Aryl Fluorides from the Reaction of Boron Trifluoride with Aryl-lead(IV) Triacetates, which may be generated *in situ* from Aryltrimethylsilanes, Triarylboroxines, and Arenes

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Aryl-lead(IV) triacetates react at room temperature with $BF_3{\cdot}Et_2O$ to give the corresponding aryl fluoride in moderate to good yields; triarylboroxines, electron-rich aryltrimethylsilanes, and some arenes, which yield aryl–lead(IV) triacetates in acid catalysed reactions with lead tetra-acetate, may be converted directly into aryl fluorides when stirred with lead tetra-acetate in $BF_3{\cdot}Et_2O$.

The growing demand for fluoroaromatic compounds, especially for the synthesis of agrochemicals and for use in the medical area, has led to a continuing search for new routes to these compounds.[1] Although a number of useful electrophilic fluorinating agents have been introduced in recent years,[1—3] their synthesis is still largely carried out by fluorinative dediazonisation, the Balz–Schiemann reaction. Pertinent to the present communication is the report by McKillop and Taylor,[4] that certain aryl-thallium(III) difluorides may be converted to aryl fluorides by heating in the presence of boron trifluoride. The method, which employs boron trifluoride gas, failed with substrates containing powerful electron-withdrawing substituents, and either oxygen or amino substituents. We now report that aryl-lead(IV) triacetates, which are readily available by direct plumbation of aromatics[5] or by metal–metal exchange,[5,6] are converted into aryl fluorides in moderate to good yields simply by mixing with excess boron trifluoride–diethyl ether complex ($BF_3{\cdot}Et_2O$) at room temperature (equation 1). Since both triarylboroxines and aryltrimethylsilanes undergo acid-catalysed metal–metal exchange when treated with lead tetra-acetate, one-pot conversions of both classes of compounds into aryl fluorides may be effected just by stirring them with a slurry of lead tetra-acetate in an excess of $BF_3{\cdot}Et_2O$ (equation 2).

$$\underset{(\mathbf{1})}{\mathrm{ArPb(OAc)_3}} \xrightarrow{\substack{\mathrm{BF_3\cdot Et_2O,}\\ \text{room temp.}}} \mathrm{ArF} + \mathrm{Pb(OAc)_2} + \mathrm{AcOBF_2} \qquad (1)$$

$$\begin{array}{c}\mathrm{ArSiMe_3}\\ (\mathbf{2})\\ \text{or } (\mathrm{ArBO})_3\\ (\mathbf{3})\end{array} \xrightarrow[\text{room temp.}]{\mathrm{Pb(OAc)_4,\ BF_3\cdot Et_2O}} \mathrm{ArF} \qquad (2)$$

$$\mathrm{ArH} \xrightarrow[\text{room temp.}]{\mathrm{Pb(OAc)_4,\ BF_3\cdot Et_2O,\ Hg(OAc)_2\ catalyst}} \mathrm{ArF} \qquad (3)$$

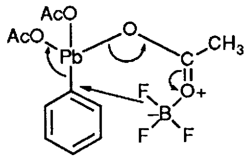
Our initial study of the isolated aryl-lead triacetates (equation 1) was carried out with compounds (**1a**)—(**1g**), and the results are recorded in Table 1. These show that yields of aryl fluoride were highest for the α- and β-naphthyl derivatives, (**1f**) and (**1g**) respectively; phenyl-lead triacetate (**1c**) and *p*-tolyl-lead triacetate (**1b**) gave good yields of the fluoride, while even the compounds containing electron-withdrawing groups, the *p*-fluoro derivative (**1d**) and *p*-trifluoromethyl compound (**1e**), reacted to produce satisfactory yields of the corresponding aryl fluoride. Of particular interest with regard to the scope of the reaction was the relatively high yield obtained with *p*-anisyl-lead triacetate (**1a**), in which BF_3 complexing with the ether oxygen may have been expected to lower the reactivity. Except with substrate (**1g**), a small amount of the product of protodemetallation was also formed, presumably owing to the incomplete exclusion of moisture, or the presence of some residual acetic acid in the aryl-lead triacetate.

Table 1. Reaction of aryl-lead(IV) triacetates with $BF_3{\cdot}Et_2O$.[a]

$ArPb(OAc)_3$ Ar=		ArF/%[b]	ArH/%[b]
p-$MeOC_6H_4$	(**1a**)	66	<5
p-MeC_6H_4	(**1b**)	82	<5
Ph	(**1c**)	62	6
p-FC_6H_4	(**1d**)	49	7
p-$CF_3C_6H_4$	(**1e**)	68	11
α-Naphthyl	(**1f**)	78	11
β-Naphthyl	(**1g**)	78 (62)[c]	0

[a] $ArPb(OAc)_3$ (0.2 mmol) was stirred in $BF_3{\cdot}Et_2O$ (5 ml) overnight at room temperature. [b] Yields were determined by GC analysis. [c] Isolated yield from a reaction on a 3.3 mmol scale.

Initial attempts to synthesise aryl fluorides by generating aryl-lead triacetates *in situ* from arylboronic acids[6c] and arylstannanes[6a] were disappointing; however, cyclic anhydrides of arylboronic acids, triarylboroxines, and to a lesser extent aryltrimethylsilanes, proved to be satisfactory substrates, and the results obtained for reactions carried out as indicated in equation (2) are included in Table 2. As can be seen from the results, both trimethylphenylsilane (**2c**) (entry 3) and trimethyl-(*p*-tolyl)silane (**2b**) (entry 2) produced the corresponding aryl fluoride in good yield; however, the yield from *p*-anisyltrimethylsilane (**2a**) (entry 1) was poor, while with *p*-trifluoromethylphenyltrimethylsilane (**2e**) (entry 5) less



(**4**)

Table 2. Reaction of aryltrimethylsilanes and triarylboroxines with $Pb(OAc)_4$–$BF_3{\cdot}Et_2O$.[a]

Entry	Substrate		ArF/%[b]	ArH/%[b]
1	*p*-$MeOC_6H_4SiMe_3$	(**2a**)	23	0
2	*p*-$MeC_6H_4SiMe_3$	(**2b**)	77	<5
3	$PhSiMe_3$	(**2c**)	83	6
4	*p*-$FC_6H_4SiMe_3$	(**2d**)	43	0
5	*p*-$CF_3C_6H_4SiMe_3$	(**2e**)	<5	<5
6	(*p*-$MeOC_6H_4BO)_3$	(**3a**)	47	0
7	$(PhBO)_3$	(**3b**)	68	1
8	(*p*-$CF_3C_6H_4BO)_3$	(**3c**)	50	1

[a] The silane (0.2 mmol) or boroxine (0.066 mmol) and lead tetra-acetate (0.24 mmol) was stirred in $BF_3{\cdot}Et_2O$ (5 ml) overnight at room temperature. [b] Yields were determined by GC analysis.

than 5% of the fluoride was produced. The low reactivity of the last two compounds is presumably due to a slow silicon–lead exchange, resulting from electron withdrawal, which in the case of the methoxy group would be due to complexing with BF_3. The moderate yield of *p*-difluorobenzene obtained from the reaction of *p*-fluorophenyltrimethylsilane (**2d**) (entry 4) is in keeping with the above order of reactivity.

In contrast to the silanes, all three boroxines, (**3a**)—(**3c**) (entries 6—8), gave synthetically useful yields of the corresponding aryl fluoride, and we attribute this difference in behaviour to the greater speed of the boron–lead exchange reaction.[6c]

The direct acid-catalysed plumbation of arenes, although not a widely applicable route to aryl–lead triacetates, has also been shown by us to be a potential method for the direct introduction of fluorine in a limited number of aromatics (equation 3). When benzene (10 mmol) was stirred overnight at room temperature in $BF_3{\cdot}Et_2O$ (30 ml) containing lead tetra-acetate (1.2 mol equiv.) and mercury(II) acetate (0.2 mol equiv.), the mixture was shown by GC analysis to contain fluorobenzene (39% yield) and benzene (42% recovery). A reaction of toluene under the same conditions gave rise to a mixture containing *p*-fluorotoluene (43% yield), *o*-fluorotoluene (12% yield), *m*-fluorotoluene (4% yield), and toluene (13% recovery).

The above routes to fluoroaromatics, the scope of which is being further investigated by us, should provide useful inexpensive alternatives in many cases to the current methods of synthesis. Although the mechanism of displacement of lead by fluoride is yet to be examined, we suggest that it may be either concerted as depicted in structure (**4**), or involve an initial dissociation to an aryl cation.

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