplanarity of the two SnSCS four-membered rings (the dihedral angle between the planes SnS(1)C(1)S(2) and SnS(1′)C(1′)S(2′) is only 4.35°).

Description of the Structure of ^{t}Bu$_2$SnCl(Et$_2$dtc). Relevant bond lengths and angles are given in Table V. The unit cell contains two independent molecules that are practically superimposable. In fact a computer fitting of molecules A and B shows only a very marginal difference in the orientation of one end of the ethylenic chains of the ligand Et$_2$dtc. One of the two molecules is represented in Figure 2 with its numbering scheme. The geometry is loosely based on a trigonal bipyramid, with atoms C(6)S(1)C(10) occupying equatorial positions. The tin atom deviates only by 0.13 Å from the plane formed by these three atoms. The Cl atom occupies approximately one apical position of the trigonal bipyramid. Conversely, being part of a chelate, the atom S(2) cannot occupy exactly the corresponding trans axial position, the angle Cl–Sn–S(2) being 153.19 (6)°.

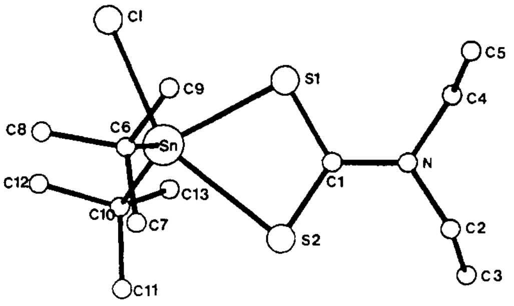


Figure 2. PLUTO diagram of ^{t}Bu$_2$SnCl(S$_2$CNEt$_2$).

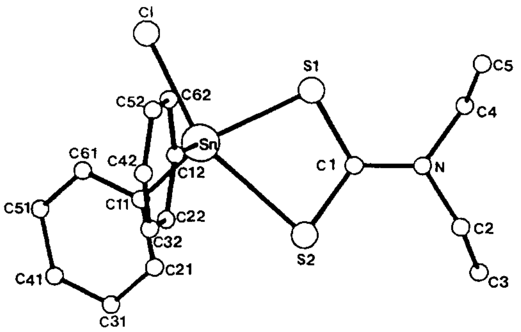


Figure 3. PLUTO diagram of Ph$_2$SnCl(S$_2$CNEt$_2$).

Table VI. Selected Bond Distances (Å) and Angles (deg) for Ph$_2$SnCl(Et$_2$dtc)

Sn–Cl	2.440 (1)	Sn–C(1,2)	2.127 (5)
Sn–S(1)	2.445 (1)	S(2)–C(1)	1.701 (4)
Sn–S(2)	2.716 (1)	S(1)–C(1)	1.744 (5)
Sn–C(1,1)	2.131 (5)	N–C(1)	1.327 (5)
Cl–Sn–S(2)	157.85 (4)	S(2)–Sn–S(1,2)	91.4 (1)
Cl–Sn–S(1)	88.42 (4)	Sn–S(2)–C1	82.1 (2)
S(2)–Sn–S(1)	69.59 (4)	Sn–S(1)–C1	89.9 (2)
S(1)–Sn–C(1,1)	122.7 (1)	C(1,1)–Sn–C(1,2)	117.6 (2)
S(2)–Sn–C(1,1)	96.1 (1)	C(1,2)–Sn–Cl	96.8 (1)
S(1)–C(1)–S(2)	118.0 (2)	C(1,1)–Sn–Cl	98.2 (1)
S(1)–Sn–C(1,2)	118.0 (1)		

Description of the Structure of Ph$_2$SnCl(Et$_2$dtc). Relevant bond lengths and angles are given in Table VI. A PLUTO diagram of the molecule showing the numbering scheme is given in Figure 3.

The geometry differs only slightly from that found in compound ^{t}Bu$_2$SnCl(Et$_2$dtc) and in other molecules of the same type previously studied, e.g., Ph$_2$SnCl(^{i}Pr(xan)) and Me$_2$SnCl(Et$_2$dtc). Essentially, the same approximate trigonal-bipyramidal geometry applies to all of these molecules. As an indication the sum of the equatorial angles formed at the Sn atom by the two coordinated carbon atoms and one sulfur atom deviates at most by 3° from the expected 360°. Again, due to the constraint of the chelate [the angle S(1)–Sn–S(2) is not 90° but only 69.54 (4)°], the S(2) atom cannot exactly occupy one of the two axial positions of the trigonal bipyramid.

Conclusions

There are a number of inter- and intramolecular exchange processes which affect the coordination environment of hypervalent tin(IV) dithiolate complexes in solution. In general, intermolecular dithiolate ligand exchange is slow on the NMR time scale at room temperature. On the other hand, the equilibrium involving intramolecular monodentate–bidentate dithiolate exchange can vary appreciably as a function of temperature. This work demonstrates the potential risk in attempting to assign coordination geometry solely on the basis of NMR data obtained at a single temperature. Indeed, the study of stereochemical nonrigidity and ligand dynamics in hypervalent tin(IV) requires investigation of a judicious range of complexes using both solution- and solid-state techniques. Generally the structures adopted at low temperature approximate those found in the solid state. However, the example of $^{t}Bu_2Sn(Et_2dtc)_2$ indicates that stereochemical nonrigidity for hypervalent tin(IV) compounds in solution can still be rapid even at −100 °C.

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Supplementary Material Available: Tables of crystal data, atomic coordinates, anisotropic thermal parameters, and hydrogen atom positions and ORTEP diagrams (10 pages); listings of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.