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AROMATIC LEAD(IV) COMPOUNDS

XII *. ^{207}Pb FT NMR INVESTIGATIONS ON ARYLLEAD(IV) COMPOUNDS

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Summary

^{207}Pb FT NMR data for a number of aromatic lead(IV) compounds are reported. The chemical shifts of the compounds cover a range of about 900 ppm. Compounds Ar_4Pb give resonances at about 150—200 ppm upfield from tetramethyllead. Downfield shifts are observed for compounds Ar_3PbR (R = alkyl) and Ar_3PbX (X = halogen or acetate). With increasing number of electronegative substituents the lead resonance is shifted towards high field. The observed phenomena are discussed on the bases of Ramsey's paramagnetic term, anisotropy contributions and the influence of the coordination number.

Introduction

^{1}H- and ^{13}C-NMR spectroscopy have proved to be very useful tools in the study of organometallic compounds [2]. In those cases involving metals with naturally occurring isotopes with spin $\neq 0$ additional information can be derived from $J(M—^1H)$ and $J(M—^{13}C)$ coupling constants and/or from chemical shift data of the metal nucleus in question.

In contrast to e.g. ^{119}Sn NMR spectroscopy [3,4], there have been relatively few reports concerning ^{207}Pb NMR spectroscopy of organometallic compounds [5—16]. Inspection of the nuclear properties of the isotope ^{207}Pb (natural abundance 21.11%; spin 1/2) with respect to natural abundance × relative sensitivity at constant field (9.13×10^{-3} relative to ^{1}H [17]) reveals that ^{207}Pb NMR spectra should be recorded easily. It was demonstrated by the elegant studies of Kennedy et al. that there is an analogy between ^{119}Sn- and ^{207}Pb-

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* Part XI, see ref. 1.

NMR, the lead shielding being more sensitive to changes in the environment of the nucleus than the tin shielding [12].

Up to now most data involve alkyllead compounds. We present here chemical shift data for aromatic lead(IV) compounds derived by means of Fourier transform NMR spectroscopy. This technique has the advantage of an increased signal-to-noise ratio compared with direct observation or INDOR experiments, thus facilitating the determination of the chemical shift of compounds in lower concentrations.

Results and discussion

The chemical shift data of the aromatic lead(IV) compounds measured are presented in Tables 1—4. Compared with the overall chemical shift variations for organolead compounds, the δ-values of the tetraaryllead compounds (Table 1) cover only a small range. Replacement of one aryl group by an alkyl group results in a low field shift of about 50 ppm. The trends observed in the series Ar_3PbMe are similar to those in the Ar_4Pb series. Variation of the alkyl group has little effect upon the lead shielding (Table 2). As can be seen from Tables 3 and 4 replacement of one aryl group by a more electronegative substituent also results in a shift to low field compared to the compounds Ar_4Pb, the magnitude of the deshielding depending on the nature of the electronegative substituent. With increasing number of electronegative substituents large high field shifts are observed.

It is generally accepted that Ramsey's paramagnetic term dominates the shielding of heavy metal nuclei. A simplified expression for this term is given by Jameson and Gutowski [17] (eq. 1).

$$\sigma_p = -(2e^2h^2/3m^2c^2\Delta E)(\langle 1/r^3\rangle_{np}P_u + \langle 1/r^3\rangle_{nd}D_u) \qquad (1)$$

ΔE is the mean excitation energy, which may be considered as approximately constant within closely related series of compounds. $\langle 1/r^3\rangle_{np}$ and $\langle 1/r^3\rangle_{nd}$ are the mean inverse cubes of the valence p and d electron nuclear distances and the terms P_u and D_u represent the amount of electron imbalance associated with the valence p and d orbitals of the metal atom.

TABLE 1

$\delta(^{207}Pb)$ VALUES OF COMPOUNDS Ar_4Pb [a]

Ar	para	meta	ortho
C_6H_5	—178.0 (—179) [b]		
$(CH_3)_3CC_6H_4$	—181.8		
$CH_3OC_6H_4$	—152.0 (—153) [b]	—166.5 (—166) [b]	—195.6
$CH_3C_6H_4$	—166.6 (—168) [b]	—175.3 (—174) [b]	—161.6
ClC_6H_4	—157.1	—169.1	
FC_6H_4	—156.2 [c] (—153.5) [e]	—171.1 [d]	
2,4-$(CH_3O)_2C_6H_3$	—185.5		
2,5-$(CH_3O)_2C_6H_3$	—188.7		

[a] δ in ppm (reference: external tetramethyllead (TML); 70% in toluene). [b] See ref. 13. [c] $^5J(^{207}Pb—^{19}F)$ = 23 Hz. [d] $^4J(^{207}Pb—^{19}F)$ = 40 Hz. [e] See ref. 9.

TABLE 2

$\delta(^{207}Pb)$ VALUES OF COMPOUNDS Ar_3PbR [a]

Ar	R	
C_6H_5	CH_3	—118.9
p-$CH_3OC_6H_4$	CH_3	—103.9
p-$CH_3C_6H_4$	CH_3	—113.4
p-ClC_6H_4	CH_3	—100.2
p-FC_6H_4	CH_3	—101.2 (—102.6) [b]
C_6H_5	C_2H_5	—116.2
C_6H_5	i-C_3H_7	—120.1
C_6H_5	t-C_4H_9	—111.5
C_6H_5	$(CH_3)_3CCH_2$	—141.8

[a] δ in ppm (reference external TML). [b] See ref. 9.

Other terms which may contribute to the shielding of a metal nucleus are σ_E contributions, arising both from the electric field effect due to permanent dipole moments in the molecule and from Van der Waals interactions between the atoms, and σ_{anis} contributions according to eq. 2.

$$\sigma_{anis} = 1/3\, H_0 R^3_{AB} \Delta\chi_B (1 - 3\cos^2\theta) \qquad (2)$$

$\Delta\chi_B$ is the magnetic anisotropy centered on atom B in an A—B bond axis, θ is the angle between the line joining the anisotropy site on the A—B bond axis to the nucleus for which the σ_{anis} contributions are calculated and the direction of the magnetic field H_0 [18].

Inspection of the data in Table 1 reveals that the effect of *ortho*, *meta* or *para* substitution in tetraaryllead compounds upon the ^{207}Pb shift is only small. No definite correlation could be found between the chemical shift of the lead atom and substituent constants (e.g. Hammett σ). Although there are relatively few data for tetraaryltin compounds, a similar phenomenon was observed for those compounds [3]. In the case of *ortho*-substituted tetraaryllead compounds a high field shift is observed for *ortho*-methoxy groups. This might be caused by the bulk of the substituent on the aromatic ring, although it is not clear why a similar high field shift is not observed with tetrakis(*o*-methylphenyl)lead.

TABLE 3

$\delta(^{207}Pb)$ VALUES OF COMPOUNDS Ar_nPbX_{4-n} [a]

Ar	n	X	
C_6H_5	3	Cl	(33) [b]
C_6H_5	3	Br	0.6 (—3) [b]
C_6H_5	3	I	—127.5 (—131) [b]
C_6H_5	2	I	—391.8
p-$CH_3OC_6H_4$	3	Cl	76.8
p-$CH_3OC_6H_4$	3	Br	34.9
p-$CH_3OC_6H_4$	3	I	—152.8
p-$CH_3OC_6H_4$	2	I	—393.5

[a] δ in ppm (reference external TML). [b] See ref. 13.

TABLE 4

$\delta(^{207}Pb)$ VALUES OF COMPOUNDS $Ar_nPb(OAc)_{4-n}$ [a]

	$n = 4$	$n = 3$	$n = 2$	$n = 1$	$n = 0$
C_6H_5	−178.0 (−179) [b]	−89.4 (−93) [b]	−611.6 (−688) [b]	−857.4	−1869 [b]
p-$CH_3OC_6H_4$	−152.0 (−153) [b]		−490.1	−795.5	−1869 [b]
m-$CH_3OC_6H_4$	−166.5 (−166) [b]	−87.5	−591.0		−1869 [b]
o-$CH_3OC_6H_4$	−195.6	−115.2	−561.5	−848.7	−1869 [b]

[a] δ in ppm (reference external TML). [b] See ref. 13.

Replacement of an aryl group in compounds Ar_4Pb by a substituent with different electronegativity will result in an increase of the p-electron imbalance P_u, and hence lead to a low field shift of the lead absorption. This low field shift is observed in compounds of the types Ar_3PbR (R = alkyl; Table 2) and Ar_3PbX (X = halogen; Table 3). In the case of the latter compounds the magnitude of the low field shift depends also on the electronegativity of the halogen atom. For example in the series $(C_6H_5)_3PbX$ the lead resonance is shifted from −127.5 ppm in $(C_6H_5)_3PbI$ towards +33 ppm in $(C_6H_5)_3PbCl$. This may be attributed to the increasing electronegativity of the halogen atom, resulting in an increase of the nuclear charge of the lead atom. This leads to an increase of the contraction of the valence p-electrons [19]. Replacement of a second aryl group by an iodine results in a large high field shift. In the case of compounds R_nSnX_{4-n} the same phenomenon was noted. Increase of the nuclear charge of the metal atom due to substitution by more electronegative groups will result in a decrease of the p-electron imbalance P_u [20]. Furthermore, σ_E - and σ_{anis} contributions have been invoked to explain the observed high field shifts [18].

Similar explanations can be given for compounds $Ar_nPb(OAc)_{4-n}$ (Table 4). Replacement of one aryl group by an acetate group results in a low field shift. For alkyllead compounds this low field shift is usually much more pronounced (e.g. $(CH_3)_4Pb$, δ 0 ppm; $(CH_3)_3PbOAc$, δ 428 ppm [13]). It is likely that the difference in electronegativity between the organic groups at the lead atom is responsible.

When the number of acetate groups at the lead atom is further increased, a large high field shift is observed. Along with a possible anisotropy contribution according to eq. 2, another factor may contribute to the high field shift with growing number of acetate groups, viz., the change of the coordination number of the lead atom. In the case of organotin compounds high field shifts are observed with increasing coordination number of the tin atom [3,4] and a similar effect was noted for some alkyllead compounds [12]. Investigations by IR spectroscopy showed that acetate groups in organolead acetates are bidentating [21]. Starting with tetraaryllead compounds, where the lead atom is four coordinated, the coordination number of the lead atom increases with growing number of acetate groups. A maximum value of eight is reached in lead(IV) acetate [22].

In conclusion it can be stated that ^{207}Pb chemical shifts are very sensitive to changes in the environment of the lead atom, the chemical shift range for organolead compounds being several thousand ppm. Although no quantitative interpretation of the NMR data is yet possible for the aryllead compounds, there is qualitative agreement with the trends in ^{119}Sn NMR, as reported for alkyllead compounds [12].

Experimental

The compounds were made by published procedures [21,23].

The spectra were recorded on a Bruker WH 90 Multinuclear NMR Spectrometer, operating at a frequency of 18.83 MHz. The compounds were examined in $CDCl_3$ solutions (concentration ca. 20% w/v) at 25° C, using the deuterium signal of the solvent for field/frequency stabilization. The spectra were recorded under conditions of proton/noise decoupling. Tetramethyllead (TML; 70% in toluene) was used as an external reference to avoid redistribution reactions. The chemical shifts are accurate within 0.1 ppm. The normal sign convention is used, positive chemical shift values being downfield from TML.

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