The Mechanism of the Spin-Spin Coupling of Dimethyllead(IV) Complexes with ONNO Quadridentate Schiff Base Ligands and the Magnetically Non-equivalent Methyl Protons of a Dimethyllead(IV) Complex

Tetsuro Majima and Yoshikane Kawasaki*
Department of Petroleum Chemistry, Osaka University, Yamadakami, Suita, Osaka 565

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Several dimethyllead(IV) complexes with ONNO quadridentate Schiff base ligands have been prepared. The spin-spin couplings between the lead nucleus and the azomethine proton of the ligands, $^3J(^{207}Pb\text{-}N{=}CH)$, as well as the lead-methyl proton couplings, $^2J(^{207}Pb\text{-}CH_3)$, have been observed in various solvents. Both J values inclease with an increase in donor strength of the solvents. The mean excitation energy, the ΔE term in the Fermi contact term plays a dominating role for the lead-proton spin-spin coupling constants. Two methyl proton signals were, for the first time, found to be magnetically non-equivalent in the dimethyllead(IV) complex of sapr.

The metal-proton spin-spin coupling constants, J(M, H), in methyl compounds of Sn, Hg, Tl, and Pb have been known to sensitively reflect changes in the configuration and electronic state around the central metal.[1)] The various studies on the coupling mechanism of J(M,H), have been considered to be mainly governed by the Fermi contact interaction as approximately expressed by[2)]

$$J(\mathrm{M,H}) = \mathrm{const}\cdot\alpha_{\mathrm{M}}^2\cdot a_{\mathrm{M}}(ns)\cdot a_{\mathrm{H}}(1s)/\Delta E, \quad (1)$$

where α_M^2 is the s character of the metal orbitals in the metal–carbon bonds, $a_M(ns)$ and $a_H(ls)$ are the hyperfine coupling constants of the ns electron in a metal atom and the 1s electron of a proton respectively. ΔE is the mean singlet-triplet excitation energy.

It has been reported that in methyltin compounds the $^2J(^{119}Sn\text{-}CH_3)$ values depend almost entirely on the s character of the tin orbitals used in the tin–carbon bonds,[1b,3)] and in the methyl compounds of Hg and Tl, the effective nuclear charge is the dominating factor in addition to the s character.[4)] In dimethyllead(IV) compounds changes of the $^2J(^{207}Pb\text{-}CH_3)$ values with the solvent depends largely on the ΔE term.[5)]

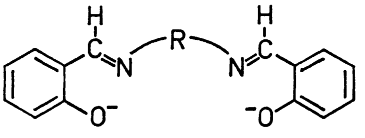
In dimethyllead(IV) complexes, the spin-spin coupling constants between the lead nucleus and the ligand protons have, in most cases, not been observed, for example in $(CH_3)_2Pb(acac)_2$ (acac=acetylacetonato).[5a)] The $^2J(^{207}Pb\text{-}CH_3)$ values have however been observed. One of the possible explanations is ligand dissociation; Eq. 2 and/or intermolecular exchange of the acac; Eq. 3 on the ^{1}H NMR time scale.[6)]

$$(CH_3)_2Pb(acac)_2 \rightleftharpoons (CH_3)_2Pb(acac)^+ + acac^- \quad (2)$$

$$(CH_3)_2Pb(acac)_2 + (CH_3)_2Pb(acac^*)_2 \rightleftharpoons 2(CH_3)_2Pb(acac)(acac^*) \quad (3)$$

Therefore, the mechanism of the lead-proton spin-spin coupling of dimethyllead(IV) complexes has been discussed mainly on the basis of changes in the $^2J(^{207}Pb\text{-}CH_3)$ values.[1e,5a–f,7)] However, observation of the lead-ligand protons spin-spin coupling constants are of importance to verify our previous assumptions that changes of the spin-spin coupling constants of dimethyllead(IV) complexes depend on changes in the ΔE term.[5)]

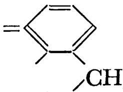
In this work, ONNO quadridentate Schiff base ligands, shown below, were selected, since these ligands have been known to coordinate storongly to the central metal atom[8)] and a spin-spin coupling constant between the lead nucleus and the azomethine proton of the ligands, $^3J(^{207}Pb\text{-}N{=}CH)$, may be predicted.

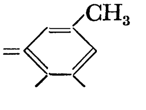


L

R = $-CH_2CH_2-$; N,N'-ethylenebis(salicylideneaminato): saln

R = $-CH_2CH(CH_3)-$; N,N'-propylenebis(salicylideneaminato): sapr

R =  ; N,N'-*o*-phenylenebis(salicylideneaminato): saph

R =  ; N,N'-(4-methyl-1,2-phenylene)-bis(salicylideneaminato): sato

Experimental

Materials. Dimethyllead dichloride was prepared by the chlorination of tetramethyllead in ethyl acetate at −10 °C.[9)] Schiff bases, N,N'-alkyl- or -aryl-substituted-bis(salicylideneamine)s (H_2**L**) were prepared from dehydration reactions between salicylaldehyde and the corresponding diamines by refluxing in ethanolic solution.[10)] The solvents used were reagent grade and purified according to the standard method except for $CDCl_3$ which was used as supplied.

*Preparation of $(CH_3)_2Pb$**L**$\cdot S$ (**L**=saln, sapr, saph, and sato; $S=CH_3OH$ or H_2O).* Dry methanol solution (20 dm^3) of the sodium salts of an appropriate Schiff base (Na_2**L**), prepared from sodium methoxide in methanol (Na; 0.5 g, 20 mmol) and H_2**L** (10 mmol), was added dropwise under stirring to dimethyllead dichloride (2.5 g, 10 mmol) in dry methanol (30 dm^3) and the mixture was stirred for a few hours. The precipitates were filtered, washed with benzene and methanol, and recrystallized from hot methanol. The crystalline complexes obtained in this manner contained one molecule of methanol or water.[11)]

Molecular Weight and Conductivity Measurements. The molecular weight of $(CH_3)_2Pb(saln)\cdot CH_3OH$ in $CHCl_3$

(0.5 wt %) was established using a Mechrolab vapor-pressure osmometer at 25 °C and was found to be 562 (504 calcd for $(CH_3)_2Pb(saln)$). This suggests that the methanol in the complex is free in solvents.[12] Molar conductances in DMSO were measured by a Yokogawa F-225A Universal bridge and a cell with a cell constant of 0.377 cm^{-1} at 25±0.1 °C. The specific conductance of DMSO used was $\kappa=4.2\times10^{-7}\ \Omega^{-1}\ cm^{-1}$. Molar conductances ($\Lambda_m$) of $(CH_3)_2Pb\mathbf{L}\cdot S$ in DMSO (10^{-3} mol dm^{-3}) were $<0.8\ \Omega^{-1}$ cm^2 mol^{-1} (Table 1). All complexes were found to be non-electrolytes.

The IR, ^1H NMR, and UV Spectra. The IR spectra were recorded on a Hitachi 225 spectrophotometer. The ^1H NMR studies were conducted on a JEOL-PS-100 spectrometer operating at 100 MHz. All data were obtained in *ca.* 4 wt %. Chemical shifts were measured wih TMS as internal standard at ambient temperature. The UV spectra were recorded on a Hitachi model 356 spectrophotometer with 0.1 cm quartz cells.

Analytical data, physical properties, and IR, ^1H NMR, and UV spectral data for the dimethyllead(IV) complexes prepared in this study are summarized in Tables 1—6.

Results and Discussion

As expected, the spin-spin coupling constants between the azomethine proton and the lead nucleus, $^3J(^{207}Pb\text{–}N{=}CH)$, were observed for all complexes; $(CH_3)_2Pb\mathbf{L}\cdot S$ ($\mathbf{L}$=saln, sapr, saph, and sato; S=CH_3OH or H_2O) (Tables 2—5).[13] The chemical shifts of the ligand protons, in all cases, moved to a higher magnetic field upon complex formation. In the case of the sapr complex two azomethine proton signals with different $^3J(^{207}Pb\text{–}N{=}CH)$ values were observed, thought due to the effect of the methyl group in the propylene unit in sapr and the difference in the strength of coordination of the two azomethine nitrogen atoms to the lead atom. One azomethine proton being closer to the methyl group (H_a) is more shielded (up-field shifts of *ca.* 0.05 ppm) and has a larger spin-spin coupling to the lead nucleus than the other (H_b). Similarly, in the sato complex two azomethine proton signals were observed, the difference in chemical shift being smaller than in the sapr complex, and the two $^3J(^{207}Pb\text{–}N{=}CH)$ values were equal within experimental error. Assignment of two signals is difficult to make from this result only. In IR spectra (Table 1), the stretching frequencies of the C–N double bond in CH_2Cl_2 (1608—1620 cm^{-1}) and in hexamethylphosphoric triamide (HMPA) (1608—1625 cm^{-1}) are almost the same but move to lower frequencies from those of the free Schiff bases (1618, 1620, 1628, and 1635 cm^{-1} for H_2saln, H_2sapr, H_2saph, and H_2sato in CH_2Cl_2 respectively). None of these complexes exhibited electric conductivity in DMSO (Table 1). Consequently, the ligand in these complexes may be assumed to coordinate to the lead atom as ONNO quadridentate ligands in all the solvents, according to a similar discussion in the dimethyllead complexes series.[5] In the UV spectra of $(CH_3)_2Pb(saln)\cdot CH_3OH$ (Table 6), a blue shift for the longest wavelength band was observed in the change from

TABLE 1. ANALYTICAL DATA, PHYSICAL PROPERTIES, AND IR SPECTRAL DATA OF $(CH_3)_2Pb\mathbf{L}\cdot S$

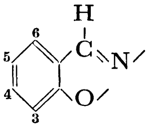
$(CH_3)_2Pb\mathbf{L}\cdot S$		Color	Mp (°C)	Found (Calcd) (%)				Λ_m[a)] (Ω^{-1} cm^2 mol^{-1})	Found (Calcd) mol wt[b)]	ν(C=N) (cm^{-1}) in CH_2Cl_2[c)] (in HMPA)[c)]
L	S			C	H	N	Pb			
saln	CH_3OH	yellow	180[d)]	42.42 (42.61)	4.13 (4.52)	5.30 (5.23)	38.44 (36.68)	0.75	562 (504)[e)]	1620 (1625)
sapr	CH_3OH	yellow	143[d)]	44.07 (43.71)	5.02 (4.77)	4.97 (5.09)	37.41 (37.69)	0.53	—[f)]	1616 (1615)
saph	CH_3OH	orange-yellow	148[d)]	47.12 (47.33)	4.06 (4.14)	4.73 (4.80)	35.29 (35.50)	0.50	—[f)]	1607 (1605)
sato	H_2O	orange-yellow	152[d)]	47.15 (47.33)	4.00 (4.14)	4.77 (4.80)	35.59 (35.50)	0.71	—[f)]	1608 (1606)

a) In DMSO. b) In $CHCl_3$. c) 5 wt %. d) Decompose. e) Calcd for $(CH_3)_2Pb(saln)$. f) Not measured.

TABLE 2. THE ^1H NMR SPECTRAL DATA OF $(CH_3)_2Pb(saln)\cdot CH_3OH$

Solvent	δ(N=CH) (ppm)	δ(ring proton)[a)] (ppm)				$\delta(CH_2)$ (ppm)	$\delta(OCH_3)$ (ppm)	$\delta(Pb\text{–}CH_3)$ (ppm)	$^2J(^{207}Pb\text{–}CH_3)$ (Hz)	$^3J(^{207}Pb\text{–}N{=}CH)$ (Hz)
		4-H[b)]	6-H[c)]	3-H[c)]	5-H[b)]					
$CDCl_3$	7.86	7.24	7.00	6.60	6.42	3.90	3.43	2.06	157.8	23.4
CH_2Cl_2	7.88	7.16	7.03	6.53	6.37	3.88	3.22	1.99	162.1	24.1
CH_3OH	8.00	7.14	7.09	6.60	6.48	3.93	—[d)]	2.02	163.8	25.9
$(CH_3O)_3PO$	7.98	7.07	7.04	6.36	6.25	—[d)]	—[d)]	1.86	172.8	27.0
Pyridine	7.97	—[d)]	—[d)]	6.54	6.32	3.67	—[d)]	2.03	180.0	28.1
DMSO	7.99	7.09	7.06	6.43	6.27	3.81	—[d)]	1.77	178.8	29.0
HMPA	8.16	7.04	7.06	6.36	6.17	3.89	—[d)]	1.78	187.5	29.3

a)



b) dd signal. c) d signal. d) Obscured by the resonance peaks of the solvents.

non-coordinating solvent to donor solvent. Other bands exhibited small changes. This, however, is quite different for $(CH_3)_2Pb(ox)_2$ (ox=8-quinolinolato) in which the red shift was obtained at the longest wavelength[5c] and this may arise from a difference in coordination to the lead atom.

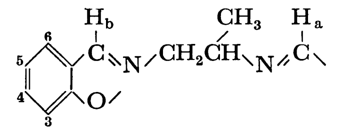
The $^2J(^{207}Pb\text{-}CH_3)$ values of these complexes in $CDCl_3$ (154—158 Hz) are comparable to those of many dimethyllead(IV) complexes having a six-coordinate configuration with a linear C–Pb–C skeleton (for

TABLE 3. THE ^{1}H NMR SPECTRAL DATA OF $(CH_3)_2Pb(sapr)\cdot CH_3OH$[a)]

Solvent	$\delta(N{=}CH_a)$ $\delta(N{=}CH_b)$ (ppm)	δ (ring proton) (ppm) 4-H[b)]	6-H[c)]	3-H[d)]	5-H[e)]	δ(-CH-)[f)] (ppm)	$\delta(CH_2)$[f)] (ppm)
$CDCl_3$	7.82 7.87	7.12	7.01	6.60	6.41	7.12	3.86
CH_2Cl_2	7.82 7.87	7.14	7.02	6.56	6.40	7.14	3.85
CH_3OH	8.03 8.08	7.20	7.16	6.64	6.51	7.20	—[h)]
$(CH_3O)_3PO$	7.97 8.02	7.13	6.99	6.35	6.24	7.13	—[h)]
Pyridine	—[h)]	—[h)]	—[h)]	6.62	6.53	—[h)]	3.60
DMSO	7.96 8.01	7.08	7.03	6.40	6.27	7.08	—[h)]
HMPA	8.04 8.09	7.05	6.98	6.33	6.14	7.05	—[h)]

Solvent	$\delta(CH_3)$[g)] (ppm)	$\delta(Pb\text{-}CH_3)$ (ppm)	$^2J(^{207}Pb\text{-}CH_3)$ (Hz)	$^3J(^{207}Pb\text{-}N{=}CH_a)$ $^3J(^{207}Pb\text{-}N{=}CH_b)$ (Hz)
$CDCl_3$	1.32	2.03 2.06	160.5	23.2 22.2
CH_2Cl_2	1.30	1.99 2.01	161.4	24.1 22.1
CH_3OH	1.30	1.93 1.96	164.4	24.9 23.5
$(CH_3O)_3PO$	1.27	1.84 1.85	168.6	25.1 23.7
Pyridine	1.11	1.99 2.02	177.6	—[h)]
DMSO	1.18	1.75 1.76	181.4	30.0 27.8
HMPA	1.19	1.73 1.75	186.0	30.5 27.9

a)

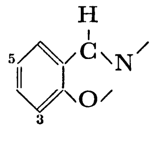


b) dt signal. c) dt signal. d) d signal. e) dd signal. f) m signal. g) d signal, coupling constant with the adjacent methine proton is 6 Hz. h) Obscured by the resonance peaks of the solvents.

TABLE 4. THE ^{1}H NMR SPECTRAL DATA OF $(CH_3)_2Pb(saph)\cdot CH_3OH$

Solvent	$\delta(N{=}CH)$ (ppm)	δ (ring proton)[a)] (ppm) 3-H[b)]	5-H[c)]	Others	$\delta(Pb\text{-}CH_3)$ (ppm)	$^2J(^{207}Pb\text{-}CH_3)$ (Hz)	$^3J(^{207}Pb\text{-}N{=}CH)$ (Hz)
$CDCl_3$	8.23	6.69	6.50	7.4—7.1	1.93	154.7	18.8
CH_2Cl_2	8.29	6.63	6.49	7.4—7.2	1.89	158.4	19.8
CH_3OH	8.33	6.76	6.60	7.4—7.2	1.78	165.3	20.7
$(CH_3O)_3PO$	8.32	6.53	6.41	7.4—7.1	1.71	174.3	23.4
Pyridine	—[d)]	6.56	6.40	—[d)]	1.95	177.2	—[d)]
DMSO	8.30	6.52	6.36	7.4—7.1	1.59	175.8	25.0
HMPA	8.38	6.44	6.23	7.4—7.0	1.60	190.4	27.0

a)

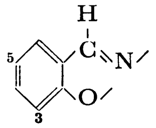


b) d signal. c) dd signal. d) Obscured by the resonance peaks of the solvents.

TABLE 5. THE ^{1}H NMR SPECTRAL DATA OF $(CH_3)_2Pb(sato) \cdot H_2O$

Solvent	δ(N=CH)	δ(ring proton)$^{a)}$ (ppm)			$\delta(CH_3)^{d)}$	δ(Pb-CH$_3$)	^2J(^{207}Pb-CH$_3$)	^3J(^{207}Pb-N=CH)
	(ppm)	3-H$^{b)}$	5-H$^{c)}$	Others	(ppm)	(ppm)	(Hz)	(Hz)
$CDCl_3$	8.25 8.26	6.74	6.53	7.4—7.1	2.45	1.94	154.4	18.6
CH_2Cl_2	8.25 8.26	6.61	6.48	7.4—7.1	2.43	1.88	158.7	19.1
CH_3OH	8.36 8.38	6.66	6.56	7.4—7.1	2.44	1.79	160.8	19.4
$(CH_3O)_3PO$	8.36 8.38	6.54	6.41	7.4—7.1	2.42	1.72	174.8	24.0
Pyridine	—$^{e)}$	6.56	6.40	—$^{e)}$	2.35	1.94	177.0	—$^{e)}$
DMSO	8.38 8.39	6.61	6.44	7.4—7.1	—$^{e)}$	1.63	178.7	26.3
HMPA	8.38 8.42	6.50	6.29	7.4—7.0	—$^{e)}$	1.62	189.1	28·4

a)



b) d signal. c) dd signal. d) Methyl proton of 4-methyl-1,2-phenylene group. e) Obscured by the resonance peaks of the solvents.

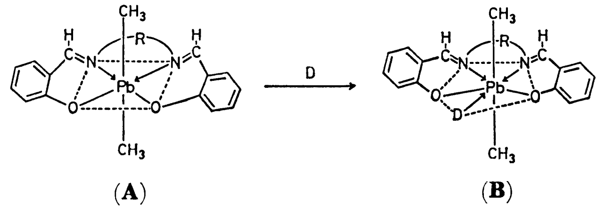
TABLE 6. THE UV SPECTRAL DATA OF $(CH_3)_2Pb(saln) \cdot CH_3OH$ IN SEVERAL SOLVENTS$^{a)}$

Solvent	λ (nm) (log ε)				
C_6H_6	—$^{b)}$	—$^{b)}$	—$^{b)}$	314(3.14)	397(3.90)
$CHCl_3$	252(4.56)	263(sh) (4.35)	278(sh) (4.02)	311(3.74)	393(3.77)
CH_2Cl_2	252(4.44)	260(sh) (4.23)	270(sh) (4.03)	316(3.93)	388(3.68)
Pyridine	—$^{b)}$	—$^{b)}$	—$^{b)}$	309(3.67)	379(4.00)
DMSO	260(4.24)	270(sh) (4.15)	278(sh) (3.97)	310(3.67)	378(3.93)
HMPA	259(4.31)	265(sh) (4.37)	275(sh) (3.93)	318(3.49)	379(3.83)

a) 5×10^{-4} mol dm^{-3}. Wavelengths (λ) and absorption coefficients (ε (mol^{-1} cm^2)) refer to band maxima and shoulders (sh). b) Obscured by absorption of the solvents.

example, 154.7 and 152.5 Hz in $(CH_3)_2Pb(acac)_2$$^{5a)}$ and $(CH_3)_2Pb(ox)_2$$^{5c)}$ respectively in $CDCl_3$). It is, therefore, reasonable to assume that these complexes have a six-coordinate configuration (**A**) in such non-coordinating solvents as $CDCl_3$ and CH_2Cl_2.

The proton resonances of the methyl groups attached to the lead atom, δ(Pb–CH$_3$), shift to a higher magnetic field and the ^2J(^{207}Pb–CH$_3$) values increase with an increase in donor strength of the solvents,$^{14)}$ as in the case of other dimethyllead(IV) complexes; $(CH_3)_2PbL_2$ (L=ox, acac, $OCOC_6H_5$).$^{5)}$ Therefore, the present complexes, $(CH_3)_2Pb\mathbf{L} \cdot S$, with ONNO quadridentate Schiff base ligands take a seven-coordinate configuration (**B**) in such donor solvents as DMSO and HMPA and this is supported by the ^2J(^{207}Pb–CH$_3$) values (175—190 Hz) which are comparable to or larger than those of an isolated seven-coordinated complex, $(CH_3)_2Pb(gbha)(H_2O)$ (gbha=2,2′-(ethanediylidenediimino) diphenolato) (178—181 Hz).$^{15)}$



(**A**) (**B**)

D=HMPA, DMSO, pyridine, $(CH_3O)_3PO$, CH_3OH.

One of remarkable features in ^{1}H NMR spectral data shown in Tables 2—5 is that the ^3J(^{207}Pb–N=CH) values increase with the ^2J(^{207}Pb–CH$_3$) values. The ^3J(^{119}Sn–N=CH) values of $(CH_3)_2Sn(saln)$ have been reported to decrease with an increase in donor strength of the solvents, although the ^2J(^{119}Sn–CH$_3$) values increase.$^{16)}$ Figures 1 and 2 show the linear relationships between the δ(Pb–CH$_3$) values and the ^2J(^{207}Pb–CH$_3$) and ^3J(^{207}Pb–N=CH) values for the dimethyllead complexes of saln and sapr respectively in various solvents. (The linear relationship was also obtained for saph and sato complexes.) In Figs. 3 and 4, the higher magnetic field shifts of the phenol ring proton resonances in these complexes with the methyl protons attached to the lead atom are shown. Interestingly, the amount of up-field shifts for 3-H and 5-H (*o*- and *p*-position to the oxygen atom respectively) are significantly larger than those for 4-H and 6-H (*m*-positions). This indicates that coordination of the solvent molecule brings about some electron donation to the lead atom and ligand, resulting in a decrease of the positive charge on the lead atom and an increase of electron density on the oxygen atom.

These results support a previous suggestion that a change of the mean excitation energy, ΔE, in the Fermi contact term plays a dominant role on the solvent dependence of the ^2J(^{207}Pb–CH$_3$) values.$^{5)}$ Namely,

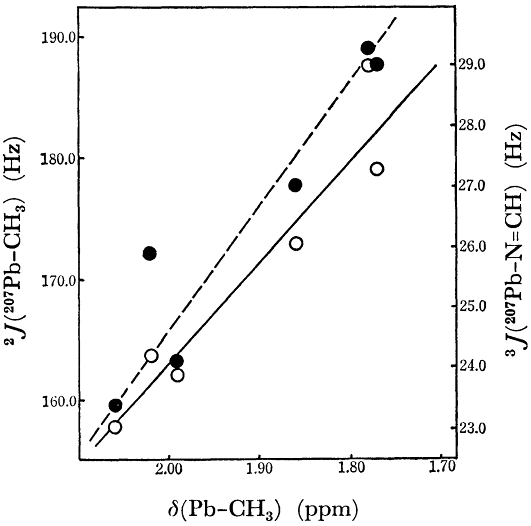


Fig. 1. Plots of the $^2J(^{207}\text{Pb-CH}_3)$ (—O—) and $^3J(^{207}\text{Pb-N=CH})$ (--●--) vs. δ(Pb-CH$_3$) values for $(\text{CH}_3)_2\text{Pb})(\text{saln})\cdot\text{CH}_3\text{OH}$ in several solvents.

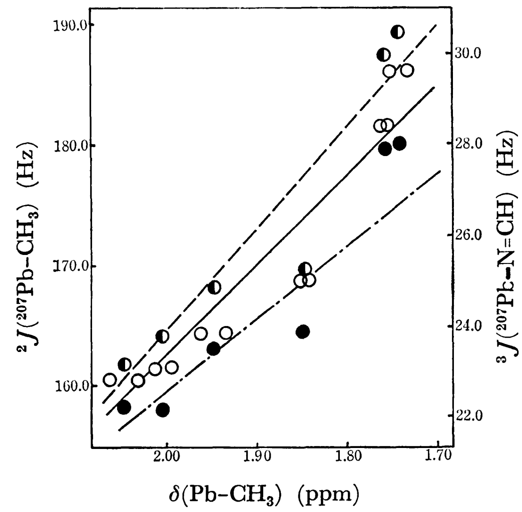


Fig. 2. Plots of the $^2J(^{207}\text{Pb-CH}_3)$ (—O—) vs. two δ(Pb-CH$_3$) values and of the $^3J(^{207}\text{Pb-N=CH}_a)$ --◐--) and $^3J(^{207}\text{Pb-N=CH}_b)$ (-·—●—·-) vs. the average of two δ(Pb-CH$_3$) values for $(\text{CH}_3)_2\text{Pb}(\text{sapr})\cdot\text{CH}_3\text{OH}$ in several solvents. See Table 3, regarding sings of azomethine protons.

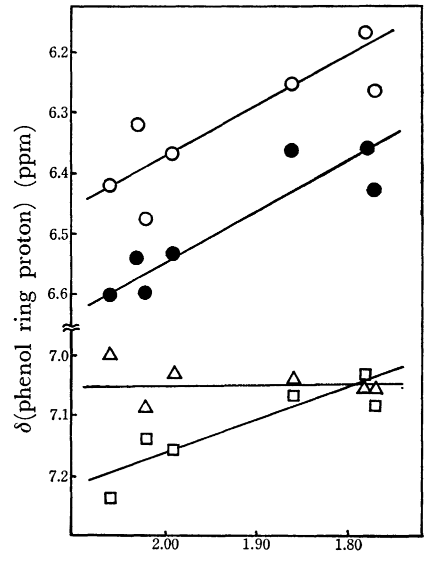


Fig. 3. Plots of the δ(phenol ring proton) vs. δ(Pb-CH$_3$) values for $(\text{CH}_3)_2\text{Pb}(\text{saln})\cdot\text{CH}_3\text{OH}$ in several solvents; 5-H (—O—), 3-H (—●—), 6-H (—△—), and 4-H (—□—). Signs of these protons are written in Table 2.

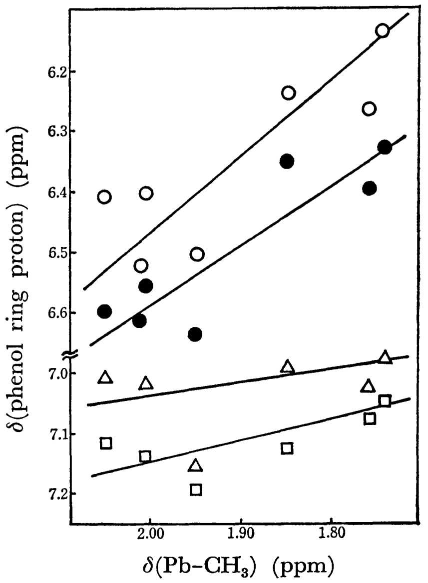


Fig. 4. Plots of the δ(phenol ring proton) vs. δ(Pb-CH$_3$) values for $(\text{CH}_3)_2\text{Pb}(\text{sapr})\cdot\text{CH}_3\text{OH}$ in several solvents; 5-H (—O—), 3-H (—●—), 6-H (—△—), and 4-H (—□—). Signs of these protons are written in Table 3.

the increase of the $^2J(^{207}\text{Pb-CH}_3)$ values together with the $^3J(^{207}\text{Pb-N=CH})$ values depend on a decrease of ΔE, which results from a decrease in the positive charge on the lead atom as a result of electron donation from the solvent molecules. It is difficult to interpret the results by the d-s mixing scheme,[1e] which has been proposed to account for the increase in the $^2J(^{205}\text{Tl-CH}_3)$ values of some dimethylthallium compounds in donor solvents. If the d-s mixing scheme were dominating, the s electron of the lead atom in the coordination plane of the ligands would transfer to the C–Pb–C bond, resulting in an increase of the s character of the lead atom for Pb–C bonds and a decrease in the coordination plane of ligands. Therefore, decrease in the $^3J(^{207}\text{Pb-N=CH})$ values was expected when the $^2J(^{207}\text{Pb-CH}_3)$ values increased, and *vice versa*. This is not consistent with the results reported here. Similarly, the results can not be explained in terms of the change of $a_{\text{Pb}}(6\text{ s})$ term in Eq. 1 which decreases with decreasing positive charge on the lead atom.

From Tables 2—5, it may be seen that the δ(N=CH) values shift to a lower magnetic field with an increase in donor strength of the solvents. This change may be accounted for by two compensating factors; 1) the down-field shift due to hydrogen bonding with oxygen atom of the solvents, which grows stronger with an increase of donor strength of the solvents, (the down-field shift of the azomethine proton for free H_2saln is as follows: 8.32, 8.53, 8.60, 8.73, 8.73, and 9.04 in $CDCl_3$, CH_2Cl_2, CH_3OH, $(CH_3O)_3PO$, DMSO, and HMPA respectively.) and 2) the up-field shift caused by the coordination of the solvent molecules to the lead atom. Indeed, the down-field shift of the N=CH proton in the saln complex from in $CDCl_3$ to in HMPA; 0.30 ppm was observed and is much smaller than that in H_2saln; 0.72 ppm. (These behaviors were observed also in sapr, saph, and sato complexes.)

It shoud be noted that the two methyl groups attached to the lead atom show different chemical shifts in the case of $(CH_3)_2Pb(sapr)\cdot CH_3OH$, although the $^2J(^{207}Pb–CH_3)$ values were the same within experimental error. In the other three complexes only one methyl signal was observed. The magnetic non-equivalence of the methyl protons is attributed to the rigidity of the N–C–C–N skeleton of the sapr ligand and to no dissociation of the ligand attached to the lead atom. The location of the methyl group of the propylene unit outside the coordination plane, induces magnetic non-equivalence above and below the coordination plane. The sapr complex is the first example of a dimethyllead(IV) complex that has magnetically non-equivalent methyl protons, a similar observation found in the case of $[(CH_3)_2Tl($*cis-syn-cis*-6,7,9,-10,17,18,20,21-octahydrodibenzo[*b.k*][1,4,7,10,13,16]-hexaoxacyclooctadecin$)]^+[\text{picrato}]^-$.[17]

In conclusion, from the present work on dimethyllead(IV) complexes with ONNO quadridentate Schiff base ligands, together with a series of spectroscopic studies for several other dimethyllead(IV) complexes previously reported,[5] the ΔE term in the Fermi contact term plays a dominant role in the solvent dependence of the indirect spin-spin coupling between the lead nucleus and proton, J(M,H).

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12) Since it is known that the addition of methanol to chloroform causes an increase of vapor pressure, the obserbed value (562) should be larger than 504 calculated for $(CH_3)_2Pb(saln)$, suggesting that $(CH_3)_2Pb\mathbf{L}\cdot S$ exists as a monomer and S (methanol or water in the crystals is completely free in solution: J. H. Perry, "Perry's Chemical Engineer's Handbook," 4th ed, McGraw-Hill, New York (1963), pp. 13—15.

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