Mechanism of arylation of nucleophiles by aryllead triacetates. Part 3. Concerning their reaction with phenols and X-ray molecular structure of p-methoxyphenyllead triacetate

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(6-Methoxy-2,3,4-trimethylphenyl)phenyllead diacetate 17, the methyl ether of one of the two possible intermediates in the ortho phenylation of 3,4,5-trimethylphenol by phenyllead triacetate, is synthesised and shown to be unchanged in $CHCl_3$–pyridine at 60 °C even after 6 days, thus excluding diaryllead diacetates as intermediates in this supposed ligand coupling process. A study of the arylation of a number of methyl substituted phenols by p-methoxyphenyllead triacetate shows that, in general, the rate of ortho arylation increases with methyl substitution; however, ortho methyl groups have a much greater effect than those in the meta and para positions. These results support the view that the arylation of phenols proceeds by an initial ligand exchange (or ligand exchange and pseudorotation) to produce an intermediate in which π-donation by the aryloxy ligand and electron release to the ortho position(s) are important factors. Phenols which are poor π-donors do not undergo the reaction.

In Part 1 of this series[1] we addressed the possibility that the C-arylation of nucleophiles such as β-dicarbonyl compounds, nitroalkanes and phenols may be proceeding by a mechanism involving aryl free radicals. Such a pathway appeared to be a distinct possibility if an initial electron transfer from the nucleophile to the aryllead triacetate were to occur. In that work we employed the o-allyloxyphenyllead compound 1, and could find no evidence for the formation of dihydrobenzofuran derivatives which would result from the intramolecular trapping of such a radical. For example, the aryllead compound 1 reacted with mesitol (2,4,6-trimethylphenol) 2 under our usual arylation conditions to give the 6-arylcyclohexa-2,4-dienone 3 (Scheme 1) in 50% yield.
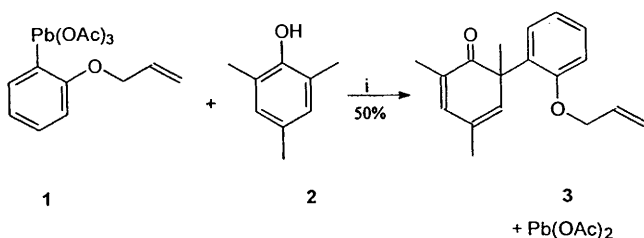
Scheme 1 Reagents and conditions: i, $CHCl_3$, pyridine, 40 °C, 20 h

With the exclusion of the involvement of aryl free radicals, a search for evidence for ligand coupling[2] pathways has been undertaken. In the case of phenol arylation by aryllead triacetates, attempts to observe an intermediate which might be involved in such a coupling have been fruitless.[3,4] Other attempts have been directed towards the detection of an intermediate in β-dicarbonyl arylation with similar results; however, here indirect evidence for ligand coupling has been obtained.[5] This derived from the reactions of the silyl enol ethers of a number of alkyl phenyl ketones with p-methoxyphenyllead triacetate 4 as shown in Scheme 2. The products of these reactions, the diorganolead diacetates 5, were thermally unstable at 60 °C (except where $R^1 = R^2 = H$) yielding the α-arylated ketone 6, which in some cases was accompanied by the corresponding α-acetoxy ketone 7. In keeping with the hypothesis that intermediates similar to compound 5 were involved in β-dicarbonyl arylation, their thermal instability increased in the series 5 ($R^1 = R^2 = H$) < 5 ($R^1 = Me, R^2 = H$) < 5 ($R^1 = R^2 = Me$), and free radical intermediates were shown not to be involved.[5]
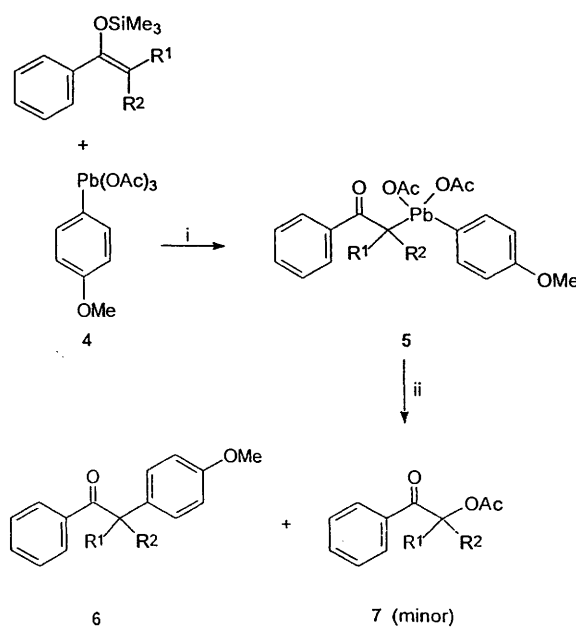

Scheme 2 Reagents and conditions: i, BF_3·Et_2O; ii, $CHCl_3$, 60 °C

Results and discussion

In our initial study of the ortho arylation of methyl substituted phenols, where we employed a 1 : 1 ratio of aryllead triacetate to the phenol, we found that unless both ortho positions were substituted by methyl groups the reaction was quite slow and yields were low.[3] In more recent work, during a search for an intermediate in this arylation, Barton and his colleagues found that 3,5-di-tert-butylphenol underwent slow diarylation to yield terphenyls of structure 11 if four equivalents of aryllead compound were employed[4] (Scheme 3). In the light of this work and our earlier findings concerning the effect of the number and positions of methyl groups on the rate of the arylation reaction, we have examined the reactions of 3,5-dimethylphenol 9 and 3,4,5-trimethylphenol 10 with p-methoxyphenyllead triacetate 4.

Not surprisingly, under the more forcing conditions employed with 3,5-di-tert-butylphenol, diarylation occurred with both phenols, 9 and 10, to produce the terphenyls 12 and
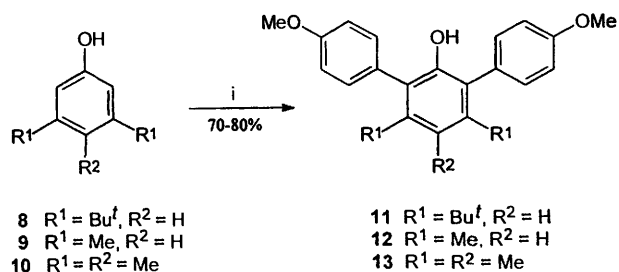
Scheme 3 Reagents and conditions: i, p-MeOC$_6$H$_4$Pb(OAc)$_3$, CHCl$_3$, pyridine

8 R^1 = Bu^t, R^2 = H
9 R^1 = Me, R^2 = H
10 R^1 = R^2 = Me

11 R^1 = Bu^t, R^2 = H
12 R^1 = Me, R^2 = H
13 R^1 = R^2 = Me

13, respectively, in good yield (80 and 70% respectively). Just as with 3,5-di-*tert*-butylphenol, the rate of the second arylation was similar to that of the initial reaction, and therefore these reactions were only useful for producing the symmetrical terphenyls 11. Interestingly, there was no evidence for diarylation at the same *ortho* position, which would have resulted in formation of a 6,6-diarylcyclohexa-2,4-dienone. The relatively high reactivity of 3,4,5-trimethylphenol to arylation made it a particularly useful substrate with which to probe further the mechanism of phenol arylation. There appeared to be two possible intermediates, 14 and 15, which could be involved in the arylation of phenol 10 by a ligand coupling pathway, and a route to the latter seemed possible by our recently reported general synthesis of diaryllead diacetates.[6]

The compound we chose for our initial study was the methyl ether 17 rather than the corresponding phenol, the synthesis of which would have been less straightforward. Its synthesis was readily achieved by treating the arylboronic acid 16 with phenyllead triacetate as outlined in Scheme 4. The diaryllead

14

15

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17
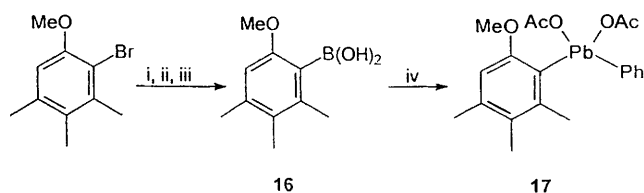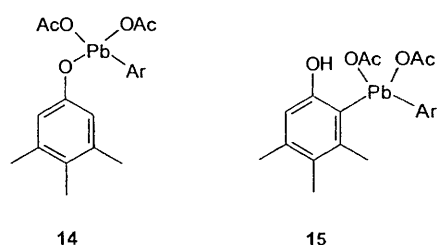
Scheme 4 Reagents and conditions: i, BuLi, −78 °C; ii, B(OPr^i)$_3$, −78 °C; iii, H$_2$O; iv, PhPb(OAc)$_3$, CHCl$_3$

compound 17 failed to yield a biaryl under the usual arylation conditions (chloroform–pyridine at 30 °C) and was unchanged even when kept at 60 °C for 6 days. Therefore, we believe the phenol arylation proceeds by a ligand coupling mechanism within an intermediate of type 14.

A number of single-crystal X-ray analyses of Pb^{IV} compounds,[5,7,8] including that of p-methoxyphenyllead triacetate 4 (see below), have shown that the central Pb atom is generally heptacoordinate with approximate pentagonal bipyramidal geometry, and, therefore, we propose that phenol arylation proceeds by an initial ligand exchange, or ligand exchange followed by a pseudorotation, to give an intermediate in which the aryl group occupies an axial position and the aryloxy ligand has an equatorial configuration (see Scheme 5). In such a structure the π systems of the two aromatic rings can overlap, and a ligand coupling at the *ortho* position of the aryloxy group is then possible, to yield an *o*-arylphenol *via* an
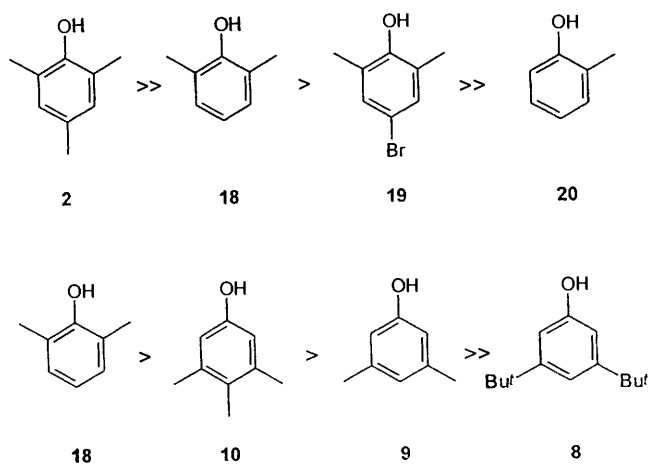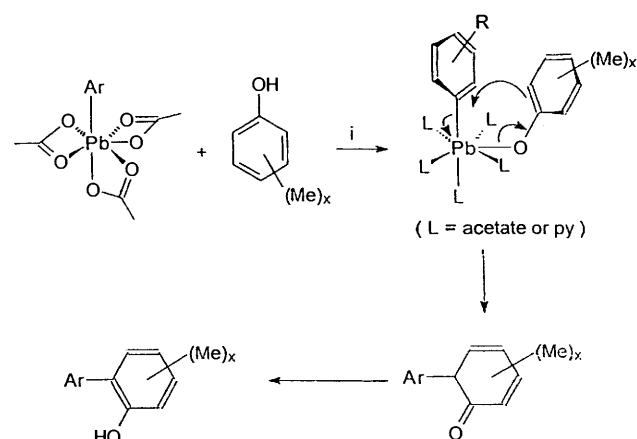
Fig. 1 Reactivity of phenols to *ortho* arylation by p-methoxyphenyllead triacetate

2   18   19   20

18   10   9   8

(L = acetate or py)

Scheme 5 Reagents and conditions: i, CHCl$_3$, pyridine

intermediate dienone. An electrophilic arylation of this type would be expected to proceed most readily with phenols which were good π donors, and we have examined a range of methyl substituted phenols to determine whether this is so. The first series of compounds examined were the four phenols, 2, 18, 19 and 20. Each was reacted with p-methoxyphenyllead triacetate 4 in chloroform–pyridine under a standard set of conditions, and showed the order of reactivity indicated in Fig. 1. Mesitol 2 had reacted completely in less than 1 h, to give the 6-arylcyclohexa-2,4-dienone in high yield, while *o*-cresol (2-methylphenol) 20 reacted very slowly; it was 85% unreacted after 5 h, and from the ^{1}H NMR spectrum of the reaction mixture it appeared that a mixture of approximately equal amounts (< 10% in total) of products arising from arylation at the two *ortho* positions had been formed. 2,6-Dimethylphenol 18 and 4-bromo-2,6-dimethylphenol 19 showed reactivity intermediate between mesitol and *o*-cresol, but unlike the latter compound good yields of 6-(p-methoxyphenyl)-6-methyl-cyclohexa-2,4-dienones were produced when the reactions were allowed to proceed to completion (24–48 h). In the reaction of 2,6-dimethylphenol 18, only 15% of the phenol remained unreacted after 5 h and after 13 h the yield (^{1}H NMR spectrum) of 6-(p-methoxyphenyl)-2,6-dimethylcyclohexa-2,4-dienone was approximately 93%. In keeping with our proposal that phenol reactivity towards arylation depends on the π-donor property of the phenol, 4-bromo-2,6-dimethylphenol 19 was less reactive than 2,6-dimethylphenol 18. Under the standard conditions it was 35% unreacted at 5 h, and produced the arylated product, 4-bromo-6-(p-methoxyphenyl)-2,6-dimethylcyclohexa-2,4-dienone in approximately 60% yield after 13 h.
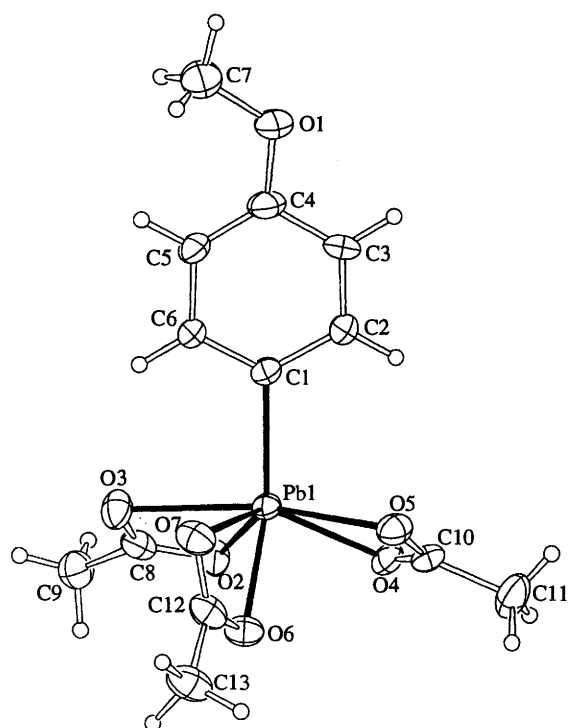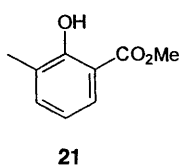
Fig. 2 X-Ray molecular structure of *p*-methoxyphenyllead triacetate **4** (with atomic numbering used in the crystallographic data)

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In addition to the π-donor property of phenols, the reactivity of phenols to arylation is significantly affected by the presence or absence of *ortho* methyl groups. Although it was expected that 3,4,5-trimethylphenol **10** would show greater reactivity to arylation than 2,6-dimethylphenol **18**, it was considerably less reactive, being 30% unreacted at 5 h. In keeping with the reduction in reactivity on reducing the number of methyl groups, 3,5-dimethylphenol **9** was 70% unreacted after 5 h under the standard conditions. Thus the order of reactivity to arylation of the phenols **18**, **10** and **9** is as shown in Fig. 1. In the light of these results, it would appear that, although the π-donor property of the phenol is a significant factor in its reactivity to arylation, electron release at the *ortho* position further enhances reactivity. As can be seen in Fig. 1, 3,5-di-*tert*-butylphenol **8** is considerably less reactive than 3,5-dimethylphenol **9** in the arylation reaction and this is no doubt due to steric hindrance in the ligand coupling.

There is now ample evidence that electron withdrawing groups in the phenol lower reactivity to *ortho*-arylation (see ref. 3 and above), and this has been further reinforced in the present work, with the finding that the methyl salicylate derivative **21** is completely inert to *p*-methoxyphenyllead triacetate under the reaction conditions used in this study.

A single crystal X-ray analysis (see Experimental section) of *p*-methoxyphenyllead triacetate showed that the structure consists of neutral monomeric units as shown in Fig. 2. The Pb has a distorted pentagonal bipyramidal geometry, with the *p*-methoxyphenyl group occupying an axial position and a C1–Pb–O6 bond angle of 146°. The two oxygens of each acetate unit are bonded unsymmetrically to Pb, which is also the situation in other aryllead triacetates.[7] The Pb–C bond length [2.167(11) Å] is similar to that in (*p*-methoxyphenyl)-α-

methylphenacyllead diacetate [2.156(8), 2.223(8) Å] as is the range of Pb–O bond lengths (2.18–2.53 Å) and (2.29–2.63 Å), respectively.[6]

Experimental

Synthesis of 6-methoxy-2,3,4-trimethylphenylboronic acid 16

Butyllithium (2.5 M solution in hexanes, 5.0 mmol) was added over 5 min to a stirred suspension of 2-bromo-3,4,5-trimethyl-anisole[11] (1.15 g, 5.0 mmol) in dry THF (15 cm³) at − 78 °C under nitrogen. The suspension was allowed to warm up until all solid had dissolved (*ca.* 10 °C), then recooled to − 78 °C, and stirred for 1 h. Triisopropyl borate (0.941 g, 5.0 mmol) was added over 5 min and the mixture was stirred at − 78 °C for 1.5 h under nitrogen. The solution was warmed to room temperature and water (5 cm³) added with stirring, then the mixture was partitioned between diethyl ether (80 cm³) and water (30 cm³). The diethyl ether layer was washed with saturated aqueous Na₂SO₄ (30 cm³), dried (Na₂SO₄), filtered and the solvent evaporated at 35 °C. The crude boronic acid was pulverised, air dried for 2 days, then stirred with pentane (20 cm³) for 2 h and the washings were discarded. The *title compound* **16** (0.70 g, 72%) was obtained as crystals of high purity, mp 115–117 °C (Found: C, 61.7; H, 8.0. $C_{10}H_{15}BO_3$ requires C, 61.9; H, 7.8%); δ_H(CDCl₃) 2.13 (3 H, s, Me), 2.31 (3 H, s, Me), 2.44 (3 H, s, Me), 3.82 (3 H, s, OMe), 5.63 [2 H, s, exch., B(OH)₂] and 6.59 (1 H, s, 5-H); *m/z* 195 (M + 1, 12%), 194 (100), 193 (31), 179 (14), 161 (11), 135 (22), 133 (10), 132 (13) and 117 (14).

Synthesis of (6-methoxy-2,3,4-trimethylphenyl)phenyllead diacetate 17

6-Methoxy-2,3,4-trimethylphenylboronic acid **16** (194 mg, 1.0 mmol) was added to phenyllead triacetate (461 mg, 1.0 mmol) in dry chloroform (6 cm³) and the mixture was stirred at room temperature for 2 days. The suspension was washed with water (2 × 3 cm³), and the chloroform solution dried (Na₂SO₄) and the solvent evaporated. Crystallisation from chloroform–light petroleum gave the *title compound* **17** (440 mg, 80%) as colourless crystals, mp 177–179 °C (Found: C, 43.8; H, 4.6. $C_{20}H_{24}O_5Pb$ requires C, 43.5; H, 4.4%); δ_H(CDCl₃) 1.99 (6 H, s, 2 × OCOMe), 2.14 (3 H, s, ²⁰⁷Pb satellites gave $J_{Pb,Me}$ 13.1, ArMe), 2.30 (3 H, s, ²⁰⁷Pb satellites gave $J_{Pb,Me}$ 8.6, ArMe), 2.48 (3 H, s, ²⁰⁷Pb satellites gave $J_{Pb,Me}$ 17.3, ArMe), 3.87 (3 H, s, OMe), 6.77 (1 H, s, ²⁰⁷Pb satellites gave $J_{Pb,H}$ 127, aryl 5-H), 7.45 (1 H, m, phenyl 4-H), 7.60 (2 H, m, phenyl 3- and 5-H) and 7.82 (2 H, m, ²⁰⁷Pb satellites gave $J_{Pb,H}$ 183, phenyl 2- and 6-H); δ_C(CDCl₃) 15.6 (²⁰⁷Pb satellites gave $J_{Pb,Me}$ 17.8, Me), 20.6 (²⁰⁷Pb satellites gave $J_{Pb,Me}$ 79.7, Me), 21.4 (Me), 22.3 (2 × OCO*Me*), 56.5 (OMe), 111.1 (²⁰⁷Pb satellites gave $J_{Pb,C}$ 104, aryl C-5), 130.4 (²⁰⁷Pb satellites gave $J_{Pb,C}$ 186, phenyl C-3 and C-5), 130.5 (²⁰⁷Pb satellites gave $J_{Pb,C}$ 38, phenyl C-4), 133.2 (²⁰⁷Pb satellites gave $J_{Pb,C}$ 134, phenyl C-2 and C-6), 140.6 (²⁰⁷Pb satellites gave $J_{Pb,C}$ *ca.* 16, quaternary C), 140.9 (²⁰⁷Pb satellites gave $J_{Pb,C}$ *ca.* 20, quaternary C), 149.5 (quaternary C), 155.0 (²⁰⁷Pb satellites gave $J_{Pb,C}$ 60.4, *C*-OMe), 162.8

(quaternary C) and 180.9 (2 × C=O); ν_{max}(Nujol)/cm^{-1} 1462 and 1377.

Attempted thermolysis of (6-methoxy-2,3,4-trimethylphenyl)-phenyllead diacetate 17

The title compound (82 mg, 0.15 mmol) in dry deuteriochloroform (1 cm^3) was heated at 60 °C for 18 h. The solution was monitored by ^{1}H NMR spectroscopy and it was found that no significant reaction had occurred. Deuteriopyridine (120 μl, 1.5 mmol) was added and heating continued at 60 °C for 6 days with continued occasional monitoring. A small amount (ca. 5%) of the protodemetallation product, 3,4,5-trimethylanisole, was identified but the lead compound 17 remained otherwise unreacted.

General methods for the reaction of phenols with p-methoxy-phenyllead triacetate

The phenol, p-methoxyphenyllead triacetate 4 and [^{2}H$_5$]pyridine in the molar ratio of 1:4:10, respectively, were dissolved in deuteriochloroform (1 cm^3 per 0.15 mmol of phenol) according to Method B of Barton[4] and kept at 30 °C. NMR spectroscopic scale reactions were performed on a 0.5 cm^3 scale in NMR tubes, with periodic shaking, while preparative scale reactions were performed on a 10 cm^3 scale in stoppered flasks, with stirring. The progress of the reactions was monitored by ^{1}H NMR spectroscopy over 48 h at 30 °C. The addition of extra solvent at 24 h, as described by Barton, was found to be unnecessary because reactant solubilities were not a problem in the cases examined. The rate of progress of each reaction was gauged by the decline of reactant signals and the appearance of new methyl signals for the mono- and di-arylated phenol species. These new signals were readily identifiable by comparison with data for previously isolated compounds,[3] and for compounds 12 and 13 (see below).

In the NMR scale reactions of excess 4-methoxyphenyllead triacetate 4 with the phenols 2, 8–10 and 18–20, the fastest reaction occurred with mesitol 2 (complete in 40–60 min). In decreasing speed of reaction, the approximate percentages of unreacted phenol at 5 h in the other reactions were: 2,6-dimethylphenol 18, 15%; 3,4,5-trimethylphenol 10, 30%; 4-bromo-2,6-dimethylphenol 19, 35%; 3,5-dimethylphenol 9, 70%; o-cresol 20, 85% and 3,5-di-tert-butylphenol 8, 90%.†

In a separate experiment, it was established that the rate of arylation of phenol 2 was not significantly reduced when 2 equiv. of the aryllead triacetate 4 were used in place of the usual 4 equiv. with all other reaction conditions unaltered. This addressed the problem of comparing the rates of arylation of phenols which underwent monoarylation with phenols which could diarylate in the presence of excess aryllead triacetate.

Preparative scale reactions were carried out in order to isolate and characterise the products of diarylation of phenols 9 and 10. 3,5-Dimethylphenol 9 gave 2,6-bis(4-methoxyphenyl)-3,5-dimethylphenol 12 in 80% yield (by NMR) after 72 h reaction, while 3,4,5-trimethylphenol 10 gave 2,6-bis(4-methoxyphenyl)-3,4,5-trimethylphenol 13 in 70% yield (by NMR) after 48 h.

2,6-Bis(4-methoxyphenyl)-3,5-dimethylphenol 12

The crude arylation product was chromatographed on silica gel in ethyl acetate–light petroleum (1:10) to give the title compound as prisms, mp 147–148 °C (from light petroleum) (Found: C, 78.9; H, 6.6; M$^+$, 334.1569. C$_{22}$H$_{22}$O$_3$ requires C, 79.0; H, 6.6%; M$^+$, 334.1569); δ_H(CDCl$_3$) 2.10 (6 H, s, 2 × Me),

3.85 (6 H, s, 2 × OMe) 4.77 (1 H, OH), 6.80 (1 H, s, 4-H), 6.99 and 7.24 (8 H, AA'BB', 3'- and 5'-H, and 2'- and 6'-H, respectively); δ_C(CDCl$_3$) 20.3 (Me), 55.2 (OMe), 114.3 (C-3' and C-5'), 123.2 (C-4), 125.4 (C-1'), 128.4 (C-2 and C-6), 131.4 (C-2' and C-6'), 136.4 (C-3 and C-5), 150.4 (C-1) and 158.9 (C-4'); m/z 335 (M + 1, 25%), 334 (100); ν_{max}(Nujol)/cm^{-1} 3449, 1606, 1560 and 1514; λ_{max}(EtOH)/nm 278 and 284sh (ε/dm^3 mol^{-1} cm^{-1} 5950 and 5700).

2,6-Bis(4-methoxyphenyl)-3,4,5-trimethylphenol 13

The crude arylation product was chromatographed on silica gel in ethyl acetate–light petroleum (1:10) to produce the title compound as very pale yellow crystals, mp 130–131 °C (from chloroform–light petroleum) (Found: C, 79.4; H, 7.1. C$_{23}$H$_{24}$O$_3$ requires C, 79.3; H, 7.0%); δ_H(CDCl$_3$) 2.07 (6 H, s, 2 × Me), 2.23 (3 H, s, Me), 3.84 (6 H, s, 2 × OMe), 4.60 (1 H, OH), 6.99 and 7.21 (8 H, AA'BB', 3'- and 5'-H, and 2'- and 6'-H, respectively); δ_C(CDCl$_3$) 16.1 (4-Me), 18.0 (3- and 5-Me), 55.2 (OMe), 114.2 (C-3'- and C-5'), 125.7 (quaternary C), 126.9 (quaternary C), 129.2 (C-2 and C-6), 131.5 (C-2' and C-6'), 134.9 (C-3 and C-5), 148.3 (C-1) and 158.8 (C-4'); m/z 349 (M + 1, 27%) and 348 (100); ν_{max}(Nujol)/cm^{-1} 3488, 1606, 1560 and 1510; λ_{max}(EtOH)/nm 278 and 284 (ε/dm^3 mol^{-1} cm^{-1} 6100 and 6150).

Crystal structure analysis of p-methoxyphenyllead triacetate 4

Crystal data. Formula C$_{13}$H$_{16}$O$_7$Pb, M = 491.47, monoclinic space group C2/c, a = 21.086(5), b = 10.831(4), c = 15.899(4) Å; β = 118.93(2)°, V = 3178(2) Å^3, D$_c$ (Z = 8) = 2.056 g cm^{-3}. F(000) = 1856, μ = 106.93 cm^{-1}, λ(Mo-Kα) = 0.710 69 Å. Specimen: colourless prisms, 0.35 × 0.32 × 0.20, number of reflections measured (N) = 3045, number of reflections refined (N$_o$) = 2056, T$_{max,min}$ = 0.123, 0.031, I > 2.5σ(I), h,k,l −25 ⟶ 25, 0 ⟶ 12, 0 ⟶ 18, R = 0.048, R' = 0.051, w = 1.70/[σ^2(F$_o$) + 0.0014F$_o^2$]. Residual extrema, 4.0 and −1.2 e Å^{-3}.‡

Data collection and processing. Lattice parameters at 21 °C were determined by a least-squares fit to the setting parameters of 25 independent reflections. Data were measured on an Enraf-Nonius CAD4F four-circle diffractometer within the limits 1 < θ < 25°, with graphite monochromated Mo-Kα radiation. Data reduction and application of Lorentz, polarisation, decomposition (57%) and Gaussian absorption corrections were carried out using the Enraf-Nonius Structure Determination Package.[12]

Structure analysis and refinement. The structure was solved by heavy atom methods using SHELX-76[13] and the solution was extended by difference Fourier methods. Hydrogen atoms were included at calculated sites (C–H 0.97 Å) with group isotropic thermal parameters and all other atoms were refined anisotropically. Refinement was by full-matrix least-squares methods using SHELX-76.[13] Scattering factors and anomalous dispersion terms used for Pb (neutral Pb) were taken from International Tables[14] and all others used were those supplied in SHELX-76.[13] All calculations were carried out using SHELX-76[13] and plots were drawn using ORTEP.[15] The atom numbering scheme is given in Fig. 1. Atomic coordinates, bond lengths and bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, J. Chem. Soc., Perkin Trans. 1, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207137.

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† In the NMR scale reactions of the aryllead compound 4 with the phenols, the relative rates of reaction were based on the percentage of phenol remaining, having ascertained that the loss of phenol by oxidation was negligible.

‡ $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $R_w = \Sigma(w^{\frac{1}{2}}||F_o| - |F_c||)/\Sigma w^{\frac{1}{2}}|F_o|$.

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