

Account / Revue

# Addition reactions of fullerenes <sup>☆</sup>

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## Abstract

A summary of the work of the Sussex fullerene research group is described. The work encompasses a range of fullerene additions including the formation of hydrides, hydroxides, halides, oxides, alkyl- and arylfullerenes, and cycloadducts are described and reveal a number of important properties of fullerenes, such as the tendency to form aromatic derivatives, as well as the formation of novel unsuspected structures. *To cite this article: R. Taylor, C. R. Chimie 9 (2006).*

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## 1. Introduction

Following the discovery of [60]fullerene, the chemistry of this fascinating spherical molecule has been intensively investigated. It is now well established that the chemical reactivity of [60]fullerene is typical of an electron-deficient olefin. Indeed [60]fullerene reacts readily with nucleophiles and is a reactive  $2\pi$  component in cycloadditions. Our group has been involved in the development of various tools for the chemical modification of  $C_{60}$ . Over the years, we have shown that fullerene chemistry is governed largely by a combination of steric effects, electron withdrawal by the cages, a drive to increase their aromaticity, and an increase in localization of  $\pi$ -electrons following a first addition. A number of these features are summarized in the present account.

## 2. Factors governing addition

Fullerenes are not fully aromatic, since the required delocalisation would increase the double bond character of bonds in pentagonal rings, with consequent increase in strain [1]. Thus the double bonds are localised as shown in Fig. 1a, and 1,2-addition occurs readily across a bond between two hexagons ('6,6-bond').

There have been many theoretical discussions as to whether there would be any electron delocalisation (i.e. aromaticity) at all in fullerenes, e.g. [2]; an unambiguous conclusion was obtained through hydrogenation (Section 3.1).

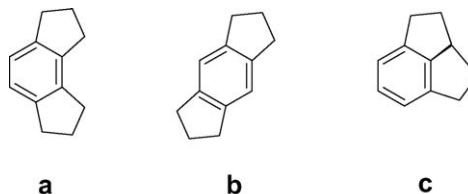


Fig. 1. The three possible arrangements of two pentagons and a hexagon in fullerenes.

<sup>☆</sup> The original manuscript prepared by Roger Taylor has been revised according to the referee's comments by J.-F. Nierengarten (Toulouse, France).

<sup>†</sup> Deceased on 1 February 2006.

### 3. Reduction–formation of fullerene hydrides

The reduction of [60]fullerene by sodium and liquid ammonia gave the addition of 36 and 18 hydrogens [3]. The proposed  $T_h$  symmetry structure for  $C_{60}H_{36}$  was most improbable, requiring total non-conjugation in the product, and was disproved later (Sections 5.2 and 5.4).

Hydrogenation of [60]fullerene in benzene using hydrogen at atmospheric pressure with catalysts such as Pt/C and Pd/C, gave a solid on removal of the solvent from the resultant yellow solution that would only re-dissolve in aqueous acetone. Reduction by hydrogen transfer from cyclohexadiene gave the same result. (Hydrogen transfer was concurrently being investigated by other workers [4].) The cause was the rapid allylic oxidation of hydrofullerenes to fullerenols (see also [5]). Cage reduction could not be effected with Raney nickel catalyst [6], a feature used in some cycloadditions described below (Section 9).

#### 3.1. Reduction by di-imide

Using reduction by di-imide produced all eight possible isomers of  $C_{60}H_4$ , and  $C_{60}H_2$  [6] (also produced by reduction via hydroboration [5] and hydrozirconation [7]). (The assignment of singlets due to the 1,2,18,36- and 1,2,55,60 isomers, was updated later [8].)

Some 30% of the tetrahydro[60]fullerene mixture consisted of the 1,2,3,4-isomer (Fig. 2). If there was no delocalisation in [60]fullerene, the  $\pi$ -density of a (localised) double bond in any hexagon would not be altered significantly by this addition. Hence subsequent addition should occur equally at any of the remaining eight (different) bonds (except for the double bond opposite on the cage which is statistically disadvantaged by a factor of 4:1). The preferential formation of the 1,2,3,4-tetrahydro derivative showed the cage to be partly aromatic. Addition in one hexagon causes localisation of the remaining electrons in that ring so favouring further addition there. This pattern is found in a number of other reactions. Extension of the arguments predicted that further addition should give rise to the ‘S’ and ‘T’ patterns (Fig. 3) [9] observed for example in epoxide formation [10].

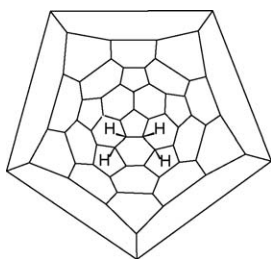


Fig. 2. Schlegel diagram of the principle (1,2,3,4) isomer of tetrahydro [60]fullerene.

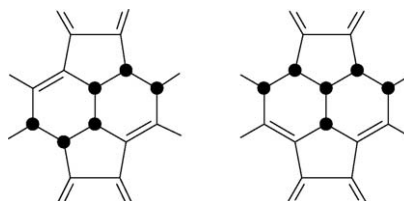
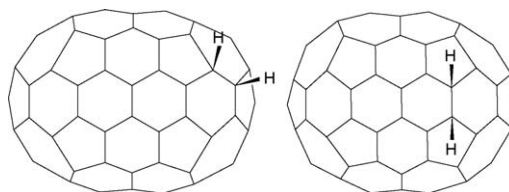


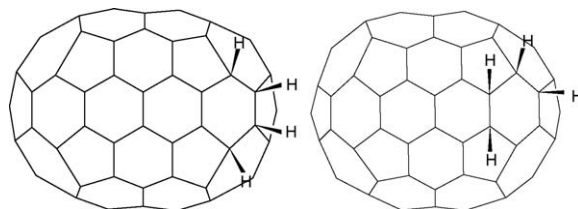
Fig. 3. Localisation-driven ‘S’ and ‘T’ addition patterns for fullerenes; • = addend.

Di-imide reduction of [70]fullerene produced 1,2- and 5,6-dihydro[70]fullerenes (Fig. 4) in a 25:1 ratio [6], cf. 2:1 for hydrogenation via hydroboration [11], demonstrating the greater reactivity of the 1,2- compared to the 5,6-bond [12]. The 5,6-bond has the slightly higher  $\pi$ -bond order [13] but greater curvature favours addition across the 1,2-bond. The  $^1H$ -NMR signal for the 2-hydrogen (attached to the more electronegative *a*-carbon [14]) is 0.5 ppm downfield relative to that for the 1-hydrogen (attached to a *b*-carbon), a feature used in characterising fullerene derivatives.

Further di-imide reduction of [70]fullerene gave six tetrahydro[70]fullerenes, the 1,2,3,4 and 1,2,5,6 isomers (Fig. 5) each comprising about 25% of the total due to the effect of  $\pi$ -bond localisation. The more equal amounts of the two main isomers compared to the dihydro precursors is a statistical effect.



Figs. 4. Structures of 1,2- (left) and 5,6-dihydro[70]fullerenes (right).



Figs. 5. 1,2,3,4- (left) and 1,2,5,6-tetrahydro-[70]fullerenes (right).

### 3.2. Reduction by Zn/HCl

[60]Fullerene in e.g. benzene is rapidly reduced by Zn/HCl, a method that gives no byproducts;  $C_{60}H_{36}$  is produced which on strong heating degrades  $C_{60}H_{18}$ . As in all other reactions, [70]fullerene is less reactive than [60]fullerene and gives  $C_{70}H_{36}$ ,  $C_{70}H_{38}$  (main) and  $C_{70}H_{40}$  [15], as it does in fluorination (Section 5.2).

Reduction of the higher fullerenes yielded  $C_{78}H_{36-48}$  and  $C_{84}H_{48-52}$  as major components [16]. At higher DCI probe temperatures (EI ms) the  $C_{84}$  derivative gave a strong signal for the (less volatile)  $C_{84}H_{40}$  showing it to be particularly stable (cf. fluorination, Section 5.3).

Degradation of the higher fullerenes occurs to give hydrides of the lower one and methylene derivatives, presumably from cage degradation. Formation of methylene derivatives is a common feature of many fullerene reactions, e.g. [17].

Reduction with Zn/DCI gave higher addition levels, i.e. up to  $C_{60}D_{44}$  and  $C_{70}D_{48}$ , attributed to the greater stabilities of C-D vs C-H bonds providing greater compensation for the increased steric compression and loss of (aromatic) resonance energy that accompanies further addition.

Calculations [18] supported our proposal that  $C_{60}H_{36}$  contains four planar aromatic rings (*T* symmetry, Fig. 6) due to the removal of strain from the adjacent pentagons [19]. Indirect proof was obtained from fluorination (isostructural with hydrogenation, but not subject to oxidative instability) which showed that  $C_1$  and  $C_3$  isomers were also present, Section 5.2). Recently these isomers were isolated in hydrogenation (the assumed structure of the  $C_1$  isomer being slightly in error by virtue of a 1,3-hydrogen shift) [20].

The best hydrogenation method is to heat fullerenes with hydrogen under pressure, control of the hydrogenation level depending upon temperature and pressure.  $C_{60}H_{18}$  made in this way has the crown structure (Fig. 7,  $\bullet = H$ ) [16] predicted by calculations [21] with a central planar aromatic ring. The structure is a sub-set

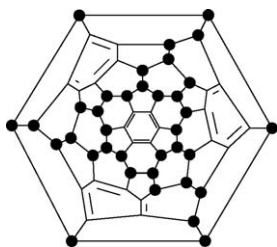


Fig. 6. Schlegel diagram showing *T* symmetry  $C_{60}X_{36}$  ( $\bullet = H$  or F).

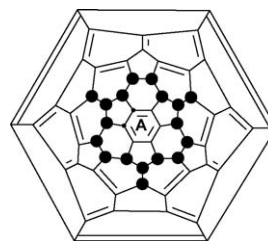


Fig. 7. Schlegel diagram of  $C_{60}X_{18}$  ( $\bullet = H, F$ ), showing the central aromatic ring.

of *T*-symmetry  $C_{60}H_{36}$  and contains a threefold combination of either of the ‘S’ or ‘T’ patterns (Fig. 3).

Reduction of  $(C_{59}N_2)$  with Zn/HCl produces  $C_{59}NH_5$ , the conjectured structure being shown in Fig. 8 [22]. This is stable due to the formation of a  $6\pi$ -electron (aromatic) pentagonal ring, consequently there is a high energy barrier to further reduction. This result contrasts with that observed in fluorination (Section 5.5).

### 3.3. Reduction by hydrogen sulphide

If traces of  $CS_2$  used for extracting fullerene soot are not completely removed, then on passing down an alumina column (containing traces of water), this becomes converted into  $H_2S$ ,  $COS$ ,  $CO$  and  $CO_2$  (a little-known reaction [23]). The  $H_2S$  then reduces the fullerene and is converted into sulphur (Scheme 1). Separate experiments showed that  $C_{60}$  converts  $H_2S$  into sulphur [24].

## 4. Hydroboration

Hydroxyfullerenes (fullerenols) are water soluble, and can be converted into a variety of polymers with very strong cross linking. They are made by nitration followed by substitution of  $NO_2$  by  $OH$  [25], and also

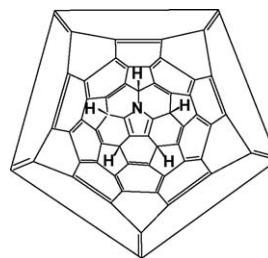
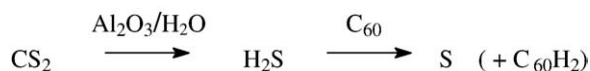
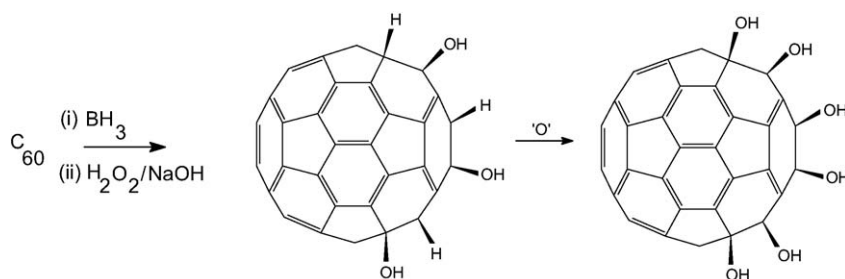


Fig. 8. Schlegel diagram of conjectured structure for  $C_{59}NH_5$ .



Scheme 1. [60]Fullerene-catalysed conversion of  $CS_2$  into sulphur.



Scheme 2. Representation of fullerene formation via allylic oxidation of hydroborated intermediates.

by hydroboration (reaction with  $\text{BH}_3/\text{THF}$  complex followed by  $\text{H}_2\text{O}_2/\text{NaOH}$ ) [26]. The ready occurrence of allylic oxidation means that multiple addition of H and OH pairs in the latter reaction (Scheme 2) can only be achieved if the reaction is performed under  $\text{N}_2$ . Otherwise the product shows an IR spectrum similar to that obtained by the nitration route. Allylic oxidation is also responsible for a typical fullerene IR spectrum being obtained on quenching the organoborane intermediate with glacial acetic acid.

## 5. Fluorination

Both fluorination and hydrogenation have low steric requirements, consequently give similar polyaddition patterns. However, the low activation energy for fluorination makes the reaction very hard to control. Fluorination has been reviewed recently [27].

### 5.1. Fluorination by $F_2, F_2$ -inert gas complexes, and by interhalogens

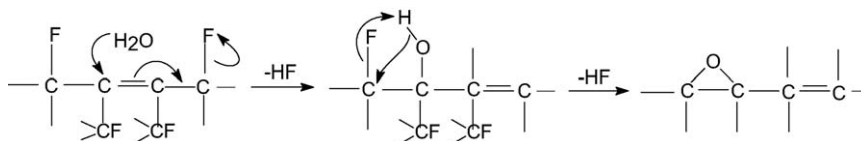
Initial experiments used pure samples of [60]fullerene fluorinated by either  $\text{F}_2$  gas or  $\text{XeF}_2$  at  $70^\circ\text{C}$ . The slow fluorination rate (many days) [28] contrasted with another report [29] because pure [60]fullerene (then unavailable elsewhere) in which the molecular close packing restricts lattice penetration of fluorine, was used. This also explains why reaction of [60]fullerene with fluorine gas at  $70^\circ\text{C}$  for 24 h, gives a product consisting of a mixture of highly fluorinated- and unreacted fullerene [30]. The packing in [70]fullerene is also poorer than in [60]fullerene, consequently it fluorinates

faster; [30] in other reactions it is less reactive. The mass spectra of the products show a very wide distribution of fluorinated species making isolation of individual components by this route unfeasible.

The hopes that fluorofullerenes would be superlubricants [31], neglected their inability to assume the eclipsing-avoiding twisted backbone of Teflon, so are very susceptible to nucleophilic substitution. Dry solid fluorofullerenes are stable and hydrophobic, but addition of a cosolvent to water e.g. acetone, gives an immediate exothermic reaction evolving HF and formation of epoxides [32]. Fluorofullerenes are therefore lubricants but can, however, be useful synthons, e.g. reaction with various carbon nucleophiles [32]. Given that an  $\text{S}_{\text{N}}2$  reaction is sterically impossible a  $\text{S}_{\text{N}}2'$  mechanism was proposed (Scheme 3, see also Section 7).

In the spectrum of the product of fluorination of [60] fullerene, species corresponding to  $\text{C}_{60}\text{F}_{18}$  and  $\text{C}_{60}\text{F}_{36}$  were dominant, providing the first indication that the regiochemistry of fluorination parallels that for hydrogenation [32].  $\text{CF}_3$  groups are formed through fragmentation, and  $\text{CF}_2$ -containing species are present, attributed to cage fragmentation followed by addition to another cage (cf. hydrogenation, Section 3.2).

The lability of bromine and chlorine in fullerenes [33,34] was employed to limit the extent of fluorine addition i.e. fluorinate a halogenofullerenes and then dehalogenate by heating. Though the derivatives tended to form complex degradation products, isolation of the mixed halogenated fullerene  $\text{C}_{60}\text{F}_{14}\text{Cl}_{18}$  indicated that the differing halogen sizes would permit formation of compounds of general approximate formula  $\text{C}_{60}\text{F}_{48-2n}\text{Cl}_n$  [35].



Scheme 3. Mechanism for nucleophilic substitution of fluorofullerenes, followed by epoxide formation.

$C_{60}F_{48}$  obtained by high temperature, was the first fluorofullerene to be characterised [36–38]. It forms a red crystalline charge-transfer complex with toluene, and deeper coloured complexes (bathochromic shift) with more alkylated benzenes [37].  $C_{60}F_{48}$  can also be produced by fluorinating with  $KrF_2$  [39]; hyperfluorination, which requires cage-opening, also occurs giving up to  $C_{60}F_{78}$ . Hyperfluorination occurs during fluorinating with  $F_2$  under UV irradiation (giving  $C_{60}F_{76}$ ) [40], and with  $TbF_4$  (giving  $C_{60}F_{70}$ ) [41].

## 5.2. Fluorination with transition metal fluorides

### 5.2.1. [60]Fullerene

Fluorination with transition metal fluorides was introduced by DuPont in 1947, fine control being achieved by adjusting the fluorine-release temperature [42]. The method is ideal for use with involatile solids such as fullerenes, especially as the fluorofullerenes are more volatile, and under vacuum these can be swept away from the reaction zone so that limited fluorination can be achieved [43]. By selection of the metal fluoride and reaction temperature, specific derivatives can be obtained. The high polarity of the C-F bond and the solubility of fluorofullerenes, allows HPLC purification and separation of species of identical fluorine content.

Reaction with  $K_2PtF_6$  produced fully characterised  $C_{60}F_{18}$  (Fig. 7, ● = F) [44]. The concentration of the fluorines at one end of the molecule (shown by the single-crystal X-ray structure, Fig. 9 [45]) gives it a very high dipole moment (ca. 6 Debye) [46] and a very long HPLC retention time. Reaction proceeds via cascade processes (see Section 3.1).

$C_{60}F_{18}O$  (Fig. 10) was the first oxahomofullerene (fullerene ether) to be isolated and characterised [47]; other fluorofullerene ethers and bis ethers have been obtained subsequently [48].

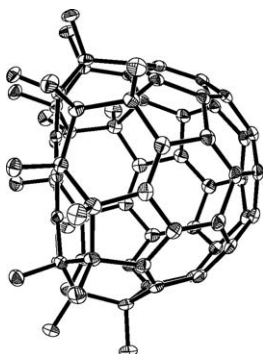


Fig. 9. X-ray structure for  $C_{60}F_{18}$ .

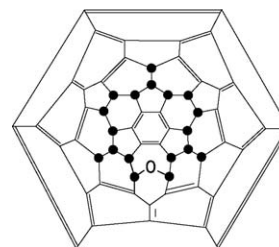


Fig. 10. Schlegel diagram of  $C_{60}F_{18}O$ ; ● = F.

As well as the *T* isomer of  $C_{60}F_{36}$  (Fig. 6), the X-ray structure of which showed it to be the most distorted fullerene (Fig. 11) [49], the  $C_3$  and  $C_1$  isomers have also been isolated from fluorination with  $MnF_3$  (Fig. 12). All three differ only through 1,3-fluorine shifts [50,51]; the *T* isomer contains four planar aromatic rings whilst the other isomers each have three.

Fluorination with  $TbF_4$  is more aggressive and gives mainly  $C_{60}F_{42}$  and  $C_{60}F_{48}$  at 320 °C and 350 °C, respectively [52]. Partially characterised compounds  $C_{60}F_{26}$ ,  $C_{60}F_{28}$ ,  $C_{60}F_{30}$  and  $C_{60}F_{22}$  have been isolated from fluorination with  $MnF_3$  [53], whilst the same reagent gave fully characterised  $C_{60}F_{38}$ . Very complex analysis of the spectroscopic details revealed the latter structure to be that shown in Fig. 12c [54], whereby disruption of one of the aromatic rings of  $C_{60}F_{36}$  occurs on addition of two fluorine atoms.

The lowest fluorinated species  $C_{60}F_2$  has also been isolated along with  $C_{60}F_4$ ,  $C_{60}F_6$  and  $C_{60}F_8$ , this series demonstrating the sequential 1,2-addition pattern, but also a departure to a 1,4-addition pattern in  $C_{60}F_8$  (Fig. 13) [55,56]. Related patterns have been obtained in the series  $C_{60}F_nO$ ,  $n = 2, 4, 6, 8, 10$  [56,57].

Other novel product is  $C_{60}F_{16}$  which differs from  $C_{60}F_{18}$  only in the absence of two fluorines that lie

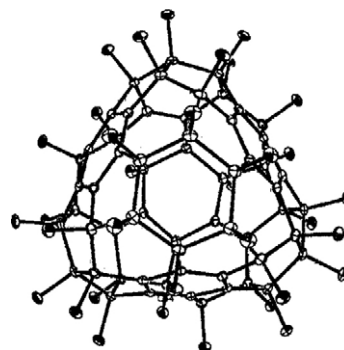


Fig. 11. X-ray structure of *T*- $C_{60}F_{36}$ .

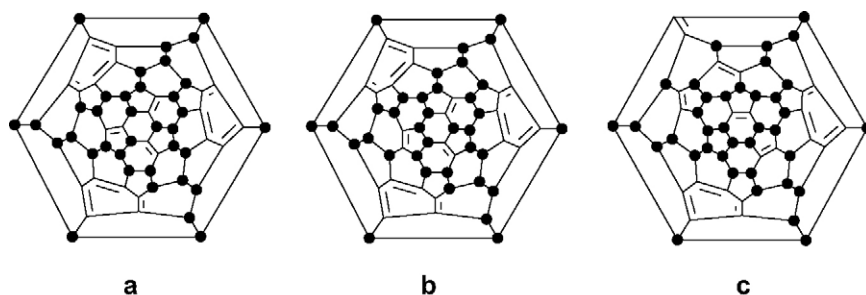


Fig. 12. Schlegel diagrams of the  $C_3$  and  $C_1$  isomers of  $C_{60}F_{36}$ , and the  $C_1$  isomer of  $C_{60}F_{38}$ .

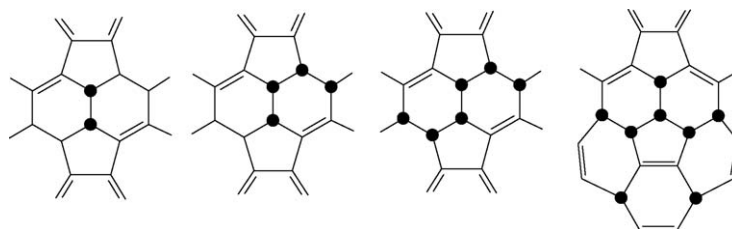


Fig. 13. Motifs for  $C_{60}F_n$  ( $n = 2, 4, 6, 8$ ).

along one of the symmetry planes [58]. But why the loss of only two fluorines, i.e., one could expect to find  $C_{60}F_{14}$  and  $C_{60}F_{12}$ ? Furthermore, the HPLC retention time is more than double that of  $C_{60}F_{18}$ , whilst that of  $C_{60}F_{16}O$  (ca. 150 min, [59]), grossly exceeds that of any other fluorofullerene. The existence of dimers cannot be discounted, especially as  $C_{60}F_{16}$  is readily made by pyrolysis of  $C_{60}F_{18}$  [60].

$C_{60}F_{20}$  ('Saturnene') is unique in having all equatorial fluorines creating a flattened structure (Fig. 14) [61].

Fragmentation of the fluorofullerene cages accompanies fluorination, producing  $:CF_2$  carbenes which can insert into C–F bonds giving derivatives such as  $C_{60}F_{17}CF_3$  (Fig. 15) and  $C_{60}F_{17}CF_2CF_3$  one isomer of

the former being chiral [62]. Up to threefold addition should be possible but there is only scant spectroscopic evidence for this.

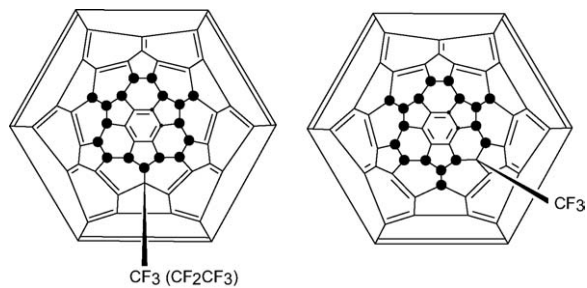


Fig. 15. Schlegel diagrams for  $C_{60}F_{17}CF_3/C_{60}F_{17}CF_2CF_3$ .

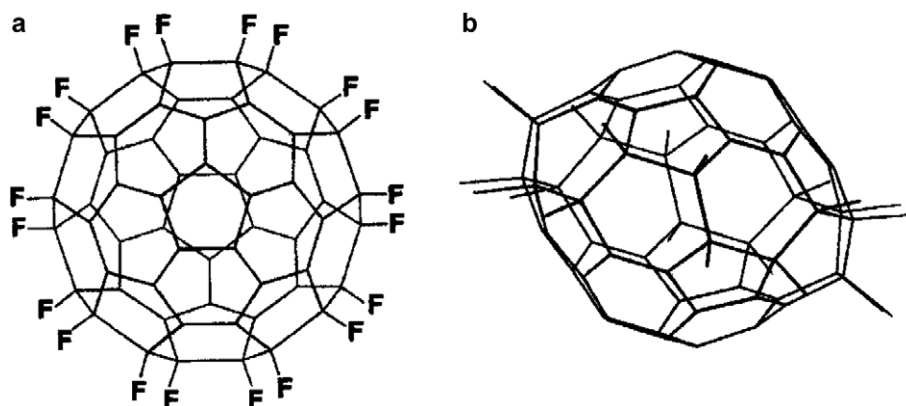
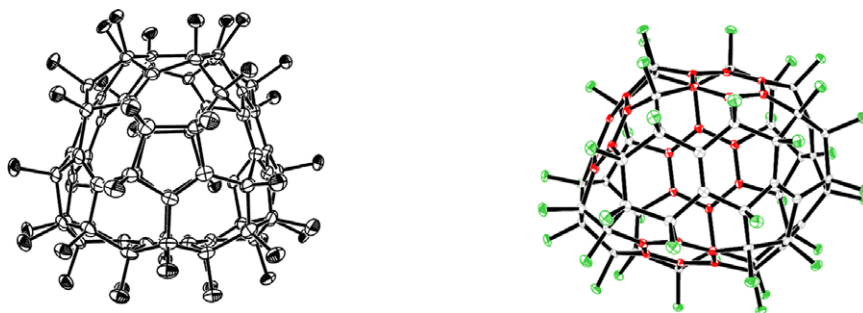


Fig. 14. Structure of  $C_{60}F_{20}$  ('Saturnene').



Figs. 16.  $C_2$  (left) and  $C_1$  (right)  $C_{70}F_{38}$ ; the end-on view of the former illustrates the distortion.

### 5.2.2. [70]Fullerene

The main product of fluorination with  $MnF_3$  is  $C_{70}F_{38}$  together with smaller amounts of  $C_{70}F_{36}$  and  $C_{70}F_{40}$ , so paralleling hydrogenation. These components (and numerous isomers) have been isolated by HPLC; there are marked differences in polarities and symmetries (variously  $C_3/C_2$  and  $C_1$ ) of some [63]. Our proposal that the specific addition levels observed indicated aromatic structures [64] has been confirmed by X-ray characterisation of the  $C_2$  and  $C_1$  isomers of  $C_{70}F_{38}$  (Fig. 16, which shows the distortion) These contain 3- and 4-planar aromatic rings, respectively, cf.  $C_{60}F_{36}$  [65].

### 5.2.3. Higher fullerenes

Fluorination of higher fullerenes by  $MnF_3$  and  $CeF_4$  yields  $C_{76}F_{38}$ ,  $C_{78}F_{38}$ ,  $C_{82}F_{40}$ ,  $C_{84}F_{40}$  and  $C_{84}F_{44}$ , with  $C_{84}F_{40}$  being by the most abundant species [66], paralleling the high stability noted above (Section 3.2) for  $C_{84}H_{40}$ . The structures of  $C_{84}F_{40}$  (Fig. 17) and  $C_{84}F_{44}$  are cubic [67].

### 5.4. Fluorination of $i\text{-}^3\text{He}[60]\text{fullerene}$

The shift in location of the single line in the  $^3\text{He}$ -NMR spectra of fullerenes containing  $^3\text{He}$  within the cage is a measure only of the change in aromaticity of the cage surface. The  $^3\text{He}$ -NMR spectra of  $i\text{-}^3\text{He}C_{60}F_{18}$

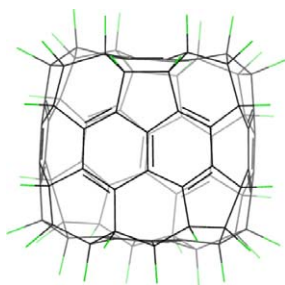


Fig. 17. The cubic structure of  $C_{84}F_{40}$ .

and  $i\text{-}^3\text{He}C_{60}F_{36}$  are virtually identical to those of the corresponding hydrogenated species thereby confirming their isostructural relationships [68]. Moreover, the spectra for  $T$  and  $C_3$  isomers of  $C_{60}X_{36}$  consist of two lines in ca. 1:3 intensity ratio, the chemical shifts relative to the parent fullerene being predicted accurately [68].

### 5.5. Fluorination of $C_{59}N$

Whereas hydrogenation of  $C_{59}N$  produces  $H_5C_{59}N$  (Fig. 8), fluorination by  $MnF_3$  produces  $C_{59}NF_{33}$  [69]. As noted (Section 3.2) hydrogenation of  $C_{59}N$  creates an increase in aromatic stability, so reaction does not readily proceed further. However, the much lower activation energy for fluorination overcomes the barrier to further reaction.

In e.g.  $T C_{60}F_{36}$  (Fig. 6) many pentagons containing three fluorines. If two fluorines are removed from one of these rings and the remaining C–F bond is replaced by N, this creates a  $10\pi$  aromatic circuit and enhanced aromatic stability (Fig. 18).

Other species isolated from this work include  $C_{59}NF$ ,  $C_{59}NF_{17}$ ,  $C_{59}NF_{37}$ ,  $C_{59}NF_4CF_3$ ,  $C_{59}NF_3(CF_3)_2$  and  $C_{59}NF_2(CF_3)_3$  and structures for these have been proposed.

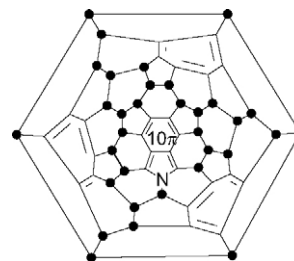
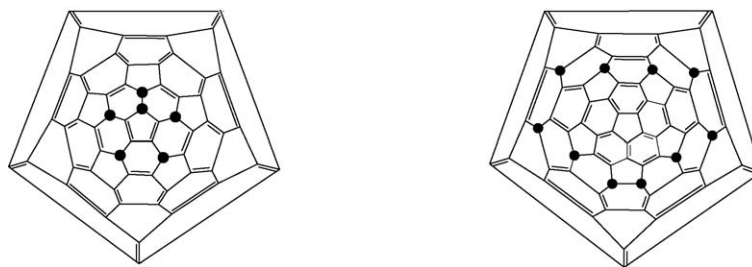


Fig. 18. Conjectured structure for  $C_{59}NF_{33}$  based on  $T C_{60}F_{36}$  (● = F); similar structures can be obtained from the other  $C_{60}F_{36}$  isomers.



Figs. 19. Schlegel diagrams for  $C_{60}Cl_6$  (left) and  $C_{70}Cl_{10}$  (right);  $\bullet = Cl$ .

## 6. Bromination and chlorination

These radical reactions have steric requirements different from fluorination resulting in quite different regiochemistry, with 1,4-addition being a dominant feature.

### 6.1. Formation of $C_{60}Cl_6$ and $C_{70}Cl_{10}$

Chlorination of [60]- and [70]fullerenes by ICl gives  $C_{60}Cl_6$  and  $C_{70}Cl_{10}$ , respectively (Fig. 19) [70,71].

Since the end cap motif of [70]fullerene is isostructural with that in [60]fullerene, chlorination could have been expected to give  $C_{70}Cl_6$ . The formation of  $C_{70}Cl_{10}$  was attributed to the unfavourable bond disposition around the equator of [70]fullerene due to the need to have double bonds exocyclic to the pentagons [71]. It can be ameliorated by consecutive 1,4-additions around the equator, resulting in two adjacent chlorines as in  $C_{60}Cl_6$ ; the resultant steric compression creates regions of high reactivity. The structure is calculated to be of low energy [72] and many other isostructural compounds are now known.

### 6.2. Formation of $C_{60}Br_{24}$ , $C_{60}Br_8$ and $C_{60}Br_6$

Bromination of [60]fullerene by bromine gives either  $C_{60}Br_{24}$ ,  $C_{60}Br_8$  or  $C_{60}Br_6$  (isostructural with  $C_{60}Cl_6$ ) depending upon the solvent employed [73, 74]. The motif in  $C_{60}Br_6$  is found in many other derivatives, whereas the  $C_{60}Br_8$  motif has been found only

in  $C_{60}Me_8$  [75].  $C_{70}Br_{10}$  has been isolated from bromination of [70]fullerene (cf. Section 6.1) [76] (Fig. 20).

## 7. Nucleophilic substitution–electrophilic aromatic substitution

Nucleophilic substitution follows two mechanisms: in the absence of a Lewis acid catalyst, an  $S_N2'$ -type of mechanism must apply. In the presence of a catalyst, the mechanism proceeds via the formation of an intermediate cation (or partial cation) feasible here due to the strong electron-withdrawing property of the cage being reduced by the presence of less electronegative  $sp^3$ -hybridised carbons [77]. When the nucleophile is an aromatic compound, the reaction becomes an *electrophilic aromatic substitution* by the halogenofullerene.

### 7.1. Nucleophilic substitution of fluorofullerenes

#### 7.1.1. Reaction of fluorofullerenes with water

A range of specific derivatives of fluorofullerenes have been isolated. Replacement of F by OH is followed by elimination of HF, and this can be repeated. Further elimination involving loss of CO from the epoxides may occur, giving species such as  $C_{59}F_{34}$  [78]. In a more detailed investigation specific  $C_1$  isomers of  $C_{60}F_{35}OH$  have been obtained from  $C_3$  and  $C_1$   $C_{60}F_{36}$  [79]. This work identified the motif required for ready substitution, viz. the presence of two CF bonds adjacent to at least on end of a double bond (Scheme 3), so that

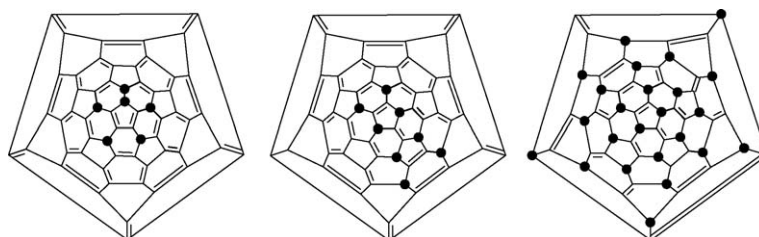
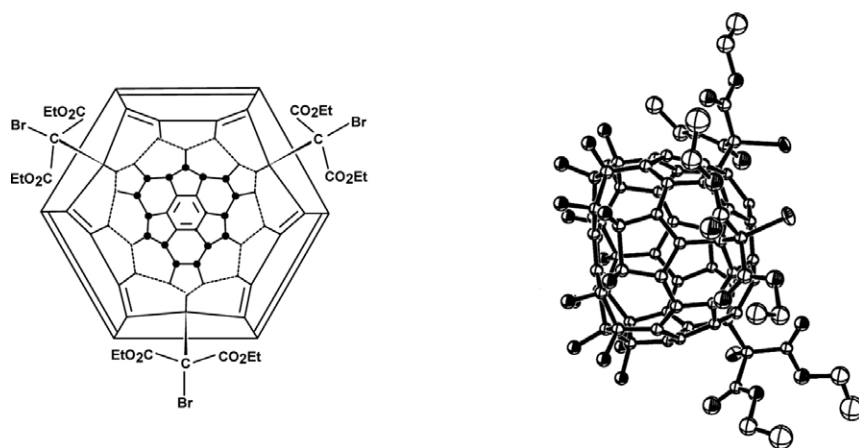


Fig. 20. Schlegel diagrams of the structures of  $C_{60}Br_6$ ,  $C_{60}Br_8$  and  $C_{60}Br_{24}$  ( $\bullet = Br$ ).





Figs. 21. Schlegel diagram (left; dotted line is delocalised chain) and X-ray structure (right) of a trannulene.

$T\text{C}_{60}\text{F}_{36}$  is unreactive and likewise is  $\text{C}_{60}\text{F}_{18}$ . The motifs in  $\text{C}_{60}\text{F}_{48}$  require that only 12 fluorines can be replaced, so giving it a relatively high hydrolytic stability [80].

#### 7.1.2. Reaction of $\text{C}_{60}\text{F}_{18}$ with bulky carbon nucleophiles – formation of trannulenes by the $\text{S}_{\text{N}}2''$ reaction

Reaction of bulky carbon nucleophiles with  $\text{C}_{60}\text{F}_{18}$  leads to the formation of trannulenes, a new class of compounds having around the equatorial region, a fully delocalised  $18\pi$  aromatic chain with all bonds of equal length; the compounds are bright emerald-green, are exceptionally stable and have a barrel-like structure (Fig. 21) [81]. This unique organic reaction, defined as an  $\text{S}_{\text{N}}2''$ , (or extended  $\text{S}_{\text{N}}2'$ ) reaction, involves an incoming nucleophile displacing a fluorine at the  $\delta$ -position. Two further types of trannulenes have since been discovered in other reactions [82].

#### 7.1.3. Reaction of $\text{C}_{60}\text{F}_{18}$ with aromatics—the ‘triumphenes’

In the presence of a  $\text{FeCl}_3$ , either one, two, or three of the outermost fluorines of  $\text{C}_{60}\text{F}_{18}$  can be substituted

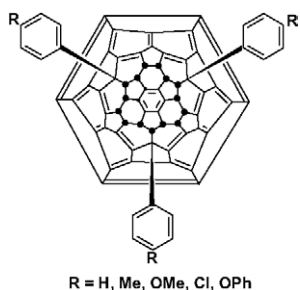


Fig. 22. Schlegel diagram of tris-substituted  $\text{C}_{60}\text{F}_{15}\text{Ar}_3$  derivatives.

by aromatics (Fig. 22), an electrophilic substitution of the fluorofullerene into the aromatic. Hence more reactive aromatics are substituted more readily [83]. A very surprising result was the formation of  $\text{C}_{60}\text{Ph}_{18}$ , the most phenylated organic compound known. The phenyl groups are almost certainly located in the positions formerly occupied by fluorine, creating an exceptional structure.

Electrophilic substitution of  $\text{C}_{60}\text{F}_{18}$  into phenols occurs at both *ortho* and *para* positions. The former products then undergo 1,3-fluorine migration being followed by HF elimination between the phenolic OH group giving benzo[2',3':10,11]hexadecafluoro[60]fullerene (Fig. 23) and derivatives; complete defluorination can also occur [84].

#### 7.2. Chlorofullerenes as electrophiles

Reaction of  $\text{C}_{60}\text{Cl}_6$  with benzene/ $\text{FeCl}_3$  produces  $\text{C}_{60}\text{Ph}_5\text{Cl}$  (Fig. 24, X = Cl), which on reaction with  $\text{PPh}_3/\text{H}_2\text{O}$  yields  $\text{C}_{60}\text{Ph}_5\text{H}$  (Fig. 24, X = H) [85]. Other aromatics give the corresponding  $\text{C}_s$  symmetric deriva-

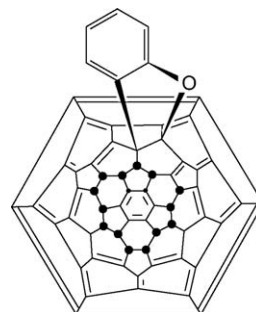
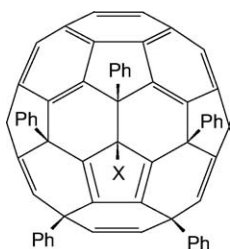


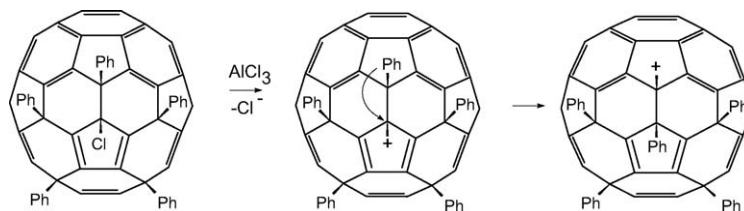
Fig. 23. Benzofurano[2',3':10,11]hexadecafluoro[60]fullerene from  $\text{C}_{60}\text{F}_{18}$  and phenol.

Fig. 24. Structure of  $C_{60}Ph_5X$  ( $X = Cl, H$ ).

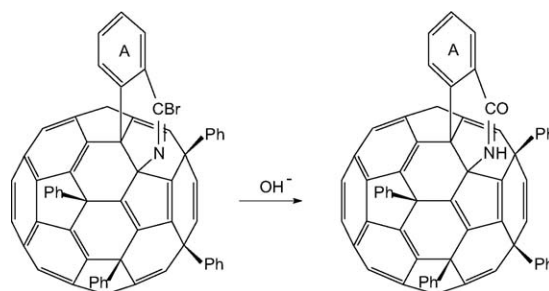
tives [77], and as in the case of aryldefluorination above, steric hindrance causes either largely or exclusively *para* substitution in the aromatics. Steric hindrance prevents mesitylene from reacting, and likewise causes substitution at the *para* position in trimethylsilylbenzene instead of cleavage of the trimethylsilyl group (*ipso* substitution), normally the much more facile reaction [86].

The entering aryl groups occupy the positions of the departing chlorines showing reaction to occur via an intermediate cation proved by the isolation of  $C_{60}Ph_5^+$  [77]. Removal of the chlorine creates an anti-aromatic structure, so a 1,2-shift of an aryl group occurs and probably is synchronous with the departure of the chlorine (Scheme 4). The location of the positive charge is confirmed by single crystal X-ray structures of derivatives formed by reaction with nucleophiles e.g.  $CN^-$  (from  $Me_3SiCN$ ) [87]; a further rearrangement must also occur since a second unsymmetrical uncharacterised derivative is formed. Chemical shifts ( $^{13}C$ -NMR) for the on-axis carbons on the cage opposite to the cation, indicate endohedral homoconjugation.

Replacement of the sixth chlorine by aryl is sterically hindered, so that although attack by aryl at the carbocation in the right hand structure of Scheme 5 gives  $C_s$   $C_{60}Ph_6$ , an unsymmetrical isomer is also obtained; 2-D and temperature-dependent NMR studies indicate the presence of three adjacent phenyl groups in this [88]. By contrast, reaction with the less sterically demanding allyl group (from allyltrimethylsilane catalysed by  $TiCl_4$ ) readily gives  $C_s$   $C_{60}(allyl)_6$  and  $C_{60}(allyl)_5Cl$  [89].

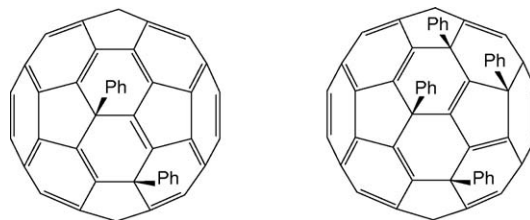


Scheme 4. Formation and stabilisation of a penta-aryl[60]fullerene cation.

Scheme 5. Formation of an isoquinolono[60]fullerene from reaction of  $C_{60}Ph_5Cl$  with  $CNBr/FeCl_3$ .

Symmetrical  $C_{60}Ph_2$ , unsymmetrical  $C_{60}Ph_4$  (Fig. 25), and traces of  $C_{60}Ph_3H_3$  are obtained as by-products from the  $C_{60}Cl_6$ /benzene/ $FeCl_3$  reaction; [90] the formation of hydro derivatives is a common feature of many fullerene reactions (see e.g., Section 7.3). Pathways involving either 1,2-, 1,4-, or 1,6- $Cl_2$  loss from either the precursor or partially phenylated intermediates can be envisaged for the formation of the main products. This combination of elimination and nucleophilic substitution of chlorine is also found in reactions with alkoxy nucleophiles [91] and in the reactions of  $C_{70}Cl_{10}$ .

The reaction between  $C_{60}Ph_5Cl$  and  $CNBr/FeCl_3$  produces a bromoisoquinolono-[60]fullerene due to nucleophilic replacement of the chlorine by  $N\equiv C-Br$ , followed by electrophilic substitution into the *ortho* position of the adjacent phenyl ring (Scheme 5); this latter is inhibited by electron withdrawal in the aryl ring, hence the corresponding fluorophenyl derivatives is unreactive. Subsequent reaction with hydroxide ion occurs readily and gives isoquinolono[3',4':1,2][60]fullerene

Fig. 25. Structures of symmetrical  $C_{60}Ph_2$  and unsymmetrical  $C_{60}Ph_4$ .

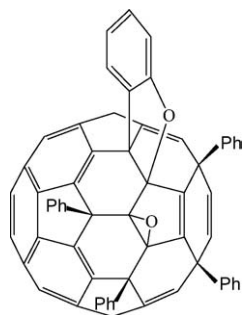


Fig. 26. A di-epoxy derivative of a benzo[*b*]furano[60]fullerene.

[92]. Reversal of the positions of attachment of the nitrogen and the aryl group A cannot be excluded.

A related ring closure involves conversions of  $C_{70}Ph_5H$  into  $C_{60}Ph_4C_6H_4O_2$  a benzo[*b*]furano[60]fullerene (Fig. 26) [93,94]. Facile spontaneous oxidation of the C–H bond to C–OH creates steric compression with the adjacent aryl group, so oxidative coupling occurs. The oxides undergo fragmentation under EI mass spectrometry to give  $C_{58}$  derivatives. Formation of benzo-furano[60]fullerenes likewise occurs spontaneously from aryloxy[60]fullerene precursors (obtained from reaction of phenols with  $C_{60}Cl_6$  [95], a reaction that parallels the reaction of phenols with  $C_{60}F_{18}$  (Fig. 23).

Reaction of  $C_{70}Cl_{10}$  with benzene/ $FeCl_3$  produces  $C_{70}Ph_8$  and  $C_{70}Ph_{10}$  as major products (Fig. 27) and  $C_{70}Ph_{2/4/6}$  as minor ones [96].  $C_{70}Ph_{10}$  is not formed directly from the chloro precursor, but is produced by phenylation of  $C_{70}Ph_8$  (which is formed more readily) so the adjacent and eclipsed chlorines are preferentially lost during the reaction, as for example they are in alkoxylation of  $C_{60}Cl_6$ ; this reaction sequence means that the final two aryl groups can be made to differ from the others, simply by reacting  $C_{70}Ph_8$  with  $ArH/FeCl_3$ .

Minor products from the above reaction are  $C_{70}Ph_9OH$ , the first monohydroxyfullerene to be isolated, and  $C_{70}Ph_8(OH)_2$  (Fig. 27) [97]. The mechanism of their formation is unclear.

A unique reaction occurred on allowing  $C_{70}Ph_8$  to stand in light, whence it changed into a bis lactone,

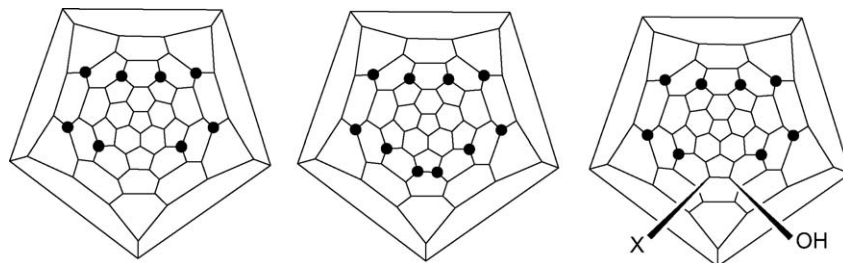


Fig. 27. Schlegel diagrams for  $C_{70}Ph_8$ ,  $C_{70}Ph_{10}$  (● = Ph),  $C_{70}Ph_9OH$  (X = Ph), and  $C_{70}Ph_8(OH)_2$  (X = OH).

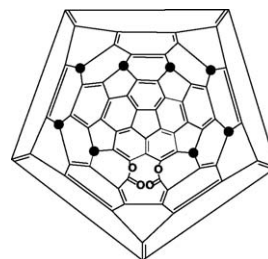


Fig. 28. Structure of the spontaneously formed bis lactone,  $C_{70}Ph_8O_4$ ; ● = Ph.

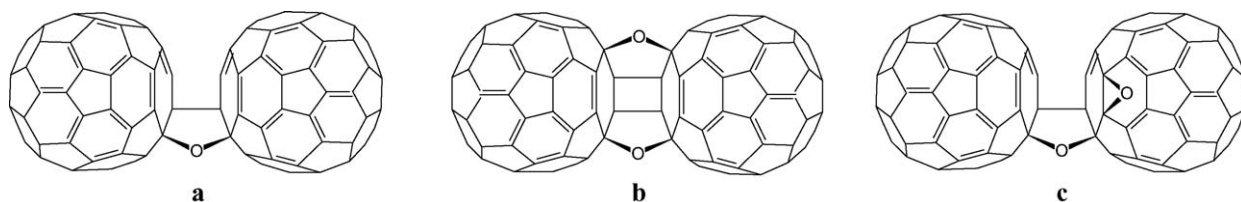
$C_{70}Ph_8O_4$  which has an 11-member hole in it (Fig. 28), the first [70]fullerene derivative to have an opened cage [98].

### 7.3. Bromo[60]fullerenes as electrophiles

Heating a solution of benzene, bromine (which increases the electrophilicity of the cage), and  $FeCl_3$ , gives many products including:  $C_{60}Ph_5H$  (main product),  $C_{60}Ph_n$  ( $n = 4, 6, 8, 10, 12$ ),  $C_{60}Ph_nO_2$  ( $n = 4, 6, 8, 10, 12$ ),  $C_{60}Ph_nOH$  ( $n = 7, 9, 11$ ),  $C_{60}Ph_n = 4, 10$ ,  $C_{60}Ph_4H_4$ ,  $C_{60}Ph_5H_3$ ,  $C_{60}Ph_nO_2H$  ( $n = 5, 9$ ),  $C_{60}Ph_4C_6H_4O_2$  [formed by spontaneous oxidation of  $C_{60}Ph_5H$  (see Section 7.2)],  $C_{60}Ph_9OH_3$ , and  $C_{60}Ph_{11}O_3H_2$  [99,100]. The corresponding reaction with toluene and chlorobenzene produced as main products,  $C_{60}(MeC_6H_4)_4$  and  $C_{60}(ClC_6H_4)_5H$ , respectively. However, specific derivatives are more easily obtained by reaction of chlorofullerenes (Section 7.2).

## 8. Formation and reactivity of oxides

Despite claims to the contrary, fullerenes do not occur naturally because of their high susceptibility to oxidation [101], the first fullerene reaction to be qualitatively observed. Films of pure fullerenes on rotovap flasks acquired a pinkish hue after a few days and would not then redissolve due to oxide formation [102]. This air oxidation is photocatalysed [103]; the product has been shown to be  $C_{120}O$  (Fig. 29a), is pre-



Figs. 29. a, b, c Structures of  $C_{120}O$  and major (b) and minor (c) isomers of  $C_{120}O_2$ .

sent in *all* samples of  $C_{60}$ , and is believed to be formed from a [2 + 2] reaction between  $C_{60}$  and  $C_{60}O$  [104].

The structures of  $C_{120}O$  [105] and two isolated isomers of  $C_{120}O_2$  (Fig. 29) [106] were determined by NMR. The structure of the main isomer (Fig. 29b) was deduced also by application of the principle of minimisation of double bonds in pentagons, and other geometrical constraints [107]. Semi-empirical calculations for  $C_{120}O$ ,  $C_{120}O_2$ , (and also  $C_{130}O$ ,  $C_{130}O_2$ ,  $C_{140}O$  and  $C_{140}O_2$ ), confirmed that the assigned structures are the most stable ones amongst a number of possibilities [108]. The structures of  $C_{120}O_2$  also follow the principle (Fig. 2) that a second addition will preferentially occur adjacent to the first.

Some higher fullerenes (especially [78]fullerene can undergo rapid spontaneous oxidation, to give completely insoluble material. The extreme insolubility was at first attributed to graphitisation [109] matrix-isolated  $CO_2$  was found to be produced (IR) on heating KBr discs. (This KBr/fullerene matrix is quite remarkable, the  $CO_2$  being stable indefinitely at room temperature, or at 225 °C.) Since  $C_{60}O$ ,  $C_{70}O$ ,  $C_{120}O$  etc. behave similarly, the insoluble material consists of oxides (probably polymerised) [110]. The question as to how  $CO_2$  could be produced from a mono-oxide was an-

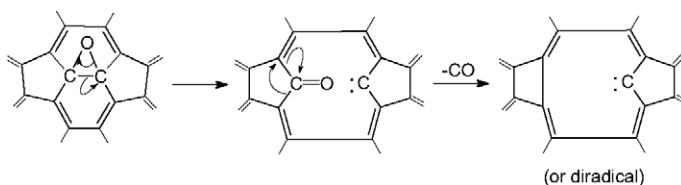
swered by the isolation of  $C_{119}$ , formation of which was consistent with Eq. (1) [110].



$C_{119}$  is more usually obtained by heating a mixture of  $C_{60}$  and  $C_{60}O$ , which is believed to lose CO to give an intermediate carbene (Scheme 6), having a strained four-member ring, (or a diradical). This may then either add to a 6:6 bond [104] or insert into a 6:5 bond of [60] fullerene, such addition/insertions being common in fullerene chemistry [105]. These intermediates are then conjectured to undergo intramolecular [2 + 2] cycloaddition, the product that results from the 6:5 insertion being the major one [106] because it is less strained.

Substituted fullerenes can lose both CO and  $CO_2$ . For example heating KBr discs of  $C_{70}F_{38}O$  reveals the formation of matrix-isolated CO [110] and ms. shows the formation of  $C_{69}F_{38}$ ; this species, and others produced from similar oxides, are particularly stable since the doubly charged ions have greatly enhanced intensities [111]; the reason for this stability is not yet understood.

Loss of CO or  $CO_2$  on heating can result in the formation of lower fullerenes, which must contain seven-member rings [99]. Thus loss of 2  $CO_2$  from  $C_{70}Ph_8O_4$



Scheme 6. Loss of CO from  $C_{60}O$  to give an intermediate carbene ( $C_{59}$ ) which then reacts with  $C_{60}$  to give  $C_{119}$ .

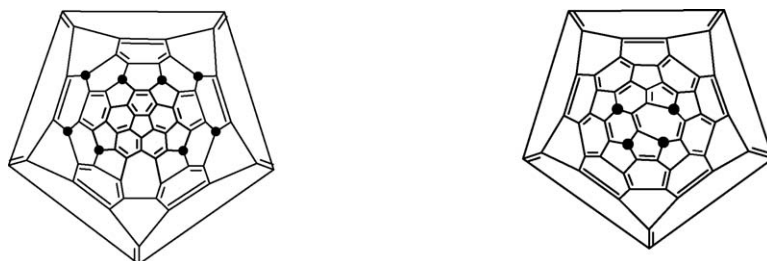


Fig. 30. Conjectured structures of  $C_{68}Ph_8$  and  $C_{58}Ph_4$  (● = Ph).

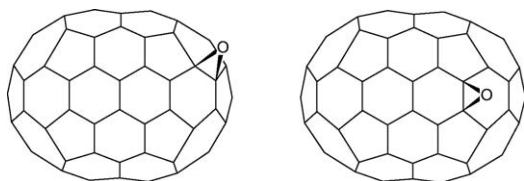


Fig. 31. 1,2-Epoxy[70]fullerene and 5,6-epoxy[70]fullerene.

and of 2 CO from  $C_{60}Ph_4O_2$  yields  $C_{68}Ph_8$  and  $C_{58}Ph_4$ , respectively (Fig. 30). These products have adjacent five-member rings, but are allowable because the neighbouring seven-member rings and the presence of the  $sp^3$ -hybridised carbons in the five-member rings combine to reduce strain.

[70]Fullerene epoxidises across the 1,2- and 5,6-bonds in a 43:57 ratio [112,113]. An unresolved general problem is why different reactions give such a wide variation in the relative proportions of the addition ratios [12] (see also Section 3.1). The epoxidation ratio is independent of formation during the arc-discharge fullerene production process [112] or by peracid oxidation of [70]fullerene [113] (Fig. 31).

## 9. Methylation

Methylation is important because although the introduced functional group is not very amenable to further reactions, the methylfullerenes are very much more soluble in a range of solvents, especially acetone and THF than the parent molecules [114–118]. The reaction can therefore be used to increase the solubility of other derivatives.

Methylation of [60]fullerene with Li/MeI gives  $C_{60}Me_n$  ( $n = 2, 4, 6, 8, 10, 12, 14$  and  $> 16$ ) together with some oxide derivatives [114]. Both 1,2- $Me_2$ - and 1,4- $Me_2$ - $C_{60}$  have been isolated and characterised (the former gives five oxide derivatives), along with  $C_{60}Me_8$  which is isostructural with  $C_{60}Br_8$  (Fig. 20), these being the only two derivatives having this motif. On reduction, 1,2- $Me_2C_{60}$  gives  $C_{60}Me_2H_{16}$ , whilst 1,4- $Me_2C_{60}$  gives  $C_{60}Me_2H_{34}$  these results showing how important



Fig. 33. The cage-opened bis-epoxide ketone  $C_{60}Me_5O_3H$ .

are the 18 And 36 site occupancies in [60]fullerene addition.

Reaction of  $C_{60}Cl_6$  with MeLi yielded a range of fully characterised compounds (Fig. 32), and these confirmed the conjectured location of epoxy and OH groups obtained in related phenylated compounds [115]. Especially notable was the isolation of the bis-epoxide ketone (Fig. 33) a cage-opened tautomer of the bis-epoxide fullereneol,  $C_{60}Me_5O_2OH$  [116].

Methylation of [70]fullerene by Li/MeI gives mainly a 3.4:1 ratio of the 1,2- and 5,6- $C_{70}Me_2$  isomers (cf. epoxidation, Section 8) [114,117], accompanied by five others, one of which is probably the 7,21-isomer (obtained also by reaction of  $C_{70}Cl_{10}$  with MeLi). Other uncharacterised products were  $C_{70}Me_n$  ( $n = 4, 6, 8, 10$ ), which may involve addition in the equatorial region. This was definitely shown to be the case on reaction of [70]fullerene with Al-Ni-NaOH in DMSO-THF followed by quenching with MeI. A sequential addition pathway from  $C_{70}Me_2$  to  $C_{70}Me_{10}$  occurs, starting with addition across the 7,23 bond, shown in Fig. 34, thereby confirming the previously conjectured pathway for phenylation. Just as  $C_{70}Ph_8$  becomes oxidised on standing to the cage-opened bis lactone  $C_{70}Ph_8O_4$  so  $C_{70}Me_8$  is converted to  $C_{70}Me_8O_4$ , which is probably isostructural [117].

Methylation of [76]fullerene by the Al-Ni-NaOH method gives mainly five isomers of  $C_{76}Me_2$ , one of which has been characterised as 1,6- $Me_2C_{76}$  together with some methyleneated compounds,  $C_{76}(CH_2)_n$  ( $n = 2-4$ ). The first oxahomo derivative of a higher fullerene 1,6- $Me_2C_{76}O$  was also obtained (oxygen inserts into the 1,6-bond) and also the first bis-oxahomo deri-

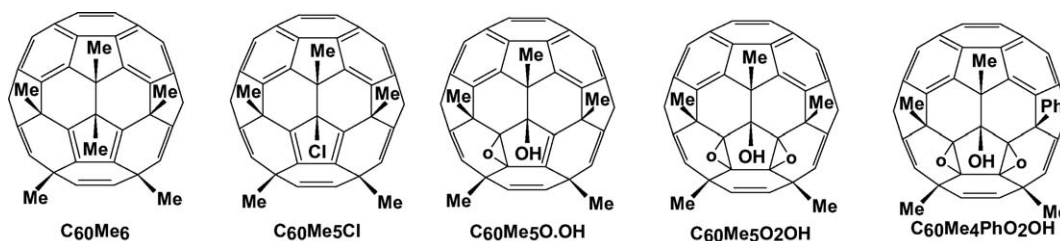


Fig. 32. Products obtained from reaction of  $C_{60}Cl_6$  with MeLi.

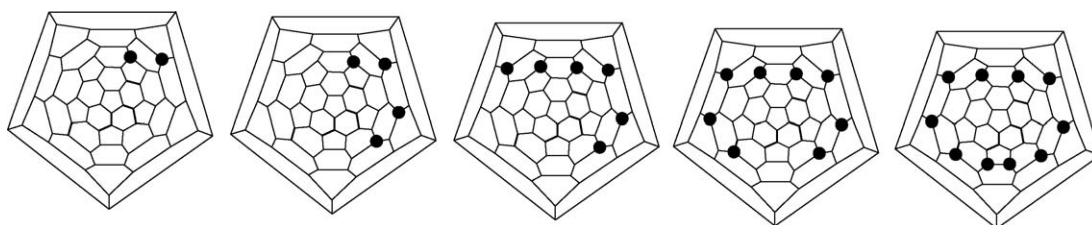


Fig. 34. Stepwise addition pathway for methylation of [70]fullerene (● = Me, double bonds omitted for clarity).

vative  $C_2$   $C_{76}Me_2O_2$ . [118]. Methylation of [84]fullerene takes place less readily, giving four dimethyl derivatives, one of  $C_1$  symmetry, the other being  $C_s$  or  $C_2$  [118].

## 10. Some cycloadditions

### 10.1. Benzyne

The [2 + 2] reaction of benzyne with [70]fullerene gave four monoadducts, whereas three had been observed in any other [70]fullerene cycloaddition [119]. These were characterised ( $^1H$ -NMR) as 1,2-, 7,21-, 5,6-, and 7,23-benzo[70]fullerenes [120], with a 1,2-/5,6-ratio of 3.5. Re-investigation involving  $^{13}C$ -NMR showed that the supposed 7,23-derivative (based on addition to these sites in other reactions) was the 7,8-derivative (both give the same  $^1H$ -NMR pattern [121]; 7,23-bridging by the aryl group apparently involves too much strain. Both 7,8- and 7,23-addition relieve the unfavourable bond fixation that exists in the equatorial region of [70]fullerene.

### 10.2. Cyclopentadiene

The adduct formed by [4 + 2] cycloaddition of cyclopentadiene to [60]fullerene readily undergoes the retro Diels-Alder reaction, which can be prevented by either hydrogenation or bromination of the double bond of the addend. Uniquely, bromine adds *cis* instead of the normal *trans*, both pointing away from the cage surface (Fig. 35), attributable the unusual steric hindrance on the cage side of the double bond. Likewise the oxygen of the epoxide (produced by reaction of the cycloadduct with perbenzoic acid) also points away from the cage [122].

Steric hindrance also governs the reaction of pentamethylcyclopentadiene with [60]fullerene, so that the methyl group on the single carbon bridge points away from the cage [123]. Comparison of the methyl chemical shifts for the [60]- and [70]fullerene derivatives provided the first evidence that that electron withdrawal by

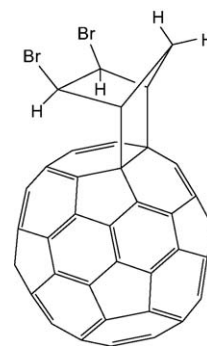


Fig. 35. The product of bromine addition to 2',3'-1'H-1,2-[(1,3)epicyclopenta][60]fullerene.

[60]fullerene is the greater. This work also provided the first example of the differential chemical shifts between hydrogens which point towards the electronegative cage, and those which point away from it.

### 10.3. Anthracene

Anthracene adds readily to 6,6-bonds of fullerenes in a [4 + 2] cycloaddition, and has been used to direct further additions [124]. A unique example of addition to a 5,6-bond occurs in the reaction with  $C_{70}Ph_8$ , in which the disposition of the phenyl groups causes the 5,6-bond (C48–C49) to be a *double* bond, and addition takes place there in preference to any other bond [125].

Because the Diels–Alder reaction of anthracene is readily reversible, the anthracene group could be expected to migrate across fullerene cages. However, this could not be proven without a reference marker, now provided in the addition of anthracene to  $C_{60}F_{18}$ . Three of the possible four monoadducts were isolated, the two main isomers having  $C_s$  and  $C_1$  symmetry. The latter is the more crowded and rearranges to the former on standing, the first example of ring-walking anthracene [126].

The only known reaction of  $C_{60}F_{20}$  ('Saturnene') occurs with anthracene giving an oxidised anthracene derivative (Fig. 36). The mechanism for this has been fully rationalised and commences with oxygen addition

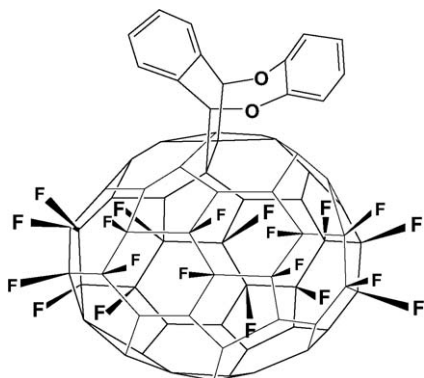


Fig. 36. Product of the reaction of anthracene with  $C_{60}F_{20}$  ('Saturnene').

across the 9,10-bond of anthracene, followed by rearrangements and subsequent addition [127].

#### 10.4. 1,3-dipolar cycloadditions

The [3 + 2] cycloaddition of  $C_{60}F_{18}$  with sarcosine and formaldehyde, gave two mono- and five bis-addition products. The monoadduct obtained in the larger amount is the least hindered  $C_s$  derivative, the other having  $C_1$  symmetry, both being fully characterised. Use of benzaldehyde gave three unresolved monoadducts and two bisadducts [128]. Further derivatisation of these adducts is feasible.

#### 10.5. Reaction of $C_{60}F_{18}$ with tetrathiafulvalene

Reaction of tetrathiafulvalene (TTF) to  $C_{60}F_{18}$  takes place uniquely with concurrent [2 + 2] cycloaddition and loss of two fluorines to give a  $C_{60}F_{16}$  derivative (Fig. 37). Addition of  $CDCl_3$  triggered a sterically driven elimination of thioketene (Fig. 37) observed when samples were being prepared for NMR spectroscopy. A

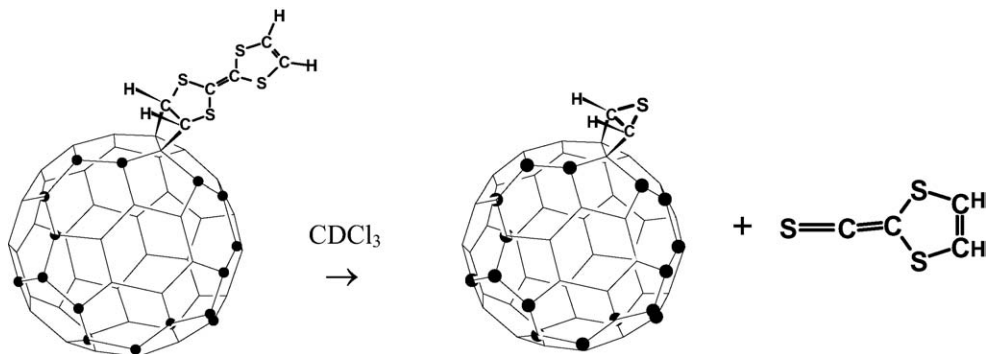


Fig. 37. Product of the reaction of  $C_{60}F_{18}$  with tetrathiafulvalene (TTF), and subsequent elimination of dithioketene (● = F).

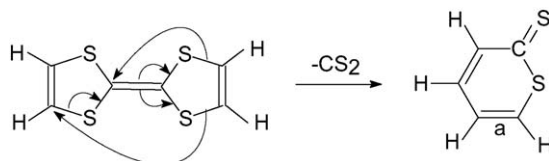


Fig. 38. Conjectured mechanism for loss of  $CS_2$  from TTF to give a thiolactone which then adds to  $C_{60}F_{18}$  with concurrent loss of 2 F.

further simultaneous unique reaction is the loss of  $CS_2$  from TTF to give a thiolactone intermediate (Fig. 38) which then adds via bond *a* to  $C_{60}F_{18}$  with concurrent loss of 2 F; the elimination of  $CS_2$  may be catalysed by the fluorofullerene [129].

#### 10.6. Addition/insertion of methylene and derivatives

Methylene species,  $C_{60}CH_2$  and  $C_{70}CH_2$  [130], are formed during hydrogenation [15] indicating that cage degradation gives carbenes, which then either add or insert to other cages; likewise formation of  $CF_2$  adducts accompanies fluorination [39].

Polymethylene adducts, e.g.  $C_{60}(CH_2)_{1-6}$  and  $C_{70}(CH_2)_{1,2}$  [130,131], are obtained in particular on heating fullerenes or bromofullerenes with THF, the trimethylene derivatives dominating [132]. These appear to be propano compounds since they lose 2H during mass spectrometry (not possible if separate methylene groups were involved). The mechanism may involve elimination of formaldehyde from THF, since the corresponding reaction with dihydropyran gives preferential formation of derivatives containing four methylene groups.

Methanofullerenes  $C_{60}(CHCN)$  and  $C_{70}(CBr_2)$ , obtained by reaction of [60]fullerene with either  $CH_2BrCN$  or  $CHBr_3$  in the presence of LDA, have synthetic potential yet to be explored [133].

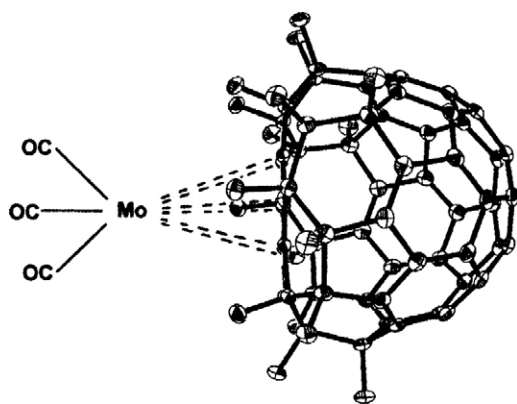


Fig. 39. Structure of  $[\text{MoC}_{60}\text{F}_{18}(\text{CO})_3]$ .

### 11. $\eta^6$ co-ordination to a fullerene

The ability to co-ordinate a transition metal to a fullerene has long been sought, but has been denied by the lack of aromaticity, so co-ordination with fullerenes has been limited to  $\eta^2$  (typical of an alkene) [134] or  $\eta^5$  (to a cyclopentadienide ring) [135].

The first example of  $\eta^6$  co-ordination has now been obtained through reaction of  $\text{C}_{60}\text{F}_{18}$  (which has a fully aromatic planar ring) with  $[\text{Mo}(\text{CH}_3\text{CN})_3(\text{CO})_3]$  whereby displacement of acetonitrile gives the product shown in Fig. 39. It was not possible to obtain a single-crystal X-ray structure, but the characterisation was accomplished by a very detailed mass spectrum; the compound is quite stable to the extent that a parent ion at 1244 amu was readily obtainable [136].

### 12. Conclusion

The present paper summarizes the work accomplished in our group on the chemical modification of fullerenes. Fluorine addition to  $\text{C}_{60}$  can be performed with a variety of agents. The difficulty of controlling the reaction provides a complex mixture of products with varying numbers of fluorine atoms attached to the carbon cage and inhibits the isolation of the early compounds of fluorine addition. Nonetheless, many fluorofullerene derivatives have been characterized over the years. In general, fluorine addition to fullerenes presents two main features: the fluorine atoms are attached to the cage as fluorine pairs across 6,6-bonds, and the fluorination has a general tendency to create structures with increased aromaticity relative to the fullerene precursor and hence with increased stability. In other words, the aromatic character of the fluorofullerenes

increases with increasing number of fluorine atoms attached to the cage. Because fullerenes are moderately aromatic, addition of the first fluorine pair increases the localization of the electrons for the remaining double bonds of the two hexagons involved, so that further addition to these hexagons becomes thermodynamically favoured. Chlorination and bromination reactions have also been studied. These radical reactions have steric requirements different from fluorination resulting in quite different regiochemistry, with 1,4-addition being a dominant feature. Other investigations of the chemistry of fullerenes have been concerned with their use as electrophiles for aromatic substitution, initial reactions being carried out using unhalogenated [60]fullerene in a Friede-Crafts reaction. Other studies involved the use of the more electrophilic halogenofullerenes. These can be generated in situ, for example, using a mixture of aromatic compounds, bromine, ferric chloride and [60]fullerene, but like the foregoing reactions, gave products that were difficult to separate and/or characterise. The most successful studies have used reactions of preformed chlorofullerenes with aromatic compounds (mostly benzene), which proceed via intermediate formation of fullerene carbocations. The use of a fluorofullerene as an electrophile has also been reported involving the  $\text{FeCl}_3$ -catalysed reaction of  $\text{C}_{60}\text{F}_{18}$  with benzene, which produced the triphenyl derivative ('triumphene') (1, Ar = Ph). In conclusion, our studies have clearly shown how fullerene chemistry is governed by a combination of steric effects, electron withdrawal by the cages, a drive to increase their aromaticity, and an increase in localization of  $\pi$ -electrons following a first addition.

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