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PMR SPECTRA OF SOME DIMETHYLMETAL (Sn, Pb, Tl) COMPOUNDS IN STRONG ACIDS

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Summary

In strong acids, the indirect spin—spin coupling constants, $J(\mathrm{M—CH_3})$ (M = Sn, Tl and Pb), of some dimethylmetal compounds were found to be smaller and the proton resonances of the methyl groups attached to the metal atom shifted to lower magnetic field. From the correlation of the spin—spin coupling constant, $J(\mathrm{M—CH_3})$, and the methyl proton chemical shift, $\delta(\mathrm{M—CH_3})$, the decrease of the spin—spin coupling constants of these compounds with the increase of acid strengths is regarded to be mainly due to the increase of the mean singlet—triplet excitation energy in the Fermi contact term. The lowering of the metal—carbon bond strengths in strong acids, which was revealed from metal—carbon stretching frequencies, may also be responsible for the decrease of the spin—spin coupling constants.

Introduction

The spin—spin coupling constants, $J(\mathrm{M—CH_3})$, of some methylmetal cations which contain solvent molecules in the first coordination sphere have been reported by several workers [1-8]. However, little information is available on the effects of coordinating solvent molecules [4] and acid strengths [1,9] on the $J(\mathrm{M—CH_3})$ values for methylmetal cations. Recently some dimethyllead compounds, $(\mathrm{CH_3})_2\mathrm{PbX_2}$ (X = benzoato and oxinato), have been found to form seven-coordinate complexes in solution with several donor molecules and the increase of the $J(^{207}\mathrm{Pb—CH_3})$ values in coordinating solvents has been found mainly due to decrease of the mean singlet—triplet excitation energy in the Fermi contact term as a result of electron donation from the coordinating solvents [10-13]. If this explanation is reasonable, the hydrated dimethyllead cation would be expected to give large $\delta(\mathrm{Pb—CH_3})$ and small $J(^{207}\mathrm{Pb—CH_3})$

values, in strong acids, in which the effective positive charge would be increased as a result of decrease of its hydration number. Therefore, we have measured these values for some dimethyllead compounds in strong acids, and also PMR data for dimethyltin oxide and some dimethylthallium compounds in strong acids and Raman spectra of some dimethylmetal (Sn, Tl and Pb) compounds have been obtained and investigated.

Experimental

Preparation of compounds

Dimethyllead dichloride was prepared by chlorination of tetramethyllead in ethyl acetate at about —10°C [14]. Dimethyllead oxide was prepared by the reaction of dimethyllead dichloride and silver oxide in water [3]. The other dimethyllead compounds, $(CH_3)_2PbX_2$ ($X = NO_3$, ClO_4, p-$CH_3C_6H_4SO_3$, F and CF_3CO_2), were prepared by reaction of dimethyllead oxide (2.5 g, 10 mmol) and an appropriate acid (20 mmol) in about 50 ml of water. The precipitates were obtained by removing water under reduced pressure and were recrystallized from water/dioxane mixtures. The compound, $(CH_3)_2Pb(O_3SC_6H_4CH_3\text{-}p)_2$, m.p. 211-213°C (dec.), is new. Anal. Found: C, 33.06; H, 3.60. $C_{16}H_{20}O_6S_2Pb$ calcd.: C, 33.15; H, 3.48%. Dimethylbis(acetylacetonato)lead was prepared by the literature method [15].

Dimethylthallium compounds, $(CH_3)_2TlX$ ($X = NO_3$ and ClO_4), were prepared by the reaction of dimethylthallium chloride (2.7 g, 10 mmol) with an appropriate silver salt (10 mmol) in about 50 ml of water, concentration and cooling of the reaction mixture yielded the crystalline compound. Dimethyl(acetylacetonato)thallium was prepared by the reaction of dimethylthallium chloride (2.7 g, 10 mmol) with thallous acetylacetonato (3 g, 10 mmol) in methanol (100 ml).

TABLE 1

M—C SYMMETRIC STRETCHING FREQUENCY (cm^{-1}) OF $(CH_3)_2PbX_2$, $(CH_3)_2TlX$ AND $(CH_3)_2SnX_2$

M	X	Solvent	ν(M—C)
Pb	NO_3	CF_3COOH	467
Pb	NO_3	HNO_3 (60%)	471
Pb	NO_3	HCOOH	474
Pb	NO_3	H_2O	475[a]
Pb	NO_3	H_2O	480[b]
Pb	NO_3	DMSO	467
Tl	NO_3	CF_3COOH	490
Tl	NO_3	HNO_3 (60%)	494
Tl	NO_3	H_2O	493
Tl	NO_3	H_2O	498[c]
Tl	ClO_4	DMSO	486[d]
Sn	O/2	$HClO_4$ (60%)	525
Sn	O/2	HNO_3 (60%)	529
Sn	NO_3	H_2O	529[e]
Sn	ClO_4	H_2O	530[e]

[a] Ref. 12. [b] Ref. 3. [c] Ref. 29. [d] Ref. 4. [e] Ref. 1.

TABLE 2

$J(^{207}Pb{-}CH_3)$, $J(^{13}C{-}H)$ AND $\delta(Pb{-}CH_3)$ VALUES OF $(CH_3)_2PbX_2$ IN STRONG ACIDS AND COORDINATING SOLVENTS

Solvent	X = NO_3			X = ClO_4		X = CF_3COO		X = acac		
	$J(Pb{-}CH_3)$ (Hz)	$J(C{-}H)$ (Hz)	$\delta(CH_3)$ (ppm)	$J(Pb{-}CH_3)$ (Hz)	$\delta(CH_3)$ (ppm)	$J(Pb{-}CH_3)$ (Hz)	$\delta(CH_3)$ (ppm)	$J(Pb{-}CH_3)$ (Hz)	$J(C{-}H)$ (Hz)	$\delta(CH_3)$ (ppm)
$HClO_4$ (70%)	101.5	[a]	3.20	101.0	3.20	101.0	3.19	101.5	[a]	3.18
$HClO_4$ (65%)	108.5	[a]	3.10	108.5	3.12	[b]	[b]	109.2	[a]	3.12
$HClO_4$ (60%)	114.9	149.6	2.98	115.1	2.98	[b]	[b]	114.9	149.5	3.02
CF_3COOH	117.4	147.7	2.94	117.0	2.93	117.0	2.91	117.7	148.2	2.92
HNO_3 (60%)	122.8	147.0	2.92	122.6	2.93	122.6	2.93	123.4	147.5	2.94
$HClO_4$ (40%)	126.0	147.3	2.80	[b]	[b]	[b]	[b]	[b]	[b]	[b]
HCOOH	130.4	146.8	2.71	130.2	2.72	129.7	2.75	130.9	146.5	2.73
$HClO_4$ (20%)	132.6	147.5	2.65	[b]	[b]	[b]	[b]	[b]	[b]	[b]
H_2O	135.0	145.1	2.55	135.2	2.54	135.2	2.54	[a]	[a]	[a]
CH_3OH	142.6	[a]	2.42	140.0	2.40	143.7	2.39	163.4 [c]	146.1 [c]	1.98 [c]
TMP	145.8	[a]	2.36	144.3	2.29	151.4	2.28	169.1	146.5	1.90
DMF	143.5	[a]	2.55	143.4	2.56	152.3	2.50	172.1 [c]	146.0 [c]	1.91 [c]
DMSO	148.6	[a]	2.33	148.8	2.28	151.1	2.31	171.2 [c]	147.0 [c]	1.80 [c]
HMPA	[d]	[d]	[d]	[d]	[d]	[d]	[d]	182.7 [c]	153.6 [c]	1.79 [c]

[a] Solubility is insufficient for measurements. [b] Not measured. [c] Ref. 17. [d] Obscured by the resonance peaks of the solvent.

Raman spectra

The Raman spectra were recorded on a JEOL model JRS-02AS spectrometer by using 4880 Å light. The carbon—metal symmetric stretching frequencies of dimethylmetal (Sn, Tl and Pb) compounds in several strong acids are shown in Table 1. The concentration of the dimethylmetal compounds is about 20% by weight.

PMR spectra

The PMR measurements were recorded with a JEOL model JNM-PS-100 spectrometer operating at 100 MHz. The chemical shifts were measured relative to tetramethylsilane or sodium 2,2-dimethyl-2-silapentane-5-sulfonate, DSS, as internal standard. The concentration dependence of the $J(^{207}\text{Pb—CH}_3)$ and $\delta(\text{Pb—CH}_3)$ values (1-20 wt%) was within 1 Hz and 0.02 ppm, respectively. The PMR data obtained in about 10 wt% solutions of dimethyllead compounds are shown in Table 2. The PMR data for dimethyllead difluoride and di-*p*-toluenesulfonate are not given in Table 2, since the data were quite similar to those of dimethyllead dinitrate. In Table 3, the PMR data of some dimethylthallium compounds measured in about 5% wt solution are given. Table 4 gives the PMR data of the dimethyltin cation which was produced by dissolving dimethyltin oxide (10 wt%) in strong acids.

Inorganic acids obtained from commercial sources were used without further purification. The organic acids and the coordinating solvents dried over a desiccant were purified by distillation.

The specific conductance of DMSO used in conductivity measurements was 1.03×10^{-7} ohm^{-1} cm^{-1} at 25°C.

TABLE 3

$J(^{205}\text{Tl—CH}_3)$ AND $\delta(\text{Tl—CH}_3)$ VALUES OF $(\text{CH}_3)_2\text{TlX}$ IN STRONG ACIDS AND COORDINATING SOLVENTS

Solvent	X = NO_3		X = ClO_4		X = acac	
	$J(\text{Tl—CH}_3)$ (Hz)	$\delta(\text{CH}_3)$ (ppm)	$J(\text{Tl—CH}_3)$ (Hz)	$\delta(\text{CH}_3)$ (ppm)	$J(\text{Tl—CH}_3)$ (Hz)	$\delta(\text{CH}_3)$ (ppm)
$\text{SbCl}_5/\text{SO}_2$	336 [a]	1.76 [a]	[b]	[b]	[b]	[b]
HClO_4 (65%)	362	1.57	361	1.57	362	1.58
HClO_4 (60%)	372	1.53	372	1.52	374	1.53
CF_3COOH	361	1.52	361	1.52	364	1.51
HNO_3 (60%)	383	1.45	383	1.44	387	1.42
HCOOH	389	1.38	389	1.38	[b]	[b]
HClO_4 (40%)	391	1.34	[b]	[b]	[b]	[b]
HClO_4 (20%)	400	1.14	[b]	[b]	[b]	[b]
H_2O	406	1.12	407	1.12	[b]	[b]
CH_3OH	414	1.02	414	1.03	417	0.95
TMP	438	0.94	436	0.92	[c]	[c]
DMF	438	1.05	434 [d]	1.10 [d]	435	0.82
DMSO	443	0.88	442 [d]	0.90 [d]	438	0.71
HMPA	471	0.93	475 [d]	0.95 [d]	447	0.74

[a] Value for $(\text{CH}_3)_2\text{TlCl}$. [b] Not measured. [c] Solubility is insufficient for measurements. [d] Ref. 4.

TABLE 4

$J(^{119}Sn{-}CH_3)$, $J(^{13}C{-}H)$ AND $\delta(Sn{-}CH_3)$ VALUES OF $(CH_3)_2SnX_2$ IN STRONG ACIDS

X	Solvent	$J(Sn{-}CH_3)$ (Hz)	$J(C{-}H)$ (Hz)	$\delta(CH_3)$ (ppm)
Cl [a]	HSO_3F	88.0		
Cl [a]	H_2SO_4 (100%)	89.8		
Cl [a]	H_2SO_4 (95%)	88.9		
O/2	HSO_3CF_3	89.4	[b]	[c]
O/2	$HClO_4$ (70%)	93.6	138.6	1.58
O/2	$HClO_4$ (65%)	95.6	138.3	1.46
O/2	HCl (36%)	96.2	138.2	1.49
O/2	$HClO_4$ (60%)	97.9	137.7	1.36
O/2	$HClO_4$ (50%)	102.5	137.1	1.21
O/2	HNO_3 (60%)	105.0	136.5	1.35
O/2	$HClO_4$ (40%)	105.2	136.2	1.12
O/2	$HClO_4$ (20%)	109.3	136.1	1.00
Cl	H_2O	107.4	135.3	1.05
O/2	$HClO_4$ (10%)	109.3	135.4	0.97

[a] Ref. 9. [b] Could not be measured because of broadening of the main peak. [c] DSS is decomposed.

Results and discussion

The structures of several dimethyllead compounds have been investigated in the solid state and in solution by means of their infrared and Raman spectra [3,5,12,15,16]. For dimethyllead dihalides, it was concluded that in the solid state these compounds have a linear C—Pb—C skeleton from the absence of the C—Pb—C symmetric and the antisymmetric stretching bands in the infrared and Raman spectra, respectively [16]. The compounds give a strong C—Pb—C symmetric stretching band at about 450 cm^{-1} in the Raman spectrum and a weak C—Pb—C antisymmetric band at about 530 cm^{-1} in the infrared spectrum. Most of the other dimethyllead compounds have also been reported to have the linear C—Pb—C skeleton [3,5,10,15-18], although a bent C—Pb—C arrangement has been suggested for some dimethyllead complexes of tridentate Schiff bases on the basis of measurements of molecular weights and coupling constants, $J(^{207}Pb{-}CH_3)$[19].In the case of dimethyllead dinitrate in strong acids, the linear C—Pb—C skeleton is probably formed, since only one strong C—Pb—C symmetric stretching band has been observed at about 470 cm^{-1} in the Raman spectrum (see Table 1), as has been reported for the dimethyllead cation in aqueous solution [3].

The appearance of only one C—M—C symmetric stretching band for dimethyltin oxide and dimethylthallium nitrate in strong acids indicates that the dimethylmetal cation with a linear C—M—C skeleton has also been produced by dissociation of an anionic group.

The C—M—C symmetric stretching band of all the dimethylmetal cations shifts a little to lower frequencies when the acid strength becomes larger (see Table 1).

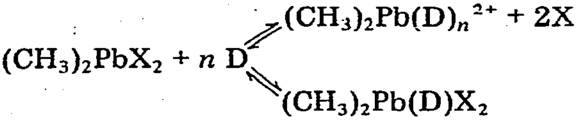
The PMR data of dimethyllead dinitrate in Table 2 show that the proton resonances of the methyl groups attached to the lead atom shift to lower magnetic field and at the same time the spin—spin coupling constant between the methyl groups and the lead nucleus, $J(^{207}Pb—CH_3)$, becomes smaller as the acid strength becomes larger or the concentration of the acids increases. The chemical shifts of the methyl groups, $\delta(Pb—CH_3)$, and the spin—spin coupling constants, $J(^{207}Pb—CH_3)$, of the dimethyllead compounds in strong acids do not depend on the anionic groups. The anionic groups, therefore, are completely dissociated in strong acids and the dimethyllead moiety forms a hydrated species. The downfield shift of the methyl resonance in strong acids is probably due to

$$(CH_3)_2PbX_2 + n\ H_2O \rightleftharpoons (CH_3)_2Pb(OH_2)_n{}^{2+} + 2\ X^-$$

$$(CH_3)_2Pb(OH_2)_n{}^{2+} + m\ H^+ \rightleftharpoons (CH_3)_2Pb(OH_2)_{n-m}{}^{2+} + m\ H_3O^+$$

a decrease of the hydration number of dimethyllead—water complexes and the resulting increased effective positive charge on the lead atom in these media. As can be seen from Table 2, the spin—spin coupling constant between the proton and the carbon nucleus of the methyl group, $J(^{13}C—H)$, increases in strong acids, although there is some scattering in the value. The result is not incompatible with the above results, since it has been reported [20-22] that the $J(^{13}C—H)$ value of the methyl group increases when the positive charge is accumulated on the atom to which the methyl group is attached.

In organic coordinating solvents, the methyl resonance of the dimethyllead compounds shifts to higher magnetic fields and the $J(^{207}Pb—CH_3)$ value increases when the donor strength [23] of the solvent molecules increases. The $\delta(Pb—CH_3)$ and $J(^{207}Pb—CH_3)$ values in each solvent are independent of the anionic group, X, when X is a perchlorato, nitrato, fluoro or *p*-toluenesulfonato group. The molar conductances of dimethyllead dinitrate and di-*p*-toluenesulfonate in DMSO have been found to be 53.8 and 58.0 $ohm^{-1}\ cm^2\ mol^{-1}$, respectively at the concentration of 10^{-3} mol l^{-1} (25.0 ± 0.1°C). These values are about twice the values for 1:1 electrolytes in DMSO (25-40 $ohm^{-1}\ cm^2\ mol^{-1}$) at the concentration of about 10^{-3} mol l^{-1} [24]. Therefore, the dimethyllead compounds with these anionic groups probably become solvated cations, $(CH_3)_2Pb(D)_n{}^{2+}$, in coordinating solvents; on the other hand, when the anionic groups are benzoato, acetylacetonato or oxinato groups, the $\delta(Pb—CH_3)$ and $J(^{207}Pb—CH_3)$ values in coordinating solvents depend on the anionic groups. Thus, in DMSO the $\delta(Pb—CH_3)$ values are 2.15, 1.80 and 1.70 ppm and the $J(^{207}Pb—CH_3)$ values are 159.6, 171.2 and 176.4 Hz, respectively [11,12,17]. These compounds have been reported to be non-electrolytes in coordinating solvents forming seven-coordinate complexes [11,12,17]. As can be seen from Table 2, dimethyl-



$$(CH_3)_2PbX_2 + n\ D \begin{array}{l} \nearrow (CH_3)_2Pb(D)_n{}^{2+} + 2X \\ \searrow (CH_3)_2Pb(D)X_2 \end{array}$$

bis(acetylacetonato)lead in coordinating solvents gives large $J(^{207}Pb—CH_3)$ and and small $\delta(Pb—CH_3)$ values in comparison with the solvated dimethyllead cation, $(CH_3)_2Pb(D)_n{}^{2+}$. These results indicate that the $J(^{207}Pb—CH_3)$ value depends on the positive charge on the central lead atom. In the case of dimethyllead di-trifluoroacetate, the dissociation of the anionic groups may be incomplete in coordinating solvents, since the $J(^{207}Pb—CH_3)$ value is somewhat larger

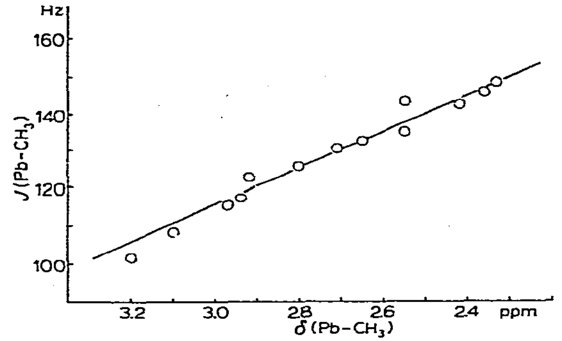


Fig. 1. Correlation between $\delta(Pb{-}CH_3)$ and $J(Pb{-}CH_3)$ for $(CH_3)_2Pb(NO_3)_2$.

than that for the solvated dimethyllead cation in each coordinating solvent.

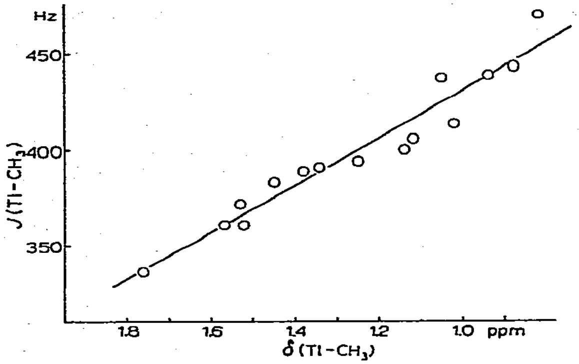
The relationship between the $\delta(Pb{-}CH_3)$ values and the $J(^{207}Pb{-}CH_3)$ values for dimethyllead dinitrate is shown in Fig. 1. Regression analysis for these quantities gives eq. 1, where r is the correlation coefficient. Fig. 1 shows

$$J(^{207}Pb{-}CH_3) = -51.7(\pm 2.6) \cdot \delta(Pb{-}CH_3) + 269.7(\pm 18.2) \quad r = 0.986 \qquad (1)$$

that the $J(^{207}Pb{-}CH_3)$ values decrease when the methyl proton resonance shifts to lower magnetic fields, which probably reflects the increase of the effective positive charge on the lead atom.

Effects of solvent coordination on $J(M{-}CH_3)$ values have been discussed in terms of the following two schemes: (1) the change of the *s* character of the metal orbital in the metal—carbon bond as a result of change of *d*—*s* mixing by coordination of solvent molecules, and (2) the change of the mean singlet—triplet excitation energy, ΔE, in the Fermi contact term.

The first scheme postulated by Shier and Drago [4] has been used for the explanation of the increase of the $J(^{205}Tl{-}CH_3)$ values of several solvates of the dimethylthallium cation with increasing donor strengths of the solvents. The involvement of the d_{z^2} orbital of the metal atom in the metal—ligand bond has originally been reported by Orgel [25] to explain the stereochemical preference of linear mercury compounds. However, a recent molecular orbital study of $J(^{199}Hg{-}CH_3)$ for several methylmercury compounds has shown that there is no support for significant employment of a mercury 5*d* orbital in bonding [26]. We have proposed the second scheme to explain the dependence of the $J(M{-}CH_3)$ values of dimethyllead and dimethylthallium compounds on $\delta(M{-}CH_3)$ values, dielectric constant of solvents and absorption maxima of the oxinato group [13]. In these complexes, the $J(M{-}CH_3)$ values have been found to be larger with a decrease of the positive charge on the central metal atom, which is mainly deduced from the upfield shift of the methyl resonances. Recently, the $J(^{207}Pb{-}CH_3)$ and $J(^{207}Pb{-}N{=}C{-}H)$ values of a dimethyllead complex of α,α'-(ethylenedinitrilo)-dicresol (Salen) have been found to increase from 157.8 to 187.5 Hz and from 23.4 to 29.3 Hz, respectively, by accompanying the upfield shift of the methyl proton resonance, when solvents have been changed from $CDCl_3$ to HMPA [27]. These findings favor a second scheme in which the decrease of the $J(^{207}Pb{-}CH_3)$ value for dimethyllead compounds in strong acids is mainly due to an increase



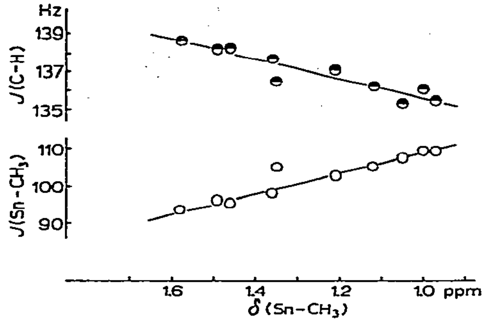


Fig. 2. Correlation between $\delta(Tl—CH_3)$ and $J(Tl—CH_3)$ for $(CH_3)_2TlNO_3$.

Fig. 3. Correlations between $\delta(Sn—CH_3)$ and $J(Sn—CH_3)$ and between $\delta(Sn—CH_3)$ and $J(C—H)$ for $(CH_3)_2SnO$.

of the mean singlet—triplet excitation energy in the Fermi contact term. The increase of the atomic hyperfine coupling constant of the metal, $a_M(ns)$, which is produced by an increase of the positive charge on the metal atom and induces the increase of the spin—spin coupling constant [27], is overcome by the increase of the mean singlet—triplet excitation energy.

The lowering of the metal—carbon bond strength in strong acids may be another factor which decreases the spin—spin coupling constant, because there is some low frequency shift of the metal—carbon stretching band (see Table 1).

The relations between the $J(M—CH_3)$ and $\delta(M—CH_3)$ values for dimethyltin oxide and dimethylthallium nitrate in strong acids and in coordinating solvents are shown in Figs. 2 and 3. The correlation between these quantities are expressed by eqs. 2 and 3. The relation between the $J(^{13}C—H)$ value of the methyl groups attached to tin and $\delta(Sn—CH_3)$ values for dimethyltin oxide dissolved in strong acids is shown in Fig. 3 and is expressed by eq. 4. The relation shown in Figs. 2 and 3 is similar to that obtained for dimethyllead dinitrate in Fig. 1.

$$J(Tl—CH_3) = —126.4(\pm 26.2) \cdot \delta(Tl—CH_3) + 559.5(\pm 40.5)\ r = 0.950 \qquad (2)$$

$$J(Sn—CH_3) = —25.6(\pm 7.1) \cdot \delta(Sn—CH_3) + 134.4(\pm 9.2)\ r = 0.946 \qquad (3)$$

$$J(^{13}C—H) = 5.2(\pm 1.6) \cdot \delta(Sn—CH_3) + 130.4(\pm 2.1)\ r = 0.933 \qquad (4)$$

Therefore, the same factor may be applied for the solvent dependence of the $J(M—CH_3)$ values for all dimethylmetal compounds studied in this report, since the C—M—C skeleton of these compounds is supposed to be similar from the Raman spectral data in Table 1.

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