Lead-207 Shielding in Organolead Compounds

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^{1}H-$\{{}^{207}$Pb$\}$Double-resonance experiments have been used to determine lead chemical shifts in 33 organolead compounds under a variety of conditions. $\delta({}^{207}Pb)$ broadly parallels $\delta({}^{119}Sn)$ in similar species, but its sensitivity to changes in chemical environment is some three times greater. The chemical shifts appear to be dominated by the paramagnetic contribution to the shielding. Changes in $\delta({}^{207}Pb)$ with concentration can be used to study reversible equilibria between species with four- and five-co-ordinate lead, the latter generally having the more highly shielded ^{207}Pb nucleus.

It is reasonable to expect that as a particular group of the Periodic Table is descended there will be marked similarities of behaviour with respect to trends in nuclear shielding induced by changes in chemical environment. In practice it is difficult to confirm this because of the way in which sufficiently abundant nuclei with suitable magnetic properties are distributed throughout the Periodic Table. Specifically, the differences in the chemistry of first- and second-row elements (particularly with reference to d_π–p_π bonding) are usually sufficient to frustrate comparisons here, while too small a proportion of heavier nuclei has been studied in sufficient detail for general conclusions to be drawn. However, it is known [1] that ^{77}Se and ^{125}Te chemical shifts run closely parallel in similar compounds, being related by a factor of *ca.* 1.8 which can be ascribed to the greater value of the radial-expansion term for the valence-p electrons in the case of tellurium, and ${}^{111/113}$Cd and ^{199}Hg shieldings also appear to show some similarities.[2,3]

The most attractive area of the Periodic Table for this type of study is Group 4 since it has no less than four elements with nuclei of spin quantum number $I = \frac{1}{2}$ and adequate natural abundance. Of these, ^{13}C, ^{29}Si, and ^{119}Sn have been studied [4-8] well enough to provide a good basis for comparison, but ^{207}Pb has been somewhat neglected even though it has $I = \frac{1}{2}$ and a natural abundance of *ca.* 20%. With the rapid growth in the availability of pulsed Fourier-transform spectrometers and the attractiveness of ^{207}Pb for study in this way (the sensitivity to detection is 0.09% of that of the proton, and the maximum ^{207}Pb-$\{{}^{1}$H$\}$ nuclear Overhauser effect is 350%) it seemed appropriate to conduct a survey of lead shieldings in a representative series of molecules, especially in view of the importance of being able rapidly to identify lead compounds found in the environment. In this paper we report measurements of lead chemical shifts in a range of organolead compounds selected partly on the basis of their suitability for comparison with tin analogues and partly on the basis of ease of preparation. It was convenient to use ^{1}H-$\{{}^{207}$Pb$\}$ double-resonance experiments to determine the lead chemical shifts: this approach has the disadvantage that the compound studied must contain protons which are spin-coupled to lead, but offers an improvement in sensitivity over direct observation and is also more economical when a range of different nuclei are of interest. Previously, ^{207}Pb chemical shifts have been obtained by direct observation in some 15 species,[9,10] and there are a few isolated reports of determinations of lead resonance frequencies by double-resonance methods.[10-12]

EXPERIMENTAL AND RESULTS

Most of the compounds studied were prepared by literature methods,[13] and correct physical properties and the absence of spurious peaks in the proton n.m.r. spectrum were used as criteria of purity. Other compounds were made as follows.

$PbMe_3(SEt)$.—Triethylamine (1.11 g, 11 mmol) was added to a mixture of ethanethiol (1.0 g, 11 mmol) and trimethyllead bromide (3.34 g, 10 mmol) in benzene (50 cm^3). The mixture was heated under reflux for 1 h, precipitated triethylamine hydrochloride was filtered off, benzene was removed *in vacuo*, and the product was distilled to give a clear liquid (b.p. 60 °C, 0.08 mmHg) † in 80% yield (Found: C, 19.3; H, 4.45. $C_5H_{14}PbS$ requires C, 19.2; H, 4.50%). Similarly prepared were: $PbMe_3(SPr^i)$, b.p. 55 °C (0.09 mmHg) (Found: C, 22.2; H, 5.0. $C_6H_{16}PbS$ requires C, 22.0; H, 4.95%); $PbMe_3(SBu^t)$, b.p. 56 °C (0.15 mmHg) (Found: C, 24.6; H, 5.40. $C_7H_{18}PbS$ requires C, 24.7; H, 5.30%); and $PbMe_3(SCH_2Ph)$, b.p. 118 °C (0.3 mmHg) (Found: C, 32.5; H, 4.35. $C_{10}H_{16}PbS$ requires C, 32.0; H, 4.30%). Bromotrimethyl-lead–pyridine (1/1) was obtained as white crystals, m.p. 68 °C, when a warm solution of $PbBrMe_3$ in pyridine was allowed to cool (Found: C, 23.0; H, 3.40; N, 3.2. $C_8H_{14}BrNPb$ requires C, 23.4; H, 3.45; N, 3.4%).

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† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

[1] H. C. E. McFarlane and W. McFarlane, *J.C.S. Dalton*, 1973, 2416.

[2] C. J. Turner and R. F. M. White, *J. Magnetic Resonance*, 1977, **26**, 1.

[3] A. P. Tupčiauskas, N. M. Sergeyev, Y. A. Ustynyuk, and A. N. Kashin, *J. Magnetic Resonance*, 1972, **7**, 124; J. D. Kennedy and W. McFarlane, *J.C.S. Faraday II*, 1976, 1653; *J.C.S. Perkin II*, 1977, 1187.

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[5] G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley–Interscience, New York, 1972.

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[13] L. C. Willemsens, 'Organolead Chemistry,' Internat. Lead Zinc Res. Org., New York, 1964.

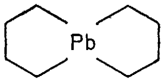
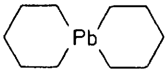
The solvents and concentrations were as specified in Table 1 and all the measurements were made at 24 ± 2 °C in spinning tubes (outside diameter 5 mm). The spectrometer was a JEOL C-60H instrument operating at a proton frequency of 60 MHz and with an extra transmitter coil to permit simultaneous irradiation of the sample at the ^{207}Pb resonance frequency of 12.50 MHz.[14] Radiofrequency power at this frequency was provided *via* a tuned amplifier by a Schlumberger FS-30 frequency synthesizer which was also used to control the r.f. oscillator of the spectrometer. Proton spectra were recorded by sweeping either the magnetic field or the r.f. frequency as convenient, and were calibrated by conventional audio-sideband techniques. The ^{207}Pb chemical shifts are quoted relative to $PbMe_4$ (δ 0 p.p.m.), the sign convention being that a shift to low field of the reference is positive. Note that this convention requires chemical shifts and shieldings to be of opposite sign.

The ^{207}Pb resonance frequency in $PbMe_4$ itself was found to be 20.920 597 MHz when corrected to a polarizing field strength such that $SiMe_4$ gives a proton resonance at exactly 100 MHz.

The procedure adopted to determine the lead resonance frequency was to monitor continuously a ^{207}Pb satellite

TABLE 1

Lead-207 chemical shifts in organolead compounds

	Compound	$\delta(^{207}Pb)$ [a]	Conditions	(^{119}Sn) [b]
(1)	$PbMe_4$	0	Containing 15% $CH_3C_6H_5$	0
(2)	$PbClMe_3$	$+432 \pm 1$	Satd. soln. in CH_2Cl_2	$+160$
(3)	$PbBrMe_3$	$+367 \pm 4$	Satd. soln. in CH_2Cl_2	$+128$
		$+329 \pm 5$	Satd. soln. in $CHCl{:}CCl_2$	
		$+276 \pm 5$	10% w/v thf [c]	
		$+193 \pm 5$	10% w/v PMe_2Ph	
		$+256 \pm 1$	10% w/v Me_2SO	
		$+163 \pm 1$	10% w/v $P(NMe_2)_3O$	
(4)	$PbIMe_3$	$+203.6 \pm 0.3$	10% Soln. in CH_2Cl_2	$+39$
(5)	$PbMe_3(SMe)$ [d]	$+214 \pm 1$	Neat liquid	
		$+239 \pm 1$	10% Soln. in CH_2Cl_2	$+90$
(6)	$PbMe_3(SEt)$ [e]	$+194 \pm 1$	Neat liquid	$+78$
		$+215 \pm 1$	10% Soln. in CH_2Cl_2	
(7)	$PbMe_3(SPr^i)$ [f]	$+177.5 \pm 1$	Neat liquid	$+70$
		$+197 \pm 1$	8% Soln. in CH_2Cl_2	
(8)	$PbMe_3(SBu^t)$ [g]	$+147.8 \pm 1$	Neat liquid	$+56$
		$+161.4 \pm 1$	10% Soln. in CH_2Cl_2	
(9)	$PbMe_3(SPh)$ [h]	$+243 \pm 1$	Neat liquid	$+91$
		$+255 \pm 1$	50% Soln. in CH_2Cl_2	
(10)	$PbMe_3(SCH_2Ph)$ [i]	$+208.1 \pm 1$	Neat liquid	
		$+217.4 \pm 1$	50% Soln. in CH_2Cl_2	
(11)	$PbMe_3(NEt_2)$	$+242 \pm 5$	20% Soln. in C_6H_6	$+58$
(12)	$PbMe_3(NMePh)$	$+226 \pm 4$	10% Soln. in C_6H_6	$+73$
(13)	$PbMe_3(SeMe)$	$+98 \pm 1$	20% Soln. in C_6H_6	$+46$
(14)	$PbMe_3(SePh)$	$+133 \pm 1$	50% Soln. in CH_2Cl_2	$+55$
(15)	$PbMe_3(PPh_2)$	$+40 \pm 4$	25% Soln. in C_6H_6	-4
(16)	$PbMe_3(SnMe_3)$	-324 ± 2	Satd. soln. in C_6H_6	-110
(17)	$PbMe_3(SnPh_3)$	-263 ± 5	Satd. soln. in C_6H_6	-92
(18)	$(PbMe_3)_2$	-281 ± 1	Satd. soln. in OEt_2	-57
(19)	$PbMe_3[B(NMeCH_2CH_2NMe)]$	-362 ± 2	30% Soln. in thf [c]	-150
(20)	$PbEt_4$	$+73.3 \pm 0.1$	Neat liquid	$+1$
		$+74.8 \pm 0.1$	17% Soln. in CH_2Cl_2	
(21)	$PbIEt_3$	$+303 \pm 4$	Satd. soln. in CH_2Cl_2	$+39$
(22)	$PbEt_3(SMe)$	$+298 \pm 2$	30% Soln. in CH_2Cl_2	
(23)	$PbEt_3(SEt)$	$+282 \pm 2$	50% Soln. in CH_2Cl_2	
(24)	$PbEt_3(SBu^t)$	$+236 \pm 2$	50% Soln. in CH_2Cl_2	
(25)	$PbEt_3(SCH_2Ph)$	$+282 \pm 4$	40% Soln. in CH_2Cl_2	
(26)	$Pb(CH_2CMe_3)_4$	$+47 \pm 8$	15% Soln. in CH_2Cl_2	
(27)	$PbBr(CH_2CMe_3)_3$	$+384 \pm 2$	Satd. soln. in CH_2Cl_2	
(28)	$PbI(CH_2CMe_3)_3$	$+336 \pm 2$	Satd. soln. in CH_2Cl_2	
(29)	$Pb(OH)(CH_2CMe_3)_3$	$+288 \pm 4$	Satd. soln. in CH_2Cl_2	
(30)	$[Pb(CH_2CMe_3)_3]_2$	-237 ± 2	Satd. soln. in CH_2Cl_2	
(31)		$+416.3 \pm 0.2$	Neat liquid	$+121$
(32)		-199 ± 8	50% Soln. in CH_2Cl_2	-80
(33)	$PbBrMe_3{\cdot}C_5H_5N$	$+194 \pm 1$	10% Soln. in C_5H_5N	
		$+373 \pm 1$	Satd. soln. in CH_2Cl_2	

[a] In p.p.m. to low field of $PbMe_4$. [b] In p.p.m. to low field of $SnMe_4$. This refers to the tin chemical shift of the analogous tin compound. See refs. 7 and 15—19. [c] thf = Tetrahydrofuran. [d] $^2J(^{207}Pb \cdots H) = -67.6 \pm 0.2$ Hz. [e] $^2J(^{207}Pb \cdots H) = -65.1 \pm 0.3$ Hz. [f] $^2J(^{207}Pb \cdots H) = -64.9 \pm 0.2$ Hz. [g] $^2J(^{207}Pb \cdots H) = -64.2 \pm 0.2$ Hz. [h] $^2J(^{207}Pb \cdots H) = -64.1 \pm 0.2$ Hz. [i] $^2J(^{207}Pb \cdots H) = -64.8 \pm 0.3$ Hz.

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[14] W. McFarlane and D. S. Rycroft, *J.C.S. Dalton*, 1973, 2162.

(preferably of a lead-methyl group) in the proton spectrum, and then sweep the output of the frequency synthesizer through an appropriate range. Once a perturbation was obtained the amplitude of the irradiating r.f. field was progressively reduced to permit accurate measurement of the optimum frequency. In many of the compounds studied it was possible to detect fine structure in the ^{207}Pb spectrum arising from splitting by coupled protons, and when this was so it was generally possible to determine $\nu(^{207}\mathrm{Pb})$ to within a few Hz, although it was then necessary to ensure that the central transitions were correctly identified. In other cases, coupling to several different kinds of proton caused the ^{207}Pb resonance to be effectively a broad envelope whose position could be determined to ±20—50 Hz. However, in view of the wide range of ^{207}Pb chemical shifts, these potential errors of 2—4 p.p.m. are not important unless detailed solvent studies are being undertaken.

DISCUSSION

Table 1 contains the lead chemical shifts measured in this work and also, for comparison, ^{119}Sn chemical shifts from various sources.[15–19] It is apparent that there are broad parallels in the general behaviour, but a plot (Figure 1) of $\delta(^{207}\mathrm{Pb})$ against $\delta(^{119}\mathrm{Sn})$ for corresponding species shows a moderately wide scatter of the points about a line of gradient 3.0. This is in marked contrast to a similar plot of $\delta(^{125}\mathrm{Te})$ against $\delta(^{77}\mathrm{Se})$ in which the spread is quite small.[1] It is to be expected that the shielding of heavy nuclei like tin and lead will be dominated by the paramagnetic term of Ramsey and an approximation to this will be given by an equation [20] such as (1). In this ΔE is a mean energy of electronic excitation from the ground state to states which can be mixed in by the magnetic field, $\langle r_{np}^{-3}\rangle$ and $\langle r_{nd}^{-3}\rangle$ are radial-expansion terms for the valence electrons, and Q_p and Q_d represent the degree of ground-state electron imbalance in the bonds to the central atom associated with the p and d components of the hybridized orbitals. For tin and lead in many of their four-co-ordinate compounds (and especially many of those studied in the present work) the terms $\langle r_{nd}^{-3}\rangle$ and Q_d may be ignored. The quotient $\langle r_{6p}^{-3}\rangle(\mathrm{Pb})/\langle r_{5p}^{-3}\rangle(\mathrm{Sn})$ is *ca.* 1.4 and $\Delta E(\mathrm{Sn})/\Delta E(\mathrm{Pb})$ is unlikely to exceed 1.25 in similar molecules, and so the expected gradient of the plot of chemical shift is *ca.* 1.8. The observed gradient of 3.0 therefore suggests that the electronic environment of the lead nucleus as measured by Q_p is more sensitive to changes in the chemical bonds than is that of tin. A similar phenomenon is noted in corresponding shieldings involving cadmium or mercury [2,3] and is quite reasonable in view of the greater polarizability of the fifth-row elements.

$$\sigma_p = -\frac{2e^2\hbar^2}{3m^2c^2\Delta E}\left(\langle r_{np}^{-3}\rangle Q_p + \langle r_{nd}^{-3}\rangle Q_d\right) \qquad (1)$$

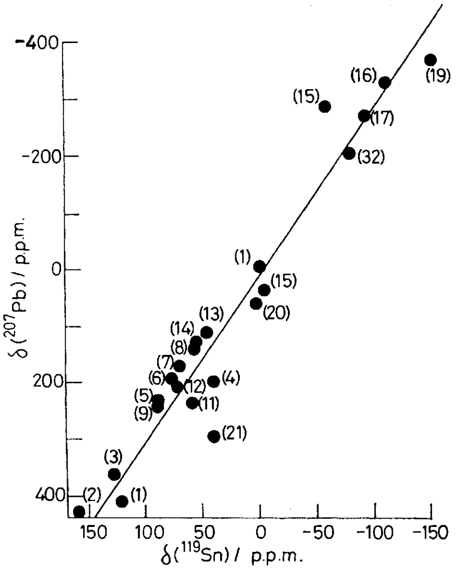

FIGURE 1 Plot of chemical shifts for lead and tin in analogous compounds. The numbers refer to the entries in Table 1

When one of the methyl groups in tetramethyl-lead (1) is replaced by an electronegative atom the lead chemical shift moves to lower field, *e.g.* in compounds (2)—(15), and the extent of the shift is dependent on the electron-withdrawing ability of the substituent group. Thus in the series of thioderivatives (5)—(10), $\mathrm{PbMe_3(SPh)}$ has the least and $\mathrm{PbMe_3(SBu^t)}$ the most shielded lead. This is in line with the Taft constants of the organo-groups in the parent thiol, although it should be pointed out that the β and γ substituents may affect the shielding (*cf.* mercury compounds) in a way not yet completely understood. Similar considerations apply to the trineopentyl-lead species (26)—(30). This behaviour is clearly related to the changes in effective nuclear charge of the lead atom and in electronic imbalance in the valence p orbitals of the lead atom brought about by substituents of differing effective electronegativity, and is similar to that which has been noted previously for ^{13}C, ^{29}Si, and ^{119}Sn.[21] However, other factors may also contribute when the atomic number of the atom(s) attached to lead changes considerably. It is now well established that the shielding of a number of nuclei, including ^{13}C, ^{29}Si, ^{119}Sn, ^{103}Rh, ^{195}Pt, and ^{199}Hg, can be increased dramatically by heavy atoms with electron lone pairs,[22] although the origin of this effect is still a matter of debate. In the case of ^{13}C, neighbouring-atom diamagnetism can satisfactorily account for this effect,[23] but this is not generally so for the

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[15] J. D. Kennedy, W. McFarlane, G. S. Pyne, P. L. Clarke, and J. D. Wardell, *J.C.S. Dalton*, 1975, 1234.

[16] J. D. Kennedy and W. McFarlane, *J.C.S. Perkin II*, 1974, 146.

[17] J. D. Kennedy, W. McFarlane, G. S. Pyne, and B. Wrackmeyer, *J.C.S. Dalton*, 1975, 386.

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[20] C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 1964, **40**, 1914.

[21] W. McFarlane and R. J. Wood, *J. Organometallic Chem.*, 1972, **40**, C17.

[22] H. C. E. McFarlane, W. McFarlane, and R. J. Wood, *Bull. Soc. chim. belges*, 1976, **85**, 864; W. McFarlane, *J.C.S. Dalton*, 1974, 324; P. L. Goggin, R. J. Goodfellow, S. R. Haddock, B. F. Taylor, and I. R. H. Marshall, *ibid.*, 1976, 459; E. M. Hyde, J. D. Kennedy, B. L. Shaw, and W. McFarlane, *ibid.*, 1977, 1571.

[23] J. Mason, *J. Chem. Soc.* (*A*), 1971, 1038.

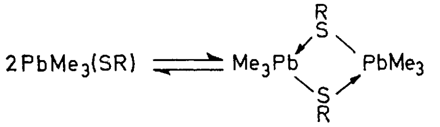
shielding of heavier nuclei. Indeed, recent indications [24] that the effect does not occur when the heavy atom has no electron lone pairs support the view that d_π–p_π interactions may be involved. Our present results show that ^{207}Pb shieldings exhibit similar behaviour. Thus, in passing from (2) to (3) to (4), $\delta(^{207}\text{Pb})$ decreases by 65 and 153 p.p.m. respectively, and decreases by *ca.* 100 p.p.m. between analogous sulphur and selenium derivatives, although these two elements have very similar electronegativities.

Any $p_\pi \rightarrow d_\pi$ interactions should lead to partial occupancy of the 6*d* orbitals of lead and hence might be expected to make Q_d non-zero and so lead to a reduction of the lead shielding which is opposite to the effect actually observed. However, this would also reduce the effective electronegativity of the substituent atom and thus may give a compensating reduction in the *p*-electron imbalance which would tend to increase the shielding, and the net effect might well be an increase in shielding as is observed. Certainly the effect of $p_\pi \rightarrow d_\pi$ interactions should be to increase the mobility of the valence-electron cloud about the lead atom and so increase the lead shielding, although in these circumstances the mean-excitation-energy approximation used in equation (1) may not be valid. Furthermore, this kind of interaction might increase ΔE, thus reducing the paramagnetic term and increasing the central-atom shielding.

In contrast, there is actually an increase in $\delta(^{207}\text{Pb})$ of 43 p.p.m. in passing from (16) to (18) even though the electronegativities of tin and lead are such as to lead one to predict a change in the opposite direction. The most noteworthy feature is that directly bound atoms of low electronegativity can cause high-field ^{207}Pb shifts even when they are light, as for example with boron in (19).

Detailed studies have shown that abnormal interbond angles at tin can cause exceptional ^{119}Sn chemical shifts, with incorporation of the tin atom into a five-membered ring producing a low-field shift, and into a six-membered ring a high-field one.[19] Comparison of the values of $\delta(^{207}\text{Pb})$ in (31) and (32) with those for tetra-alkyl-leads [*e.g.* (1), (20), and (26)] shows that this effect operates here also, and is of substantially greater magnitude. This last feature can be ascribed partly to the greater sensitivity of lead shielding to electronic changes as compared with tin, but will also be due to the greater length (typically 220 compared with 214 pm) of a lead–carbon bond. This has the effect of necessitating a greater reduction of the C–Pb–C interbond angle when the lead atom is incorporated in a five-membered ring.

Many four-co-ordinate tin compounds with one or more electronegative atoms attached to tin have a tendency to auto-associate in solution or to form complexes in the presence of donor molecules.[25-27] This increases the co-ordination number of the tin atom and there is generally a concomitant increase (which may amount to several hundred p.p.m.) in the ^{119}Sn shielding which offers a convenient means of studying the process. The data in Table 1 for the thio-derivatives (5)—(10) at two concentrations suggest that lead behaves similarly and that a reversible associative equilibrium such as (2) may be involved in which the monomer containing four-co-ordinate lead will predominate at low concentrations. Under no conditions of measurement used by us was more than one lead-methyl resonance observed which indicates that any equilibrium is rapid on an n.m.r. time scale. More detailed study revealed a monotonic relation between $\delta(^{207}\text{Pb})$ and concentration, and over the range from neat liquid to 10% w/w in CH_2Cl_2 the increases in $\delta(^{207}\text{Pb})$ for species (5)—(8) were 26, 21, 17, and 14 p.p.m. respectively. These small changes suggest that the position of equilibrium (2) is well to the left, but that there is a steady decrease in the degree of association in the neat liquid as the bulk of the alkyl group on sulphur is increased, a situation which is paralleled by the effect of bulky *O*-substituents on the auto-association of organotin alkoxides.[27] In the thio-derivatives of triethyl-lead the changes of $\delta(^{207}\text{Pb})$ on dilution in methylene chloride were much less, which indicates that steric hindrance at lead can also inhibit auto-association. An extreme example of the effect on $\delta(^{207}\text{Pb})$ of an increase in the co-ordination number of the lead atom from four to five is provided by (33), the pyridine adduct of $PbBrMe_3$ (3). This can be isolated as a solid when it is presumably stabilized by crystal-lattice forces, but in very dilute solution in methylene chloride it is apparently dissociated to such an extent that the lead chemical shift is very similar to that in the uncomplexed species. [In fact it may be that only (3) and not its pyridine adduct is soluble in methylene chloride.] In dilute solution in pyridine, however, the lead chemical shift moves *ca.* 179 p.p.m. to high field indicating that the position of equilibrium has moved substantially to favour the five-co-ordinate species. This change in $\delta(^{207}\text{Pb})$ is accompanied by a change in $^2J(^{207}\text{Pb} \cdots \text{H})$ from -66.6 to -79.3 Hz. We have also noticed that in organolead carboxylates this coupling is sensitive to concentration.



(2)

In order to define this effect more closely, we studied the behaviour of $PbClMe_3$ and $PbIMe_3$, together with their tin analogues, in the presence of the strong stanno- and plumbo-philic ligands Me_2SO and $P(NMe_2)_3O$ (Table 2). The tin compounds show the expected increase in metal nuclear shielding on increase in co-ordination number on formation of $SnXMe_3{\cdot}Me_2SO$ and $SnXMe_3{\cdot}P(NMe_2)_3O$, but it is interesting to note that for a given ligand the shielding of the five-co-ordinate adduct

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[24] J. D. Kennedy, W. McFarlane, R. J. Puddephatt, and P. J. Thompson, *J.C.S. Dalton*, 1976, 874.

[25] V. N. Torochesnikov, A. P. Tupčiauskas, N. M. Sergeyev, and Yu. A. Ustynyuk, *J. Organometallic Chem.*, 1971, **29**, 245.

[26] J. D. Kennedy, *J.C.S. Perkin II*, 1977, 242.

[27] J. D. Kennedy, W. McFarlane, L. Smith, P. J. Smith, and R. F. M. White, *J.C.S. Perkin II*, 1973, 1785.

TABLE 2

Lead-207 and ^{119}Sn chemical shifts and coupling constants for trimethylmetal halides in donor solvents [a]

Compound	Solvent	$\delta(^1H)$/p.p.m.	$^2J(M \cdots {}^1H)$/Hz	$\delta(M)$ [b]
$PbClMe_3$	CH_2Cl_2 [c]	+1.53	68.5 ± 0.5	+432 ± 1
$PbBrMe_3$	CH_2Cl_2 [c]	+1.60	66.0 ± 0.5	+367 ± 4
$PbIMe_3$	CH_2Cl_2 [c]	+1.80	65.0 ± 0.5	+204 ± 1
$PbClMe_3 \cdot Me_2SO$	Me_2SO	+1.87	82.5 ± 0.5	+258 ± 1
$PbBrMe_3 \cdot Me_2SO$	Me_2SO	+1.99	82.0 ± 0.5	+256 ± 1
$PbIMe_3 \cdot Me_2SO$	Me_2SO	+2.16	80.5 ± 0.5	+251 ± 1
$PbClMe_3 \cdot P(NMe_2)_3O$	$P(NMe_2)_3O$	+1.83	87.5 ± 0.5	+168 ± 1
$PbBrMe_3 \cdot P(NMe_2)_3O$	$P(NMe_2)_3O$	+1.97	87.0 ± 0.5	+163 ± 1
$PbIMe_3 \cdot P(NMe_2)_3O$	$P(NMe_2)_3O$	+2.14	85.5 ± 0.5	+152 ± 1
$SnClMe_3$	CH_2Cl_2	+0.65	58.7 ± 0.5	+168 ± 2
$SnIMe_3$	CH_2Cl_2	+1.13	57.5 ± 0.5	+47 ± 2
$SnClMe_3 \cdot Me_2SO$	Me_2SO	+0.54	69.5 ± 0.5	−3 ± 2
$SnIMe_3 \cdot Me_2SO$	Me_2SO	+0.61	69.0 ± 0.5	+6.5 ± 2
$SnClMe_3 \cdot P(NMe_2)_3O$	$P(NMe_2)_3O$	+0.525	72.5 ± 0.5	−47.5 ± 2
$SnIMe_3 \cdot P(NMe_2)_3O$	$P(NMe_2)_3O$	+0.59	72.0 ± 0.5	−48.5 ± 2

[a] 10% w/v solutions, except where indicated. [b] In p.p.m. to low field of MMe_4. [c] Saturated solution.

is independent (within ±5 p.p.m.) of the nature of the halogen atom. This is in marked contrast to the behaviour of the four-co-ordinate species and suggests that in these five-co-ordinate compounds the heavy-atom shielding effect referred to above may be relatively unimportant and that the tin chemical shift may depend more on the electronic asymmetry about the nucleus. That this conclusion also holds for lead is supported by the data for the trimethyl-lead halides which similarly show halogen-independent chemical shifts for the five-co-ordinate adducts of Me_2SO and $P(NMe_2)_3O$. In this context the shielding of $PbIMe_3 \cdot Me_2SO$ is of particular relevance since the resonance is actually to low field of the uncomplexed iodide, the first example of an increase in co-ordination number of a Group 4B metal being accompanied by a *decrease* in metal nuclear shielding. This novel observation was confirmed by a more careful study of the behaviour of $SnIMe_3$ and $PbIMe_3$ in the presence of Me_2SO; the results are presented graphically in Figure 2, and show that while $^2J(^{119}Sn \cdots H)$ and $^2J(^{207}Pb \cdots H)$ are affected similarly by changes in concentration, the tin and lead shieldings display opposite trends. The variations in the coupling constants and proton chemical shifts also rule out equilibrium (3).

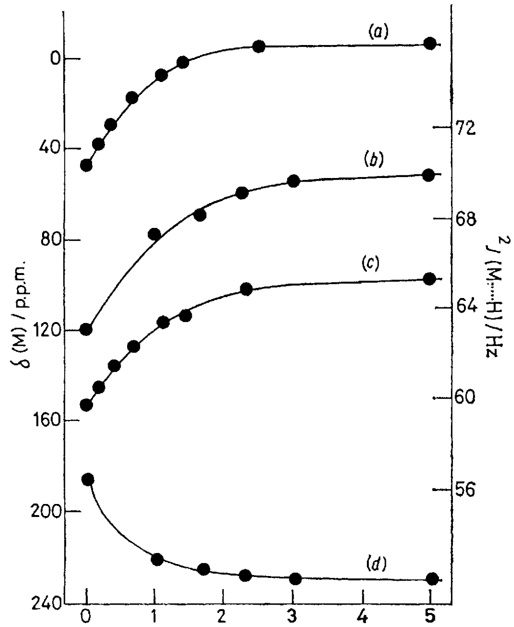

FIGURE 2 Effects on metal chemical shifts and metal–proton coupling constants of adding dimethyl sulphoxide to solutions of $SnIMe_3$ and $PbIMe_3$ in methylene dichloride: (*a*) $\delta(^{119}Sn)$, (*b*) $-^2J(^{207}Pb \cdots H)$, (*c*) $^2J(Sn \cdots H)$, and (*d*) $\delta(^{207}Pb)$

$$PbXMe_3 + Me_2SO \rightleftharpoons [PbMe_3(OSMe_2)]X \quad (3)$$

In conclusion it can be stated that lead chemical shifts follow the same overall pattern as those of tin in similar molecules, the sensitivity to equivalent changes in chemical environment being larger by a factor of *ca.* 3. There are differences of detail, but it will be generally possible to use the large body of data on tin shielding to predict that of lead and thus use measurements of $\delta(^{207}Pb)$ either directly by pulsed Fourier-transform n.m.r. or by ^1H-$\{^{207}Pb\}$ double-resonance in structural work. In addition, detailed studies of the changes in lead shielding should provide information on the thermodynamics of complex formation and auto-association by lead compounds.

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