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HIGH RESOLUTION CPMAS ^{13}C NMR OF ORGANOMETALLIC SOLIDS. OBSERVATION OF *J* COUPLING TO TIN

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Summary

Chemical shift and $^1J(^{117,119}\text{Sn}, ^{13}\text{C})$ data from cross polarization magic angle spinning (CPMAS) proton-decoupled solid-state ^{13}C NMR experiments are given for the methyltin carbon in $(\text{Me}_2\text{SnS})_3$, Me_3SnOAc, $\text{Me}_2\text{Sn(acetylacetonate)}_2$, $\text{Me}_2\text{SnCl}_2 \cdot 2\text{(dimethylsulfoxide)}$, and amorphous $(\text{Me}_2\text{SnO})_n$. The relationship between the magnitude of the coupling constant and the coordination at tin is examined by reference to X-ray structure data. The tin-methyl ^{13}C chemical shift was sensitive to slight variations in bond angles and bond lengths. The presence of isotopically abundant NMR-active nuclei in the molecule broadens lines, and can prevent resolution of the *J* coupled interaction.

^{13}C NMR chemical shifts and coupling constants are powerful tools for determining the structure and bonding of organometallic compounds in solution [1]. Their interpretation, however, is generally based on solid-state structural data and is, therefore, subject to uncertainties arising from solvation and dynamic effects. The solid-state NMR parameters of structurally characterized organometals should provide the basis for more accurate interpretation of their solution NMR spectra and may permit rigorous testing of the relationships between NMR parameters and structural features such as bond angles, bond lengths, and steric environment. Nevertheless, while *J* coupling between ^{13}C and spin-$\frac{1}{2}$ metal nuclei should be evident in high resolution solid-state NMR spectra of many organometals, few examples have appeared [2].

We report here the first observation of *J* coupling to ^{117}Sn and ^{119}Sn, $^1J(^{117,119}\text{Sn}, ^{13}\text{C})$ (abundances 7.6 and 8.6%, respectively; both spin-$\frac{1}{2}$), in solid-state ^{13}C NMR

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TABLE 1

^{13}C CHEMICAL SHIFTS, $|J(^{117,119}Sn, ^{13}C)|$ FOR METHYL BONDED TO TIN IN METHYLTIN(IV) SOLIDS

Compound	^{13}C Chemical shift (ppm) [a]	$\|J(^{117,119}Sn, ^{13}C)$ [b]$\|$ (Hz)		LW [d] (Hz)	Tin geometry
		Solid [b]	Solution [c]		
$(Me_2SnS)_3$ **(1)**	7.7, 8.5, 12.1 (1/1/1)	420	398	10	tetrahedral
Me_3SnOAc **(2)**	−0.1, 1.7 (1/2)	530	401	7	trigonal bipyramidal
$Me_2Sn(acac)_2$ **(3)**	11.4	1125, 1175	966	5	octahedral (*trans*-Me)
$Me_2SnCl_2 \cdot 2DMSO$ [e] **(4)**	23.5, 28.5 (1/1)	1040	1009	14	octahedral (*trans*-Me)
$(Me_2SnO)_n$ **(5)**	6.4	640		21	trigonal bipyramidal

[a] ± 0.1 ppm; relative areas in parentheses. [b] Av. of $^1J(^{117}Sn, ^{13}C)$ and $^1J(^{119}Sn, ^{13}C)$ except for entry **3** for which ^{117}Sn, ^{119}Sn satellites were resolved. [c] $J(^{119}Sn, ^{13}C)$ in solution: Entry **2**, **4** this work; $CDCl_3$, DMSO solvent, resp. Entry **1** in $CDCl_3$ reported by G. Domazetis, R.J. Magee, B.D. James, J. Inorg. Nucl. Chem., 43 (1981) 1351. Entry **3** in $CDCl_3$, see ref. 6. [d] Full width at half-height. [e] DMSO = dimethyl sulfoxide.

experiments with methyltin(IV) solids. Examination of a representative series of compounds has allowed us to study the relationship between the magnitude of the J coupling ($|J|$) and the coordination at tin, and has revealed the sensitivity of chemical shift to subtle structural factors. We also demonstrate the potential of the method for the structural analysis of intractable organometallic polymers.

The ^{13}C NMR spectra of five methyltin(IV) solids were obtained in cross polarization magic angle spinning (CPMAS), proton-decoupled experiments; ^{13}C chemical shifts and coupling constants for the methyl carbons bonded to tin are given in Table 1. The $^{117,119}Sn$ satellites were identified on the basis of the following observations: (1) symmetrical displacement about the uncoupled resonance; (2) relative to the total signal, their area is equal to the sum of the natural abundances of ^{117}Sn and ^{119}Sn. (3) for $Me_2Sn(acac)_2$ (acac = acetylacetonate) the ^{117}Sn and ^{119}Sn satellites were resolved (Fig. 1) a $J(^{119}Sn, ^{13}C)/J(^{117}Sn, ^{13}C)$ is equal to the ratio of the gyromagnetic ratios of the tin isotopes (1.05).

$|J|$ has been related to the percent *s* character in the Sn–C bond [4]. For the structurally characterized polycrystalline compounds examined (**1**–**4**, Table 1), $|J|$ increases as the *s* character in the Sn–C bond increases from sp^3 (tetrahedral tin) to sp^2 (trigonal bipyramidal, equatorial Me) to *sp* (octahedral, *trans* Me) [5]. $|J|$ of the solids agrees well with the solution values (Table 1), except for Me_3SnOAc which undergoes a change in coordination number on dissolution (tetracoordinate in solution [4b], pentacoordinate polymer in the solid-state [6]), and $Me_2Sn(acac)_2$. The 200 Hz difference between the solid and solution J values of $Me_2Sn(acac)_2$ is intriguing. We speculate that it may reflect a decrease in the Me–Sn–Me bond angle (with a concurrent decrease in the *s* character of the bond to Me) in going from the solid (180.0°) [7] to solution. Consistent with this explanation, $|J|$ of $Me_2SnCl_2 \cdot 2DMSO$, (Me–Sn–Me angle 170°) [8], is also much smaller than the $Me_2Sn(acac)_2$ solid-state value.

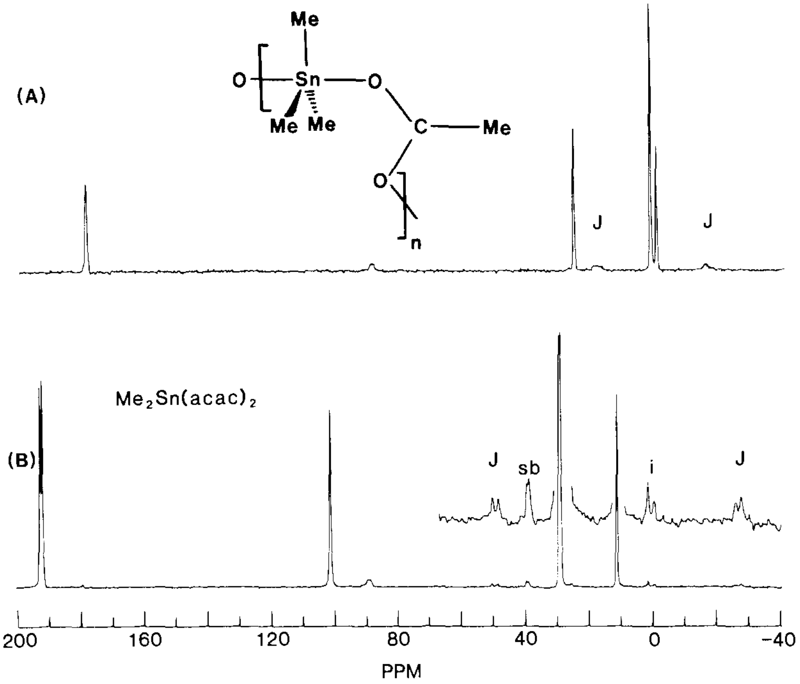

Fig. 1. Solid-state proton-decoupled CPMAS ^{13}C NMR spectra of polycrystalline Me_3SnOAc (a) and $Me_2Sn(acac)_2$(*trans*-Me) (b) solids. The signal at 89.1 ppm is polyoxymethylene, the internal reference. ^{117,119}Sn satellites are labelled *J*; spinning side band, sb; unidentified resonance, i.

Dimethyltin oxide, $(Me_2SnO)_n$, is an intractable, amorphous polymer not amenable to X-ray crystallography [9]. Nevertheless, the Sn satellites were well resolved from the central resonance and provide insight into the structure of this compound. Based on a comparison with the other methyltin(IV) solids, we deduce that polymeric dimethyltin oxide is pentacoordinate at tin, as has been suggested from Mössbauer evidence [9].

The structure observed for the tin-methyl carbon resonances (Table 1) in these experiments illustrates the sensitivity of the chemical shift to subtle differences in the bonding environment. The multiplets are composed of resonances in integer ratios and are thus attributed to magnetic inequivalences within the repeating molecular structure of each compound. Close examination of the X-ray structures of these compounds reveals plausible intramolecular sources of the tin-methyl multiplicities which are summarized below:

(1) Me_3SnOAc crystallizes as a linear polymer [6] with the repeating unit shown in Fig. 1. Because of restricted rotation of the trimethyl trigonal plane, the methyl group lying in the plane that contains Sn and the bridging carboxylates (assigned to the upfield resonance) is resolved from the methyls which lie out of the plane of the acetate group (assigned to the downfield resonance). (2) Three sharp methyl resonances are observed for polycrystalline dimethyltin sulfide, $(Me_2SnS)_3$, which exists in a twist-boat conformation [10]. A C_2 axis of symmetry interconverts three unique pairs of methyls and accounts for the observed multiplicity. (3) The *trans* methyl groups in $Me_2SnCl_2 \cdot 2DMSO$ [8] differ somewhat in their intramolecular bond

angles and through-space distances to the other atoms. These relatively small differences (5–10° between corresponding C–Sn–X angles, up to 0.2 Å in non-bonded C–X distances) are evidently sufficient to produce a large difference in chemical shift (5 ppm).

(4) The sensitivity of the solid-state NMR experiment to small differences in bonding is further emphasized in the spectrum of $Me_2Sn(acac)_2$ (Fig. 1). X-ray studies have revealed [7] that each acac ligand is unsymmetrical due to partial bond localization [HC–C(O) bond lengths of 1.36 and 1.44 Å, respectively] which gives rise to partially resolved doublets for the acac carbonyl (191.4, 192.2 ppm) and methyl (29.2, 29.5 ppm) resonances.

The presence of isotopically abundant NMR active nuclei (e.g., ^{14}N, ^{19}F, ^{31}P, or $^{35,37}Cl$) broadens [11] the ^{13}C resonance and may prevent resolution of the J coupled interaction. For example, we could not resolve the J coupling in Me_2SnCl_2 (linewidth ~ 200 Hz) which exists in a hexacoordinate configuration [12] in the solid state, each tin bonded closely to two chlorines and weakly to two others. Remarkably, on forming the DMSO adduct, $Me_2SnCl_2 \cdot 2DMSO$, the linewidth was reduced to 21 Hz.

Experimental

Materials. Me_3SnOAc [13], $Me_2Sn(acac)_2$ [7], and $Me_2SnCl_2 \cdot 2DMSO$ [16] were prepared as described in the literature. The other methyltin(IV) compounds were commercially available.

NMR spectroscopy. ^{13}C CPMAS spectra were obtained at 15.08 MHz on a homebuilt instrument. Spectra were acquired with the following: (1) 60 MHz high power proton decoupling; (2) spin locking cross-polarization with the ^1H and ^{13}C fields matched at 57 kHz for 2 ms; (3) magic angle spinning at 2300 Hz in an Andrew-type rotor with 0.4 g sample and 5 mg Delrin (polyoxymethylene) as a secondary chemical shift standard; (4) signal averaging of 5 to 25 K scans at a dwell time of 50 μs and repetition rates of 8 s. Solution ^{13}C NMR experiments were run at 100 MHz on a Bruker WM-400 spectrometer. All solutions were < 10% by weight in methyltin(IV); line widths at half-height were < 5 Hz.

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