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Note

^{207}Pb NMR Chemical Shifts of Aryllead Tricarboxylates

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ABSTRACT: ^{207}Pb NMR spectroscopy was used to investigate the nature of aryllead(IV) tricarboxylate species in solution. The ^{207}Pb chemical shifts of *p*-Br- and *p*-MeO-aryllead tricarboxylates were found to depend on both electronic (as measured by the pK_a of the parent acid) and steric effects of the neighbouring carboxylic acid ligands. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{207}Pb NMR; organolead compounds

INTRODUCTION

As part of ongoing investigations into various aspects of the Pinhey arylation[1] (Scheme 1), we have utilized ^{207}Pb NMR spectroscopy as a tool to probe the nature of lead(IV) tetracarboxylates.[2] We have shown recently, by using ^{207}Pb NMR spectroscopy, that intermolecular ligand exchange occurs in lead(IV) tetracarboxylates, and that this process becomes slow on the NMR timescale at low temperatures.[3,4] This behaviour suggests that in arylation reactions containing a variety of carboxylate ligands, many different lead(IV) species could be present, any of which could, in principle, mediate the arylation. That such ligand equilibration could be important in arylation reactions is supported by recent results indicating that only low levels of enantioselectivity can be achieved in reaction mixtures in which a mixture of chiral and achiral ligands are present.[5]

We are interested in the effect that changing the carboxylate groups on the intermediate aryllead tricarboxylate has on the course of the Pinhey arylation. With this in mind, we would like to use ^{207}Pb NMR as a convenient means of identifying which aryllead species are formed in solution as the reaction proceeds, which should then give a greater insight into the effects of different carboxylate ligands on the reactivity of lead(IV) compounds. As part of this investigation, we report here the ^{207}Pb NMR chemical shifts for a wide range of aryllead tricarboxylates, and demonstrate the influence of electronic and steric factors.

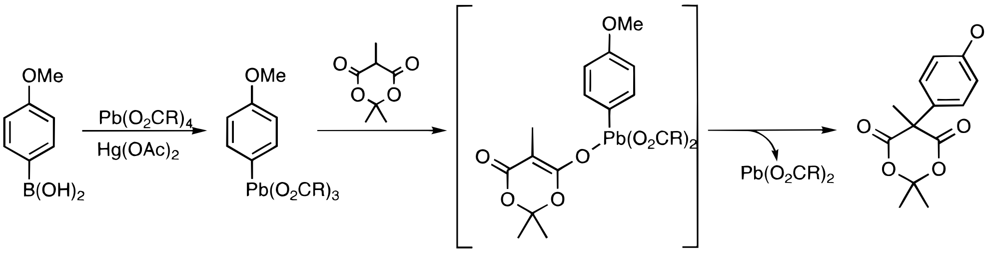
RESULTS AND DISCUSSION

Two aryllead triacetates (*p*-BrPhPbOAc$_3$ and *p*-MeOPhPbOAc$_3$) were prepared by standard procedures.[6] These had ^{207}Pb NMR resonances in good accord with literature values.[7]

When *p*-toluic acid (T) was titrated into a sample of *p*-methoxyphenyllead triacetate (ArPbA$_3$) at 218 K, four resonances, corresponding to the species ArPbA$_3$, ArPbA$_2$T, ArPbAT$_2$ and ArPbT$_3$, were seen (Fig. 1). This is consistent with a dynamic intermolecular exchange process involving the carboxylate ligands but not the aryl group.

This titration process was repeated for a wide range of different carboxylic acids, and the ^{207}Pb resonance chemical shifts of the aryllead diacetate monocarboxylate for each acid are given in Table 1. A similar set of experiments was carried out using lead tetraacetate as the starting material and chemical shifts of the lead triacetate monocarboxylate species are also presented in Table 1.

A plot of the chemical shift of the aryllead diacetate monocarboxylate against the pK_a of the parent acid[8,9] indicates a general trend of increasing chemical shift (i.e. more positive) with decreasing pK_a. Figure 2 shows the results for the *p*-Br-aryllead species; similar trends were observed for the *p*-MeO-aryllead species. These results mirror those for ^{29}Si NMR[10] and ^{119}Sn NMR.[11]



Scheme 1.

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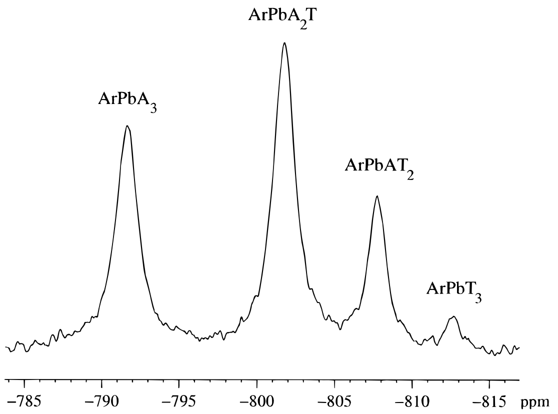

Figure 1. 52.2 MHz ^{207}Pb NMR spectra at 218 K: *p*-MeO-phenyllead triacetate with toluic acid; external reference 80% $Pb(CH_3)_4$ in toluene.

A lower pK_a value reflects a more electron-deficient carboxylate group, which would be expected to deshield the lead nucleus. This effect corresponds to a change of about 15 ppm per pK_a unit, similar to that found in triorganotin carboxylates.[11] We assume that other factors, such as the anisotropy of the electron distribution in the aryl–lead bond and the bond lengths in the lead–carboxylate unit, will remain broadly constant over each series that we have examined, since the differences between ligands are three bonds removed from the lead atom.

There is, however, a secondary effect in evidence. Those carboxylates with an *ortho* substituent on an aromatic ring have a chemical shift about 10 ppm to lower frequency than would be expected purely on the electronic grounds discussed above (these are given the plot symbol ◆). Moreover, the larger the substituent, the more pronounced the deviation is, as exemplified by the *o*-halobenzoic acids (**3**, **5**, **7** and **9**). Conversely, those carboxylic acids with less substituted sp^3 or sp^2 centres adjacent to the carboxylate (acetate, the phenyl acetates and cinnamates; plot symbol ●) have a chemical shift to higher frequency. It therefore appears that there exists a steric factor influencing the chemical shift, with increased crowding around the lead(IV) centre causing a resonance shift to low frequency, analogous to the 'γ-

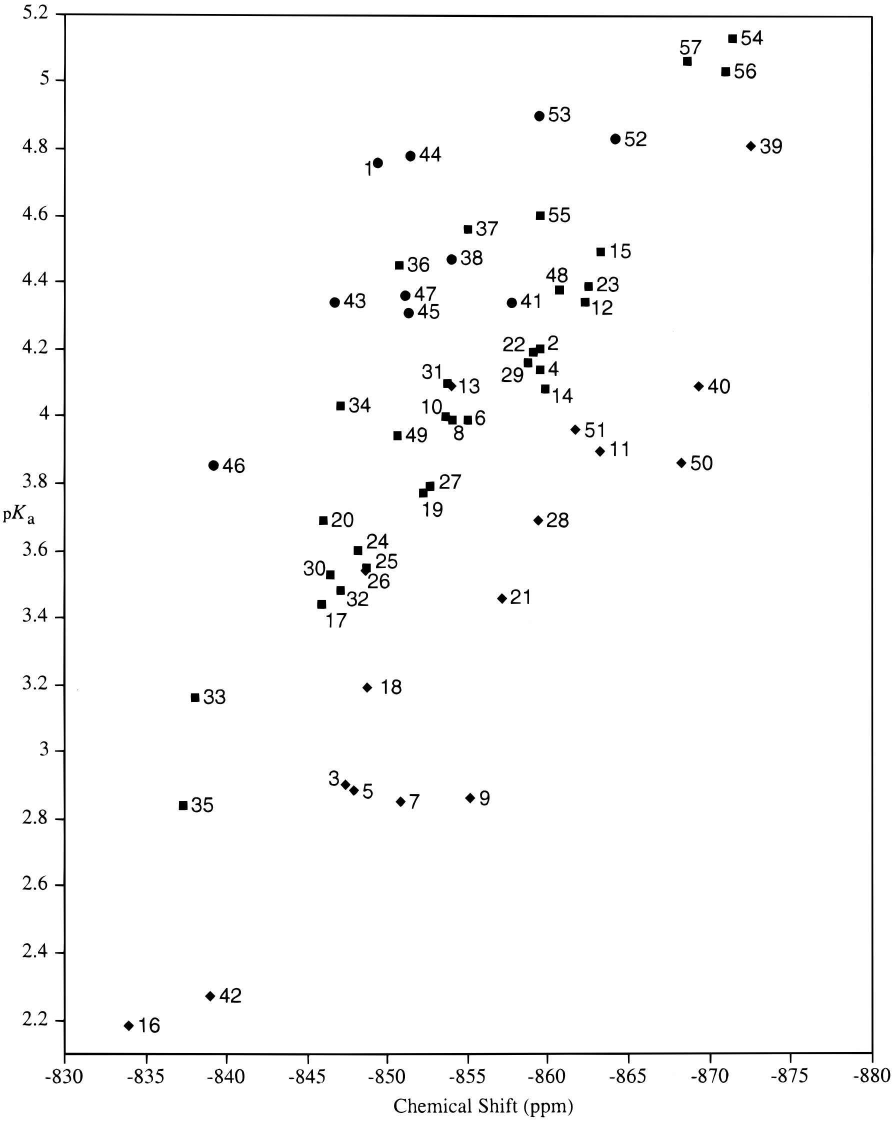

Figure 2. Chemical shifts of *p*-Br-phenyllead diacetate monocarboxylate plotted against pK_a.

Table 1. Chemical shifts of p-Br-phenyllead diacetate monocarboxylate, p-MeO-phenyllead diacetate monocarboxylate and lead triacetate monocarboxylate

No.	X	Plot symbol	p-BrPhPb(OAc)$_2$X	p-MeOPhPb(OAc)$_2$X	PbOAc$_3$X	pK_a	Source[a]
1	Acetate	●	−849.4	−789.0	−1883.1	4.76	A
2	Benzoate	■	−859.6	−796.8	−1886.9	4.20	A
3	o-F-benzoate	◆	−847.4	−786.0	−1878.5	2.90	A
4	p-F-benzoate	■	−859.6	−798.8	−1888.2	4.14	A
5	o-Cl-benzoate	◆	−847.9	−781.2	−1886.4	2.88	A
6	p-Cl-benzoate	■	−855.1	−792.7	−1887.9	3.99	A
7	o-Br-benzoate	◆	−850.8	−785.5	−1902.9	2.85	A
8	p-Br-benzoate	■	−854.1	−794.1	−1887.8	3.99	A
9	o-I-benzoate	◆	−855.2	−792.1	−1936.9	2.86	A
10	p-I-benzoate	■	−853.7	−794.4	−1888.5	4.00	A
11	o-Me-benzoate	◆	−863.3	−801.5	−1882.8	3.90	A
12	p-Me-benzoate	■	−862.4	−799.0	−1886.5	4.34	A
13	o-MeO-benzoate	◆	−854.1	−793.2	−1877.7	4.09	A
14	m-MeO-benzoate	■	−859.9	−797.6	−1888.7	4.08	A
15	p-MeO-benzoate	■	−863.3	−801.1	−1886.8	4.49	A
16	o-NO$_2$-benzoate	◆	−834.0	−765.3	−1883.4	2.18	A
17	p-NO$_2$-benzoate	■	−845.9	−782.8	−1888.3	3.44	A
18	o-CF$_3$-benzoate	◆	−849.0	−786.5	−1889.7	3.19	B
19	m-CF$_3$-benzoate	■	−852.3	−783.4	−1888.2	3.77	B
20	p-CF$_3$-benzoate	■	−846.1	−782.7	−1887.8	3.69	B
21	o-Ph-benzoate	◆	−857.2	−798.6	−1886.5	3.46	A
22	p-Ph-benzoate	■	−859.1	−799.8	−1886.7	4.19	B
23	p-Bu^t-benzoate	■	−862.6	−803.9	−1886.4	4.39	A
24	m-CN-benzoate	■	−848.2	−785.3	−1887.8	3.60	A
25	p-CN-benzoate	■	−848.7	−786.9	−1888.3	3.55	A
26	o-Benzoylbenzoate	◆	−848.7	−787.8	−1891.1	3.54	A
27	p-Benzoylbenzoate	■	−852.7	−788.2	−1887.6	3.79	B
28	1-Naphthoate	◆	−859.4	−797.3	−1881.9	3.69	A
29	2-Naphthoate	■	−858.8	−796.3	−1887.3	4.16	A
30	2-Thiophenecarboxylate	■	−846.5	−785.0	−1885.3	3.53	A
31	3-Thiophenecarboxylate	■	−853.8	−792.6	−1881.9	4.10	A
32	Benzo[*b*]thiophene-2-carboxylate	■	−847.1	−787.4	−1886.0	3.48	B
33	2-Furoate	■	−838.1	−778.4	−1876.9	3.16	A
34	3-Furoate	■	−847.1	−785.8	−1876.8	4.03	B
35	5-Br-2-furoate	■	−837.3	−777.7	−1879.3	2.84	B
36	2-Pyrrolecarboxylate	■	−850.8	−785.5	−1877.9	4.45	A
37	*N*-Methyl-2-pyrrolecarboxylate	■	−855.1	−792.9	−1871.7	4.56	B
38	Cinnamate	●	−854.0	−795.4	−1882.5	4.47	A
39	α-Me-cinnamate	◆	−872.6	−813.6	−1895.9	4.81	B
40	α-Ph-cinnamate	◆	−869.4	−808.2	−1895.3	4.09	B
41	2-Thienylacrylate	●	−857.8	−795.5	−1882.4	4.34	B
42	Phenylpropiolate	◆	−839.0	−774.1	-1876.2	2.27	A
43	Vinylacetate	●	−846.8	−783.8	−1881.5	4.34	A
44	4-(2-Thienyl)butyrate	●	−851.5	−789.5	−1881.0	4.78	B
45	Phenylacetate	●	−851.4	−788.0	−1884.0	4.31	A
46	p-NO$_2$-phenylacetate	●	−839.2	−776.6	−1883.2	3.85	A
47	p-MeO-phenylacetate	●	−851.2	−788.3	−1883.8	4.36	A
48	2-Phenylpropionate	■	−860.8	−798.8	−1886.5	4.38	A
49	Diphenylacetate	■	−850.7	−787.2	−1885.0	3.94	A
50	2,2-Diphenylpropionate	◆	−868.3	−804.9	−1892.2	3.86	B
51	Triphenylacetate	◆	−861.8	−800.4	−1891.3	3.96	A
52	Cyclopropanecarboxylate	●	−864.3	−802.8	−1884.6	4.83	A
53	Cyclohexanecarboxylate	●	−859.5	−798.6	−1881.0	4.90	A
54	1-Me-Cyclohexanecarboxylate	■	−871.5	−812.9	−1885.9	5.13	A
55	Isobutyrate	■	−859.6	−800.6	−1884.5	4.6	A
56	Pivalate	■	−871.1	−812.3	−1889.5	5.03	A
57	Adamantanecarboxylate	■	−868.7	−807.1	−1883.7	5.06	B

[a] A, Literature values;[8] B, calculated values.[9]

gauche'-type shielding effect observed in ^{13}C NMR spectroscopy.[12]

The results for aryllead tricarboxylates contrast markedly with those for the lead(IV) tetracarboxylate series, where no correlation with pK_a could be discerned (Fig. 3). However, the evidence suggests that steric factors are still influential, again with the general trend being that increased steric crowding induces shifts to low frequency (although the evidence is not as clear as for the aryllead tricarboxylates). These are under further investigation.

It can be concluded that three influences are evident in the chemical shifts of aryllead tricarboxylates. The effect of changes in the aryl group have been known for some time, where electron-donating substituents cause a shift to higher frequency.[7] Here we have also demonstrated that the carboxylate ligands have two effects; electronic and steric. Carboxylates derived from weaker acids (higher pK_as) and those which are more crowded about the lead centre (particularly *ortho*-substituted benzoic acids) tend to exhibit chemical shifts of lower frequency.

EXPERIMENTAL

^{207}Pb NMR spectra were measured on a Bruker AM250 spectrometer with a broadband probe, using 10 mm tubes. Obervation of the ^{207}Pb nucleus was at 52.2 MHz, with broadband proton decoupling. The probe temperature was 218 K. The spectra were referenced externally to 80% $Pb(CH_3)_4$ in toluene, whereby the reference frequency of this standard was calculated[13] from $\Xi(^{207}\mathrm{Pb}) = 20.920\,597$ MHz.[13,14] Samples were 0.15 mmol of the aryllead triacetate and 0.15 mmol of the appropiate carboxylic acid in 4 ml of $CDCl_3$–$CHCl_3$ (1 : 1) solution. Samples of the lead tetracarboxylate contained 0.25 mmol of both lead tetraacetate and the additional carboxylic acid. Other acquisition parameters are given in Table 2.

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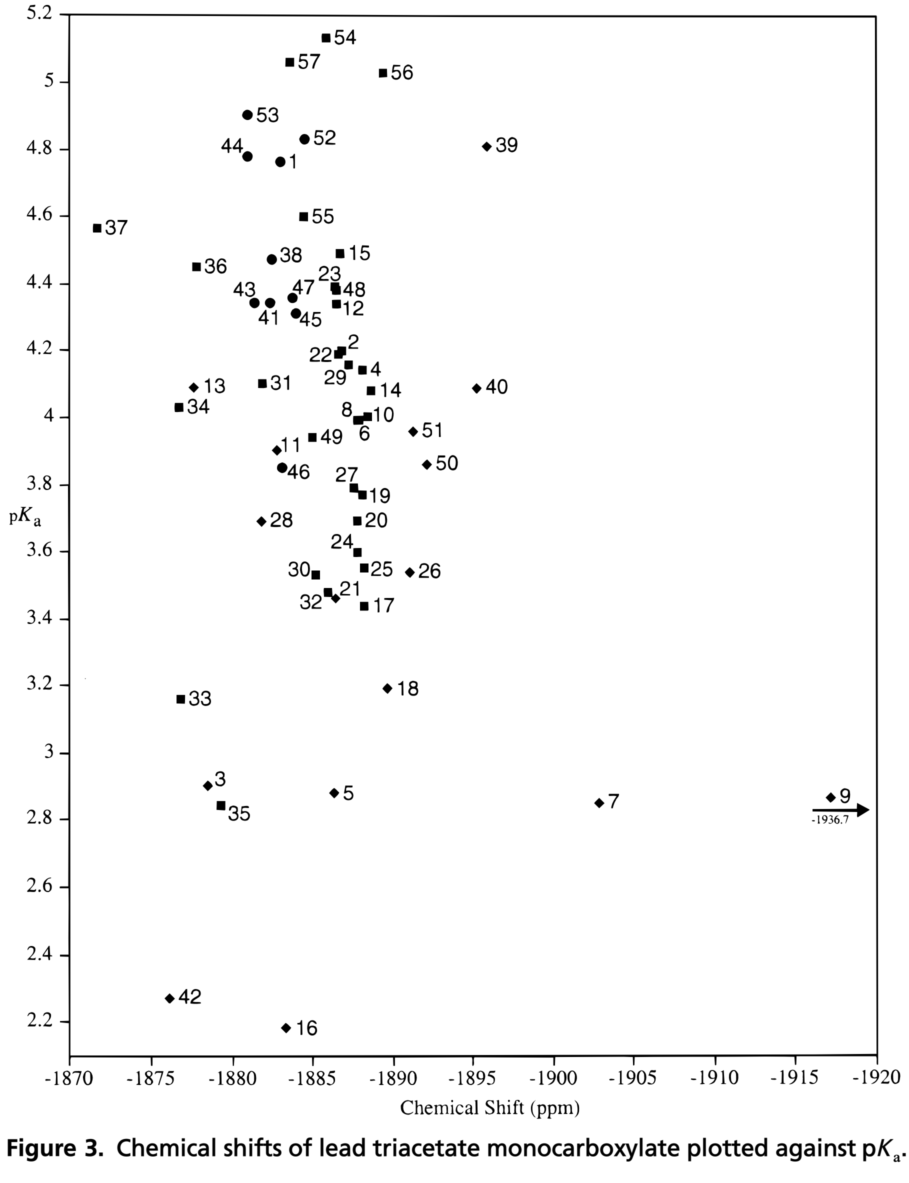

Figure 3. Chemical shifts of lead triacetate monocarboxylate plotted against pK_a.

Table 2. Acquisition parameters

Parameter	Lead tetracarboxylates	Aryllead tricarboxylates
Pulse width (μs)	12(70°)	16(90°)
Acquisition time (ms)	620	390
Spectral width (kHz)	13	2.6
Relaxation delay (s)	1	None
Datapoints	16K	2K
Digital resolution (Hz per point)	1.6	2.5
Number of transients	~400	~1000
Line broadening (Hz)	4	4

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