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ipso-Fluorination of aryltrimethylsilanes using xenon difluoride

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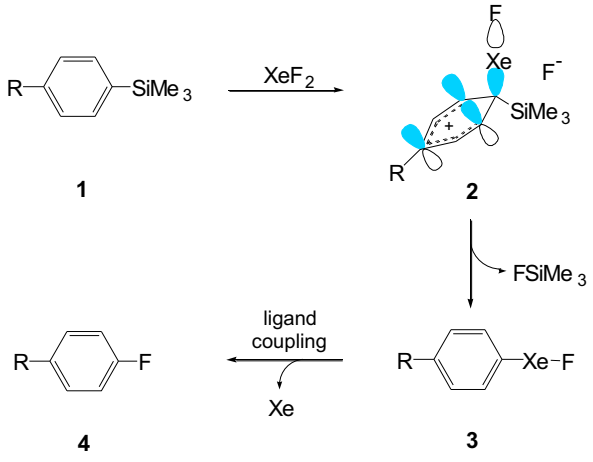
ABSTRACT

Reaction of aryltrimethylsilanes with xenon difluoride in C_6F_6/Pyrex® at room temperature gives aryl fluorides in good yield. The reaction is inhibited when acetonitrile is used as solvent but proceeds well in $CFCl_3$/Pyrex® or CH_2Cl_2/Pyrex®. Pyrex® appears to be a very effective heterogeneous catalyst for this *ipso*-fluorination. The reaction does not proceed in PTFE, quartz, soda glass or glassy-carbon flasks or Pyrex® flasks pre-rinsed with 2 M NaOH. Aryltrimethylstannanes and arylboronic acids and their esters do not undergo *ipso*-fluorination under similar conditions. Plausible mechanisms involving electrophilic addition of polarised xenon difluoride [$FXe^{\delta+}\cdots F\rightarrow Pyrex^{\delta-}$] followed by ligand coupling are discussed.

1. Introduction

Regioselective introduction of a fluoro substituent into an aromatic ring in high yield is often difficult and usually fluorine is incorporated at the beginning of a synthetic sequence. There are, however, situations when it is desirable to incorporate fluorine at a late stage: an extreme example is the introduction of ^{18}F ($t_{1/2}$ 110 min,) for positron emission tomography (PET) studies.[1] With PET methodology in mind, our interest in hypervalent reagents[2] led us to investigate electrophilic fluorination of aryltrimethylsilanes **1** using xenon difluoride. It is known that hypervalent iodine reagents react with aryltrimethylsilanes **1** to give diaryliodonium salts.[3] We anticipated that, in a similar manner, xenon difluoride would give the intermediate cation **2**, which can be stabilized by both the β-effect of the trimethylsilyl substituent and interaction with the non-bonding molecular orbital associated with the hypervalent xenon bonds. Subsequent elimination of fluorotrimethylsilane (Me_3SiF) can lead to an aryl xenon derivative **3**, which undergoes ligand coupling to form the desired aryl fluoride **4** (Scheme 1).

Our initial experiment using 4-*tert*-butylphenyltrimethylsilane **1** (R=^{t}Bu) and XeF_2 in C_6F_6 at room temperature rapidly gave an almost quantitative yield (by ^1H NMR) of 1-*tert*-butyl-4-fluorobenzene **4** (R=^{t}Bu) and Me_3SiF.[4] Fig. 1(a) shows the ^1H NMR of the reaction mixture after 1 h. Fig. 1(b) shows (after dilution with $CDCl_3$) the results of a similar reaction using 4-chlorophenyltrimethylsilane



Scheme 1.

1 (R=Cl); 1-chloro-4-fluorobenzene **4** (R=Cl) is formed in virtually quantitative yield. In both reactions the singlet due to the trimethylsilyl group has been replaced by a doublet due to Me_3SiF, which is expanded in Fig. 1(b). Volatile Me_3SiF is easily removed from the reaction mixture.

Our initial results were reported in a communication.[4] We now describe the results of a study of a series of aryltrimethylsilanes **1** and demonstrate that the outcome of the reaction depends on the nature of the substituent R, the solvent and the catalytic properties of the reaction vessel.

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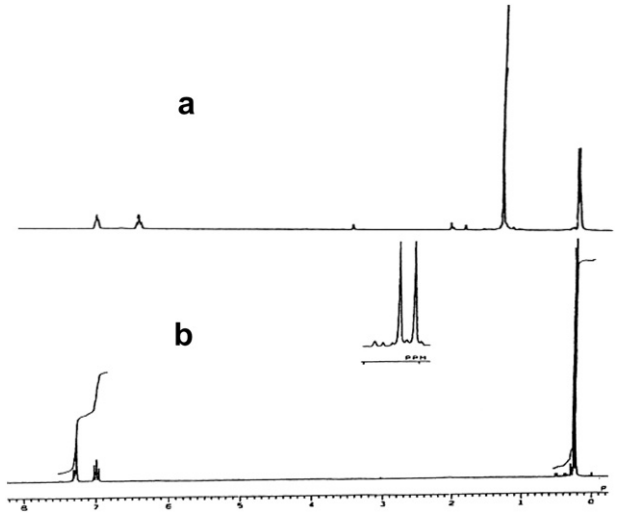


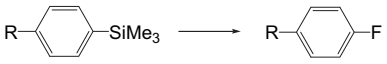
Fig. 1. ^{1}H NMRs of reaction mixtures showing quantitative formation (a) 1-*tert*-butyl-4-fluorobenzene and (b) 1-chloro-4-fluorobenzene, together with trimethylsilyl fluoride.

2. Results and discussion

We investigated a series of twelve 4-substituted phenylsilanes **1** (Table 1, entries 1–12). Phenylsilanes that are not commercially available were made by reaction of an arylmetal reagent (usually Grignard) with trimethylsilyl chloride. 4-Nitrophenyltrimethylsilane **1** (R=NO_2) was made in 35% yield by nitration of 1,4-bis(trimethylsilyl)benzene **1** (R=$SiMe_3$), and was accompanied by a 3% yield of 1,4-bis(trimethylsilyl)-2-nitrobenzene. The acetamide derivative **1** (R=NHAc) was made by reduction of the nitro derivative followed by acetylation. Aryl fluorides were available commercially with the exception of 4-*tert*-butyl-1-fluorobenzene, which was prepared by reaction of the corresponding diazonium salt with piperidine and treatment of the resulting triazine with HF–pyridine complex.

All the arylsilanes were reacted with 2 equiv of XeF_2 in hexafluorobenzene solution in a Pyrex® flask at room temperature and compositions of the reaction mixtures were analysed by ^{1}H NMR after 1 h. Yields were easily assessed by a combination of NMR and GC–MS and major products were shown to be identical to authentic samples. In most cases it was not necessary to isolate and fully characterize the aryl fluoride. We found it necessary to use 2 equiv of XeF_2 to drive the reaction to completion and give a clean reaction mixture.

Table 1
Yields of aryl fluorides **4** from silanes **1** and XeF_2



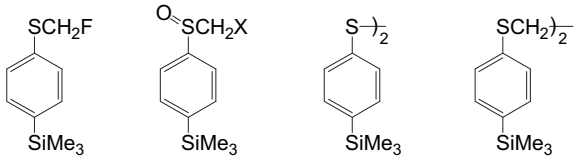
1 **4**

Entry	Substituent R	Solvent (% yield of product 4)[a]				
		C_6F_6	MeCN	CH_2Cl_2	$CHCl_3$	$CFCl_3$
1	H	65	—	—	—	—
2	Me	69	2	—	38	48
3	^{t}Bu	>95 (85)[a]	2	—	39	85
4	F	>95	0	>95 (73)[a]	—	—
5	Cl	82	4	—	0	32
6	OMe	61	—	—	—	—
7	$SiMe_3$	60	0	—	—	77
8	NO_2	8	0	—	0	0
9	COMe	9	0	—	0	0
10	COPh	<5	0	—	—	—
11	NHCOMe	0	—	—	—	—
12	SMe	4[b]	0	—	—	—

[a] Isolated yield.
[b] Using 1 equiv of XeF_2.

The observed substituent effects for the reaction **1**→**4** in C_6F_6 (Table 1) suggest that the reaction has the characteristics of an electrophilic substitution and this is consistent with a mechanism involving the intermediate **2**. An exception is the acetamide derivative (entry 11) for which the arylsilane **1** (R=NHCOMe) was largely recovered. This may have been due to a problem with solubility. The case of the methylsulfanyl derivative **1** (R=SMe) (entry 12) is different. Thioethers are readily oxidized by XeF_2 and this substrate gave a complex mixture of products, which included the derivatives **5** (8%), **6** (34%), **7** (11%), **8** (18%) and **9** (16%), in accord with earlier studies of thioethers.[5–8] Use of 1 equiv of XeF_2 gave a very low yield of the aryl fluoride **4** (R=SMe)(4%), together with starting material **1** (R=SMe)(27%), **5** (33%) and **7** (35%).

When the reactions were carried out using acetonitrile as solvent fluorodesilylation was almost completely suppressed (Table 1). We have observed similar behaviour in other reactions of XeF_2 in acetonitrile.[9–12] The Pyrex® surface of the vessel catalyses reaction of XeF_2 and we have proposed that the borosilicate glass (13% B_2O_3 and 2% Al_2O_3) acts as a heterogeneous acid catalyst, facilitating the electrophilic reactions [$FXe^{\delta+}\cdots F\rightarrow Pyrex^{\delta-}$]. Whether the Pyrex® surface acts as a Lewis acid or a Brønsted acid is not clear but acetonitrile appears to behave as a weak base inhibiting the catalytic activity. The only derivative that reacted in acetonitrile solution was the thioether **1** (R=SMe), which gave primarily the products **5** and **7**, and none of the fluoride **4** (R=SMe). The products **5** and **7** probably arise from XeF_2 reacting via an alternative single electron transfer (SET) mechanism that is not catalysed.



5 **6** (X = F) **7** (X = H) **8** **9**

To further investigate the catalytic effect of the Pyrex® surface, the reaction of 4-tolyltrimethylsilane **1** (R=Me) with XeF_2 in C_6F_6 was investigated using a number of other vessels. No reaction occurred in flasks made of PTFE, quartz, soda glass or glassy carbon. When a Pyrex® flask was pre-washed with 2 M NaOH and then rinsed with acetone and dried no reaction took place implying that the acidic catalytic sites had been neutralized. The Pyrex® surface could be reactivated by washing with chromic acid, rinsing with acetone and drying. These reactions were repeated several times using new, old and reused flasks and the results were repeatable and consistent.

Use of chloroform as solvent led to poorer yields of the fluorides **4** (Table 1) together with formation of solvent-derived by-products, including the chloride (~10%) and trichloromethyl derivatives (~30%). We have previously described an investigation of the reaction of XeF_2 with chloroform and have suggested that formation of the cation CCl_3^+ leads to the trichloromethyl derivatives via electrophilic substitution of $SiMe_3$.[13] In trichlorofluoromethane (Freon®, $CFCl_3$) yields were better than in $CHCl_3$ but inferior to those using C_6F_6 (Table 1).

Subsequent to our studies using the solvents described above, we investigated the stability of XeF_2 in a variety of solvents including CH_2Cl_2 using ^{1}H and ^{19}F NMR and found that in Pyrex® the half-life for complete decomposition in CH_2Cl_2 ($t_{1/2}$ 0.7 h) is significantly longer than that in $CHCl_3$ ($t_{1/2}$ 0.2 h).[14] Since fluorodesilylation (**1**→**4**) is a rapid reaction we considered that the increased stability in CH_2Cl_2 might make it an alternative solvent that is more convenient than C_6F_6. Previously Bardin and Frohn[15] investigated the fluorodesilylation of 4-fluorophenyltrimethylsilane **1** (R=F) in an

FEP container using CH_2Cl_2 as solvent and $BF_3{\cdot}OEt_2$ as a homogeneous Lewis acid catalyst. This led to a complex mixture of at least seven ring-derived products including the difluoride **4** (R=F)(34%). We therefore decided to investigate the same reaction using Pyrex® as a heterogeneous catalyst.

When 4-fluorophenyltrimethylsilane **1** (R=F) was reacted with 2 equiv of XeF_2 in CH_2Cl_2 in a Pyrex® flask a GC–MS analysis of the crude reaction mixture after 1 h showed almost quantitative formation of 1,4-difluorobenzene **4** (R=F). After conventional workup, the isolated yield was 73%. A separate reaction using CD_2Cl_2 as solvent was monitored by ^{1}H NMR. Fig. 2(b) shows the ^{1}H NMR of the reaction mixture when the reaction was almost complete with a small amount of the starting silane visible, together with Me_3SiF (doublet at ~0 ppm). Fig. 2(a) shows the ^{1}H NMR of the starting material **1** (R=F) with an Me_3Si singlet at ~0 ppm, and Fig. 2(c) shows the ^{1}H NMR of authentic 1,4-difluorobenzene **4** (R=F). Use of Pyrex® as catalyst rather than $BF_3{\cdot}OEt_2$ is clearly advantageous.

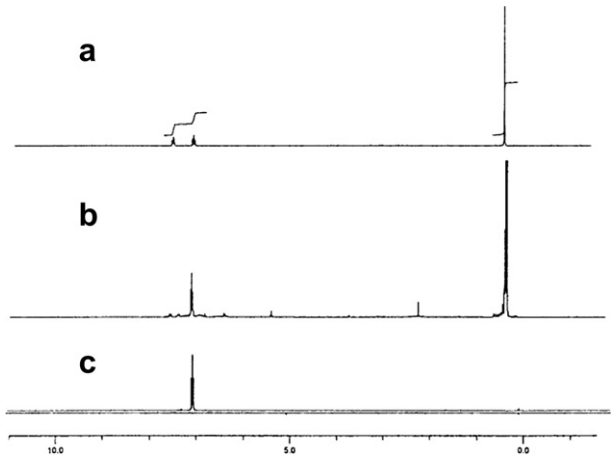
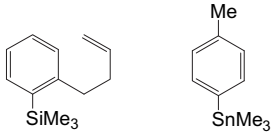


Fig. 2. ^{1}H NMR of (a) 4-fluorophenyltrimethylsilane, (b) reaction mixture after treatment of 4-fluorophenyltrimethylsilane with XeF_2 in CH_2Cl_2 at room temperature and (c) authentic 1,4-difluorobenzene.

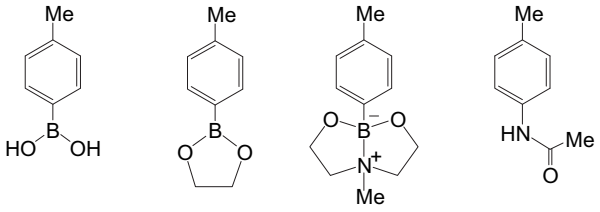
To investigate a system in which XeF_2 might give differing products depending upon the reaction conditions, we prepared 2-(but-3-en-1-yl)phenyltrimethylsilane **10** from 2-trimethylsilyl-(bromomethyl)benzene[16] and allyl magnesium bromide. When this derivative was reacted with XeF_2 in either C_6F_6 or MeCN in Pyrex® no reaction was observed. This lack of reactivity may be due to steric hindrance, particularly for fluorodesilylation which may well occur on the flask surface.

Aryltrimethylstannanes are known to undergo *ipso*-fluorination using electrophilic fluorinating agents, such as caesium fluoroxysulfate[17] and F-TEDA-BF4 with AgOTf.[18] We investigated the reactions of the trimethyltin derivative **11** with XeF_2 in Pyrex®/C_6F_6 and Pyrex®/$CFCl_3$. In both reactions ~70% starting material **11** was recovered. In contrast to the corresponding trimethylsilane (Table 1, entry 2) only a trace (~3%) of the fluoride **4** (R=Me) was detected and the only other product was toluene (20–30%). When the reaction in $CFCl_3$ was pushed to completion by addition of another 2 equiv of XeF_2, the main product was toluene (65%) together with 4-fluorotoluene (33%). The mechanism of protodestannylation is not clear: it may involve formation of HF or alternatively SET resulting in homolytic cleavage of the C–Sn bond.



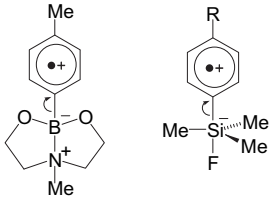
10 **11**

We considered it possible that a boron substituent could act as both an intramolecular Lewis acid and a leaving group leading to an aryl fluoride, and we therefore investigated the boronic acid **12** and its derivatives **13** and **14**.[19] Reaction of the boronic acid **12** with 2 equiv of XeF_2 in MeCN in a PTFE vessel gave 4′-methylacetanilide **15** (40%) as the only significant organic product. The solvent (MeCN) clearly participates in the reaction displacing boron. Prakash and co-workers[20] have recently described similar reactions of a series of boronic acids with XeF_2/MeCN with yields varying in the range 13–95%. They proposed a SET initiated mechanism in accord with our previous proposals that XeF_2 reacts with organic substrates via SET in MeCN solution.[9,11,12,21] Reaction of the boronic acid **12** with XeF_2 in CH_2Cl_2 gave a dark brown fuming solution, which was shown to be a complex mixture containing a tiny amount of 4-fluorotoluene **4** (R=F) (^{19}F NMR −119 ppm).



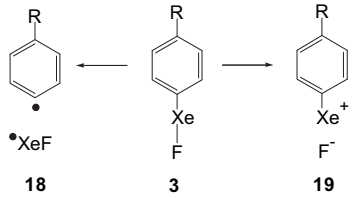
12 **13** **14** **15**

Similar results were obtained using the derivatives **13** and **14**. The boronic ester **13** gave the acetanilide **15** in 37% yield and the 1,3-dioxa-6-aza-2-boracine **14** gave the same product **15** in 73% yield. Reaction of compound **14** in CH_2Cl_2 gave significant amounts of 4-chlorotoluene suggesting the formation of 4-tolyl radicals after initial SET, possibly because the tetravalent boron undergoes heterolytic cleavage from the aryl radical cation fragment **16**. No other products of interest were detected in the reactions of compounds **13** and **14** with XeF_2 in CH_2Cl_2.



16 **17**

In our original communication,[4] we suggested that additional solvent-derived products, formed during reaction of 4-*tert*-butylphenyltrimethylsilane **1** (R=^{t}Bu) with XeF_2 in $CHCl_3$, were formed from 4-*tert*-butylphenyl radicals **18** (R=^{t}Bu), generated via the intermediate **17** (R=^{t}Bu) or by homolytic C–Xe bond cleavage of the intermediate **3** (R=^{t}Bu). Since XeF_2 rapidly decomposes in $CHCl_3$,[13] it is possible that the observed 1-*tert*-butyl-4-trichloromethylbenzene $ArCCl_3$ (11%) is formed by electrophilic *ipso*-substitution mediated by CCl_3^+.[13] Formation of 1-*tert*-butyl-4-chlorobenzene ArCl (28%) is less likely to occur via an electrophilic mechanism and its formation via an aryl radical **18** is plausible. This product is also formed in $CFCl_3$ (7%). Alternatively, the C–Xe–F hypervalent bond might undergo heterolytic cleavage with loss of fluoride (**3**→**19**). Elimination of Xe^0 could then lead to a reactive aryl cation. Salts of the type $ArXe^+$ Y^- have been characterized when Y is a non-nucleophilic anion.[22–25]



Although the proposal of an aryl xenon intermediate **3** was the basis for our original investigation, there is no direct evidence that these species are intermediates in the fluorodesilylations **1**→**4**. These reactions do have the characteristics of electrophilic substitutions and formation of intermediates **3** is consistent with XeF_2 reacting as $FXe^{\delta+}\cdots F\rightarrow Pyrex^{\delta-}$ (i.e., as an FXe^{+} equivalent). A number of aryl xenon species of the type Ar–Xe–X have been isolated and characterized, including Ar–Xe–F[25–27] and Ar–Xe–OCOR.[28,29] These species do undergo ligand coupling with elimination of Xe,[25] and there is evidence that the hypervalent C–Xe bond undergoes homolytic cleavage.[26,30] If this is the case, formation of the radical pair **18** within an unreactive solvent shell can account for the formation of the aryl fluorides **4**.

3. Conclusions

We have shown that under specific conditions aryltrimethylsilanes **1** that do not carry an electron-withdrawing substituent can give the corresponding aryl fluoride **4** rapidly at room temperature. A recent study has shown that palladium-catalysed silylation of aryl chlorides gives good yields of aryltrimethylsilanes **1**.[31] Fluorodesilylation therefore provides a potentially convenient way of converting aryl chlorides to aryl fluorides. Since [^{18}F]XeF_2 is now available on a production scale using a micro-reactor,[21,32] this methodology provides a potential route to [^{18}F]-substituted aromatic rings for PET studies.

4. Experimental section

4.1. General

Melting points were determined using a Reichert Kofler Block apparatus and are uncorrected. Infrared spectra were recorded on Perkin–Elmer paragon 1000 FT-IR or Perkin–Elmer 881 spectrophotometers. Unless otherwise stated IR spectra were measured as KBr discs. NMR spectra were recorded at ambient temperature using a Bruker Avance DPX300 NMR spectrometer at 300, 75.5 and 282 MHz for ^{1}H, ^{13}C and ^{19}F spectra, respectively. Chemical shifts are quoted relative to TMS as an external standard (for ^{1}H, ^{13}C) or $CFCl_3$ (for ^{19}F). Gas chromatography–mass spectrometry was carried out with a Hewlett–Packard 5890 gas chromatograph coupled to a 5970B mass selective detector (quadrupole mass spectrometer using 70 eV electron impact ionization). Chromatography was performed on an immobilized polydimethylsiloxane phase in a fused silica column (12 m×0.2 mm) (SGE, Milton Keynes, UK). Helium was used as a carrier gas at 1 mL min^{-1}. Elemental analyses were determined using a Perkin–Elmer 240 CHN Elemental Analyser. Accurate mass spectra were performed by the EPSRC National Mass Spectrometry Service. All solvents were pre-distilled and dried appropriately prior to use. Flash chromatography was performed using silica gel (Janssen Chimica) 0.035–0.07 mm. Short path distillations were performed using a Buchi GKR-51 Kugelrohr Distillation Kit. Concentration and evaporation refer to the removal of volatile materials under reduced pressure on a Büchi Rotovapor.

4.2. Aryltrimethylsilanes

Phenyltrimethylsilane **1** (R=H), 4-fluorophenyltrimethyl-silane **1** (R=F) and 1,4-bis(trimethylsilyl)benzene **1** (R=$SiMe_3$) were purchased from Sigma–Aldrich, UK. 4-Methyl-phenyltrimethylsilane **1** (R=Me) and 4-chlorophenyltrimethylsilane **1** (R=Cl) were purchased from ABCR GmbH & Co. KG, Germany. 4-Methoxyphenyltrimethylsilane **1** (R=OMe) (5.8 g, 25%); ^{1}H NMR ($CDCl_3$) δ 0.36 (s, 9H, $SiMe_3$), 3.89 (s, 3H, OMe), 7.5 (dd *J* 8.0 and 1.0 Hz, 4H, aromatic H); MS (EI) *m*/*z* 180 (M$^{\bullet+}$) (14%), 165 (100%) was prepared as a colourless oil by the method of Effenberger and Häbich.[33] 4-Acetylphenyltrimethylsilane **1** (R=COMe) (3.4 g, 60%), colourless oil, bp 170 °C at 55 mmHg [lit.,[34] 65 °C at 0.4 mmHg]; ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 9H, $SiMe_3$), 2.6 (s, 3H, COMe), 7.65 (d *J* 8.2 Hz, 2H, ArH) and 7.9 (d *J* 8.2 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) −1.8 (SiMe), 26.0 (Me), 126.8 (CH), 133.1 (CH), 136.8 (CSi), 146.5 (CAc) and 197.4 (CO); IR (liquid film) ν_{max}/cm^{-1} 3072, 1688, 1596, 1388, 1252 and 839; MS (EI) *m*/*z* 192 (M$^{\bullet+}$), 177 (100%), 162, 134, 119 and 91, was prepared according to the procedure of Eaborn and co-workers.[34] An analogous procedure gave 4-benzoylphenyltrimethylsilane **1** (R=COPh) (6.75 g, 89%), colourless oil, bp 75–77 °C at 0.1 mmHg [lit.,[35] 156 °C at 3 mmHg]; ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 9H, $SiMe_3$) and 7.4–7.9 (m, 9H, ArH); ^{13}C NMR ($CDCl_3$) −1.6 (SiMe), 127.9 (CH), 128.7 (CH), 129.6 (CH), 132.0 (CH), 132.8 (CH), 137.2 (CSi), 137.4 (C.COPh), 145.7 (C.COAr) and 196.0 (CO); IR (liquid film) ν_{max}/cm^{-1} 3067, 2956, 1662, 1598, 1281 and 847; MS (EI) *m*/*z* 254 (M$^{\bullet+}$), 239 (100%), 165, 134, 105 and 77.

*4.2.1. 4-tert-Butylphenyltrimethylsilane **1** (R=^{t}Bu).* This derivative was prepared by the method outlined by Eaborn.[36] To Mg turnings (2.05 g, 85.5 mmol) suspended with stirring in dry ether (50 mL) was rapidly added 1-bromo-4-*tert*-butylbenzene (15.2 g, 71.0 mmol) in dry ether (50 mL). A small amount of iodine and 1,2-dibromoethane (3 drops) were added to initiate the reaction, and dry ether (100 mL) was then rapidly added. When formation of the Grignard reagent was complete, trimethylsilyl chloride (7.74 g, 71.0 mmol) in dry ether (50 mL) was added over 30 min. The mixture was then stirred and heated under reflux overnight. Most of the solvent was then evaporated and the residue treated with satd aq NH_4Cl solution (50 mL). The ether layer was separated and the aqueous layer extracted with ether (2×50 mL). The combined ether layers were dried ($MgSO_4$) and evaporation gave a solid product, which after recrystallisation from EtOH/H_2O was identified as compound **1** (R=^{t}Bu) (12.2 g, 83%), colourless crystals, mp 78 °C [lit.,[36] 78 °C]; ^{1}H NMR ($CDCl_3$) δ 0.31 (s, 9H, $SiMe_3$), 1.37 (s, 9H, CMe_3) and 7.48 (dd *J* 8.3 Hz, 4H, ArH); IR (KBr) ν_{max}/cm^{-1} 3050, 2960, 1250, 838 and 759; MS (EI) *m*/*z* 206 (M$^{\bullet+}$) (10%), 191 (100%). Anal. Calcd for $C_{13}H_{22}Si$: C, 75.65; H, 10.74. Found: C, 75.70; H, 10.70%.

An analogous procedure using 4-bromothioanisole gave 4-methylsulfanylphenyltrimethylsilane **1** (R=SMe) (4.80 g, 95%), yellow oil, bp 216 °C at 760 mmHg [lit.,[37] 121 °C at 10 mmHg]; ^{1}H NMR ($CDCl_3$) δ 0.30 (s, 9H, $SiMe_3$), 2.40 (s, 3H, SMe) and 7.2–7.5 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$) −1.3 (SiMe), 15.0 (SMe), 125.4 (CH), 128.6 (CS), 133.5 (CH) and 139.3 (CSi); IR (liquid film) ν_{max}/cm^{-1} 3063, 2955, 1582, 1251, 839 and 804; MS (EI) *m*/*z* 196 (M$^{\bullet+}$), 181 (100%), 151, 105, 91 and 43.

*4.2.2. 4-Nitrophenyltrimethylsilane **1** (R=NO_2).* A solution 1,4-bis (trimethylsilyl)benzene **1** (R=$SiMe_3$) (5.0 g, 22.5 mmol) in acetic anhydride (14.0 mL) was heated under reflux and a solution of 90% fuming nitric acid (6.0 mL) in acetic anhydride (10.0 mL) was added over 1.5 h. After cooling, water (100 mL) was added and the aqueous solution extracted with Et_2O. The organic phase was washed with aq NaOH and with H_2O, dried (Na_2SO_4) and evaporated. The residue was purified by column chromatography (silica gel: eluent,

petroleum ether (bp 60–80 °C)) to give compound **1** (R=NO_2) (1.69 g, 35%), colourless prisms, mp 36–7 °C [lit.,[38] 38–9 °C]; ^{1}H NMR ($CDCl_3$) δ 0.3 (s, 9H, $SiMe_3$), 7.65 (d *J* 7.8 Hz, 2H, ArH) and 8.15 (d *J* 7.8 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) -1.60 (SiMe), 122.1 (CH), 134.0 (CH), 147.4 (CSi) and 149.8 (CNO_2); IR (KBr) ν_{max}/cm^{-1} 1519, 1352, 1251 and 837; MS (EI) *m*/*z* 195 (M$^{\bullet+}$), 180 (100%), 164, 134, 119 and 105, and 1,4-bis(*trimethylsilyl*)-2-*nitrobenzene* (0.15 g, 3%), colourless crystals, mp 30–35 °C; ^{1}H NMR ($CDCl_3$) δ 0.3 (s, 9H, $SiMe_3$), 0.4 (s, 9H, $SiMe_3$), 7.7 (m, 2H, ArH) and 8.4 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$) −1.4 (SiMe), 0.5 (SiMe), 128.3 (CH), 135.5 (CH), 137.9 (CH), 144.0 (CSi) and 153.2 (CNO_2); IR (KBr) ν_{max}/cm^{-1} 3067, 2955, 1700, 1664, 1653, 1533, 1506, 1353, 1252, 836 and 749; MS (EI) *m*/*z* 252 (M$^{\bullet+}$−Me), 207, 177, 133 and 83. Anal. Calcd for $C_{12}H_{21}NO_2Si_2$: C, 53.89; H, 7.91; N, 5.24. Found: C, 53.90; H, 8.29; N, 5.31%.

*4.2.3. N-[4-(Trimethylsilyl)phenyl]acetamide **1** (R=NHCOMe).* A solution 4-nitrophenyltrimethylsilane **1** (R=NO_2) (0.5 g, 2.6 mmol) in toluene (50 mL) together with 10% Pd/C catalyst (100 mg) was stirred under hydrogen (1 atm pressure) until uptake of hydrogen was complete. After filtration through Celite and evaporation, Kugelrohr distillation of the residue gave 4-(trimethylsilyl)aniline **1** (R=NH_2) (3.71 g, 89%), pale yellow oil, bp 240 °C at 350 mmHg [lit.,[39] 130–132 °C at 30 mmHg]; ^{1}H NMR ($CDCl_3$) δ0.1(s, 9H, $SiMe_3$), 3.3 (s, 2H, NH_2), 6.35 (d *J* 8.3 Hz, 2H, ArH) and 7.05 (d *J* 8.3 Hz, 2H, ArH); MS (EI) *m*/*z* 165 (M$^{\bullet+}$), 133, 120, 106, 77, 65 and 43. The product **1** (R=NH_2) (0.19 g, 1.2 mmol) in dry toluene (5.0 mL) was stirred vigorously and acetic anhydride (0.11 mL, 1.2 mmol) and pyridine (0.10 mL, 1.2 mmol) were added. After stirring at room temperature (3 h) a white crystalline solid had separated from the orange solution. This was collected and identified as compound **1** (R=NHCOMe)(0.13 g). The solution was evaporated and the orange residue was purified by chromatography (silica gel: eluent, petroleum ether (bp 60–80 °C)/ethyl acetate 4:1) to give an additional batch (0.04 g). The batches were combined to give compound **1** (R=NHCOMe) (0.17 g, 71%), colourless plates, mp 170–171 °C [lit.,[40] 169–170 °C]; ^{1}H NMR ($CDCl_3$) δ 0.25(s, 9H, $SiMe_3$),2.15 (s, 3H, Me) and 7.5 (m, 4H, ArH); IR (KBr) ν_{max}/cm^{-1} 3255, 1670, 1590, 1540, 1248 and 840; HRMS *m*/*z* calcd for $C_{11}H_{17}NOSi$ 207.1079, found 207.1082.

*4.2.4. 2-(But-3-en-1-yl)phenyltrimethylsilane **10**.* To a stirring solution of 2-trimethylsilyl-(bromomethyl)benzene[16] (1.0 g, 4.0 mmol) in THF (5.0 mL), under an argon atmosphere, allyl magnesium bromide (21.0 mL, 21.0 mmol) was added dropwise. The solution darkened with formation of a white precipitate. The mixture was then heated under reflux (1 h), cooled to 0 °C and carefully quenched with 2 M H_2SO_4. Water was then added and the two phases separated. The aqueous layer was extracted with Et_2O, dried ($MgSO_4$) and evaporated to give a yellow oil (0.58 g), which was Kugelrohr distilled to give compound **10** (0.51 g, 61%), pale yellow oil, bp 135–140 °C at 40 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.2 (s, 9H, $SiMe_3$), 2.3 (m, 2H, CH_2), 2.8 (m, 2H, CH_2), 4.95 (m, 2H, CH_2), 5.85 (m, 1H, CH) and 7.0–7.4 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$) 0.4 (SiMe), 35.4(CH_2), 36.5 (CH_2), 114.8 (CH_2), 125.2 (CH), 128.5 (CH), 129.2 (CH), 134.5 (CH), 138.0 (CCH_2) and 147.6 (CSi); IR (KBr) ν_{max}/cm^{-1} 3058, 2956, 1438, 1262, 1249, 1128, 912, 849, 837, 752 and 621; MS (EI) *m*/*z* 204 (M$^{\bullet+}$), 189, 163, 129, 105, 59(100%) and 31. Anal. Calcd for $C_{13}H_{20}Si$: C, 76.40; H, 9.86. Found: C, 76.15; H, 9.60%.

4.3. Fluorodesilylations using xenon difluoride

Xenon difluoride was purchased from Apollo Scientific Ltd, UK. Reactions were carried out in conventional round bottom Pyrex® flasks (10 mL). In early studies reactions were carried out in a glove box under an atmosphere of dry nitrogen but it was subsequently found that this was unnecessary. In a typical procedure, the aryltrimethylsilane **1** (0.74 mmol) in the appropriate solvent (5 mL) was stirred at room temperature and xenon difluoride (250 mg, 1.48 mmol) was quickly added. Stirring was continued (1 h) and the mixture then analysed by ^{1}H NMR and GC–MS. If required, the aryl fluoride **4** was isolated by evaporation followed by chromatography (silica gel: eluent, petroleum ether (bp 60–80 °C)/ethyl acetate). Typically, this procedure using hexafluorobenzene as solvent gave 4-*tert*-butyl-fluorobenzene **4** (R=^{t}Bu) (96 mg, 85%), colourless oil, identical with an authentic sample, and using dichloromethane as solvent gave 1,4-difluorobenzene **4** (R=F) (62 mg, 73%), colourless liquid, identical with an authentic sample.

4.4. Fluoroarenes 4

Authentic samples of the fluoroarenes **4** (R=H, Me, F, Cl, OMe, $SiMe_3$, NO_2, COMe, COPh, SMe) were purchased from Sigma–Aldrich, UK. 4′-Fluoroacetanilide **4** (R=NHCOMe) was purchased from Apollo Scientific Ltd, UK.

*4.4.1. 4-tert-Butyl-fluorobenzene **4** (R=^{t}Bu).* 4-*tert*-Butylaniline (4.5 g, 0.03 mol) and water (20 mL) were cooled in an ice bath and HCl (37%) (6.0 g, 0.06 mol) in water (40 mL) was then added with stirring at 0 °C. After 10 min, $NaNO_2$ (2.08 g, 0.03 mmol) in water (12 mL) was added slowly, keeping the temperature below 5 °C, and the mixture turned yellow. After a further 30 min, piperidine (11.73 g, 0.138 mol) in water (10 mL) was added. Orange crystals formed on top of the yellow liquid and these were collected, washed, dried under vacuum and identified as 1-(4-*tert*-butylphenyl)-3,3-(1,5-pentadienyl)triazine (6.86 g, 93%), orange prisms; ^{1}H NMR ($CDCl_3$) δ 1.3(s, 9H, CMe_3),1.6 (m, 6H, CH_2), 3.7 (br s, 4H, NCH_2) and 7.3 (s, 4H, ArH), which was used as follows without further purification. The triazine (4.48 g, 0.018 mol) was dissolved in a minimum amount of toluene in a diaflon (polytrifluoromonochloroethylene) vessel and HF–pyridine complex (2.61 g, 5 equiv) was added slowly. The mixture was stirred (30 min) and then heated to 50 °C (10 min). After cooling, the mixture was neutralised using aq NaOH (ca. 4 mL) and water (25 mL) was added. The aqueous mixture was extracted with ether (3×25 mL) and the combined ether layers were washed with dil HCl, dried ($MgSO_4$) and distilled to afford 4-*tert*-butyl-fluorobenzene **4** (R=^{t}Bu) (0.53 g, 19%), colourless oil, bp 167–172 °C [lit.,[41] bp 172 °C]; ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 9H, CMe_3),7.05(m, 2H, ArH) and 7.40 (m, 2H, ArH); ^{19}F NMR ($CDCl_3$) −119.0 (s, CF); IR (liquid film) ν_{max}/cm^{-1} 3060, 2965, 1392, 1364 and 1230; MS (EI) *m*/*z* 152 (M$^{\bullet+}$) (20%), 137 (100%), 121, 115, 109, 101, 95, 80, 74, 63 and 57.

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