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Indirect Nuclear Spin-Spin Coupling of Lead-207 to Other Magnetic Nuclei

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Coupling constants $^1J_{207\text{Pb-X}}$ ($X = \text{H, B, C, N, P, Se, Sn, Pb}$) and other NMR parameters are reported for model lead compounds. Comparison of the reduced coupling constants $^1K_{\text{Pb-X}}$ and $^1K_{\text{Sn-X}}$ in analogous compounds shows no clear pattern and it is concluded that these couplings depend significantly upon β_{PbX} and β_{SnX} , the *s*-overlap integrals between lead or tin and the element X, in addition to the expected factors α_s^2 and $\psi^2(0)$.

Introduction

The element lead has been unduly neglected by NMR spectroscopists: the nucleus of the isotope ^{207}Pb has $I = 1/2$, a natural abundance of ca. 21%, and a sensitivity to NMR detection which is 0.9% of that of the proton, and yet very few studies have appeared of either lead shielding or electron-mediated spin coupling to nuclei other than the proton.¹ This is the more surprising in view of the ease with which the problems of sensitivity can be overcome by modern pulsed Fourier transform and/or double-resonance techniques and in view of the current interest in all types of lead compounds.

One might expect to find broad parallels in the behavior of both coupling constants and nuclear shieldings as a particular group in the periodic table is descended. However, recent work on cadmium² and mercury³ chemical shifts and also on the remarkable sensitivity⁴ of tin-tin coupling constants to changes of substituent suggests that these may not always occur; certainly there are sufficient differences between the chemistry of tin and lead to warrant proper investigation. In the present paper we report the results of a study of coupling constants $^1J_{207\text{Pb-X}}$ ($X = ^1\text{H, }^{11}\text{B, }^{13}\text{C, }^{15}\text{N, }^{31}\text{P, }^{77}\text{Se, }^{119}\text{Sn, }^{207}\text{Pb}$) performed with the object of comparing these parameters with the corresponding ones involving ^{119}Sn or ^{13}C . Although direct ^{207}Pb Fourier transform spectra could yield the required magnitudes of the coupling constants, their signs are more conveniently got from $^1\text{H}\{^{207}\text{Pb}\}$ double-resonance experiments, and this is the approach we adopted. The principal obstacles to such an investigation are preparative ones as many compounds with a direct bond between lead and another element of interest are rather unstable; for this reason the range of molecules studied is more restricted than in our earlier work on tin.⁵

Experimental Section

Subdued lighting and anaerobic conditions were used throughout the preparations in order to minimize decomposition. Samples were generally stored at -78°C until immediately prior to insertion in the spectrometer (probe temperature 23°C).

$\text{Me}_3\text{PbPbMe}_3$ was prepared by a method given in the literature⁶ and had the correct melting point and appearance. In addition, the absence of spurious peaks in the proton NMR spectrum indicated that the purity was high.

Me_3PbSeMe . Hexamethyllead (0.836 g, 1.67 mmol) and dimethylidisenium (0.361 g, 1.67 mmol) were dissolved in dry benzene (0.4 ml) at 24.3°C . The proton NMR spectrum of the mixture showed that no reaction had occurred. After 12 h the proton NMR spectrum of the mixture showed that reaction to form the desired product was quantitative and essentially complete; the benzene was removed under vacuum (15 mmHg) and the product was distilled [bp $50\text{--}51^\circ\text{C}$ (1.0 mm); lit.⁷ 75°C (3 mm)] to give the product as a yellow oil which had a proton NMR spectrum fully consistent with the proposed formulation. Also, the double-resonance experiments demonstrated unequivocally the presence of a lead-selenium bond. An attempt to prepare $\text{Me}_3\text{PbPbMe}_2$ similarly by reaction between $\text{Me}_3\text{PbPbMe}_3$ and Me_2PbMe_2 was unsuccessful, decomposition to metallic lead and other products occurring before any significant amount of the desired product was formed.

$\text{Me}_3\text{PbNEt}_2$. This compound was prepared by the standard method⁸ from lithium diethylamide and trimethyllead bromide in diethyl ether-hexane at -20°C and was purified by crystallization from pentane at -78°C . [NMR parameters: $\delta(^1\text{H})(\text{Me-Pb}) +1.23$, $\delta(^1\text{H})(\text{CH}_2\text{-N}) +3.50$, $\delta(^1\text{H})(\text{CH}_3) +1.31$, $\delta(^{207}\text{Pb}) +242 \pm 8$ ppm; $^2J_{207\text{Pb-H}} = 61.5$, $^3J_{207\text{Pb-H}} = 93.0$ Hz; 20% w/v in C_6H_6 at 23°C .]

$\text{Me}_3\text{PbSnMe}_3$. Trimethyltin hydride (0.44 g, 2.68 mmol) was added to trimethyllead diethylamide (0.88 g, 2.71 mmol) in benzene (7 ml) and the mixture was homogenized. The more volatile components were removed under vacuum (20°C (0.1 mm)), and the residue was dissolved in benzene (1.0 ml) and centrifuged to remove solid material. The yellow supernatant liquid had a proton NMR spectrum which showed it contained the desired product (i.e., both the *Sn*-methyl and the *Pb*-methyl resonances had both $^{117/119}\text{Sn}$ and ^{207}Pb satellites whose identities were confirmed by the heteronuclear double-resonance⁹ experiments (see Figure 1). It was not possible to isolate pure material from this solution which deposited metallic lead and/or tin quite rapidly and which was therefore used for the measurements.

$\text{Me}_3\text{PbSnPh}_3$, $\text{Me}_3\text{PbPPh}_2$, and $\text{Me}_3\text{Pb}^{15}\text{NMePh}$ (enriched to ca. 95% in ^{15}N) were prepared similarly by the reaction between equimolar amounts of trimethyllead diethylamide and triphenyltin hydride, diphenylphosphine, or *N*-methylaniline enriched to 96% in ^{15}N , respectively. In all cases the products were too unstable to be isolated in an analytically pure state, but their proton NMR spectra in benzene solution and the results of the double-resonance experiments clearly showed that these species were the major ones present. All of the samples prepared from trimethyllead diethylamide contained up to 10 mol % of diethylamine. Attempts to remove this more effectively resulted in longer working times which permitted extensive decomposition of the product to occur.

$\text{Me}_3\text{PbB}(\text{NMeCH}_2)_2$. Trimethyllead bromide (1.65 g, 5 mmol) was stirred with freshly cut lithium metal (0.5 g, a large excess) in tetrahydrofuran (10 ml) at -78°C for 2 h to give a green solution whose behavior was consistent with its containing Me_3PbLi . $\text{ClB}(\text{NMeCH}_2)_2$ (0.66 g, 5 mmol) was then added at -78°C and after 1 h the reaction mixture was warmed to -10°C . The solvent was then removed (-10°C (0.01 mm)), and the residue was dissolved in benzene (3 ml) to give a solution which was stable for several days at -10°C but which deposited lead quite rapidly at the spectrometer probe temperature of 23°C . The presence of a lead-boron bond in this product was confirmed by the observation in the $^1\text{H}\{^{207}\text{Pb}\}$ experiments that the ^{207}Pb spectrum consisted of four regions of equal intensity due to coupling to boron (^{11}B has $I = 3/2$, abundance 82%) with $J_{207\text{Pb-}^{11}\text{B}} = 1330$ Hz. Other species which were present in the samples of this compound were small amounts of tetrahydrofuran, tetramethyllead, hexamethyldilead, and unreacted $\text{ClB}(\text{NMeCH}_2)_2$, which were identified by ^1H and $^1\text{H}\{X\}$ NMR.

$\text{Me}_3\text{SnB}(\text{NMeCH}_2)_2$ was also prepared by the above method.⁸ $^1\text{H}\{X\}$ ($X = ^{11}\text{B, }^{13}\text{C, }^{15}\text{N, }^{31}\text{P, }^{77}\text{Se, }^{119}\text{Sn, }^{207}\text{Pb}$) experiments were performed as described elsewhere⁹ on a modified JEOL spectrometer operating at a measuring frequency of 60 MHz. Frequency-locking circuits to the Schlumberger FS-30 frequency synthesizer eliminated drift between the various frequencies used and spectra were calibrated using a frequency counter. Table I lists the NMR parameters of the compounds studied in this work; where possible the relative signs are based upon $^1J_{^{13}\text{C-H}}$ being positive and are otherwise based upon $^2J_{207\text{Pb-H}}$ being negative—none of the atoms bound to lead is sufficiently electropositive for there to be any doubt about this latter assumption. $\mathcal{Z}(X)$ is the resonant frequency of X corrected¹⁰ to a polarizing field strength at which Me_4Si gives a proton resonance of exactly 100 MHz. No specific problems were encountered

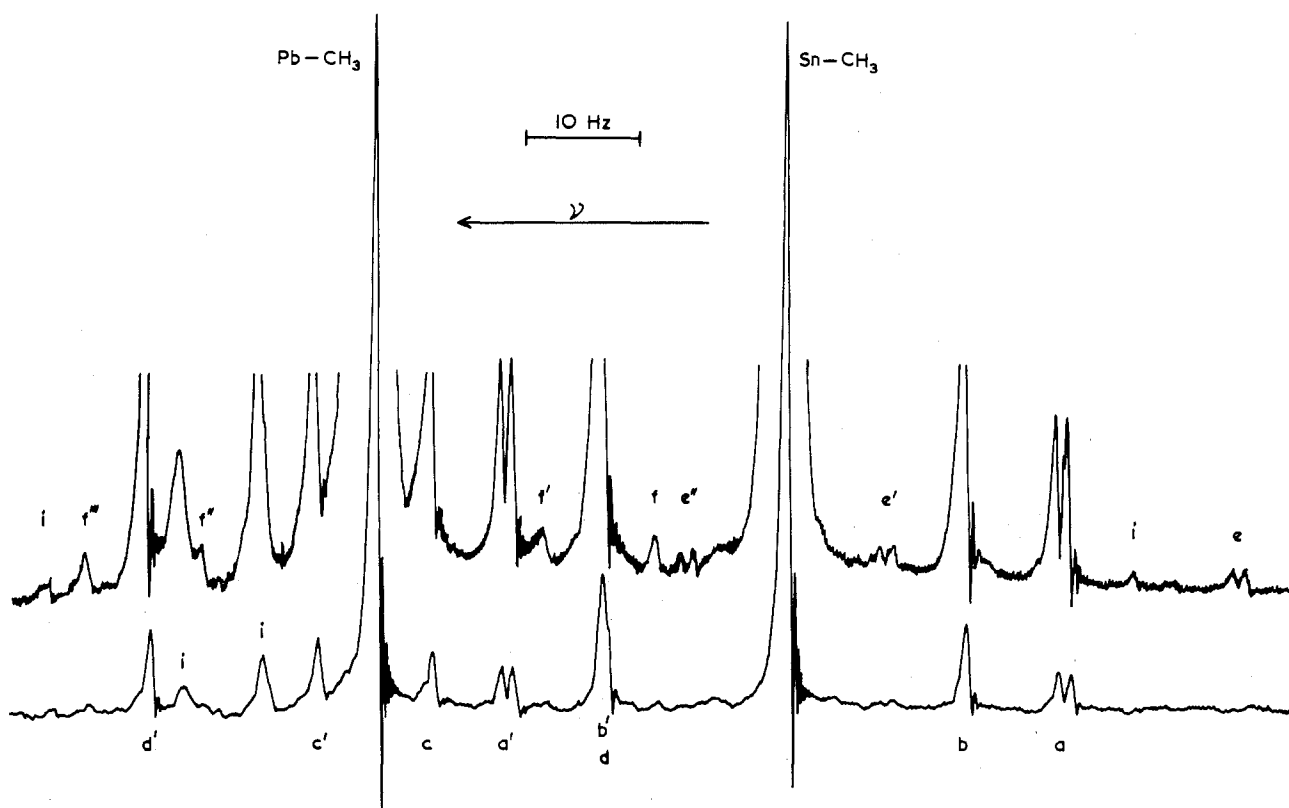


Figure 1. The 60-MHz frequency sweep proton NMR spectrum of $\text{Me}_3\text{PbSnMe}_3$ in benzene solution (upper trace at higher spectrometer gain) showing satellites (a-f''') due to the species $\text{Me}_3^{207}\text{PbSnMe}_3$, $\text{Me}_3\text{Pb}^{117}\text{SnMe}_3$, $\text{Me}_3\text{Pb}^{119}\text{SnMe}_3$, $\text{Me}_3^{207}\text{Pb}^{117}\text{SnMe}_3$, and $\text{Me}_3^{207}\text{Pb}^{119}\text{SnMe}_3$. Lines marked i are due to either impurities or ^{13}C satellites.

Table I. Data for Newly Measured Species^a

	$\text{Me}_3\text{PbPbMe}_3$ ^b (40% in C_6H_6)	$\text{Me}_3\text{PbSnMe}_3$ ^c (30% in C_6H_6)	$\text{Me}_3\text{PbSnPh}_3$ ^c (20% in C_6H_6)	$\text{Me}_3\text{PbSeMe}_3$ ^d (20% in C_6H_6)	$\text{Me}_3\text{PbNMePh}$ ^e (20% in C_6H_6)	$\text{Me}_3\text{PbPPh}_2$ ^f (30% in C_6H_6)	$\text{Me}_3\text{PbB-}$ $(\text{NMeCH}_2)_2$ ^g (30% in THF)
$\Xi(\text{Pb})$	20 914 717 ± 20	20 913 820 ± 15	20 915 092 ± 3	20 922 280 ± 15	20 925 340 ± 50	20 921 447 ± 70	20 913 020 ± 50
$\Xi(\text{X})$	20 914 717 ± 20	37 288 540 ± 50	37 286 200 ± 40	19 067 780 ± 15	10 133 508 ± 2	40 479 336 ± 8	32 085 330 ± 30
$\delta(\text{Pb})^h$	-281 ± 1	-323.8 ± 1.2	-263.1 ± 0.2	+80.5 ± 1	+226.5 ± 2.5	+40.5 ± 4	-362.0 ± 2
$\delta(\text{X})$	-281 ± 1	-57.0 ± 1.5 ⁱ	-119.5 ± 1.5 ⁱ	-196.5 ± 1 ^j	+15.5 ± 0.2 ^k	-35.9 ± 0.4 ^l	+41.7 ± 1 ^m
$^1J_{\text{PbX}}$	+290 ± 10	-3570 ± 100	-2800 ± 50	-1170 ± 100	+261 ± 5	-1335 ± 10	+1330 ± 30
$^2J_{\text{PbH}}$	-42.1 ± 0.1	-40.1 ± 0.2	-46.8 ± 0.1	-61.9 ± 0.2	-65.3 ± 0.1	-52.0 ± 0.2	-43.1 ± 0.2
$^3J_{\text{PbH}}$	+22.9 ± 0.1	+31.9 ± 0.2	41 ± 2	44.5 ± 0.1	44.5 ± 0.1		<i>n</i>
$^2J_{\text{XH}}$	-42.1 ± 0.1	+50.4 ± 0.2	9.7 ± 0.5	<0.3			$\nu_{1/2}^o =$ 2.25 Hz
$^3J_{\text{XH}}$	+22.9 ± 0.1	-10.2 ± 0.2	-12.1 ± 0.1	Not obsd	0.48 ± 0.02	1.75 ± 0.1	$\nu_{1/2}^o =$ 1.5 Hz
$\delta(^1\text{H})(\text{PbCH}_3)$	+1.01 ± 0.01	+1.05 ± 0.02	+1.13 ± 0.02	+1.01 ± 0.02	+0.948 ± 0.02	+0.87 ± 0.02	1.12 ± 0.01
$\delta(^1\text{H})(\text{XCH}_3)$	+1.01 ± 0.01	+0.44 ± 0.02	+1.98 ± 0.02	+3.06 ± 0.02			<i>p</i>

^a J and Ξ in Hz; δ in ppm to low field of reference. ^b $\text{X} = ^{207}\text{Pb}$; see also R. J. H. Clark, A. G. Davies, R. J. Puddephatt, and W. McFarlane, *J. Am. Chem. Soc.*, **91**, 1334 (1969); and ref 11. ^c $\text{X} = ^{119}\text{Sn}$. ^d $\text{X} = ^{77}\text{Se}$. ^e $\text{X} = ^{15}\text{N}$. ^f $\text{X} = ^{31}\text{P}$. ^g $\text{X} = ^{11}\text{B}$. ^h Relative to $\text{Me}_4\text{Pb} = 0$. ⁱ Relative to $\text{Me}_4\text{Sn} = 0$. ^j Relative to $\text{Me}_2\text{Se} = 0$. ^k Relative to $\text{Me}_2\text{N}^+\text{I}^- = 0$. ^l Relative to 85% $\text{H}_3\text{PO}_4 = 0$. ^m Relative to $\text{Et}_2\text{O} \cdot \text{BF}_3 = 0$. ⁿ $^4J_{^{207}\text{PbBNC}_2\text{H}_5} = -6.6 \pm 0.1$ Hz; $^4J_{^{207}\text{PbBNC}_2\text{H}_5} = 1.8 \pm 0.1$ Hz. ^o Width of resonance at half-height. ^p $\delta(^1\text{H})(\text{NCH}_3) + 2.87 \pm 0.01$ ppm; $\delta(^1\text{H})(\text{NCH}_3) + 3.17 \pm 0.01$ ppm.

with the measurements: it was always possible to observe enough satellite lines in the proton spectrum to get the required data, although with ^{119}Sn and ^{77}Se the accuracy was limited somewhat by the low abundances (8.6 and 7.5%, respectively) of these isotopes. The special case of $\text{Me}_3\text{PbPbMe}_3$ which gives an $\text{A}_9\text{A}'_9\text{XX}'$ spectrum when both leads are magnetic has been discussed elsewhere,¹¹ and to illustrate the procedure followed for the other molecules we describe the case of $\text{Me}_3\text{PbSnMe}_3$ in some detail. The proton spectrum given by the methyl groups is shown in Figure 1, the main resonance at higher field arising from the *Sn*-methyl protons. The lines marked a, a' and b, b' are the $^{117/119}\text{Sn}$ and ^{207}Pb satellites of this resonance, respectively, and this was confirmed by $^1\text{H}\{^{119}\text{Sn}\}$ and $^1\text{H}\{^{207}\text{Pb}\}$ experiments which also gave the frequencies of the centers of the ^{119}Sn and ^{207}Pb spectra.

The same values for these frequencies were obtained from similar experiments on c, c' and d, d' which are the $^{117/119}\text{Sn}$ and ^{207}Pb satellites of the *Pb*-methyl resonance. In order to determine $^1J_{^{207}\text{Pb-}^{119}\text{Sn}}$ it is necessary to study molecules which are doubly labeled (i.e., $\text{Me}_3^{207}\text{Pb}^{119}\text{SnMe}_3$ —note ^{119}Sn has a natural abundance of 8.6%) and these give rise to "satellites of satellites" in the proton spectrum. The visible satellites of the *Sn*-methyl resonance are labeled e through e'', and those of the *Pb*-methyl resonance, f through f'''. The ^{119}Sn and ^{207}Pb frequencies determined from these satellites will differ by $\pm 1/2(^1J_{^{207}\text{Pb-}^{119}\text{Sn}})$ from the central frequencies. The ^{119}Sn and ^{207}Pb frequencies associated with f''' were 1785 Hz lower and higher, respectively, than the corresponding central frequencies thus showing that (i) $^1J_{^{207}\text{Pb-}^{119}\text{Sn}}/2J_{^{207}\text{Pb-H}} > 0$ (note that $\gamma(^{119}\text{Sn})$ is negative), (ii)

$^1J_{^{207}\text{Pb}-^{119}\text{Sn}}/^3J_{^{119}\text{Sn}-\text{H}} > 0$, and (iii) $^1J_{(^{207}\text{Pb}-^{119}\text{Sn})} = -3570$ Hz. These results were confirmed by observing f and f' (f' is partially hidden), and observations of e and e' similarly gave the sign of $^1J_{^{207}\text{Pb}-^{119}\text{Sn}}$ relative to $^2J_{^{119}\text{Sn}-\text{H}}$ and $^3J_{^{207}\text{Pb}-\text{H}}$. The precision of these measurements was limited primarily by the complexity of the ^{119}Sn and ^{207}Pb spectra and the rather poor signal-to-noise ratio at which the relevant proton lines were observable.

Similar methods were used for the determination of the parameters given in Table I for the other compounds; the quoted errors reflect the precision with which it was possible to perform the measurements. Benzene was chosen as solvent since with the molecules studied it can be expected to act essentially as a diluent which would not be the case if donor solvents were used. Chlorinated solvents lead to accelerated decomposition of the compounds. The principal effect of benzene would be due to its diamagnetic anisotropy which might affect chemical shifts by 1 ppm or so; any effect upon coupling constants will be negligible. The instability of the compounds and the need to achieve an adequate signal-to-noise ratio for the doubly labeled species of low abundance precluded any studies of the temperature or concentration dependence of the couplings. However, large variations of the NMR parameters of group 4 compounds are generally found only when strong associative interactive processes are occurring; the nature of the compounds and solvents used in this work are such that these are highly improbable. The small amounts of impurities (arising mainly from decomposition of the compound under investigation) were generally of such a nature as to render insignificant any effect upon the measured NMR parameters. This is supported by the fact that these parameters did not change with time although the amounts of the impurities did. A possible exception to this generalization is diethylamine, which was present in several of the samples and was not completely removed for the reasons given above. In fact, the amount present was small, and as no changes in the parameters were observed when the concentration of this contaminant was altered over a fairly wide range, its presence can be disregarded.

An important point which arises from this work is the value of heteronuclear double resonance as a diagnostic technique. The high degree of instability of the compounds studied prevented their isolation in analytically pure form, and yet it was possible from the various double-resonance experiments to demonstrate unequivocally that these were the species present.

Discussion

As some of the nuclei with which we are concerned in this work (notably ^{15}N and ^{119}Sn) have negative magnetogyric ratios γ , it is convenient to conduct the discussion in terms of reduced coupling constants K , defined by $K_{XY} = J_{XY} \cdot (4\pi^2)/\gamma_X\gamma_Y h$, in order to avoid dependence upon individual nuclear properties.¹² Coupling constants between lead and the nuclei of other directly bound elements are presented and compared with the corresponding couplings involving tin in Table II. It is immediately apparent from the wide range of variation in the ratio of the two couplings given in the last column of Table II that there is no simple relationship between them. This is perhaps surprising: in the classification scheme developed by Jameson and Gutowsky¹³ both tin and lead are class B atoms, that is, ones which have an accessible open s-shell electronic configuration which then leads to a positive nuclear spin-electron spin interaction. If, as is likely, the coupling mechanism is dominated by the Fermi contact interaction, this situation will then lead to a dependence of the signs of coupling constants involving directly bound tin or lead upon the class to which the other atom belongs.¹³ Furthermore when the other atom belongs to class A or B (i.e., either actually has or has accessible an open s-shell configuration), then the reduced coupling constant should be positive and should be described by the equation¹²

$$^1K_{XY} = \frac{4e^2h^2}{9m^2c^2\Delta E} \psi_X^2(0)\psi_Y^2(0)\alpha_X^2\alpha_Y^2 \quad (1)$$

where α^2 and $\psi^2(0)$ represent respectively the s character of the hybrid orbital used to form the X-Y bond and the valence s-electron density of the nucleus, and ΔE is a mean electronic

Table II. Comparison of Lead and Tin Coupling Constants in Similar Molecules

Compd ⁱ (M = Sn or Pb)	$^1J_{\text{SnX}}^a$	$^1J_{\text{PbX}}^a$	$^1K_{\text{SnX}}^b$	$^1K_{\text{PbX}}^b$	$^1K_{\text{PbX}}/^1K_{\text{SnX}}^c$
$\text{Me}_3\text{M}-\text{H}$	-1744 ^d	+2674 ^d	+39.0	+106.7	+2.73
$\text{Me}_3\text{M}-\text{B}(\text{NMeCH}_2)_2$	-930 ± 30 ^e	+1330 ^e	+64.8	+165	+2.55
$\text{Me}_3\text{M}-\text{CH}_3$	-340 ^f	+250 ^g	+30.2	+39.6	+1.31
$\text{Me}_3\text{M}-\text{NMePh}$	+2 ^h	+261 ± 5 ^e	+0.44	-103	-233
$\text{Me}_3\text{M}-\text{PPh}_2$	+596 ± 2 ^j	+1335 ± 10 ^e	-33.0	-131.5	+4.00
$\text{Me}_3\text{M}-\text{SeMe}$	+1015 ± 10 ^k	-1170 ± 100 ^e	-119	-244	+2.06
$\text{Me}_3\text{M}-\text{SnMe}_3$	+4462 ^e	-3570 ± 100 ^e	+268	+382	+1.42
$\text{Me}_3\text{M}-\text{SnPh}_3$	+4240 ± 80 ^e	-2800 ± 50 ^e	+254	+299	+1.18
$\text{Me}_3\text{M}-\text{PbMe}_3$	-3570 ± 100 ^e	+290 ± 10 ^l	+382	+55.3	+0.14

^a In Hz. ^b In nm⁻³. ^c $\psi_s^2(0)(\text{Pb})/\psi_s^2(0)(\text{Sn}) = 1.69$ on the basis of values from ref 13. ^d C. Schumann and H. Dreeskamp, *J. Magn. Reson.*, **3**, 204 (1970). ^e This work. ^f W. McFarlane, *J. Chem. Soc. A*, 528 (1967). ^g W. McFarlane, *Mol. Phys.*, **13**, 587 (1967). ^h J. D. Kennedy, W. McFarlane, G. S. Pyne, and B. Wrackmeyer, to be submitted for publication. ⁱ Element X in italics. ^j H. Elser and H. Dreeskamp, *Ber. Bunsenges. Phys. Chem.*, **73**, 619 (1969). ^k J. D. Kennedy and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 2134 (1973). ^l Reference 11.

excitation energy. On this basis then, one might expect close similarities of behavior between tin and lead since one should not expect great differences in either α^2 or $\psi^2(0)$ for these two elements in similar compounds. [Note¹³ that $\psi^2(0)(\text{Pb})/\psi^2(0)(\text{Sn}) = \text{ca. } 1.69$.]

In compounds of the type studied here, this relationship appears to hold to certain extent for lead or tin bound directly to hydrogen, carbon, or boron.

When one of the elements bound to tin or lead belongs to class C (i.e., no accessible open s-shell configuration), then a negative reduced coupling constant is predicted by Gutowsky and Jameson.¹³ In the molecules considered here nitrogen, phosphorus, and selenium belong to this class, yet for nitrogen $^1K_{\text{SnN}}$ is actually positive (though very small) and it therefore appears that this treatment is not fully adequate. An alternative approach due to Pople and Santry¹² is to introduce the mutual polarizability²⁰ (π_{XY}) of the valence s orbitals of X and Y into the right-hand side of (1) to give eq 2. π_{XY}

$$^1K_{XY} = \frac{4e^2h^2}{9m^2c^2} \psi_X^2(0)\psi_Y^2(0)\pi_{XY} \quad (2)$$

can be of either sign, being negative when β_{XY} , the s-overlap integral between X and Y, is small and positive when it is large; thus the sign variation of K_{XY} can be explained. For covalently bound atoms (class A or B) of relatively low polarizability both β_{XY} and π_{XY} will be relatively large and positive and thus changes in the substituents of X or Y will proportionately affect α^2 and $\psi^2(0)$ more than they do β_{XY} , and so relation 1 in its unmodified form should describe adequately the coupling constant K_{XY} . When X or Y belongs to class C, variations in β_{XY} may be relatively important (when fluorine is involved, it appears that β_{XF} is often so small, and hence π_{XF} has such a substantial negative value that simple dependence upon α^2 and $\psi^2(0)$ again occurs), and the pattern of variation of coupling constants will become complex. Furthermore, if X or Y is large and polarizable yet not a member of class C, β_{XY} often may be small enough for π_{XY} to be quite close to zero so that changes in substituents have a large relative effect. We believe this to be the case with lead and to some extent tin. This then accounts for the variability of the entries in the last column of Table II: the values of α_s^2

and $\psi^2(0)$ are no doubt quite similar for tin and lead in the various molecules examined (except for a simple constant numerical factor (ca. 1.7) in the case of the latter) but because the s-overlap integrals can be rather small, especially in the case of lead, small differences in these are able to produce large apparent anomalies in the pattern of coupling constants. This is well illustrated by the Pb-Pb, Sn-Sn, and Pb-Sn bonds, as would also be expected on general chemical grounds. We conclude therefore that relations of the type of (1) cannot describe $^1K_{\text{PbX}}$ or $^1K_{\text{SnX}}$ and that attempts to obtain sets of parameters analogous to the Malinowski parameters¹⁴ for $^1J_{^{13}\text{C-H}}$ cannot succeed.

The other coupling constants listed in Table I serve largely to confirm the foregoing conclusion. Thus $^2J_{^{207}\text{Pb-H}}$ varies in a systematic way largely in response to changes in the electronegativity of X, having its most negative values when the electronegativity of X is greatest. This behavior parallels that of other geminal coupling constants involving protons and a heavier element and supports the idea that α^2 and $\psi^2(0)$ for the lead atom are varying in the manner which chemical intuition would suggest. Some care must be used in the interpretation of the vicinal couplings $^3J_{\text{Pb-H}}$ since these probably have a marked stereochemical dependence, as will $^4J_{^{207}\text{Pb-H}}$. This last point is demonstrated vividly by the different values of the four-bond couplings to CH_3 and to CH_2 in $\text{Me}_3\text{PbB}(\text{NMeCH}_2)_2$.

The lead chemical shifts are consistent with the view that heavy-atom substituents produce shifts to higher applied magnetic field when they possess one or more electron lone pairs but shifts to lower field when they do not. Similar conclusions have been drawn from work on ^{195}Pt shielding,¹⁵ and the ^{11}B chemical shifts for the species $(-\text{CH}_2\text{MeN})_2\text{BX}$ are also consistent with this. Thus for the series $\text{X} = \text{Cl}, \text{Br},$ and I the boron chemical shift moves to higher field as the atomic number of X increases,¹⁶ whereas for $\text{X} = \text{C}, \text{Si}, \text{Sn},$ and Pb it moves to lower field.^{5,17} These results indicate that the neighboring diamagnetic contribution to the shielding cannot be a dominant factor.¹⁸

It is clear from this preliminary survey that the coupling constants $^1J_{\text{PbX}}$ between lead and a directly bound element X are extraordinarily sensitive to the nature of the Pb-X bond (compare for example the widely different values of $^1J_{^{207}\text{Pb-}^{119}\text{Sn}}$ in $\text{Me}_3\text{PbSnMe}_3$ and $\text{Me}_3\text{PbSnPh}_3$). While this behavior has the disadvantage that it cannot be explained simply in terms of variations of α_s^2 and $\psi^2(0)$ for Pb and/or X, it does provide an extremely sensitive probe for the study of these bonds and no doubt will be greatly utilized with the growing availability

of Fourier transform spectrometers.¹⁹

In connection with the structural uses of this type of measurement it is important to be aware that there is in general no close parallel between coupling constants involving tin and those involving lead and further that any attempts to extrapolate from the large body of carbon-13 data to lead may go seriously astray.

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Registry No. Me_3SnH , 1631-73-8; Me_3PbH , 7442-13-9; $\text{Me}_3\text{SnB}(\text{NMeCH}_2)_2$, 36333-59-2; $\text{Me}_3\text{PbB}(\text{NMeCH}_2)_2$, 58747-16-3; Me_3SnCH_3 , 594-27-4; Me_3PbCH_3 , 75-74-1; $\text{Me}_3\text{SnNMePh}$, 1076-10-4; $\text{Me}_3\text{PbNMePh}$, 58747-17-4; $\text{Me}_3\text{SnPPH}_2$, 1213-51-0; $\text{Me}_3\text{PbPPH}_2$, 58747-18-5; Me_3SnSeMe , 17719-49-2; Me_3PbSeMe , 58747-19-6; $\text{Me}_3\text{SnSnMe}_3$, 661-69-8; $\text{Me}_3\text{PbSnMe}_3$, 58747-20-9; $\text{Me}_3\text{SnSnPh}_3$, 1235-18-3; $\text{Me}_3\text{PbSnPh}_3$, 58747-21-0; $\text{Me}_3\text{PbPbMe}_3$, 6713-83-3; $\text{Me}_3\text{PbNEt}_2$, 58747-22-1; dimethylid-selenium, 7101-31-7; trimethyllead bromide, 6148-48-7; $\text{ClB}(\text{NMeCH}_2)_2$, 17739-11-6; ^{11}B , 14798-13-1; ^{13}C , 14762-74-4; ^{15}N , 14390-96-6; ^{77}Se , 14681-72-2; ^{119}Sn , 14314-35-3; ^{207}Pb , 14119-29-0.

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Organolanthanide Tetrahydroborates.

Ligation Geometry and Coordinative Saturation

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This work reports the synthesis and spectral (infrared, Raman) characterization of the series of compounds $(\eta^5\text{-C}_5\text{H}_5)_2\text{LnBH}_4\cdot\text{THF}$, where $\text{Ln} = \text{Sm}, \text{Er}, \text{Yb}$. Vibrational spectra indicate that the mode of BH_4^- coordination is sensitive to the metal ionic radius. The $\text{Ln} = \text{Sm}$ compound is proposed to have tridentate BH_4^- ligation, whereas the $\text{Ln} = \text{Yb}$ compound is proposed to have bidentate ligation. The tetrahydrofuran can be removed for $\text{Ln} = \text{Yb}$ and Er to yield complexes of the composition $(\eta^5\text{-C}_5\text{H}_5)_2\text{LnBH}_4$. Vibrational spectra are similar to those of $\text{Be}(\text{BH}_4)_2$ and $\text{CH}_3\text{Zn}(\text{BH}_4)$, suggesting a polymeric structure with bridging BH_4^- groups. All data suggest appreciable ionic character in the bonding of the tetrahydroborate ligand to the trivalent lanthanides.

In recent years there has been a growing interest in the chemistry and bonding properties of the tetrahydroborate

ligand, BH_4^- .³ Organometallic tetrahydroborates are known for a large number of main group, transition metal, and

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