bridging species have been proposed in the studies by Eisenberg[4] with $IrH_2Br(CO)(dppe)$, by Harrod[3] with $Ir(PPh_3)_2(CO)H_3$, and most notably by Moore in the reaction of Cp_2WH_2 with $[M(PPh_3)_2H_2(acetone)_2]^+$ (M = Rh, Ir).[14]

We suspect that the driving force for the transfer of dihydrogen to another metal can be attributed not only to a stronger metal-hydrogen bond for iridium but also to a greater thermodynamic stability of the dehydrogenated product **2**. The latter molecule is found to be quite unreactive: **2** is stable thermally up to 200 °C and only slowly reacts with refluxing methyl iodide.

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Registry No. 1, 81368-84-5; **2**, 75359-46-5; **3**, 29638-05-9; **4k**, 87985-33-9; **4t**, 88035-04-5; $Re(PPh_3)_3H_5$, 12104-75-5; $Re(PPh_3)_2H_7$, 12103-40-1; cyclopentadiene, 542-92-7; cyclopentene, 142-29-0; hydrogen, 1333-74-0.

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Structural Investigations by Solid-State ^{13}C NMR. Dependence of $|^1J(^{119}Sn,^{13}C)|$ on the Me-Sn-Me Angle in Methyltin(IV)s†

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An essentially unexploited aspect of solid-state NMR is its ability to provide NMR data for compounds in the same state of matter where their structure may be accurately determined by X-ray diffraction. In this way is offered the opportunity to establish directly the relationship between NMR and structural parameters and a means of relating solution NMR data to X-ray diffraction results. Recently, we detected $^1J(^{119}Sn,^{13}C)$, J, in the ^{13}C solid-state NMR of several structurally characterized methyltin(IV)s.[2] The resonance multiplicity was sensitive to slight structural variations, and the dependence of $|J|$ on tin coordination number was examined.

We report the first examination of J coupling as a function of molecular geometry (from X-ray) for di- and trimethyltin(IV)s. A simple, linear relationship between $|J|$ and the Me-Sn-Me angle, θ, obtains. This empirical relationship can be used to estimate the bonding geometry of uncharacterized methyltin(IV) solids and methyltin(IV)s in solution and may provide the basis for developing and evaluating theoretical models of J coupling involving Sn.

$|J|$ has been determined for nine compounds in CPMAS (cross-polarization, magic angle spinning), proton-decoupled solid-state ^{13}C NMR experiments (Table I). The ^{117}Sn and ^{119}Sn satellites could be resolved for $Me_2Sn(acac)_2$ (acac = acetyl acetonate) which has a single, narrow Sn-methyl resonance[2] though, in general, the combination of multiple Sn-methyl resonances and two spin-$^1/_2$ isotopes of Sn ($\gamma_{^{119}Sn}/\gamma_{^{117}Sn} = 1.046$, natural abundances 7.6% and 8.6%, respectively) gave rise to unresolved satellites. In these cases, $|J|$ was measured from the center of the satellite resonances.

Table I. CPMAS ^{13}C NMR of Methyltin(IV) Solids: $|^1J(^{119}Sn,^{13}C)|$ vs. Me-Sn-Me Angle

compd[a]	coord no.	Me-Sn-Me angle, deg	ref	$\vert^1J(^{119}Sn,^{13}C)\vert$,[b] Hz
Me_4Sn (**1**)	4	109.5	*c*	336[c]
$(Me_2SnS)_3$ (**2**)	4	118	*d*	430
Me_3SnCl (**3**)	5[e]	117.2	*f*	470
Me_3SnOAc (**4**)	5[e]	120	*g*	540
$Me_2PhSnOAc$ (**5**)	5[e]	128.1	*h*	610
$Me_2Sn(oxinate)_2$ (**6**)	6	110.7	13	630
$(Me_2SnCl_2 \cdot lut\text{-}N\text{-}O)_2$ (**7**)	6	145.3	*i*	810
$Me_2SnCl_2 \cdot 2DMF$ (**8**)	6	165.0	*j*	990
$Me_2SnCl_2 \cdot 2Me_2SO$ (**9**)	6	170.4	*k*	1060
$Me_2Sn(acac)_2$ (**10**)	6	180.0	*l*	1175[m]

[a] Abbreviations: OAc = acetate; oxinate = anion of 8-hydroxquinoline; lut-N-O = lutidine *N*-oxide; DMF = *N,N*-dimethylformamide; Me_2SO = dimethyl sulfoxide; acac = acetyl acetonate. [b] Calculated from center of unresolved $^{119}Sn,^{117}Sn$ satellites ($|J_{obsd}| \times 1.023$). [c] Average solution value: Petrosyan, V. S.; Permin, A. B.; Reutov, O. A.; Roberts, J. D. *J. Magn. Reson.* **1980**, *40*, 511. Tetrahedral geometry assumed. [d] Tetragonal modification: Menzebach, B.; Bleckmann, P. *J. Organomet. Chem.* **1975**, *91*, 291. [e] These compounds associate via bridging Cl and OAc groups in the solid state. [f] Lefferts, J. L.; Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J. *J. Organomet. Chem.* **1982**, *240*, 349. [g] Chih, H.; Penfold, B. R. *J. Cryst. Mol. Struct.* **1973**, *3*, 285. [h] Heeg, M. J.; Amini, M. M.; Zuckerman, J. J., unpublished results. [i] Ng, S.-W.; Barnes, C. L.; van der Helm, D.; Zuckerman, J. J. *Organometallics* **1983**, *2*, 600. [j] Aslanov, L. A.; Ionov, V. M.; Attiya, V. M.; Permin, A. B.; Petrosyan, V. S. *J. Struct. Chem.* **1973**, *91*. [k] Isaacs, N. W.; Kennard, C. H. L. *J. Chem. Soc. A* **1970**, 1257. Aslanov, L. A.; Ionov, V. M.; Attiya, W. M.; Permin, A. B.; Petrosyan, V. S. *J. Organomet. Chem.* **1978**, *144*, 39. [l] Miller, G. A.; Schlemper, E. O. *Inorg. Chem.* **1973**, *12*, 677. [m] $|^1J(^{119}Sn,^{13}C)|$ observed directly.

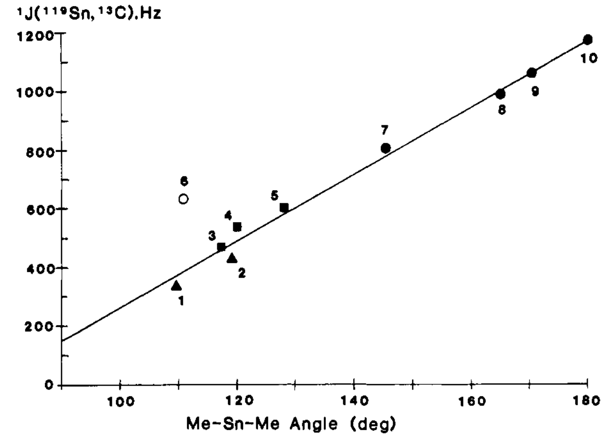

Figure 1. Plot of $|^1J(^{119}Sn,^{13}C)|$ vs. Me-Sn-Me bond angle, θ. Compound numbers defined Table I. Key: (●) hexacoordinated, (■) pentacoordinated, (▲) tetracoordinated methyltin(IV). Open circle, **6**, omitted from linear regression (see text).

A plot of $|J|$ against θ for the tetra-, penta-, and hexacoordinated methyltin(IV)s reveals a linear relationship (Figure 1). Omitting $Me_2Sn(oxinate)_2$ (oxinate = 8-hydroxyquinoline), a marked outlier,[3] a linear regression gives

$$|^1J(^{119}Sn,^{13}C)| = 11.4(\theta) - 875 \qquad r = 0.995; \quad n = 9$$

From this empirical relationship, the Me-Sn-Me angle of as yet uncharacterized or amorphous methyltin(IV) solids can be estimated. Further, because $|J|$ in the solid state is similar to that in solution (absent a structural change),[2] the relationship may also be used to detect changes in θ for methyltin(IV)s on disso-

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† In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Group IA and IIA become groups 1 and 2. The d-transition elements comprise group 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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(2) Manders, W. F.; Lockhart, T. P. *J. Organomet. Chem.*, in press.

(3) In benzene-d_6 solution $|J|$ of $Me_2Sn(oxinate)_2$ is 632 Hz.

lution. Thus, $|J|$ of $Me_2Sn(acac)_2$ in $CDCl_3$ solution, 966 Hz,[4] indicates a decrease in θ from 180° in the solid to 161°.[5] In this way solid-state NMR can help to elucidate solvation and other medium effects.

The magnitude of J in solution has been related to the Sn coordination number (CN)[4,6] and provides a qualitative probe of organotin(IV) structure. Our data for structurally characterized solids indicate that for tetracoordinated methyltin(IV)s $|J| \leq 430$ Hz, pentacoordinated 470–610 Hz, and hexacoordinated ≥630 Hz. However, the NMR data show the relationship of $|J|$ to Sn CN to be indirect. Because of the strong dependence of $|J|$ on θ, greatly distorted tetrahedral, trigonal bipyramidal, or *trans*-dimethyl octahedral geometries may produce values of $|J|$ outside of these ranges and caution should be used when assigning CN on the basis of this criterion.

The Fermi contact term, usually assumed to make the largest contribution to $|J|$ for group 14 nuclei,[7–10] is a linear function of the electron density at each of the two coupled nuclei[11] and reflects the s-character of the bonded orbitals. Because the methyl substituent is the same throughout, to a first approximation changes in $|J|$ can be attributed to changes in the Sn contribution. The close dependence of $|J|$ on θ appears to be consistent with the dominance of the Fermi contact term and the substantial, nonzero extrapolated value of $|J|$ for $\theta = 90°$ (150 Hz), where percent s character should be zero,[12] may provide an empirical estimate of the contribution of the orbital and dipolar terms to $|J|$.

The different behavior of $Me_2Sn(oxinate)_2$ is not readily understood. The Sn–C distance, 2.16 (2) Å,[13] is intermediate among the hexacoordinated compounds examined. It has been suggested that Sn uses sp^3-hybridized orbitals to bond to methyl ($\theta = 110.7°$) in this complex[13,14] but the large deviation from the other $|J|/\theta$ data, and particularly from tetracoordinated methyltin(IV)s Me_4Sn and $[Me_2SnS]_3$, suggests that such a simple picture is incorrect. Other hexacoordinated compounds with $\theta < 140°$ will be examined to determine if the deviation is general for contracted Me–Sn–Me bond angles [which could reflect either the importance of the non-Fermi contact terms in determining $|J|$ or a change in Sn hybridization—perhaps the inclusion of d orbitals[8b]—in cis-hexacoordinated methyltin(IV)s].

NMR data obtained on structurally characterized compounds must form the basis for examining the structural dependence of NMR parameters. We hope that the availability of these and other $|J|$/structure data will stimulate theoretical investigations of the J coupling of Sn and other heavy nuclei.

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Formation of Interstitial Pd–C Phase by Interaction of Ethylene, Acetylene, and Carbon Monoxide with Palladium[†]

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Palladium is an important catalyst, widely employed in industrial processes and in the laboratory practice. Its interaction with various gases has been extensively investigated from the point of view of catalytic[1] and surface[2] properties. Structural changes are known to occur in an hydrogen environment due to formation of palldium hydrides,[3] but little attention has been paid so far to changes of the bulk structure of palladium caused by interaction with carbon-containing gas molecules.[4] Among the catalytically important group 8–10 metals, only Fe, Ni, and Co form stable carbides; reports of palladium carbides[4b,4c] have not been substantiated.[5] In this context then, it appears of interest to report that a stable palladium phase, containing up to 13 atom % of carbon, readily occurs on heating metallic palladium in a flow of ethylene, acetylene, or carbon monoxide. Formation, stability, and some properties of that phase are the subject of this paper.

Palladium black (Aesar, Cat. No. 12066) was heated in 50 °C increments in the microreactor of a θ–θ X-ray diffractometer described earlier.[6] In separate experiments, ethylene, 1% acetylene in helium, and carbon monoxide were allowed to flow through the diffractometer chamber at 40 mL/min. At each temperature 20–30-min diffraction scans were taken. A phase transformation of Pd was observed at approximately 150 °C in C_2H_4, 250 °C in 1% C_2H_2/He, and 500 °C in CO, manifested by an expansion of the Pd unit cell. For example, Figure 1 shows the diffraction pattern of Pd black in a flow of 1% C_2H_2/He at selected temperatures. While there is no change in the structure on exposure of Pd to C_2H_2 at room temperature, a shift of peak positions is noticeable above 100 °C. At 200 °C each reflection is split into two components indicating a coexistence of two phases, both of which show lattice expansion with reference to pure Pd. Only

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[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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