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AROMATIC LEAD(IV) COMPOUNDS

VIII*. ^{13}C FT-NMR SPECTROSCOPY OF COMPOUNDS $Ar_nPb(CH_3)_{4-n}$ (n = 0-4)

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Summary

^{13}C chemical shifts and ^{207}Pb—^{13}C coupling constants are reported for some arylmethyllead compounds. The value of $J(^{207}Pb—^{13}C)$ is shown to depend on the number and the nature of the aryl groups.

Introduction

Recently ^{13}C data for some organolead compounds were published [2,3]. Continuing our investigations on the ^{1}H NMR spectroscopy of the compounds $(p\text{-}XC_6H_4)_nPb(OAc)_{4-n}$ (X = CH_3O, CH_3, Cl) [4] we have now studied a series of arylmethyllead compounds $Ar_nPb(CH_3)_{4-n}$ (see Fig. 1) in order to obtain more insight into the nature of the ^{207}Pb—^{13}C interactions.

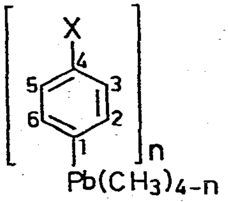

Fig. 1. Compounds $Ar_nPb(CH_3)_{4-n}$ (X = H, Cl, CH_3, CH_3O; n = 0-4).

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* Part VII see ref. [1].

Results and discussion

The ^{13}C chemical shifts and ^{207}Pb—^{13}C coupling constants are listed in Table 1. Replacement of methyl by phenyl groups in $C_6H_5Pb(CH_3)_3$ leads to a downfield shift of the ^{13}C resonance for all carbon atoms, as expected from electronegativity considerations. ^{1}H NMR resonances likewise show a downfield shift: $C_6H_5Pb(CH_2CH_3)_3$ δ(H(2,6)) 7.37, δ(H(3,5)) 7.20, δ(H(4)) 7.11 ppm [8], $(C_6H_5)_4Pb$ δ(H(2,6)) 7.59, δ(H(3,5)) 7.39, δ(H(4)) 7.32 ppm [9], (cf. δ(H(2,6)) and δ(H(3,5)) for the $(p\text{-}FC_6H_4)_nPb(CH_3)_{4-n}$ series [10]).

In phenylmethyltin compounds an upfield shift for C(1) was observed, and was explained in terms of differences in β effect between a methyl and a phenyl group [2]. In the compounds $(p\text{-}FC_6H_4)_nPb(CH_3)_{4-n}$ the upfield shift in ^{207}Pb and ^{19}F NMR observed with increasing number of phenyl groups was attributed to d_π—p_π bonding in the metal—carbon bond [10].

The ^{13}C shifts in the compounds Ar_3PbCH_3 vary in the expected way with the nature of the substituent X. A strong resemblance between the trends in the ^{13}C shifts in these and that in the corresponding ArH compounds [11] was observed, indicating that there is no special influence of the lead substituent. An attempt was made to establish the relation between the ^{13}C shifts and the electronic effects of the substituents X by means of a least square analysis based

TABLE 1

CHEMICAL SHIFTS (ppm) [a] AND ^{207}Pb—^{13}C COUPLING CONSTANTS (Hz) [b] FOR COMPOUNDS $Ar_nPb(CH_3)_{4-n}$ (n = 0–4) [c]

Compound [d]	C(1)	C(2,6)	C(3,5)	C(4)	C(X) [e]	C(CH$_3$)
$Pb(CH_3)_4$	—	—	—	—	—	−3.2 [f]
	(—)	(—)	(—)	(—)	(—)	(251) [g]
$C_6H_5Pb(CH_3)_3$ [h]	148.5	136.5	128.5	127.5	—	−2.2
	(348) [i]	(63)	(66)	(16)	(—)	(274)
$(C_6H_5)_2Pb(CH_3)_2$	149.0	136.6	128.7	127.8	—	−1.0
	(395)	(65)	(72)	(19)	(—)	(295)
$(C_6H_5)_3PbCH_3$	149.6	137.1	129.2	128.3	—	0.2
	(439)	(67)	(77)	(19)	(—)	(321)
$(C_6H_5)_4Pb$	150.1	137.7	129.5	128.6	—	—
	(481)	(68)	(80)	(20)	(—)	(—)
$(p\text{-}ClC_6H_4)_3PbCH_3$	146.8	138.0	129.4	134.7	—	0.8
	(438)	(74)	(81)	(21)	(—)	(357)
$(p\text{-}CH_3C_6H_4)_3PbCH_3$	145.8	137.0	130.0	137.6	21.2	0.0
	(459)	(68)	(78)	(18)	(11)	(325)
$(p\text{-}CH_3OC_6H_4)_3PbCH_3$	140.0	138.1	115.0	159.9	54.8	0.0
	(471)	(77)	(84)	(18)	(—)	(336)
$(p\text{-}ClC_6H_4)_4Pb$	146.6	138.3	129.8	135.4	—	—
	(506)	(77)	(87)	(23)	(—)	(—)
$(p\text{-}CH_3C_6H_4)_4Pb$	146.4	137.5	130.2	138.0	21.4	—
	(492) [j]	(69)	(83)	(19)	(12)	(—)
$(p\text{-}CH_3OC_6H_4)_4Pb$	140.4	138.4	115.2	160.0	54.9	—
	(522)	(79)	(89)	(19)	(—)	(—)

[a] Reference TMS. [b] In parentheses. [c] In $CDCl_3$. [d] Prepared according to known methods [5]. [e] Carbon of the substituent at the phenyl ring [f] From ref. [6]. [g] Cf. ref. [7] 249 Hz. [h] Cf. ref. [2] 148.9, 136.7, 128.8 and 127.7 ppm. [i] Cf. ref. [2] 364 Hz. [j] Cf. ref. [2] 488 Hz.

on eqn. 1, where σ_I and σ_R are substituent constants [12].

$$\delta(^{13}C) = \rho_I\sigma_I + \rho_R\sigma_R + C \quad (1)$$

Although a satisfactory fit was not obtained in all cases, the results were similar to those for carbon, silicon and germanium compounds [12].

From Table 1 it appears that the magnitude of $J(^{207}Pb-^{13}C)$ depends for all carbons on the number of aryl groups attached to the lead atom. The numerical largest change occurs at $J(^{207}Pb-^{13}C(1))$: 348 Hz for $C_6H_5Pb(CH_3)_3$ versus 481 Hz for $(C_6H_5)_4Pb$. The same phenomenon has been observed in ^1H NMR: $J(^{207}Pb-H(2,6))$ 68.0 Hz in $C_6H_5Pb(CH_3)_3$ versus 80.1 Hz in $(C_6H_5)_4Pb$. The Fermi contact term being assumed to dominate the M—X coupling, the coupling constant is given by eqn. 2, in which C is a summation of constants, Δ the mean excitation energy, and $\psi^2{}_{ns}(0)$ the valence s-electron density at the nucleus; α^2 represents the s-character of the hybride orbital used to form the M—X bond.

$$J(M-X) = (C/\Delta)\,\alpha^2(M)\,\alpha^2(X)\,\psi^2(0)_{ns(M)}\,\psi^2(0)_{ns(X)} \quad (2)$$

An increase of $J(^{207}Pb-^{13}C)$ may be due to (a) a decrease of Δ (b) an increase of the effective nuclear charge on the coupled nuclei and (c) an increase of the s-electron content of the C—Pb bond. Aritomi and Kawasaki [13] suggest, in explaining the increase in $J(^{207}Pb-H(CH_3))$ in dimethylbis(oxinato)lead complexes in several solvents, that amongst other factors, decrease of the excitation energy plays an important role on the basis of the highfield shift of the proton resonances of the methyl groups attached to the lead atom. The assumption of increase of positive charge on the lead atom was abandoned by these authors because the $J(^{207}Pb-H(CH_3))$ values did not correlate simply with the $J(^{13}C-H)$ values.

It seems thus to be useful to consider also the $J(^{207}Pb-H(CH_3))$ values for the compounds $(C_6H_5)_nPb(CH_3)_{4-n}$ (n = 0-3) which are presented in Table 2. It can be readily seen from Table 2 that $\delta(H(CH_3))$ and $J(^{207}Pb-H(CH_3))$ increase with increasing number of phenyl groups. This was also the case for $\delta(^{13}C(CH_3))$ and $J(^{207}Pb-^{13}C(CH_3))$. Moreover a linear relation between $J(^{207}Pb-^{13}C(CH_3))$ and $J(^{207}Pb-^1H(CH_3))$ was found: $J(^{207}Pb-^1H(CH_3))$ 0.111 (±0.009), $J(^{207}Pb-^{13}C(CH_3))$ + 0.32 (±0.03). Therefore the decrease in mean excitation energy is not considered to be the major contribution to the increase in $J(^{207}Pb-^{13}C)$. Taking into account the difference in electronegativity between a phenyl

TABLE 2

^1H NMR DATA FOR COMPOUNDS $(C_6H_5)_nPb(CH_3)_{4-n}$ [a] (n = 0-3)

Compounds	$\delta(H(CH_3))$ [b] (ppm)	$J(^{207}Pb-H(CH_3))$ (Hz)
$Pb(CH_3)_4$	0.74	60.5 [c]
$C_6H_5Pb(CH_3)_3$	0.88	63.2
$(C_6H_5)_2Pb(CH_3)_2$	1.09	64.7
$(C_6H_5)_3PbCH_3$	1.30	68.5

[a] In $CDCl_3$. [b] Reference TMS. [c] Cf. ref. [7] 61.2 Hz.

TABLE 3

VALUES ρ_I, ρ_R AND C FITTING THE EQUATION $J(^{207}Pb—^{13}C) = \rho_I\sigma_I + \rho_R\sigma_R + C$ FOR COMPOUNDS Ar_3PbCH_3

	C(1)	C(2,6)	C(3,5)	C(4)	C(CH$_3$)
ρ_I	−51 (±22)	9.021 (±0.007)	3.70 (±0.15)	6.93 (±0.47)	73 (±18)
ρ_R	−69 (±20)	−12.403 (±0.007)	−9.80 (±0.13)	4.58 (±0.42)	13 (±15)
C	444 (±6)	66.998 (±0.002)	77.03 (±0.04)	18.98 (±0.12)	325 (±5)

and a methyl group, the increase in $J(^{207}Pb—^{13}C)$ with increasing number of phenyl groups may be mainly attributed to the growing effective nuclear charge on the lead atom, next to the greater s electron content in the C—Pb bonds.

The magnitude of the $^{207}Pb—^{13}C$ coupling is also determined by the nature of the aryl group e.g. $J(^{207}Pb—^{13}C(1))$ 439 Hz in $(C_6H_5)_3PbCH_3$ verus $J(^{207}Pb—^{13}C(1))$ 471 Hz in $(p\text{-}CH_3OC_6H_4)_3PbCH_3$. Regression analysis with the aid of the J analogue of eqn. 1 was performed to explain the differences in terms of electronic substituent effects. The results are presented in Table 3. Although a satisfactory fit was not obtained in all cases the relative (reversed) importance of the electronic influences is indicated.

Experimental

The compounds were synthesized by published procedures [5]. Trimethylphenyllead was purified very carefully.

All ^{13}C and ^1H NMR spectra were recorded on a JEOL-Ps-100 NMR spectrometer, equipped with a JEOL-JNM-PFT-100 pulse unit and a JEOL-JEC-6 computer. Field/frequency stabilisation was established by the deuterium signal of $CDCl_3$. The compounds were examined as c. 20% solutions in $CDCl_3$ (minimum 1000 pulses). The chemical shifts are expressed in ppm relative to internal TMS and are believed to be accurate to 0.1 ppm. The spectra have been taken under conditions of proton-noise decoupling.

Regression analysis was performed on an IBM 370/158 computer.

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