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Aryl Fluoride Syntheses Involving Reaction of Aryllead Triacetates with Boron Trifluoride–Diethyl Ether Complex†

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Abstract: Aryllead(IV) triacetates react at room temperature with $BF_3.Et_2O$ to give the corresponding aryl fluoride in moderate to good yields; triarylboroxines, electron rich aryltrimethylsilanes and some arenes, which yield aryllead triacetates in acid catalysed reactions with lead tetraacetate, are converted directly into aryl fluorides when stirred with lead tetraacetate in $BF_3.Et_2O$. An investigation of the mechanism of the fluoro–deplumbation reaction indicates that it probably proceeds by acid catalysed heterolytic cleavage of the C–Pb bond to produce an aryl cation.

With the growing demand in recent years for fluoroaromatics for use in the synthesis of agricultural and pharmaceutical chemicals, there has been considerable activity in the search for methods for the selective introduction of fluorine into aromatic compounds. Although a number of very useful electrophilic fluorinating agents for achieving this operation have been developed,[1-3] the most widely used methods are those which are based on the replacement of groups by fluoride ion. These procedures, which are less hazardous than the former type of reaction, include the Balz–Schiemann reaction[4] and the nucleophilic displacement of activated halides, nitro groups and alkoxy groups.[1] We report here a further example of the latter type of reaction; this involves fluorinative deplumbation of aryllead triacetates and, like fluorinative dediazonisation, proceeds without the need for activation of the aromatic nucleus by electron withdrawing groups.

Aryllead triacetates have been shown by us to be highly useful reagents for the C–arylation of a range of soft carbon nucleophiles such as β–dicarbonyl compounds,[5,6] nitroalkanes,[6,7] and phenols.[6,8] Attempts to extend these uncatalysed reactions of aryllead(IV) compounds, for which there is evidence pointing to a mechanism involving ligand coupling,[9-12] have been largely unsuccessful. The only non–carbon nucleophiles which have been found to undergo the simple ligand coupling type process are iodide[6] and azide[13] ions. A second type of reaction of aryllead triacetates was discovered by Professor Sir Derek Barton; he has shown that with copper catalysis N–arylation can be effected to provide a useful synthesis of aromatic amines.[14] The third type of reaction of these compounds proceeds under strong acid conditions, and here we have proposed that an aryl cation (or incipient aryl cation) is involved.[6,15,16]

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†Dedicated to Professor Sir Derek Barton on the occasion of his 75th birthday.

The last type of reaction of aryllead triacetates was one of the first reactions of these compounds investigated by us. It was found that, when dissolved in trifluoroacetic acid at room temperature, aryllead tricarboxylates were generally converted in high yield into aryl trifluoroacetates (as in reaction 1).[15] A study of the mechanism of the reaction indicated that it probably proceeds by heterolytic cleavage of the C–Pb bond to give an aryl cation,[15,16] which may be trapped by an aromatic to yield a biaryl (as in reaction 2). During this work, we found that replacement of trifluoroacetic acid by boron

$$ArPb(OCOCF_3)_3 \xrightarrow{CF_3CO_2H} ArOCOCF_3 + Pb(OCOF_3)_2 \qquad (1)$$

(1b) (2)

trifluoride–diethyl ether complex in reaction 2 led to an increase in the yield of 4–methylbiphenyl, but also resulted in the formation of some *p*–fluorotoluene. When this reaction was reinvestigated recently it was found that, by treating *p*–tolyllead triacetate (1b) with a large excess of $BF_3.Et_2O$ in the absence of benzene, *p*–fluorotoluene could be obtained in high yield (Table 1). Our investigation of the scope of this potentially useful synthesis of aryl fluorides (reaction 3) is the subject of this paper.[17] In addition, since it appeared likely that the mixture $Pb(OAc)_4$–$BF_3.Et_2O$ may be useful for the *in situ* generation of aryllead triacetates by metal–metal exchange, and by direct plumbation of arenes, we have explored three variations in order to eliminate the need to use the isolated aryllead triacetate.

Reaction of Aryllead Triacetates with $BF_3.Et_2O$

As can be seen from Table 1, the aryllead triacetates (1a) – (1e) and (1h) – (1k) gave moderate to good yields of the corresponding aryl fluoride when stirred with $BF_3.Et_2O$ at room temperature (reaction 3). Since this group contains compounds with electron rich aromatic rings and some, such as (1e) and (1h), substituted by electron withdrawing substituents, it would appear that the reaction will be applicable to a wide range of aryllead tricarboxylates. Two compounds which failed to react, or gave a very low yield of aryl fluoride, were *o*–fluorophenyllead triacetate (1g) and *o*–methoxyphenyllead triacetate (1f). The reason for the failure of these compounds to behave like the corresponding *para* isomers, (1e) and (1d) respectively, is not clear; however, in view of the possibility of BF_3 complexing with both the fluoro and methoxy groups, it appeared likely that this was giving rise to an '*ortho* effect'.

In most of the reactions listed in Table 1, the aryl fluoride was accompanied by a small amount of the product of proto–deplumbation. This is probably arising due to the incomplete exclusion of moisture from the reactions, or because of the presence of a trace of acetic acid in the aryllead triacetate. Interestingly, a reaction of *o*–fluorophenyllead triacetate (1g) under forcing conditions (120°C for 1.5 h)

again failed to yield any *o*-difluorobenzene, but it did produce fluorobenzene in high yield (90%). We believe that, at the higher temperature, a free radical mechanism is operating; that is, C-Pb bond homolysis leads to an *o*-fluorophenyl radical which then abstracts hydrogen from diethyl ether.

$$ArPb(OAc)_3 + BF_3.Et_2O \xrightarrow{\Delta} ArF + Pb(OAc)_2 + AcOBF_2 \qquad (3)$$

Table 1. Reaction of aryllead triacetates with $BF_3.Et_2O$.[a]

$ArPb(OAc)_3$ Ar-		ArF(%)[b]	ArH(%)[b]
Ph	(1a)	62	6
p-MeC_6H_4	(1b)	82	<1
p-PhC_6H_4	(1c)	74	2
p-$MeOC_6H_4$	(1d)	66	<5
p-FC_6H_4	(1e)	49	7
o-$MeOC_6H_4$	(1f)	14	7
o-FC_6H_4	(1g)	0	<1
o-FC_6H_4	(1g)	0	90[c]
p-$CF_3C_6H_4$	(1h)	68	11
α-Naphthyl	(1j)	78	11
β-Naphthyl	(1k)	78	0

[a] Reactions were conducted at room temperature unless otherwise indicated. [b] Yields were determined by GC analysis. [c] Reaction temperature was 120°C.

We have demonstrated the usefulness of this new route to aryl fluorides with a preparative scale (3.3 mmol) synthesis of 2-fluoronaphthalene from the lead compound (1k) in an isolated yield of 62%. This example was chosen to highlight the main advantage of the method, the avoidance of carcinogenic aromatic amines of the Balz-Schiemann synthesis.

Reaction of Aryltrimethylsilanes with a $Pb(OAc)_4$ - $BF_3.Et_2O$ Mixture

In our early study of the synthesis of aryllead tricarboxylates, we had shown that aryltrimethylsilanes readily undergo Si-Pb exchange with lead tetraacetate in trifluoroacetic acid to yield aryllead tristrifluoroacetates, which were converted under the conditions of the reaction into aryl trifluoroacetates (see reaction 1), at a rate dependent on the nature of substituents in the aromatic ring (reaction 4).[6,18] The possibility of replacing trifluoroacetic acid by $BF_3.Et_2O$ in the Si-Pb exchange reaction, led us to

question whether a 'one-pot' conversion of aryltrimethylsilanes into aryl fluorides might be achieved (reaction 5).

$$ArSiMe_3 \xrightarrow{Pb(OAc)_4,\ CF_3CO_2H} ArOCOCF_3 \quad (4)$$

$$ArSiMe_3 \xrightarrow{Pb(OAc)_4,\ BF_3.Et_2O} ArF \quad (5)$$

Table 2. Reaction of aryltrimethylsilanes with $Pb(OAc)_4$–$BF_3.Et_2O$.[a]

$ArSiMe_3$ Ar=		ArF(%)[b]	ArH(%)[b]
Ph	(2a)	83	6
p-MeC_6H_4	(2b)	77	<5
p-$MeOC_6H_4$	(2c)	23	0
p-FC_6H_4	(2d)	43	0
p-$CF_3C_6H_4$	(2e)	<5	<5
α-Naphthyl	(2f)	73	4
β-Naphthyl	(2g)	64	0
4,4'-Biphenylyl-disilane	(3a)	68[c]	0

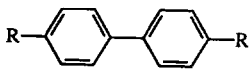
[a] See Experimental for conditions. [b] Yields were determined by GC analysis, unless otherwise specified. [c] Isolated yield of 4,4'-difluorobiphenyl(3b).

Trimethylphenylsilane (2a) was the first compound examined, and was found to react readily at room temperature, as indicated in reaction (5), to give fluorobenzene in high yield (83%). However, from an inspection of the results of our study of a range of silanes (Table 2), it can be seen that the reaction has more limitations than that of the isolated aryllead compounds.

The unsubstituted aromatics (2a), (2f) and (2g), and the *p*-tolylsilane (2b) gave good yields of the corresponding aryl fluoride, while the *p*-fluorophenyl compound (2d) afforded a moderate yield of *p*-difluorobenzene, which was similar to that obtained with the corresponding aryllead compound (1e). Reactions of the *p*-methoxyphenylsilane (2c) and the *p*-trifluoromethylphenylsilane (2e), on the other hand, failed to produce useful yields of the aryl fluorides, in contrast to the corresponding aryllead compounds (1d) and (1h), respectively. The poor results obtained with silanes (2c) and (2e) are no doubt due to a slow electrophilic substitution of silicon by lead. This is understandable in the case of

compound (2e), which has a strong electron-withdrawing group in the *para* position, and with the *p*-anisyl compound (2c) where the BF_3 complexed methoxyl group would have a similar effect.

In syntheses of 1-fluoronaphthalene and 2-fluoronaphthalene on a preparative scale (2.0 g), best yields were obtained by reacting the trimethylnaphthylsilane with a mixture of lead tetraacetate (1.2 mol equiv.) and $BF_3.Et_2O$ (1.2 mol equiv.) in chloroform at a lower temperature and then adding excess $BF_3.Et_2O$. In this way, 1-fluoronaphthalene and 2-fluoronaphthalene were isolated in yields of 60 and 61%, respectively. Also, by use of the same procedure, 4,4'-difluorobiphenyl (3b) was isolated in 68% yield from a reaction of the bis(silyl)biphenyl (3a).



(3a), R = Me_3Si

(3b), R = F

Reaction of Triarylboroxines with a $Pb(OAc)_4$-$BF_3.Et_2O$ Mixture

The metal-metal exchange reactions of aryltributylstannanes[19] and arylboronic acids[13,20] have been used by us as a source of aryllead triacetates, but both classes of compounds failed to produce significant amounts of aryl fluorides when treated with $Pb(OAc)_4$-$BF_3.Et_2O$ mixtures. Since, with the boronic acids, the major product resulted from boron-proton exchange, we explored aprotic conditions by employing their cyclic anhydrides, the triarylboroxines.

$$(ArBO)_3 \xrightarrow{Pb(OAc)_4,\ BF_3.Et_2O} 3ArF \qquad (6)$$

Table 3. Reaction of triarylboroxines with $Pb(OAc)_4$ in $BF_3.Et_2O$.[a]

$(ArBO)_3$ Ar-		ArF(%)[b]	ArH(%)[b]
Ph	(4a)	68	1
p-$MeOC_6H_4$	(4b)	47	0
m-$MeOC_6H_4$	(4c)	41	2
p-$CF_3C_6H_4$	(4d)	50	1

[a] See Experimental for conditions. [b] Yields were determined by GC analysis.

When these compounds were treated with $Pb(OAc)_4$–$BF_3.Et_2O$ in the same way as the silanes above, synthetically useful yields of aryl fluorides were obtained (reaction 6). Although a smaller number of compounds was investigated (see Table 3), the results indicate that the method should be more widely applicable than that employing the silanes. The best yield was obtained with triphenylboroxine (**4a**); however, even with a *para* CF_3 substituent, compound (**4d**), a 50% yield of aryl fluoride was obtained, in contrast to the corresponding silane (**2e**). The moderate yields obtained with *p*–methoxyphenyl and *m*–methoxyphenyl derivatives, (**4b**) and (**4c**) respectively, also contrast with the poor result achieved with *p*–methoxyphenyltrimethylsilane (**2c**). We attribute the improved results for the triarylboroxines to a faster boron–lead exchange, a feature previously noted in the case of arylboronic acids and their esters.[13,20]

Reaction of Arenes with a $Pb(OAc)_4$–$BF_3.Et_2O$ Mixture

The direct plumbation of aromatics is an important but limited route to aryllead triacetates.[6] Although these reactions are generally performed in acetic acid or a haloacetic acid, it has been found in the present work that the mixture $Pb(OAc)_4$–$BF_3.Et_2O$ containing a catalytic amount of mercury(II) acetate will also effect this plumbation, and under the reaction conditions replacement of the tricarboxylead group by fluoride occurs (reaction 7).

$$ArH \xrightarrow{Pb(OAc)_4,\ BF_3.Et_2O,\ Hg(OAc)_2\ cat.} ArF \qquad (7)$$

Table 4. Reaction of arenes with a $Pb(OAc)_4$ – $BF_3.Et_2O$, $Hg(OAc)_2$ mixture.[a]

Substrate		ArF (%)[b]	Unreacted Substrate[b]
Benzene	(**5a**)	39	42
Toluene	(**5b**)	77 (*o*:*m*:*p* = 19:4:77)	7
p-Xylene	(**5c**)	46 (2-fluoro)	21
		13 (difluoro)[c,d]	
m-Xylene	(**5d**)	73 (4-fluoro)	0
o-Xylene	(**5e**)	53 (4-fluoro)	16
		7 (3-fluoro)	
Cumene	(**5f**)	61 (*o*:*m*:*p* = 13:7:80)	21
Mesitylene	(**5g**)	76[c]	0

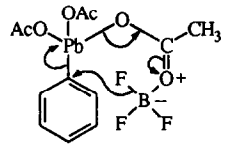
[a] See Experimental for conditions. [b] Yields were determined by GC analysis. [c] Established by GC-MS. [d] Structure unknown.

In Table 4 the results of reactions of the aromatics (**5a**) – (**5g**) are shown. It is clear from the data that, except in special cases such as *m*–xylene (**5d**) and mesitylene (**5g**), the reaction will be of

little use synthetically, because of the similar boiling points of isomers and unreacted substrates. In a preparative scale reaction (40 mmol) with *m*-xylene (5d), in which it was necessary to moderate the reaction by dilution with chloroform, 4-fluoro-*m*-xylene was obtained in a 61% isolated yield.

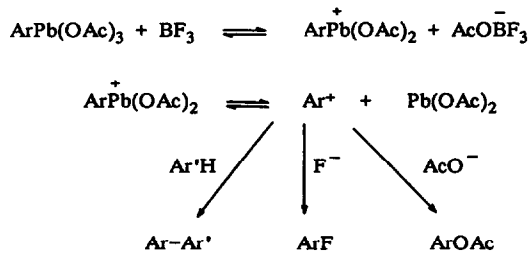
Mechanism of the Fluoro-deplumbation Reaction

Unlike the reactions of aryllead triacetate with iodide and azide ions referred to in the introduction to this paper, phenyllead triacetate failed to produce any fluorobenzene when treated with potassium fluoride or tetrabutylammonium fluoride in dimethyl sulfoxide. It would appear that fluoro-deplumbation requires the strong Lewis acid, BF_3, and we believe that it proceeds through an aryl cation (or incipient aryl cation) as proposed for other reactions of aryllead tricarboxylates which require strongly acidic conditions.[6,15,16]



(6)

Previously, we put forward a concerted mechanism as indicated in structure (6) as an alternative possibility;[17] however, the results of two reactions designed to probe the mechanism are more in keeping with the aryl cation proposal. In the first of these *p*-tolyllead triacetate (1b) (0.2 mmol) was dissolved in a large excess of benzene and stirred at room temperature for 20 minutes with $BF_3.Et_2O$ (1.6 mmol). Analysis of the reaction mixture by GC showed it to contain 4-methylbiphenyl (8%), *p*-tolyl acetate (5%) and *p*-fluorotoluene (33%). When the above reaction was repeated with mesitylene in place of benzene, analysis showed the presence of 2,4,4',6,-tetramethylbiphenyl (5%), *p*-tolyl acetate (5%) and *p*-fluorotoluene (19%). The results would suggest that BF_3 brings about heterolytic C-Pb bond cleavage as indicated in Scheme 1 to produce an aryl cation, which then reacts indiscriminately with the available nucleophiles.



Scheme 1

EXPERIMENTAL

Melting points are uncorrected. NMR spectra were run in deuterochloroform with TMS as internal standard on Bruker AMX-400 and AC-200F and Varian EM-390 spectrometers. *J* values are given in Hz and fluorine chemical shifts are referenced to $CFCl_3$. Column chromatography and flash chromatography were carried out on Merck Kieselgel 60 (70-230 mesh) and (230-400 mesh), respectively. Light petroleum refers to the fraction of b.p. 60-80°C. Gas chromatography (GC) was performed on a Hewlett Packard 5890A instrument fitted with an SGE 25QC2/BP20-0.25 capillary column (25m x 0.22 mm i.d. x 0.25 μm film thickness). Quantitative determinations were made by the addition of a measured amount of internal standard to both reaction product and standard solution. GC-MS investigations were performed on a Hewlett Packard 5890 Series II GC/5989A MS instrument fitted with a BP20 column as above.

Anhydrous $BF_3.Et_2O$ was obtained from Aldrich Chemical Co., or was freshly distilled from calcium hydride and ether under reduced pressure.

4,4'-Bis(trimethylsilyl)biphenyl was prepared in 80% yield by the method of Curtis and Allred,[21] but deleting the treatment with sulfuric acid during work-up.

1-and 2-Trimethylsilylnaphthalenes were prepared by reaction of the respective lithio derivatives with chlorotrimethylsilane in tetrahydrofuran at -78°C in 82% and 89% yield, respectively.

Reaction of Aryllead Triacetates with $BF_3.Et_2O$ as Reported in Table 1

The aryllead triacetate (0.2 mmol) was suspended in $BF_3.Et_2O$ (5 ml) and the mixture stirred overnight at room temperature under anhydrous conditions. The mixture was diluted with ice-cold ether (20 ml) and washed with iced water (25 ml) and water (2 x 25ml), and dried (Na_2SO_4). The mixture was analysed by GC and yields determined by comparison to a standard solution, with the aid of a suitable internal standard.

Reactions of Aryltrimethylsilanes and Triarylboroxines with $Pb(OAc)_4$-$BF_3.Et_2O$ in Tables 2 and 3

The aryltrimethylsilane (0.2 mmol) or triarylboroxine (0.067 mmol) was mixed with dry $Pb(OAc)_4$ (106.4 mg, 0.24 mmol, 1.2 mol equiv.) in $BF_3.Et_2O$ (5 ml) and the mixture stirred overnight at room temperature under anhydrous conditions. The mixture was worked up and analysed by GC as above.

Reaction of Arenes with $Pb(OAc)_4$-$BF_3.Et_2O$ as Reported in Table 4

(Method a) The arene (10 mmol), lead tetraacetate (5.32 g, 12 mmol) and mercury(II) acetate (0.64 g, 2 mmol) were dissolved in $BF_3.Et_2O$ (30 ml) and stirred overnight at room temperature under anhydrous conditions. The mixture was diluted with ice-cold ether (120 ml), washed with iced water (120 ml) and water (2 x 120 ml) and dried (Na_2SO_4). The mixture was analysed by GC as above. This method was used for compounds (**5a**) and (**5b**).

(Method b) Method (a) was followed except that lead tetraacetate (4.88 g, 11 mmol) and mercury(II) acetate (0.32 g, 1 mmol) were used. This method was employed with compounds (**5c**), (**5e**) and (**5f**).

(Method c) As for method (b) except that $BF_3.Et_2O$ (15 ml) and dry chloroform (15 ml) were used. The method was used for compounds (**5d**) and (**5g**).

Synthesis of 2-Fluoronaphthalene by Reaction of 2-Naphthyllead Triacetate with $BF_3.Et_2O$

2-Naphthyllead triacetate (1.7 g, 3.3 mmol) was stirred at room temperature with $BF_3.Et_2O$ (100 ml) for 24 h. The mixture was diluted with ether (100 ml), and washed in turn with water (200 ml), dilute hydrochloric acid (150 ml, 1.5 M), saturated sodium hydrogencarbonate (100 ml), water (2 x 200 ml) and brine (200 ml). The solution was dried (Na_2SO_4), filtered, and the solvent evaporated. The crude product was purified by column chromatography in pentane, and recrystallized from ethanol to give 2-fluoronaphthalene (0.31 g, 62%) m.p. 55-57°C (lit.[22] 59°C) δ_H ($CDCl_3$) 7.25 (1H, dt, $J_{F,2}$ and $J_{2,3}$ 8.79 Hz, $J_{1,2}$ 2.59 Hz, H-3), 7.38-7.54 (3H, m, H-1, H-6, H-7), 7.75-7.86 (3H, m, H-4, H-5, H-8); δ_C ($CDCl_3$) 110.85 (d, *J* 20.2 Hz, C-1), 116.24 (d, *J* 25.3 Hz, C-3), 125.06 (d, *J* 2.2 Hz, C-5), 126.83 (s, C-6), 127.24 (d, *J* 5.3 Hz, C-7), 127.86 (s, C-4a), 130.17 (s, C-4), 130.35 (s, C-8a), 134.12 (d, *J* 9.8 Hz, C-8), 160.58 (d, *J* 244.1 Hz, C-2).

Preparation of 1-Fluoro-2,4-dimethylbenzene by Reaction of *m*-Xylene with $Pb(OAc)_4$-$BF_3.Et_2O$

$BF_3.Et_2O$ (60 ml) was added under anhydrous conditions to a stirred solution of *m*-xylene (4.25 g, 40 mmol), dry lead tetracetate (19.50, 44 mmol) and mercury(II) acetate (1.27 g, 4 mmol) in dry chloroform (60 ml) at -10°. The mixture was allowed to warm slowly to room temperature and was stirred for 24 h. It was then diluted with ice-cold ether (500 ml), washed with iced water (200 ml) and water (2 x 200 ml) and dried (Na_2SO_4). The solvent was carefully removed by distillation at atmospheric pressure and the brown residue fractionated by column chromatography in pentane. The solvent was removed by careful distillation at atmospheric pressure to give 1-fluoro-2,4-dimethylbenzene (3.03 g, 61%) as a colourless oil, b.p. 142-143°C (lit.[23] 142-143°C). δ_H ($CDCl_3$) 2.23 (3H, d, $J_{F,Me}$ 1.77 Hz, 2-Me), 2.27 (3H, s, 4-Me), 6.80-7.0 (3H, m, H-3, H-5, H-6); δ_C ($CDCl_3$) 14.39 (s, Me), 20.52 (s, Me), 114.53 (d, *J* 21.9 Hz, CH), 124.25 (d, *J* 17.4 Hz, C-2), 127.50 (d, *J* 8.5 Hz, CH), 131.92 (d, *J* 4.2 Hz, CH), 133.01 (d, *J* 3.5 Hz, C-4), 159.58 (d, *J* 241.8 Hz, C-1); δ_F ($CDCl_3$) -122.72 (lit.[24] -122.4). *m/z* 124 (M^+, 46%), 123 (25), 109 ($M-CH_3$, 100), 77 (11).

Preparation of 4,4'-Difluorobiphenyl (3b)

4,4'-Bis(trimethylsilyl)biphenyl (1.49 g, 5 mmol) and dry lead tetraacetate (5.32 g, 12 mmol) were dissolved in dry chloroform (20 ml) under anhydrous conditions and cooled to 10°C. $BF_3.Et_2O$ (1.5 ml, 12 mmol) was added over 1 min to the stirred solution and the mixture stirred for 1 h at 10°. Additional $BF_3.Et_2O$ (58.5 ml) was added over 5 min, and the mixture stirred for 1h at 10°C, and then for 24h at room temperature. The reaction mixture was diluted with ice-cold light petroleum (150 ml) and washed with iced water (75 ml) and water (2 x 75 ml), and dried (Na_2SO_4). The solvent was removed by careful distillation at atmospheric pressure. The crude product was purified by flash chromatography in light petroleum to give 4,4'-difluorobiphenyl (0.65 g, 68%), m.p. 88-90°C (lit.[4] 90°C).

Preparation of 1-Fluoronaphthalene

1-Fluoronaphthalene was prepared from 1-(trimethylsilyl)naphthalene (2.004 g, 10 mmol) and dry lead tetraacetate (5.32 g, 12.mmol) by the method used above for thesynthesis of compound (3b). The title compound (0.881 g, 60%) was obtained after distillation as a colourless oil, b.p. 215-216°C (lit.[25] 215°C).

Preparation of 2-Fluoronaphthalene

2-Fluoronaphthalene was prepared from 2-(trimethylsilyl)naphthalene (2.004 g, 10 mmol) by the method used above for 1-fluoronaphthalene, with two important modifications. The initial reaction temperature was -40°C, and after addition of the second portion of $BF_3.Et_2O$ (58.5 ml) the mixture was stirred for 2.5 h at -40°C. The title compound (0.890 g, 61%) was obtained as colourless crystals, m.p. 57-58°C (lit.[4] 60°C).

Reaction of *p*-Tolyllead Triacetate (1b) with $BF_3.Et_2O$ in the Presence of Arenes

(a) *p*-Tolyllead triacetate (1b) (95 mg, 0.2 mmol) was dissolved in benzene (3.12 g, 40 mmol) and $BF_3.Et_2O$ (0.18 g, 1.6 mmol) was added to the solution. The mixture was stirred for 20 min at room temperature and worked up with ether and water as for experiments reported in Table 1. Quantitative GC analysis showed the presence of 4-methylbiphenyl (8% yield), *p*-fluorotoluene (33% yield) and *p*-tolyl acetate (5% yield).

(b) The lead compound (1b) (0.2 mmol), mesitylene (40 mmol) and $BF_3.Et_2O$ (1.6 mmol) were reacted as in reaction (a) above, and the mixture was worked up in the same way. The crude reaction mixture was shown by GC to contain *p*-fluorotoluene (19% yield), 2,4,4',6-tetramethylbiphenyl (5% yield) and *p*-tolyl acetate (5% yield).

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