

Ligand exchange and catalysis in phenylation reactions mediated by lead tetracarboxylates

Mark G. Moloney ^{a,*}, Diana R. Paul ^a, Russell M. Thompson ^b, Emma Wright ^a

^a *The Department of Chemistry, Dyson Perrins Laboratory, University of Oxford, South Parks Rd, Oxford, OX1 3QY, UK*

^b *Associated Octel Company, Ellesmere Port, South Wirral, L65 4HF, UK*

Received 25 October 1997

Abstract

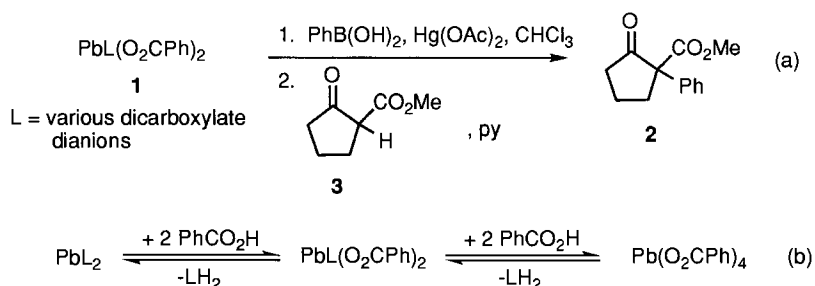
An investigation of catalysis and ligand exchange in the arylation of nucleophiles with phenylboronic acid and mixed ligand lead(IV) complexes is described. Although this reaction is known to be catalyzed by mercury(II) acetate, other heavy metals have been shown to have a similar effect, albeit less efficiently. The effect of pyridine has been investigated with a range of chelating ligands containing a pyridine sub-unit. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Lead(IV); Ligand modification; Phenylation; Catalysis; Mercury(II)

1. Introduction

The arylation of nucleophiles with phenylboronic acid and lead tetraacetate with mercuric acetate catalysis has been extensively developed, and provides an important source of phenyl cation synthetic equivalents [1]; it is also well documented that pyridine is important in these reactions [2]. In previous work, we described the use of novel chiral and achiral lead(IV) complexes such as **1** in place of lead tetraacetate (LTA) for Pinhey arylation, and demonstrated that comparable yields of

the expected product **2** could be obtained, although in the case of chiral ligands, only low enantioselectivity in the reaction was observed (Scheme 1(a)) [3–5]. Since we have recently shown that rapid ligand exchange occurs in a mixture of lead(IV) tetraacetate/tetrabenzoate [6,7], it seemed likely that similar equilibration in lead(IV) complexes such as **1** would scramble the ligands (Scheme 1(b)), thereby providing several different coordinated species with varying reactivity. This would be similar to the equilibrium which exists in some ligand-modified transition metal mediated reactions, in which



Scheme 1.

* Corresponding author. E-mail: mark.moloney@chem.ox.ac.uk

it is now well established that there a number of reactive entities in solution which often possess differing reactivity patterns [8]. Furthermore, the need to use both heavy metal cation (Hg(II)) catalysis and pyridine in the Pinhey arylation procedure [2] introduces additional ligands, which can further complicate the lead(IV) coordination chemistry. We therefore examined both the need for, and nature of, suitable catalysts and additives in arylation reactions; of particular interest was their effect upon rate and enantioselectivity.

2. Synthesis and reactivity of lead(IV) complexes

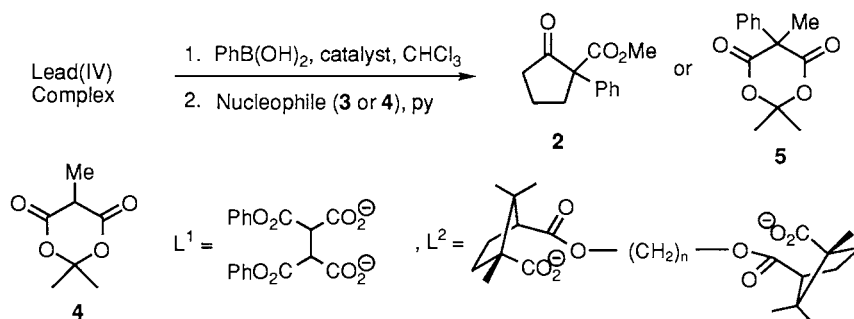
One particularly valuable approach to the arylation reaction involves initial in situ formation of the intermediate phenyllead species by boron/lead exchange in the presence of a suitable catalyst, followed by treatment with a β -dicarbonyl (e.g. **3** or **4**) and pyridine (Scheme 2) [9]. In the first step, mercury(II) acetate catalysis (0.1 equiv.) has been found to be necessary. Using these conditions, the products **2** or **5** were obtained in 70 and 71% yield respectively (Scheme 2 and Table 1, entries 2 and 3), but in the absence of mercury acetate none of the desired product was obtained (entry 1). Mercury chloride and lead(II) acetate, however, were also found to be effective catalysts, giving product **5** in good yield, although lower than that obtained with mercury(II) acetate (entries 4–6). The poorer yield for the lead(II) catalyst is possibly due to its lower solubility in chloroform. Despite a recent report which indicated that fluoride was an effective catalyst for palladium-mediated coupling reactions of boronic acids with aryl bromides, [10] neither caesium nor potassium fluoride were useful in these lead(IV)-mediated reactions (entries 7 and 8).

It was also shown that the mercuric chloride catalyzed arylation of β -dicarbonyl **3** could be achieved using lead complexes other than LTA. Thus, the lead(IV) complexes prepared from ligands L^1 and L^2 ($n = 1, 2$) (ligands derived from tartrate and camphoric acid, respectively) [11] were satisfactorily used in this procedure (entries 9–14), giving yields almost as high as LTA in some cases (entries 9, 10).

Examination of the ^{207}Pb -NMR of mixtures of lead(IV) tetrabenzoate (LTB) and mercuric(II) salts indicated that ligand exchange depended on the nature of the counter anion; thus, when 0.1 equivalents of mercuric acetate was added to LTB in solution, species in the LTA/LTB equilibrium system were observed (Fig. 1(a)). However, the addition of mercuric chloride to LTB gave no change in δ_{Pb} , consistent with the absence of ligand exchange (Fig. 1(b)).

Pyridine has long been known to be useful for the lead(IV)-mediated arylation reaction, giving cleaner reactions and better yields of product [2]. It has been suggested that pyridine is either a σ -donor for lead(IV), since spectroscopic evidence for the formation of an adduct with LTA has been reported, [12,13] or alternatively, a base which catalyses the keto-enol tautomerization of the substrate. In order to exploit the benefits of pyridine, complexes in which the pyridine unit is tethered to a carboxylic acid ligand were prepared; the synthesis of the required ligands **6–8** has been reported [11]. Complexes derived from these ligands, along with acetic, benzoic, cyclohexanecarboxylic, and cinnamic acids, were prepared using standard methodology (Table 2, Schemes 2 and 3) [5,14]. The latter three acids were chosen on the basis of their known electron-donating properties [7] to observe the possible effects on the stability, solubility and reactivity of the derived complexes; benzoic acid is more electron-donating than acetate, while cyclohexanecarboxylic acid and cinnamic acid are both less electron-donating. The derived complexes were orange or yellow non-crystalline materials which were readily soluble in chloroform, and possessed greater hydrolytic stability than LTA.

Characterization of the lead(IV) complexes showed in general that the acid carbonyl stretching frequencies had disappeared from the infra-red spectrum, and only the ester carbonyl functions (C10) of the chiral ligands were observed as sharp peaks in the ^{13}C -NMR spectrum. No large changes were observed in ^1H -NMR spectra of the complexes when compared to the free ligand, although small changes did occur in the pattern of signals corresponding to the side-chain methylene groups in most complexes. Thus, in the case of ligand **6**



Scheme 2.

Table 1
Reaction of Nucleophiles **3** or **4** with Phenylboronic acid and lead complexes and catalysts according to Scheme 2

Entry	Lead(IV) Complex	Catalyst	Nucleophile	Product	Yield(%)
1	Pb(OAc) ₄	None	3	—	0
2	Pb(OAc) ₄	Hg(OAc) ₂ (0.1 eq)	3	2	70
3	Pb(OAc) ₄	Hg(OAc) ₂ (0.1 eq)	4	5	71
4	Pb(OAc) ₄	HgCl ₂ (0.1 eq)	3	2	58
5	Pb(OAc) ₄	HgCl ₂ (1 eq)	3	2	53
6	Pb(OAc) ₄	Pb(OAc) ₂ (0.1 eq)	4	5	39
7	Pb(OAc) ₄	CsF	3	2	5
8	Pb(OAc) ₄	KF	3	2	0
9	PbL ¹ (O ₂ CPh) ₂	Hg(OAc) ₂ (0.1 eq)	3	2	71
10	PbL ¹ (O ₂ CPh) ₂	HgCl ₂ (1 eq)	3	2	65
11	PbL ¹ (O ₂ CAr) ₂ ^a	Hg(OAc) ₂ (0.1 eq)	3	2	58
12	PbL ¹ (O ₂ CAr) ₂ ^a	HgCl ₂ (1 eq)	3	2	54
13	PbL ² (O ₂ CPh) ₂ ^b	HgCl ₂ (0.1 eq)	3	2	16
14	PbL ² (O ₂ CPh) ₂ ^c	HgCl ₂ (0.1 eq)	3	2	57

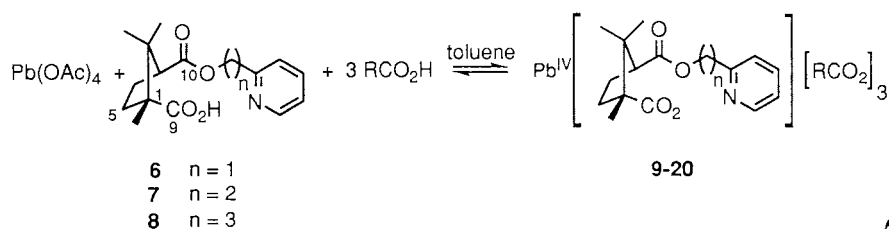
^a Ar = *p*-MeC₆H₄-;

^b *n* = 1;

^c *n* = 2.

(*n* = 1), the C(11)H₂ methylene signal appeared as a close double doublet when bound to lead(IV), in comparison with a singlet for the free ligand, and in the case of ligand **7** (*n* = 2), the C(12)H₂ methylene signal became a very much more complicated multiplet on coordination to lead(IV); this could be due to restricted rotation in their derived complexes, resulting from N–Pb co-ordination, causing the benzylic protons to exhibit substantial chemical shift differences. ²⁰⁷Pb-NMR spectroscopy provided some evidence for the solution structure of these complexes, and multiplet patterns of the simple mixed ligand systems which have previously been observed, [6,7] and indicative of slow ligand equilibration (on the NMR timescale), were not generally seen. Indeed, only complex **18** gave four resonances, consistent with complete ligand exchange. Five complexes (**11**, **12**, **15**, **19** and **20**) gave broad single resonances, and three (**9**, **13** and **16**) gave two broad resonances. [6,7] However, more detailed examination of complexes **14** and **18** by ¹H n.o.e. spectroscopy did not allow the determination of the detailed solution structure. Moreover, none of the above data allowed the conformational assignment for the cyclopentyl ring; this could be either diequatorial or diaxial.

The potential of these 12 novel complexes to mediate Pinhey's arylation reaction was initially tested using the phenylation of methyl Meldrum's acid **4** (Scheme 2). Pyridine was used in the second step of all of these reactions since an initial study in which pyridine was replaced with complex **8** failed to yield any product. Thus, the lead(IV) complex, phenylboronic acid and a HgCl₂ catalyst were dissolved in dry CHCl₃ and stirred at 40°C for 2 h; the substrate **4** in pyridine was then added, and the mixture stirred at 40°C for 2 h then overnight at room temperature. Only four complexes showed any phenylated product (Table 2). All three tris(cyclohexanecarboxylate) complexes **11**, **15** and **19** were reactive, as was the triacetate complex **17**. The lack of reactivity in the cases of the three tricinnamate complexes **12**, **16** and **20**, was probably due to the insolubility of these complexes in the reaction medium. The lead(IV) complexes **10**, **11**, **13**, **14** and **18** were unreactive to phenylation, possibly due to electronic stabilization or steric protection by the ligands, and it would seem that electron deficient Pb^{IV} centres, particularly those with acetate ligands, are the more reactive; this is in keeping with earlier results [4,5]. However, by carrying out the second step of the phenylation reaction



Scheme 3.

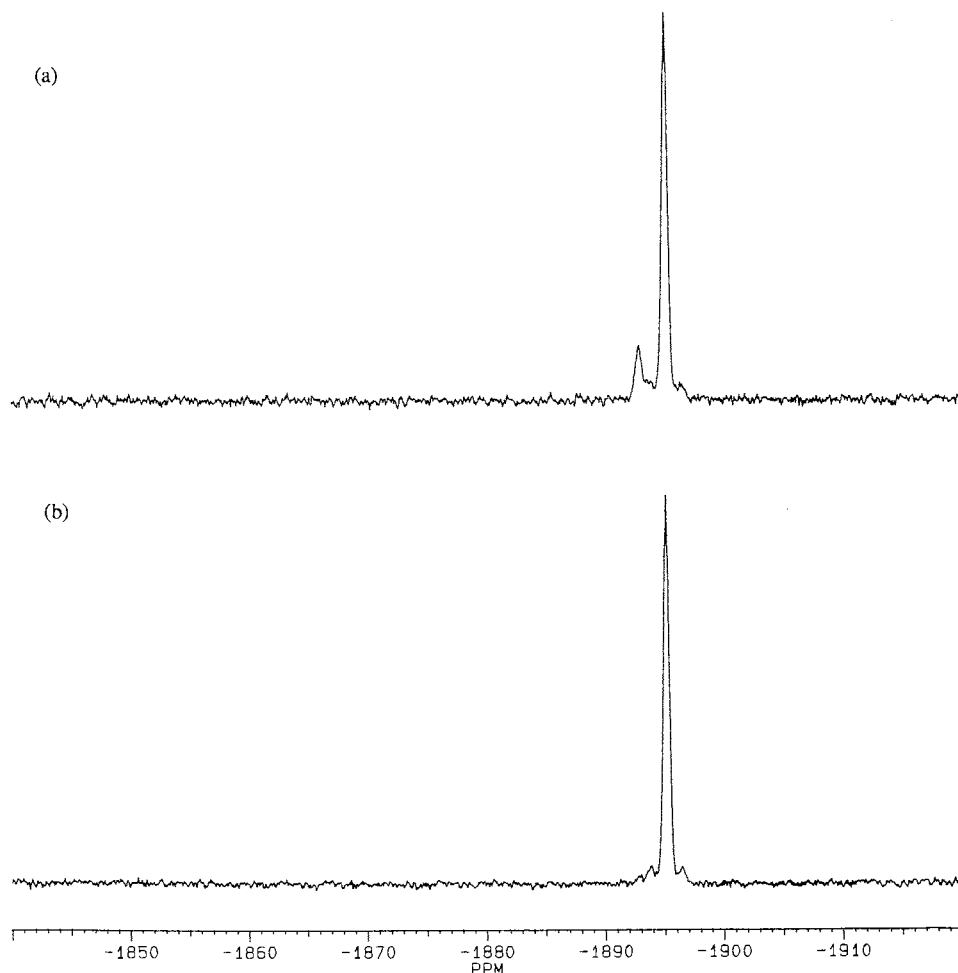
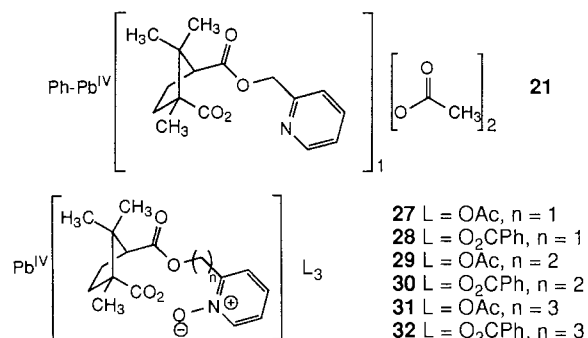


Fig. 1. ^{207}Pb -NMR spectrum of LTB with 0.1 equiv. of (a) HgOAc_2 ; and (b) HgCl_2 .

under refluxing conditions, six of the complexes showed reactivity (Table 2), giving much higher yields of the phenylated product.

Quite unusually, the tribenzoate complex **18** which did show rapid ligand exchange by ^{207}Pb -NMR spectroscopy, gave no product in an attempted phenylation reaction under either set of reaction conditions. This would thus confirm that rapid ligand exchange is not a sole requirement for the observation of reactivity.

An attempt was made to isolate the presumed phenyllead(IV) intermediate in these arylation reactions. [9] Complex **9**, phenylboric acid and HgCl_2 were dissolved in dry chloroform and stirred at 40°C for 2 h. The reaction mixture was then filtered through Celite[®] and, after work-up, the majority of solvent was removed to give a concentrated solution to which petroleum ether was then added (1:10 ratio of CHCl_3 :Petrol 40–60). A pale yellow precipitate formed on overnight storage at 0°C , which after filtration, was shown spectroscopically to be **21**. Reaction with methyl Meldrum's acid **4** and pyridine in dry chloroform gave the phenylated product **5** in 46% yield.



3. Asymmetric reactivity

Those complexes which displayed good reactivity under the more vigorous refluxing conditions were tested for asymmetric induction in phenylation reaction on substrate **3** (Scheme 2). Thus, a lead(IV) complex, phenylboric acid and HgCl_2 were dissolved in dry CHCl_3 and stirred at 40°C for 2 h. Methyl 2-oxocyclopentane-carboxylate **3** in pyridine was added to the cloudy

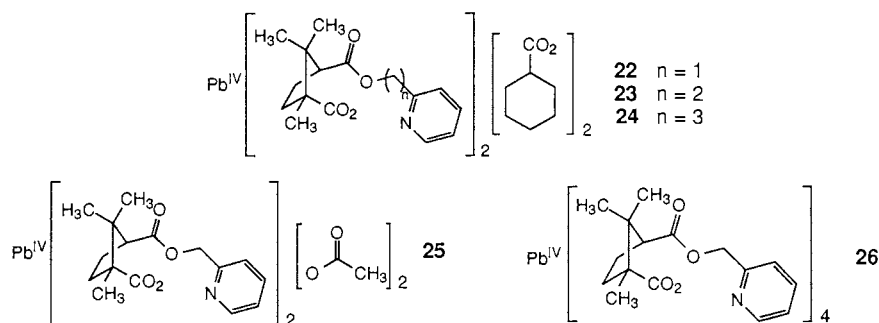
Table 2
Preparation of Complexes (Scheme 3) and their Reaction with **4** (Scheme 2)

Complex	<i>n</i>	R	Yield (%) of 5
9	1	CH ₃ –	No reaction (78 ^a)
10	1	C ₆ H ₅ –	No reaction (56 ^a)
11	1	C ₆ H ₁₁ –	34 (54 ^a)
12	1	C ₆ H ₅ CH=CH–	No reaction
13	2	CH ₃ –	No reaction
14	2	C ₆ H ₅ –	No reaction
15	2	C ₆ H ₁₁ –	34 (57 ^a)
16	2	C ₆ H ₅ CH=CH–	No reaction
17	3	CH ₃ –	42–52 (49 ^a)
18	3	C ₆ H ₅ –	No reaction
19	3	C ₆ H ₁₁ –	41 (72 ^a)
20	3	C ₆ H ₅ CH=CH–	No reaction

^a Stage two at reflux (see General Method).

suspension which was then heated under reflux for 18 h. After work-up, the product **2** was purified by flash column chromatography (2:1 DCM:Petrol 40–60) Table 3.

Substrate **3** was found to be less reactive than methyl Meldrum's acid **4**, requiring extended heating in the second step to give acceptable yields. However, the enantiomeric excesses (determined by chiral shift NMR spectroscopy) were very low, the highest value being only 8%. These low e.e. values could be the result of a number of factors; the stereogenic centre of the ligand could be too far removed from the lead(IV) centre, or alternatively it is conceivable that the extended heating of the second stage either re-establishes a facile ligand exchange equilibrium, which possibly generates a more reactive but achiral complex, or overwhelms the small energy difference of the diastereomeric transition states, ultimately giving essentially racemic product [5].



Interestingly, the application of the complexes **22–26**, prepared in an analogous fashion to the previous complexes, containing more than one chiral ligand, failed to give any arylated product with substrate **4**, even when the reaction was carried out under refluxing conditions. It would appear that the introduction of too much steric bulk and/or electron density in close proximity to the lead(IV) centre does indeed result in substantial

deceleration of the ligand-coupling reaction. Furthermore, the complexes **27–32**, prepared from the corresponding pyridine *N*-oxide ligands, were also found to be completely inert to phenylation reactions.

This variable reactivity of the lead(IV) complexes is not dissimilar to the reported reactivity of a variety of chiral hypervalent iodine compounds [15], in which variable and at best moderate stereoselectivity was observed [16–18].

Thus, we have shown that a number of mercury(II) and lead(II) salts are useful catalysts for phenyl boron/lead exchange and subsequent arylation reactions, and that such catalysis can be achieved without the complication of existing ligand equilibria. We believe that such systems, in which ligand exchange is minimized, will be important in improving the yield in these arylation reactions, and will prove to be instrumental in permitting the formation of non-racemic products.

4. Experimental

General experimental procedures have been described [5].

5. General procedure for phenylation reactions [9]

5.1. Stage one

The lead(IV) complex (1 eq.), phenylboric acid (1 eq.) and the catalyst (0.1 eq.) were dissolved in dry CHCl₃ (20–40 ml) and stirred at 40°C for 1 h. The resulting cloudy solution was stirred overnight at room temperature.

5.2. Stage two

The substrate **3** or **4** (0.91 eq.) in pyridine (3.03 eq.) was added to the above solution, which was stirred at 40°C for 1 h and at room temperature overnight. The resulting solution was filtered through Celite[®] and the solid was washed with CHCl₃ (2–3 × 25 ml). The com-

bined organic layers were washed with 3 M H₂SO₄ (25–50 ml) and the CHCl₃ layer was separated. The aqueous phase was extracted with CHCl₃ (2 × 15 ml), the combined organic layers were dried (MgSO₄) and the solvent was removed in vacuo to give the crude product.

In the case of substrate **3**, the crude product was purified by silica chromatography (3:1 DCM:petrol, gradient to DCM) to give **2** as a colourless oil (0.70 g, 70%). *R_f* 0.34 (DCM); ν_{\max} (film) 2954 m, 1750 s, 1722 s, 1449 m and 1256 s cm⁻¹; ¹H-NMR δ_{H} (200 MHz, CDCl₃) 1.82–2.13 (2H, m, CH₂), 2.28–2.62 (3H, m, CH₂), 2.83–2.93 (1H, m, CH₂), 3.72 (3H, s, CH₃) and 7.30–7.41 (5H, m, ArH); δ_{C} (50.3 MHz, CDCl₃) 19.19, 34.92, 37.75 (3 × CH₂), 53.00 (CH₃), 65.05, 127.54, 127.92, 128.78 (3 × ArCH), 136.32 (ArC), 171.52 (CO₂Me) and 211.95 (C=O); *m/z* (CI (NH₃)) 236 (M + NH₄⁺, 53%), 219 (100, MH⁺), 204 (8), 190 (12) and 159 (13).

In the case of **4**, the crude product was purified by flash column chromatography eluting with either i) 1:9-EtOAc:petrol, or ii) 1:3-DCM:petrol, gradient to 100% DCM gave 5-phenyl-2,2,5-trimethyl-1,3-dioxane-4,6-dione **5**, m.p. 133–135°C; *R_f* 0.44 (100% DCM); ν_{\max} (Nujol) 1776 m, 1735 s, 1302 s, 1159 s, 1070 m cm⁻¹; δ_{H} (200 MHz, CDCl₃) 1.27 (3H, s, CH₃), 1.74 (3H, s, CH₃), 1.88 (3H, s, CH₃), 7.33–7.44 (5H, m, ArCH); δ_{C} (50.3 MHz, CDCl₃) 26.19, 27.11 and 29.32 (3 × CH₃), 55.42 (C5), 105.56 (C2), 125.60, 128.77 and 129.68 (3 × CH), 136.95 (*ipso*-C), 167.44 (C=O); *m/z* (CI(NH₃)) 252 (82%, [MNH₄⁺]), 150 (13), 132 (100%), 122 (15), 104 (51), 76 (83).

6. General method for the preparation of lead complexes

LTA (1 equiv), monodentate carboxylic acid A (*n* equiv.) and monodentate carboxylic acid B (*m* equiv.), (where *n* + *m* = 4), were combined in dry toluene (20–40 ml). The solvent was removed in vacuo (20–70 mbar, 20°C) to give a residue which was then redissolved in toluene (20–40 ml) and the solvent again removed in vacuo. This process was continued to remove acetic acid, as shown by ¹H-NMR spectroscopy.

7. Lead(IV) triacetate mono((1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-pyridinylmethyl)ester) **9**

LTA (0.076 g, 0.17 mmol) and ligand **6** (0.050 g, 0.17 mmol) were reacted according to the General Method to give complex **9** as a bright yellow foam. $[\alpha]_{\text{D}}^{23}$ – 4.5 (*c* = 1.05, CHCl₃); ν_{\max} (film) 2973 s, 1733 s, 1596 m,

1574 s, 1540 s, 1439 s, 1376 s, 1309 s, 1267 s, 1169 s, 1130 m, 1054 m, 1011 m, 816 w, 791 w, 769 m, 733 m, 700 m cm⁻¹; δ_{H} (200 MHz, CDCl₃) 0.91 (3H, s, CH₃), 1.29 (6H, s, 2 × CH₃), 1.60–1.72 (1H, m, C5HH'), 1.82–1.98 (1H, m, C4HH'), 2.15 (9H, s, (OC(O)CH₃)₃), 2.15–2.34 (1H, m, C4HH'), 2.45–2.57 (1H, m, C5HH'), 2.92 (1H, t, *J* = 9.5 Hz, C3H), 5.25 (1H, d, *J* = 12.5 Hz, C11HH'), 5.26 (1H, d, *J* = 12.5 Hz, C11HH'), 7.22 (1H, m, C15H), 7.38 (1H, d, *J* = 8.0 Hz, C13H), 7.73 (1H, m, C14H), 8.61 (1H, d, *J* = 5.0 Hz, C16H); δ_{C} (50.3 MHz, CDCl₃) 18.02 ((OC(O)CH₃)₃), 21.15 (CH₃), 22.41 (2 × CH₃), 22.72 (C4), 33.59 (C5), 47.30 (C2), 52.27 (C3), 56.60 (C1), 66.81 (C11), 122.27 (C13), 123.17 (C15), 137.19 (C14), 149.57 (C16), 155.92 (C12), 173.66 (C10), 180.82 (C=O); δ_{Pb} (52.3 MHz, CDCl₃, 223K) – 1877.6, – 1883.4 to – 1885.0 (broad).

8. Lead(IV) tribenzoate mono((1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-pyridinylmethyl)ester) **10**

LTA (0.076 g, 0.17 mmol), benzoic acid (0.063 g, 0.52 mmol) and ligand **6** (0.050 g, 0.17 mmol) were reacted according to the General Method to give complex **10** as a yellow foam. $[\alpha]_{\text{D}}^{23}$ + 5.1 (*c* = 0.88, CHCl₃); ν_{\max} (film) 3060 w, 2966 w, 1732 s, 1592 s, 1488 s, 1440 s, 1388 s, 1315 m, 1274 s, 1156 s, 1117 m, 1070 m, 1024 m, 938 m, 853 m, 761 m, 714 s, 681 s cm⁻¹; δ_{H} (200 MHz, CDCl₃) 0.95 (3H, s, CH₃), 1.32 (6H, s, 2 × CH₃), 1.62–1.99 (2H, m, C5HH' and C4HH'), 2.17–2.36 (1H, m, C4HH'), 2.51–2.67 (1H, m, C5HH'), 2.93 (1H, t, *J* = 9.0 Hz, C3H), 5.26 (1H, d, *J* = 13.5 Hz, C11HH'), 5.30 (1H, d, *J* = 13.5 Hz, C11HH'), 7.27 (1H, t, *J* = 5.0 Hz, C15H), 7.37–7.49 (7H, m, 6 × ArH and C13H), 7.58–7.61 (3H, m, 3 × ArH), 7.65–7.77 (1H, m, C14H), 8.11 (6H, d, *J* = 7.5 Hz, 6 × ArH), 8.64 (1H, d, *J* = 5.0 Hz, C16H); δ_{C} (50.3 MHz, CDCl₃) 21.18 (CH₃), 22.47 (2 × CH₃), 22.76 (C4), 33.53 (C5), 47.35 (C2), 52.34 (C3), 56.64 (C1), 66.34 (C11), 122.52 (C13), 123.44 (C15), 128.76 (ArC), 131.54 (ArC), 134.31 (ArC), 137.74 (C14), 149.16 (C16), 155.78 (C12), 173.73 (C10), 174.68 (C=O), 175.37 (C=O).

9. Lead(IV) tris(cyclohexanecarboxylate) mono((1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-pyridinylmethyl)ester) **11**

LTA (0.076 g, 0.17 mmol), cyclohexanecarboxylic acid (0.066 g, 0.52 mmol) and ligand **6** (0.050 g, 0.17 mmol) were reacted according to the General Method to give complex **11** as a pale yellow foam. $[\alpha]_{\text{D}}^{21}$ + 5.4 (*c* = 0.89, CHCl₃); ν_{\max} (CDCl₃) 2979 s, 2858 s, 1732 s, 1704 s, 1311 m, 1285 m, 1268 m, 1230 m, 1171 s, 1138

m, 1053 m, 1013 m, 950 m, 927 m cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 0.91 (3H, s, CH_3), 1.28–1.96 (38H, m, $2 \times \text{CH}_3$, $\text{C5HH}'$, $\text{C4HH}'$ and $30 \times$ cyclohexyl protons), 2.15–2.35 (1H, m, $\text{C4HH}'$), 2.50–2.57 (4H, m, $\text{C5HH}'$ and $3 \times \text{C1'H}$), 2.92 (1H, t, $J = 9.5$ Hz, C3H), 5.26 (1H, d, $J = 12.5$ Hz, $\text{C11HH}'$), 5.27 (1H, d, $J = 12.5$ Hz, $\text{C11HH}'$), 7.22–7.29 (1H, m, C15H), 7.39 (1H, d, $J = 7.5$ Hz, C13H), 7.73 (1H, m, C14H), 8.62 (1H, d, $J = 4.5$ Hz, C16H); δ_{C} (50.3 MHz, CDCl_3) 21.22 (CH_3), 22.40 ($2 \times \text{CH}_3$), 22.69 (C4), 25.20 (C3'), 25.49 (C4'), 29.53 (C2'), 33.46 (C5), 42.16 (C1'), 47.17 (C2), 52.30 (C3), 56.68 (C1), 66.65 (C11), 122.29 (C13), 123.19 (C15), 137.26 (C14), 149.45 (C16), 155.88 (C12), 173.75 (C10), 175.37 (C=O); δ_{Pb} (52.3 MHz, CDCl_3 , 223K) – 1876.8 (broad).

10. Lead(IV) tricinnamate mono((1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-pyridinylmethyl)ester) 12

LTA (0.076 g, 0.17 mmol), cinnamic acid (0.076 g, 0.52 mmol) and ligand **6** (0.050 g, 0.17 mmol) were reacted according to the General Method to give complex **12** as a pale yellow solid. $[\alpha]_{\text{D}}^{25} - 3.9$ ($c = 0.26$, CHCl_3); ν_{max} (CHCl_3) 3021 s, 1693 s, 1639 s, 1595 s, 1450 s, 1410 s, 1127 s, 840 m, 798 m, 794 cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 0.79–1.09 (3H, m, CH_3), 1.14–1.40 (6H, m, $2 \times \text{CH}_3$), 1.57–1.76 (1H, m, $\text{C5HH}'$), 1.81–2.11 (1H, m, $\text{C4HH}'$), 2.13–2.38 (1H, m, $\text{C4HH}'$), 2.54–2.72 (1H, m, $\text{C5HH}'$), 2.96 (1H, t, $J = 9.0$ Hz, C3H), 5.20–5.37 (2H, s, C11H_2), 6.64 (3H, d, $J = 16.0$ Hz, $3 \times \text{CH}=\text{CHCO}_2$), 7.23–7.29 (1H, m, C15H), 7.34–7.64 (16H, m, C13H and $15 \times \text{ArCH}$), 7.69–7.80 (1H, m, C14H), 7.88 (3H, d, $J = 16.0$ Hz, $3 \times \text{CH}=\text{CHCO}_2$), 8.64–8.66 (1H, m, C16H); δ_{C} (50.3 MHz, CDCl_3) 21.23 (CH_3), 22.49 (CH_3), 22.76 (C4), 33.57 (C5), 47.36 (C2), 52.38 (C3), 66.65 (C11), 122.34 (C13), 123.24 (C15), 125.51 and 128.45 ($\text{CH}=\text{CHCO}_2$), 128.70 (CH), 129.22 (CH), 131.19 (CH), 134.28 (C), 137.38 (C14), 149.42 (C16), 155.89 (C12), 173.75 (C10); δ_{Pb} (52.3 MHz, CDCl_3 , 253 K) – 1878.6 (broad).

11. Lead(IV) triacetate mono((1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-(2-pyridinyl)ethyl)ester) 13

LTA (0.073 g, 0.16 mmol) and ligand **7** (0.050 g, 0.16 mmol) were reacted according to the General Method to give complex **13** as a yellow gum. ν_{max} (film) 2971 s, 1727 s, 1636 m, 1595 s, 1571 m, 1541 s, 1476 s, 1458 s, 1374 s, 1308 s, 1174 s, 1119 w, 1057 w, 1013 m, 764 m, 693 cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 0.80 (3H, s, CH_3), 1.12 (3H, s, CH_3), 1.25 (3H, s, CH_3), 1.56–1.89 (2H, m, $\text{C5HH}'$ and $\text{C4HH}'$), 2.04–2.30 (10H, m, $\text{C4HH}'$ and

(OC(O)CH_3), 2.39–2.55 (1H, m, $\text{C5HH}'$), 2.76 (1H, t, $J = 8.0$ Hz, C3H), 3.16 (2H, t, $J = 7.0$ Hz, C11H_2), 4.40–4.60 (2H, m, C12H_2), 7.18–7.28 (2H, m, C14H and C16H), 7.65 (1H, m, C15H), 8.58 (1H, d, $J = 5.0$ Hz, C17H); δ_{C} (50.3 MHz, CDCl_3) 20.69 ($(\text{OC(O)CH}_3)_3$), 24.65, 24.83, 26.10 and 27.93 ($3 \times \text{CH}_3$ and C4), 31.46 (C5), 37.15 (C11), 48.15 (C2), 52.79 (C3), 54.89 (C1), 63.32 (C12), 121.90 (C14), 123.79 (C16), 136.82 (C15), 149.49 (C17), 157.58 (C13), 174.01 (C=O); δ_{Pb} (52.3 MHz, CDCl_3 , 223 K) – 1876.6 (broad), – 1882.7 (broad).

12. Lead(IV) tribenzoate mono((1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-(2-pyridinyl)ethyl)ester) 14

LTA (0.073 g, 0.16 mmol), benzoic acid (0.060 g, 0.49 mmol) and ligand **7** (0.050 g, 0.16 mmol) were reacted according to the General Method to give complex **14** as a bright orange solid. ν_{max} (film) 2964 m, 1725 s, 1593 m, 1525 s, 1442 m, 1392 s, 1315 m, 1273 m, 1175 m, 1158 m, 1117 w, 1070 m, 1025 m, 851 m, 768 m, 717 s, 682 cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 0.75 (3H, s, CH_3), 1.10–1.25 (6H, s, $2 \times \text{CH}_3$), 1.29–2.77 (5H, m, C4H_2 and C5H_2 and C3H), 3.16–3.22 (2H, m, C11H_2), 4.42–4.52 (2H, m, C12H_2), 7.17–7.47 (11H, m, $9 \times \text{ArH}$, C14H and C16H), 7.62–7.69 (1H, m, C15H), 7.98 (6H, d, $J = 7.5$ Hz, $6 \times \text{ArH}$), 8.63–8.65 (1H, m, C17H); δ_{C} (50.3 MHz, CDCl_3) 21.09 (CH_3), 21.51 (CH_3), 22.33 (C4), 22.57 (CH_3), 32.37 (C5), 36.60 (C11), 46.56 (C2), 52.76 (C3), 57.10 (C1), 63.48 (C12), 122.30 (C14), 124.14 (C16), 128.31 (ArCH), 130.08 (ArCH), 132.83 (ArCH), 137.55 (C15), 148.91 (C17), 157.86 (C13), 173.62 (C=O), 174.34 (C=O).

13. Lead(IV) tris(cyclohexanecarboxylate) mono-((1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-(2-pyridinyl)ethyl)ester) 15

LTA (0.073 g, 0.16 mmol), cyclohexanecarboxylic acid (0.061 g, 0.48 mmol) and ligand **7** (0.050 g, 0.16 mmol) were reacted according to the General Method to give complex **15** as a pale yellow/green gum. $[\alpha]_{\text{D}}^{20} + 5.9$ ($c = 0.51$, CHCl_3); ν_{max} (CDCl_3) 2937 s, 2858 s, 1727 s, 1538 s, 1452 s, 1350 m, 1285 m, 1230 m, 1177 s, 1021 cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 0.82 (3H, s, CH_3), 1.12 (3H, s, CH_3), 1.20–2.00 (35H, m, CH_3 , $\text{C4HH}'$, $\text{C5HH}'$ and $30 \times$ cyclohexyl protons), 2.12–2.30 (1H, m, $\text{C4HH}'$), 2.43–2.61 (4H, m, $\text{C5HH}'$ and $3 \times \text{C1'H}$), 2.75 (1H, t, $J = 9.0$ Hz, C3H), 3.16 (2H, t, $J = 6.5$ Hz, C11H_2), 4.44–4.56 (2H, m, C12H_2), 7.18–7.28 (2H, m, C14H and C16H), 7.64 (1H, t, $J = 7.5$ Hz, C15H), 8.59 (1H, d, $J = 5.0$ Hz, C17H); (50.3 MHz, CDCl_3) 21.10 (CH_3), 21.19 ($2 \times \text{CH}_3$), 22.39 (C4), 25.23 (C4'), 25.51

(C3'), 29.52 (C2'), 33.40 (C5), 36.95 (C11), 42.37 (C1'), 46.90 (C2), 52.37 (C3), 56.64 (C1), 63.61 (C12), 122.03 (C14), 123.87 (C16), 137.01 (C15), 149.38 (C17), 158.08 (C13), 174.02 (C10), 184.74 (C=O); δ_{Pb} (52.3 MHz, CDCl_3 , 223 K) – 1875.9 (broad).

14. Lead(IV) tricinnamate mono((1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-(2-pyridinyl)ethyl)ester) 16

LTA (0.073 g, 0.16 mmol), cinnamic acid (0.071 g, 0.48 mmol) and ligand **7** (0.050 g, 0.16 mmol) were reacted according to the General Method to give complex **16** as a bright yellow foam. ν_{max} (CDCl_3) 3031 m, 2972 m, 1726 s, 1635 s, 1579 s, 1498 s, 1452 s, 1310 m, 1254 s, 1180 s, 1072 m, 982 s, 927 s, 686 s cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 0.86 (3H, s, CH_3), 1.14 (3H, s, CH_3), 1.29 (3H, s, CH_3), 1.55–1.90 (2H, m, $\text{C4HH}'$ and $\text{C5HH}'$), 2.11–2.35 (1H, m, $\text{C4HH}'$), 2.46–2.65 (1H, m, $\text{C5HH}'$), 2.77 (1H, t, $J=8.5$ Hz, C3H), 3.16 (2H, t, $J=6.5$ Hz, C11H_2), 4.44–4.57 (2H, m, C12H_2), 6.48 (3H, d, $J=16.0$ Hz, $3 \times \text{CH}=\text{CHCO}_2$), 7.18–7.27 (2H, m, C14H and C16H), 7.35–7.65 (16H, m, C15H and $15 \times \text{ArCH}$), 7.90 (3H, d, $J=16.0$ Hz, $3 \times \text{CH}=\text{CHCO}_2$), 8.56 (1H, d, $J=4.0$ Hz, C17H); δ_{C} (50.3 MHz, CDCl_3) 20.72 (CH_3), 22.29 ($2 \times \text{CH}_3$ and C4), 31.48 (C5), 36.88 (C11), 54.89 (C3), 63.33 (C12), 121.04 (C14), 122.12 (CH), 123.99 (C16), 128.44 (CH), 128.53 (CH), 129.12 (CH), 130.82 (CH), 134.49 (C), 137.22 (C15), 149.17 (C17); δ_{Pb} (52.3 MHz, CDCl_3 , 223K) – 1879.7, – 1881.2 (broad).

15. Lead(IV) triacetate mono((1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(3-(2-pyridinyl)propyl)ester) 17

LTA (0.070 g, 0.16 mmol) and ligand **8** (0.050 g, 0.16 mmol) were reacted according to the General Method to give complex **17** as a bright orange gum. ν_{max} (film) 2964 s, 1729 s, 1592 m, 1475 m, 1436 m, 1364 m, 1259 m, 1173 s, 1117 m, 1053 m, 1019 m, 768 m cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 0.90 (3H, s, CH_3), 1.27 (6H, s, $2 \times \text{CH}_3$), 1.44–2.62 (15H, m, (OC(O)CH_3)₃, C5H_2 , C4H_2 and C12H_2), 2.73–2.91 (3H, m, C3H and C11H_2), 4.10–4.16 (2H, m, C13H_2), 7.13–7.29 (2H, m, C15H and C17H), 7.58–7.65 (1H, m, C16H), 8.54 (1H, d, $J=4.0$ Hz, C18H); δ_{C} (50.3 MHz, CDCl_3) 18.04 ((OC(O)CH_3)₃), 21.16 (CH_3), 22.43 ($2 \times \text{CH}_3$), 22.58 (C4), 28.49 (C12), 33.58 (C5), 34.34 (C11), 47.11 (C2), 52.29 (C3), 56.50 (C1), 63.92 (C13), 121.56 (C15), 123.16 (C17), 137.01 (C16), 149.30 (C18), 160.91 (C14), 173.98 (C10), 180.66 (C=O).

16. Lead(IV) tribenzoate mono((1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(3-(2-pyridinyl)propyl)ester) 18

LTA (0.070 g, 0.16 mmol), benzoic acid (0.059 g, 0.48 mmol) and ligand **8** (0.050 g, 0.16 mmol) were reacted according to the General Method to give complex **18** as a yellow gum. $[\alpha]_{\text{D}}^{21} + 8.6$ ($c=0.71$, CHCl_3); ν_{max} (CHCl_3) 3600–3200 br, 2969 m, 1725 br s, 1593 s, 1533 s, 1416 s, 1228 s, 1203 s, 1178 s, 1125 s, 1072 s, 1027 m cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 0.85–0.98 (3H, m, CH_3), 1.13–1.40 (6H, m, $2 \times \text{CH}_3$), 1.40–3.06 (9H, m, C5H_2 , C4H_2 , C12H_2 , C11H_2 and C3H), 4.17–4.23 (2H, m, C13H_2), 7.11–7.28 (2H, m, C15H and C17H), 7.42–7.75 (10H, m, $9 \times \text{ArH}$ and C16H), 8.12 (6H, d, $J=7.0$ Hz, $6 \times \text{ArH}$), 8.60–8.69 (1H, m, C18H); δ_{C} (50.3 MHz, CDCl_3) 21.22 (CH_3), 22.54 ($2 \times \text{CH}_3$), 22.55 (C4), 28.67 (C12), 33.62 (C5), 33.91 (C11), 47.19 (C2), 52.37 (C3), 56.64 (C1), 63.85 (C13), 121.98 (C15), 123.55 (C17), 128.76 (ArCH), 131.62 (ArCH), 134.28 (ArCH), 137.81 (C16), 148.69 (C18), 160.62 (C14), 174.07 (C10), 175.79 (C=O); δ_{Pb} (52.3 MHz, CDCl_3 , 223 K) – 1885.6, – 1888.0, – 1892.7, – 1895.4.

17. Lead(IV) tris(cyclohexanecarboxylate) mono((1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(3-(2-pyridinyl)propyl)ester) 19

LTA (0.070 g, 0.16 mmol), cyclohexanecarboxylic acid (0.061 g, 0.48 mmol) and ligand **8** (0.050 g, 0.16 mmol) were reacted according to the General Method to give complex **19** as a bright yellow gum. $[\alpha]_{\text{D}}^{21} + 12.2$ ($c=0.55$, CHCl_3); ν_{max} (film) 3600–3100 br, 2933 s, 2856 s, 1729 s br, 1542 s, 1452 s, 1349 s, 1285 m, 1175 s, 1022 m, 950 m, 811 m, 733 m cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 0.90 (3H, s, CH_3), 1.20–1.45 (14H, m, $2 \times \text{CH}_3$ and $8 \times$ cyclohexyl protons), 1.45–1.83 (16H, m, $\text{C5HH}'$, $\text{C4HH}'$ and $14 \times$ cyclohexyl protons), 1.83–2.30 (11H, m, $\text{C4HH}'$, C12H_2 and $8 \times$ cyclohexyl protons), 2.45–2.68 (4H, m, $\text{C5HH}'$ and $3 \times \text{C1'H}$), 2.78 (1H, t, $J=9.5$ Hz, C3H), 2.88 (2H, t, $J=7.5$ Hz, C11H_2), 4.14 (2H, t, $J=6.5$ Hz, C13H_2), 7.11–7.17 (2H, m, C15H and C17H), 7.61 (1H, m, C16H), 8.55 (1H, d, $J=5.0$ Hz, C18H); δ_{C} (50.3 MHz, CDCl_3) 21.24 (CH_3), 22.46 ($2 \times \text{CH}_3$), 22.46 (C4), 25.17 (C3'), 25.45 (C4'), 28.49 (C12), 29.64 (C2'), 33.52 (C5), 34.37 (C11), 41.76 (C1'), 47.03 (C2), 52.31 (C3), 56.57 (C1), 63.89 (C13), 121.56 (C15), 123.14 (C17), 136.97 (C16), 149.35 (C18), 160.91 (C14), 174.09 (C10), 184.93 (C=O); δ_{Pb} (52.3 MHz, CDCl_3 , 223K) – 1877.0 (broad).

18. Lead(IV) tricinnamate mono((1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(3-(2-pyridinyl)propyl)ester) 20

LTA (0.070 g, 0.16 mmol), cinnamic acid (0.070 g, 0.47 mmol) and ligand (0.050 g, 0.16 mmol) were reacted according to the General Method to give complex **20** as a pale yellow solid. ν_{\max} (CHCl₃) 3029 m, 2968 m, 1733 s, 1698 s, 1654 m, 1636 s, 1283 s, 1232 s, 1158 m cm⁻¹; δ_{H} (200 MHz, CDCl₃) 0.97 (3H, s, CH₃), 1.32 (6H, s, 2 × CH₃), 1.47–1.99 (2H, m, C5HH' and C4HH'), 2.04–2.27 (3H, m, C4HH' and C12H₂), 2.50–2.65 (1H, m, C5HH'), 2.81 (1H, t, *J* = 9.5 Hz, C3H), 2.91 (2H, t, *J* = 7.5 Hz, C11H₂), 4.15 (2H, t, *J* = 6.5 Hz, C13H₂), 6.47 (3H, d, *J* = 16.0 Hz, 3 × CH=CHCO₂), 7.13–7.20 (2H, m, C15H and C17H), 7.27–7.66 (16H, m, C16H and 15 × ArH), 7.86 (3H, d, *J* = 16.0 Hz, 3 × CH=CHCO₂), 8.58 (1H, d, *J* = 4.5 Hz, C18H); δ_{C} (50.3 MHz, CDCl₃) 21.28 (CH₃), 22.46 (C4), 22.59 (2 × CH₃), 28.49 (C12), 33.70 (C5), 34.08 (C11), 47.13 (C2), 52.44 (C3), 63.85 (C13), 121.82 (C15), 123.40 (C17), 125.49 and 128.45 (CH=CHCO₂), 128.61, 129.18, 131.00, 134.40, 137.48 (C16), 149.94 (C18), 160.75 (C14), 174.15 (C10); δ_{Pb} (52.3 MHz, CDCl₃, 253K) –1878.4 (broad).

19. Lead(IV) bis(cyclohexanecarboxylate) bis((1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-pyridinylmethyl)ester) 22

LTA (0.076 g, 0.17 mmol), cyclohexanecarboxylic acid (0.044 g, 0.34 mmol) and ligand **6** (0.100 g, 0.34 mmol) were reacted according to the General Method to give complex **22** as a pale yellow/green gum. $[\alpha]_{\text{D}}^{20} + 9.1$ (*c* = 0.81, CHCl₃); ν_{\max} (CHCl₃) 2937 s, 2858 m, 1732 s, 1703 s, 1454 s, 1228 s, 1170 s, 909 m cm⁻¹; δ_{H} (200 MHz, CDCl₃) 0.89 (6H, s, 2 × CH₃), 1.25 and 1.28 (2 × 6H, 2 × s, 4 × CH₃), 1.08–2.85 (30H, m, 2 × C5H₂, 2 × C4H₂ and 22 × cyclohexyl protons), 2.90 (2H, t, *J* = 9.5 Hz, 2 × C3H), 5.24 (2H, d, *J* = 14.0 Hz, 2 × C11HH'), 5.25 (2H, d, *J* = 14.0 Hz, 2 × C11HH'), 7.21–7.26 (2H, m, 2 × C15H), 7.37 (2H, d, *J* = 7.5 Hz, 2 × C13H), 7.71 (2H, m, 2 × C14H), 8.60 (2H, d, *J* = 5.0 Hz, 2 × C16H); δ_{C} (50.3 MHz, CDCl₃) 21.23 (CH₃), 21.63 (CH₃), 22.53 (CH₃), 22.77 (C4), 25.38 (C3'), 25.67 (C4'), 29.05 (C2'), 32.61 (C5), 45.21 (C1'), 46.79 (C2), 52.75 (C3), 66.43 (C11), 122.33 (C13), 123.21 (C15), 137.37 (C14), 149.34 (C16), 155.95 (C12), 174.06 (C10), 183.92 (C=O); δ_{Pb} (52.3 MHz, CDCl₃, 223 K) –1876.1.

20. Lead(IV) bis(cyclohexanecarboxylate) bis((1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-(2-pyridinyl)ethyl)ester) 23

LTA (0.073 g, 0.16 mmol), cyclohexanecarboxylic acid (0.042 g, 0.33 mmol) and ligand **7** (0.100 g, 0.33 mmol) were reacted according to the General Method to give the complex **23** as a pale yellow/green gum. $[\alpha]_{\text{D}}^{20} + 8.1$ (*c* = 0.35, CHCl₃); ν_{\max} (CHCl₃) 2937 s, 2858 s, 1725 s, 1534 s, 1453 s, 1392 s, 1350 s, 1228 s, 1176 s cm⁻¹; δ_{H} (200 MHz, CDCl₃) 0.79 (6H, s, 2 × CH₃), 1.22–2.09 (36H, m, 4 × CH₃, 2 × C4HH', 2 × C5HH' and 20 × cyclohexyl protons), 2.14–2.35 (2H, m, 2 × C4HH'), 2.40–2.61 (4H, m, 2 × C5HH' and 2 × C1'H), 2.73 (2H, t, *J* = 9.0 Hz, 2 × C3H), 3.14 (4H, t, *J* = 6.5 Hz, 2 × C11H₂), 4.39–4.61 (4H, m, 2 × C12H₂), 7.18–7.29 (4H, m, 2 × C14H and 2 × C16H), 7.58–7.65 (2H, m, 2 × C15H), 8.55 (2H, d, *J* = 4.5 Hz, 2 × C17H); δ_{C} (50.3 MHz, CDCl₃) 21.16 (CH₃), 21.40 (2 × CH₃ and C4), 25.25 (C3'), 25.65 (C4'), 29.21 (C2'), 32.95 (C5), 36.94 (C11), 41.06 (C1'), 46.67 (C2), 52.56 (C3), 56.64 (C1), 63.52 (C12), 122.02 (C14), 123.87 (C16), 137.01 (C15), 149.34 (C17), 158.08 (C13), 174.18 (C10), 184.10 (C=O); δ_{Pb} (52.3 MHz, CDCl₃, 223 K) –1875.7.

21. Lead(IV) bis(cyclohexanecarboxylate) bis((1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(3-(2-pyridinyl)propyl)ester) 24

LTA (0.069 g, 0.16 mmol), cyclohexanecarboxylic acid (0.040 g, 0.31 mmol) and ligand **8** (0.100 g, 0.31 mmol) were reacted according to the General Method to give complex **24** as a pale yellow gum. $[\alpha]_{\text{D}}^{20} + 9.2$ (*c* = 0.25, CHCl₃); ν_{\max} (CHCl₃) 3600–3200 br, 2936 s, 2857 m, 1723 s, 1593 m, 1452 m, 1403 s, 1228 s, 1206 s, 1174 s cm⁻¹; δ_{H} (200 MHz, CDCl₃) 0.91 (6H, s, 2 × CH₃), 1.21–2.28 (42H, m, 4 × CH₃, 2 × C12H₂, 2 × C4H₂, 2 × C5HH' and 20 cyclohexyl protons), 2.45–2.74 (4H, m, 2 × C5HH' and 2 × C1'H), 2.78 (2H, t, *J* = 9.5 Hz, 2 × C3H), 2.88 (4H, t, *J* = 7.5 Hz, 2 × C11H₂), 4.14 (4H, t, *J* = 6.5 Hz, 2 × C13H₂), 7.11–7.20 (4H, m, 2 × C15H and 2 × C17H), 7.61 (2H, dt, *J* = 7.5, 1.5 Hz, 2 × C16H), 8.55 (2H, d, *J* = 4.5 Hz, 2 × C18H); δ_{C} (50.3 MHz, CDCl₃) 21.37 (CH₃), 21.63 (CH₃), 22.45 (C4), 22.91 (CH₃), 25.48 (C3'), 25.71 (C4'), 28.55 (C12), 29.20 (C2'), 32.41 (C5), 34.23 (C11), 41.15 (C1'), 46.64 (C2), 52.82 (C3), 63.74 (C13), 121.65 (C15), 123.25 (C17), 137.15 (C16), 149.19 (C18), 160.88 (C14), 174.49 (C10), 184.24 (C=O); δ_{Pb} (52.3 MHz, CDCl₃, 223 K) –1876.4.

22. Lead(IV) diacetate bis((1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-pyridinylmethyl)ester) 25

LTA (0.076 g, 0.17 mmol) and ligand **6** (0.100 g, 0.34 mmol) were reacted according to the General Method to give the complex **25** as a pale yellow/green gum. $[\alpha]_{\text{D}}^{20} + 7.2$ ($c = 0.20$, CHCl_3); ν_{max} (CHCl_3) 2972 s, 1732 s, 1596 m, 1537 m, 1439 s, 1392 s, 1311 m, 1228 s, 1170 s, 1053 m, 997 m, 815 w, 794 w, 723 m, 700 cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 0.92 (6H, s, $2 \times \text{CH}_3$), 1.28–1.30 ($2 \times 6\text{H}$, $2 \times \text{s}$, $2 \times \text{C}6\text{H}_3$ and $2 \times \text{C}8\text{H}_3$ or $\text{C}7\text{H}_3$), 1.61–1.72 (2H, m, $2 \times \text{C}5\text{H}\text{H}'$), 1.82–2.38 (10H, m, $2 \times \text{C}4\text{H}_2$ and $2 \times \text{OC}(\text{O})\text{CH}_3$), 2.46–2.60 (2H, m, $2 \times \text{C}5\text{H}\text{H}'$), 2.93 (2H, t, $J = 9.5$ Hz, $2 \times \text{C}3\text{H}$), 5.26 (2H, d, $J = 12.5$ Hz, $2 \times \text{C}11\text{H}\text{H}'$), 5.27 (2H, d, $J = 13.5$ Hz, $2 \times \text{C}11\text{H}\text{H}'$), 7.20–7.31 (2H, m, $2 \times \text{C}15\text{H}$), 7.39 (2H, d, $J = 7.5$ Hz, $2 \times \text{C}13\text{H}$), 7.74 (2H, m, $2 \times \text{C}14\text{H}$), 8.61 (2H, d, $J = 4.5$ Hz, $2 \times \text{C}16\text{H}$); δ_{C} (50.3 MHz, CDCl_3) 21.44, 21.73, 22.62 and 22.99 ($3 \times \text{Me}$, O_2CCH_3 and C4), 31.67 (C5), 46.81 (C2), 52.78 (C3), 66.55 (C11), 122.10 (C13), 122.94 (C15), 136.96 (C14), 149.22 (C16), 155.70 (C12), 173.80 (C10), 180.32 (C=O); δ_{Pb} (52.3 MHz, CDCl_3 , 223 K) – 1877.6.

23. Lead(IV) tetra((1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-pyridinylmethyl)ester) 26

LTA (0.069 g, 0.16 mmol) and ligand **6** (0.180 g, 0.62 mmol) were reacted according to the General Method to give the complex **26** as a pale yellow gum. $[\alpha]_{\text{D}}^{23} - 2.5$ ($c = 0.40$, CHCl_3); ν_{max} (CHCl_3) 1733 s, 1702 s, 1170 cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 0.83 (12H, s, $4 \times \text{CH}_3$), 1.19 and 1.24 ($2 \times 12\text{H}$, $2 \times \text{s}$, $8 \times \text{CH}_3$), 1.56–1.76 (4H, m, $4 \times \text{C}5\text{H}\text{H}'$), 1.75–1.97 (4H, m, $4 \times \text{C}4\text{H}\text{H}'$), 2.03–2.37 (4H, m, $4 \times \text{C}4\text{H}\text{H}'$), 2.48–2.71 (4H, m, $4 \times \text{C}5\text{H}\text{H}'$), 2.87 (4H, t, $J = 9.5$ Hz, $4 \times \text{C}3\text{H}$), 5.23 (4H, d, $J = 14.0$ Hz, $4 \times \text{C}11\text{H}\text{H}'$), 5.25 (4H, d, $J = 14.0$ Hz, $4 \times \text{C}11\text{H}\text{H}'$), 7.21–7.26 (4H, m, $4 \times \text{C}15\text{H}$), 7.36 (4H, d, $J = 7.5$ Hz, $4 \times \text{C}13\text{H}$), 7.69 (4H, m, $4 \times \text{C}14\text{H}$), 8.58 (4H, d, $J = 3.0$ Hz, $4 \times \text{C}16\text{H}$); δ_{C} (50.3 MHz, CDCl_3) 21.13 (CH_3), 21.62 (CH_3), 22.56 (CH_3), 22.78 (C4), 32.48 (C5), 46.85 (C2), 52.67 (C3), 66.63 (C11), 122.34 (C13), 123.17 (C15), 137.23 (C14), 149.54 (C16), 156.00 (C12), 174.06 (C10); δ_{Pb} (52.3 MHz, CDCl_3 , 223 K) – 1877.9.

24. Lead(IV) triacetate mono((1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-methylpyridine-*N*-oxide)ester) 27

LTA (0.072 g, 0.16 mmol) and (1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-methylpyridine-*N*-oxide)ester [11] (0.050 g, 0.16 mmol) were

reacted according to the General Method to give the title compound **27** as a deep yellow foam. ν_{max} (film) 3600–3300 br, 2967 m, 1734 s, 1559 m, 1497 m, 1439 m, 1376 m, 1222 m, 1162 s, 1050 m, 1015 m, 852 m, 772 m, 669 cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 0.81–1.02 (3H, m, CH_3), 1.20–1.41 (6H, m, $2 \times \text{CH}_3$), 1.56–2.79 (13H, m, $\text{C}5\text{H}_2$, $\text{C}4\text{H}_2$ and $(\text{OC}(\text{O})\text{CH}_3)_3$), 2.87–3.04 (1H, m, $\text{C}3\text{H}$), 5.25–5.54 (2H, m, $\text{C}11\text{H}_2$), 7.25–7.54 (3H, m, $\text{C}13\text{H}$, $\text{C}14\text{H}$ and $\text{C}15\text{H}$), 8.38–8.45 (1H, m, $\text{C}16\text{H}$).

25. Lead(IV) tribenzoate mono((1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-methylpyridine-*N*-oxide)ester) 28

LTA (0.072 g, 0.16 mmol), benzoic acid (0.059 g, 0.49 mmol) and (1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-methylpyridine-*N*-oxide)ester [11] (0.050 g, 0.16 mmol) were reacted according to the General Method to give the title compound **28** as a bright yellow foam. ν_{max} (film) 3061 w, 2966 w, 2630 w, 1712 s, 1593 s, 1529 s, 1444 m, 1392 s, 1316 m, 1269 m, 1217 s, 1175 m, 1119 m, 1070 m, 1025 m, 938 m, 849 m, 770 m, 681 cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 0.75–1.02 (3H, m, CH_3), 1.20–1.51 (7H, m, $2 \times \text{CH}_3$ and $\text{C}5\text{H}\text{H}'$), 1.61–2.95 (4H, m, $\text{C}5\text{H}\text{H}'$, $\text{C}4\text{H}_2$ and $\text{C}3\text{H}$), 5.45–5.63 (2H, m, $\text{C}11\text{H}_2$), 7.20–7.59 (12H, m, $\text{C}13\text{H}$, $\text{C}14\text{H}$, $\text{C}15\text{H}$, $6 \times \text{ArH}$ and $3 \times \text{ArH}$), 8.05 (6H, d, $J = 7.5$ Hz, $6 \times \text{ArCH}$), 8.49–8.56 (1H, m, $\text{C}16\text{H}$).

26. Lead(IV) triacetate mono((1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-ethylpyridine-*N*-oxide)ester) 29

LTA (0.069 g, 0.16 mmol) and (1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-ethylpyridine-*N*-oxide)ester [11] (0.050 g, 0.16 mmol) were reacted according to the General Method to give the title compound **29** as a bright yellow foam. ν_{max} (film) 3600–3200 br, 2968 m, 1727 s, 1559 s, 1492 m, 1441 s, 1376 s, 1213 s, 1171 s, 1115 m, 1056 m, 1015 m, 852 m, 772 m, 669 cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 0.70–0.87 (3H, m, CH_3), 1.04–1.29 (6H, m, $2 \times \text{CH}_3$), 1.54–1.68 (1H, m, $\text{C}5\text{H}\text{H}'$), 1.70–2.62 (12H, m, $\text{C}5\text{H}\text{H}'$, $\text{C}4\text{H}_2$ and $(\text{OC}(\text{O})\text{CH}_3)_3$), 2.65–2.80 (1H, m, $\text{C}3\text{H}$), 3.25–3.41 (2H, m, $\text{C}11\text{H}_2$), 4.45–4.63 (2H, m, $\text{C}12\text{H}_2$), 7.22–7.37 (3H, m, $\text{C}14\text{H}$, $\text{C}15\text{H}$ and $\text{C}16\text{H}$), 8.44 (1H, d, $J = 6.0$ Hz, $\text{C}17\text{H}$).

27. Lead(IV) tribenzoate mono((1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-ethylpyridine-*N*-oxide)ester) 30

LTA (0.037 g, 0.08 mmol), benzoic acid (0.031 g, 0.25 mmol) and (1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-di-

carboxylic acid mono-3-(2-ethylpyridine-*N*-oxide)ester [11] (0.027 g, 0.08 mmol) were reacted according to the General Method to give the title compound **30** as a bright yellow gum. ν_{\max} (film) 3068 w, 2971 w, 1728 s, 1643 m, 1601 s, 1531 s, 1496 s, 1448 s, 1392 s, 1315 s, 1290 s, 1208 s, 1176 s, 1118 m, 1070 m, 1036 m, 940 m, 850 m, 719 s cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 0.86 (3H, s, CH_3), 1.16 (3H, s, CH_3), 1.27 (3H, s, CH_3), 1.59–1.88 (2H, m, $\text{C5HH}'$ and $\text{C4HH}'$), 2.09–2.24 (1H, m, $\text{C4HH}'$), 2.42–2.69 (1H, m, $\text{C5HH}'$), 2.74 (1H, t, $J = 8.0$ Hz, C3H), 3.33 (2H, t, $J = 6.0$ Hz, C11H_2), 4.53 (2H, t, $J = 6.0$ Hz, C12H_2), 7.22–7.33 (3H, m, C14H , C15H and C16H), 7.40–7.64 (9H, m, $6 \times \text{ArH}$ and $3 \times \text{ArH}$), 8.10 (6H, d, $J = 7.5$ Hz, $6 \times \text{ArH}$), 8.45 (1H, d, $J = 5.5$ Hz, C17H).

28. Lead(IV) triacetate mono((1*R*,1*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-propylpyridine-*N*-oxide)ester) **31**

LTA (0.044 g, 0.10 mmol) and (1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-propylpyridine-*N*-oxide)ester [11] (0.033 g, 0.10 mmol) were reacted according to the General Method to give the title compound **31** as a bright yellow/orange gum. ν_{\max} (film) 3600–3300 br, 2963 m, 1727 s, 1539 s, 1493 m, 1441 s, 1408 s, 1210 s, 1159 s, 1115 m, 1067 m, 1019 m, 877 m, 846 m, 772 s, 728 m cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 0.83–0.96 (3H, m, CH_3), 1.12–1.25 (6H, m, $2 \times \text{CH}_3$), 1.31–1.48 (1H, m, $\text{C5HH}'$), 1.54–2.91 (15H, m, $\text{C5HH}'$, C4H_2 , C12H_2 , C3H and $(\text{OC}(\text{O})\text{CH}_3)_3$), 3.01–3.11 (2H, m, C11H_2), 4.12–4.21 (2H, m, C13H_2), 7.19–7.36 (3H, m, C15H , C16H and C17H), 8.39 (1H, d, $J = 6.0$ Hz, C18H).

29. Lead(IV) tribenzoate mono((1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-propylpyridine-*N*-oxide)ester) **32**

LTA (0.066 g, 0.15 mmol), benzoic acid (0.055 g, 0.45 mmol) and (1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-propylpyridine-*N*-oxide)ester [11] (0.050 g, 0.15 mmol) were reacted according to the General Method to give the title compound **32** as a yellow foam. ν_{\max} (film) 2964 m, 1725 s, 1548 s, 1445 s, 1208 s, 1071 m, 1018 m, 849 m, 728 m cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 0.89–0.97 (3H, m, CH_3), 1.20–1.29 (6H, m, $2 \times \text{CH}_3$), 1.51–2.37 (5H, m, $\text{C5HH}'$, C4H_2 and C2H_2), 2.49–2.68 (1H, m, $\text{C5HH}'$), 2.74–2.86 (1H, m, C3H), 3.03–3.15 (2H, m, C11H_2), 4.12–4.22 (2H, m, C13H_2), 7.24–7.59 (12H, m, C15H , C16H , C17H , $9 \times \text{ArH}$), 8.06 (6H, d, $J = 7.5$ Hz, $6 \times \text{Aru}$), 8.52 (1H, d, $J = 6.0$ Hz, C18H); δ_{Pb} (52.3 MHz, CDCl_3 , 223 K) –1883.8, –1888.2, –1893.5.

30. Phenylation of methyl Meldrum's acid with isolation of PhPbL_3 intermediate

Lead(IV) triacetate mono((1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-methylpyridine)ester) **9** (0.338 g, 0.50 mmol), phenylboric acid (0.067 g, 0.55 mmol) and HgCl_2 (0.136 g, 0.50 mmol) were dissolved in dry CHCl_3 (15 ml) and stirred 40°C for 2 h. The reaction mixture was then filtered through Celite[®], and the solid washed with CHCl_3 (3×20 ml). The organic layer was washed with H_2O (1×50 ml), the aqueous layer being further extracted with CHCl_3 (2×25 ml). The combined organic fractions were again filtered through Celite[®] and then concentrated to a volume of 10 ml. Petrol (60 ml) was added to the solution which was then stored at 0°C overnight. Filtration of the resulting precipitate gave a pale yellow crystalline solid, phenyl lead(IV) diacetate mono((1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-methylpyridine)ester) **21** (0.135g, 39%) ν_{\max} (film) 1729 s, 1546 m, 1432 s, 1382 m, 1264 m, 1162 s, 990 m, 725 s, 692 m, 666 s cm^{-1} ; δ_{H} (200 MHz, CDCl_3) 0.89 (3H, s, C7H_3 or C8H_3), 1.28 and 1.31 ($2 \times 3\text{H}$, $2 \times \text{s}$, $2 \times \text{CH}_3$), 1.51–1.74 (1H, m, $\text{C5HH}'$), 1.76–1.99 (1H, m, $\text{C4HH}'$), 2.11 (6H, s, $2 \times \text{OC}(\text{O})\text{CH}_3$), 2.12–2.35 (1H, m, $\text{C4HH}'$), 2.49–2.70 (1H, m, $\text{C5HH}'$), 2.93 (1H, t, $J = 9.5$ Hz, C3H), 5.27 (1H, d, $J = 14.0$ Hz, $\text{C11HH}'$), 5.28 (1H, d, $J = 14.0$ Hz, $\text{C11HH}'$), 7.23–7.66 (7H, m, C15H , C13H and C_6H_5), 7.69–7.78 (1H, m, C14H), 8.60 (1H, d, $J = 5.0$ Hz, C16H); δ_{C} (125.8 MHz, CDCl_3) 21.24, 21.42, 21.78 and 22.38 ($3 \times \text{CH}_3$ and C4), 22.72 ($\text{OC}(\text{O})\text{CH}_3$), 32.65 (C5), 47.10 (C2), 52.60 (C3), 56.19 (C1), 66.76 (C11), 122.25 (C13), 123.00 (C15), 129.48, 131.23 and 135.97 ($3 \times \text{ArCH}$), 136.94 (C14), 149.41 (C16), 155.84 (C12), 173.65 (C10).

Phenyl lead(IV) diacetate mono ((1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid mono-3-(2-methylpyridine)ester) **21** (0.103 g, 0.15 mmol) was dissolved in dry CHCl_3 (10 ml). Methyl Meldrum's acid **4** (0.024 g, 0.15 mmol) in pyridine (0.035 g, 0.45 mmol) was added to the above stirring solution, which was then heated under reflux for 5 h. The reaction mixture was filtered through Celite[®] and the solid residue washed with CHCl_3 (3×25 ml). The combined organic fractions were then concentrated in vacuo. Purification by flash column chromatography (eluting 100% DCM) gave the phenylated product **6** (0.016g, 46%).

Acknowledgements

We thank DTI, EPSRC and Associated Octel Company for funding of studentships to D.R.P. and E.W., and we wish to gratefully acknowledge the use of the EPSRC's Chemical Database Service at Daresbury [19]

and the EPSRC Mass Spectrometric Service Centre at Swansea. We thank Dr T. Claridge for assistance with obtaining ^{207}Pb -NMR spectra.

References

- [1] For some useful leading references, see: J.T. Pinhey, in: A. McKillop (Ed.), *Comprehensive Organometallic Chemistry II*, vol. 11, Pergamon, Oxford, 1995.
- [2] J.T. Pinhey, *Aust. J. Chem.* 44 (1991) 1353.
- [3] M.G. Moloney, D.R. Paul, R.M. Thompson, *Main Group Metal Chem.* 18 (1995) 295.
- [4] M.G. Moloney, R.M. Thompson, E. Wright, *Main Group Metal Chem.* 19 (1996) 133.
- [5] M.G. Moloney, D.R. Paul, S.C. Prottey, R.M. Thompson, E. Wright, *J. Organometal. Chem.* 534 (1997) 195.
- [6] J.E.H. Buston, T.D.W. Claridge, M.G. Moloney, *J. Chem. Soc. Perkin Trans. II* (1995) 639.
- [7] T.D.W. Claridge, E.J. Nettleton, M.G. Moloney, *Mag. Res. Chem.* 35 (1997) 159.
- [8] D.J. Berrisford, C. Bolm, K.B. Sharpless, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1059.
- [9] J. Morgan, J.T. Pinhey, *J. Chem. Soc. Perkin Trans. 1* (1990) 715.
- [10] S.W. Wright, D.L. Hagemann, L.D. McClure, *J. Org. Chem.* 59 (1994) 6095.
- [11] M.G. Moloney, D.R. Paul, E. Wright, R.M. Thompson, *Tetrahedron Asymmetry* 6 (1996) 2551.
- [12] H.C. Bell, G.L. May, J.T. Pinhey, S. Sternhell, *Tetrahedron Lett.* (1976) 4303.
- [13] H.C. Bell, J.T. Pinhey, S. Sternhell, *Aust. J. Chem.* 32 (1979) 1551.
- [14] J.E.H. Buston, A. Coop, R. Keady, M.G. Moloney, R.M. Thompson, *J. Chem. Res. (M)* (1994) 1101.
- [15] P.J. Stang, V.V. Zhdankin, *Chem. Rev.* 96 (1996) 1123.
- [16] T. Imamoto, H. Koto, *Chem. Lett.* (1986) 967.
- [17] E. Hatzigrigoriou, A. Varvoglis, M. Bakola-Christianopolou, *J. Org. Chem.* 55 (1990) 315.
- [18] D.G. Ray, G.F. Koser, *J. Am. Chem. Soc.* 112 (1990) 5672.
- [19] D.A. Fletcher, R.F. McMeeking, D. Parkin, *J. Chem. Inf. Comput. Sci.* 36 (1996) 746.