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PROTON AND CARBON-13 NMR STUDY OF GROUP IVB (^{117,119}Sn, ^{207}Pb) AND MERCURY (^{199}Hg) ORGANOMETALLICS

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Summary

Proton and carbon-13 data of $(CH_3)_3SnX$, $[(CH_3)_3CCH_2]_3SnX$, $(CH_3)_3PbX$, $[(CH_3)_3CCH_2]_3PbX$, and $(CH_3)_3CCH_2HgX$, where X = Me, Et, i-Pr, t-Bu, neo-Pent, CH=CH$_2$, Cl, Br, I, or OH, are reported. The effects of electronic and steric factors on ^1J(MC) and ^2J(MH) (M = Sn, Pb, and Hg) have been studied. Linear relationships exist between ^1J(MC) and ^2J(MH). These relationships are discussed in terms of the mechanisms of the coupling constants.

The understanding of the mechanism of heavy nuclei spin—spin coupling with directly bonded carbon-13 and with geminal protons (M—C—H) is of interest particularly to gain insight into the bonding and structure of organometallic molecules. Although several studies describing substituent effects on geminal tin—proton, lead—proton, and mercury—proton coupling constants have been reported in the recent years relatively few reports are available on the corresponding one-bond metal—carbon coupling constants. In this paper, we report M—C and M—C—H coupling constants of trimethyl- and trineopentyl-tin and -lead derivatives and neopentylmercury derivatives and discuss them qualitatively in terms of the relative importance of their mechanisms of coupling.

According to the theory of spin—spin interaction developed by Ramsey [1], coupling is determined by the sum of three terms: (1) the Fermi contact; (2) the interaction between the electron spin and the nuclear dipole, J(dipole); and (3) the interaction of the magnetic field of the nuclear dipole with orbital magnetic moment of the electron, J(orb). The contact term is usually considered to be dominant in the coupling between directly bonded nuclei [2,3]. However, the other terms, particularly the dipole term can make significant contribution to one-bond metal—carbon coupling.

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Results

Tables 1-4 list the ^{1}H NMR data of tin and lead compounds, R_3MX (R = CH_3, $CH_2C(CH_3)_3$). The spectra of the compounds with X = alkyl and vinyl were run on pure liquids as well as in deuterochloroform (1/1 by volume), and no concentration effect on ^{117,119}Sn—^{1}H and ^{207}Pb—^{1}H coupling constants was detected. Also in the spectra of $(CH_3)_3SnCl$ and $(CH_3)_3SnBr$, measured at 0.1-3.0 *M* concentration range in $CDCl_3$, no concentration dependence of the tin—proton coupling constants was observed. Our values were essentially the same as reported by Lorbeth and Vahrenkamp [4] at ~0.25 *M* concentration in CCl_4. However, lead—proton coupling constants of trimethyllead halides increased with concentration (see Table 3). The increase in ^2J(PbH) is attributed to the self-association of these compounds in solution. No concentration effect on the terminal lead—proton coupling was noted in trineopentyllead halides and hydroxide.

The ^{13}C NMR spectra of tin, lead, and mercury compounds were also run in $CDCl_3$. The pertinent data are listed in Tables 5, 6 and 7. Mercury—carbon coupling constants particularly ^1J(HgC), like ^2J(HgH) [5], in neopentylmercuric cyanide, chloride, and acetate show considerable concentration dependence.

^1J(PbC) and ^2J(PbC) in hexaorganodilead. McFarlane et al. [6], determined the lead—carbon coupling constants of hexamethyldilead by heteronuclear magnetic double resonance and, surprisingly, assigned the larger coupling constant (+92 Hz) to ^2J(PbC) and the smaller (+28 Hz) to ^1J(PbC). By comparison, in hexamethylditin $^1J(^{119}$SnC) (—240 Hz) is numerically considerably greater than $^2J(^{119}$SnC) (—56 Hz) [7]. The negative signs of these coupling constants are due to the negative magnetogyric ratio of ^{119}Sn. (Note: For convenience,

TABLE 1

PROTON NMR DATA OF TRIMETHYLTIN COMPOUNDS, $(CH_3)_3SnX$

	CH_3				
X	$\delta(CH_3)$ (ppm) [a]	$^2J(^{117}SnH)$ (Hz)	$^2J(^{119}SnH)$ (Hz)	$^1J(^{13}CH_3)$ (Hz)	X
Me	0.07 [27]	52.0 [27]	54.3 [27]	128 [28]	
Et	0.03 [27]	50.5 [27]	52.8 [27]		
i-Pr	0.00	48.6	50.8	128	$\delta(CH_3)$, 1.18 ppm [a]; $^3J(^{117}SnH)$, 70.2 Hz; $^3J(^{119}SnH)$, 72.7 Hz
t-Bu	0.00	48.0	50.0	128	$\delta(CH_3)$, 1.08 ppm [a]; $^3J(^{117}SnH)$, 62.8 Hz; $^3J(^{119}SnH)$, 65.5 Hz
$CH{=}CH_2$	0.13	53.5	56.5	129	
$Sn(CH_3)_3$	0.32	46.4	48.5	128	
Cl	0.61 [4]	55.7 [4]	58.1 [4]	133	
Br	0.73 [4]	55.2 [4]	57.8 [4]	131	
I	0.88 [4]	54.7 [4]	57.2 [4]		
OH [b]	0.37	59.0 [c]			

[a] Downfield from internal TMS. [b] About 0.5 *M* in $CDCl_3$. [c] ^{117}Sn and ^{119}Sn satellites unresolved.

TABLE 2

PROTON NMR DATA OF TRINEOPENTYLTIN COMPOUNDS, $[(CH_3)_3CCH_2]_3SnX$

X	$\delta(CH_2)$ (ppm) [a]	$\delta(CH_3)$ (ppm) [a]	$^2J(^{117}SnH)$ (Hz)	$^2J(^{119}SnH)$ (Hz)	$^4J(SnH)$ (Hz)	$^1J(^{13}CH_2)$ (Hz)
$CH_2C(CH_3)_3$	1.20	1.02	46.8	49.0	~2.7	126
$Sn[CH_2C(CH_3)_3]_3$	1.40	1.00	41.0	43.0	~2.4	
Cl	1.55	1.06	47.0	49.0	4.0	

[a] Downfield from internal TMS.

the signs of ^1J(MC) and ^2J(MH) coupling constants have been disregarded in this paper).

Our present study with neopentyllead compounds indicates a possible need to interchange the assignments of the lead—carbon coupling constants in hexamethyllead. For example, in hexaneopentyldilead, we have measured and assigned 58 Hz and 19 Hz to ^1J(PbC) and ^2J(PbPbC), respectively, on the following basis. A comparison of ^1J(PbC) and ^2J(PbCC) in the other neopentyllead derivatives (Table 6) indicates that the former coupling is usually several-folds greater than the latter. The ^2J(PbCC) in hexaneopentyldilead is 24 Hz, which means the assignment of the 58 Hz coupling to ^1J(PbC) is more consistent with the trend than if it were assigned the smaller coupling of 19 Hz. Likewise, in hexamethyldilead also the larger lead—carbon coupling probably belongs to ^1J(PbC) and the smaller to ^2J(PbPbC).

(continued on p. 257)

TABLE 3

PROTON NMR DATA OF TRIMETHYLLEAD COMPOUNDS, $(CH_3)_3PbX$

X	CH_3				X
	$\delta(CH_3)$	$^2J(PbH)$		$^1J(^{13}CH_3)$	
Me	0.74 [25]	61.8 [25]		134 [28]	
Et	0.67	56.4			$\delta(CH_3)$, 1.42 ppm [a]; $^3J(PbH)$, 151.4 Hz
i-Pr	0.67	51.3			$\delta(CH_3)$, 1.43 ppm [a]; $^3J(PbH)$, 150.5 Hz
neo-Pent	0.72 [25]	55.5 [25]		134	
$CH{=}CH_2$	0.77	65.0		135	$J(HH_{trans})$, 19.8 Hz; $J(HH_{cis})$, 12.2 Hz; $J(HH_{gem})$, 3.0 Hz
$Pb(CH_3)_3$	0.97	41.5			
		2 *M*	0.2 *M*		
Cl	1.60	76.0	66.0	70 [29]	
Br	1.67	72.0	64.0	68 [29]	
I	1.83	64.0	63.0	63 [29]	
OH	1.53 [29]			76 [29]	

[a] Downfield from internal TMS.

TABLE 4

PROTON NMR DATA OF TRINEOPENTYLLEAD COMPOUNDS, $[(CH_3)_3CCH_2]_3PbX$

X	$CH_2C(CH_3)_3$					X
	$\delta(CH_2)$ (ppm) [a]	$\delta(CH_3)$ (ppm) [a]	$^2J(PbH)$ (Hz)	$^4J(PbH)$ (Hz)	$^1J(^{13}CH_2)$ (Hz)	
Me	1.65 [25]	0.98 [25]	40.5 [25]	5.5 [25]	132	$\delta(CH_3)$, 0.81 ppm [a]; $^2J(PbH)$, 44.2 Hz [25]
Et	1.67 [25]	1.00 [25]	36.4 [25]	5.5 [25]		[25]
i-Pr	1.68 [25]	1.00 [25]	32.5 [25]	4.6 [25]		[25]
t-Bu	1.73 [25]	1.02 [25]	27.5 [25]	4.6 [25]		[25]
neo-Pent	1.78 [25]	1.02 [25]	33.8 [25]	5.3 [25]	131	
$CH{=}CH_2$	1.75	1.01	42.0	5.8		$J(HH_{trans})$, 19.5 Hz; $J(HH_{cis})$, 15.5 Hz; $J(HH_{gem})$, 4.5 Hz
Pb(neo-Pent)$_3$	2.01 [24]	1.03 [24]	19.8 [24]	5.0 [24]		
Cl	2.45 [24]	1.12 [24]	30.0 [24]	8.0 [24]		
Br	2.53 [24]	1.11 [24]	28.0 [24]	8.0 [24]	135	
I	2.70	1.11	25.0	7.1		
OH	2.13	1.10	37.6	7.4		

[a] Downfield from internal TMS.

TABLE 5

CARBON-13 NMR DATA OF TIN COMPOUNDS, R_3SnX

X	R	CH_3			$\overset{1}{C}H_2\overset{2}{C}(\overset{3}{C}H_3)_3$					
		Concentration in $CDCl_3$	δ(C) (ppm)[a]	$^1J(^{119}SnC)$ (Hz)	δ(C(1)) (ppm)[a]	δ(C(2)) (ppm)[a]	δ(C(3)) (ppm)[a]	$^1J(^{119}SnC)$ (Hz)	^2J(SnC) (Hz)	^3J(SnC) (Hz)
Me	Me			337.8 [30]						
CH=CH_2	Me	1/1[b]	10.0[c]	353(337)[d]						
$Sn(CH_3)_3$	Me			240 [7]						
Cl	Me	3 *M*	0.7[c]	379(365)[d]						
Br	Me	3 *M*	0.8[c]	365(349)[d]						
neo-Pent	neo-Pent	0.5 *M*			33.3	32.5	33.8	302(290)[d]	15[e]	32[e]
Sn(neo-Pent)$_3$	neo-Pent	0.2 *M*			33.3	32.5	33.9	222(212)[d]		29[e]
Cl	neo-Pent	0.5 *M*			40.5	32.3	33.2	327(312)[d]	24[e]	42[e]

[a] Downfield from internal TMS. [b] By volume. [c] Upfield from internal TMS. [d] Values in parentheses are $^1J(^{117}SnC)$ coupling constants. [e] ^{117}Sn and ^{119}Sn satellites unresolved.

TABLE 6

CARBON-13 NMR DATA OF LEAD COMPOUNDS, R_3PbX

X	R	CH_3			$\overset{1}{C}H_2\overset{2}{C}(\overset{3}{C}H_3)_3$					
		Concentration in $CDCl_3$	δ(C) (ppm)[a]	^1J(PbC) (Hz)	δ(C(1)) (ppm)[a]	δ(C(2)) (ppm)[a]	δ(C(3)) (ppm)[a]	^1J(PbC) (Hz)	^2J(PbC) (Hz)	^3J(PbC) (Hz)
Me	Me			251 [17]						
CH=CH_2	Me	1/1[b]	3.0[c]	279						
$Pb(CH_3)_3$	Me			92[d]						
Br	Me	0.2 *M*	15.2	246						
$CH_2C(CH_3)_3$	Me	1/1[b]	3.0[c]	194	39.6	33.1	33.1	336	37	61
Me	neo-Pent	1/1[b]	1.3	98	41.8	33.4	33.4	222	34	51
neo-Pent	neo-Pent	1.0 *M*			43.7	33.7	33.7	168	33	48
$\overset{4}{C}H=\overset{5}{C}H_2$[e]	neo-Pent	1/1[b]			44.4	33.1	33.5	241		54
Pb(neo-Pent)$_3$[f]	neo-Pent	~0.3 *M*[g]			45.6	34.0	34.0	58[d]	24	40
Br	neo-Pent	0.5 *M*			61.3	34.9	33.4	133	34	66

[a] Downfield from internal TMS. [b] By volume. [c] Upfield from internal TMS. [d] See text for assignment of these values. [e] δ(C(4)), 151.1 ppm[a]; δ(C(5)), 130.6 ppm[a]. [f] ^2J(PbPbC), 19 Hz[d]. [g] Saturated.

TABLE 7

CARBON-13 AND PROTON NMR DATA OF $(\overset{3}{C}H_3)_3\overset{2}{C}\overset{1}{C}H_2HgX$

X	Concentration in $CDCl_3$	δ(C(1)) (ppm) [a]	δ(C(2)) (ppm) [a]	δ(C(3)) (ppm) [a]	^1J(HgC) (Hz)	^2J(HgC) (Hz)	^3J(HgC) (Hz)	^2J(HgH) [b] (Hz)
Me		62,5 [b]	33,3 [b]	35,2 [b]	690 [5]	30 [5]		102
neo-Pent	1/1 [c]	63,0	33,9	35,7	690	29	72	94
$CH{=}CH_2$		55,7 [b]	33,7 [b]	35,6 [b]	820 [5]	31 [5]		109
CN	5 M	47,7 [b]	33,2 [b]	34,7 [b]	1404 [5]	51 [5]	120 [5]	180
	3 M	47,7	33,3	34,6	1374		118	177
	2 M	47,8	33.4	34,7	1362		117	
	1 M							174
	0 M [d]				1330			173
Cl	5 M	52,7 [b]	33,4 [b]	34,2 [b]	1514 [5]	70 [5]	149 [5]	202
	3 M	52,5		34,1	1488		148	199
	2 M	52,5	33.4	34,2	1472		147	
	1 M							195
	0 M [d]				1448			193
$OCOCH_3$ [e]	5 M	45,2 [b]	33,0 [b]	33,9 [b]	1563 [5]	71 [5]	150 [5]	210
	3 M	45,2	33,1	33,9	1546		149	208
	2 M	45,4	33,1	34,0	1529		148	
	1 M							205
	0 M [d]				1506			204
ONO_2	0,5 M	46,9 [b]	30,0 [b]	33,2 [b]		85 [5]	170	222

[a] Downfield from internal TMS. [b] Calculated from the chemical shifts given in ref. 5 using CS_2 chemical shift of 192,7 ppm downfield from internal TMS. [c] By volume. [d] Extrapolated. [e] The $^{13}CH_3$ (3 M solution) appeared at 23.9 ppm [a].

Discussion

Theoretical studies indicate that Fermi contact is the dominant term which determines the magnitude of geminal tin—proton [8-10], lead—proton [8-10], and mercury—proton [8-12] coupling constants. Smith [13] extended the original valence-bond theory of geminal proton—proton [14] and carbon—proton [15] coupling to the geminal metal—proton couplin in $(CH_3)_4M$ (M = Sn and Pb) and $(CH_3)_2Hg$. According to his extension, a simplified Fermi contact term for ^2J(M—C—H) can be written as:

$$^2J(\mathrm{M{-}C{-}H}) \propto \gamma_M\gamma_H(\alpha_{MC})^2(\alpha_{HC})^2 \left(\frac{Z_M^*}{n_M}\right)^3 \left(\frac{Z_H^*}{n_H}\right)^3 \Delta E^{-1} \qquad (1)$$

where γ's are nuclear magnetogyric ratios, $(\alpha_{MC})^2$ and $(\alpha_{HC})^2$ are the fractional *s* characters of the orbitals of M and H respectively involved in bonding to carbon, Z_M^* and Z_H^* are the effective nuclear charges of these orbitals, *n* is the principal quantum number of the period to which the atom belongs, and ΔE is the average energy approximation term. The $(\alpha_{HC})^2$, n_H, and Z_H^* are equal to 1.

In the trimethyl-tin and -lead series the geminal metal—proton coupling increases with the substituent electronegativity OH > Cl > Br > I ≃ $CH{=}CH_2$ > Alk. This is understandable from the expected increase in $(\alpha_{MC})^2$ and Z_M^* with increase in the substituent electronegativity. According to Bent's isovalent model [16] the *s* character tends to concentrate in orbitals directed toward more electropositive groups. However, this is not so particularly in the trineopentyllead halides in which the geminal lead—proton coupling constants are smaller than those in the alkyltrineopentyllead compounds. Although considerably more *s* character is expected in the Pb—C bonds of the trineopentyllead halides than of the alkyltrineopentyllead compounds not only because of the higher electronegativities of the halides compared to those of the alkyl groups but also because of the steric opening of the $\text{neo-Pentyl}_3\text{Pb}$ group due to the polarizability of the $Pb^{\delta+}$—$X^{\delta-}$ bond in the former compounds.

The anomalous trend in ^2J(PbH) suggests that one or more assumptions on which eqn. 1 is based are probably not valid for the organolead compounds. It is most likely that the ΔE term is not constant. Carbon-13 data provides more intimate information on this point. For example, Roberts et al. [17,18], related two-bond metal—carbon coupling constants to two-bond metal—proton coupling constants by

$$^2J(\mathrm{MC}) = a\ ^2J(\mathrm{MH}) \qquad (2)$$

where *a* is a constant. Eqn. 2 is a simple extension of the relationship derived by Karabatsos [15] for hydrocarbon systems (M = H) and can be derived from eqn. 1 and a similar expression written for ^2J(MC). The average energy approximation usually holds for hydrocarbons and *a* = 0.3, 0.4, and 0.61 for sp^3, sp^2, and *sp* hybridized carbons, respectively.

We have calculated the *a* values of pertinent neopentyl-tin, -lead, and -mercury compounds (Table 8). In alkyl- and vinyl-neopentylmercurials the *a* values are approximately equal to 0.3. But they are higher in neopentylmercuric chloride (0.35), acetate (0.34), and nitrate (0.38) which we previously interpret-

TABLE 8

a VALUES IN THE EXPRESSION $^2J(MC) = a\ ^2J(MH)$ OF PERTINENT NEOPENTYL-TIN, -LEAD, AND -MERCURY COMPOUNDS

Compound	$a = {}^2J(MC)/{}^2J(MH)$
$[(CH_3)_3CCH_2]_4Sn$	0.31
$[(CH_3)_3CCH_2]_3SnCl$	0.49
$(CH_3)_3CCH_2Pb(CH_3)_3$	0.68
$[(CH_3)_3CCH_2]_3PbCH_3$	0.85
$[(CH_3)_3CCH_2]_4Pb$	0.95
$[(CH_3)_3CCH_2]_3PbBr$	1.25
$(CH_3)_3CCH_2HgCH_3$	0.29
$[(CH_3)_3CCH_2]_2Hg$	0.31
$(CH_3)_3CCH_2HgCH{=}CH_2$	0.28
$(CH_3)_3CCH_2HgCl$	0.35
$(CH_3)_3CCH_2HgOCOCH_3$	0.34
$(CH_3)_3CCH_2HgONO_2$	0.38

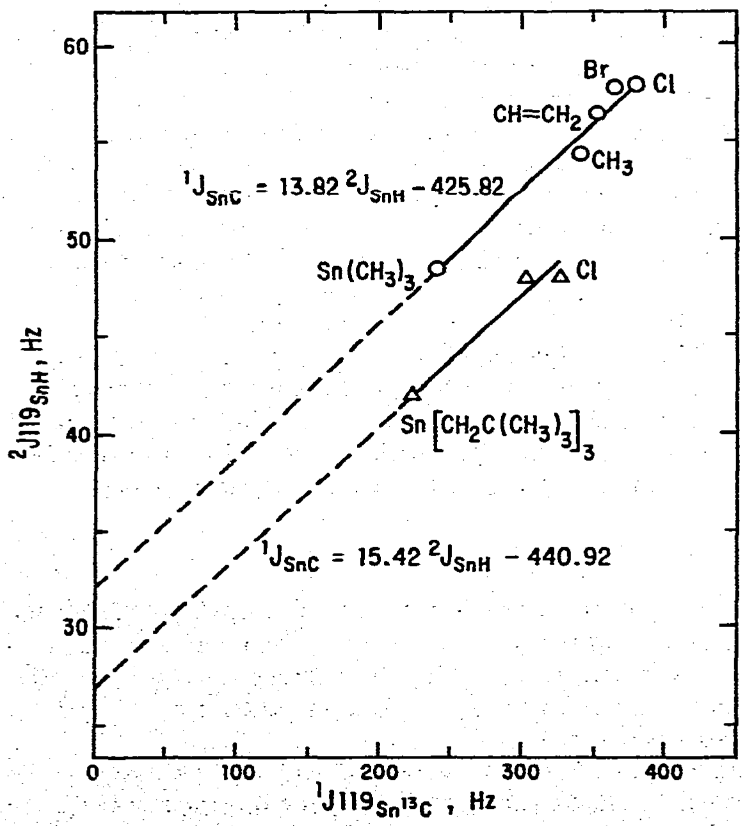

Fig. 1. Linear relationships between $^1J(^{119}Sn^{13}C)$ and $^2J(^{119}SnH)$ in $(CH_3)_3SnX$ (○) and $[(CH_3)_3CCH_2]_3SnX$ (△) derivatives.

ed in terms of hyperconjugative $d\pi$—$p\pi$ bonding involving $6d$ or $6(p + d)$ orbitals of mercury and the adjacent C—H bonds [5]. However, from the results of present study of neopentyl-tin and -lead compounds it appears that the hyperconjugative interaction might not be of as much significance as was originally thought. For example, in trineopentyltin chloride and all the neopentyllead compounds, including the mixed methyl-neopentyllead derivatives, the a values are much higher than expected (0.3-0.4) for any incipient double bond between the metal and carbon, M=--C- - -H. Consequently, the high values of a can be better explained by a possible failure of the average energy approximation than by hyperconjugative $d\pi$—$p\pi$ bonding alone. From this empirical analysis of the results in Table 8 it appears that the breakdown of the energy term (ΔE) in the neopentyl organometallics occurs in the following order: Pb > Sn > Hg.

Relationships between $^1J(MC)$ and $^2J(MH)$. Linear plots of ^1J(MC) vs. ^2J(MH) of tin, lead, and mercury compounds are shown in Figs. 1, 2 and 3, respectively. The relationships of tin and lead compounds when extrapolated give large intercepts for ^2J(MH). McFarlane [19] observed similar intercept for

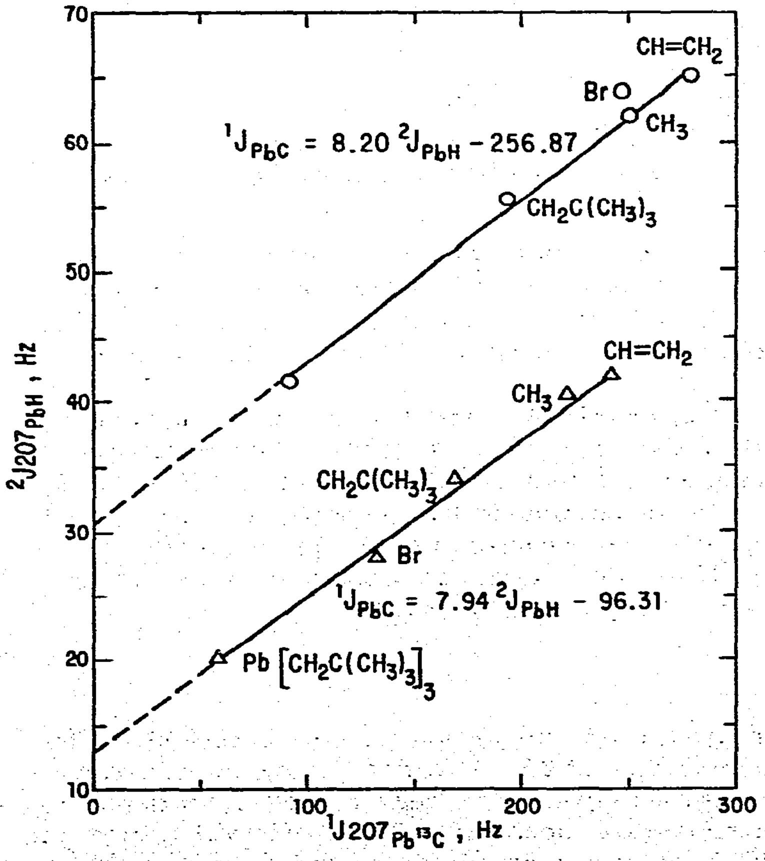

Fig. 2. Linear relationships between $^1J(^{207}Pb^{13}C)$ and $^2J(^{207}PbH)$ in $(CH_3)_3PbX$ (○) and $[(CH_3)_3CCH_2]_3PbX$ (△) derivatives.

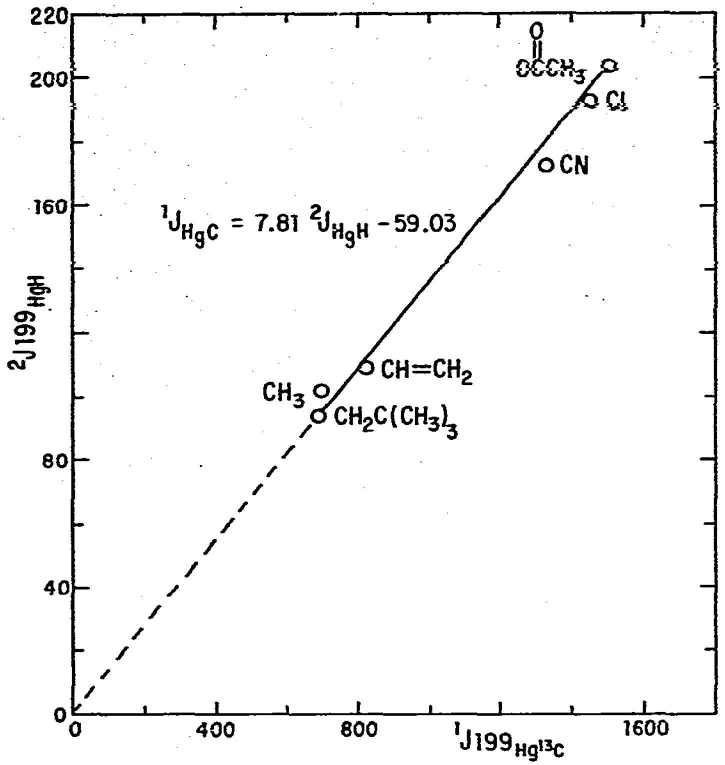

Fig. 3. Linear relationship between $^1J(^{199}Hg^{13}C)$ and $^2J(^{199}HgH)$ in $(CH_3)_3CCH_2HgX$ derivatives.

^2J(SnH) in a series of methyltin compounds and interpreted that one of these coupling constants receives significant contribution from J(dipole) and/or J(orb). Most probably it is J(dipole) which contributes significantly to ^1J(SnC) and ^1J(PbC) because the dipole term is usually strong when heavy nuclei are involved.

By comparison, the ^1J(HgC)—^2J(HgH) correlation in Fig. 3 when extrapolated passes almost through the origin, suggesting that Fermi contact is the dominant mechanism of coupling between directly bonded mercury and carbon. In other words, the dipole term makes practically no contribution to ^1J(HgC). This is probably due to high degree of s character ($\geq$50%) in the mercury orbitals bonding to carbon. The dipole interaction usually decreases with increasing s character and is zero for pure s orbitals [20].

Experimental

NMR spectra. Proton spectra were run on Varian Associates A60 or T60 spectrometer at a probe temperature of 35 ± 1°C. The ^{13}C spectra were run on a Bruker HFX-90 spectrometer equipped with a Digilab NMR-3 Fourier transform accessory. The spectrometer was operated at 22.63 MHz with a time-shared deuterium lock on $CDCl_3$, and using a broadband proton noise decoupler to eliminate $^{13}C—^1H$ couplings. Single coil Fourier transform operation was used with exciting rf pulses of about 10 microseconds. The system was operated with an 8192 point data file and 5000 Hz bandwidth. Good spectra were generally obtained with 1000-5000 scans, except that in the case of 0.2 *M* solution of $(CH_3)_3PbBr$ 35000 scans were used.

Compounds. Trimethyltin and trimethyllead compounds used in this study are known compounds and were prepared by the methods described in literature [21,22]. Tetraneopentyltin, trineopentyltin chloride, and hexaneopentylditin were prepared by Zimmer et al. [23], who also supplied the samples used in this study. Neopentyllead derivatives have become available from our previous studies [24,25]. New trineopentyllead compounds prepared for this study are described below.

Vinyltrineopentyllead. To a suspension of 5.0 g (0.01 mol) of trineopentyllead bromide in 100 ml of anhydrous ether at —30°C was added dropwise during stirring 13.3 ml (0.02 mol) of 1.5 *M* solution of vinylmagnesium chloride in tetrahydrofuran. Dry nitrogen atmosphere was maintained throughout the addition of the Grignard reagent. The reaction mixture was decomposed with 50 ml of ice-cold water. The organic layer was separated and dried over anhydrous sodium sulfate. The volatiles were removed in vacuo at room temperature and remaining liquid was distilled under reduced pressure. Vinyltrineopentyllead distilled at 71-72°C/0.25 mmHg as a colorless liquid n_D^{25} 1.5063. Yield was 3.2 g (72%). Anal. Found: C, 45.92; H, 8.11. $C_{17}H_{36}Pb$ calcd.: C, 45.62; H, 8.05%.

Its infrared spectrum (neat) showed absorptions at 3040w, 2956s, 2905s, 2866s, 1455m, 1374w, 1352w, 1230s, 1112m, 995w, 925m, and 722m cm^{-1}.

Trineopentyllead iodide. A solution of 2.54 g (0.01 mol) of iodine in 60 ml of anhydrous benzene was added dropwise during stirring to a solution of 8.40 g (0.01 mol) of hexaneopentyldilead in 100 ml of anhydrous benzene. Benzene was removed in vacuo and the remaining solid was crystallized from aqueous ethanol. Trineopentyllead iodide was obtained as white solid in 95% yield; m.p. 106-107°C. Anal. Found: C, 33.31; H, 5.92. $C_{15}H_{33}IPb$ calcd.: C, 32.90; H, 6.03%.

Trineopentyllead hydroxide. To a suspension of 2.74 g (0.005 mol) of trineopentyllead iodide in 50 ml of distilled water was added a solution of 0.40 g (0.01 mol) of sodium hydroxide in 20 ml of distilled water. The mixture was stirred for 1 hour and filtered. Trineopentyllead hydroxide was obtained as white solid in almost quantitative yield. It was crystallized from aqueous ethanol; m.p. 175-177°C. Anal. Found: C, 41.35; H, 7.52. $C_{15}H_{34}OPb$ calcd.: C, 41.17; H, 7.77%.

Its infrared spectrum (KBr) showed absorptions at 3200w (broad OH stretch) [26], 2960s, 2865s, 1600w(br), 1455s, 1360s, 1312m (in plane OH deformation) [26], 1235s, 1114s, 1100m, 1005m, and 743s cm^{-1}.

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