ponential.[7] This requires that the formation of the biradical is much faster than its decay ($k_{cl} >> 1/\tau$). This assumption was checked by Stern–Volmer quenching experiments on the triplet states of the precursor ketones. With the exception of cycloheptanone all triplets have lifetimes of substantially less than 10 ns. The lifetime of **3** was obtained by fitting the data to a double exponential.

The results are summarized in Table I. The observed biradical lifetimes are relatively long and show not much variation within the series. As might be expected, branching of the alkyl end of the biradical increases the disproportionation to cyclization ratio. Although the structural variation within the series is not large, the small differences in τ and the long lifetimes suggest that the kinetics are controlled by spin dynamics.[8]

The last two columns in Table I give previously unavailable information on the mechanism of intersystem crossing in biradicals. To elaborate, it should be pointed out that in the absence of a magnetic field the eigenstates of biradicals of the type included here are close to pure singlets and triplets because the mixing interactions, V_{st}, are small compared to the singlet–triplet energy gap, $2J$.[9] Time-dependent perturbation theory predicts the intersystem crossing rate constant (k_{st}) to be proportional to

$$k_{(s,t)} \propto V_{st}^2/(V_{st}^2 + J^2)$$

An external magnetic field, B_0 (in our experiments $B_0 = 1.41$ T), changes this for two of the three triplet levels to

$$k_{s,t\pm} \propto V_{st}^2/[V_{st}^2 + (2J \mp g\beta B_0)^2]$$

where β is the Bohr magneton and g the electron g factor. Since J is dependent on the conformation of the biradical which is itself time dependent, it can be seen that the rate is a complex function of the conformational dynamics, the magnitude of the field that determines the energy gap between the triplet levels and the singlet, and the magnitude of V_{st}.[10]

The last column of Table I lists the measured enhancement factors, EF for the disproportionation products as fractions of their maxima. Here EF_{max} is the computed enhancement obtained for a hypothetical biradical in which T_+-S and all nuclear spin-independent mixing processes are negligible. The magnitude of EF_{max} is dependent on the number of protons carrying hyperfine interaction and, within the model, is independent of J. The results show that hyperfine interactions provide only a small fraction of the singlet–triplet mixing, with the major components coming from other mechanisms.[12] Two-center spin orbit coupling at the point of ring closure induced by the presence of an acyl function is a likely contributor.[9] Within the series, the importance of the hyperfine mechanism increases with increased branching as evidence by a rise in EF/EF_{max}. This presumably reflects a larger hyperfine interaction in the branched compounds. Also, the importance of hyperfine-induced mixing is less in the 1,8 series than in the 1,7 series, in agreement with previous studies.[9]

In conclusion, it should be pointed out that the relatively long lifetime of triplet biradicals must be attributed to the poor energy match of singlet and triplet levels rather than to a lack of mixing interactions. It can be easily shown that for a radical pair in which triplet and singlet are strictly degenerate, the hyperfine interactions of typical alkyl radicals alone are large enough to cause intersystem crossing in less than 10 ns. We have confirmed this by attempting to measure the geminate radical recombination resulting from the photolysis of dibenzyl ketone. The process is complete in less than 25 ns, the present time resolution of our experiment.[6]

Registry No. $\cdot CH_2(CH_2)_6\dot{C}O$, 69245-22-3; $(CH_2)_2\dot{C}(CH2)_6\dot{C}O$, 96897-00-6; $\cdot CH2(CH_2)_5\dot{C}O$, 96897-01-7; $CH_3\dot{C}H(CH_2)_5\dot{C}O$, 96897-02-8; $(CH_3)_2\dot{C}(CH_2)_5\dot{C}O$, 96897-03-9; $\overline{CH_2CH_2\dot{C}HCH_2C}H(CH_2)_2\dot{C}O$, 82352-63-4; cycloheptanone, 502-42-1; cyclooctanone, 502-49-8; 2,2-dimethylcycloheptanone, 7228-52-6; 2,2-dimethylcyclooctanone, 42393-51-1; 2-methylcycloheptanone, 932-56-9; 2-bicyclo[3.2.1]octanone, 5019-82-9.

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[7] The signal intensity in the 1,8 biradicals at early times in not proportional to the product formation because the triplet sublevels react with different rates and give different polarization patterns. This has been taken into account and will be explained in detail in a separate publication.

[8] This conclusion has been expressed previously by: Scaiano, J. C. *Tetrahedron* **1982**, *38*, 819.

[9] Closs, G. L. *Adv. Magn. Res.* **1974**, *1*, 157. Closs, G. L. *NATO Adv. Study Inst. Ser., Ser. C* **1979**, *34*, 225.

[10] The CIDNP spectra resulting from these dynamics have been modeled by: de Kanter, F. J. J.; den Hollander, J. A.; Huizer, A. H.; Kaptein, R. *Mol. Phys.* **1977**, *34*, 857. Doubleday, C., Jr. *Chem. Phys. Lett.* **1981**, *77*, 131; **1982**, *85*, 65.

[11] Nuclear spin independent processes are assumed to be negligibly small for the calculation of EF_{max}.

[12] This conclusion has been anticipated in ref 9 and by: de Kanter, F. J. J.; Kaptein, R. *J. Am. Chem. Soc.* **1982**, *104*, 4759.

The Direct Intermolecular Transfer of Dihydrogen between Two Transition-Metal Complexes

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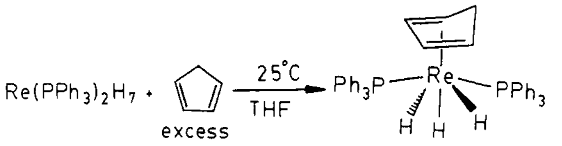
The reaction of dihydrogen with coordinately unsaturated 16-electron metal complexes in low oxidation states commonly leads to oxidative addition, a concerted process in which both hydrogen atoms are bound to the metal.[1] This process is often reversible, and reductive elimination of dihydrogen is also a common process. Only rarely have examples of hydrogen atom transfer from one metal to another been observed,[2] and cases in which two hydrogen atoms are transferred are even rarer.[3-5] We present here evidence for the direct transfer of dihydrogen from rhenium to rhenium and rhenium to iridium.

In 1980, Ephritikhine and Felkin reported the preparation of $CpRe(PPh_3)_2H_2$ by treatment of $Re(PPh_3)_2H_7$ with a slight excess of cyclopentadiene in THF.[6] The reaction was reported to proceed to completion in 15 min at 60 °C. Recently, we have found that $Re(PPh_3)_2H_7$ reacts with cyclopentadiene in THF (1:4 v/v) at 25 °C to give (η^4-C_5H_6)$Re(PPh_3)_2H_3$ (**1**) in high yield (eq 1).[7]



(1)

1

Compound **1**, isolated as colorless crystals, only slowly undergoes loss of dihydrogen at 60 °C to produce the dihydride complex $CpRe(PPh_3)_2H_2$ (**2**) ($\tau_{1/2} = 100$ min). The reluctance of **1** to undergo conversion to **2** at 60 °C seemed to rule out this species as an intermediate in the reaction of cyclopentadiene with $Re(PPh_3)_2H_7$ under the conditions employed by Ephritikhine and Felkin.

[†] Alfred P. Sloan Fellow, 1984-1986.

[1] Halpern, J. *Acc. Chem. Res.* **1970**, *3*, 386-392. Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransitionmetal Chemistry"; University Science: Mill Valley, CA, 1980.

[2] See, for example: McCullen, S. B.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 7496-7500. Jones, W. D.; Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4415-4423. Lehnig, M. *Tetrahedron Lett.* **1977**, *41*, 3663-3666.

[3] Drouin, M.; Harrod, J. F. *Inorg. Chem.* **1983**, *22*, 999-1001. Harrod, J. F.; Yorke, W. J. *Inorg. Chem.* **1981**, *20*, 1156-1159.

[4] Johnson, C. E.; Fisher, B. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1983**, *105*, 7772-7774. Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.*, **1985**, *107*, 3148-3160.

[5] Hazel, N. J.; Howard, J. A. K.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 1663-1664.

[6] Ephritikhine, M.; Felkin, H. *J. Organomet. Chem.* **1982**, *224*, 363-376. Baudry, D.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1980**, 249-250.

[7] Jones, W. D.; Maguire, J. A. *Organometallics* **1985**, *4*, 951-953.

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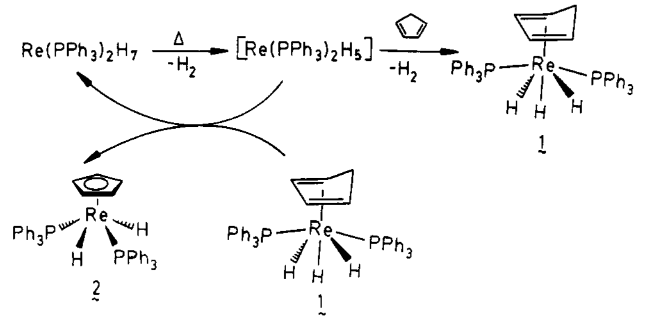
Scheme I

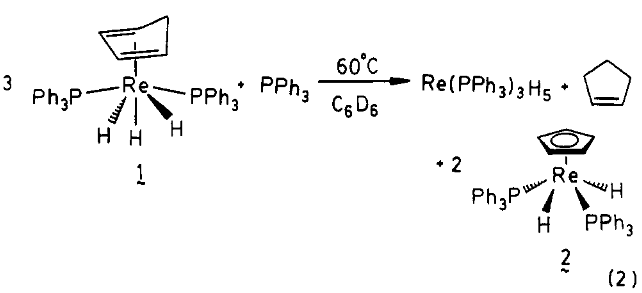


We have repeated the reaction of $Re(PPh_3)_2H_7$ with 2 equiv of cyclopentadiene in THF-d_8 at 60 °C and discovered an unusual sequence of events while monitoring the reaction by ^1H NMR spectroscopy. During the first 5 min of reaction at 60 °C, the cyclopentadiene and the $Re(PPh_3)_2H_7$ are observed to disappear smoothly as compound **1** and cyclopentene (1:1) appear.[8] Only traces of **2** (5–10%) are seen during this period, and all of the cyclopentadiene is found to be consumed (7–8 min). During the next 6–7 min of reaction, compound **1** is observed to rapidly undergo dehydrogenation to compound **2**. The rapidity of the latter reaction was surprising in view of its half-life in pure form. The solution remains colorless and none of the red dimer $Re_2(PPh_3)_4H_8$ is observed.[9]

The key to this dehydrogenation can be attributed to the small amount of $Re(PPh_3)_2H_7$ that is present. The latter complex, or more likely a derivative formed by loss of dihydrogen, is apparently capable of catalyzing the dehydrogenation reaction of **1**. This hypothesis was confirmed by heating a mixture of pure isolated **1** with 0.1 equiv of $Re(PPh_3)_2H_7$ in benzene solution (0.08 M, 0.008 M) at 60 °C. The half-life for dehydrogenation of **1** to **2** was found to be only 20 min, and the quantity of $Re(PPh_3)_2H_7$ was unchanged during the reaction. A separate experiment using 1 equiv of $Re(PPh_3)_2H_7$ as catalyst (0.04 M) was found to have a half-life of only ~7 min at 60 °C.[10]

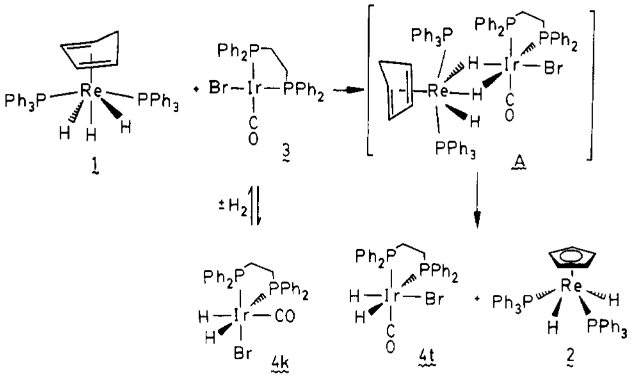
Scheme I shows a proposed mechanism for the dehydrogenation of **1** by $Re(PPh_3)_2H_7$. Since $Re(PPh_3)_2H_7$ is known to lose hydrogen upon heating,[6] the transfer of dihydrogen between **1** and $[Re(PPh_3)_2H_5]$ is the most plausible pathway for the catalysis.[11] Cyclopentadiene is capable of intercepting this intermediate and produces more **1**.

Further evidence for the catalysis of the dehydrogenation of **1** by $[Re(PPh_3)_2H_5]$ comes from heating **1** in benzene solution to 60 °C in the presence of 2 equiv of PPh_3. While **1** is still found to disappear under these conditions, the formation of **2** is strongly inhibited ($\tau_{1/2} \approx 7$ h). The only products observed are $Re(PPh_3)_3H_5$ (presumably from scavenging of incipient $[Re(PPh_3)_2H_5]$), cyclopentene, and **2** in a 1:1:2 ratio (eq 2). When $P(C_6D_5)_3$ is used, no evidence for the incorporation of deuterated phosphine into unreacted **1** is found and no free $P(C_6H_5)_3$ is observed.

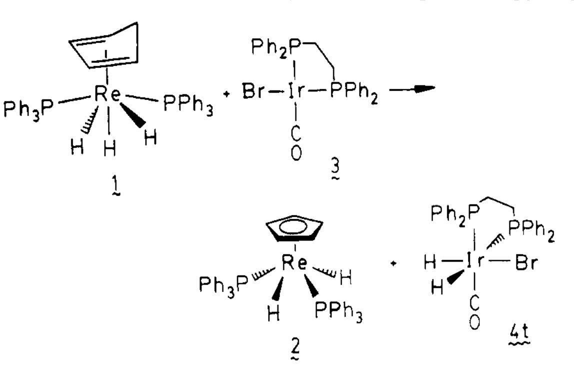


(2)

Scheme II



The transfer of dihydrogen from **1** to another metal can also be effected by using the remarkably reactive cis analogue of Vaska's complex discovered by Eisenberg and co-workers, IrBr(CO)(dppe) (**3**).[4] Treatment of **1** with 1 equiv of **3** in C_6D_6 solution (1.65 mM each) at 30.5 °C results in the slow second-order ($k = 8.7 \times 10^{-3}$ M^{-1} s^{-1}) formation of **2** and $IrH_2Br(CO)(dppe)$, as evidenced by ^1H NMR spectroscopy (eqn 3).[12]



(3)

Furthermore, the isomer of $IrH_2Br(CO)(dppe)$ formed exclusively is the thermodynamically favored isomer which has hydride trans to phosphorus and bromide, **4t**. Eisenberg, Fisher, and Johnson have recently investigated the addition of H_2 to **3** and found that the kinetic isomer formed instantly is $IrH_2Br(CO)(dppe)$ in which hydride is trans to phosphorus and carbon monoxide (**4k**).[4] **4k** prepared by treatment of **3** with 600 mmH$_2$ only slowly isomerizes to **4t** at 30.5 °C, ultimately giving an ~97:3 ratio of **4t** to **4k**. Consequently, dehydrogenation of **1** clearly does not proceed by reductive elimination of dihydrogen from the Re metal center followed by oxidative addition of hydrogen to **3**.

A control experiment rules out the possibility that **4k** is indeed formed initially but is then catalytically isomerized to **4t** by **1**. Treatment of **3** with dihydrogen (580 mm) in benzene solution containing **1** rapidly produces a mixture of the kinetic isomer **4k** and **1**. A second-order reaction to form **2** and **4t** is then observed as **1** and **4k** are consumed.[13]

Scheme II shows a possible mechanism for the dehydrogenation by **3**. The proposed bridging dihydride **A** could be either a transition state or intermediate in the dihydrogen transfer. Similar

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[8] ^1H NMR data for **1** (C_6D_6, 25 °C): δ 7.90 (s, 12 H), 7.06 (m, 18 H), 5.76 (s, 1 H), 3.94 (s, 2 H), 3.35 (s, 1 H), 2.72 (s, 2 H), −5.51 (br s, 3 H). For **2** (C_6D_6, 25 °C): δ 7.63 (m, 12 H), 6.97 (m, 18 H), 4.27 (s, 5 H), −9.95 (t, J = 40 Hz, 2 H).

[9] Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 695–696.

[10] Temperature equilibration in the NMR probe requires ~3 m. Actual half-lives at 60 °C are probably somewhat smaller.

[11] See also: Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc.* **1980**, 1243–1244.

[12] ^1H NMR data for **3** (C_6D_6, 25 °C): δ 7.88 (m, 4 H), 7.54 (m, 4 H), 7.00 (m, 6 H), δ 6.96 (m, 6 H), δ 1.99 (ddd, J = 25.8, 14.2, 8.3 Hz, 2 H), 1.68 (ddd, J = 26.3, 14.1, 8.2 Hz, 2 H). Hydride region ^1H NMR data for **4t** (C_6D_6, 25 °C): δ −8.34 (dd, J = 132.9, 17.2 Hz, 1 H), −17.48 (dd, J = 16.6, 8.6 Hz, 1 H). For **4k** (C_6D_6, 25 °C): δ −7.87 (dd, J = 152.2, 14.2 Hz, 1 H), −8.94 (t, J = 19.3 Hz, 1 H).

[13] The second-order rate of reaction increases upon addition of H_2 ($k = 1.28 \times 10^{-2}$ M^{-1} s^{-1}). The kinetic isomer **4k** quantitatively forms rapidly, suggesting that another mechanism might be responsible for the dehydrogenation under these conditions. In addition, PPNBr (saturated solution in benzene) now slows the rate of reaction 10-fold. Details of this related reaction are under further study.

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.

Acknowledgment is made to the U.S. Department of Energy (83ER13095) for their support of this research. We are also indebted to Prof. Richard Eisenberg and Dr. Curt Johnson for discussions involving the use of iridium as a dihydrogen abstractor and to Amanda Kunin for a loan of IrBr(CO)(dppe).

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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(14) Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E.; Alcock, N. W. *J. Chem. Soc., Dalton Trans* **1982**, 541–548.

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	$\lvert ^1J(^{119}Sn,^{13}C)\rvert$,[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.

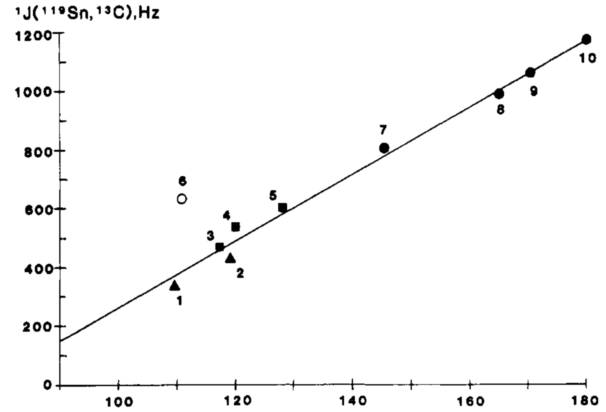

Figure 1. Plot of $|^1J(^{119}Sn,^{13}C)|$ vs. Me–Sn–Me bond angle, θ. Compound numbers defined Table I. Key: (●) hexacoordinated, (■) pentacoordinated, (▲) tetracoordinated methyltin(IV). Open circle, **6**, omitted from linear regression (see text).

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.)

(1) (a) National Research Council-National Bureau of Standards Postdoctoral Research Associate, 1983–1985. (b) University of Oklahoma.

(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.