Arylation of [60]fullerene *via* electrophilic aromatic substitution involving the electrophile $C_{60}Cl_6$: frontside nucleophilic substitution of fullerenes

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Reaction of $C_{60}Cl_6$ and ferric chloride with aromatic compounds gives the corresponding C_s-symmetric aryl derivatives $C_{60}Ar_5Cl$, where Ar = phenyl, tolyl, anisyl, *tert*-butylphenyl, fluorophenyl, trimethylsilylphenyl and thienyl. The derivatives arising from exclusive *para* substitution in anisole and fluorobenzene, together with $C_{60}(4\text{-}FC_6H_4)_5H$ have been isolated and fully characterised. Toluene undergoes substitution in the *ortho* as well as the *para* position. Traces of octaaryl derivatives are obtained in the reaction with toluene and anisole. The steric bulk of the chlorofullerene (the largest electrophile known) accounts for the failure to achieve substitution in mesitylene and the abnormal deprotonation rather than desilylation in the reaction with trimethylsilylbenzene. Protiodesilylation of the trimethylsilylphenyl derivative was achieved by reaction with acid. With triphenylphosphine, $C_{60}Ar_5Cl$ compounds react to give $C_{60}Ar_5H$ and with toluene/$FeCl_3$, $C_{60}Ph_5Cl$ gives $C_{60}Ph_5$tolyl. $C_{60}(4\text{-}FC_6H_4)_5H$ showed a marked tendency to acquire oxygen, suggesting that this oxygenation is facilitated by electron withdrawal. FAB mass spectrometry of $C_{60}(4\text{-}FC_6H_4)_5H$, $C_{60}Ph_5Cl$, $C_{60}Ph_5H$ and also of $C_{70}Ph_{10}$ shows addition of up to $9C_2$ fragments in each case; this parallels two previous reports of C_2 addition during FAB mass spectrometry. The replacement of chlorine by aryl groups at the same site indicates that frontside nucleophilic substitution on the cage must occur, involving a cationic fullerene intermediate.

Formation of arylfullerenes[1] is a particularly fruitful area of fullerene research. Not only are the compounds relatively stable, but they are fairly easy to prepare and purify, survive EI mass spectrometry, give considerable ^1H and ^{13}C NMR information due to the aryl rings, and provide the potential for a huge range of derivatives. In a preliminary publication we outlined details for the preparation of the [60]fullerene derivatives $C_{60}Ph_5X$ (X = Cl, H).[2] We now describe the formation of a range of aryl derivatives prepared from $C_{60}Cl_6$, the preparation of which was described earlier.[3]

The derivatives of [60]fullerene was prepared as described in the Experimental section. A problem encountered in this work is that substitution can in principle occur both *ortho* and *para* to the substituent X in PhX compounds. Since five aryl groups became attached to the cage, the number of possible products is 28. For this reason we have not completely characterised some of the derivatives, but in the case of substitution in fluorobenzene and anisole, *para* orientation is strongly favoured,[4] permitting isolation and full characterisation of a single derivative with relative ease.

Experimental and discussion

NMR spectra ($CDCl_3$ used throughout) were obtained at the following field strengths: ^1H, 50 MHz; ^{13}C, 125.8 MHz; ^{19}F, 282.2 MHz. EI mass spectra were obtained using a 70 eV ionisation potential. *J* Values are given in Hz.

$C_{60}Ph_5Cl$ and $C_{60}Ph_5H$

These were prepared as described previously,[2] the structures (Fig. 1, X = Cl, H), being proved by both ^{13}C and ^1H NMR spectroscopy[2] together with NOE couplings for X = H (Fig. 1). If the formation of $C_{60}Ph_5Cl$ is carried out at room temperature, the reaction takes many weeks for completion, and two other compounds, $C_{60}Ph_2$ and $C_{60}Ph_4$ (which have been characterised)[5] can be isolated.

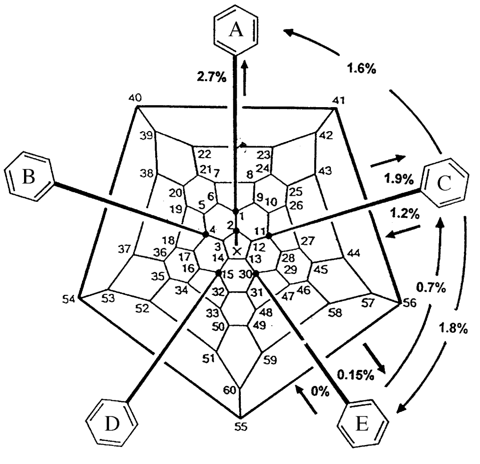

Fig. 1 Schlegel diagrams of the $C_{60}Ph_5X$ (X = Cl, H) structures. The NOE couplings (for X = H) are those between (*a*) the cage hydrogen and the *ortho* hydrogens of the phenyl rings and (*b*) the *ortho* hydrogens of the phenyl rings.

$C_{60}(4\text{-}FC_6H_4)_5Cl$

This was prepared in the general manner,[2] using fluorobenzene as the aromatic to give, after work up, red plates of C_{60}-$(4\text{-}FC_6H_4)_5Cl$, 10 mg, 63%. *m/z* = 1230, 1196. The ^{13}C NMR spectrum has 28 peaks in the cage sp^2 region confirming the C_s symmetry: δ_C 156.07 (2C), 153.20 (2C), 150.45 (2C), 149.68 (2C), 148.59 (2C), 148.57 (1C), 148.56 (2C), 148.55 (2C), 148.48 (2C), 148.27 (2C), 148.10 (2C), 148.01 (1C), 147.63 (2C), 147.13 (2C), 146.99 (2C), 145.99 (2C), 144.78 (2C), 144.62 (2C), 144.45 (2C), 144.30 (2C), 144.20 (2C), 144.14 (2C), 143.51 (2C), 143.47

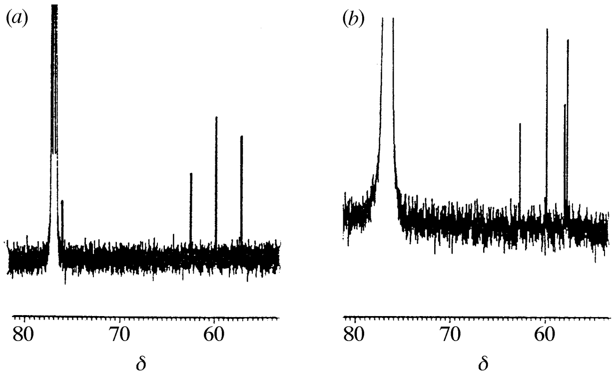

Fig. 2 ^{13}C NMR spectra (sp^3 region) for (*a*) $C_{60}(4\text{-}FC_6H_4)_5Cl$; (*b*) $C_{60}(4\text{-}FC_6H_4)_5H$

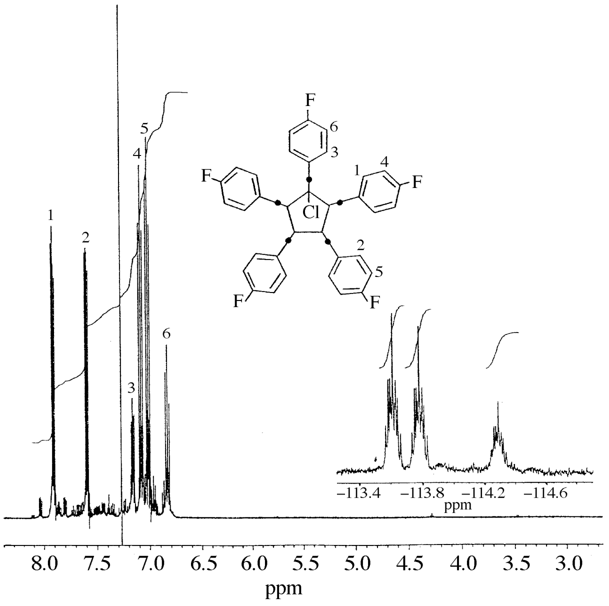

Fig. 3 ^1H NMR spectrum of $C_{60}(4\text{-}FC_6H_4)_5Cl$ (motif) showing assignments; inset shows the ^{19}F NMR spectrum

(2C), 143.10 (2C), 142.86 (2C), 142.83 (2C), 142.74 (2C). The fluorine-bearing *ipso* carbons appeared as doublets at δ_C 162.1 (2C, *J* 249.5), 162.15 (2C, *J* 249.6) and 161.7 (1C, *J* 249.2); the other *ipso* carbons could not be resolved. The symmetry is also confirmed by four peaks in the sp^3 region: δ_C 76.1 (1C), 62.4 (1C), 59.7 (2C), 57.0 (2C); the most downfield peak is attributed to C-1 which bears the chlorine [Fig. 2(*a*)].

The ^{19}F NMR (inset, Fig. 3) shows three multiplets with intensity ratios of 2:2:1 as required.

The peaks in the ^1H NMR spectrum (Fig. 3) are identified by the following argument:

(1) There are two groups of peaks (1,2,3), (4,5,6) each with a 2:2:1 intensity ratio (*J* 8.7–8.9).

(2) Peaks 1,2 and 4,5 must be due to hydrogens on the two pairs of equivalent rings.

(3) Hydrogens (*ortho*) nearest to the cage will be more sensitive to change in environment than those (*meta*) further away. Peaks 1, 2 and 3, being spread further apart, must therefore be due to the *ortho* hydrogens. This is also confirmed by (*i*) additional splitting of peaks 1, 2 and 3 due to through-space interactions and (*ii*) peaks 4, 5 and 6 show larger splitting due to coupling with the adjacent fluorines.

$C_{60}(4\text{-}FC_6H_4)_5H$

The above chloride (17.3 mg) was dissolved in benzene (15 cm^3) and triphenylphosphine (excess) was added. The solution darkened and after *ca.* 30 min a red microcrystalline solid precipitated. After a further 4 h (at which time precipitation was complete) the solution was decanted from the solid which was washed with benzene. The mother liquors and washings were evaporated under reduced pressure, and the residue dissolved in CCl_4 was passed through a short silica gel column. Solvent was removed from an orange fraction, to give a red solid which was combined with the precipitate and the whole recrystallised from benzene to give 1,2,4,11,15,30-hexahydro-1,4,11,15,30-penta-(4′-fluorophenyl)[60]fullerene (67%).

The ^{13}C NMR spectrum has 28 peaks in the sp^2 cage region confirming the C_s symmetry: δ_C 155.45 (2C), 152.05 (2C), 151.51 (2C), 150.77 (2C), 148.56 (2C), 148.52 (2C), 148.38 (2C), 148.12 (2C), 147.98 (2C), 147.89 (1C), 147.83 (2C), 147.45 (2C), 147.00 (2C), 146.87 (2C), 146.79 (2C), 146.59 (1C), 145.33 (2C), 145.27 (2C), 145.06 (2C), 144.72 (2C), 144.14 (2C), 144.13 (2C), 144.05 (2C), 143.95 (2C), 143.85 (2C), 143.82 (2C), 143.10 (2C), 142.97 (2C), and four peaks in the sp^3 region: 62.7 (1C), 59.8 (2C), 57.9 (1C), 57.7 (2C). Compared to the spectrum for the chloro precursor, the peaks due to C-1 and C-2 are more upfield (by 4.2 and 13.4 ppm, respectively) due to replacement of chlorine by hydrogen [*cf.* Figs. 2(*a*), (*b*)]. The fluorine-bearing *ipso* carbons appeared as doublets at δ_C 162.09 (2C, *J* 248.8), 161.98 (2C, *J* 248.3) and 161.2 (1C, *J* 248.2). The peaks for the other aryl carbons fall between δ_C 134.91 and 115.25 and are noticeably more upfield than those for the analogous pentaphenyl compound.[2]

The ^1H NMR spectrum resembles that of the chloro precursor: δ_H 7.69–7.74, 4 H, dd, *J* 8.9; 7.56–7.53, 4 H, dd, *J* 8.9; 7.36–7.33, 2 H, dd, *J* 8.9; 7.09–7.06, 4 H, dd, *J* 8.75; 6.95–6.93, 4 H, dd, *J* 8.75; 6.91–6.875, 2 H, dd, *J* 8.75. The loss of chlorine causes a slight upfield shift in peak positions, except for those due to the hydrogens on ring A which are shifted slightly downfield, a similar result being obtained for the pentatolyl compound (below); the singlet due to the hydrogen on the cage appears at δ 5.23, very slightly downfield from that for $C_{60}Ph_5H$.[2]

The mass spectrum indicated the presence in this compound of small amounts of the hexaaryl derivative (*m/z* 1290) and mono- and di-oxygenated derivatives (*m/z* 1212 and 1228, respectively). Recently we have found that $C_{60}Ph_5H$ is converted completely to two dioxygenated derivatives on standing over a period of 12 months.[6] One compound is a benzo[*b*]furanyl derivative and the mechanism for its formation seems to involve initial oxygen insertion into the C–H bond; consistent with this view is our observation that fullerenes $C_{60}Ph_x$ (*x* even) are more stable. The fluoro compound is particularly susceptible to oxygenation and rapidly adds oxygen on standing in air for only a few days.

$C_{60}(4\text{-}MeOC_6H_4)_5Cl$

Anisole (1 cm^3) was added to $C_{60}Cl_6$ (42 mg) dissolved in dry CH_2Cl_2 (100 cm^3). $TiCl_4$ (0.5 cm^3 of a 1.0 M solution in CH_2Cl_2) was added and the mixture was stirred at room temperature for 24 h. After work up as above, the product was filtered through Celite to remove titanium salts and precipitated from excess anisole by the addition of pentane. ($FeCl_3$ may also be used as catalyst, but this gives a greater number of byproducts which follows from the greater susceptibility of anisole to electrophilic aromatic substitution.)

Column chromatography (silica gel, dichloromethane), gave four orange–red products, with R_f values of 0.58, 0.50, 0.40 (31 mg, 54%) and 0.21. The first two fractions gave a main peak at 1241 amu, consistent with the presence of a deoxygenated derivative, whilst the latter contained a mixture of $C_{60}(4\text{-}MeOC_6H_4)_5OH$ (*m/z* 1273), $C_{60}(4\text{-}MeOC_6H_4)_6$ (*m/z* 1363), $C_{60}(4\text{-}MeOC_6H_4)_8$ (*m/z* 1578) [and $C_{60}(4\text{-}MeOC_6H_4)_7$ at *m/z* 1471 and presumably a fragment of the octaaryl component]; demethylated fragments were also evident in all three fractions and it is probable that chlorine (readily lost under EIMS conditions) was present in some. The main component gave *m/z* = 1257 (Fig. 4).

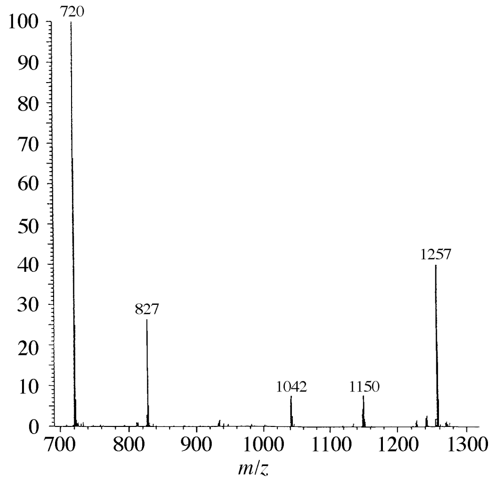

Fig. 4 EI mass spectrum for $C_{60}(4\text{-}MeOC_6H_4)_5Cl$

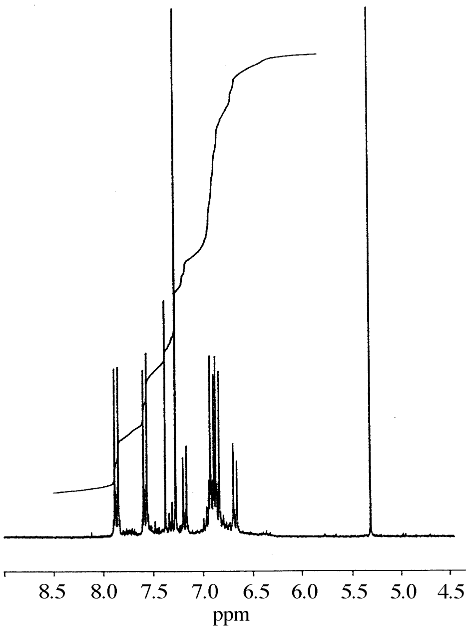

Fig. 5 ^{1}H NMR spectrum for $C_{60}(4\text{-}MeOC_6H_4)_5Cl$

The ^{1}H NMR spectrum for the aryl hydrogens: δ_H 7.86, 4 H, d, J 17.7; 7.58, 4 H, d, J 17.7; 7.18, 2 H, J 17.7; 6.90, 4 H, J 17.7; 6.85, 4 H, J 17.7; 6.67, 2 H, J 17.7 (Fig. 5), is similar to that for the corresponding fluoro compound and confirms the peak assignments made above. Thus whereas the peaks corresponding to set (1,2,3) in Fig. 3 (those nearest the cage) are in virtually the same positions, the peaks corresponding to set (4,5,6) (those nearest the substituent), are each more upfield (by δ 0.17) as expected from the different electronic effects of MeO and F. The methyl protons appeared at δ 3.85, 3.84 and 3.82 (2:2:1 ratio).

Reaction of $C_{60}Cl_6$ with toluene

A pure product could not be obtained here for reasons given in the introduction to the Experimental: the steric effect of methyl is insufficient to prevent some substitution occurring *ortho* to it in some of the aryl rings.

$C_{60}Cl_6$ (43 mg) was dissolved in dry redistilled toluene (50 cm^3), a catalytic amount of ferric chloride was added, and the mixture stirred for 24 h, during which time the solution changed colour from orange to dark green. The mixture was washed with water (2 × 15 cm^3) whence the colour reverted to orange and the organic layer was separated and dried ($MgSO_4$). The solvent was removed and the dark-red residue washed with pentane. Purification was effected either by allowing a CCl_4 solution to stand giving crystals (this took 4 d), or by column chromatography (silica gel, CCl_4), which gave $C_{60}(4\text{-}MeC_6H_4)_5Cl$, (61%), ν/cm^{-1} 3024, 2920, 1518, 1419, 1187, 1021, 1021, 762, 718, 650, 586, 564, 554, 498, 477, 462 and 445.

The ^{13}C NMR spectrum was similar to that for the fluoro compound in showing four peaks in the sp^3 region at 76.25, 63.0, 60.4 and 57.8 ppm (1:1:2:2 intensity ratio); peaks at 21.0 ppm (4 C) and 20.8 ppm (1 C) are due to the methyl carbons. However, a number of other peaks were present (including one notably downfield at 96 ppm, which may indicate the presence of an OH group on the cage), showing that the compound was not a single isomer. This was confirmed by the mass spectrum (Fig. 6) which showed the main component to contain five *p*-tolyl groups but with traces of up to eight present. Moreover, the ^{1}H NMR spectrum which showed a number of minor peaks in addition to the main aryl-H ones (which occurred *ca.* 0.1 δ upfield from those for $C_{60}Ph_5Cl$[2]).

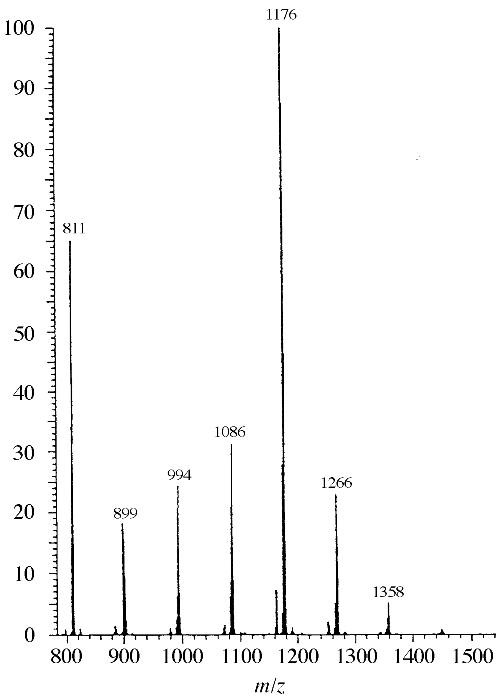

Fig. 6 EI mass spectrum for $C_{60}(4\text{-}MeC_6H_4)_5Cl$

The fact that the two most reactive aromatics used in this study each showed the formation of some octaaryl derivatives could reflect the presence in the $C_{60}Cl_6$ starting material of some $C_{60}Cl_8$, and which is less reactive. Alternatively, direct arylation at non-chlorinated sites may be occurring with reactive aromatics. We believe this latter pathway to be the more likely and hope to investigate it further in due course.

$C_{60}(4\text{-}MeC_6H_4)_5H$

$C_{60}(4\text{-}MeC_6H_4)_5Cl$ (23.4 mg) was dissolved in benzene (10 cm^3) and triphenylphosphine (excess) was added. Precipitation of a dark-red solid began almost immediately. The mixture was left for a further 12 h after which the precipitate was collected by decantation, washed with benzene and dried under vacuum to yield $C_{60}(4\text{-}MeC_6H_4)_5H$ (18.8 mg, 83%), ν/cm^{-1} 3027, 2921, 2853, 1510, 1478, 1461, 1420, 1378, 1187, 1021, 883, 844, 816, 777, 756, 728, 676, *m/z* 1176, 1086, 994, 902, 811, 720. δ_H 7.62, 4 H, d, J 8.1; 7.45, 4 H, d, J 8.1; 7.27, 2 H, dd, J 8.1; 7.10, 4 H, d, J 7.90; 6.98, 4 H, d, J 7.9; 6.935, 2 H, J 7.9; 5.22, 1 H, s (hydrogen on C-2); 2.36 (6 H, s, 4-Me in rings B,C), 2.30 (6 H, s, 4-Me in rings D,E) and 2.26 (3 H, s, 4-Me in ring A). The ring methyl assignments were determined by NOE analysis, which confirmed both the aryl ring dispositions as shown in Fig. 1, and the correlation of the NMR resonances with the aryl hydrogens as deduced for both the fluoro derivative (Fig. 2) and the methoxy derivative (Fig. 5).

The aryl-H peaks occur slightly upfield compared to those for the chloro precursor, except for those adjacent to the cage in ring A. Indeed there is an approximately linear correlation between the differential shifts (chloro *vs.* hydro compound) for both the fluoro and methyl compounds.

The ^{13}C NMR spectrum shows four peaks at 62.8, 60.6, 58.6 and 58.5 ppm (1:2:1:2 ratio) and the upfield shifts for C-2 and C-1 due to replacement of chlorine by hydrogen (13.3 and 4.1 ppm, respectively) are virtually identical to those found for the fluoro compound (above) and the parent pentaphenyl compound.[2] Peaks due to the methyl carbons appeared at 21.0, 20.95 and 20.8 ppm (2:2:1 ratio). In the sp^2 region, 43 peaks were found (*cf.* 40 required) reflecting the presence of traces of impurities; the *ortho* and *meta* carbons of rings B–E, gave signals (not distinguished) at δ 129.37, 129.12, 127.90 and 127.77.

Reaction of $C_{60}Cl_6$ with *tert*-butylbenzene

tert-Butylbenzene (four drops) was added to $C_{60}Cl_6$ (4 mg) dissolved in freshly distilled dichloromethane (5 cm^3). $FeCl_3$ was added and the mixture stirred at room temperature for 16 h. The reaction mixture was washed with water (3 × 5 cm^3), the orange organic layer was collected, dried ($MgSO_4$) and evaporated under reduced pressure to remove unreacted *tert*-butylbenzene. The mass spectrum showed $C_{60}(4\text{-}Bu^tC_6H_4)_5Cl$ (*m/z* = 1388) to be the major product, possibly containing two additional hydrogen atoms (products containing two additional hydrogen atoms have been observed also in reaction of [60]fullerene with bromine–benzene–ferric chloride);[7] the ^{1}H NMR spectrum indicated that it was rather impure. Similar results were obtained if the reaction was carried out with excess *tert*-butylbenzene as solvent instead of dichloromethane.

Reaction of $C_{60}Cl_6$ with thiophene

$C_{60}Cl_6$ (12 mg) was dissolved in thiophene and ferric chloride was added to the solution, which was warmed to 70 °C and stirred under argon for 2 h. The cooled mixture was washed with water (3 × 10 cm^3) and the separated organic layer dried ($MgSO_4$). Removal of thiophene under reduced pressure gave a dark-brown oil to which pentane was added causing precipitation of a light-coloured solid. The filtered solid was dissolved in CCl_4 and chromatographed on a silica-gel column. The major fraction which eluted as an orange solution gave, after removal of solvent, $C_{60}(\text{thienyl})_5Cl$ (7.1 mg, 49%); substitution is assumed to have entered the more-reactive 2-position of thiophene. The mass spectrum, obtained after the sample had been standing for a week or so, shows the attachment of five thienyl rings to the fullerene cage (*m/z* 1132), though there appears to be some hydrogen loss on addition of the fifth thienyl group, possibly due to some couplings between adjacent rings. A substantial amount of a monooxygenated derivative is also present (*m/z* 1150). The aromatic region of the ^{1}H NMR spectrum could not be clearly resolved and we hope to investigate this reaction on larger samples in due course.

$C_{60}Ph_5(4\text{-}MeC_6H_4)$

$C_{60}Ph_5Cl$ (8 mg) was dissolved in toluene (10 cm^3) and ferric chloride was added. The mixture was heated to 50 °C and stirred for 30 min. The cooled product was washed with water (2 × 10^3 cm^3) and the separated organic fraction dried ($MgSO_4$). The residue remaining after solvent removal was washed with pentane, but the product could not be crystallised. The mass spectrum (Fig. 7) confirmed the formation of $C_{60}Ph_5(4\text{-}MeC_6H_4)$. Whilst the structure is presently unknown, the greater ease of addition of this sixth (more reactive) aryl group to the cage, suggests that this reactivity enables some steric hindrance to be overcome.

$C_{60}(X\text{-}Me_3SiC_6H_4)_5Cl$ (X = *para* and/or *meta*)

Because cleavage of the aryl–silicon bond normally takes place much more readily than cleavage of the aryl–hydrogen bond,[8] it was anticipated that reaction of chlorofullerene with phenyltrimethylsilane would take place very rapidly, possibly to the extent of requiring only a very mild catalyst or even none at all. In the event desilylation did not occur and we attribute this to steric hindrance at the *ipso* carbon in phenyltrimethylsilane. Steric hindrance at this site has been proposed previously to account for the greater rate of nitrosodesilylation of arylsilanes compared to nitrodesilylation, whereas the nitrosonium ion is normally a less reactive electrophile than the nitronium ion.[9]

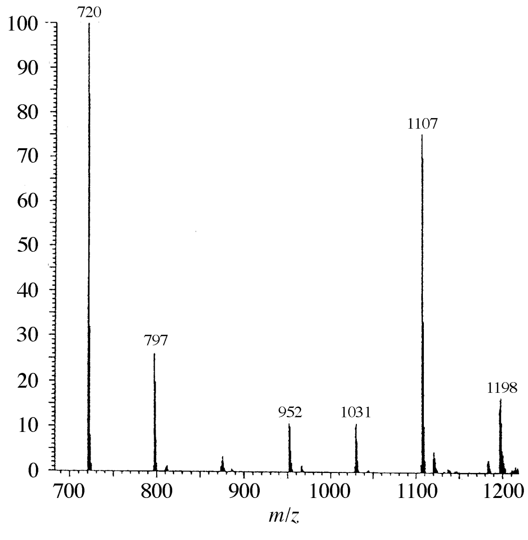

Fig. 7 EI mass spectrum of $C_{60}Ph_5(C_6H_4Me)$

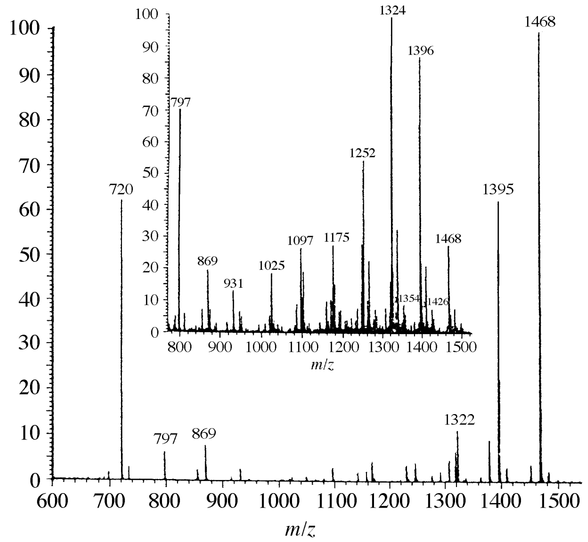

Fig. 8 EI mass spectrum of $C_{60}[3(\text{and/or})4\text{-}Me_3SiC_6H_4]_5Cl$. (This compound may be a dihydro derivative.) Inset spectrum shows the product after partial protiodesilylation by acid.

Phenyltrimethylsilane (0.2 cm^3) was added to $C_{60}Cl_6$ (12 mg), dissolved in redistilled dichloromethane (20 cm^3), the mixture stirred for a few minutes and then ferric chloride was added. After being stirred for a further 2 h the orange mixture became red–brown, but on washing with water (3 × 10 cm^3) the organic layer became orange again. This was separated, dried ($MgSO_4$) and the solvent removed to give a dark-red oil, which, on addition of pentane, precipitated as a solid. Column chromatography (silica gel) of the solid with elution first by pentane (to remove unreacted phenyltrimethylsilane) and then by carbon tetrachloride gave an orange fraction shown, by MS (Fig. 8), to be $C_{60}(X\text{-}Me_3SiC_6H_4)_5Cl$ (X = *para* or *meta*); this product may contain two extra hydrogen atoms, as was indicated for the corresponding *tert*-butyl derivative, above. The ^{1}H NMR

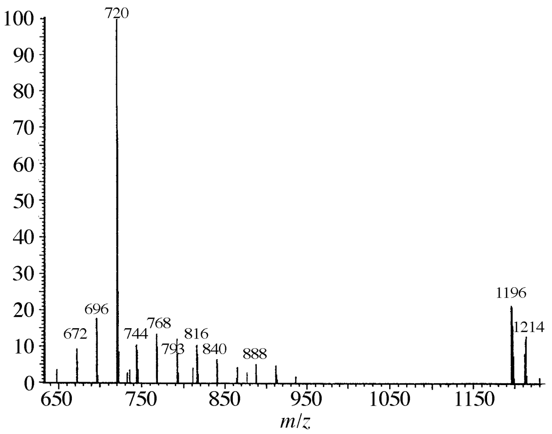

Fig. 9 FAB mass spectrum of $C_{60}(4\text{-}FC_6H_4)_5Cl$ showing the presence of C_2 insertion species

spectrum indicated that the product is not a pure component, due probably to some substitution having occurred *meta* to the trimethylsilyl group, which has only a small positional discrimination effect ($\sigma^+_m = -0.16$; $\sigma^+_p = -0.09$).[10]

In contrast to the usual behaviour of trimethylsilyl compounds during mass spectrometry (the most intense peak occurring at $M^+ - 15$), such peaks are only trivial in the mass spectrum of the fullerene derivative. Instead, the $SiMe_3$ groups are lost as a whole; for example peaks at $m/z = 1395$ and 1322 are due to loss of two such groups. These peaks are not due to a mixture of phenyl and trimethylsilyl groups in the product, because there is no evidence for $C_{60}Ph_5Cl$ in the mass spectrum. Further evidence is adduced below.

Protiodesilylation of $C_{60}(X\text{-}Me_3SiC_6H_4)_5Cl$ (X = *para* and/or *meta*)

The formation of [60]fullerene possessing trimethylsilylphenyl addends offers the possibility of preparing other derivatives through cleavage of the trimethylsilyl group by electrophiles. Preliminary experiments were carried out to see if such cleavage could be achieved, given the extremely strong electron-withdrawing effect of the fullerene cage. A suspension of $C_{60}(X\text{-}Me_3SiC_6H_4)_5Cl$ in HCl–MeOH was heated to 60 °C for several days. The mass spectrum of the product (inset to Fig. 8) showed a substantial change in relative peak intensities, indicating that protiodesilylation had partly occurred.

Attempted reaction with mesitylene

The attempted reaction of $C_{60}Cl_6$ with mesitylene in the above general manner failed, despite the considerable higher reactivity of the aromatic. We attribute this to steric hindrance arising from two methyl groups *ortho* to the normal reaction site in mesitylene.

C_2 insertion reactions

During FAB mass spectrometry (*m*-NBA matrix) of some of our derivatives [$C_{60}Ph_5H$, $C_{60}(4\text{-}FC_6H_4)_5Cl$, $C_{60}Ph_5Cl$] and also of $C_{70}Ph_{10}$, we observed insertion of up to nine C_2 units into the cages. Fig. 9 shows the mass spectrum for the fluoro compound. Others have also observed C_2 insertion reaction under FAB conditions: Chiang *et al.* found that the FAB/LSIMS spectrum of the 4-bromophenyl derivative of [60]fullerenols showed numerous C_2 insertions above *m/z* 900 (all the way up to C_{122}) and attributed the result to recombination of fragments produced under the MS conditions.[11] This explanation has also been advanced by Pradeep and Cooks who analysed the product (FAB/LSIMS) resulting from bombardment of [60]fullerene with a $Cr(CO)_6{}^+$ beam of 1800 eV. C_2 insertion products up to at least C_{108} were observed, and similar insertions were also observed in experiments involving [70]fullerene.[12]

Our studies show that aromatics with a greater electron availability are more readily substituted by the fullerene electrophile and we find that $AlCl_3$ is a more potent Lewis acid catalyst than $FeCl_3$, in turn more reactive than $TiCl_4$. These features are consistent with the operation of a normal mechanism of electrophilic substitution and since the incoming phenyl groups occupy the same sites as the departing chlorines, an addition–elimination mechanism (proposed to account for the nucleophilic substitution in fluorofullerenes)[13] cannot apply. The need to form an electrophilic species from the fullerene suggests that a process of the S_N1 type applies, which conflicts with the expectation that the extreme electron-withdrawing ability of the cage would render this difficult. However, it is known that the electron withdrawal diminishes markedly with extent of addition (as shown for example for the positions of the ^1H NMR signals for hydrogenated fullerenes).[14] It may be therefore that the presence of the chlorine atoms actually aids formation of a partial carbocation, exactly the opposite of what might, *a priori*, be expected. Moreover, the Lewis acid acatalyst (not present in nucleophilic substitution of fluorofullerenes) must aid fullerene–Cl polarisation in the required direction.

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References

1 S. H. Hoke, J. Molstad, G. L. Payne, B. Kahr, D. Ben-Amotz and R. G. Cooks, *Rapid Commun. Mass Spectr.*, 1991, **5**, 472; G. A. Olah, I. Bucsi, C. Lambert, R. Anisfeld, N. J. Trivedi, D. K. Sensharma and G. K. S. Prakash, *J. Am. Chem. Soc.*, 1991, **113**, 9385, 9387; R. Taylor, G. J. Langley, M. F. Meidine, J. P. Parsons, A. K. Abdul-Sada, T. J. Dennis, J. P. Hare, H. W. Kroto and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1992, 667.

2 A. G. Avent, P. R. Birkett, J. D. Crane, A. D. Darwish, G. J. Langley, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1994, 1463.

3 P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1993, 1230.

4 R. Taylor, *Electrophilic Aromatic Substitution*, Wiley, Chichester, 1989, ch. 11.

5 P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor and D. R. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1997, 457.

6 A. D. Darwish, A. G. Avent, H. W. Kroto, R. Taylor and D. R. M. Walton, unpublished work.

7 A. D. Darwish, P. R. Birkett, G. J. Langley, H. W. Kroto, R. Taylor and D. R. M. Walton, *Fullerene Sci. Technol.*, in press.

8 Leading references are given in ref. 4, ch. 4 (sect. 7) and ch. 10.

9 Ref. 3, pp. 413–414, 434; R. Taylor, *Specialist Periodical Report on Aromatic and Heteroaromatic Chemistry*, The Chemical Society, London, 1976, vol. 4, p. 259.

10 E. Glyde and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1632.

11 L. Y. Chiang, R. B. Upasani and J. W. Swirczewski, *J. Am. Chem. Soc.*, 1992, **114**, 10154.

12 T. Pradeep and R. G. Cooks, *Int. J. Mass Spectrom., Ion Procs.*, 1994, **135**, 243.

13 R. Taylor, J. H. Holloway, E. G. Hope, A. G. Avent, G. J. Langley, T. J. Dennis, J. P. Hare, H. W. Kroto and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1992, 665.

14 A. G. Avent, A. D. Darwish, D. K. Heimbach, H. W. Kroto, M. F. Meidine, J. P. Parsons, C. Remars, R. Roers, O. Ohashi, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1994, 15.

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