Infrared, Raman, and Hydrogen-1, Carbon-13, and Lead-207 Nuclear Magnetic Resonance Spectra of Hexamethyldilead

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Abstract: The infrared and Raman spectra of hexamethyldilead have been recorded over the range 5000–70 cm^{-1}, both in the solid state and in solution, and assignments for the various fundamentals made. The spectra suggest that the skeletal symmetry of the molecule is D_{3d}. Using a simple valence force field, the following force constants were derived from the a_{1g} skeletal frequencies: $K_1 = 1.81$ (PbC stretching), $K_2 = 0.05$ (CPbC bending), and $K_3 = 0.83$ mdyn/Å (PbPb stretching). The values of K_1 and K_2 are very similar to the values of the corresponding force constants for tetramethyllead. From the three force constants, values for the two a_{2u}, three e_u, and three e_g skeletal frequencies have been calculated and found to be in reasonable agreement with the experimental values. The infrared spectrum of hexamethylditin has been measured in the range 200–70 cm^{-1} in order to locate the CSnC bending frequencies. Corresponding force constant and frequency calculations have also been carried out for this molecule, giving the results $K_1 = 2.21$, $K_2 = 0.09$, and $K_3 = 0.99$ mdyn/Å. The ^{1}H, ^{13}C, and ^{207}Pb nmr spectral parameters for hexamethyldilead are given and compared with the corresponding ones for hexamethylditin. The direct CPb coupling constant is surprisingly small, implying an unusually high per cent s character for the PbPb bond. The ^{207}Pb chemical shift is to high field of that found for tetramethyllead and appears to depend on factors other than the paramagnetic contribution.

The infrared and Raman spectra of the compounds $(CH_3)_6M_2$ (M = Si, Ge, or Sn) have all been closely studied, but the spectra of hexamethyldilead have not yet been reported. It has been deduced[2,3] that hexamethyldisilane has either D_{3h} (eclipsed methyl groups) or D_{3h}' (free rotation about the SiSi bond) symmetry. The Raman spectrum of hexamethyldigermane[4] and the infrared[5] and Raman[4] spectra of hexamethylditin have also been reported, but no deductions were made as to their stereochemistries. However, electron diffraction data on the corresponding lead compound are consistent[6] with its having a staggered ethane type structure (D_{3d} symmetry) and PbC and PbPb bond lengths of 2.25 and 2.88 Å, respectively. We considered it desirable to record the complete infrared and Raman spectra of hexamethyldilead for comparison with those above and in order to confirm the skeletal symmetry of the molecule. Certain force constants for the molecule have been calculated from the data on the basis of a simple valence force field. Similar calculations were made for hexamethylditin, and infrared measurements in the 200–70-cm^{-1} region were necessary in order to check certain calculated frequencies with the experimental ones.

The ^{1}H nmr spectrum of hexamethylditin has recently been completely interpreted,[7] and it was of interest to compare it with that of hexamethyldilead. The occurrence of peaks due to the molecule $(CH_3)_3{}^{207}Pb^{207}Pb(CH_3)_3$ allows the relative signs of J(PbCH) and J(PbPbCH) to be determined. Double resonance studies have also given the signs and magnitudes of the PbC coupling constants in this molecule.

Experimental Section

Preparation. Hexamethyldilead, mp 38°, was prepared by the method of Calingaert and Soroos[8] ($PbCl_2$ and CH_3MgBr at $-10°$ in ether). The compound blackened rapidly in air and hence it was purified immediately before use by dissolving it in ether, filtering off the metallic lead, and then pumping off the solvent; cream crystals remained. Solutions of the compound in benzene or cyclohexane were fairly stable, but those in carbon tetrachloride decomposed very rapidly.

Hexamethylditin (mp 28°) was obtained from Aldrich Chemicals and purified as described previously.[7]

Physical Measurements. The infrared spectra were recorded on Perkin-Elmer 225 and Grubb-Parsons GM3 spectrometers. The solid was run both as a Nujol and as a hexachlorobutadiene mull, while for solutions three solvents (benzene, cyclohexane, and carbon tetrachloride) were required to cover the full frequency range. Sodium chloride, potassium bromide, cesium iodide, or polythene plates or cells were used where appropriate.

The Raman spectra were recorded on a Cary 81 spectrometer fitted with a helium–neon (6328-Å) laser source. Spectra were recorded both on the solid powder, packed into the standard metal cone supplied with the instrument, and as solutions sealed into glass capillaries.

The force constants were calculated using a program devised for the Atlas computer of the University of London.

The ^{1}H nmr spectrum of hexamethyldilead (40% solution in benzene) was recorded on a Varian HA 100-Mcs spectrometer.

Heteronuclear magnetic double resonance experiments were performed on a JEOL C-60-H spectrometer modified by the addition of an extra coil within the probe. Power at the ^{13}C and ^{207}Pb resonant frequencies was provided by a Schlumberger frequency synthesizer, and the relative drift of the crystal controlled oscillators of the spectrometer and the synthesizer was found to be less than 1 in 5 × 10^7 during the course of the experiments.

The sample was a freshly prepared saturated solution (at 25°) of $(CH_3)_6Pb_2$ (containing ^{13}C and ^{207}Pb in natural abundance) in benzene, and the signal from the solvent was used to actuate the field-frequency locking circuits of the spectrometer. The proton spectrum was recorded in frequency-sweep mode, and ^{13}C and

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(1) (a) University College; (b) Sir John Cass College.

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Table I. The Infrared (Ir) and Raman (R) Spectra of Hexamethyldilead

	Solid		Solution[a]	
Assignment	R	Ir	R	Ir
$\nu_a(CH_3) + \delta_a(CH_3)$		4364 vw, br		4398 vw, br
$\nu_a(CH_3) + \delta_s(CH_3)$		4134 vw, br		4140 vw, br
$\nu_s(CH_3) + \delta_s(CH_3)$?		4053 vw, br		4060 vw, br
$\nu_a(CH_3)$	2997 w, br	2997 m		3000 m
$\nu_s(CH_3)$	~2912 w	2920 s		2922 s
		2856 w		
$2\delta_s(CH_3)$		2301 w		
$2\delta_s(CH_3)$		2269 m		2273 m
$\delta_a(CH_3) + \nu(PbC)$		1909 vw		
$\delta_s(CH_3) + \nu(PbC)$		1600 w		1601 w
$\delta_a(CH_3)$		~1455 w, br		~1445 w, br
$\delta_a(CH_3)$		~1383 w, br		~1383 w, br
$\delta_s(CH_3) + \delta(CPbC)$		1260 w		
$\delta_s(CH_3)$	1151 ms	1151 s	1162 s, pol	1153 s
$\delta_s(CH_3)$	1138 ms	1143 s	1143 ms	1145 ms
		1095 vw		~1100 vw, br
		1017 vw		
$\rho(CH_3)$		~742 vvs, v br		760 vs, br
		692 sh, br		
$\nu(PbPb) + \nu(PbC)$				590 w
				546 w
$\nu(PbC)$		464 vvs		467 vvs
	460 vs		458 vs, pol	
		448 vs		448 vs
$\delta(CPbC)$		117 s, br		118 s, br
$\delta(CPbC)$, $\nu(PbPb)$	121 s		116 vs, pol	

[a] Solutions are in benzene, cyclohexane, or carbon tetrachloride above 500 cm^{-1} and in benzene below 500 cm^{-1}. All measured frequencies were within 1 cm^{-1} of each other in different solvents.

Table II. Distribution and Approximate Description of the Normal Modes of Vibration of the C_6M_2 Skeleton of the Hexamethyldimetal Compounds

	$\nu_1\nu_2\nu_3$	ν_4	$\nu_5\nu_6$	$\nu_7\nu_8\nu_9$	$\nu_{10}\nu_{11}\nu_{12}$		
	D_{3h} a_1'	a_1''	a_2''	e'	e''		
	R, pol		Ir	R, Ir	R	Degrees of freedom	Distinct modes of vibration
	D_{3d} a_{1g}		a_{2u}	e_u	e_g		
	R, pol	a_{1u}	Ir	Ir	R		
$\nu(MC)$	1		1	1	1	6	4
$\nu(MM)$	1					1	1
$\delta(CMC)$	1		1	1	1	6	4
torsion		1				1	1
$\delta(CMM)$				1	1	4	2
Total	3	1	2	3	3	18	12

^{207}Pb line positions were determined by tickling experiments as described elsewhere.[7] The ^{13}C and ^{207}Pb frequencies were converted to Ξ values[9] by first correcting to the field strength appropriate to a TMS proton resonance at *exactly* 60 Mcps, and then multiplying by $^{10}/_6$. The precision of the ^{13}C measurements was limited by signal-to-noise ratio considerations, and possibly by two-bond $^{13}C \cdots H$ coupling; that of the ^{207}Pb measurements was limited chiefly by the complexity of the lead spectrum.

Results and Discussion

A. Infrared and Raman Spectra. The band maxima in the infrared and Raman spectra of hexamethyldilead are listed in Table I and are conveniently discussed in terms of methyl-group vibrations, PbC stretching vibrations, PbPb stretching vibrations, and CPbC bending vibrations. The vibrational representation of the skeletal modes is $3a_1' + a_1'' + 2a_2'' + 3e' + 3e''$ in D_{3h} and $3a_{1g} + a_{1u} + 2a_{2u} + 3e_u + 3e_g$ in D_{3d} (Table II).

Methyl-Group Vibrations. As found for tetramethyllead[10] and for the methyllead halides,[11] there is little coupling between the different methyl groups of hexamethyldilead. Hence the spectrum in this region is the same as that of a single methyl group attached to a heavy point mass. The piling up of fundamental frequencies in the spectra of lead compounds has been interpreted in terms of the large size and mass of the central atoms.[12] The assignments of the various vibrations of the methyl groups are thus obvious and are included in Table I without further discussion.

Lead–Carbon Stretching Frequencies. On the basis of previous work,[11] the PbC stretching frequencies in hexa-

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Table III. Force Constant Data for $(CH_3)_6Sn_2$ and $(CH_3)_6Pb_2$[a]

	$\nu_1(a_{1g})$	$\nu_2(a_{1g})$	$\nu_3(a_{1g})$	$\nu_5(a_{2u})$	$\nu_6(a_{2u})$	$\nu_7(e_u)$	$\nu_8(e_u)$	$\nu_9(e_u)$	$\nu_{10}(e_g)$	$\nu_{11}(e_g)$	$\nu_{12}(e_g)$
$(CH_3)_6Sn_2$: $K_1 = 2.21$, $K_2 = 0.09$, $K_3 = 0.99$ mdyn/Å											
Calcd	512	200	117	479	175	541	171	97	539	165	132
Obsd	512	190	126	499	142	520	142	<75	512	126 ?	...
$(CH_3)_6Pb_2$: $K_1 = 1.81$, $K_2 = 0.05$, $K_3 = 0.83$, mdyn/Å											
Calcd	458	136	90	458	116	474	124	74	474	119	88
Obsd	458	116	116	448	118	467	118	<75	458	116	<60

[a] The frequency numbering scheme is that of ref 3. ν_4 is the torsional mode which is inactive in D_{3d} (a_{1u} species).

methyldilead appeared most likely to yield structural information. Thus if the compound has D_{3d} symmetry with the staggered conformation of methyl groups, the four PbC stretching fundamentals belong to the species a_{1g} and e_g (Raman active only) and a_{2u} and e_u (infrared active only). On the other hand, for the eclipsed conformation (D_{3h} symmetry) the PbC stretching vibrations belong to the species a_1' and e'' (Raman active only), e' (both infrared and Raman active), and a_2'' (infrared active only). The second set of selection rules would also apply if the molecule has free rotation about the PbPb bond (D_{3h}' symmetry).

In practice, there is no infrared–Raman coincidence in the 450-cm^{-1} region, and hence the data conform to D_{3d} selection rules, in agreement with the conclusions from the electron diffraction data. There are two bands (at 448 and 467 cm^{-1}) in the solution infrared spectrum of the compound attributable to PbC stretching modes, whereas the solution Raman spectrum contains one such band at 458 cm^{-1}. The latter arises mainly from the a_{1g} vibration as the depolarization ratio (ρ) is 0.43; however, the e_g mode is probably coincident with it (Figure 1). Hexamethylditin also has two bands in its infrared spectrum attributable to SnC stretching vibrations (at 499 and 520 cm^{-1})[5] and only one such band in the Raman spectrum (at 512 cm^{-1});[4] as the latter is not coincident with the infrared bands, it is probable that this compound has D_{3d} symmetry also.

Lead–Lead Stretching Vibration and Skeletal Bending Vibrations. The infrared spectrum of the compound contains but a single band between 448 and 70 cm^{-1} (the limit of the present instrument), at 118 cm^{-1}. This band clearly arises from the infrared-active CPbC bending modes (a_{2u} and e_u in D_{3d}) in view of its similarity in frequency to the analogous bands of tetramethyllead (~ 130 cm^{-1}).[10] In view of the convergence of fundamental frequencies in methyllead compounds, the corresponding Raman-active bands (a_{1g} and e_g) would be expected at nearly the same frequency, and indeed the Raman spectrum of the compound contains a strong, polarized ($\rho = 0.42$) band at 116 cm^{-1}. However, this is also the region in which the PbPb stretching frequency (likewise a_{1g} symmetry) is expected to occur (*cf.* that in hexaphenyldilead[13] at 109 cm^{-1}); the phenyl–lead–phenyl bending vibrations occur at or below 74 cm^{-1} in the Raman spectra of the latter compound. We are thus led to assign the Raman band at 116 cm^{-1} to the superposition of the a_{1g} and e_g CPbC bending modes with the a_{1g} PbPb stretching mode. It seems surprising that two vibrations of the same symmetry could be degenerate, but it is highly improbable that the PbPb stretching frequency could be below the region scanned (limit 60 cm^{-1}). This result suggests that owing to the high mass of the lead atoms, and hence their very slight movement in each normal mode, the frequency of the CMC bending vibration is not affected by whether the PbPb stretching vibration is in or out of phase with it. The decoupling of skeletal vibrations in $(CH_3)_6M_2$ compounds as M gets heavier is clearly shown in Figure 2.

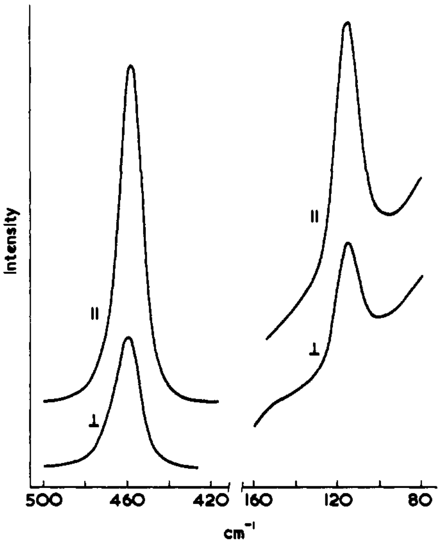

Figure 1. Raman spectrum of $(CH_3)_6Pb_2$, including polarization data.

Force-Constant Calculations. Assuming a diatomic model and an effective mass for lead of 207.2, the PbPb stretching force constant is calculated to be 0.82 mdyn/Å. On the same basis, the Sn–Sn stretching force constant of hexamethylditin is 1.26 mdyn/Å. In an attempt to define the force field a little more closely, we have also used the simple valence force field devised by Howard[14] for ethane; the field does not distinguish between D_{3d}, D_{3h}, and D_{3h}' symmetries, but the first is assumed for reasons outlined above. All bond angles were assumed to be tetrahedral, in agreement with the assumption of the electron diffraction study.[6] The effective mass of the methyl group was taken to be 15.0. This treatment leads to a cubic equation for the three a_{1g} skeletal frequencies in terms of the following force constants: K_1, PbC stretching; K_2, CPbC bending; K_3, PbPb stretching. The values for the force constants which give the best fit between calculated and

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(13) R. J. H. Clark, A. G. Davies, and R. J. Puddephatt, *Inorg. Chem.*, **8**, 457 (1969).

(14) J. B. Howard, *J. Chem. Phys.*, **5**, 442 (1937).

Table IV. Species Present in Hexamethyldilead

	Molecule	Abundance, %	Lines in ^1H spectrum
A	$(CH_3)_3PbPb(CH_3)_3$	56.03	9
B	$(CH_3')_3{}^{207}PbPb(CH_3)_3$	32.72	H′ 6, 12; H 7, 11
C	$(CH_3)_3{}^{207}Pb^{207}Pb(CH_3)_3$	4.78	8, (9), 10
D	$(^{13}CH_3')(CH_3)_2PbPb(CH_3)_3$	3.76	H′ 3, 15
E	$(^{13}CH_3')(CH_3)_2{}^{207}PbPb(CH_3)_3$	1.10	H′ 1, 5, 13, 17
F	$(^{13}CH_3')(CH_3)_2Pb^{207}Pb(CH_3)_3$	1.10	H′ 2, 4, 14, 16
G	$(^{13}CH_3')(CH_3)_2{}^{207}Pb^{207}Pb(CH_3)_3$	0.32	Not observed

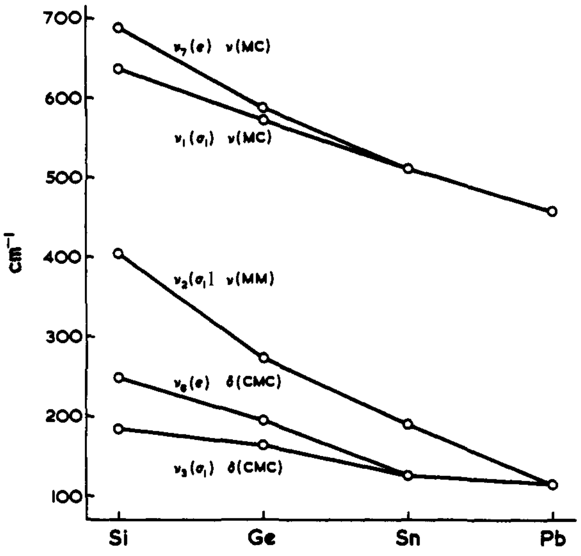

Figure 2. Some Raman-active fundamentals of the molecules $(CH_3)_6M_2$ (M = Si, Ge, Sn, or Pb) in the range 700–70 cm^{-1} using the frequency numbering scheme of ref 3, and D_3 nomenclature (as the silicon and germanium compounds are thought [2-4] to have D_{3h} or D_{3h}' skeletal symmetry).

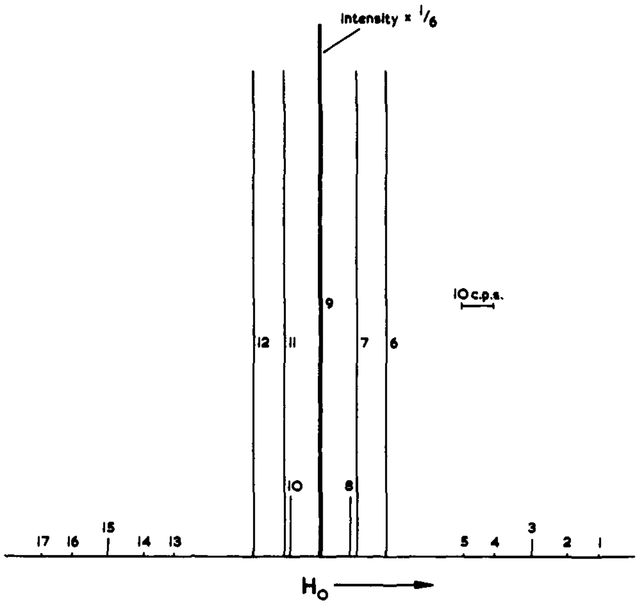

Figure 3. ^1H nmr spectrum of $(CH_3)_6Pb_2$.

observed frequencies are given in Table III. We have also recalculated the corresponding force constants of hexamethylditin and obtained slightly better agreement between the calculated and observed frequencies than obtained originally;[4] the results are also in Table III.

It is observed that by use of this model, although ν_1 can be fitted exactly, ν_2 and ν_3 are calculated to be further apart than they occur in practice, the deviation being more marked for lead than for tin. It seems probable that the neglect of interaction constants, in particular that connecting CMC bending with MM stretching, is the principal cause of these deviations. It has previously been recognized that this three-constant potential function for ethane exaggerates the extent of the coupling of the HCH bending and CC stretching motions.[15] Nevertheless, the derived force constants are closely similar to those calculated for other similar molecules. For example, for $(CH_3)_4Sn$ and $(CH_3)_4Pb$, the MC stretching (K) and CMC bending (K_δ/l^2) force constants, on the simple valence force field model, are calculated to be $K = 2.27$, $K_\delta/l^2 = 0.07$ (for tin) and $K = 1.88$, $K_\delta/l^2 = 0.05$ mdyn/Å (for lead). The metal–metal stretching force constants are a little lower than those calculated for $(CH_3)_6Ge_2$ (1.34 mdyn/Å)[4] and H_6Ge_2 (1.29 mdyn/Å).[16] They are also lower than those calculated for the molecules Hg_2Cl_2 and Hg_2Br_2.[17] It is also interesting that the PbPb stretching force constant calculated in this way is not significantly different from that calculated assuming a diatomic model (*vide supra*).

From the force constants, the two a_{2u}, the three e_u, and the three e_g frequencies for $(CH_3)_6Sn_2$ and $(CH_3)_6Pb_2$ have been calculated in each case using the equations derived by Howard[14] and Stitt.[15] The agreement between the calculated and the observed frequencies is satisfactory (Table III). The calculations indicate that of the two infrared-active MC stretching frequencies, $\nu_7(e_u)$ lies above $\nu_5(a_{2u})$.

The interesting torsional mode (a_{1u} species) is inactive in both the infrared and the Raman spectra; it is, however, permitted in combination with each of the three e_g modes. Unfortunately, there should be a large number of binary combination bands of skeletal fundamentals for hexamethyldilead (66, of which 33 are infrared active, 28 are Raman active, and 5 are inactive), but very few are in practice observed. We were thus unable to determine its frequency and obtain a measure of the barrier to rotation about the PbPb bond.

B. Nmr Spectra. The observed ^1H nmr spectrum of hexamethyldilead is illustrated in Figure 3 and has contri-

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(16) D. A. Dows and R. M. Hexter, *ibid.*, 24, 1029 (1956).
(17) H. M. Gager, J. Lewis, and M. J. Ware, *Chem. Commun.*, 616 (1966).

Table V. Nmr Data for Hexamethyldilead

Coupling constant[a]	Cps	Chemical shift	
$^1J(^{13}C–H)$[e]	$+134.4 \pm 0.2$	$\tau(CH_3)$[b]	8.99 ± 0.01 ppm
$^1J(^{207}Pb–^{13}C)$	$+28 \pm 2$	$\delta(^{13}C)$[c]	$+172.3 \pm 0.1$ ppm
$^2J(^{207}Pb–H)$	-42.1 ± 0.1	$\delta(^{207}Pb)$[d]	$+281 \pm 1$ ppm
$^2J(^{207}Pb–^{13}C)$	$+92 \pm 2$	$\Xi(^{13}C)$	$25,144,948 \pm 1$ cps
$^3J(^{207}Pb–H)$	$+22.9 \pm 0.1$		
$^5J(H–H)$	0 ± 0.2	$\Xi(^{207}Pb)$	$20,914,810 \pm 20$ cps

[a] See text for possible need to interchange $^1J(^{207}Pb–^{13}C)$ and $^2J(^{207}Pb–H)$ with $^2J(^{207}Pb–^{13}C)$ and $^3J(^{207}Pb–H)$, respectively. [b] Measured relative to TMS as 40% solution in benzene. [c] Relative to CH_3C^*OOH. [d] Relative to $(CH_3)_4Pb$. [e] Assumed to be positive.

butions from the molecular species given in Table IV. The relative abundances are calculated from the naturally occurring isotopic abundances for ^{207}Pb and ^{13}C of 22.6 and 1.107%, respectively. Molecules containing more than one ^{13}C atom are omitted from Table III; they have a total abundance of less than 0.2%, and no peaks can be experimentally observed for these molecules. ^{207}Pb is the only naturally occurring magnetic isotope of lead and has spin $^1/_2$.

In previous nmr investigations of hexaalkylditin and dilead compounds[7,18–20] it has been assumed that the numerically larger of the two metal–proton coupling constants is the geminal one. This is not entirely reasonable, since in many ethyl derivatives $|^3J(X–H)| > |^2J(X–H)|$. However, it does appear that vicinal X–H coupling constants decrease in magnitude as the size of the intervening atoms increases, and the signs of the coupling constants determined in the present work suggest that the usual assignment is correct.

The proton chemical shift and various coupling constants are contained in Table V. Of special interest are the peaks given by species C, which contains two magnetic lead atoms. This molecule is of the type $AA'X_9X'_9$ with $J(X\cdots X') = 0$, in which half of the intensity of the ^1H resonance is contained in a sharp doublet of separation $J(AX) + J(AX')$ and most of the remainder is concealed by the central peak 9.[21] Thus, since the coupling constants $^2J(^{207}Pb–C–H) = 42.1$ cps and $^3J(^{207}Pb–Pb–C–H) = 22.9$ cps, the doublet is expected to be separated by $42.1 + 22.9 = 65.0$ cps or $42.1 - 22.9 = 19.2$ cps for coupling constants of like or unlike signs, respectively. The observed separation of the doublet is 19.3 cps, clearly indicating that these coupling constants are of opposite sign. A similar observation was made for hexamethylditin[7] although in that case the spectrum was complicated by the presence of three magnetic isotopes of tin.

The ^{207}Pb spectrum of the species B is a decet of decets (*i.e.*, 100 lines in all) which are spaced in such a way that individual lines could not be resolved by ^{207}Pb tickling. However, the center of the resonance was found to ± 20 cps, and this was sufficiently precise to compare the signs of $^2J(^{207}Pb–^{13}C)$ and $^1J(^{13}C–H)$ by observation of lines 16 and 11 in the proton spectrum. The sign of $^1J(^{207}Pb–^{13}C)$ could not be found in this way because the coupling constant is smaller than the error in the ^{207}Pb measurements. ^{13}C tickling experiments gave more accurate values of the two carbon–lead coupling constants, and also their signs relative to the corresponding lead–proton coupling constants. Since the relative signs of the last two are known from the analysis of the proton spectrum the sign information is complete.

The value of $^1J(^{207}Pb–^{13}C)$ is only one-ninth of that found in $(CH_3)_4Pb$, but the assignment of the coupling constants is thought to be correct for the reason given earlier. In hexamethylditin[7] $|^1J(^{119}Sn–^{13}C)|$ is less than in $(CH_3)_4Sn$ so some decrease in the lead compound is to be expected, but the magnitude of the change is surprising. The s character of the tin hybrid orbitals involved in the SnSn bond of $(CH_3)_6Sn_2$ has been variously calculated as 28 and 47% depending on whether the starting point was the Sn–H or the Sn–C coupling constant.[7,22] It has been shown that these coupling constants are linearly related[23] in a series of tin compounds which includes[7] hexamethylditin. However, the line does not pass through the origin so a disagreement in the results of the two calculations is inevitable. It is not known whether $^2J(^{207}Pb–H)$ and $^1J(^{207}Pb–^{13}C)$ are similarly related, but a calculation by the first method (using $^2J(^{207}Pb–H) = 62$ cps for $(CH_3)_4Pb$)[24] gives 17% for the s character of the Pb orbitals used for the PbC bonds and hence 49% for that of the PbPb bond in $(CH_3)_6Pb_2$. The second method (based on a value[25] of +250 cps for $^1J(^{207}Pb–^{13}C)$ in $(CH_3)_4Pb$) gives 2.2% s character for the PbC bonds and hence 93% for the PbPb bond.

These calculations may give spurious results for two reasons: (1) the Pb atomic hybridizations involved differ so much from true sp^3 that the quantitative basis may be seriously at fault; (2) the whole principle of relating per cent s character to coupling constants has been questioned[26] on the grounds that it ignores changes of effective nuclear charge. It is clear, however, that replacement of CH_3 by $(CH_3)_3Pb$ affects the coupling in the way to be expected of an electropositive group. It is probably qualitatively correct to say that the % s character in the PbPb bond is greater than in the SnSn one. The low PbPb force constant and the chemical properties of hexamethyldilead are consistent with this.

Many geminal coupling constants between protons are negative and similar couplings between other reasonably

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electropositive elements might be expected to have this sign. This is so for ^2J(X–C–H) in $(CH_3)_4X$ and related compounds (X = C, Si, Sn, or Pb, allowance being made for the negative magnetogyric ratios of the magnetic Si and Sn isotopes). However, it has been found[27] that the negative sign for the geminal H–H coupling applies only if the intervening atom is small (*e.g.*, C), but with other intervening atoms the coupling constant becomes positive and increases with increasing atomic number. A similar result also applies to geminal carbon to hydrogen couplings. Thus the reduced[28] *Pb*–Pb–*C* coupling constant should be positive and larger than the *Sn*–Sn–*C* one. This is the case.

The ^1H and ^{13}C chemical shifts of hexamethyldilead differ only slightly from those found for $(CH_3)_4Pb$ and may well depend on the conditions of measurement. The large high-field shift of the ^{207}Pb resonance is consistent with the corresponding value of +113 ppm for the ^{119}Sn shift in hexamethylditin, the extremely large range[30] of ^{207}Pb chemical shifts being borne in mind. It is generally considered that the local paramagnetic term is the dominant contributor to lead shielding,[31] and this depends *inter alia* on the reciprocal of ΔE (the separation between the ground and excited states) in such a way that small values of ΔE should correspond to low-field resonances. The cream color of $(CH_3)_6Pb_2$ suggests that ΔE is relatively small; hence dominance by the paramagnetic term should lead to a ^{207}Pb chemical shift in $(CH_3)_6Pb_2$ to the *low field* of $(CH_3)_4Pb$. The results for ^{59}Co and ^{195}Pt chemical shifts may be compared here.[32,33]

We therefore conclude that ^{207}Pb chemical shift differences between related lead compounds are not necessarily dominated by the paramagnetic term and the neighboring anisotropy effect of the $(CH_3)_3Pb$ group may be more important in hexamethyldilead.

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Stereochemically Nonrigid Organometallic Molecules. XX.[1] Proton Nuclear Magnetic Resonance Study of the Fluxional Behavior of Some Substituted (1,2,7-*Trihapto*benzyl)(*pentahapto*cyclopentadienyl)dicarbonyl Compounds of Molybdenum and Tungsten[2,3a]

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Abstract: Several new fluxional molecules containing substituted 1,2,7-*trihapto*benzyl groups bound to the $(C_5H_5)Mo(CO)_2$ and $(C_5H_5)W(CO)_2$ residues have been prepared and their proton magnetic resonance spectra studied with the objective of elucidating the pathway and evaluating the activation parameters concerned in the fluxional behavior of this class of molecules. The molecules are less difficult to prepare and more stable than previously reported. The chief qualitative conclusion, derived from the study of the 3,5-diisopropylbenzyl compound, is that the $(C_5H_5)Mo(CO)_2$ residue has access to all four equivalent (including enantiomorphically related) positions of attachment to the benzyl group. A plausible pathway would be *via* a *monohapto-* (*i.e.*, σ-) $C_6H_5CH_2Mo(C_5H_5)(CO)_2$ intermediate, in which rotation about the C_1–C_7 bond of the benzyl group can occur.

The first example of a compound containing a benzyl group bonded to a metal atom in a manner which could be formally considered to involve the $C_6H_5CH_2$ group serving as a 3-electron donor to the metal atom (or the $C_6H_5CH_2^-$ anion serving as a 4-electron donor to a cation) was reported in 1966 by King and Fronzaglia.[4] The compound in question is $(C_6H_5CH_2)(C_5H_5)Mo(CO)_2$ and King and Fronzaglia proposed that the benzyl group is attached to the molybdenum atom through an allylic sequence of three carbon atoms, one of which is the exocyclic methylene carbon atom. In short, the suggested structure was that which would be designated in a recently proposed notation[5] as (1,2,7-*trihapto*benzyl)(*pentahapto*-

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[2] A more conventional but less precise name for these compounds would be (π-benzyl)(π-cyclopentadienyl)dicarbonylmetal compounds.

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