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ORGANOLEAD CHEMISTRY

III*. ^{207}Pb CHEMICAL SHIFTS IN SOME ORGANOLEAD COMPOUNDS

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Summary

^{207}Pb chemical shifts are reported for the compounds $(CH_3)_{4-n}PbX_n$, where n = 1 - 4, X = 4-FC_6H_4—, n = 1, 2, 4, X = $CH_3C{\equiv}C$—, n = 1, 4, X = $CH_2{=}CH$—, n = 1, X = Cl—, CH_3O—, CH_3CO_2— A correlation between $\delta(^{207}Pb)$ and $\delta(^{19}F)$ for the 4-fluorophenyl derivatives is discussed, and solvent effects on $\delta(^{207}Pb)$ for the propynyl derivatives are interpreted in terms of complex formation.

Introduction

There have been several reports recently of ^{29}Si [2 - 4] and ^{119}Sn [5 - 10] chemical shifts in organometallic derivatives of these elements. While a detailed interpretation of the observed chemical shifts is not yet possible, it is already apparent that valuable information about structure and bonding in organosilicon and organotin compounds can be obtained Thus replacement of methyl groups in Me_4M (M = Si or Sn) by unsaturated organic groups such as vinyl, alkynyl or aryl groups leads to a shift of the ^{29}Si or ^{119}Sn resonance to high field [3, 10], whereas a shift to low field would be expected from simple electronegativity considerations. This high field shift has therefore been tentatively attributed to the presence of $p\pi$—$d\pi$ bonding in the metal—carbon bond [10], a theory which is supported by the observation that electronegative but saturated organic groups, such as the trichloromethyl group, cause the expected shift of the metal resonance to low field [5]. It has also been found that high field shifts are produced when the coordination number of the

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* For Part II see ref. 1.

central metal exceeds four. Thus, for example, ^{119}Sn NMR spectroscopy has been used to study complex formation and intra- and intermolecular association of organotin compounds [7, 9].

In contrast, there have been very few reports of ^{207}Pb NMR spectra of organolead compounds. It has been noted that the ^{207}Pb chemical shift difference between hexamethyldilead and tetramethyllead is larger than the difference between the ^{119}Sn chemical shifts of the analogous tin compounds [11, 12], as expected from the very large overall range of ^{207}Pb chemical shifts [13 - 15]. A preliminary report of ^{207}Pb chemical shifts in some simple methyllead compounds has appeared recently [16, 17]. We now report ^{207}Pb chemical shifts (Table 1) for some propynyl-, vinyl- and 4-fluorophenyl-lead compounds and for trimethyllead chloride, acetate and methoxide. ^{1}H and ^{19}F NMR spectra of the 4-fluorophenyl-lead compounds are also given. The trends in ^{207}Pb chemical shifts are compared with those for ^{29}Si and ^{119}Sn chemical shifts in analogous compounds of silicon and tin.

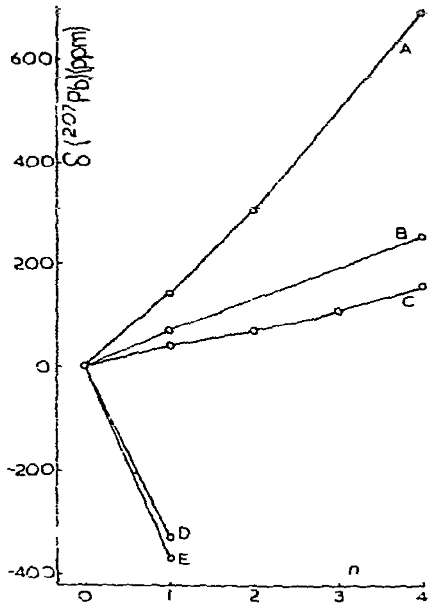
Results and Discussion

The ^{207}Pb chemical shifts obtained for some of the compounds in Table 1, in solution in non-polar solvents, are plotted in Fig. 1. It can be seen that stepwise replacement of methyl groups in tetramethyllead by propynyl, vinyl or 4-fluorophenyl groups causes a steady shift of the ^{207}Pb resonance to high field The stepwise shift for each propynyl substituent is approximately +170 ppm, for a vinyl group +62 ppm and for a 4-fluorophenyl group +36 ppm. These can be compared with those from similar studies of silicon and tin compounds. Thus in methylsilicon compounds, a vinyl substituent causes a shift of the ^{29}Si resonance [3] of +7 ppm, and a phenyl group +4 ppm while in similar tin compounds an ethynyl group causes a shift of the ^{119}Sn resonance [10] of +68.5 ppm, a vinyl group +41.5 ppm and a phenyl group +32.5 ppm.

TABLE 1

^{207}Pb CHEMICAL SHIFTS IN ORGANOLEAD COMPOUNDS

Compound	$\delta(^{207}Pb)$ (ppm)	Conditions
Me_4Pb	0	80% w/w soln. in toluene
Me_4Pb	+2.39 ± 0.05	Soln in toluene + pyridine
$Me_3PbCCMe$	+139.8 ± 0.8	Soln in benzene
$Me_3PbCCMe$	+140.9 ± 0.2	Soln in pyridine
$Me_2Pb(CCMe)_2$	+304.7 ± 0.8	Soln. in benzene
$Me_2Pb(CCMe)_2$	+311.0 ± 0.2	Soln. in pyridine
$Pb(CCMe)_4$	+685.5 ± 0.4	Soln. in benzene
$Pb(CCMe)_4$	+698.9 ± 0.8	Soln in pyridine
$Me_3Pb(C_6H_4F\text{-}4)$	+38.5 ± 0.8	Neat liquid
$Me_2Pb(C_6H_4F\text{-}4)_2$	+63.0 ± 0.8	Neat liquid
$MePb(C_6H_4F\text{-}4)_3$	+102.6 ± 0.8	Soln in CCl_4
$Pb(C_6H_4F\text{-}4)_4$	+153.5 ± 1.5	Soln in CCl_4
$Me_3Pb(CH{=}CH_2)$	+65.3 ± 0.8	Neat liquid
$Pb(CH{=}CH_2)_4$	+251.0 ± 0.8	Neat liquid
Me_3PbCl	−374.8 ± 0.8	Soln in $CDCl_3$
Me_3PbCl	−215.7 ± 0.2	Soln. in pyridine
Me_3PbO_2CMe	−304.6 ± 0.2	Satd soln in methanol
Me_3PbO_2CMe	−311.4 ± 0.2	Above soln. diluted X 3
Me_3PbO_2CMe	−264.8 ± 0.2	Satd soln in methanol + pyridine
Me_3PbOMe	−331.3 ± 0.8	Soln in dichloromethane



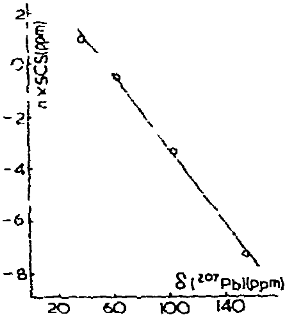


Fig 1 ^{207}Pb chemical shifts for $Me_{4-n}PbX_n$. A, X = $CH_3C{\equiv}C-$, B, X = $CH_2{=}CH-$ C X = $4\text{-}FC_6H_4-$ D, X = CH_3O-, E, X = Cl—.

Fig 2. Correlation of ^{207}Pb chemical shift with $n \times$ (^{19}F substituent chemical shift) for the compounds $Me_{4-n}(4F\text{-}C_6H_4)_nPb$

The trends in each case are clearly similar, with the incremental shift increasing with the Taft σ^* constant of the substituent [10, 17]; the magnitude of the shifts for a given substituent are in the order $^{207}Pb > {}^{119}Sn > {}^{29}Si$ as might be expected from the overall chemical shift ranges for these elements.

In order to investigate the possibility that the upfield shifts might be due to π-bonding effects, we have studied the ^{1}H and ^{19}F NMR spectra of the 4-fluorophenyllead derivatives; the results of the analysis, which was carried out by standard methods [18, 19], are given in Table 2. It is well known [20,

TABLE 2

NMR DATA FOR $Me_{4-n}Pb(C_6H_4F\text{-}4)_n$

	Me_4Pb	Me_3PbAr [a]	Me_2PbAr_2 [a]	$MePbAr_3$ [a]	$PbAr_4$ [a]
Chemical shifts (ppm)					
$\delta(^{207}Pb)$	0	38 5	63 0	102 6	153 5
$\delta(F)^b$		114 11	112 87	111.99	111 28
$\delta(H^1)^c$		7 33	7 32	7 47	7 55
$\delta(H^2)^c$		6 87	6 82	7 02	7 09
$\delta(CH_3Pb)$	0 71	0 91	1 11	1 33	
Coupling constants (Hz)					
$^2J(^{207}PbCH_3)$	-62 0	64 0	67 0	71 0	
$^5J(^{207}PbF)$		18 0	19.0	20 4	22 0
$^3J(^{207}PbH^1)^c$		68 0	68 0	75 6	76 0
$^3J(FH^2)^c$		9 0	9 1	9.2	9.3
$^4J(FH^1)^c$		6 0	6 1	6.2	6 3
$^3J(H^1H^2)^c$		8 2	8 4	8 7	8 6
$SCS(^{19}F)$ ppm		0 99	—0 25	—1.13	—1 84

[a] Ar = $4\text{-}FC_6H_4$ [b] From internal $CFCl_3$. [c] H^1 *ortho*, H^2 *meta* to Pb

21], that the ^{19}F chemical shifts in compounds 4-FC_6H_4X are determined by a combination of the σ- and π-bonding effects of the substituent X, and this information has been used successfully to investigate the importance of $p\pi$—$d\pi$ bonding in the metal—aryl bonds of several organometallics [22, 23]. The method relies on relating the substituent chemical shift (SCS) [defined as SCS = δ(F) in 4-FC_6H_4X minus δ(F) in C_6H_5F] to bonding influences. Thus σ- and π-inductive effects (+*I* and +*M*) should shield fluorine while the π-acceptor effect (—*M*), due to $p\pi$—$d\pi$ bonding, should deshield the ^{19}F nucleus. If the ^{207}Pb chemical shift is also determined by a combination of these effects then a correlation between $\delta(^{207}Pb)$ and the ^{19}F SCS value would be expected. In fact a linear correlation is observed between $\delta(^{207}Pb)$ and n × SCS, where n is the number of aryl groups present in the molecule $Me_{4-n}Pb(C_6H_4F)_n$ (Fig. 2). Thus it seems that the effects of $p\pi$—$d\pi$ bonding between lead and each aryl group, which largely determine the ^{19}F SCS value, combine in an additive manner to shield the lead nucleus This correlation lends support to the theory that the ^{207}Pb chemical shifts in these compounds are strongly influenced by π-bonding effects

Some apparently anomalous chemical shift data can be rationalised using this approach. For example, the high field ^{119}Sn chemical shift in tributyltin cyanide (+48 ppm) was tentatively attributed [5] to the presence of intermolecular association giving 5-coordinate tin, but is more likely to be due to $p\pi$—$d\pi$ bonding effects in the Sn—CN bond; the ^{119}Sn chemical shift is very close to that for the essentially isoelectronic triethyl(ethynyl)tin of +52 ppm [10].

As expected, the ^{207}Pb chemical shifts for trimethyllead chloride, acetate and methoxide are all downfield from tetramethyllead, but the dimethyllead dihalides are too insoluble for study of their ^{207}Pb NMR spectra, so that we have been unable to observe the expected increase in chemical shift on further halogen substitution [3, 5, 10]

Solvent effects

The ^{207}Pb chemical shifts of the propynyllead compounds have been measured in both benzene and pyridine solutions with the aim of investigating their ability to form complexes with pyridine. In all cases, the ^{207}Pb resonance moved to higher field in pyridine solution, the maximum solvent shift being +13.4 ppm for $Pb(C{\equiv}CCH_3)_4$, suggesting that this has the strongest acceptor properties. This shift is small, however, compared with the similar solvent shift of +159 ppm for trimethyllead chloride which is known to form a 5-coordinate complex with pyridine [24]. This suggests that complex formation by the alkynyllead compounds is rather weak, as already indicated by previous studies [1]. This conclusion should however be regarded as tentative since two opposing effects on the ^{207}Pb chemical shift are expected on complex formation. Thus the primary effect should be to cause a high-field shift, but a secondary effect will be the weakening of $p\pi$—$d\pi$ bonding in the alkynyl—lead bond which is expected to cause an opposing low-field shift.

Experimental section

General techniques have been described previously [1]. ^{19}F chemical shifts are in ppm upfield from internal $CFCl_3$. ^{207}Pb chemical shifts determined by the double resonance method [11], are in ppm upfield from Me_4Pb (as an 80% ww solution in toluene), which has a Ξ value of 20,920,657 ± 2 Hz

Organolead compounds were prepared by established methods [1,25,26], with the following exceptions.

(4-Fluorophenyl)trimethyllead was prepared by treating Me_3PbCl (7 33 g, 25 mmole) with 4-fluorophenylmagnesium bromide (30 mmole) in ether (50 ml). After hydrolysis with ammonium chloride solution, the ether layer was evaporated and the product was purified by vacuum distillation Yield 50%, b.p. 80° (15 mm). (Found: C, 30.8; H, 3.5. $C_9H_{13}FPb$ calcd : C, 31 1; H, 3.8%.) The product was hydrolysed slowly in air.

Bis(4-fluorophenyl)dimethyllead was prepared from Me_2PbCl_2 (7 4 g, 24 mmole) and 4-fluorophenylmagnesium bromide (90 mmole) in tetrahydrofuran (50 ml). After refluxing for 1 h the solvent was evaporated under vacuum and the residue was extracted with pentane. After evaporating the pentane extracts, the product, a viscous liquid, was purified by vacuum distillation Yield 55%; b.p. 170° (1 mm) (Found. C, 38.9; H, 3 6, Pb, 49.3. $C_{14}H_{14}F_2Pb$ calcd . C, 39 3; H, 3 3; Pb, 48.5%.)

Tris(4-fluorophenyl)methyllead was prepared by treating tris(4-fluorophenyl)leadmagnesium bromide, prepared from lead chloride (5 g, 0.018 mole) and 4-fluorophenylmagnesium bromide (0.054 mole) in dry tetrahydrofuran (50 ml), with excess methyl iodide. After hydrolysis, extraction with chloroform and evaporation of the organic extracts, the product was recrystallised from methanol Yield 2 5 g (46%); m.p. 89-90°. (Found C, 44 56, H, 2 72; Pb, 39 91. $C_{19}H_{15}F_3Pb$ calcd · C, 44 90; H, 2.90, Pb, 40.71%.)

Tetrakis(4-fluorophenyl)lead was prepared by refluxing lead dichloride (5 g, 0 018 mole) and 4-fluorophenylmagnesium bromide (0.036 mole) in a mixture of ether (100 ml) and toluene (100 ml) for 24 h. The mixture was hydrolysed, the toluene layer was evaporated and the product was recrystallised from chloroform. Yield 4 g (71%), m.p. 144-145°. (Found· C, 49.32, H, 2 60; Pb 34.91. $C_{24}H_{16}F_4Pb$ calcd : C, 49.20, H, 2.71, Pb 35.30%)

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