

## Stable [60]fullerene carbocations

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**[60]Fullerene derivatives,  $C_{60}Ar_5Cl$  (Ar = Ph or 4-FC<sub>6</sub>H<sub>4</sub>), react with  $AlCl_3$  in solution at room temperature to form  $C_s$  symmetrical pentaaryl[60]fullerene carbocations,  $C_{60}(Ar)_5^+$ .**

A number of stable [60]fullerene derivatives which are anions have been synthesised and characterised in solution.<sup>1</sup> In contrast no carbocationic [60]fullerene derivatives have been described to date. However, the non-functionalised [60]fullerene radical carbocation,  $C_{60}^+$ , has been identified by *in situ* EPR and NMR spectroscopy in super acid media<sup>2</sup> and the fullerene cationic salt [ $C_{76}^+$ ][ $CB_{11}H_6Br_6^-$ ] has been fully characterised.<sup>3</sup> Photo-induced electron transfer (PET) has recently been used to generate  $C_{60}^+$  which was functionalised *in situ* by reaction with hydrogen donor molecules, such as alcohols, resulting in the formation of 1-substituted 1,2-dihydro[60]fullerene derivatives.<sup>4</sup> Our studies of Friedel–Crafts reactions between chloro-fullerenes and aromatic compounds with  $FeCl_3$ ,<sup>5</sup> a moderately strong Lewis acid, imply the formation of either fullerene carbocation intermediates (or of donor–acceptor complexes which subsequently undergo front-side displacement by an aromatic group, which is unlikely). We have now prepared and characterised the first examples of [60]fullerene derivative carbocations,  $C_{60}Ar_5^+$  (Ar = Ph or 4-FC<sub>6</sub>H<sub>4</sub>), which are formed by cleaving the fullerene–Cl bond of  $C_{60}Ar_5Cl$  (Ar = Ph **1**;<sup>5a</sup> 4-FC<sub>6</sub>H<sub>4</sub> **2**<sup>5c</sup>) using a strong Lewis acid,  $AlCl_3$ .

The reaction of either **1** or **2** in  $CH_2Cl_2$ ,  $CHCl_3$  or  $CS_2$  with  $AlCl_3$  at room temperature over 30 min results in a change from an orange solution to an intense purple–red indicating the formation of new [60]fullerene derivatives. *In situ* <sup>1</sup>H NMR spectra ( $CS_2$ – $CD_2Cl_2$ ) of the above reactions showed that, in each case, complete conversion to a new  $C_s$  symmetric pentaarylated [60]fullerene derivative occurs as each spectrum has the same number and intensities of signals as the  $C_s$  symmetric starting material; however, the chemical shifts of the signals are significantly different. For example, in the reaction of **2** with  $AlCl_3$  the two multiplets due to the Hs of the unique aryl ring (A) are shifted downfield in the reaction product (Fig. 1). Unequivocal assignments for the signals of the pairs of aryl rings (BC and DE) are not possible as NOE experiments result in equal saturation transfer to all similar signals in the spectrum. Irradiation of the highest field 3-H multiplet of the spectrum in Fig. 1(a), which is due to one of the two pairs of aryl rings of the reaction product from **2**, results in the equal collapse of the two other 3-H signals (including that of the unique aryl ring). The foregoing data is consistent with the proposal that the  $AlCl_3$  is able to abstract the chlorine atom from **1** or **2** generating the carbocations **3** or **4** which are expected to have considerable anti-aromatic character due to their  $4\pi$  electron systems (Scheme 1). 1,2-Phenyl migration then occurs producing the carbocations **7**<sup>‡</sup> and **8**.<sup>§</sup> The fact that the NOE data shows equal saturation transfer to all five aryl rings in both of the reaction products implies that there is a dynamic equilibrium between the initial carbocation formed, which can be viewed as the  $C_s$  symmetric anti-aromatic cyclopentadienyl carbocations, **5** and **6**, and the subsequent major reaction products, **7** and **8**, respectively. However, variable temperature NMR spectra of

both reaction products to 233 K failed to produce any evidence for the presence of **5** or **6**.

The *in situ* <sup>13</sup>C NMR spectra of both **7** and **8** have the required number of signals due to the fullerene carbon atoms [ $28 sp^2$  ( $26 \times 2C$  and  $2 \times 1C$ ), three  $sp^3$  ( $2 \times 2C$  and  $1 \times 1C$ ) and one carbocationic carbon ( $1 \times 1C^+$ )] in addition to those of the aryl carbons. The signal due to the *ipso*-carbon attached to the fullerene cage of the unique aryl ring A is not observed in the spectrum of **8** and is most probably masked by one of the other *ipso*-signals. The formation of donor–acceptor type complexes can be ruled out as the chemical shifts,  $\delta$  173.74 and 171.67, of the signals due to the carbon atoms bearing the positive charge in **7** and **8** respectively are much too low field. However, these values are relatively high-field for carbocationic centres and reflect the exchange of the aryl groups detected by <sup>1</sup>H NMR spectroscopy. Other factors, such as the positively charged carbon atom having an empty  $sp^3$ -like orbital due to the strained ring system being unable to rehybridise to form a planar  $sp^2$  orbital, should however also be considered. The positive charge is localised mostly at or near to the site of its generation in both **7** and **8**. Consequently the carbon atoms immediately adjacent to the carbon atom bearing the positive charge undergo a large downfield shift ( $> \delta 4$ ) compared with those more remote to the positive centre. This situation is analogous to the observed localisation of either the negative charge in the monoaddended fullerene anions<sup>1a–e</sup> or to the radical electron in mono-radical addition to fullerenes.<sup>7</sup> The signals due to the readily identifi-

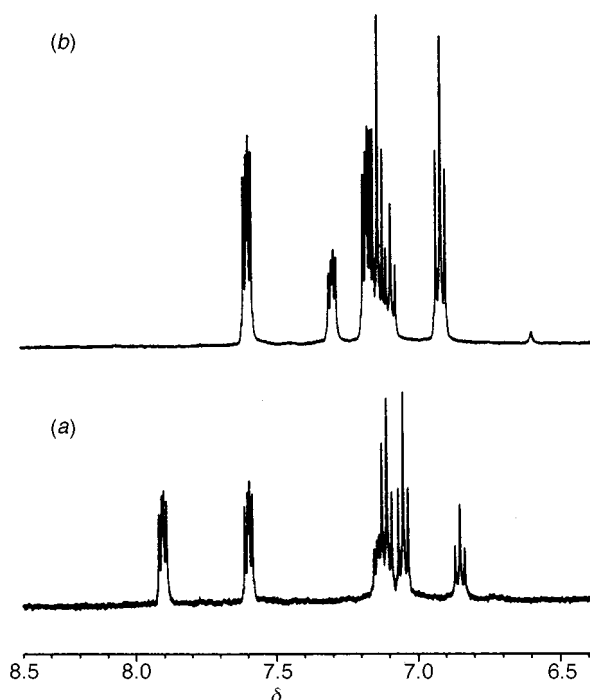
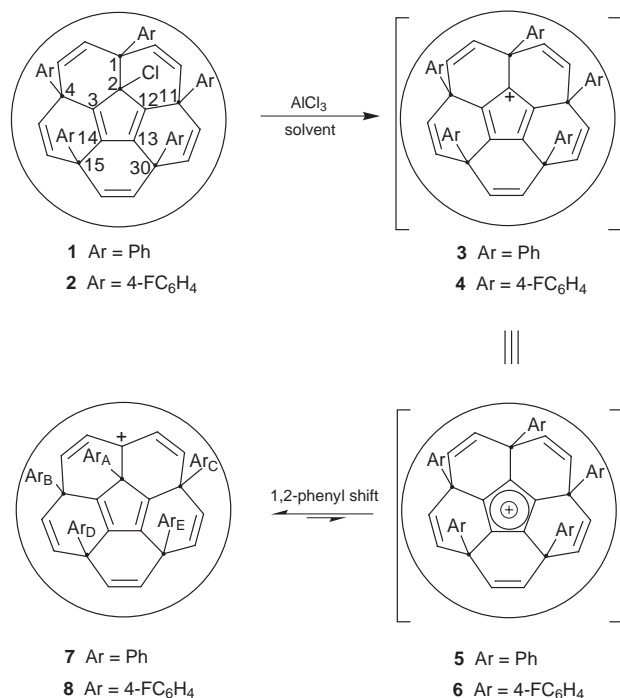


Fig. 1 The <sup>1</sup>H NMR spectra of (a) **2** and (b) the reaction product **8** from the *in situ* reaction of **2** with  $AlCl_3$



**Scheme 1** The proposed reaction sequence for the formation of the carbocations **7** and **8**. Only the five-membered ring around which the phenyl groups are situated in [60]fullerene is shown; the C atoms are numbered using the IUPAC system<sup>6</sup> and the aromatic labels, e.g. Ar<sub>A</sub>, in **7** and **8** correspond to those used in the text.

able (single intensity) symmetry plane sp<sup>2</sup> carbon atoms (C55/C60 carbons), which are located at the opposite pole of the [60]fullerene cage, undergo anomalously large downfield shifts of  $\delta$  2.67 and 2.66 in **7** and  $\delta$  1.86 and 1.72 in **8** probably due to the presence of endohedral homoconjugation, *i.e.* overlap of the rear nodes of the orbitals of the sp<sup>2</sup> carbons C55 and C60 with those of the carbocationic carbon C1 and the sp<sup>3</sup> carbon C2 through the interior of the cage. A transannular interaction of this type was first suggested by Olah *et al.* to explain the observed downfield shift of the bridgehead Hs in the <sup>1</sup>H NMR spectrum of the 1-adamantyl carbocation.<sup>8</sup> Moreover, endohedral homoconjugation has recently been observed by cyclic voltammetry in the pentaphenylcyclopentadienyl[60]fullerene anion, C<sub>60</sub>Ph<sub>5</sub><sup>-</sup>.<sup>9</sup>

Further studies to examine the scope, nature, properties, spectroscopy and chemical reactivity of this new fullerene species are in progress.

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## Notes and References

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‡ Selected data for **7**:  $\delta_{\text{H}}$ [500 MHz; CS<sub>2</sub>-CD<sub>2</sub>Cl<sub>2</sub> (lock)] 7.14 (t, *J* 7.3, 4 H, H-3 and H-5 aryl BC/DE), 7.19 (d, *J* 7.0, 4 H, H-2 and H-6 aryl BC/DE), 7.28 (t, *J* 7.2, 2 H, H-4 aryl BC/DE), 7.32 (t, 2 H, H-3 and H-5 aryl A), 7.36 (d, 2 H, H-2 and H-6 aryl A), 7.30–7.38 (1 H, H-4 aryl A), 7.39 (t, *J* 7.2, 4 H, H-3 and H-5 aryl BC/DE), 7.46 (t, *J* 7.3, 2H, H-4 aryl BC/DE), 7.66 (t, *J* 7.1 *J* 7.3, 4 H, H-2 and H-6 aryl BC/DE);  $\delta_{\text{C}}$ [125.76 MHz; CDCl<sub>3</sub> (lock)] (number of carbon atoms) 58.56 (2 C), 63.06 (2 C), 66.77 (1 C), 127.50 (2

C, Ar), 127.71 (3 C, Ar), 128.84 (1 C, Ar), 129.11 (4 C, Ar), 129.32 (2 C, Ar), 129.46 (2 C, Ar), 129.69 (2 C, Ar), 133.61 (2 C, Ar), 134.31 (1 C, *ipso*-Ar A), 136.03 (2 C, *ipso*-Ar BCDE), 137.42 (2 C, *ipso*-Ar BCDE), 139.39 (2 C), 141.46 (2 C), 141.52 (2 C), 141.94 (2 C), 142.25 (2 C), 142.58 (2 C), 142.80 (2 C), 144.18 (2 C), 145.03 (2 C), 145.09 (2 C), 145.48 (2 C), 145.69 (2 C), 146.06 (2 C), 146.11 (2 C), 146.71 (2 C), 146.80 (2 C), 147.64 (2 C), 147.69 (2 C), 148.36 (2 C), 148.86 (2 C), 148.89 (2 C), 149.14 (2 C), 149.53 (1 C, C55/C60), 150.45 (1 C, C55/C60), 152.15 (2 C), 153.91 (2 C), 154.81 (2 C), 163.54 (2 C), 173.74 (1 C, C1);  $\lambda$ (cyclohexane)/nm 429, 562.

§ Selected data for **8**:  $\delta_{\text{H}}$ [500 MHz; CS<sub>2</sub>-CD<sub>2</sub>Cl<sub>2</sub> (lock)] 6.89–6.93 (m, 4 H, H-3 and H-5 aryl BC/DE), 7.06–7.11 (m, 2 H, H-3 and H-5 aryl BC/DE), 7.11–7.15 (m, 4 H, H-3 and H-5 aryl BC/DE), 7.16–7.19 (m, 4 H, H-2 and H-6 aryl BC/DE), 7.28–7.31 (m, 2 H, H-2 and H-6 aryl A), 7.57–7.61 (m, 4 H, H-2 and H-6 aryl BC/DE);  $\delta_{\text{C}}$ [125.76 MHz; CS<sub>2</sub>-CD<sub>2</sub>Cl<sub>2</sub> (lock)] (number of carbon atoms) 57.81 (2 C), 62.26 (2 C), 65.70 (1 C), 116.95 (4 C, d, C-3,5 aryl BC/DE, <sup>2</sup>*J*<sub>CF</sub> 22), 116.90 (4 C, d, C-3,5 aryl BC/DE, <sup>2</sup>*J*<sub>CF</sub> 22), 117.99 (2 C, d, C-3,5 aryl A, <sup>2</sup>*J*<sub>CF</sub> 22), 128.00 (2 C, d, C-2,6 aryl A, <sup>3</sup>*J*<sub>CF</sub> 9), 129.42 (4 C, d, C-2,6 aryl BC/DE, <sup>3</sup>*J*<sub>CF</sub> 8), 129.57 (4 C, d, C-2,6 aryl BC/DE, <sup>3</sup>*J*<sub>CF</sub> 9), 131.83 (2 C, d, C-1 aryl BC/DE, <sup>4</sup>*J*<sub>CF</sub> 3), 133.08 (2 C, d, C-1 aryl BC/DE, <sup>4</sup>*J*<sub>CF</sub> 3), 139.31 (2 C), 140.89 (2 C), 141.69 (2 C), 141.72 (2 C), 142.41 (2 C), 142.48 (2 C), 142.76 (2 C), 144.08 (2 C), 144.83 (2 C), 145.24 (2 C), 145.40 (2 C), 145.72 (2 C), 146.21 (2 C), 146.29 (2 C), 146.65 (2 C), 146.77 (2 C), 147.15 (2 C), 147.73 (2 C), 148.40 (2 C), 148.95 (2 C), 149.04 (2 C), 149.32 (2 C), 149.73 (1 C), 150.43 (1 C), 152.44 (2 C), 153.95 (2 C), 154.46 (2 C), 162.32 (2 C), 163.00 (2 C, d, C4 aryl BC/DE, <sup>1</sup>*J*<sub>CF</sub> 251), 163.05 (2 C, d, C-4 aryl BC/DE, <sup>1</sup>*J*<sub>CF</sub> 252), 163.35 (1 C, d, C-4 aryl A, <sup>1</sup>*J*<sub>CF</sub> 253), 171.66 (1 C);  $\delta_{\text{F}}$ [282.2 MHz; CS<sub>2</sub>-CD<sub>2</sub>Cl<sub>2</sub> (lock)] –113.77 (septet, 2 F, aryl BC/DE), –112.95 (septet, 2 F, aryl BC/DE), –111.12 (septet, 1 F, aryl A);  $\lambda$ (cyclohexane)/nm 429, 562.

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