The influence of ligands in Pinhey phenylation reactions using lead(IV) tetracarboxylates

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Abstract

Lead(IV) tetracarboxylates, prepared from achiral and chiral carboxylic acids, have been shown to undergo metal–metal exchange with phenylboronic acid, and the phenyllead(IV) carboxylates thus generated in situ can be used for Pinhey phenylation reactions. Although the yields of these reactions are generally moderate to good, only low levels of asymmetric induction at best were observed. Possible reasons for this lack of enantioselectivity are discussed.
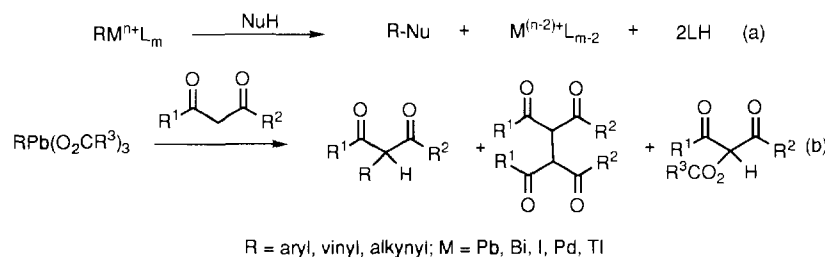
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1. Introduction

Cross coupling processes are now recognised to be especially useful, often mediating the formation of synthetically valuable products under very mild conditions (for some useful leading references, see Ref. [1]). Notable amongst these are transition-metal catalysed reactions, and palladium particularly finds extensive application in, for example, Suzuki- [2–5], Stille- [6,7], and Heck-type couplings [8–10]. More recently, the use of chiral ligands has allowed enantioselective carbon–carbon bond forming reactions to be developed [11,12] in, for example, asymmetric Heck reactions [13]. Main group metals are also known to mediate a variety of cross coupling reactions, and in recent years the application of lead(IV) [14,15], bismuth(V), [16] iodine(III) [17] and thallium [18] have been investigated in detail [19]. Generally, an organometallic derivative of one of these main group metals will react with a nucleophile with formation of a new carbon–carbon or carbon–heteroatom bond (Scheme 1(a)); what is unusual about these processes is that the organometallic compound reacts as a carbocation synthetic equivalent, rather than

a carbanionic species, and therefore the couplings are examples of umpolung [20,21]. There is now considerable evidence that these latter processes occur by ligand coupling [22,23] involving a reductive elimination at the lead [24,25] or bismuth centre [26], and the possible intermediacy of radicals under the conditions of these reactions appears to have been excluded [27]. These processes are made all the more valuable in that the carbocation synthetic equivalents — those of phenyl-, vinyl- or alkynylcations — are not easily prepared by alternative routes. However, although such examples of umpolung of organometallic compounds are not exclusively restricted to main group metals, since Pd(II) for example is known to mediate similar reactions [28], they are more common because the extremely high oxidising potential of these metals provides an efficient electron sink, promoting collapse with two electron reduction of the metal cation and generation of an incipient carbocation [14]. The application of lead(IV) has been especially productive, and organolead(IV) tricarboxylates have been found to mediate arylations, vinylations and alkynylations of a variety of nucleophilic substrates, especially soft carbon nucleophiles such as β-dicarbonyl compounds (Scheme 1(b)), but also some heteronucleophiles, for example iodide or azide. However, oxidative dimerisation or α-carboxyla-

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$$RM^{n+}L_m \xrightarrow{\text{NuH}} R\text{-Nu} + M^{(n-2)+}L_{m-2} + 2LH \quad (a)$$

$$RPb(O_2CR^3)_3 \xrightarrow{\quad\quad}$$

R = aryl, vinyl, alkynyl; M = Pb, Bi, I, Pd, Tl

Scheme 1.

tion of the nucleophilic substrate by the organolead(IV) reagent can be competitive reactions [14].

In recent years, the importance of ligands in many metal mediated reactions [11] has been amply demonstrated (e.g. catalytic reduction [29], Sharpless allylic epoxidation [30], dihydroxylation [31] and aminohydroxylation [32]) and it has therefore been of interest to us to examine the effect of ligands on the coupling reactions mediated by lead(IV). Although much work has been done using isolated organolead triacetates [14,15], it has also been shown more recently that these compounds can be generated in situ from other readily available organometallic compounds (e.g. organostannanes, mercurials and boronic acids) and used directly in reactions with nucleophiles [33]. This type of approach to the generation of reactive lead(IV) compounds is attractive because their often troublesome isolation is avoided, and because the potential for general and flexible application is greater, allowing the use of any lead(IV) tetracarboxylate as a source of lead(IV). Although lead tetraacetate (LTA) has generally been used for these metal–metal exchanges, a recent report described that lead tetrabenzoate [34] was superior. This suggested that modification of the ligands may be used to influence the efficiency of the cross coupling reactions, perhaps extending the scope of the reaction to a wider range of nucleophiles or permitting enantioselective cross coupling. The identification of other ligands for lead(IV) is not immediately obvious because many possible electron donors, for example amines, alcohols and thiols, were expected to be unsuitable, having been reported to be readily oxidised by lead(IV) [35,36]. However, carboxylates have been widely used as ligands for lead(IV) [35,37,38], since these are electron donors which are nonetheless oxidatively stable under mild conditions, and are known to satisfy the co-ordination requirement for lead(IV) by acting as either monodentate or bidentate ligands. We have shown that a wide range of simple lead(IV) tetracarboxylates are accessible by ligand exchange with LTA, and that these compounds are not chemically inert, reacting with allylstannanes to give the corresponding allyl carboxylates in excellent yield [39]. In a continuation of this work, we have examined and now report the application of more highly functionalised achiral and chiral carboxylic

acids as ligands, and to this end have prepared a range of lead(IV) tetracarboxylates derived from mixed ligand systems, and examined their reactivity. This represents the first detailed study of such compounds, and the effect of ligands upon Pinhey phenylation reactions. Some of the results of this work have been published in preliminary form [40,41].
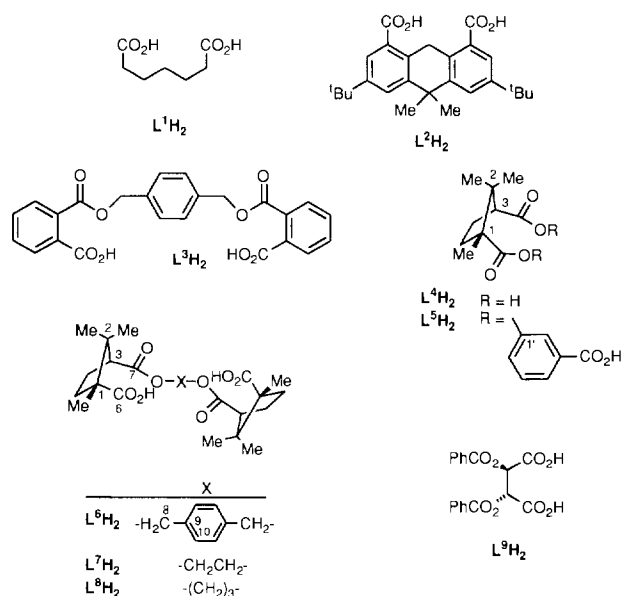
2. Results and discussion

Complexation was readily achieved by metathesis of the required carboxylate ligand and LTA in toluene at about 40 °C to give the corresponding lead(IV) complexes, for example, lead tetra(o-benzoylbenzoate) 1 and lead tetra(p-toluate) 2 (Table 1). The former compound was readily crystallised and shown by crystallographic analysis to be mononuclear, possessing a somewhat distorted trigonal dodecahedron structure [42]. This contrasts with an earlier report of the structure of LTA, which was oligomeric [43]. Mixed ligand complexes (Table 1, compounds 3–9) were also found to be readily available by using the appropriate stoichiometry of monocarboxylic acid ligands (2:2 for 3,4,6,8 or 3:1 for 5,7,9) in the metathesis reaction. Characterisation of these complexes was by a combination of combustion analysis and/or spectroscopic procedures. ^{1}H NMR spectroscopy was used to confirm both the absence of acetate as well as the ligand ratio, and it was noted that the carboxylic acid carbonyl absorption in the IR spectrum, which was very strong for the free ligand, was

Table 1
Lead(IV) compounds $Pb(O_2CR^1)_m(O_2CR^2)_n$ available by metathesis with LTA and carboxylic acids

Complex	R^1	m	R^2	n
1	o-PhCOC$_6$H$_4$–	4	—	—
2	p-MeC$_6$H$_4$–	4	—	—
3	p-MeC$_6$H$_4$–	2	Me	2
4	Ph	2	PhCH=CH–	2
5	Ph	3	PhCH=CH–	1
6	Ph	2	C$_6$H$_{11}$–	2
7	Ph	3	C$_6$H$_{11}$–	1
8	Ph	2	o-PhCOC$_6$H$_4$–	2
9	Ph	3	o-PhCOC$_6$H$_4$–	1

absent, and in the ^{13}C NMR spectra the carboxylate carbonyl was broadened or absent altogether. This is most likely due to the same rapid ligand exchange which has recently been observed by NMR spectroscopy in simpler systems [44]. Of interest, however, was that this ligand exchange was also observed in the [207]Pb NMR spectra; thus, complexes 4–9 all gave multiple signals, corresponding to more than one species in solution. Although these results demonstrated that mixed ligand systems were accessible, it was clear that facile ligand exchange occurred in solution, a phenomenon previously described for lead(IV) carboxylates [37].

Similarly readily available were the complexes obtained from the dicarboxylic acid ligands L^1H_2 and L^2H_2 (Table 2), and [207]Pb NMR spectroscopic analysis again indicated that rapid ligand exchange occurred, even for Rebek's diacid [45] L^2H_2. The large number of resonances which were observed for complex 10 is probably indicative of the presence of oligomeric, in addition to monomeric, species in solution.

Table 2
Lead complexes $PbL_x(O_2CR)_y$ available by metathesis of LTA with carboxylic acids

Complex	L	R	x	y	Complex	L	R	x	y
10	L^1	m-MeOC$_6$H$_4$	1	2	18	L^5	Ph	1	2
11	L^2	Ph	1	2	19	L^6	—	2	0
12	L^3	—	2	0	20	L^6	Me	1	2
13	L^3	Me	1	2	21	L^6	Ph	1	2
14	L^3	Ph	1	2	22	L^7	Ph	1	2
15	L^4	—	2	0	23	L^8	Ph	1	2
16	L^4	Me	1	2	24	L^9	Ph	1	2
17	L^5	—	2	0	25	L^9	p-MeC$_6$H$_4$	1	2

reaction reported to occur at temperatures as low as 50 °C when camphoric acid is treated with LTA and pyridine [47,48], did not occur. In general, all complexes were more stable than LTA, although diacetates 13, 16 and 20 were found to be rather more unstable than the dibenzoates 14, 18, and 21–24. The bis- complexes 12 and 17 were partially chloroform soluble, but 15 was soluble only in DMSO, and all three were very stable. In the case of the complexes 19–21, substantial changes in the ^{1}H NMR spectra were observed upon complexation to lead; for example, in complex 19, the three methyl resonances, originally at δ_H 0.82, 1.24 and 1.25 changed to 0.35, 0.95 and 1.15, and the benzylic protons, appearing as a close pair of doublets ($J = 12$ Hz) in the free ligand ($\Delta\delta = 0.06$ ppm) became separated by 1.21 ppm with similar coupling constants upon complexation. Again, except in the cases of the complexes 17, 22, 24 and 25 where the resonance were broadened, the ^{13}C NMR spectra did not show the carboxylate carbonyl, indicative of rapid ligand exchange [44]. For the complexes which were amenable to [207]Pb NMR spectroscopic investigation due to their favourable solubility or stability (10, 11, 14, 18, 22, 24, 25), the presence of lead species within the characteristic lead(IV) chemical shift range (δ_{Pb} −1883 to −1899 ppm) was readily demonstrated [39]. Although combustion analysis confirmed the stoichiometry of some of the complexes, their solution structure was found by [207]Pb NMR to consist of between two and eight species as a result of a facile ligand equilibration, well known for lead(IV) [37], which was established by careful chemical shift analysis in the [207]Pb NMR spectra [49]. Unfortunately, none of the complexes could be crystallised, thereby precluding more detailed structural analysis.

In view of the ready availability of the simple lead(IV) complexes, the ligands L^3H_2–L^8H_2, readily derived from phthalic or camphoric anhydrides [46], were examined. These systems were of interest since their derived complexes were expected to be of good solubility, and, additionally, ligands L^4H_2–L^8H_2 were chiral with their stereogenic centres close to the chelating carboxylic acid. Commercially available dibenzoyltartarate L^9H_2 was also examined. By using the appropriate stoichiometry of ligands in the metathesis reaction (Scheme 2), lead(IV) bis(dicarboxylates), or (dicarboxylate)diacetates, dibenzoates or di-p-toluates were obtained (Table 2), usually as yellow or pale yellow solids. Under these conditions, decarboxylation [37], a
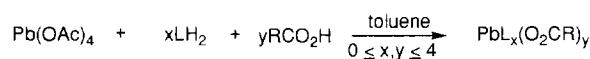
Several of these complexes were much less reactive when treated with allyltributyltin than lead(IV) compounds derived from simple carboxylic acids, a reaction we have recently shown to be extremely facile [39]; the

$$Pb(OAc)_4 \ + \ xLH_2 \ + \ yRCO_2H \xrightarrow[0 \le x,y \le 4]{toluene} PbL_x(O_2CR)_y$$

Scheme 2.

Table 3

Yields and enantiomeric excess for the products according to Scheme 3

Lead complex	26b Yield (%)[a]	27b Yield (%)[a]	27b e.e.[b]	28b Yield (%)[a]	28b e.e.[b]
5	15(36)	—		—	—
6	21(57)	—		—	—
10	15(54)	—		—	—
11	18(48)	—		—	—
14	52(–)	—		—	—
18	62(–)	44	0(–)	—	—
19	< 5(–)	10	12(4)	8	—
20	—	37	8(1)	—	—
21	52(–)	21	8(4)	17	6(4)
22	—	69	10(6)	—	—
24	—	71	4(4)	—	—
25	—	58	4(4)	—	—

[a] Isolated yields (estimated yield from the ^{1}H NMR spectrum of the crude material).

[b] e.e. by chiral shift ^{1}H NMR spectroscopy with Eu(tfc)$_3$ at 250 or 300 MHz by chiral GC (by Chiraldex™ or Lipodex™ column).

complexes 12 and 15 were, in fact, inert, although complex 14 gave allyl benzoate in 14% isolated yield and the same product could be detected by ^{1}H NMR spectroscopy, although was not isolated, for complexes 17, 18 and 21.

The synthetic utility of these complexes was examined in phenylation reactions using the in situ Pinhey arylation protocol [33]. Thus, treatment of the lead complex with phenylboronic acid in the presence of a mercury acetate catalyst in CHCl$_3$ at 40 °C for 1 h followed by overnight stirring, gave the phenyllead tricarboxylate, which was not isolated. This was treated directly with any of the nucleophiles 26a–28a in pyridine and CHCl$_3$ solution (Table 3 and Scheme 3) at 40 °C for 1 h followed by overnight stirring, to give the α-phenylated products 26b–28b in yields ranging from poor to good. The mass balance of these reactions was made up of unreacted starting material, thereby indicating that competitive oxidation of the substrate to give analogous products to those indicated in Scheme 1(b) was not occurring. Compared to the literature procedure using LTA [33], the work-up was sometimes complicated by the need to remove the ligands, although this could generally be achieved by a simple wash with

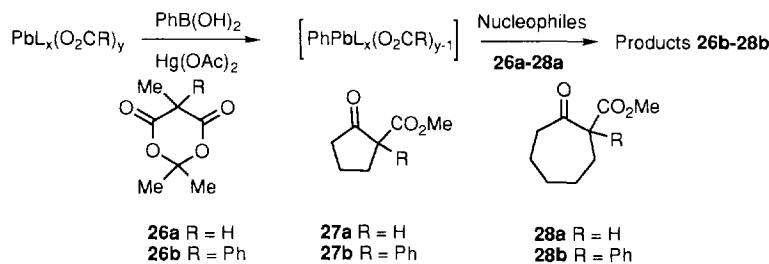Table 4

Phenylations of 27a in the presence of chiral ligands

Ligand (equiv.)	Yield 27b (%)	e.e.[a]
L^{4}H$_2$ (1)	61	0
L^{4}H$_2$ (2)	57	0
L^{6}H$_2$ (1)	28	0
L^{6}H$_2$ (2)	34	0

[a] By chiral shift NMR spectroscopy.

saturated sodium bicarbonate. Methyl Meldrum's acid 26a in some cases gave good yields, although the complex 19 gave a particularly low yield of less than 5% of 26b, in keeping with the lower reactivity which was always observed for such bis(dicarboxylate) complexes. Although the β-ketoester 27a gave in some cases very good yields of the phenylated product 27b, in particular with the complexes 22, 24, and 25, the best e.e. value which was observed was only 12%, and the tartrates 24 and 25 were notable for their very low e.e. values. A major by-product of reactions using complexes derived from the ligand L^{6}H$_2$ was camphoric anhydride, presumably arising by a highly competitive ligand degradation reaction. The more bulky cycloheptyl substrate 28a gave both a low yield and e.e. value with complex 21. The ability to enantioselectively phenylate such substrates would be an important example of the asymmetric creation of a quaternary centre [50], and be of considerable potential for natural product synthesis [51].

Phenylation reactions were also investigated by adding the ligands L^{4}H$_2$ and L^{6}H$_2$ directly to a phenylation reaction mediated by LTA, that is without isolation of the complex. Using either one or two equivalents of these ligands with the nucleophile 27a (Table 4), low to good yields of the product 27b were obtained, but with no enantioselectivity.

The low levels of asymmetric induction which were obtained could be the result of several factors. Firstly, the most successful ligands for many metal-catalysed asymmetric processes are those with chiral centres immediately proximal to the metal cation. This is clearly not possible with carboxylates, and it is feasible that the chiral centres in L^{4}H$_2$–L^{9}H$_2$ are too far removed to exert any influence on the cross coupling reaction. However, there seems to be no a priori reason why

PbL$_x$(O$_2$CR)$_y$ $\xrightarrow[\text{Hg(OAc)}_2]{\text{PhB(OH)}_2}$ [PhPbL$_x$(O$_2$CR)$_{y-1}$] $\xrightarrow[\text{26a-28a}]{\text{Nucleophiles}}$ Products 26b-28b

26a R = H
26b R = Ph

27a R = H
27b R = Ph

28a R = H
28b R = Ph

Scheme 3.

chiral carboxylates should not be successful in asymmetry transfer, and this is supported by the elegant application of chiral rhodium carboxylates pioneered by Doyle et al. [52]. Secondly, the replacement of acetate by other carboxylates results in a substantial stabilisation of the complex and deceleration of the subsequent coupling. This could be due to both electronic stabilisation or steric encumbrance of the lead(IV) by the ligand(s). In fact, the crucial importance of ligand acceleration in asymmetric processes has recently been recognised [30]. Thirdly, the occurrence of extensive ligand equilibration in solution has already been described above. In mixed ligand systems containing both chiral and achiral ligands, this equilibrium will result in the formation of some achiral lead(IV) species in solution. If these species are the most reactive — and this could be a realistic possibility simply on steric grounds — then poor overall asymmetric induction would be expected to be observed. That ligand equilibration is clearly important came from examination of the ^{207}Pb NMR spectrum of the dibenzoate 21. At room temperature, the signals in the spectrum were broad, but at lower temperature (225 K) the spectrum could be resolved into a number of peaks, and the identity of some of these were assigned by comparison to reference samples [49]. Clearly present were $Pb(O_2CPh)_4$, $Pb(OAc)(O_2CPh)_3$, $Pb(OAc)_2(O_2CPh)_2$, $Pb(OAc)_3(O_2CPh)$, and PbL_2^6, in addition to other unidentified species. Which of these species (or indeed any other) is the most reactive in phenylation reactions is unclear, but the presence of so many achiral lead(IV) species may be an important reason for the poor e.e. values which were observed. It appears that a tightly binding chiral ligand which accelerates ligand coupling could be necessary for asymmetric induction.

An attempt was made to isolate the phenyllead tricarboxylate $PhPbL^6(O_2CPh)$, the presumed phenylation intermediate. Therefore, complex 21 was combined with mercury(II) acetate in chloroform, and phenylboronic acid in chloroform was added slowly to this solution. After stirring at 40 °C for 1 h and at room temperature overnight, the solution was filtered through Celite®, and the organic layer washed and concentrated. Petrol was added to the remaining solution and the mixture stored at 0 °C overnight, after which time a white precipitate was formed. Although proton NMR spectroscopy did not allow this compound to be unambiguously identified as the phenyllead compound $PhPbL^6(O_2CPh)$, it was dissolved in chloroform and a solution of methyl 2-oxocyclopentanecarboxylate in pyridine added. The mixture was heated and stirred as normal, and on work-up the phenylated material 27b was isolated in 70% yield.

Thus, we have demonstrated that a range of lead(IV) complexes derived from dicarboxylic acids can be readily isolated as stable compounds, and that these com-

plexes are useful for the creation of new carbon–carbon bonds, although the level of asymmetric induction is very low. This could be due, at least in part, to a highly facile ligand exchange of mixed ligand complexes.

3. Experimental

^{1}H NMR spectra were recorded on Varian Gemini (200 MHz), Bruker AM-200 (200 MHz), Bruker AM-500 (500 MHz) and Bruker AMX-500 (500 MHz) spectrometers. Two-dimensional COSY spectra were recorded on a Bruker AM-500 (500 MHz) spectrometer. Proton chiral shift nuclear magnetic resonance spectra were recorded on Bruker AM-250 (250 MHz) or Bruker AM-300 (300 MHz) spectrometers. The shift reagent used was $Eu(tfc)_3$ (tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato], europium(III) derivative), 0.5 equiv. being added to separate enantiomers of methyl 1-phenyl-2-oxocyclopentanecarboxylate and 0.2 equiv. being added to separate enantiomers of methyl 1-phenyl-2-oxocycloheptanecarboxylate. ^{13}C NMR spectra were recorded on Varian Gemini and Bruker AM-200 (50.3 MHz) and Bruker AM-500 (125.8 MHz) spectrometers. ^{207}Pb NMR spectra were recorded on Bruker AM-250 (52.3 MHz) and Bruker AMX-500 (104.6 MHz) spectrometers using $CDCl_3$ as an internal lock. Chemical shifts are recorded in parts per million from Me_4Pb, using a literature value for LTA [53], and referenced to LTA. Spectra recorded on the Bruker AM-250 spectrometer were recorded at 223 K and 253 K, corresponding to probe temperatures of 208 K and 244 K respectively. Infra-red spectra were recorded using a Perkin–Elmer 1750 FT-IR spectrometer. Low resolution mass spectra (m/z) were recorded on VG Micromass ZAB1F, VG Masslab 20-250 and VG BIO-Q spectrometers using ammonia desorption chemical ionisation (DCI), chemical ionisation (CI) or negative electrospray (ES^-) techniques. Gas chromatography mass spectra (GCMS) were recorded on a VG Trio-1 spectrometer. Microanalyses were performed by the microanalytical service of the Dyson Perrins Laboratory.

Chiral gas chromatography was performed at The Associated Octel Company, Ellesmere Port. Enantiomers of methyl 1-phenyl-2-oxocyclopentanecarboxylate were separated by diluting a few microlitres of sample in 200 μl of EtOH in a vial insert and injecting 0.5 μl into a split injector. Separation was achieved on an FS-Lipodex E column (length 25 m, i.d. 0.25 mm) and determined using an FID detector. A racemic sample was used as the standard. Enantiomers of methyl 1-phenyl-2-oxocycloheptanecarboxylate were separated in a similar way using a Chiraldex Gamma-Cyclodextrin Trifluoroacetyl column (length 10 m, i.d. 0.25 mm).

LTA was obtained containing acetic acid which was not removed prior to use. Toluene was dried by distillation and stored over activated 4 Å molecular sieves.

3.1. General procedure for the preparation of lead(IV) complexes

LTA (1 equiv.) and the carboxylic acid(s) in the required stoichiometric ratio were combined in dry toluene (20–40 ml) and acetic acid (ca. 1 ml) added to aid dissolution if required. The solvent was removed in vacuo (20–70 mbar, 35 °C) to give a solid which was then redissolved in toluene (20–40 ml) and the solvent was removed in vacuo. This procedure was repeated until complexation was complete (acetate groups no longer present by proton NMR spectroscopy).

3.1.1. Lead(IV) tetra(o-benzoylbenzoate) 1

LTA (0.93 g, 2.1 mmol) and o-benzoylbenzoic acid (1.94 g, 8.40 mmol) were reacted by the general procedure to yield the product 1 as a bright yellow crystalline solid. M.p. 162–169 °C. Found: C, 60.70; H, 3.27. $C_{56}H_{36}O_{12}Pb$ requires C, 60.76; H, 3.24%. ν_{max} (Nujol/cm^{-1}) 1671 m, 1596 m, 1579 m, 1316 m. δ_H (200 MHz, CDCl$_3$) 7.41 (1H, t, $J = 7.4$ Hz, ArH p- to COAr), 7.54 (2H, t, $J = 6.6$ Hz, ArH m- to COAr), 7.62 (2H, d, $J = 6.0$ Hz, ArH o- to COAr), 7.71 (2H, t, $J = 5.7$ Hz, ArH p-, m- to CO$_2$), 8.09 (2H, d, $J = 7.7$ Hz, ArH o- to CO$_2$ and ArH o- to C=O); δ_C (50.3 MHz, CDCl$_3$) 115.41, 121.93, 124.62, 129.25 and 129.81 (ArC), 159.81 (C=O), 175.50 (CO_2).

3.1.2. Lead(IV) tetra(p-toluate) 2

LTA (0.93 g, 2.1 mmol) was reacted with p-toluic acid (1.14 g, 8.40 mmol) by the general procedure to yield the product 2 as a pale yellow powder. M.p. 164–167 °C. Found: C, 51.53; H, 3.31. $C_{32}H_{28}O_8Pb$ requires C, 51.40; H, 3.97%. ν_{max} (Nujol/cm^{-1}) 1809 w, 1694 m, 1611 s, 1588 m, 1322 m. δ_H (200 MHz, CDCl$_3$) 2.42 (3H, s, CH_3), 7.26 (2H, d, $J = 6.8$ Hz, ArH), 8.02 (2H, d, $J = 8.1$ Hz, ArH); δ_C (50.3 MHz, CDCl$_3$) 21.74 (CH$_3$), 124.10, 129.49, 132.10, 145.58 (ArC) and 175.50 (CO_2).

3.1.3. Lead(IV) diacetate di-p-toluate 3

LTA (0.44 g, 1.0 mmol) and p-toluic acid (0.28 g, 2.0 mmol) were reacted by the general procedure to yield the product 3 as a yellow/orange solid which decomposed to a brown solid over 2 days. M.p. 162–165 °C. ν_{max} (CHCl$_3$/cm^{-1}) 1757 w, 1708 s, 1610 s, 1587 s, 1430 s, 1425 s; δ_H (200 MHz, CDCl$_3$) 2.20 (6H, s, CH_3CO$_2$), 2.44 (6H, s, ArCH_3), 7.25 (4H, d, $J = 9.4$ Hz, ArH), 8.00 (4H, d, $J = 9.4$ Hz, ArH); δ_C (50.3 MHz, CDCl$_3$) 17.95 and 21.74 (CH$_3$), 129.51 and 132.21 (ArC), 145.70 (CO_2).

3.1.4. Lead(IV) dibenzoate dicinnamate 4

LTA (0.443 g, 1.00 mmol), benzoic acid (0.244 g, 2.00 mmol) and cinnamic acid (0.296 g, 2.00 mmol) were reacted by the general procedure to give the product 4 as a moisture-stable, yellow solid. M.p. 60–63 °C. Found: C, 51.85; H, 3.06. $C_{32}H_{24}O_8Pb$ requires C, 51.68; H, 3.25%. ν_{max} (Nujol/cm^{-1}) 1690 m, 1632 s, 1592 m, 1578 m, 1496 s, 1251 s, 1204 m, 1177 m, 1070 m, 1025 m, 979 m, 884 m, 775 m, 720 s, 696 s, 684 s. δ_H (200 MHz, CDCl$_3$) 6.48 (2H, d, $J = 16.0$ Hz, 2 × PhCH=CHCO$_2$), 7.18–7.56 (16H, m, 2 × C_6H_5CH=CHCO$_2$, 4 × m- and 2 × p-C_6H_5CO$_2$), 7.81 (2H, d, $J = 16.0$ Hz, PhCH=CHCO$_2$), 8.12 (4H, d, $J = 7.5$ Hz, 4 × o-C_6H_5CO$_2$); δ_C (50.3 MHz, CDCl$_3$) 128.5 (CH), 128.8 (CH), 131.4 (CH), 134.2 (CH); δ_{Pb}(52.3 MHz, CDCl$_3$, 223 K) −1882.9, −1886.8, −1890.5, −1893.9, −1897.2.

3.1.5. Lead(IV) tribenzoate monocinnamate 5

LTA (0.443 g, 1.00 mmol), benzoic acid (0.366 g, 3.00 mmol) and cinnamic acid (0.148 g, 1.00 mmol) were reacted by the general procedure to give the product 5 as a moisture-stable, yellow powder. M.p. 112–114 °C. Found: C, 50.23; H, 2.51. $C_{30}H_{22}O_8Pb$ requires C, 50.20; H, 3.09%. ν_{max} (Nujol/cm^{-1}) 1696 m, 1633 m, 1601 m, 1593 m, 1498 m, 1456 s, 1412 s, 1378 s, 1307 m, 1255 m, 1177 m, 1162 m, 1071 m, 1026 m, 885 m, 766 m, 716 s, 696 m, 683 m. δ_H (200 MHz, CDCl$_3$) 6.49 (1H, d, $J = 16.0$ Hz, PhCH=CHCO$_2$), 7.40–7.67 (14H, m, C_6H_5CH=CHCO$_2$ and 6 × m- and 3 × p-C_6H_5CO$_2$), 7.92 (1H, d, $J = 16.0$ Hz, PhCH=CHCO$_2$), 8.15 (6H, d, $J = 7.5$ Hz, 6 × o-C_6H_5CO$_2$); δ_C (50.3 MHz, CDCl$_3$) 128.78 (CH), 129.19 (CH), 131.30 (CH), 132.07 (CH), 134.57 (CH); δ_{Pb} (52.3 MHz, CDCl$_3$, 223 K) −1885.8, −1889.4, −1892.8, −1896.2.

3.1.6. Lead(IV) dibenzoate dicyclohexanecarboxylate 6

LTA (0.443 g, 1.00 mmol), benzoic acid (0.244 g, 2.00 mmol) and cyclohexanecarboxylic acid (0.256 g, 2.00 mmol) were reacted by the general procedure to give the product 6 as a moisture-stable, pale yellow crystalline solid. M.p. 128–129 °C. Found: C, 48.12; H, 4.24. $C_{28}H_{32}O_8Pb$ requires C, 47.79; H, 4.58%. ν_{max} (Nujol/cm^{-1}) 1704 s, 1593 s, 1525 s, 1462 s, 1410 s, 1377 s, 1178 s, 1070 m, 1025 s, 949 m, 883 s, 810 m, 778 m, 719 s, 694 s. δ_H (200 MHz, CDCl$_3$) 1.27–1.36 (6H, m, 6 × alicyclic protons), 1.51–1.76 (14H, m, 14 × alicyclic protons), 2.54–2.64 (2H, m, 2 × CHCO$_2$), 7.48 (4H, t, $J = 7.5$ Hz, 4 × m-C_6H_5CO$_2$), 7.64 (2H, t, $J = 7.5$ Hz, 2 × p-C_6H_5CO$_2$), 8.13 (4H, d, $J = 7.0$ Hz, 2 × o-C_6H_5CO$_2$); δ_C (50.3 MHz, CDCl$_3$) 25.22 (CH_2), 25.46 (CH_2), 29.66 (CH_2), 128.75 (CH), 131.90 (CH), 134.47 (CH); δ_{Pb} (52.3 MHz, CDCl$_3$, 223 K) −1877.6, −1883.0, −1887.9, −1892.4, −1896.4.

3.1.7. Lead(IV) tribenzoate monocyclohexanecarboxylate 7

LTA (0.443 g, 1.00 mmol), benzoic acid (0.366 g, 3.00 mmol) and cyclohexanecarboxylic acid (0.128 g, 1.00 mmol) were reacted by the general procedure to give the product 7 as a moisture-stable, pale yellow solid. M.p. 161 °C. Found: C, 48.04; H, 3.54. $C_{28}H_{26}O_8Pb$ requires C, 48.20; H, 3.76%. ν_{max} (Nujol/cm^{-1}) 1688 m, 1600 m, 1525 s, 1498 s, 1461 s, 1405 s, 1378 s, 1179 m, 884 s, 720 s, 695 s. δ_H (200 MHz, CDCl$_3$) 1.26–1.40 (3H, m, 3 × alicyclic protons), 1.58–1.76 (5H, m, 5 × alicyclic protons), 1.96–2.03 (2H, m, 2 × ring protons), 2.54–2.65 (1H, m, CHCO_2), 7.47 (6H, t, $J = 7.5$ Hz, 6 × m-C$_6$H$_5$CO$_2$), 7.63 (3H, t, $J = 7.5$ Hz, 3 × p-C$_6$H$_5$CO$_2$), 8.13 (6H, d, $J = 7.5$ Hz, 6 × o-C$_6$H$_5$CO$_2$); δ_C (50.3 MHz, CDCl$_3$) 25.33 (CH$_2$), 25.55 (CH$_2$), 29.84 (CH$_2$), 128.60 (CH), 131.95 (CH), 134.45 (CH); δ_{Pb} (52.3 MHz, CDCl$_3$, 223 K) −1883.1, −1887.9, −1892.4, −1896.3.

3.1.8. Lead(IV) dibenzoate di-o-benzoylbenzoate 8

LTA (0.100 g, 0.23 mmol), benzoic acid (0.055 g, 0.45 mmol) and o-benzoylbenzoic acid (0.102 g, 0.45 mmol) were reacted by the general procedure to give the product 8 as a moisture-stable, yellow solid. M.p. 166–167 °C. Found: C, 56.21; H, 2.98. $C_{42}H_{28}O_{10}Pb$ requires C, 56.06; H, 3.14%. ν_{max} (CHCl$_3$/cm^{-1}) 1762 s, 1600 m, 1581 m, 1497 m, 1450 m, 1412 s, 1285 m, 1180 w, 1027 w, 936 m, 892 m, 770 m, 705 m, 697 m, 687 m. δ_H (200 MHz, CDCl$_3$) 6.75–6.89 (2H, m, 2 × ArCH), 7.06 (4H, t, $J = 7.0$ Hz, 4 × ArCH), 7.37–7.71 (16H, m, 16 × ArCH), 7.74–8.12 (6H, m, 6 × ArCH); δ_C (50.3 MHz, CDCl$_3$) 127.86 (CH), 128.05 (CH), 128.35 (CH), 128.96 (CH), 129.49 (CH), 131.91 (CH), 132.17 (CH), 132.62 (CH), 133.72 (CH), 134.24 (CH), 136.85 (ArC), 142.91 (ArC), 174.86 (C=O, broad), 196.26 (C=O, broad); δ_{Pb} (52.3 MHz, CDCl$_3$, 223 K) −1895.7, −1901.5, −1906.9, −1912.0.

3.1.9. Lead(IV) tribenzoate mono-o-benzoylbenzoate 9

LTA (0.443 g, 1.00 mmol), benzoic acid (0.366 g, 3.00 mmol) and o-benzoylbenzoic acid (0.226 g, 1.00 mmol) were reacted by the general procedure to give the product 9 as a moisture-stable, yellow solid. M.p. 137–140 °C. Found: C, 52.69; H, 2.79. $C_{35}H_{24}O_9Pb$ requires C, 52.83; H, 3.04%. ν_{max} (Nujol/cm^{-1}) 1678 m, 1594 w, 1526 m, 1462 m, 1378 m, 1282 m, 1178 w, 1071 w, 1026 w, 934 w, 886 w, 770 w, 720 m, 696 m, 684 m. δ_H (200 MHz, CDCl$_3$) 7.18–7.64 (16H, m, 16 × ArCH), 7.95–8.15 (8H, m, 8 × ArCH); δ_C (50.3 MHz, CDCl$_3$) 127.47 (CH), 128.60 (CH), 128.82 (CH), 129.61 (CH), 131.22 (CH), 131.32 (CH), 133.20 (CH), 134.05 (CH), 137.36 (ArC); δ_{Pb} (52.3 MHz, CDCl$_3$, 223 K) −1895.2, −1900.8.

3.1.10. Lead(IV) di-m-methoxybenzoate monopimelate 10

LTA (0.443 g, 1.00 mmol), m-methoxybenzoic acid (0.304 g, 2.00 mmol) and pimelic acid L^1H_2 (0.160 g, 1.00 mmol) were reacted by the general procedure to give the product 10 as a moisture-stable, bright yellow solid. M.p. 76–82 °C. Found: C, 41.20; H, 3.30. $C_{23}H_{24}O_{10}Pb$ requires C, 41.38; H, 3.62%. ν_{max} (Nujol/cm^{-1}) 1700 s, 1601 s, 1587 s, 1532 s, 1321 s, 1286 s, 1246 s, 1184 s, 1127 s, 1114 s, 1077 s, 995 m, 935 m, 921 m, 874 m, 823 s, 762 s. δ_H (200 MHz, CDCl$_3$) 1.40–1.55 (2H, m, CH_2), 1.65–1.80 (4H, m, 2 × CH_2), 2.40–2.55 (4H, m, 2 × CH_2), 3.83 (6H, s, 2 × OCH_3), 7.15–7.24 (2H, m, 2 × CH), 7.38 (2H, t, $J = 8.0$ Hz, 2 × CH), 7.62 (2H, s, 2 × CH), 7.72 (2H, d, $J = 8.0$ Hz, 2 × C(4)H); δ_C (50.3 MHz, CDCl$_3$) 25.26 (CH$_2$), 28.18 (CH$_2$), 31.71 (CH$_2$), 55.51 (OCH$_3$), 115.46 (CH), 121.97 (CH), 124.59 (CH), 128.02 (C(3)), 129.88 (CH), 160.08 (C(1)), 175.98 (ArCO$_2$), 183.55 (pimelate C=O); δ_{Pb} (52.3 MHz, CDCl$_3$, 223 K) −1868.7, −1875.8, −1881.7, −1882.9, −1887.1, −1889.0, −1894.7, −1900.2.

3.1.11. Lead(IV) dibenzoate mono(2,7-di-t-butyl-9,9-dimethyl-4,5-xanthenedicarboxylate) 11

LTA (0.443 g, 1.00 mmol), 2,7-di-t-butyl-9,9-dimethyl-4,5-xanthenedicarboxylic acid [45] L^2H_2 (0.410 g, 1.00 mmol) and benzoic acid (0.244 g, 2.00 mmol) were reacted by the general procedure to give the product 11 as a yellow solid. M.p. 182–185 °C. ν_{max} (Nujol/cm^{-1}) 1723 s, 1602 br s, 1531 s, 1264 s, 1176 s, 1124 s, 1070 m, 1026 m, 938 m, 886 m, 860 m, 796 m, 722 s, 695 s. δ_H (200 MHz, CDCl$_3$) 1.35 (18H, s, 2 × C(CH_3)$_3$), 1.66 (6H, s, C(CH_3)$_2$), 7.47 (4H, t, $J = 7.5$ Hz, 4 × ArH), 7.59–7.80 (4H, m, 4 × ArH), 8.17 (6H, m, 6 × ArH); δ_C (50.3 MHz, CDCl$_3$) 31.20 (C(CH$_3$)$_3$), 32.39 (2 × CH$_3$), 34.39 (4°C), 34.61 (4°C), 128.76 (CH), 130.10 (CH), 130.30 (CH), 132.20 (CH), 134.60 (CH), 147.01 (ArC); δ_{Pb} (52.3 MHz, CDCl$_3$, 223 K) −1879.8, −1884.4, −1886.8, −1890.5, −1895.2.

3.1.12. Lead(IV) bis[1,1'-(benzene-1,4-dimethyl)diphthalate] 12

LTA (0.20 g, 0.46 mmol) and 1,1'-(benzene-1,4-dimethyl)diphthalate [46] L^3H_2 (0.40 g, 0.92 mmol) were reacted by the general procedure to give the product 12 as a pale yellow solid. M.p. 105–110 °C (decomp.). ν_{max} (Nujol/cm^{-1}) 1724 s, 1581 w, 1536 m, 1285 s, 1123 m and 1075 m. δ_H (200 MHz, CDCl$_3$) 5.40 (8H, s, ArH) 7.49–7.69 (20H, m, ArH) and 7.99–8.03 (4H, d, $J = 7.5$ Hz, ArH).

3.1.13. Lead(IV) [1,1'-(benzene-1,4-dimethyl)diphthalate] diacetate 13

LTA (0.20 g, 0.46 mmol) and 1,1'-(benzene-1,4-dimethyl)diphthalate [46] L^3H_2 (0.20 g, 0.46 mmol) were

reacted by the general procedure to give the product **13** as a pale brown solid which began to decompose immediately in the solid state and in solution. δ_H (200 MHz, CDCl$_3$) 2.16 (6H, s, 2 × CH_3), 5.40 (4H, s, 2 × CH_2), 7.54–7.65 (10H, m, ArH), 8.00 (2H, d, $J = 7.5$ Hz, ArH).

3.1.14. Lead(IV) [1,1'-(benzene-1,4-dimethyl)diphthalate] dibenzoate 14

LTA (0.22 g, 0.50 mmol), 1,1'-(benzene-1,4-dimethyl)diphthalate [46] **L^{3}H$_2$** (0.22 g, 0.50 mmol) and benzoic acid (0.12 g, 1.00 mmol) were reacted by the general procedure to give the product **14** as a yellow solid. M.p. 115–118 °C. ν_{max} (Nujol/cm^{-1}) 1728 s, 1600 w, 1530 s, 1284 m, 1123 m and 1074 s. δ_H (200 MHz, CDCl$_3$) 5.39 (4H, s, 2 × CH_2), 7.43–7.87 (16H, m, ArH), 8.01 (2H, d, $J = 7.0$ Hz, ArH) and 8.13 (4H, d, $J = 7.0$ Hz, ArH); δ_{Pb} (52.3 MHz, CDCl$_3$, 253 K) − 1889.92 and − 1893.30.

3.1.15. Lead(IV) bis[(1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylate] 15

LTA (0.20 g, 0.46 mmol) and (1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid [46] **L^{4}H$_2$** (0.20 g, 1.00 mmol) were reacted by the general procedure to give a crude product which was washed with Et$_2$O (3 × 10 ml) to give the product **15** as a white powder. M.p. > 250 °C. Found: C, 39.90; H, 4.89. C$_{20}$H$_{28}$O$_8$Pb requires C, 39.79; H, 4.67%. ν_{max} (Nujol/cm^{-1}) 1541 s, 1300 m, 1171 w and 1129 w. δ_H (500 MHz, d_6-DMSO, 373 K) 0.94, 1.14, 1.24 (3 × 6H, 3 × s, 6 × CH_3), 1.63–1.70 (2H, m, CH_2), 1.96–2.05 (4H, m, 2 × CH_2), 2.37–2.43 (2H, m, CH_2) and 2.52 (2H, t, $J = 9.8$ Hz, 2 × CH).

3.1.16. Lead(IV) bis[(1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid di(3-hydroxybenzoic acid) ester] 17

LTA (0.20 g, 0.45 mmol) and (1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid di(3-hydroxybenzoic acid) ester [46] **L^{5}H$_2$** (0.40 g, 0.91 mmol) were reacted by the general procedure, and the crude product washed with Et$_2$O (3 × 10 ml) to give the product **17** as a yellow solid. M.p. 133–135 °C (decomp.). Found: C, 53.45; H, 4.16. C$_{48}$H$_{44}$O$_{16}$Pb requires C, 53.18; H, 4.09%. ν_{max} (Nujol/cm^{-1}) 1752 s, 1536 w, 1209 s, 1140 s, 1115 m and 1079 m. δ_H (500 MHz, d_6-DMSO) 1.04 (6H, s, 2 × CH_3), 1.42 (6H, s, 2 × CH_3), 1.45 (6H, s, 2 × CH_3), 1.64–1.69 (2H, m, 2 × C(5)H), 1.98–2.05 (2H, m, 2 × C(4)H), 2.15–2.22 (2H, m, 2 × C(4)H), 2.56–2.62 (2H, m, 2 × C(5)H), (C(3)H obscured by DMSO peak), 7.31–7.35 (4H, m, 4 × C(4')H), 7.53 (4H, t, $J = 7.9$ Hz, 4 × C(2')H), 7.58–7.62 (4H, m, 4 × C(5')H) and 7.82 (4H, d, $J = 7.8$ Hz, 4 × C(6')H); δ_C (125.8 MHz, CDCl$_3$) 21.27, 21.46 (4 × CH_3), 22.39 (2 × C(4)), 23.08 (2 × CH_3), 32.32 (2 ×

C(5)), 47.00 (2 × C(2)), 52.22 (2 × C(3)), 56.24 (2 × C(1)), 122.20, 125.37, 126.62, 129.72 (ArCH), 137.10 (C(3')), 150.44 (C(1')), 169.28 (CO$_2$Pb), 172.26, 173.76 (CO$_2$Ar) and 175.00 (CO$_2$Pb).

3.1.17. Lead(IV) [(1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid di(3-hydroxybenzoic acid) ester] dibenzoate 18

LTA (0.13 g, 0.29 mmol), (1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid di(3-hydroxybenzoic acid) ester [46] **L^{5}H$_2$** (0.13 g, 0.29 mmol) and benzoic acid (0.07 g, 0.58 mmol) were reacted according to the general procedure to give the product **18** as a yellow solid. M.p. 153–154 °C (decomp.). Found: C, 48.56; H, 3.83. C$_{38}$H$_{32}$O$_{12}$Pb requires C, 51.40; H, 3.63%. $[\alpha]_D^{24}$ +0.36 (c 0.28 in CHCl$_3$). ν_{max} (Nujol/cm^{-1}) 1753 s, 1601 w, 1535 s, 1309 m, 1212 s, 1116 s and 1078 m. δ_H (200 MHz, CDCl$_3$) 1.12, 1.43, 1.49 (3 × 3H, 3 × s, 3 × CH_3), 1.59–1.84 (1H, m, C(5)H), 1.87–2.15 (1H, m, C(4)H), 2.15–2.52 (1H, m, C(4)H), 2.57–2.89 (1H, m, C(5)H), 3.12 (1H, t, $J = 9.0$ Hz, C(3)H), 7.36–7.77 (10H, m, ArH), 7.89 (2H, s, ArH), 8.04 (2H, d, $J = 7.5$ Hz, ArH) and 8.14 (4H, d, $J = 7.5$ Hz, ArH o-to CO$_2$Pb); δ_C (50.3 MHz, CDCl$_3$) 21.62 (2 × CH_3), 22.49 (C(4)), 23.07 (CH_3), 32.61 (C(5)), 47.43 (C(2)), 52.66 (C(3)), 56.57 (C(1)), 125.23, 128.15, 128.82, 129.62, 129.96, 132.19, 134.75 (ArC and ArCH), 150.84, 150.92 (2 × C(1')) and 172.38, 174.06 (CO$_2$Ar); δ_{Pb} (52.3 MHz, CDCl$_3$, 223 K) − 1895.40, − 1896.12, − 1897.51, − 1899.09, and − 1900.30.

3.1.18. Lead(IV) bis[3,3'-(benzene-1,4-dimethyl)di[(1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylate]] 19

LTA (0.22 g, 0.50 mmol) and 3,3'-(benzene-1,4-dimethyl)di[(1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylate] [46] **L^{6}H$_2$** (0.50 g, 1.00 mmol) were reacted according to the general procedure to give the product **19** as a yellow solid. $[\alpha]_D^{22}$ − 3.78 (c 0.98 in CHCl$_3$). ν_{max} (Nujol/cm^{-1}) 1733 w, 1306 s, 1156 m and 973 m. δ_H (500 MHz, CDCl$_3$) 0.35, 0.98, 1.15 (3 × 12H, 3 × s, 12 × CH_3), 1.56–1.64 (4H, m, 4 × C(5)H), 1.74–1.93 (4H, m, 4 × C(4)H), 2.23–2.36 (4H, m, 4 × C(4)H), 2.39–2.46 (4H, m, 4 × C(5)H), 2.70 (4H, t, $J = 9.1$ Hz, 4 × C(3)H), 4.59 (4H, d, $J = 11.3$ Hz, 4 × C(8)H), 5.80 (4H, d, $J = 11.3$ Hz, 4 × C(8)H) and 7.46 (8H, s, ArH).

3.1.19. Lead(IV) [3,3'-(benzene-1,4-dimethyl)di[(1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylate]] diacetate 20

LTA (0.22 g, 0.5 mmol) and 3,3'-(benzene-1,4-dimethyl)di[(1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylate] [46] **L^{6}H$_2$** (0.25 g, 0.5 mmol) were reacted by the general procedure to give the product **20** as a yellow solid which decomposed rapidly in the solid

state and in solution. δ_H (200 MHz, CDCl$_3$) 0.34 (6H, s, 2 × CH_3), 0.97 (6H, s, 2 × CH_3), 1.01–1.28 (10H, m, 2 × CH_3 and 2 × CH_2), 1.56–2.86 (12H, m, 2 × CO$_2$CH_3 and 2 × CH_2), 4.56–4.68 (2H, m, 2 × C(8)H), 5.74–5.83 (2H, m, 2 × C(8)H) and 7.35–7.46 (4H, m, ArH).

3.1.20. Lead(IV) {3,3'-(benzene-1,4-dimethyl)di[(1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylate]} dibenzoate 21

LTA (0.22 g, 0.50 mmol), 3,3'-(benzene-1,4-dimethyl)di[(1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylate] [46] L^{6}H$_2$ (0.25 g, 0.50 mmol) and benzoic acid (0.12 g, 1.00 mmol) were reacted by the general procedure to give the product 21 as a yellow foam. $[\alpha]_D^{22}$ +3.02 (c 1.00 in CHCl$_3$). δ_H (500 MHz, CDCl$_3$) 0.36–0.43 (6H, m, 2 × CH_3), 0.98–1.28 (12H, m, 4 × CH_3), 1.60–2.85 (10H, m, 2 × C(3)H, 4 × C(4)H and 4 × C(5)H), 4.59–4.72 (2H, m, 2 × C(8)H), 5.11–5.82 (2H, m, 2 × C(8)H), 7.31–7.47 (8H, m, ArH), 7.61 (2H, t, J = 7.4 Hz, ArH) and 8.10 (4H, d, J = 6.8 Hz, ArH).

3.1.21. Lead(IV) {3,3'-(ethylene-1,2-dioxy)di[(1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylate]} dibenzoate 22

LTA (0.16 g, 0.35 mmol), 3,3'-(ethylene-1,2-dioxy)di[(1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylate] [46] L^{7}H$_2$ (0.15 g, 0.35 mmol) and benzoic acid (0.09 g, 0.70 mmol) were reacted by the general procedure to give the product 22 as a yellow hygroscopic solid. $[\alpha]_D^{22}$ +0.20 (c 1.00 in CHCl$_3$). ν_{max} (Nujol/cm^{-1}) 1730 s, 1593 w, 1530 s and 1174 m. δ_H (200 MHz, CDCl$_3$) 0.91 (6H, br, s, 2 × CH_3), 1.27 (12H, br, s, 4 × CH_3), 1.54–1.76 (2H, br, m, 2 × C(5)H), 1.79–2.01 (2H, br, m, 2 × C(4)H), 2.04–2.18 (2H, br, m, 2 × C(4)H), 2.43–2.56 (2H, br, m, 2 × C(5)H), 2.75–2.84 (2H, br, m, 2 × C(3)H), 4.17–4.32 (4H, br, m, 4 × C(8)H), 7.28–7.52 (6H, br, m, ArH) and 7.90–8.13 (4H, br, m, ArH); δ_C (50.3 MHz, CDCl$_3$) 21.17 (2 × CH$_3$), 22.49 (4 × CH$_3$ and C(4)), 33.51 (C(5)), 47.14 (C(2)), 52.27 (C(3)), 56.57 (C(1)), 62.29 (C(8)), 128.68, 131.47, 134.17 (ArC and ArCH), 173.81 (C(7)), 175.14 (br, ArCO$_2$Pb) and 185.29 (br, C(6)); δ_{Pb} (52.3 MHz, CDCl$_3$, 223 K) − 1883.74, − 1887.80, − 1890.20, − 1892.74, and − 1895.32.

3.1.22. Lead(IV) {3,3'-(propylene-1,3-dioxy)di[(1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylate]} dibenzoate 23

LTA (0.18 g, 0.40 mmol), 3,3'-(propylene-1,3-dioxy)di[(1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylate] [46] L^{8}H$_2$ (0.17 g, 0.40 mmol) and benzoic acid (0.10 g, 0.79 mmol) were reacted by the general procedure to give the product 23 as an orange solid. M.p. 101–103 °C (decomp.). Found: C, 49.80; H, 5.31.

C$_{37}$H$_{44}$O$_{12}$Pb requires C, 50.05; H, 5.00%. $[\alpha]_D^{26}$ +17.5 (c 1.02 in CDCl$_3$). ν_{max} (Nujol/cm^{-1}) 1729 s, 1593 w, 1531 m, 1308 m, 1171 s, 884 s and 816 m. δ_H (200 MHz, CDCl$_3$) 0.86–1.02 (6H, br, m, 2 × CH_3), 1.09–1.27 (12H, br, m, 4 × CH_3), 1.39–2.33 (8H, m, 2 × C(5)H, 4 × C(4)H and 2 × C(9)H), 2.45–2.56 (2H, m, 2 × C(5)H), 2.80 (2H, t, J = 9.0 Hz, 2 × C(3)H), 4.06–4.17 (4H, br, m, 4 × C(8)H), 7.33–7.66 (6H, m, ArH) and 8.10 (4H, d, J = 7.0 Hz, ArH); δ_C (50.3 MHz, CDCl$_3$) 21.33, 22.64 (6 × CH$_3$, C(4)), 28.00 (C(9)), 33.65 (C(5)), 47.13 (C(2)), 52.29 (C(3)), 56.50 (C(1)), 60.99 (C(8)), 125.26, 128.19, 128.55, 128.99, 131.64, 134.28 (ArCH and ArC) and 173.54 (C(7)).

3.1.23. Lead(IV) dibenzoyl-L-tartrate dibenzoate 24

LTA (0.22 g, 0.50 mmol), dibenzoyl-L-tartaric acid L^{9}H$_2$ (0.18 g, 0.50 mmol) and benzoic acid (0.12 g, 1.00 mmol) were reacted according to the general procedure to give the product 24 as a yellow solid. M.p. 127–129 °C. Found: C, 47.71; H, 2.27. C$_{32}$H$_{22}$O$_{12}$Pb requires C, 47.70; H, 2.75%. $[\alpha]_D^{22}$ +25.2 (c 1.01 in CHCl$_3$). ν_{max} (Nujol/cm^{-1}) 1735 s, 1693 w, 1600 m, 1414 s, 1260 s and 1241 s. δ_H (200 MHz, CDCl$_3$) 5.02 (1H, br, s, OH), 6.14 (1H, br, s, CH), 7.33–7.84 (12H, m, ArH) and 8.02 (8H, d, J = 7.0 Hz, ArH); δ_C (50.3 MHz, CDCl$_3$) 72.17 (CH), 126.04, 128.32, 128.53, 129.04, 130.13, 131.83, 133.59, 134.46 (ArC and ArCH), 164.72 (PhC=O) and 175.36 (C=O); δ_{Pb} (52.3 MHz, CDCl$_3$, 223 K) − 1890.18 and − 1894.07.

3.1.24. Lead(IV) dibenzoyl-L-tartrate di-p-toluate 25

LTA (0.33 g, 0.75 mmol), dibenzoyl-L-tartaric acid L^{9}H$_2$ (0.27 g, 0.75 mmol) and p-toluic acid (0.20 g, 1.5 mmol) were reacted by the general procedure to give the product 25 as a yellow solid. M.p. 128–130 °C (decarboxylated). Found: C, 48.63; H, 3.19. C$_{34}$H$_{26}$O$_{12}$Pb requires C, 48.98; H, 3.14%. $[\alpha]_D^{22}$ +20.5 (c 1.00 in CHCl$_3$). ν_{max} (Nujol/cm^{-1}) 1734 s, 1604 m, 1587 m, 1413 s, 1261 s and 1241 s. δ_H (200 MHz, CDCl$_3$) 2.38 (6H, s, 2 × CH_3), 6.11 (2H, s, 2 × CH), 7.05–7.49 (10H, m, ArH), 7.74 (4H, br, s, ArH) and 7.99 (4H, d, J = 7.5 Hz, ArH); δ_C (50.3 MHz, CDCl$_3$) 21.76 (2 × CH$_3$), 72.41 (CH), 123.61, 128.50, 129.48, 130.27, 130.38, 132.12, 133.70 (ArC and ArCH), 145.70 (ArCCH$_3$), 165.14 (PhC=O) and 174.85 (C=O); δ_{Pb} (52.3 MHz, CDCl$_3$, 223 K) − 1888.87, − 1891.60 and − 1893.16.

3.2. Reaction of lead(IV) complexes with allyltributyltin [39]

The lead(IV) complex (0.07–0.34 mmol) and allyltributyltin (1 equiv.) were combined in CDCl$_3$ (3 ml) and stirred for 12 h, and the reaction mixture examined by proton NMR spectroscopy. For the reaction of com-

plex **3**, the crude material was purified by silica chromatography (1:1 DCM:petrol) to give allyl benzoate as a colourless oil (7 mg, 14%).

3.3. General procedure for phenylation reactions

Stage 1: the lead(IV) complex (1 equiv.), phenylboronic acid (1 equiv.) and mercury acetate (0.1 equiv.) were dissolved in dry $CHCl_3$ (20–40 ml) and then stirred at 40 °C for 1 h. The resulting cloudy solution was then stirred overnight at room temperature.

Stage 2: the nucleophile (0.91 equiv.) in pyridine (3.03 equiv.) 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 $CHCl_3$ (2 × 25 ml). The combined organic layers were washed with 3 M H_2SO_4 (25–50 ml) and the $CHCl_3$ layer was separated. The aqueous phase was extracted with $CHCl_3$ (2 × 15 ml), the combined organic layers were dried ($MgSO_4$) and the solvent was removed in vacuo to give the crude product.

3.3.1. 5-Phenyl-2,2,5-trimethyl-1,3-dioxane-4,6-dione 26b

The title compound was obtained as a white solid after purification by silica chromatography (DCM). M.p. 133–135 °C. R_f 0.44 (DCM). ν_{max} (Nujol/cm^{-1}) 1776 m, 1735 s, 1302 s, 1159 s and 1070 m. δ_H (200 MHz, CDCl$_3$) 1.28 (3H, s, C(5)CH_3), 1.74, 1.89 (2 × 3H, 2 × s, 2 × C(2)CH_3) and 7.33–7.47 (5H, m, ArH); δ_C (50.3 MHz, CDCl$_3$) 26.22, 27.12, 29.34 (3 × CH$_3$), 55.47 (C(5)), 105.70 (C(2)), 125.88, 129.02, 129.94 (3 × ArCH), 137.20 (ArC) and 167.76 (C=O). m/z (CI, NH$_3$, probe) 252 (82%, MNH$_4^+$), 150 (13), 132 (100), 122 (15), 104 (51) and 76 (83).

3.3.2. Methyl 1-phenyl-2-oxocyclopentanecarboxylate 27b

The title compound was obtained as a colourless oil after purification by silica chromatography (3:1 DCM:petrol, gradient to DCM). R_f 0.34 (DCM). ν_{max} (film/cm^{-1}) 2954 m, 1750 s, 1722 s, 1449 m and 1256 s. δ_H (200 MHz, CDCl$_3$) 1.82–2.13 (2H, m, CH_2), 2.28–2.62 (3H, m, CH_2), 2.83–2.93 (1H, m, CH_2), 3.72 (3H, s, CH_3) and 7.30–7.41 (5H, m, ArH); δ_C (50.3 MHz, CDCl$_3$) 19.19, 34.92, 37.75 (3 × CH$_2$), 53.00 (CH$_3$), 65.05 (C(1)), 127.54, 127.92, 128.78 (3 × ArCH), 136.32 (ArC), 171.52 (CO_2Me) and 211.95 (C=O). m/z (CI, NH$_3$, GCMS) 236 (53%, MNH$_4^+$), 219 (100, MH$^+$), 204 (8), 190 (12) and 159 (13).

3.3.3. Methyl 1-phenyl-2-oxocycloheptanecarboxylate 28b

The title compound was obtained as a white solid after purification by silica chromatography (1:2

Et$_2$O:petrol). M.p. 63–65 °C. R_f 0.43 (1:1 Et$_2$O:petrol). ν_{max} (Nujol/cm^{-1}) 1731 s, 1703 s, 1235 s, 1157 m and 1070 m. δ_H (200 MHz, CDCl$_3$) 1.26–1.97 (6H, m, 3 × CH_2), 2.13–2.25 (1H, m, CH_2), 2.58 (2H, t, J = 6.0 Hz, CH_2), 2.73–2.84 (1H, m, CH_2), 3.70 (3H, s, CH_3) and 7.18–7.41 (5H, m, ArH); δ_C (50.3 MHz, CDCl$_3$) 25.37, 26.36, 30.33, 33.63, 41.86 (5 × CH$_2$), 52.49 (CH$_3$), 68.21 (C(1)), 127.65, 128.63 (2 × ArCH), 139.00 (ArC), 172.86 (CO_2Me) and 208.61 (C=O). m/z (CI, NH$_3$, GCMS) 247 (100%, MH$^+$), 206 (40), 189 (95) and 173 (15).

3.4. Phenylations using LTA with the addition of chiral ligands

LTA (0.75–1.00 mmol), phenylboronic acid (1.00 equiv.) and mercury(II) acetate (0.10 equiv.) were reacted according to stage 1 of the general procedure (Section 3.3); methyl 2-oxocyclopentanecarboxylate (0.13 g, 0.91 mmol) and the ligands L^4H_2 and L^6H_2 (1.00 equiv.) in pyridine (3.03 equiv.) were added and the reaction continued according to stage 2 of the general procedure (Section 3.3). The crude product was purified by silica chromatography (1:4 EtOAc:petrol) to give methyl 1-phenyl-2-oxocyclopentanecarboxylate **27b** as a yellow oil with the yields indicated in Table 4. Chiral shift NMR spectroscopy indicated that the product was racemic.

3.5. Phenylation using phenyllead(IV) {3,3'-(benzene-1,4-dimethyl)di[(1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylate]} monobenzoate

Lead(IV) {3,3'-(benzene-1,4-dimethyl)di[(1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylate]} dibenzoate (0.48 g, 0.5 mmol) **21** and mercury(II) acetate (16 mg, 0.05 mmol) were dissolved in CHCl$_3$ (25 ml) giving a clear yellow solution. To this was added a solution of phenylboronic acid (61 mg, 0.50 mmol) in CHCl$_3$ (10 ml) over 15 min, via a dropping funnel, giving a cloudy solution which was stirred at 40 °C for 1 h and then at room temperature overnight. The reaction mixture was then filtered through Celite®, and the solid was washed with CHCl$_3$ (2 × 30 ml). The CHCl$_3$ filtrate was washed with water (40 ml) and the aqueous layer was extracted with CHCl$_3$ (2 × 80 ml). The combined organic layers were filtered through Celite® and concentrated to 50 ml in vacuo. The solution was diluted with petrol (300 ml) and left to stand at 0 °C overnight. This solution was filtered to give phenyllead(IV) {3,3'-(benzene-1,4-dimethyl)di[(1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylate]} monobenzoate as a white solid (61 mg, 13%). A satisfactory proton NMR spectrum of this product could not be obtained, but the crude material was taken on to the next stage of the reaction.

The complex (20 mg, 0.02 mmol) was dissolved in $CHCl_3$ (10 ml) and a solution of methyl 2-oxocyclopentanecarboxylate (3 mg, 0.02 mmol) and pyridine (5 mg, 0.06 mmol) in $CHCl_3$ (5 ml) added. The resulting solution was heated at 40 °C for 1 h and then at room temperature overnight. The organic layer was then washed with 2 M HCl (25 ml) and water (25 ml), dried ($MgSO_4$) and the solvent was removed in vacuo. Proton NMR spectroscopy of the crude material (11 mg) showed ca. 3 mg of this to be methyl 1-phenyl-2-oxocyclopentanecarboxylate **27b** (70%), giving around 10% yield over two steps.

Acknowledgements

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