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AROMATIC LEAD(IV) COMPOUNDS

XIII *. ^{13}C FT-NMR INVESTIGATIONS ON ALKYLPHENYLLEAD(IV) COMPOUNDS

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Summary

The ^{13}C FT-NMR data of several organolead compounds of the type Ph_nPbR_{4-n} (R = alkyl, cycloalkyl; n = 0—4) are reported. Substituent chemical shift parameters have been calculated for the triphenyllead group in alkyltriphenyllead compounds. Variations of the ^{207}Pb—^{13}C coupling constants are discussed in terms of changes of hybridisation and nuclear charge of the lead atom. Steric factors can also play an important role, especially in the compounds $Ph_3Pb(cyclo\text{-}C_nH_{2n-1})$ (n = 6, 7).

Introduction

In recent years there has been a wealth of ^{13}C NMR studies of organometallic compounds [2,3]. However only limited data on organolead compounds are available compared with those for e.g. organotin compounds [4]. In previous investigations we studied the ^{13}C NMR characteristics of several types of organolead compounds [5—8]. In the compounds Ar_3PbCH_3 the value of $^1J(^{207}Pb—^{13}C(CH_3))$ was found to depend on the nature of the aryl group. We have now investigated a number of alkylphenyllead(IV) compounds, and especially the magnitude of the ^{207}Pb—^{13}C coupling constants as a function of the alkyl group at the lead atom. Analogous studies on alkyltrimethyltin compounds were recently published by Kuivila et al. [9] and Mitchell et al. [10].

Results and discussion

a. Chemical shift data

Table 1 presents the chemical shift data for the compounds studied. Only

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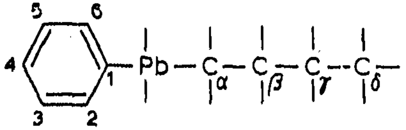
* Part XII: see ref. 1.

TABLE 1

^{13}C CHEMICAL SHIFT DATA AND SUBSTITUENT CHEMICAL SHIFTS OF COMPOUNDS Ph_nPbR_{4-n} (n = 0—4) [a]



	Compound	C(1)	C(2,6)	C(3,5)	C(4)	C_α	C_β	C_γ	C_δ
I	Ph_4Pb [b]	150.1	137.7	129.5	128.6				
II	Ph_3PbCH_3 [b]	149.6	137.1	129.2	128.3	0.2 (+2.3)			
III	$Ph_3PbCH_2CH_3$	150.5	137.5	129.1	128.1	16.6 (+10.7)	13.5 (+7.6)		
IV	$Ph_2Pb(CH_2CH_3)_2$	150.6	137.4	128.9	127.7	14.6	13.6		
V	$PhPb(CH_2CH_3)_3$	150.6	137.7	128.6	127.3	12.3	13.8		
VI	$Pb(CH_2CH_3)_4$ [c]					9.6	13.8		
VII	$Ph_3PbCH_2CH_2CH_3$	150.6	137.4	129.1	128.0	27.1 (+11.5)	22.2 (+5.9)	18.9 (+3.3)	
VIII	$Ph_3PbCH_2CH_2CH_2CH_3$	150.5	137.4	129.1	128.0	24.2 (+11.0)	30.8 (+5.8)	27.4 (+2.4)	13.5 (+0.3)
IX	$Ph_3PbCH(CH_3)_2$	151.6	137.7	129.1	128.0	33.6 (+17.5)	24.1 (+8.5)		
X	$Ph_3PbC(CH_3)_3$	152.8	137.8	129.1	128.0	49.2 (+24.0)	32.8 (+8.5)		
XI	$Ph_3PbCH(CH_3)CH_2CH_3$	151.9	137.7	129.1	127.9	43.2 (+18.2)	31.0 [d] (+6.0)	15.1 (+1.9)	
XII	$Ph_3PbCH_2CH(CH_3)_2$	151.0	137.4	129.1	128.0	36.5 (+12.2)	28.5 (+3.3)	26.7 (+2.4)	
XIII	$Ph_3PbCH_2C(CH_3)_3$	151.5	137.3	129.1	127.9	44.7 (+13.2)	32.8 (+4.9)	33.3 (+1.8)	
XIV	$Ph_3Pb(cyclo\text{-}C_3H_5)$	149.8	137.5	129.2	128.2	10.1 (+13.7)	2.5 (+5.1)		
XV	$Ph_3Pb(cyclo\text{-}C_4H_7)$	151.2	137.6	129.2	128.0	37.8 (+14.5)	31.3 (+8.0)	26.0 (+2.7)	
XVI	$Ph_3Pb(cyclo\text{-}C_5H_9)$	151.4	137.6	129.1	128.0	41.5 (+15.0)	32.6 (+6.1)	25.8 (—0.7)	
XVII	$Ph_3Pb(cyclo\text{-}C_6H_{11})$	151.8	137.7	129.1	127.9	46.0 (+18.2)	34.3 (+6.7)	29.6 (+1.8)	26.6 (—1.2)
XVIII	$Ph_3Pb(cyclo\text{-}C_7H_{13})$	152.2	137.6	129.1	127.9	46.6 (+17.2)	35.5 (+6.1)	30.4 (+1.0)	27.7 (—1.7)

[a] $\delta(^{13}C)$ in ppm (reference TMS), $\Delta\delta_i$ in parentheses. [b] See ref. 5. [c] See ref. 6. [d] $\delta(CH_3)$ 21.1 ppm (+7.9).

the resonances of the C(1) aromatic carbon atoms are significantly affected by change of the alkyl group. With increasing bulk of the alkyl group the resonance of the C(1) carbon atom shifts towards lower field.

It is possible to determine the effect of the triphenyllead group on the direction and magnitude of the ^{13}C chemical shifts of the hydrocarbon moiety R. The substituent chemical shift $\Delta\delta_i$ may be defined as $\Delta\delta_i = \delta_i(Ph_3PbR) - \delta_i(RH)$, wherein the chemical shift $\delta_i(Ph_3PbR)$ applies to a particular carbon atom in the organolead compound and $\delta_i(RH)$ to the corresponding carbon atom in the parent hydrocarbon RH [11]. The data thus obtained are also listed (in parentheses) in Table 1. It is clear that virtually all the carbon resonances show a downfield shift, the magnitude of the deshielding being determined by the distance of the triphenyllead group from the carbon atom in question. The average values of the substituent chemical shifts are: $\Delta\delta(C_\alpha)$ +14.2 ppm (number of compounds (m) 14; standard deviation 5.0 ppm), $\Delta\delta(C_\beta)$ +6.5 ppm ($m = 14$; s.d. 1.5 ppm) and $\Delta\delta(C_\gamma)$ +1.8 ppm ($m = 9$; s.d. 1.2 ppm). These data show the same trend as found for the Ar_3Pb group in compounds of the type Ar_3PbAr [7].

b. Lead—carbon coupling constants

The absolute values of the ^{207}Pb—^{13}C coupling constants are presented in Table 2. The data demonstrate that the magnitude of both $J(^{207}Pb—^{13}C(Ph))$ and $J(^{207}Pb—^{13}C(R))$ depends strongly on the number and the nature of the alkyl groups. In the series $Ph_nPb(CH_2CH_3)_{4-n}$ ($n = 0$—4; compounds I, III—VI) $^1J(^{207}Pb—^{13}C)$ is found to decrease with the number of phenyl groups. Similar trends were observed in compounds $Ph_nPb(CH_3)_{4-n}$ ($n = 0$—4) [5], although

TABLE 2

^{207}Pb—^{13}C COUPLING CONSTANTS OF COMPOUNDS Ph_nPbR_{4-n} ($n = 0$—4) [a]

Compound	C(1)	C(2,6)	C(3,5)	C(4)	C_α	C_β	C_γ	$\Sigma ^1J$
I [b]	481	68	80	20				1924
II [b]	439	67	77	19	321			1638
III	349	62	70	17	404	43		1451
IV	237	56	60	15	324	38		1122
V	143	51	51	13	256	34		911
VI [c]					200	30		800
VII	347	63	70	17	392	39	100	1433
VIII	349	62	68	17	388	38	100	1435
IX	275	58	63	16	486	18		1311
X	200	56	59	15	553			1153
XI	258	57	62	16	477	24 [d]	73	1251
XII	344	63	69	17	388	37	81	1420
XIII	341	63	68	16	387	37	70	1410
XIV	432	63	75	18	530	32		1826
XV	308	60	66	16	389	40	134	1313
XVI	297	60	65	16	455	13	90	1346
XVII	260	59	62	16	469	29	115	1249
XVIII	243	58	62	16	463	24	147	1192

[a] J in Hz. [b] See ref. 5. [c] See ref. 6. [d] $J(^{207}Pb—^{13}C(CH_3))$ 24 Hz.

the numerical decrease was much less pronounced (e.g. $^{1}J(^{207}\mathrm{Pb}—^{13}\mathrm{C(Ph)})$ = 481 Hz in $\mathrm{Ph_4Pb}$ and 143 Hz in $\mathrm{PhPb(CH_2CH_3)_3}$ versus 348 Hz in $\mathrm{PhPb(CH_3)_3}$ [5]).

In the series $\mathrm{Ph_3PbCH_{3-x}(CH_3)_x}$ (x = 0—3; compounds II, III, IX and X) substitution of an α-hydrogen by a methyl group results in a decrease of $^{1}J(^{207}\mathrm{Pb}—^{13}\mathrm{C(Ph)})$ and an increase of $^{1}J(^{207}\mathrm{Pb}—^{13}\mathrm{C(R)})$. Figure 1 shows a graph of $^{1}J(^{207}\mathrm{Pb}—^{13}\mathrm{C(Ph)})$ plotted against $^{1}J(^{207}\mathrm{Pb}—^{13}\mathrm{C(R)})$. From the linear relationship between these coupling constants it must be concluded that the factors determining the changes in the coupling constants are similar throughout this series. An analogous phenomenon was observed in compounds of the type $\mathrm{(CH_3)_3SnCH_{3-x}(CH_3)_x}$ [9].

The magnitude of the one bond lead—carbon coupling constant is dominated by the Fermi-contact term, which can be represented according to [12]:

$$^{1}J(^{207}\mathrm{Pb}—^{13}\mathrm{C}) = (C/\Delta) \times \alpha^2(\mathrm{Pb}) \times \alpha^2(\mathrm{C}) \times \psi^2_{6s\,\mathrm{Pb}}(0) \times \psi^2_{2s\,\mathrm{C}}(0)$$

Within closely related series of compounds the mean excitation energy Δ may be considered to have a constant value and differences in the coupling constants can be explained in terms of variations of α^2, the percentage s-character of the lead—carbon hybride orbitals, and $\psi^2(0)$, the s-electron density at the nucleus related to the effective nuclear charge. For the compounds II, III, VII—XIII one may assume that the hybridisation of the α-carbon atom remains unchanged. A simplification can thus be obtained by invoking only the electron density at the lead nucleus and the hybridisation of the lead atom to explain the observed phenomena.

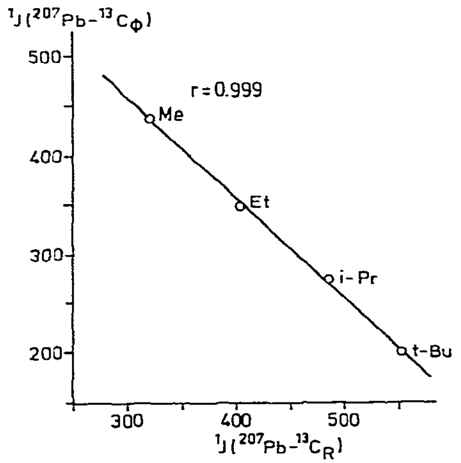


Fig. 1.

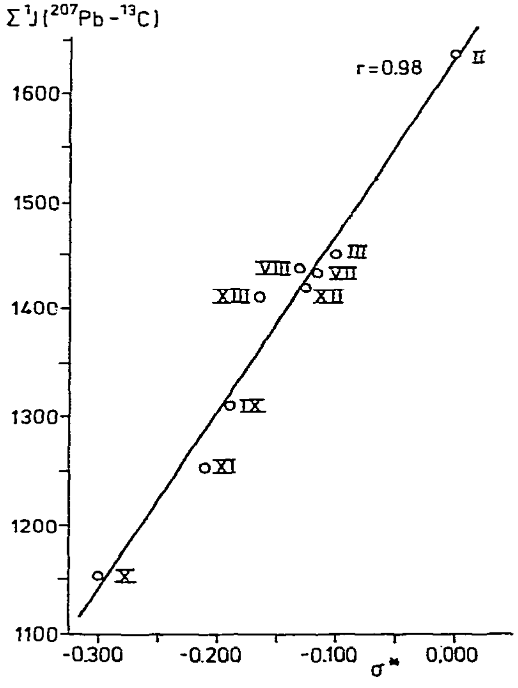


Fig. 2.

In the case of the trimethyltin compounds Bent's postulate of isovalent hybridisation [13] was taken into account to explain the direction of the changes in $^1J(^{119}Sn—^{13}C(CH_3))$ [9,10]. Although the usefulness of Bent's postulate in interpreting NMR characteristics of organolead compounds has been questioned [14], it may be relevant for the triphenyllead compounds under consideration. Thus, replacement of an alkyl group by a more electropositive one will result in an increase of $^1J(^{207}Pb—^{13}C(R))$ owing to increasing *s*-character of the lead orbital directed towards the alkyl group and hence lead to a decrease of $^1J(^{207}Pb—^{13}C(Ph))$. However, it should be noted that if isovalent hybridisation was the only factor accounting for the changes in the coupling constant values, the sum of the one bond coupling constants Σ^1J should remain constant upon variation of the alkyl group R. This was observed for the trimethyltin compounds studied by Kuivila et al. [9], but in the triphenyllead compounds studied here the value of Σ^1J varies from 1638 Hz in compound II to 1153 Hz in compound X.

In order to get more insight into the factors determining this phenomenon we have correlated Σ^1J with Taft's polar substituent constant σ^* of the alkyl group R [15]. As can be seen from Fig. 2 a linear correlation results which indicates that the decrease in Σ^1J is caused by a decrease of the effective nuclear charge of the lead atom due to increasing electropositivity of R. With the closely related compounds $(CH_3)_nSn(C_4H_9)_{4-n}$ (n = 0—4) studied by Mitchell et al. similar results were obtained [10]. Thus for the alkyltriphenyllead compounds Bent's rule alone is not useful for the explanation of the NMR results. At least also the effective nuclear charge of the lead atom should be invoked in the discussion.

The linear relationship between Σ^1J and σ^*, however, does not exclude that other factors contribute to the observed trends. We suggest that steric factors may also be important (see also Kuivila et al. [9]). Upon branching at the α-carbon atom (compounds II, III, IX—XI) $^1J(^{207}Pb—^{13}C(Ph))$ decreases significantly with increasing bulk of the substituent: from 439 Hz in compound II to 200 Hz in compound X. Branching at the β-carbon atom (compounds III, VII, XII and XIII) shows a small change (from 349 Hz in compound III to 341 Hz in compound XIII), while with substitution at the γ-carbon atom (compounds VII and VIII) the value of $^1J(^{207}Pb—^{13}C(Ph))$ is hardly affected.

Within the series $Ph_3Pb(cyclo\text{-}C_nH_{2n-1})$ (n = 3—7; compounds XIV—XVIII) it appears that although $^1J(^{207}Pb—^{13}C(Ph))$ decreases with increasing n, there is no uniform change either in $^1J(^{207}Pb—^{13}C(R))$ or in Σ^1J. Obviously with the cyclopropyl (XIV) and cyclobutyl compounds (XV) there is a large change in the hybridisation of the α-carbon atom, thus affecting the magnitude of the Fermi-contact term. Upon further increasing the ring size of the cycloalkyl group there is a steady decrease in Σ^1J, but the values of $^1J(^{207}Pb—^{13}C(R))$ do not increase simultaneously. We believe that in this case, also, steric factors play an important role, especially in the compounds with larger cycloalkyl groups (XVII and XVIII), because of the poor correlation between Σ^1J and σ^*. Similar effects were observed for the corresponding trimethyltin compounds [9].

We thus conclude that the magnitude of the lead—carbon coupling constant in compouds Ph_3PbR is determined by hybridisation and nuclear charge of the contributing atoms, in particular the lead atom. It is demonstrated that steric factors can have a great impact on the lead—carbon coupling constants: with decreasing distance to the lead atom substituents show an increasing influence.

Experimental

a. NMR spectra

The 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. The compounds were examined as ca. 20% solutions in $CDCl_3$. Field/frequency stabilisation was established by the deuterium signal of the solvent. The spectra have been taken under conditions of proton-noise decoupling. Chemical shifts are accurate to 0.02 ppm, coupling constants to 0.5 Hz.

Assignments have been made with the aid of (a) relative intensities of the carbon signals, indicating the carbon atoms without hydrogen atoms, (b) relative magnitudes of the ^{207}Pb—^{13}C-coupling constants ($^1J(^{207}\text{Pb}—^{13}\text{C}) >> {^3J}(^{207}\text{Pb}—^{13}\text{C}) > {^2J}(^{207}\text{Pb}—^{13}\text{C}) > {^4J}(^{207}\text{Pb}—^{13}\text{C})$) and (c) multiplicities in the NMR spectra recorded with off resonance decoupling.

b. Synthesis of the compounds

The compounds were synthesized either by reaction of an excess of the Grignard compound of the alkyl halide with the appropriate organolead bromide (eq. 1) or by reaction of triphenylleadmagnesium bromide with the alkyl halide (eq. 2):

$$n\ \text{RMgX} + \text{Ph}_{4-n}\text{PbBr}_n \xrightarrow{\text{THF}} \text{Ph}_{4-n}\text{PbR}_n + n\ \text{MgBrX} \quad (n = 1, 2) \tag{1}$$

$$\text{Ph}_3\text{PbMgBr} + \text{RX} \xrightarrow{\text{THF}} \text{Ph}_3\text{PbR} + \text{MgBrX} \tag{2}$$

TABLE 3

EXPERIMENTAL DETAILS FOR THE PREPARATIONS OF COMPOUNDS Ph_nPbR_{4-n} (n = 1—4)

Compound	Yield (%)	M.p. [a] (°C)	Method of preparation [b]
III	50	45—46 [c]	2
IV	83	[d]	1
V	43	[e]	3
VII	73	68—70 [f]	1
VIII	50	49—50 [g]	2
IX	8	89—91	2
X	11	150—152	1
XI	70	78—80	1
XII	84	68—69	1
XIII	82	57—59	1
XIV	52	64—66	1
XV	47	62—64	1
XVI	87	98—100	1
XVII	58	128—132	1
XVIII	48	52—54	1

[a] Dec. (uncorr.). [b] See text. [c] M.p. lit. [16] 48—50°C. [d] n_D^{20} 1.5946, d_4^{20} 1.486. [e] n_D^{20} 1.5701 (lit. [17] 1.5752). [f] M.p. lit. [16] 68—69°C. [g] M.p. lit. [18] 47—48°C.

Triethylphenyllead (V) was prepared according to eq. 3:

$$(CH_3CH_2)_3PbBr + PhMgBr \xrightarrow{THF} (CH_3CH_2)_3PbPh + MgBr_2 \tag{3}$$

The purity of the organolead compounds was checked by means of ^1H NMR spectroscopy. Yields and melting points are summarized in Table 3.

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