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On the structure and reaction with pyridine of *o*-methoxyphenyllead acetates

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Abstract

Pyridine catalyses the ligand redistribution of *o*-methoxyphenyllead triacetate to di(*o*-methoxyphenyl)lead diacetate. Characterisation of these two lead (IV) compounds by single-crystal X-ray diffraction demonstrates a weak interaction between the lead atom and the methoxy oxygen atom leading to an 8-coordinate lead atom.

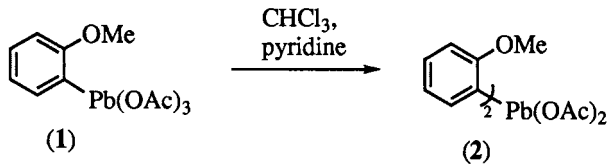
Keywords: Lead; Ligand effects; Organolead; Pyridine; Solid state structures

1. Introduction

In the course of our study of the Pinhey arylation of β-dicarbonyl compounds using aryllead triacetates [1–3], we have synthesised a range of aryllead tricarboxylates. As part of our aim to modify the Pinhey arylation by manipulating the ligands on lead (IV), we have determined the structure of these aryllead triacetates, and have also investigated the essential, but ill-understood, role that pyridine plays in these arylations. In the light of a recent report of similar organolead compounds [4], we wish to report some of our progress in this area involving an investigation of *o*-methoxyphenyl lead (IV) acetates.

2. Results

o-Methoxyphenyllead triacetate **1** was synthesised from lead tetraacetate and *o*-methoxyphenylboronic acid in the presence of a mercury (II) catalyst [5] (Scheme 1). Slow crystallisation from chloroform–hexane gave colourless crystals, from which the crystal structure was determined by X-ray diffraction. The molecular unit of triacetate **1** is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. In keeping with other aryllead triacetates [6], **1** is monomeric, with the three acetate groups binding to the lead atom in a bidentate fashion, although each acetate group is distorted so that each of the lead-oxygen bonds are non-equivalent. The range of Pb–O bond lengths observed is consistent with those found in other aryllead triacetates [6] and for lead tetracarboxylates [7]. Rather more unusual is the position of the *o*-methoxy group. It can be seen that the oxygen atom is relatively near the lead atom (Pb1–O20 = 2.91 Å), an indication of a weak interaction between the lead atom and the methoxy oxygen atom. Further evidence for this comes in the distortion of the bond angles between the lead atom and the *ortho*-substituent which, being smaller than the 120° expected for sp^2 hybridised atoms, suggests that the aryl group is being distorted to allow the closer approach of the *ortho*-substituent to the lead atom; the relevant data are compiled in Table 2. A similar Pb–O interaction resulting in distortion of sp^2 bonding angles has recently been reported for 2,4-dimethoxyphenyllead triacetate [8]. In contrast, the equivalent angles for the structures of *o*-tolyllead triacetate [9] and *o*-chlorophenyl lead triacetate [9] are also given in



(1) (2)

Scheme 1.

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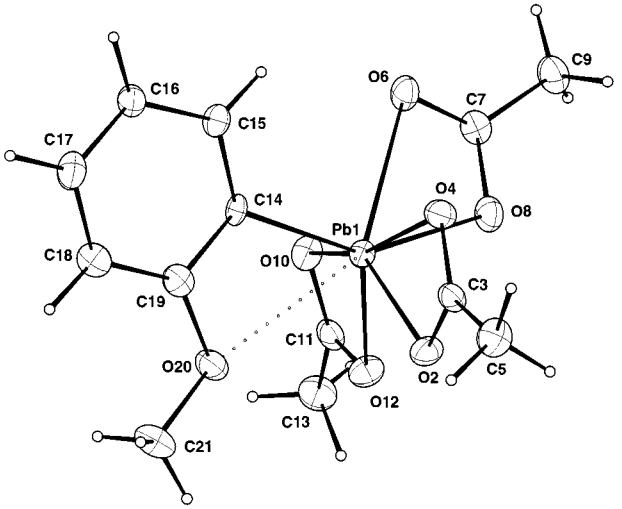


Fig. 1. Single crystal X-ray structure of *o*-methoxyphenyllead triacetate **1**. Thermal ellipsoids are shown at the 50% probability level.

Table 2. These clearly show that in these cases where there is no additional electronic interaction, the *ortho*-substituent is bent away from the lead atom as a result of an unfavourable steric interaction.

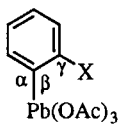
Since our interest in these lead (IV) species lies in their involvement in the Pinhey arylation [1], a reaction known to necessitate the involvement of pyridine or a similar heterocyclic base, and as we have recently investigated the synthesis and structure of a complex between pyridine and lead tetraacetate [10], we attempted to crystallise a complex of **1** with pyridine. Of particular interest was whether the σ-donor pyridine ligand would diminish the Pb–OMe stabilising interaction. After several weeks, crystals formed from a solution of **1** in neat pyridine. To our surprise these were not the desired complex, but di(*o*-methoxyphenyl)lead diacetate **2**. This compound was spectroscopically identical to a sample of **2** prepared by more conventional means, namely the reaction of the aryllead triacetate with *o*-methoxyphenylboronic acid [11].

Table 1
Selected bond lengths (Å) and angles (°) for Aryllead **1** [a]

Pb1–O2	2.202 (5)	C3–O2	1.281 (8)
Pb1–O4	2.538 (5)	C3–O4	1.288 (8)
Pb1–O6	2.537 (5)	C7–O6	1.225 (8)
Pb1–O8	2.147 (5)	C7–O8	1.298 (8)
Pb1–O10	2.487 (5)	C11–O10	1.254 (8)
Pb1–O12	2.195 (5)	C11–O12	1.286 (8)
Pb1–O20	2.915 (8)	C19–O20	1.365 (8)
Pb1–C14	2.156 (6)	O20–C21	1.443 (8)
O2–Pb1–O4	54.4 (2)	O10–Pb1–O12	55.5 (2)
O2–C3–O4	119.9 (6)	O10–C11–O12	119.6 (6)
O6–Pb1–O8	55.0 (2)	Pb1–C14–C15	123.0 (5)
O6–C7–O8	120.6 (6)	Pb1–C14–C19	113.7 (5)
C14–C19–O20	114.5 (6)		

[a] Atom numbers as in Fig. 1.

Table 2
Bond angles and distances in some aryllead triacetates



X =	Me	Cl	MeO (**1**)
α (°)	118	113	123
β (°)	121	123	114
γ (°)	123	119	114
Pb–C (Å)	2.17	2.19	2.16
Pb–X (Å)	3.39	3.39	2.91

The crystal structure of **2** was also determined and is shown in Fig. 2, with the associated data given in Table 3. This compound has a crystallographic two-fold rotational axis of symmetry. The central lead atom is formally six co-ordinate, but has weak interactions with both of the methoxy oxygen atoms (at Pb–O = 2.96 Å), which enclose the lead atom so that it, like the aryllead triacetate **1**, is monomeric. In contrast, both $Ph_2Pb(OAc)_2$ [4] and $Ph_4Pb_2(OAc)_4{\cdot}H_2O$ [12] are polymeric with acetate groups bridging two lead atoms. Thus the intramolecular stabilising effects of the *ortho*-methoxy oxygen atom are sufficient to ensure the formation of a monomeric complex.

Other standard spectroscopic data for **1** and **2** were also collected and are shown in Table 4.

Both the ^{1}H- and ^{13}C-NMR data for aryllead **1** are in close agreement to that published in the literature [9]. Data for diaryllead **2** has not been reported before, but as in other comparisons of aryllead and diaryllead compounds the differences in proton and carbon chemical shift values are not great [14]. These values are consistent a highly electropositive lead atom. There is, however, a more marked difference in the long-range J_{Pb-H} and J_{Pb-C} coupling constants. These, although still large, are considerably less for the diaryllead **2** than the aryllead **1**,

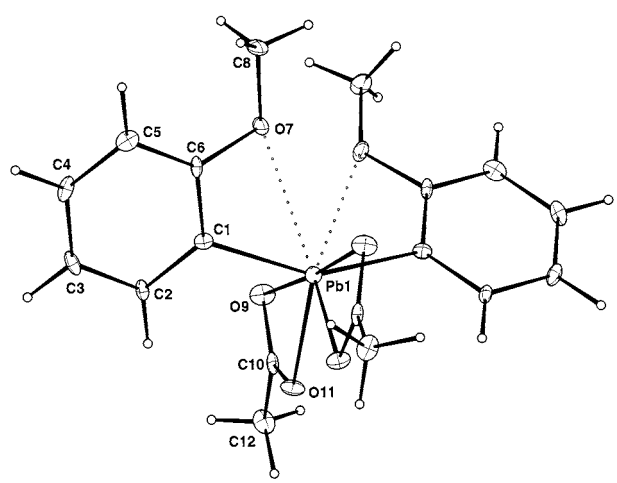


Fig. 2. Single-crystal X-ray structure of di(*o*-methoxyphenyl)lead diacetate **2**. Thermal ellipsoids are shown at the 30% probability level.

Table 3
Selected bond lengths (Å) and angles (°) for diaryllead **2**[a]

Pb1–O9	2.594 (4)	Pb1–C1	2.135 (5)
Pb1–O11	2.564 (3)	Pb1–O7	2.955 (7)
C10–O9	1.238 (5)	C6–O7	1.360 (5)
C10–O11	1.288 (6)	O7–C8	1.431 (5)
O9–Pb1–O11	53.3 (1)	Pb1–C1–C6	115.7 (3)
O9–C10–O11	121.0 (4)	Pb1–C1–C2	122.7 (3)
C6–O7–C8	118.0 (4)	C1–C6–O7	114.3 (4)

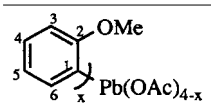
[a] Atom numbers as in Fig. 2.

for example, $^1J_{Pb-C}$ for C1 decreases from 2096 Hz (aryllead **1**) to 1272 Hz (diaryllead **2**). This is ascribed [14] to a decrease in the effective nuclear charge of the lead atom in diaryllead **2** compared to aryllead **1**, consistent with the more covalent character of the bonding in diaryllead **2**. No long-range coupling for the lead to the carbon atoms in the acetate ligands was observed. Following our observations that carboxylate ligands in lead tetracarboxylates are in very rapid exchange [15,16], and lead–carbon coupling can only be seen at low temperature when this exchange is slowed, we suggest that a similar exchange is operating in solution in these aryllead acetates.

The ^{207}Pb-NMR spectra for these two compounds was also recorded. In our laboratory we have noted that chemical shifts of lead (IV) resonances often show a distinct temperature dependance. For example lead tetracarboxylates have a upfield shift of about 5 ppm per 20°C decrease in temperature [15], and therefore the temperature should always be given whenever chemical shifts are reported. However, the chemical shift of aryllead **1** shows a smaller temperature dependance (3 ppm per 20°C decrease in temperature), but now in a downfield sense. The temperature dependance of diaryllead **2** is rather smaller but in the same sense. We have also observed considerable differences in linewidth, but all of these observed resonances were reasonably sharp ($\nu_{1/2}$: 8–35 Hz).

That crystals of diaryllead **2** were formed from aryllead **1** in pyridine suggested that pyridine can catalyse the aryl transfer necessary for the observed ligand redistribution, a reaction previously recorded only once for the rapid decomposition of 2-furyllead triacetate in the presence of pyridine [17]. In both Pinhey's example and ours it would appear that the diaryllead diacetate is the thermodynamic product. To further investigate the ligand redistribution of this aryllead triacetate to the diaryllead diacetate, we allowed samples of the aryllead-triacetate **1** (0.2 M) to stand in deuterochloroform containing pyridine and bipyridine at a range of concentrations. The progress of these reactions were followed over an extended period by ^{1}H-NMR spectroscopy, looking principally at the ratios of the methoxy resonances, (which were adequately resolved at a field of 500 MHz). These results are shown in Fig. 3. It can immediately be seen that this ligand redistribution is dependent on the concentration of pyridine, but is nevertheless very slow, with just $\sim$15% conversion after a month. Since the reaction has not progressed far, and therefore the plot of the proportion of aryllead **1** remaining against time is still linear, the gradient of the line will give a good approximation to the initial rate of the reaction, tabulated in Table 5 [18].

Table 4
Spectroscopic data for aryllead **1** and diaryllead **2**

	Aryllead **1**	Diaryllead **2**
	$x = 1$	$x = 2$
m.p. (lit)	158–159°C (148–151) [13]	186–190°C
Appearance	Colourless crystals	Colourless crystals
IR (KBr)	1596s	1595s, 1389s
($CHCl_3$ solution)	1563s	1588s, 1393s
NMR: δ_H: Oac	2.10 (s)	1.97 (s)
OMe ($^4J_{H-Pb}$)	3.92 (s) (76)	3.97 (s) (76)
ArH(3) ($^4J_{H-Pb}$)	7.06 (dd, $J = 7.4$ & 1.0) (230)	7.13 (dd, $J = 7.4$ & 0.7) (125)
ArH(4) ($^5J_{H-Pb}$)	7.48 (td, $J = 7.7$ & 1.0) (38)	7.46 (td, $J = 7.4$ & 0.7)
ArH(5) ($^4J_{H-Pb}$)	7.20 (td, $J = 7.7$ & 1.3) (134)	7.24 (td, $J = 7.6$ & 1.4) (56)
ArH(6) ($^3J_{H-Pb}$)	7.80 (dd, $J = 7.9$ & 1.3) (422)	7.80 (dd, $J = 7.6$ & 1.4) (206)
NMR: δ_C: CH_3CO_2	20.32	22.35
CH_3CO_2	179.83	181.00
Ome	56.55	56.29
ArC(1) ($^1J_{C-Pb}$)	150.58 (2096)	150.28 (1272)
ArC(2) ($^2J_{C-Pb}$)	157.77 (77)	158.83 (53)
ArCH(3) ($^3J_{C-Pb}$)	112.75 (186)	112.43 (101)
ArCH(4) ($^4J_{C-Pb}$)	131.76 (118)	132.84 (38)
ArCH(5) ($^3J_{C-Pb}$)	123.56 (344)	123.44 (169)
ArCH(6) ($^2J_{C-Pb}$)	133.18 (46)	132.34 (20)
NMR: δ_{Pb} at 313 K ($\nu_{1/2}$)	−847.0 (38 Hz)	−558.9 (7)
δ_{Pb} at 218 K ($\nu_{1/2}$)	−833.0 (13)	−556.6 (17)

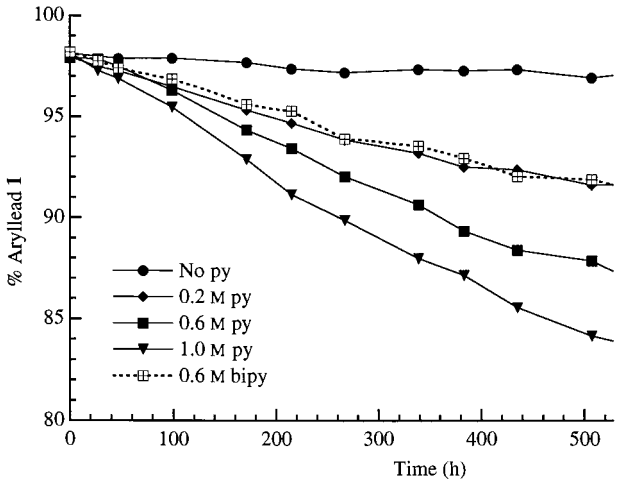


Fig. 3. The pyridine catalysed ligand redistribution of aryllead **1** to diaryllead **2**.

The effect of bipyridine was less than that of pyridine; this is surprising since bypyridine is reported to be a more effective promotor of the Pinhey arylation reaction than pyridine [19]. This ligand redistribution reaction is not unlike the well-known Kocheshkov disproportionation reaction of aryltin chlorides [20]. However, such a disproportionation will not compete with the Pinhey arylation when a β-dicarbonyl is present; such arylations are normally complete in a few hours. We have shown previously that pyridine can act as a ligand to lead (IV), and has a labilising effect on the coordination sphere (the acetate groups are in fast exchange) [10]. Here it would appear that pyridine catalyses the transfer of an aryl group from one lead atom to another, presumably to form the more thermodynamically stable diaryllead compound. It seems likely that in the Pinhey arylation, pyridine again catalyses the transfer of an aryl group; the thermodynamic driving force is the commitant reduction of lead (IV) to lead (II).

3. Conclusions

We have shown that the methoxy oxygen atom of both *o*-methoxyphenyllead triacetate and di(*o*-methoxyphenyl)lead diacetate weakly coordinate to the lead atom. Furthermore, pyridine catalyses the ligand redistribution of the aryllead triacetate to the diaryllead diacetate. It is suggested that the ability to catalyse aryl transfer reactions of lead may be the principal role of pyridine in the Pinhey arylation.

Table 5
The rate of disproportionation of aryllead **1** (0.2 M)

Additive	Concentration (M)	Relative rate
None	–	1
Pyridine	0.2	7.1
Pyridine	0.6	12.7
Pyridine	1.0	16.6
2,2-Bipyridine	0.6	7.9

4. Experimental

4.1. NMR spectroscopy

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AM500 spectrometer with a broadband probe at 300 K. Observation of the ^{1}H nucleus was at 500 MHz and the ^{13}C nucleus was at 125 MHz, with broadband proton decoupling. In both cases spectra were referenced to the residual solvent peaks. $CDCl_3$was used as the solvent for all NMR spectroscopy. Samples contained the aryllead acetates at a concentration of 0.2 M.

^{207}Pb-NMR spectra in solution were recorded on a Bruker AM250 spectrometer with a 10 mm broadband probe. Observation of the ^{207}Pb nucleus was at 52.2 MHz, with broadband proton decoupling, and a probe temperature of 295 K unless stated otherwise. The spectra were referenced externally to 80% Me_4Pb in toluene, whereby the reference frequency of this standard was calculated [21] from $\Xi(^{207}Pb) = 20.920597$ MHz [21,22] (when the ^{1}H frequency of Me_4Si is 100.000 MHz). About 64 scans for each sample were required to obtain a satisfactory signal-to-noise ratio.

4.2. Crystallography

The crystal for investigation was mounted on a glass fibre using a drop of perfluoropolyether oil. It was then plunged into a cold nitrogen stream (100 K) using an Oxford Cryosystems CRYOSTREAM cooling system. The data was collected on an Enraf-Nonius DIP2020 image-plate diffractometer using graphite monochromated Mo–K_α radiation ($\lambda = 0.71070$ Å), and the images processed using the DENZO and SCALEPACK software [23]. Data were corrected for Lorentz and polarisation effects. For aryllead compound **1** a partial absorption correction was applied by multi-frame scaling of the image-plate data using equivalent reflections. For diaryllead **2** an absorption correction was applied using DIFABS [24] with $T_{min} = 0.75$ and $T_{max} = 1.0$. The structure was solved by direct methods using the SIR92 program [25]. The structure was refined in F, using a full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were placed in calculated positions during the final cycles of refinement. A three parameter Chebychev-weighting scheme [26] was applied. All crystallographic calculations were performed using the CRYSTALS Issue 10software [27]. Neutral atom scattering factors were taken from International Tables for X-ray crystallography (974, Vol IV, table 2.2B). Crystal data, data collection and refinement parameters are shown in Table 6.

Table 6
Crystallographic parameters

	Aryllead **1**	Diaryllead **2**
Molecular formula (mass)	$C_{13}H_{16}PbO_7$ (491.5)	$C_{18}H_{20}PbO_6$ (539.5)
Crystal dimensions (mm)	Colourless, 0.4 × 0.3 × 0.3	Colourless, 0.3 × 0.2 × 0.2
Symmetry	Monoclinic, $P2_1/n$	Monoclinic, $P2/n$
a (Å)	8.241(1)	8.715(1)
b (Å)	23.795(1)	8.640(1)
c (Å)	8.341(1)	11.671(1)
α, β, γ (°)	90, 112.91(1), 90	90, 90.20(1), 90
Calculated density (Mg m^{-3})	2.17	2.04
V (Å^3), Z	1504.8, 4	878.79, 2
Collection mode	ω scans	ω scans
θ_{max} (°)	26.63	26.71
h range	−10 to +10	−10 to +10
k range	−29 to +29	−10 to +10
l range	−10 to +9	−14 to +14
μ (mm^{-1})	11.32	9.70
Measured reflections	8687	5046
Independent reflections	3046	1854
Reflections with $I>3\sigma(I)$	2475	1586
Parameters refined	191	115
Final $\Delta\rho$ (Å^{-3})	−1.71, 1.98	−1.05, 1.05
Final R and Rw	0.0379, 0.0464	0.0301, 0.0340

5. Supplementary information

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC, Nos. CCDC-103172 for (**1**) and CCDC-103173 for (**2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@chemcrys.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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