A Lead-207 and Carbon-13 Fourier-transform Nuclear Magnetic Resonance Study of Organolead Compounds

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Lead-207 and ^{13}C n.m.r. parameters have been obtained for a large number of representative organolead compounds. The lead chemical shifts determined cover a range of *ca.* 2 500 p.p.m.; similar chemical-shift trends are observed for tin and lead, but the larger lead shift range allows a clearer distinction between closely related species. Carbon-13 chemical shifts and lead–carbon coupling constants also show similar trends to the corresponding shifts and couplings for organotin compounds, but here again the parameters for the lead compounds are generally more sensitive to structural changes; this is particularly so for coupling constants. There is no clear relation between ^nJ(Sn–C) and ^nJ(Pb–C).

THE advent of Fourier-transform n.m.r. spectroscopy has led to a rapid increase in the number of papers concerned with organo-silicon and -tin compounds. However, until recently, organolead compounds had been somewhat neglected. The publication over the past few years of a number of papers [1-14] containing relatively limited amounts of spectral data prompted us to publish the following survey of a number of typical organolead compounds; many of the data reported here appear in the doctoral dissertation [15] of one of us (J. G.).

EXPERIMENTAL

Spectra were recorded in the pulse Fourier-transform mode with proton-noise decoupling using Bruker HFX-90 (^{207}Pb, 18.81 MHz; ^{13}C, 22.628 MHz) and WP-80 (^{13}C, 20.155 MHz) n.m.r. spectrometers. Typical pulse-repetition intervals and numbers of transients were: ^{207}Pb, 0.33 s, 4—16 K; ^{13}C, 0.9 s, 4—32 K. The normal operating temperature was *ca.* 40 °C; the samples (neat liquids or saturated solutions in the appropriate solvents) contained deuteriated solvents as internal lock substances. For ^{207}Pb the standard used was external $PbMe_4$ (80% in toluene) to avoid redistribution reactions; for ^{13}C, the standard was internal $SiMe_4$. The normal convention is used for chemical shifts (*i.e.* negative to high field of the standard). The substances investigated were prepared using published procedures or in a few cases were commercially available compounds.

RESULTS AND DISCUSSION

The n.m.r. parameters of the compounds are listed in Tables 1—5. No sign determinations for coupling constants were carried out: it is known from the literature [1,16] that ^1J(Pb–C) and (for Pb_2Me_6) ^2J(Pb–Pb–C) are positive. The various features of the spectra will be discussed separately.

Lead-207 Chemical Shifts.—These are collected in Tables 1 and 5; values in parentheses in Table 1 are those for the corresponding organotin compounds, taken from recent review articles [17,18] or from our own measurements. Although a comparison is possible in only a limited number of cases, it is clear that similar trends are shown by tin and lead; thus as for tin,[18] the paramagnetic contribution to the shielding is presumably dominant. The reported temperature dependence of lead chemical shifts,[4] together with the fact that lead shifts are much more sensitive to the nature of the substituents than are tin shifts [*e.g.* compounds (1)—(4) and (17)], suggests that ΔE cannot be considered to be approximately constant in a related series of organolead compounds. However, the expression used for the paramagnetic term also involves the mean inverse cubes of the valence *p*- and *d*-electron-nuclear distances, which increase on going from tin to lead thus causing an increase in the overall range of the chemical shifts; a quantification of the influence of these various factors does not appear possible at the present time.

The values for compounds (2)—(4) were obtained by allowing a 1 : 1 mixture of (1) and (17) to undergo a redistribution reaction in the presence of a small amount of $AlCl_3$. Redistribution reactions were also carried out for the systems $PbMe_4$–$PbBu_4$, $PbEt_4$–$PbBu_4$, and $PbMe_3Cl$–$PbEt_3Cl$, and led to the formation of a number of other mixed organolead species. Since compounds $PbRCl_3$ are unknown, while $PbR(O_2CMe)_3$ are unstable

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except when R = aryl, measurements for the complete series PbR_nCl_{4-n} and $PbR_n(O_2CMe)_{4-n}$ have not been carried out. However, in the acetate case, values for n = 4, 3, 2, and 0 are available when R = Me, Et, Bu, or Ph; in each case a similar pattern is observed, with that of $PbR(O_2CMe)$ shifted to low field of PbR_4, followed by a high-field shift for $PbR_2(O_2CMe)_2$ and $Pb(O_2CMe)_4$. The same trend occurs in general for compounds SnR_nX_{4-n} (X = Cl, Br, O_2CMe, *etc.*).[18]

TABLE 1

Lead-207 chemical shifts [in p.p.m.; $\delta(PbMe_4) = 0$] for organolead compounds PbR_nX_{4-n}; values for the corresponding organotins are in parentheses

Compound	R	n	X	Solvent	$\delta(^{207}Pb)$
(1)	Me	4		Toluene	0 (0)
(2)	Me	3	Et	*a*	29 (3)
(3)	Me	2	Et	*a*	53 (7)
(4)	Me	1	Et	*a*	67 (9)
(5)	Me	3	Pr^i	$CDCl_3$	62 (10)
(6)	Me	3	Bu	*b*	16 (−2)
(7)	Me	2	Bu	*b*	29 (0)
(8)	Me	1	Bu	*b*	36
(9)	Me	3	Cl	$CHCl_3$	390 (164)
				MeOH	342 (54)
(10)	Me	3	Br	$CHCl_3$	379 (128)
(11)	Me	3	I	$CHCl_3$	171 (39)
(12)	Me	3	O_2CMe	Water	428
(13)	Me	2	EtCl	$CHCl_3$ [c]	425
(14)	Me	1	Et_2Cl	$CHCl_3$ [c]	459
(15)	Me	2	Cl	dmso	−222
(16)	Me	2	O_2CMe	MeOH	−472
				Pyridine	−538
(17)	Et	4			71 (−6)
(18)	Et	3	Bu	*d*	65 (−1)
(19)	Et	2	Bu	*d*	57
(20)	Et	1	Bu	*d*	49
(21)	Et	3	Cl	$CHCl_3$	472 (153)
				C_6H_6	425
(22)	Et	3	O_2CMe	$CDCl_3$	317 (102)
(23)	Et	2	O_2CMe	$CDCl_3$	−441
(25)	Pr	3	O_2CMe	$CHCl_3$	370
(26)	Pr^i	3	Cl	$CHCl_3$	442
(27)	Pr^i	2	O_2CMe	$CHCl_3$	−497
				Pyridine	−662
(28)	Bu	4			40 (−7)
(29)	Bu	3	O_2CMe	$CHCl_3$	383 (96)
(30)	Bu	2	O_2CMe	$CDCl_3$	−448 (−195)
(31)	Bu^i	3	O_2CMe	$CHCl_3$	392
(32)		0	O_2CMe	$CDCl_3$	−1 869
(33)	Ph	4		$CDCl_3$	−179 (−137)
(34)	C_6H_4Me-*m*	4		$CDCl_3$	−174
(35)	C_6H_4Me-*p*	4		$CDCl_3$	−168
(36)	C_6H_4OMe-*m*	4		CS_2	−166
(37)	C_6H_4OMe-*p*	4		$CHCl_3$	−153
(38)	C_6H_4SMe-*p*	4		$CHCl_3$	−160
(39)	Ph	3	$PbPh_3$	$CHCl_3$	−75 (−144)
(40)	Ph	3	Cl	$CDCl_3$	33 (−63)
(41)	Ph	3	Br	$CHCl_3$	−3
				Tetrahydrofuran	−63
				Pyridine	−174
(42)	Ph	3	I	$CHCl_3$	−131 (−115)
(43)	Ph	3	O_2CMe	$CDCl_3$	−93 (−121)
(45)	Ph	2	O_2CMe	$CHCl_3$	−688
				Pyridine	−859

Data obtained using saturated solutions in the given solvent. [a] Equilibrium mixture of compounds (1)—(4) and (17). [b] Equilibrium mixture of (1), (6)—(8), and (28). [c] Equilibrium mixture of (9), (13), (14), and (21). [d] Equilibrium mixture of (17)—(20) and (28).

A further similarity between tin and lead is the high-field shift which occurs when the donor capacity of the solvent increases [*e.g.* compounds (16), (27), and (41)]. We have looked more closely at this phenomenon in the case of $PbEt_3Cl$ for which a number of shifts have been measured (see Table 5; in each case a saturated solution was studied). A plot of chemical shifts against solvent donor number[19] for six of the solvents shows a good linear correlation (r 0.985); on this basis, chloroform must function as an electron acceptor, presumably *via* an interaction between chlorine and hydrogen. We shall return to these results below.

In the cases in which literature values for lead shifts are available the agreement between these and our values is generally good. Compounds of the type $PbR_3(O_2CMe)$, (12), (22), (25), (29), and (31), have previously been investigated[14] using acetic acid as

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[19] V. Gutmann, E. Wychera, and F. Mairinger, *Monatsh.*, 1966, **97**, 1265; V. Gutmann, *Angew. Chem.*, 1967, **79**, 279.

solvent; the shifts in this solvent are 40—90 p.p.m. to lower field than those in $CDCl_3$. This difference may possibly be due to the formation in acetic acid solution of transient complex ions of the type $[PbR_3(O_2CMe)_2]^-$; we previously prepared a number of stable complexes containing this and related anions.[20]

TABLE 2

Carbon-13 n.m.r. data for methyl-lead compounds $PbMe_nX_{4-n}$

Compound	n	X	Solvent	$\delta(^{13}C)$ ^{a}	^1J-($^{207}Pb-^{13}C$) ^{b}
(1)	4		Toluene ^{c}	−4.2	250
(2)	3	Et ^{d}	*e*	−5.1	196
(3)	2	Et ^{f}	*e*	−5.9	151
(4)	1	Et ^{g}	*e*	−6.7	*h*
(5)	3	Pr^i ^{i}	$CDCl_3$	−5.1	152
(9)	3	Cl	$CDCl_3$	21.3	318
			[$^2H_5$]Pyridine	18.1	378
(10)	3	Br	$CDCl_3$	19.0	287
			CD_3OD	17.4	337
(11)	3	I	$CDCl_3$	13.6	253
(12)	3	O_2CMe	D_2O	17.9	422
(13)	2	EtCl ^{j}	*k*	19.7	215
(14)	1	Et_2Cl ^{l}	*k*	18.5	119
(15)	2	Cl	[$^2H_6$]dmso	45.1	796
(16)	2	O_2CMe	CD_3OD	36.4	779

Data obtained using saturated solutions in the given solvent. ^{a} In p.p.m., $\delta(SiMe_4) = 0$. ^{b} In Hz. ^{c} 80% v/v in toluene. ^{d} For ethyl group: $\delta(C^1)$ 10.7, $\delta(C^2)$ 13.3 p.p.m., ^1J(Pb–C) 346, ^2J(Pb–C) 37 Hz. ^{e} Equilibrium mixture of compounds (1)—(4) and (17). ^{f} For Et group: $\delta(C^1)$ 10.3, $\delta(C^2)$ 13.5 p.p.m., ^1J(Pb–C) 292, ^2J(Pb–C) 34 Hz. ^{g} For Et group: $\delta(C^1)$ 10.0, $\delta(C^2)$ 13.6 p.p.m., ^1J(Pb–C) 244, ^2J(Pb–C) 32 Hz. ^{h} Not measured. ^{i} For isopropyl group: $\delta(C^1)$ 24.1, $\delta(C^2)$ 23.5 p.p.m., ^1J(Pb–C) 431, ^2J(Pb–C) 16 Hz. ^{j} For Et group: $\delta(C^1)$ 35.6, $\delta(C^2)$ 12.2 p.p.m., ^1J(Pb–C) 396, ^2J(Pb–C) 55 Hz. ^{k} Equilibrium mixture of (9), (13), (14), and (21). ^{l} For Et group: $\delta(C^1)$ 35.7, $\delta(C^2)$ 12.5 p.p.m., ^1J(Pb–C) 296, ^2J(Pb–C) 50 Hz.

Carbon-13 *Chemical Shifts*.—These are collected in Tables 2—4. The products of the redistribution reactions $PbMe_4$–$PbEt_4$ and $PbMe_3Cl$–$PbEt_3Cl$ were also studied by ^{13}C n.m.r., the values for the mixed tetra-alkyl-leads and trialkyl-lead chlorides being given in Table 2. In the former case we can distinguish clearly between the methyl and between both ethyl signals from the various products, while in the latter case a clear distinction is only possible for the methyl signals and those due to C^2 of the ethyl group. Assignments of the signals in these mixtures were made on the basis of (*a*) relative areas, and (*b*) comparison of chemical shifts and coupling constants with those observed for the corresponding organotin compounds.[21]

A comparison with literature values for the corresponding alkyltin compounds shows that replacement of tin by lead causes a downfield shift $\Delta\delta$ for all the carbons; this shift is of the order of 1—3 p.p.m. for β-carbons and 0.5 p.p.m. for γ-carbons, and is insignificant for δ-carbons. However, values of $\Delta\delta$ up to 35 p.p.m. have been observed for the α-carbons: $\Delta\delta$ increases on going from PbR_4 to PbR_2X_2. For PbR_4 $\Delta\delta$ is 5—10 p.p.m., for PbR_3X 19—28 p.p.m., and for PbR_2X_2 >30 p.p.m. The factors which could be involved here are differences in the anisotropy, and the length and polarity of the M–C bond. The first of these corresponds to the neighbour-atom term in the Saika–Schlichter treatment of the screening expression;[22] however, it is known that the value of this term is generally small,[23] and it should furthermore be approximately constant for PbR_4, PbR_3X, and PbR_2X_2, so that although it could be used to rationalise $\Delta\delta$ for PbR_4 it cannot explain the increase in $\Delta\delta$ on going to PbR_2X_2. The change in bond length in going from Sn–C to Pb–C may be associated with changes in the paramagnetic shielding term involving ΔE and the dimensions of the bonding orbitals; however, since the Pb–C bond length is presumably approximately constant in compounds PbR_nX_{4-n} (n = 2—4), we still appear to have no explanation for the change in $\Delta\delta$ when n changes. It appears that the polarity of organolead compounds PbR_3X and PbR_2X_2 is greater than that of the corresponding organotin compounds; thus a decrease in n corresponds to an increase in the positive charge on lead, and thus to an increase in the polarity of the Pb–C bond, which in its turn is associated with a change in the paramagnetic term due to changes in ΔE and the dimensions of the bonding orbitals.

TABLE 3

Carbon-13 n.m.r. data for other alkyl-lead compounds PbR_nX_{4-n}

Compound	R	n	X	$\delta(C^1)$	$\delta(C^2)$	$\delta(C^3)$	^1J(Pb–C)	^2J(Pb–C)	^3J(Pb–C)
(17)	Et	4		9.8	13.8		202	31	
(21)	Et	3	Cl	35.0	12.9		205	43	
(22)	Et	3	O_2CMe	31.8	12.6		219	40	
(23)	Et	2	O_2CMe	53.1	11.6		504	82	
(24)	Pr	3	Cl	43.9	21.6	18.8	179	36	103
(25)	Pr	3	O_2CMe	41.7	21.5	18.6	184	31	102
(26)	Pr^i	3	Cl	48.7	23.6		110	9	
(27)	Pr^i	2	O_2CMe	72.8	22.0		300	32	
(28)	Bu	4		18.5	31.7	27.8 *	190	28	74
(29)	Bu	3	O_2CMe	39.0	30.1	27.4 *	178	29	102
(30)	Bu	2	O_2CMe	59.6	28.7	26.0 *	503	79	215
(31)	Bu^i	3	O_2CMe	51.2	28.2	26.7	166	27	82

Data were recorded using saturated solutions in $CDCl_3$, except for $PbEt_4$ and $PbBu_4$ (neat liquids). $\delta(SiMe)_4 = 0$ p.p.m., coupling constants in Hz. * $\delta(C^4)$ 13.6 p.p.m. Data for compounds (17), (22), and (23) agree with those given in ref. 13.

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[20] F. Huber and E. Schönafinger, *Angew. Chem.*, 1968, **80**, 79; *Progr. Co-ordination Chem.*, 1968, 409.

[21] T. N. Mitchell and G. Walter, *J. Organometallic Chem.*, 1976, **121**, 177.

[22] A. Saika and C. P. Schlichter, *J. Chem. Phys.*, 1954, **22**, 26.

[23] J. A. Pople, *Discuss. Faraday Soc.*, 1962, **34**, 7.

Phenyl-lead compounds also exhibit a large shift $\Delta\delta$ for the α-carbons which apparently increases on going from $PbPh_4$ to $PbPh_2X_2$, while the shifts for the remaining carbons are insignificant. The chemical shifts for the tolyl-lead compounds show that replacement of a proton by a methyl group causes the normal[24] downfield shift of *ca.* 9 p.p.m. for the ring carbon concerned; in the case of the *p*-tolyl compound, the resonance of C^1 is shifted 3.5 p.p.m. to higher field, as expected.[24]

TABLE 4

Carbon-13 n.m.r. data for phenyl-lead compounds $PbPh_nX_{4-n}$

Compound	n	X	$\delta(C^1)$	$\delta(C^2)$	$\delta(C^3)$	$\delta(C^4)$	^1J(Pb–C)	^2J(Pb–C)	^3J(Pb–C)
(33)	4		150.1	137.4	129.4	128.4	481	66	81 [a]
(34) [b]	4		150.1	137.9 [c]	138.7 [d]	129.1	470	64 (65 [e])	79 (85 [f])
(35) [g]	4		146.5	137.3	130.0	137.9	491	69	84 [h]
(39)	3	$PbPh_3$	153.0	137.8	129.5	128.0	116 [i]	71	66
(40)	3	Cl	155.7	136.1	130.3	129.9	*j*	89	105
(41)	3	Br	154.4	136.2	130.2	129.7	531	89	104
		k	156.5	136.7	130.3	129.7	590	88	102
		l	158.8	136.8	130.0	129.4	705	85	109
(43)	3	O_2CMe	158.4	136.7	130.1	129.6	*j*	90	104 [m]
(44)	2	Br	162.6	133.7	130.4	130.4	*j*	128	183
(45)	2	O_2CMe [l]	167.2	133.1	130.2	130.2	*j*	*j*	*j*

Data were recorded using saturated solutions; solvent (when not otherwise stated) $CDCl_3$. [a] ^4J(Pb–C) 20 Hz. [b] $Pb(C_6H_4Me\text{-}m)_4$. [c] $\delta(C^6)$ 134.4 p.p.m.. [d] $\delta(C^5)$ 129.1 p.p.m. [e] J(Pb–C^6). [f] J(Pb–C^5). [g] $Pb(C_6H_4Me\text{-}p)_4$. [h] ^4J(Pb–C) 18 Hz ^5J(Pb–C) 10 Hz. [i] ^2J(Pb–Pb–C) 175 Hz (see text). [j] Not measured. [k] In tetrahydrofuran. [l] In [$^2H_5$]pyridine. [m] ^4J(Pb–C) 23 Hz. The values for compounds (33) and (35) agree well with those given in ref. 9.

TABLE 5

Lead-207 and ^{13}C n.m.r. data for saturated solutions of $PbEt_3Cl$ in organic solvents

Solvent [a]	Donor number [b]	Solubility [c]	$\delta(^{207}Pb)$ [d]	δ(Pb–C) [e]	^1J(Pb–C) [f]
$CHCl_3$		2.8	472	35.0	205
C_6H_6		2.2	425	36.2	228
CCl_4		4.7	423	36.2	231
MeCN	14	0.5	416	32.8	223
Me_2CO	17	1.0	403	32.3	229
Tetrahydrofuran	20	3.7	393	33.4	226
$HCONMe_2$	27	4.9	325	32.5	260
dmso	30	12.1	310	32.4	268
Pyridine	33	11.0	305	32.9	265

[a] In some cases the deuteriated solvent was used. [b] From ref. 19. [c] At 25 °C, in mol dm^{-3}. [d] In p.p.m., $\delta(PbMe_4) = 0$. [e] In p.p.m., $\delta(SiMe_4) = 0$. [f] In Hz.

In three cases [compounds (9), (10), and (41)] chemical shifts were measured in inert and donor solvents; compounds (9) and (10) show an upfield shift for C^1 when the donor capability of the solvent increases. Table 5 contains shift values for $PbEt_3Cl$ in various solvents; in this case there is no clear correlation between δ(C) and the donor number of the solvent. However, this is perhaps not surprising since the total range of δ(C) is only *ca.* 4 p.p.m. compared with *ca.* 170 p.p.m. for δ(Pb). In contrast to these results, compound (41) shows a downfield shift for C^1 when the donor strength of the solvent increases; the reason for this difference in behaviour is unclear.

Lead–Carbon Coupling Constants.—It is generally accepted[13] that the lead–carbon coupling mechanism is dominated by the Fermi-contact term (for a discussion of the theoretical background see ref. 10); the main factors involved in determining J(Pb–C) are therefore $Z_{eff.}$ (the effective nuclear charge at lead), α^2 (the s character of the hybrid bonding orbital), and ΔE the mean excitation energy. We have previously[21] discussed variations in ^1J(Sn–C) in symmetrical tetraorganotins in terms of these parameters, and conclude that $Z_{eff.}$ plays an important role; in mixed tetraorganotins an additional factor is involved in the form of Bent's postulate,[25] which allows us to explain the differing values of ^1J(Sn–C) observed.

Similar trends are shown by ^nJ(Pb–C) and ^nJ(Sn–C); for example, replacement of one or two alkyl groups in MR_4 by electronegative residues generally leads to an increase in J(M–C) due to an increase in $Z_{eff.}$ [an exception is shown in the organolead acetate series, $PbPr_3(O_2CMe)$ and $PbBu_3(O_2CMe)$ showing a decrease compared with PbR_4; this may be due to steric effects].[26] In the case of alkyl- and (with one exception) phenyl-lead compounds the order of magnitude of ^nJ is as follows: $^1J > {}^2J < {}^3J$. The magnitude also increases on going from an inert to a donor solvent, again as observed for organotins, in the cases studied. Table 5 shows coupling-constant values for $PbEt_3Cl$ in organic solvents; these can be correlated with the donor number of the solvent (r 0.953).

It thus seems clear that both the lead chemical shifts and the lead–carbon coupling constants are a measure of the degree to which $PbEt_3Cl$ is complexed by the

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[24] W. R. Woolfenden and D. M. Grant, *J. Amer. Chem. Soc.*, 1966, **88**, 1272.

[25] H. A. Bent, *Chem. Rev.*, 1961, **61**, 275.

[26] D. C. van Beelen, D. de Vos, and J. Wolters, *Abs. 2nd Internat. Conf. Chem. Germanium, Tin, and Lead*, Nottingham, 1977, B5.

donor solvents studied. In the case of dimethyl sulphoxide (dmso) and pyridine, the solutions studied had the approximate composition $PbEt_3Cl{\cdot}L$; in the remaining cases an excess of solvent was present. Similar investigations have been carried out previously using $PbMe_3Cl$, with ^2J(Pb–H) being a measure of the degree of complexation;[27] the complexation of trialkyltin halides by donor solvents has been the subject of a large number of investigations, including calorimetric studies[28] in which it was shown that ^2J(Sn–H) could be correlated with the enthalpy of complexation.

When we compare the observed values of ^nJ(Pb–C) with ^nJ(Sn–C) for the corresponding alkyl-lead and -tin compounds we find that (for neat liquids or in inert solvents) ^1J(Pb–C) is always smaller than ^1J(Sn–C), while the reverse is true for ^2J(M–C). However, J(Pb–C)/J(Sn–C) is not constant, varying for the compounds studied here in the ranges 0.34—0.83 (^1J) and 1.1—2.5 (^2J). The magnitudes of the corresponding quotients of the reduced coupling constants K (ref. 29) can be obtained by multiplying the J quotient by 1.79; thus for ^1K we observe values between 0.61 and 1.49. Kennedy *et al.*[10] reported J ratios between −0.08 [for ^1J(M–Pb)] and 130.5 [for ^1J(M–N)] for a number of representative compounds. Thus there is no simple relation between ^1J(Pb–X) and ^1J(Sn–X). It is likely that the coupling mechanism for both elements is dominated by the Fermi-contact interaction; since ^1K(M–C) is positive for both elements, the following expression for ^1K can be used:[29]

$$^1K(\mathrm{M{-}C}) = (4e^2\boldsymbol{h}^2/9m^2c^2\Delta E)\psi_{\mathrm{M}}{}^2(0)\psi_{\mathrm{C}}{}^2(0)\alpha_{\mathrm{M}}{}^2\alpha_{\mathrm{C}}{}^2$$

α^2 and $\psi^2(0)$ are respectively the *s* character of the M–C hybrid orbital and the valence-electron density at the nucleus; ΔE is the mean electronic excitation energy. According to Jameson and Gutowsky,[30] $\psi^2(0)(\mathrm{Pb})/\psi^2(0)(\mathrm{Sn}) =$ *ca.* 1.69. Pople and Santry[29] replaced the term involving α^2 by π(M–C), the mutual polarisability of the valence *s* orbitals of M and C, to explain negative values of ^1K. π(M–C) depends in its turn on β(M–C), the *s*-overlap integral between M and C; we can expect that, for the long and relatively weak Pb–C bonds, changes in the substituents on lead will affect β(Pb–C) more than the corresponding changes will affect β(Sn–C). It is also likely that ΔE may vary over larger ranges for Pb than for Sn. A quantification of these factors is however not possible at this stage in the development of the theory of heavy-metal couplings.

The variability of ^1J(M–C) can be demonstrated by the following examples: on going from MMe_4 to MBu_4, ^1J(Sn–C) decreases by 8% while ^1J(Pb–C) decreases by 24%. Similarly, in the series $MMe_{4-n}Et_n$, $^1J(\mathrm{Sn{-}CH_2})$ decreases by 14% on going from $n = 1$ to 4 while $^1J(\mathrm{Pb{-}CH_2})$ decreases by 42%. To take a final example, ^1J(Pb–C) decreases by 40% on going from $PbMe_4$ to $PbMe_3Pr^i$ while the corresponding decrease in ^1J(Sn–C) is only 11%. Thus, since ^1J(Sn–C) in ditins is much lower than in tetra-alkyltins[31] (*e.g.* $SnMe_4$, 338; Sn_2Me_6, 244 Hz), the low value (28 Hz) found by Clark *et al.*[1] for ^1J(Pb–C) in Pb_2Me_6 is therefore not at all surprising, and Singh's assignment[8] of the couplings in hexaneopentyldilead is probably incorrect; we have assigned the smaller coupling observed for C^1 in hexaphenyldilead as ^1J(Pb–C) on this basis.

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