

**Reaction and structural chemistry
of open-cage fullerenes**

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Acknowledgement

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Chapter 1

General Introduction

1 General Introduction

The following section 1.1.1 and 1.1.2 was cited from introductory article for fullerene written by Ananthaiah.^{1a)}

1.1 The third allotrope of carbon^{1a)}

Fullerenes belong to a fundamentally new class of molecules and also constitute a new allotrope of carbon. Unlike graphite and diamond (which are the only two structurally well characterized allotropes of carbon), this new allotrope is made of hollow carbon cages. Because of its discrete molecular nature, it is the only pure form of carbon. The number of carbon atoms in each fullerene cage can vary and for this reason numerous new structures can be imagined. Generally, they are represented by the formula C_n , where n denotes the number of carbon atoms present in the cage. C_{60} (fullerene containing 60 carbon atoms) is the most abundant and well characterized member of the fullerene family and is currently dominating fullerene research.

1.1.1 Discovery of Fullerenes^{1a)}

The story of the discovery of fullerenes is fascinating because the discovery came about during an investigation into a problem of interest to astronomers. Kroto was interested in radio astronomy. In order to determine whether carbon containing molecules present in interstellar clouds were responsible for some of the signals, he began making and characterizing new carbon species in the laboratory, using microwave spectroscopy as his main tool. Interstellar cyanopolynes (HC_nN , $n = 5-11$) were discovered by Kroto and coworkers through a synergistic combination of laboratory microwave spectroscopy experiments, theoretical analysis, and observational radioastronomy. Curl, a fellow spectroscopist on the other side of the Atlantic, suggested that collaboration with Smalley would be beneficial. Smalley was interested in cluster chemistry. He had designed and built a special laser-supersonic cluster beam apparatus which could vaporize almost any known material into a plasma of atoms and lead to precise information about the pattern and distribution of the clusters. In an action packed fortnight in September 1985, Curl, Kroto and Smalley along with graduate students J R Heath and S C O'Brien began to carry out some experiments on laser vaporization of carbon.²⁾ Generally vaporized carbon is obtained by directing an intense beam of laser onto a graphite or any other carbon surface. The carbon atoms produced in this way in an inert atmosphere combine to form a series of clusters where the size varies from a few atoms to many hundreds. These experiments were aimed at synthesizing long chain carbon molecules, since the conditions might reproduce those existing in red giant stars, which give off large amounts of carbon. This would then provide good evidence to show how such molecules originate in the interstellar medium. During the course of the experiments which probed the behavior of the pure carbon clusters, a striking observation was made. Under some clustering conditions the peak corresponding to 720 mass

units appeared extremely strong.¹⁾ The intensity of this peak relative to adjacent peaks varied dramatically under different clustering conditions. Under a particular condition, the mass spectrum was totally dominated by the 720 peak, corresponding to sixty carbon atoms (Figure 1-1).

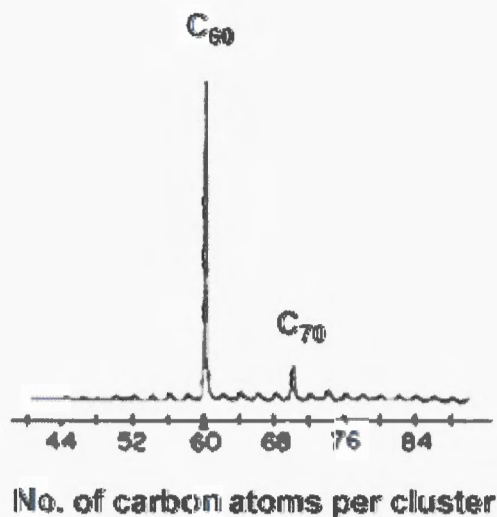


Figure 1-1

The next difficult task was to assign a structure for the 720 mass peak which could explain its unique stability. Kroto, Smalley and Curl came up with a brilliant resolution to the problem. Using handmade models, they found that the planar graphite sheet structure curls up on the introduction of a few pentagons. For a 60 atom cluster with 12 pentagons, the structure closes in on itself, forming a beautiful cage (Figure 1-2).

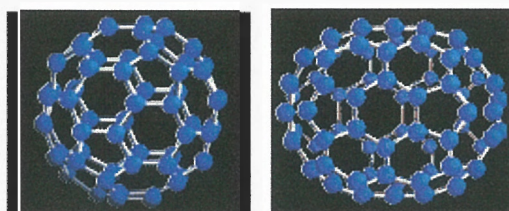


Figure 1-2



Figure 1-3

The shape is identical to that of a soccer ball (Figure 1-3). But the inspiration for the remarkable proposal of C_{60} having a spheroidal cage structure came from the geodesic domes designed by the renowned architect R Buckminster Fuller. The stability of geodesic structures was realized and exploited by this architect earlier, for example in the American pavilion in the 1967 Montreal Expo (Figure 1-4).

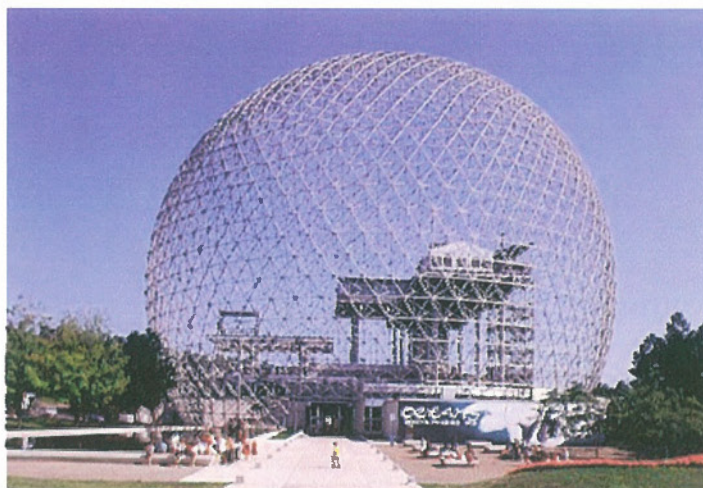


Figure 1-4

But it was not suspected that such structures could be realized on a molecular scale until 1985. Since the geodesic dome concept played an important role in arriving at the structure of C_{60} , it was given the name Buckminsterfullerene. The whole family of hollow cage carbon clusters are now called fullerenes. The most important member of the family, apart from C_{60} is C_{70} . It is usually a major contaminant in the production of C_{60} . The rugby ball shaped structure of C_{70} is shown in Figure 1-2. There were many conjectures on the possible existence of fullerenes prior to the actual discovery of these molecules. A hollow cage structure for carbon was first suggested by Osawa in 1970 and discussed further in a chapter on superaromaticity in a book by Yoshida and Osawa in 1971.^{1b,c)} Even though the discovery of C_{60} through mass spectrometry was achieved in 1985, many chemists were not fully convinced of the existence of fullerenes. The substance had been inferred in an exotic instrument, but was not made in a bottle. Kroto, Smalley and Curl followed up their original proposal with many additional experiments. They provided evidence for the cage structure by incorporating metal ions in C_{60} . But the breakthrough in synthesis came almost five years after the original discovery, from a group of physicists. Krätschmer, Lamb, Fostiropoulos, and Huffman, in following up their earlier infrared spectral observations, discovered that at 300–400°C, a solid material could be sublimed from the deposit obtained from arc-processed graphite.³⁾ They were able to crystallize the material and the X-ray and electron diffraction analyses showed that it consisted of arrays of 7 Å diameter spheroidal molecules. They also reported IR, UV/VIS, and mass spectra of this extracted

material which provided the first confirmation of the Buckminsterfullerene structural proposal. Since the discovery of the procedure by Krätschmer and Huffman for the macroscopic production of C₆₀, methods to prepare and purify fullerenes have been further developed and improved by many research groups. Even though C₆₀ is available in macroscopic quantities, conventional organic synthesis of the molecule is yet to be achieved. This is currently one of the greatest challenges of synthetic organic chemistry. Of course, there have been a few efforts in this direction involving carbon rings, smaller polycyclic condensed aromatics like corannulene, sumanene, etc. Success may not be very far. Ever since C₆₀ and C₇₀ were first detected by Kroto and others by laser vaporization of graphite, much effort has been directed to answer why C₆₀ and C₇₀ are so stable and what kinds of other fullerenes, with different sizes and shapes, can be formed as stable entities. Theoretical calculations on the higher fullerenes have predicted that all even-numbered fullerenes with the sizes larger than C₇₀ can exist, at least in the sense of a hollow-closed cage structure. Until now, eight fullerenes comprised of 60, 70, 76, 78, 82, 84, 90, 96 carbon atoms have actually been isolated and confirmed to exist as stable clusters. Further, for C₆₀, C₇₀, and C₈₄, the proposed structures have been confirmed by conventional spectroscopic tools as well as by chemical derivatization. For C₇₆ and C₇₈, the structures have been proposed by ¹³C NMR spectroscopy in solution. Several variations in the fullerene cluster shapes have been observed. Long cylindrical nanotubes, cage enclosed in a cage, onion like shapes have all been made. Usually, carbon tubules consist of hexagonal sheets folded as long cylindrical shapes capped with pentagons. This so-called carbon nanotube represents a range of structures bridging fullerenes and graphite. The spheroidal geometry of fullerenes is their most arresting feature, and it directly determines their singular electronic structure. According to Euler's theorem, a closed structure can be constructed with 12 pentagons. A general formula for fullerenes is C_{20+2n}, made up of 12 pentagons and n hexagons. For the larger fullerenes, several isomeric forms can be derived with pentagons and hexagons exclusively. Initially C₆₀ was expected to be extremely unreactive. This prediction was based on the fact that 12500 resonance structures are theoretically possible. Many of these forms apparently do not contribute to the stability of the molecule. Consequently, C₆₀ behaves like an alkene rather than as an aromatic compound. In general, fullerenes undergo all the reactions associated with poorly conjugated, electron-deficient alkenes. But their unique feature is the vast number of products possible from the addition of just one reagent.

1.1.2 Synthesis of fullerenes

Kroto et al.³⁾ vaporized graphite by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. This experiment led to an outburst of interest in the chemistry of C₆₀. Five years after the discovery of C₆₀, Krätschmer and co-workers^{4,5)} developed the first

method to obtain C_{60} in usable quantities. This method consists of the vaporization of graphite rods by resistive heating in a He atmosphere. Krätschmer and co-workers made a real breakthrough in the fullerene science; the access to sizable quantities of C_{60} changed the way in which fullerenes were studied. Moreover, their synthesis allowed the establishment of fullerene chemistry. However, this method is not very efficient, with yields lower than 1%, and it requires harsh reaction conditions (temperatures around 1300°C and pressure of 1 kbar). This method produces C_{60} and C_{70} , but it gives very low quantities of larger fullerenes such as C_{84} , and requires great effort to purify the samples (more than 20 high-performance liquid chromatography cycles for C_{84}). Because of the uncontrollable character of the reaction, it is not possible to obtain a single fullerene or a specific isomer. Since then, the scientific community has been interested in finding new methods that could be controlled to facilitate the synthesis of larger fullerenes and specific isomers with high yields and low costs. However, nowadays, the methods used for obtaining fullerenes in commercial scale are based on the vaporization of graphite by pyrolysis, radio-frequency-plasma, or arc discharge-plasma techniques⁶⁻⁹⁾ and bearing hydrocarbons.¹⁰⁾ Another procedures for the synthesis of C_{60} involves solar furnace,^{11,12)} pyrolysis of organic compounds,¹³⁾ explosive synthesis¹⁴⁾ and in supputtering.¹⁵⁾ In 2002, Scott reported total synthesis of C_{60} starting from simple chloro aromatic compound, which was submitted to flash vacuum pyrolysis (FVP) at 1100°C and 0.01 Torr¹⁶⁻¹⁸⁾ in 0.1 to 1% yield.

1.1.3 Structure of fullerene

In 1990, a team of astronomers led by Krätschmer and Huffman reported that the new allotrope of carbon C_{60} can be produced in macroscopic quantities through resistive heating of graphite under inert atmosphere. A single line ^{13}C NMR spectrum of C_{60} at 143 ppm was reported, confirming the equivalence of all carbon atoms of the highly symmetrical cage (Figure 1-5).¹⁹⁾

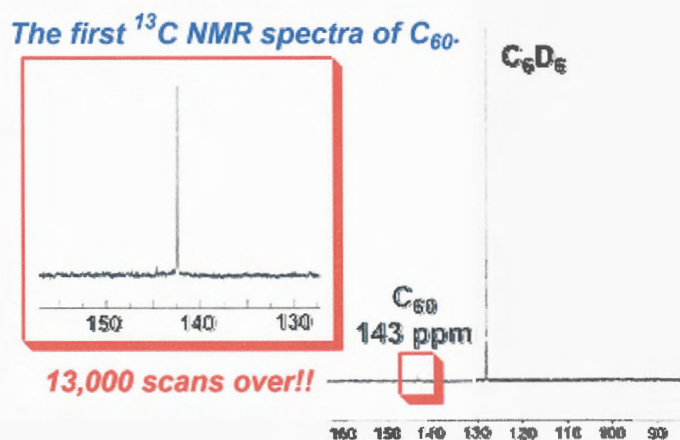


Figure 1-5

Although the icosahedral-cage structure of C_{60} was strongly suggested by ^{13}C NMR, IR, Raman and photoelectron spectroscopy, as well as by scanning tunneling microscopy (STM) imaging, the ultimate confirmation and detailed parameters of the soccer ball-shaped framework had to await X-ray crystallography. However, rapid isotropic rotational motion of the orderly packed spherical molecules in the crystal to temperatures down to 100 K have so far prevented a successful high resolution X-ray crystal structure analysis.²⁰⁾ To break the symmetry of C_{60} and prevent its rapid spinning in the crystal, Hawkins et al. prepared by osmylation a remarkable 1:1 C_{60} -osmium tetroxide adduct.²¹⁾ The crystal structure of this adduct was subsequently solved by the Berkeley group and clearly confirms the soccer ball structure of C_{60} , composed of 20 six-membered rings fused to 12 five-membered rings (Figure 1-6).

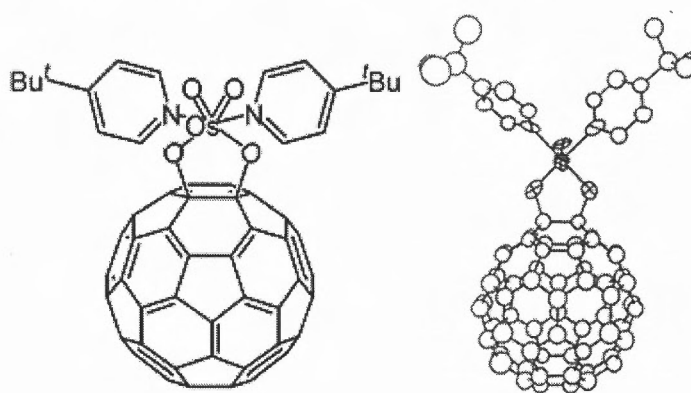


Figure 1-6

All tricoordinate carbon atoms of C_{60} are pyramidalized and lie at an average distance of 3.512(3) Å from the center of the sphere. The unfunctionalized five- and six-membered rings are all planar within ± 0.05 Å. The two bond lengths in these rings are 1.388(9) Å for the fusion between two six-membered rings and 1.432(5) Å for the fusion between a six- and a five-membered ring. At the same time, Fagan also reported X-ray crystal structure of Pt complex of C_{60} .²²⁾ The soccer ball shaped C_{60} isomer with icosahedral symmetry (I_h) is the smallest stable fullerene, because it is the first to obey the isolated pentagon rule (IPR). Due to strain and electronic arguments, the IPR predicts fullerene structures with all the pentagons isolated by hexagons to be stabilized against structures with adjacent pentagons (Figure 1-7).^{23,24)}

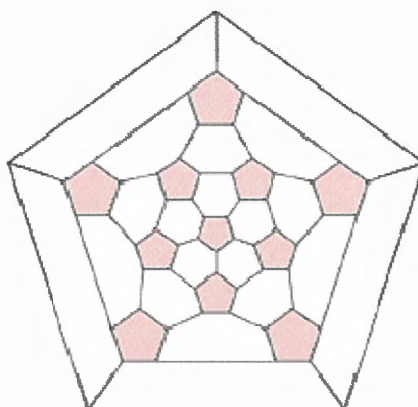


Figure 1-7 Schlegel diagram of C_{60} .

Hawkins also reported 2D INADEQUATE NMR for ^{13}C - ^{13}C couplings of Os-complex of C_{60} .²⁵⁻²⁷⁾ The necessary condition for the observation of ^{13}C - ^{13}C coupling constants is the presence of two anisochronous ^{13}C atoms in a molecule. Because of the low natural abundance of ^{13}C (1.1 %) this condition is, however, met only for few molecules in the sample (≈ 0.011 %). Line splittings as a result of ^{13}C - ^{13}C coupling are present in the ^{13}C NMR spectrum only as weak satellites accompanying the intense signals of molecules with one ^{13}C atom ; in particular, small coupling constants are difficult to measure (Figure 1-8).

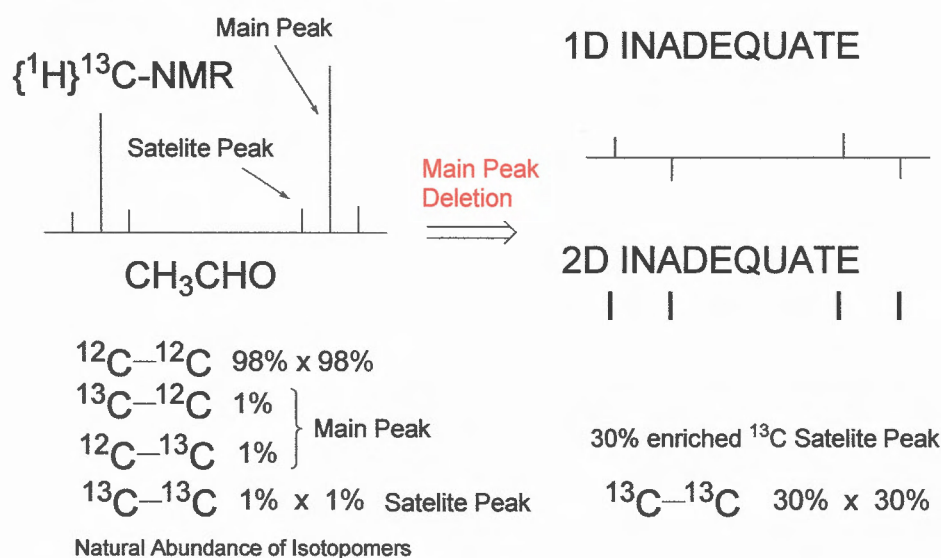


Figure 1-8

Since synthetic enrichment is possible only in a few exceptional cases, experimental methods which facilitate the measurement of J (^{13}C - ^{13}C) data are of interest. The pulse sequence INADEQUATE developed by Freeman et al.²⁸⁻³⁰⁾ for this purpose is based on the idea that by suitable treatment of the spin system consisting of the AX system of the coupled ^{13}C nuclei and the intense signal of the parent compound with only one ^{13}C , the main signal can be suppressed (Figure 1-8). Carbon-13-enriched C_{60} was prepared from cored natural abundance carbon rods

packed with ^{13}C powder and converted to Os-complex. The 1D ^{13}C NMR spectrum of enriched Os-complex showed 22 peaks. Five of the peaks were assigned to coordinated 4-*tert*-butylpyridiene. Of the 17 remaining peaks, four displayed approximately half the intensity of the other 13 peaks. This pattern agrees with the structure of Os-complex, considering that it has two approximate mirror planes. Accordingly, the C_{60} segment of Os-complex has 17 types of carbons, 13 represented four times, and four that lie on a mirror plane and are represented two times (Figure 1-9).

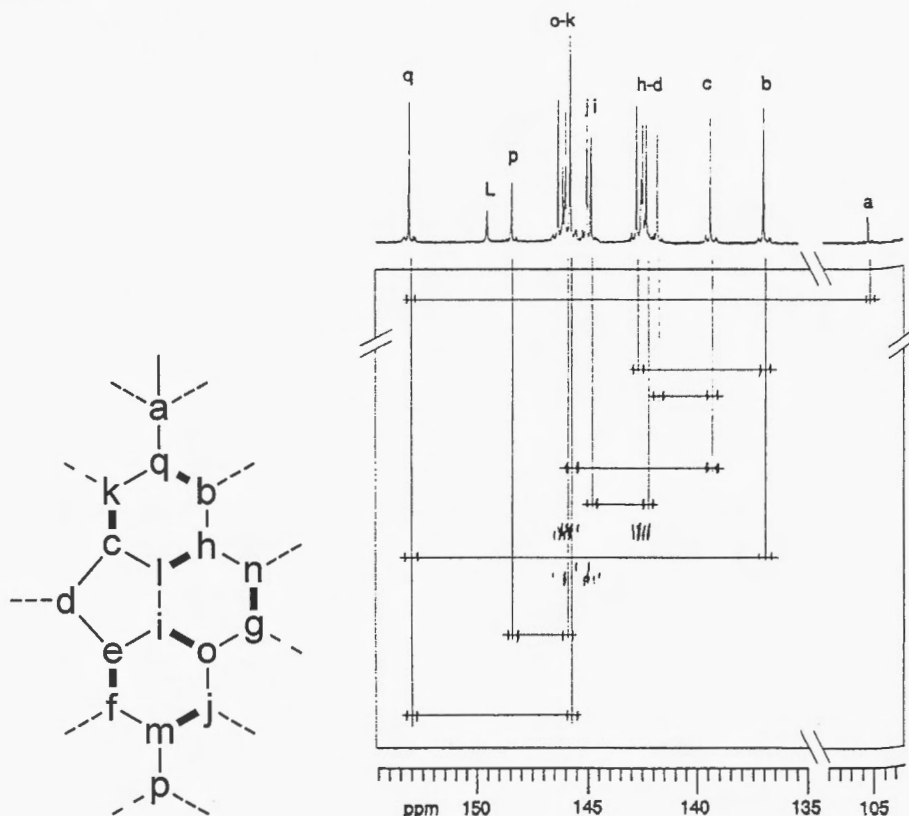


Figure 1-9

The 17 types of carbons were assigned on the basis of the connectivities derived from a 2D NMR INADEQUATE experiment (Figure 1-9). The half-intensity peaks (a, g, n and p) were assigned to the carbons on the approximate mirror planes. Peaks a and p were assigned to types 1 and 17 because they each couple with only one carbon. Of the pair, the remote upfield peak, a, was assigned to the tetracoordinate O-bonded carbon. Starting from carbon type 1, C-C connectivities provided assignments for carbon types 2-13 and 16. Types 5 and 7 were readily differentiated in that type 5 (peak c) couples with three full-intensity peaks (d, k and l), while type 7 (peak h) couples with two full-intensity peaks (b and l) and a half-intensity peak (n). The coupling between carbon types 9 and 10 (peaks d and e) was not first order, and $^1J_{\text{CC}}$ could not be measured. Peaks e and f, corresponding to types 10 and 14, are very close, and the associated cross peaks are not visible. Connectivities from carbon type 17 completed the assignments. The

up-down pattern aided assignments in complicated regions.

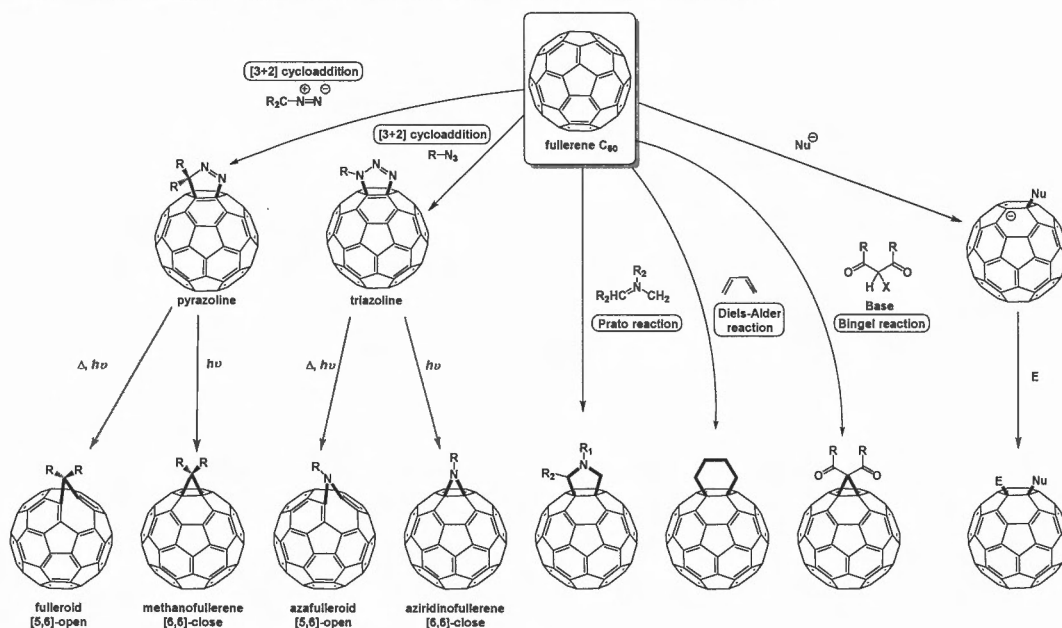
1.2 Chemical transformation of fullerenes

1.2.1 Chemical modification and reactivity of fullerenes

A complete delocalization of the conjugated π -system leading to a reactivity closely related to aromatics can be ruled out. The reactivity of C_{60} is that of a fairly localized electron deficient polyolefin on [6,6] bonds, not that of [5,6] bonds. C_{60} is an electron deficient molecule, which can be easily reduced but hardly oxidized.³¹⁻³⁴⁾ This is reflected theoretically by the MO diagram of C_{60} showing low lying triply degenerate LUMOs and five-fold degenerate HOMOs as well as experimentally by the ease of reversible one-electron reductions up to the hexaanion.³⁵⁾ Based on pioneering studies by Wudl,³⁶⁾ Taylor,³⁷⁾ Hawkins,³⁸⁾ Fagan³⁹⁾ and Haddon,⁴⁰⁾ the following rules of reactivity, can be deduced from the multitude of chemical transformations that have been carried out with C_{60} . The main type of chemical transformation are therefore additions to the 6-6 double bonds, especially, nucleophilic-, radical- and cycloaddition and the formation of η^2 -transition metal complexes; but also, for example, hydroboration and hydrometalation, hydrogenation, halogenation and Lewis acid complex formations are possible. Reactions leading to saturated tetrahedrally hybridized sp^3 carbon atoms are strongly assisted by the strain of pyramidalization present in the fullerene. In most cases, addition reactions to C_{60} are exothermic. The exothermicity of subsequent additions depends on the size and the numbers of addends are already bound to the fullerene core and decreases at a certain stage. Therefore, adducts with a high degree of addition become eventually unstable (elimination) or do not form at all, since new types of strain, for example, steric repulsion of addends or introduction of planar cyclohexane rings are increasingly built up. The interplay of these strain arguments largely determines the number of energetically favorable additions to the fullerene core. Also the reduction of C_{60} can be regarded as a strain-relief process, because many carbanions are known to prefer pyramidal geometries. The exclusive mode for typical cycloaddition and the preferred mode for addition of sterically nondemanding segregated addends is 1,2-addition to a [6,6] double bond,⁴¹⁾ since in this case no unfavorable [5,6] double bonds within the fullerene framework have to be formed. The introduction of each [5,6] double bond costs about 8.5 kcal/mol. In 1,2-additions, however, eclipsing interactions between the addends are introduced. Thus, if bulkier segregated addends are allowed to react with C_{60} , a 1,4-mode avoiding eclipsing interactions may occur simultaneously or exclusively.⁴²⁾ In 1,4-additions eclipsing 1,2-interactions are avoided but the introduction of [5,6] double bonds is required.⁴³⁾ The electronic structure of the fullerenes is such that bonds at [6,6] ring junctions have much double-bond character, while bonds at [5,6] ring junctions are essentially single bonds. This arrangement results in C_{60} having a strong bond-alternated structure which can best be described

as a spherical tessellation of [5]radialene and 1,3,5-cyclohexatriene subunits. As original type of reaction, recent interest was focused on the oxidative, nucleophilic addition,⁴⁴⁻⁴⁶⁾ solid-state dimerization⁴⁷⁾ and η^2 -pentaarylated metal complexes⁴⁸⁾ of fullerene.

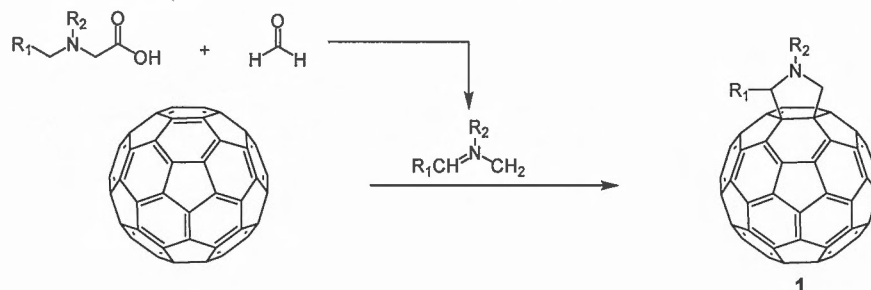
Exohedral modifications of fullerenes in three dimensions by addition reactions and the development of preparative fullerene chemistry are particularly attractive to chemists. In the meantime an entire series of successful reactions with C_{60} and also with C_{70} have been conducted, leading to well-defined fullerene derivatives (Scheme 1-1).



Scheme 1-1

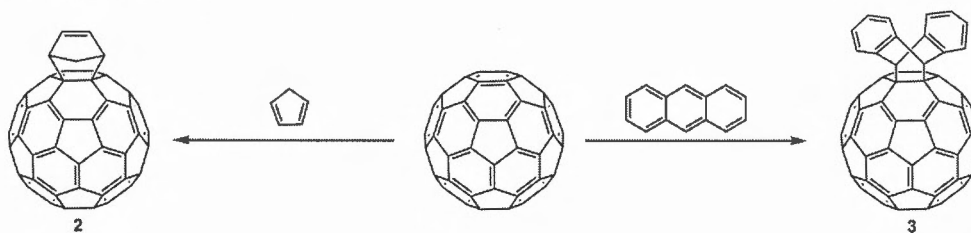
The [3+2] and [4+2] cycloaddition was shown to add regioselectively exclusively at a double bond common to two annelated six-membered ring (6-6 bond) in the fullerene framework. Up to now, 250 papers were appeared in literature. Wudl et al. and Diederich et al. showed [3+2] cycloaddition with diazoalkanes and diazoacetates provide σ - or π -homoaromatic fullerenes with methanobridges. The thermally stable final products in these reactions are the opened, π -homoaromatic compounds bridged at a [5,6] ring juncture ('fulleroid'), or the closed, σ -homoaromatic fullerenes 3 bridged at a [6,6] ring juncture ('methanofullerene'). The opened azafulleroids were obtained from C_{60} and organic azides by [3+2] cycloaddition and subsequent loss of nitrogen molecular. The details of [3+2] addition of diazo and azide compounds will be shown in next chapter. Prato et al devised a new and general fullerene functionalization, based on 1,3-dipolar cycloadditions to C_{60} . Azomethine ylides, generated in different ways, add to C_{60} affording substituted fullerene-pyrrolidine in excellent yields. A very easy way of generating azomethine ylides is the "decarboxylation route". Thus, a mixture of *N*-methylglycine and paraformaldehyde was heated at reflux in toluene in the presence of C_{60} . The reaction

proceeded very smoothly affording the *N*-methylpyrrolidine derivative after chromatography. Among other approaches, thermal ring opening of aziridines was employed and they obtained good yields of the fullerene 3,4-substituted proline (Scheme 1-2).⁴⁹⁾



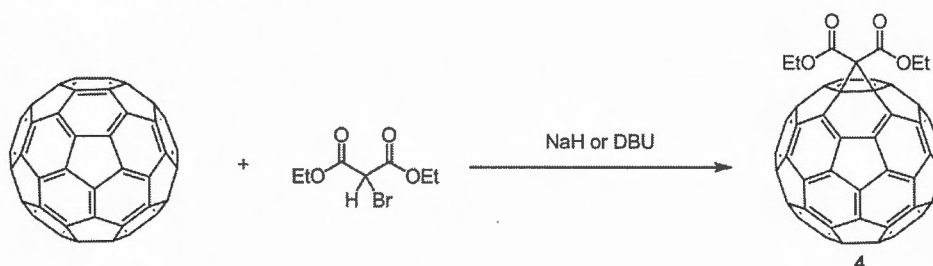
Scheme 1-2

C_{60} have low-LUMO level and only acts as dienophile like *N*-phenylmaleimide.^{50,51)} Defined, stable Diels-Alder adducts of C_{60} can be obtained from reactions with cyclopentadiene and with anthracene (Scheme 1-3).



Scheme 1-3

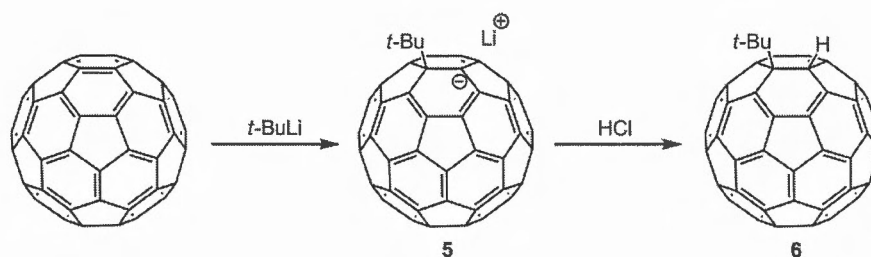
They are formed with high regioselectivity by addition to a 6-6 double bond exclusively. C_{60} is capable of reacting with nucleophiles of all types, and the intermediate anions can be trapped with suitable electrophiles. Binge demonstrated that C_{60} reacts with several stabilized α -halocarbanions to give the methanofullerenes. This reaction is formulated as an addition of the stabilized α -halocarbanion to C_{60} , followed by intramolecular displacement of halide by the anionic center generated on the fullerene sphere. The reaction is fast, clean and proceeds in fair to good yield (Scheme 1-4).⁵³⁻⁵⁷⁾



Scheme 1-4

The nucleophilic additions of Grignard and organolithium compounds and the subsequent protonation to form 1-organo-1,9-dihydrofullerenes-60 reveal much about the reactivity of C_{60}

(Scheme 1-5).⁵⁸⁻⁵⁹⁾

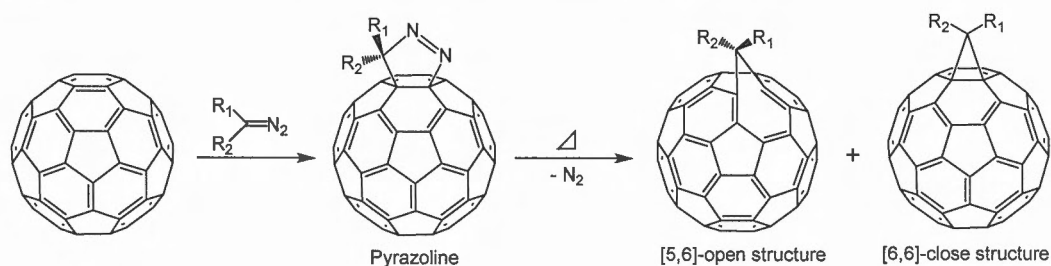


Scheme 1-5

Even in these two-step processes isomerically pure compounds are obtained. For good yield of the monoadduct, the reactions with reactive carbanionic nucleophiles must be carefully regulated. The fact that the stable final products isolated are exclusively the 1,9 derivatives clearly demonstrates that the negative charge in the anionic intermediates RC_{60}^- (*C*_s symmetry) is localized primarily on C₉.

1.2.2 Chemical modification of C₆₀ with diazo and azide compounds.

Generally, diphenyldiazomethane,⁶⁰⁻⁶⁸⁾ diazoacetate^{61,69)} and diazoanide⁷⁰⁾ add initially as a [1,3]-dipole to C₆₀, and that the pyrazoline intermediate, subsequently extrudes nitrogen molecular to give [6,6]methanofullerene and [5,6]fulleroid (Scheme 1-6).



Scheme 1-6

As a result of the presence of both five- and six-membered rings within the structure of C₆₀, there are two types of bonds – namely bonds at the junction between two six-membered rings ([6,6] bonds) and bonds at the junction between a six- and five-membered ring ([5,6] bonds). The addition of carbenes or their equivalents to the C₆₀ sphere would give an organic derivative of C₆₀, a methanofullerene. The presence of two different kinds of bonds in C₆₀ suggested that, in principle, two isomers of the methanofullerenes may be formed by such addition reactions – namely the [5,6] bridged and [6,6] bridged isomers. Further, by analogy with the methanoannulenes the possibility of valence isomerism leads to four possible isomers (Figure 1-10) depending on whether the transannular bond of the methanofullerene subunit in the fullerene sphere is 'open' or 'closed'; especially the 'open' structure is called fulleroid, which preserve 60 π electron as same as C₆₀. The stability order of the [5,6] and [6,6]-bridged isomers is

compatible with the hypothesis, wherein the [5,6] open [6,6] closed-bridged isomers are more stable than the [5,6] closed isomers and [6,6] open isomers. These have been explained by avoiding locating any double bonds within the five-membered rings of C_{60} .^{31,40,68,71-74)}

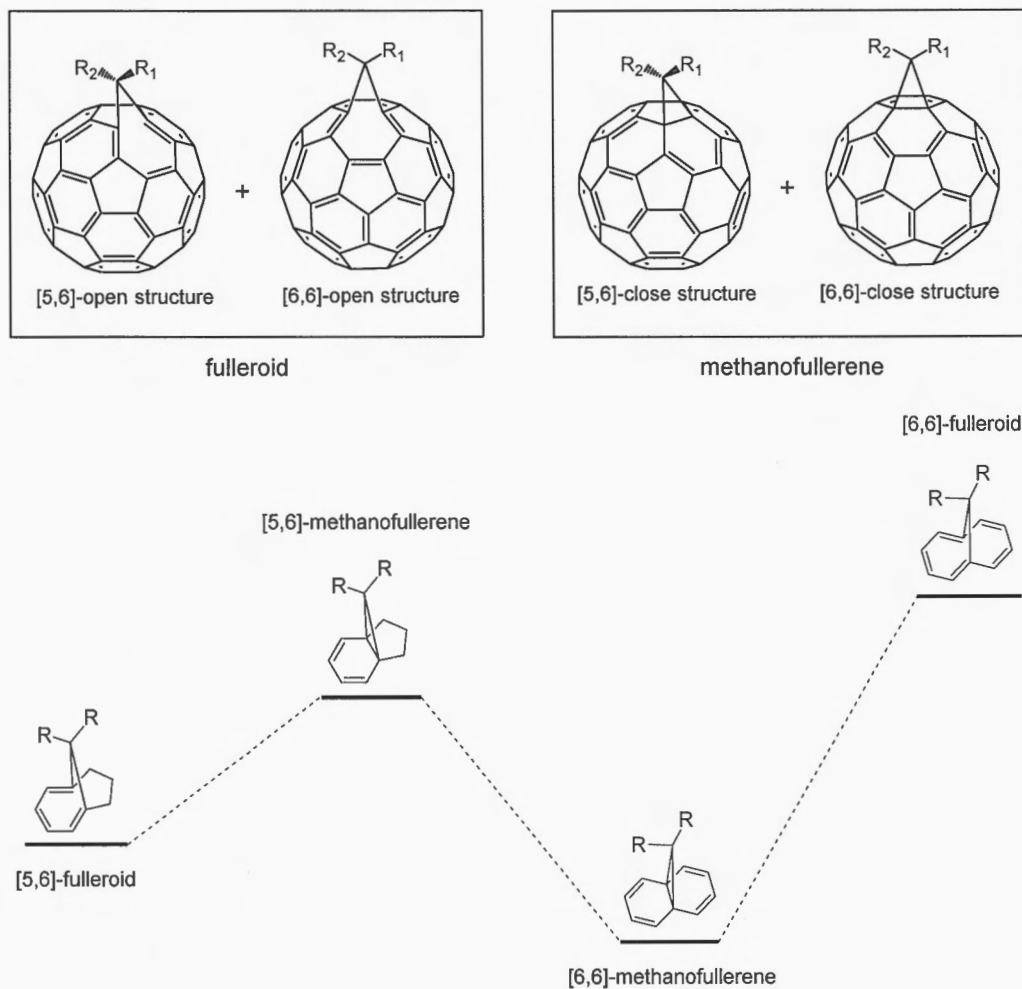
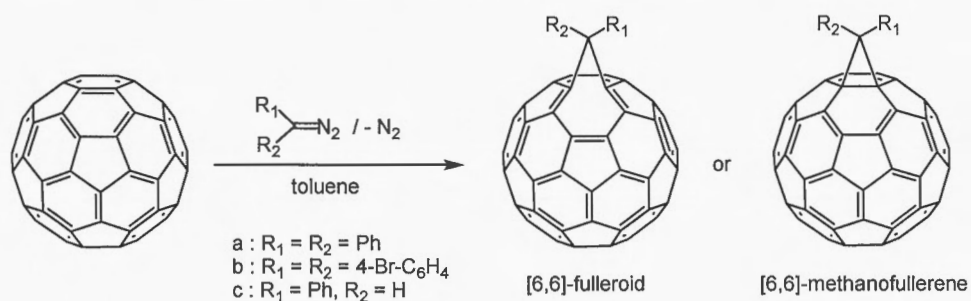


Figure 1-10

In late 1991, Wudl and co-workers reported that C_{60} reacts with diphenyldiazomethane in toluene solution at room temperature to give a [6,6] ring bridged adducts (Scheme 1-7).



Scheme 1-7

Subsequently, in an Accounts of Chemical Research article, it was shown⁶¹⁾ that this reaction tolerates the presence of substituent on the phenyl rings, implying its general applicability to the production of functionalized fullerene derivatives. This account ignited an interesting debate on the structure of methanofullerenes. In their initial report on their synthesis of methanofullerenes, Wudl and co-workers assigned a [6,6] open structure to product of addition on the basis of its ¹H NMR spectrum and the similarity of its UV/Vis spectrum and cyclic voltammogram to the corresponding data of C₆₀ itself; however, the compound was too insoluble to record a ¹³C NMR spectrum (Scheme 1-7). Subsequently, a crystal structure was reported in which the transannular bond length at the [6,6] bridged was found to be 1.84 Å, which, although shorter than an open transannular bond in methanofullerenes, is clearly much longer than the normal sp³-sp³ bond length of 1.54 Å (Figure 1-11).

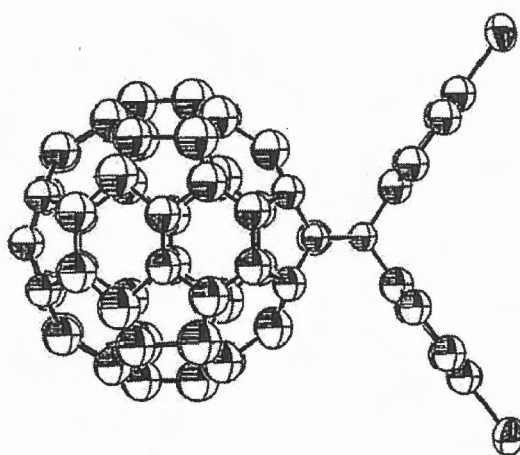
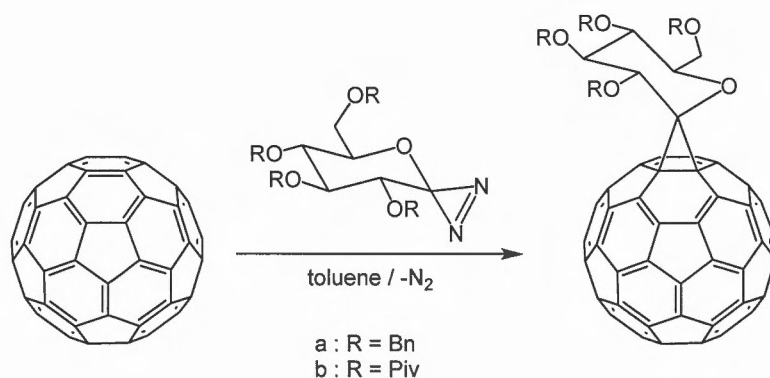


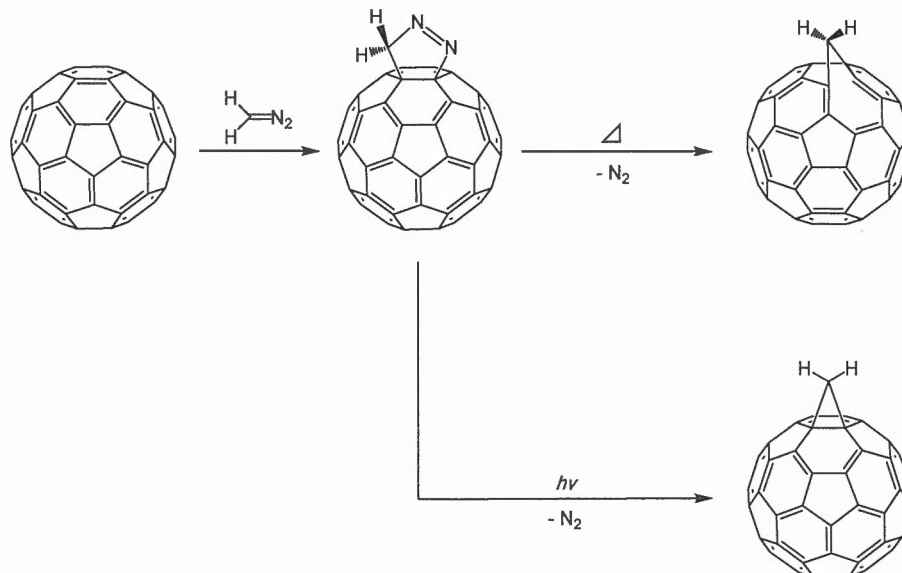
Figure 1-11

This result must however, be treated with caution since the crystals were of poor quality and probably contained more than one isomer. In addition, Wudl also determined the ¹J_{CH} coupling constant at the bridging carbon.⁶⁴⁾ The measured value of 140 Hz is almost exactly that found in 11-phenyl-1,6-methano[10]annulene with an open transannular bond, and thus was considered clear evidence for a [6,6] open structure.⁶⁴⁾ Caution should be exercised, however, since, without ¹H and ¹³C NMR spectra of all three isomers, it is impossible to distinguish whether bridging had occurred at the [5,6]- or [6,6]-ring junctions of the fullerene sphere. Despite these reservations the matter seemed settled in favor of the [6,6] open structure, at this point. However, the synthesis⁷⁵⁾ of fullerene sugars by Vasella et al. raised new questions. Sugar derivatives of fullerenes (R = Bn or Piv) were soluble enough to permit the recording of high quality ¹³C NMR spectra, which clearly showed peaks corresponding to fullerene resonances in the 70 to 80 ppm region providing evidence for a [6,6] closed structure (Scheme 1-8).



Scheme 1-8

Wudl and co-workers proposed⁶⁰⁾ that diazomethane adds initially as a [1,3]-dipole to C_{60} , and that the pyrazoline intermediate, which was not isolated, subsequently extrudes nitrogen molecular. When the addition of diazomethane to C_{60} was conducted in benzene at room temperature, a brown, thermally unstable, compound was isolated (Scheme 1-9).



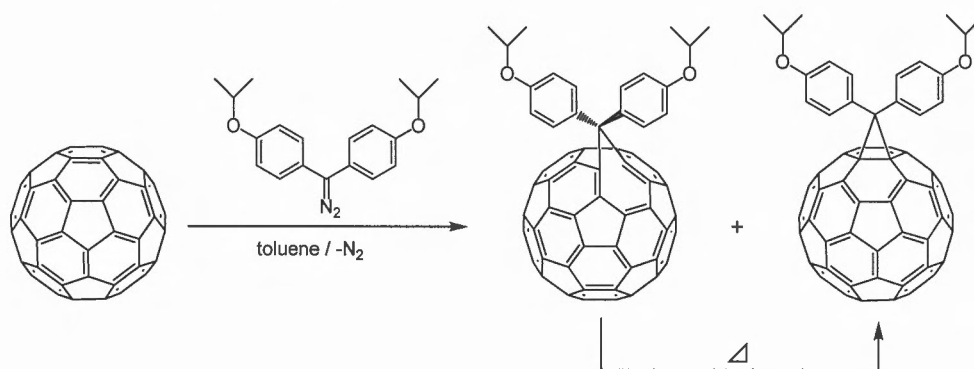
Scheme 1-9

This compound was assigned the pyrazoline structure on the basis of (i) singlet in the ^1H NMR spectrum at 6.51 ppm, (ii) the presence of 30 carbon resonances in the fullerene region of the ^{13}C NMR spectrum (consistent with the assigned C_s symmetry), and (iii) a $\text{N}=\text{N}$ stretching vibration at 1560 cm^{-1} in the infrared spectrum. Thermolysis of pyrazoline in refluxing toluene afforded [5,6] fulleroid in quantitative yield. The ^1H NMR spectrum of [5,6] fullroid showed two doublets centered at 2.87 and 6.35 ppm, and the ^{13}C NMR spectrum displayed 32 resonances between 135 and 150 ppm, in addition to a signal at 39 ppm, in agreement with the assigned [5,6] open structure (Scheme 1-9). Taken together, these experiments suggest that the initial step in the addition of diazo compounds to C_{60} is indeed a [1,3]-dipolar cycloaddition followed by thermal loss of nitrogen molecule. In the case of the parent methanofullerene C_{61}H_2 ,

it has not proved possible thermally to rearrange the [5,6] open isomer to the [6,6] closed compounds. The latter could, however, be synthesized by Smith et al. by photolysis of pyrazoline.⁶⁵⁾ This reaction afforded both isomers in a 4:3 ratio, and separation of the mixture by HPLC on a C₁₈ reverse-phase column gave [6,6] closed compound, whose structure was convincingly elucidated by ¹H and ¹³C NMR spectroscopy. The ¹³C NMR spectrum contained 18 signals, 16 between 136 and 150 ppm, and more importantly, one at 30 ppm and one at 71 ppm which was assigned to the cyclopropane carbon atoms in the fullerene sphere. Further evidence for the [6,6] closed structure was obtained from the ¹J_{CH} coupling constant at the bridging carbon atoms, which, at 167 Hz, is clearly characteristic of a cyclopropane ring. In contrast, Wudl and co-workers did not observe any resonances in the 70 - 80 ppm region in the ¹³C NMR spectrum of the [5,6] bridged isomer of C₆₁H₂. They measured a ¹J_{CH} coupling constant at the bridging carbon atom of around 146 Hz which, together with the ¹³C NMR data, provided clear evidence that the [5,6] bridged isomer of C₆₁H₂ had an open transannular bond. All these results called into question the original assignment of a [6,6] open structure⁶⁴⁾ and indeed, as this point, [6,6] open fulleroid and its derivatives were reformulated as the corresponding [6,6] closed structure. However, all of the phenyl- and diphenyl-substituted methanofullerenes isolated previously were bridged at the [6,6] ring junction, and not at the [5,6] ring junction. Thus, it was unclear whether the results obtained in the diazomethane addition, which yielded only a very small amount of the [6,6] closed isomer, applied to the reactions of C₆₀ with diazo compounds in general. In all of the previous cases, the initial product of the reaction was a mixture of at least two isomers. Furthermore, it was possible to convert this isomeric mixture thermally into a single [6,6] ring bridged compound which had high symmetry (C_{2v}) – readily identified by the simplicity of its ¹H and ¹³C NMR spectra. These two generalizations apparently did not apply to the diazomethane adduct. Thus, all the then-known [6,6] bridged methanofullerenes had a closed transannular bond. Subsequent work has shown that this statement is almost certainly true for all [6,6] bridged methanofullerenes, and that the substituent effects at the bridging carbon atoms which are observed in methanoannulenes are overwhelmed in the methanofullerenes by electronic and structural preferences of the fullerene sphere. In retrospect, it was not until [5,6] and [6,6] bridged compounds bearing the same substituent at the bridging carbon atom became available, and were fully characterized, that all of the pieces of the puzzle could be fitted together. Today, it is clear that all [5,6]-bridged compounds possess an open transannular bond, and all [6,6]-bridged compounds have a closed transannular bond.

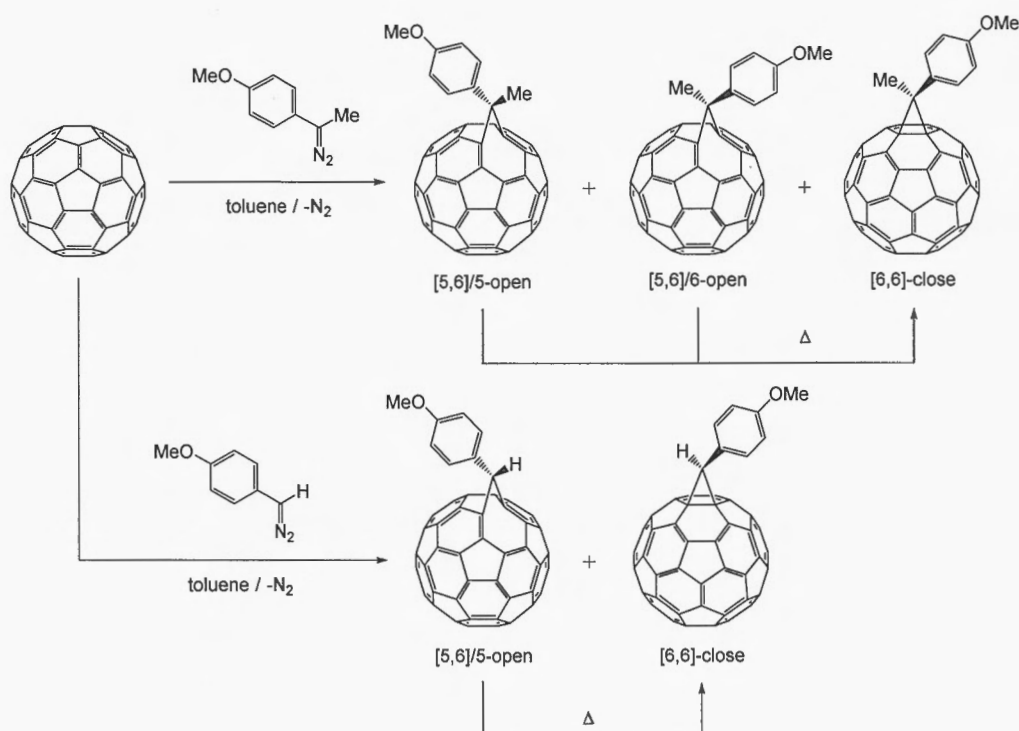
Wudl et al. showed that the initial product of addition is a mixture of methanofullerene and methanoannulene (fulleroid) isomers and that the lowest energy isomer of substituted phenyldiazomethane and substituted diphenyldiazomethane addition has [6,6] methanofullerene.

The substitution of same groups was investigated with the adduct of bis(*p*-isopropoxyphenyl)diazomethane with C₆₀. Three different para-disubstituted benzene rings (in 2:2:1 ratio) are observed in the ¹H NMR spectrum of chromatographically products. Based on the detection of NOE interactions between the respective ortho protons, two patterns (in fixed 1:1 ratio) are part of the same molecule. For this isomer, a number of ¹³C low-field resonances of the product mixture (32 from the fullerene sphere and 8 from the benzene rings) support the fulleroid structure with a [5,6] fulleroid (bridge carbon at δ 64.02). Heating the mixture converted it quantitatively to the other, already present, isomer. The latter showed only one para-disubstituted benzene system and one 2-propoxy moiety in its ¹H NMR spectrum. The ¹³C NMR spectrum exhibited 16 fullerene sphere and 4 benzene ring resonances, one resonance at δ 79.58 (bridgehead), and 3 aliphatic resonances (bridged carbon at δ 57.35). This pattern is unambiguously diagnostic for a symmetric structure with a [6,6] methanofullerene (Scheme 1-10).⁶⁶⁾



Scheme 1-10

Next, Wudl et al. investigated the unsymmetrical substitution with two unsymmetrical diazomethane adducts. Indeed, the ¹H NMR spectrum of the chromatographically pure (*p*-methoxyphenyl)diazoethane addition product revealed three distinct isomers (in 4:2:1 ratio) (Scheme 1--11)⁶⁶⁾.



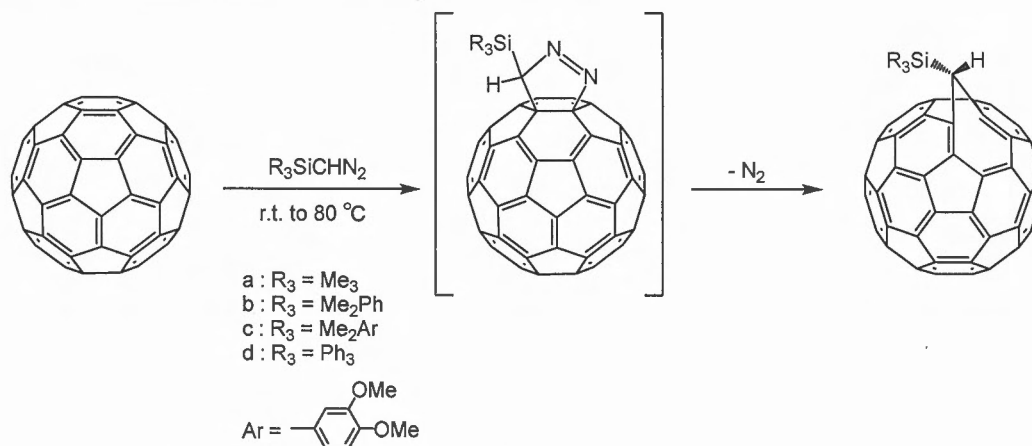
Scheme 1-11

The inseparable mixture was subjected to HETCOR analysis. In one isomer the methyl proton resonance at δ 2.52 correlates with the fullerene carbon resonance at δ 80.98, providing corroborating evidence for a methanofullerene structure for this compound. In the other two isomers, the bridgehead carbons resonate in the low-field region, supporting fulleroid structures. Upon refluxing overnight in toluene, the mixture converged cleanly to the methanofullerene. Two major isomers (in 1:1 ratio) were found in the NMR spectrum of the (*p*-methoxyphenyl)diazomethane adduct. The HETCOR analysis shows a correlation between the methine ¹H resonance at δ 5.33 and the ¹³C resonance at δ 75.61. The assignment of the methanofullerene structure to this compound is strengthened by the observed methine ¹*J*_{CH} = 163.7 Hz, typical of cyclopropane rings. For the other isomer, the methine ¹H resonance at δ 4.03 (¹*J*_{CH} = 142.0 Hz, characteristic of open [5,6] fulleroids) couples only with four ¹³C low-field resonances (one of them correlates also with phenyl protons). This result, combined with UV-vis spectroscopy (identical to C₆₀) point to the fulleroid structure for this isomer. Heating the mixture produced [6,6] methanofullerene quantitatively (Scheme 1-11).⁶⁶⁾

Wudl and co-workers found that for the addition of (*p*-methoxyphenyl)diazomethane to C₆₀, the [5,6] open diastereoisomer with the bulkier substituent located above the five-membered ring predominated in the product mixture formed under kinetic control. Related studies by Skiebe and Hirsch⁷⁶⁾ demonstrated the same phenomenon, suggesting that this diastereoselectivity in the formation of the kinetic [5,6] open isomers may be a general phenomenon. Structure of the two

[5,6] open diastereoisomers, in all cases, were assigned based on the ^1H NMR spectra which showed a strong downfield shift of the resonance for the methano bridge proton located above a pentagon as compared to the resonance of the proton above a hexagon.

Later, Kabe and Ando reported that the mono-silyl diazomethanes were added to C_{60} and the mono-adducts were isolated in moderate yield (Scheme 1-12).⁷⁷⁾



Scheme 1-12

The ^1H NMR chemical shifts of the methine proton of adducts can be used as a sensitive NMR probe for the segregated ring currents of the fullerene core. For adducts, the methine protons appeared upfield (2.47–3.43 ppm), typical for a location above the six-membered ring of a bridged fullerene subunit. In the ^1H -decoupled ^{13}C NMR spectra, 32 resonances were assigned to the C_{60} skeleton. Of the 32, 28 signals have a relative intensity of 2 and 4 signals have an intensity of 1, indicating C_s symmetry. Moreover, in the gated ^1H -coupled ^{13}C NMR spectra, the three sets of fullerene carbons at 136.7–137.0 ppm, 138.2–140.0 ppm and 143.7–143.8 ppm are split into doublets ($^2,3J_{\text{C-H}} = 5.3\text{--}7.4\text{ Hz}$) by the methine protons (Figure 1-12). ^{13}C – ^1H COLOC analysis also showed a correlation between the methine proton resonances and the same three fullerenes resonances (Figure 1-13). The ^{13}C – ^1H long range coupling supports the conclusion that adducts have [5,6] open fulleroid structures with silyl groups located above a five-membered ring (Scheme 1-12).

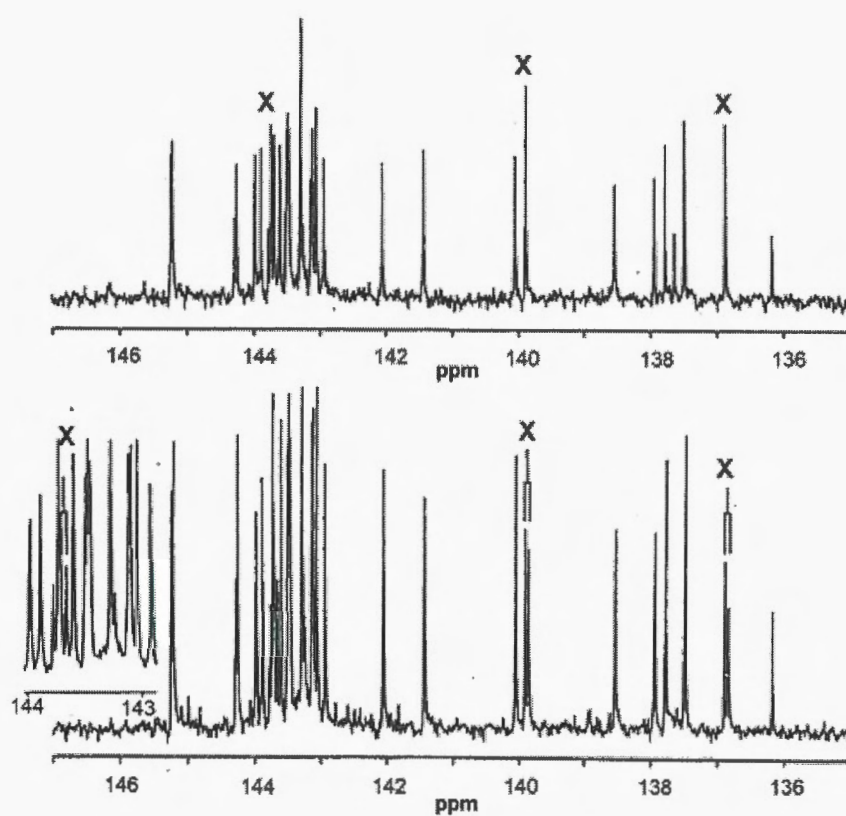


Figure 1-12

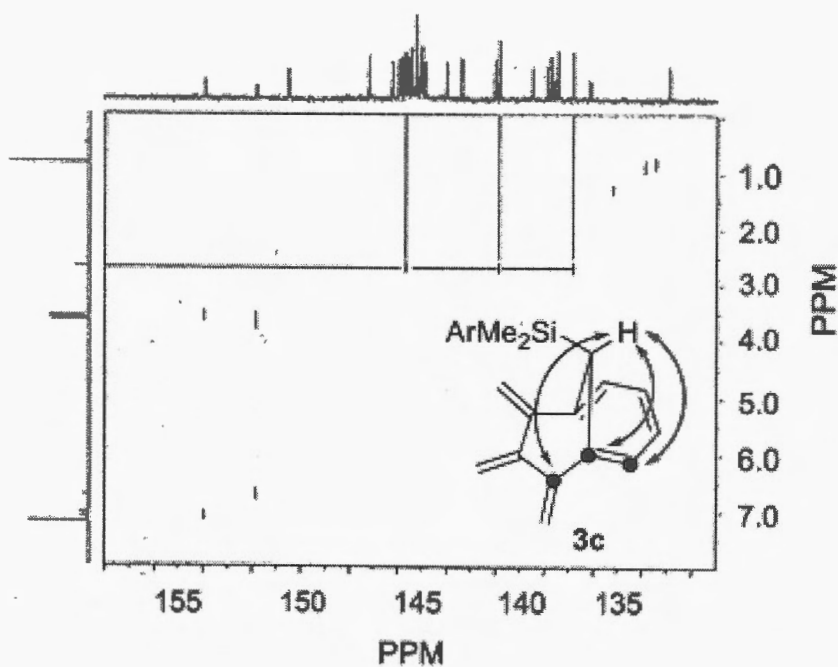
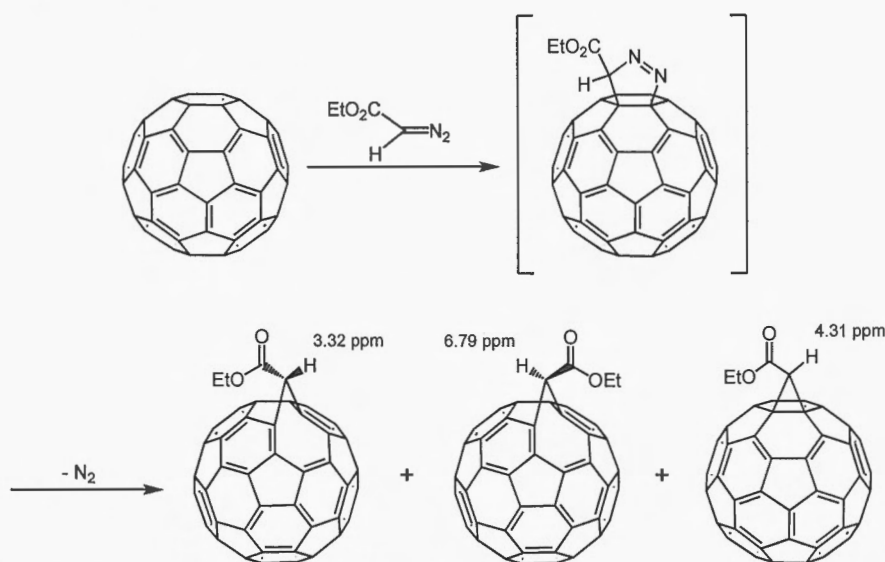


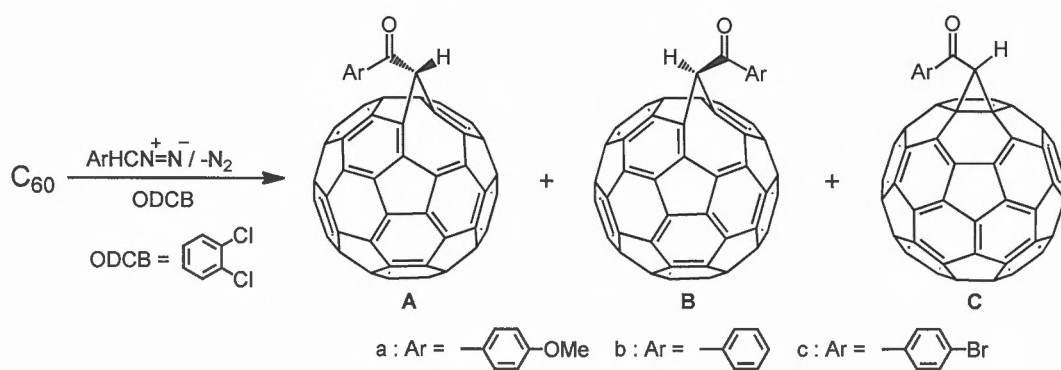
Figure 1-13

Diederich and co-workers observed that the addition of alkyl diazoacetates to C_{60} in refluxing toluene for 7 h (Scheme 1-13) gave rise to three isomeric products (as determined by 1H NMR spectroscopic analysis) under kinetic control.⁷⁸⁾ Interestingly, one of the isomers predominated by a factor of three over the other two. When this isomeric mixture, which like C_{60} solutions was purple, was heated in refluxing toluene for 24 h, a wine-red solution was produced whose 1H NMR spectrum showed only a single set of resonances. This pure compound corresponded to one of the two minor components in the isomeric mixture and was obviously thermodynamically more stable than the other two isomers. This compound was assigned the [6,6] closed structure based on its ^{13}C NMR spectrum and the $^1J_{CH}$ value for the methine carbon which clearly supported the presence of a cyclopropane ring. The 1H NMR chemical of methine proton depend on the extent segregated ring current on five- and six-membered ring of a bridged fullerene subunit (Scheme 1-13).



Scheme 1-13

Later, Nishimura et al. reported that the reactions of [60]fullerene with benzoyl diazomethane afforded mainly three products (Scheme 1-14).⁷⁹⁾ Under these reaction conditions, no dihydrofuran-fused fullerene derivatives reported in the literature were detected, since the reactions were performed at lower temperature. Both A and B are “fulleroids” with [5,6]-open structure, while C is a “methanofullerene” with [6,6]-closed structure. Fulleroids A and B are diastereoisomers to each other; the methine protons of A and B are located over a six-membered ring and five-membered ring, respectively. The isolation of each of A-C was unsuccessful due to the similar polarity. 1H NMR spectra are expected to reveal quite different features from one another, because the methine protons of A-C are situated in quite different environments. Hence, the methine proton of fulleroid A is expected to resonate at rather high fields, while that of B at rather low fields, and that of C is in the middle region between them (Figure 1-14).



Scheme 1-14

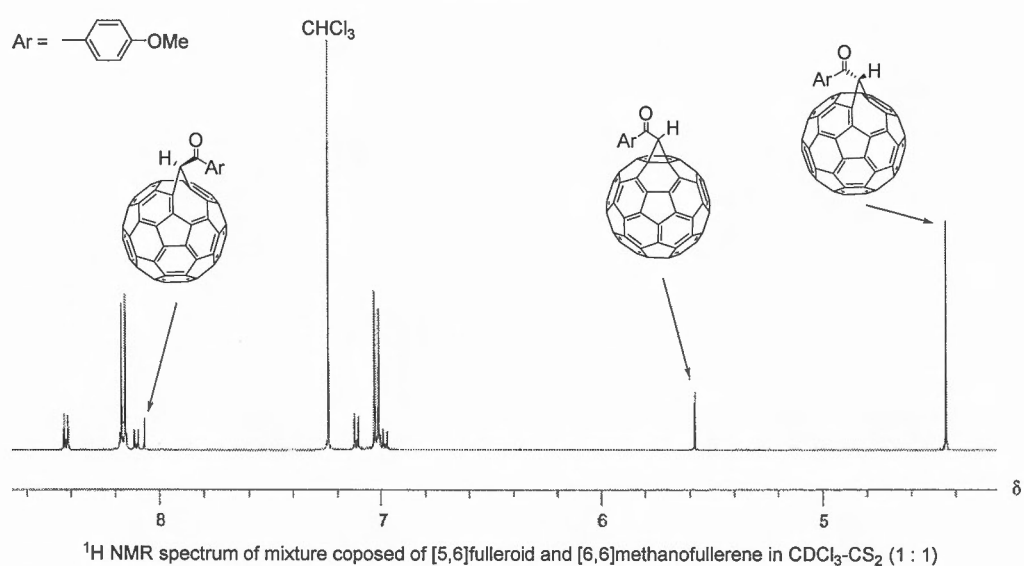
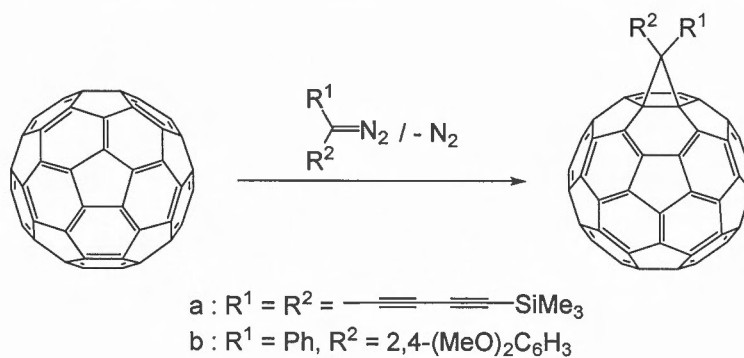


Figure 1-14

Finally, Diederich group have reported on the crystal structure analysis of [6,6] methanofullerene. The first accurate X-ray data for [6,6] methano-bridged fullerenes definitively confirm the preference for a closed [6,6] structure (Scheme 1-15 and Figure 1-14).⁸⁰⁾



Scheme 1-15

Brock and co-workers reported the first X-ray crystal structure of a C_{70} -fulleroid, and established that indeed, CCl_2 insertion to the [5,6] single bond and the structure is an opened homo conjugated annulene (Figure 1-15(c)).⁸¹⁾ In the related halo carbene, Sidorov and co-workers reported⁸²⁾ that CF_2 addition to C_{60} provided unprecedented [6,6]fulleroid of $C_{60}CF_2$ based on NMR spectra. The ^{13}C NMR spectrum showed 16 singlet signals and one singlet for CF_2 carbon at 111 ppm with ^{19}F - ^{13}C coupling ($^1J_{CF} = 267$ Hz) for [6,6] $C_{60}CF_2$ molecular with C_{2v} symmetry (Scheme 1-16 and Figure 1-16). Later, X-ray structure of bis[6,6]fulleroid, $C_{60}(CF_2)_2$ and mono fulleroid $C_{70}(CF_2)_2$ were also reported.^{83,84)}

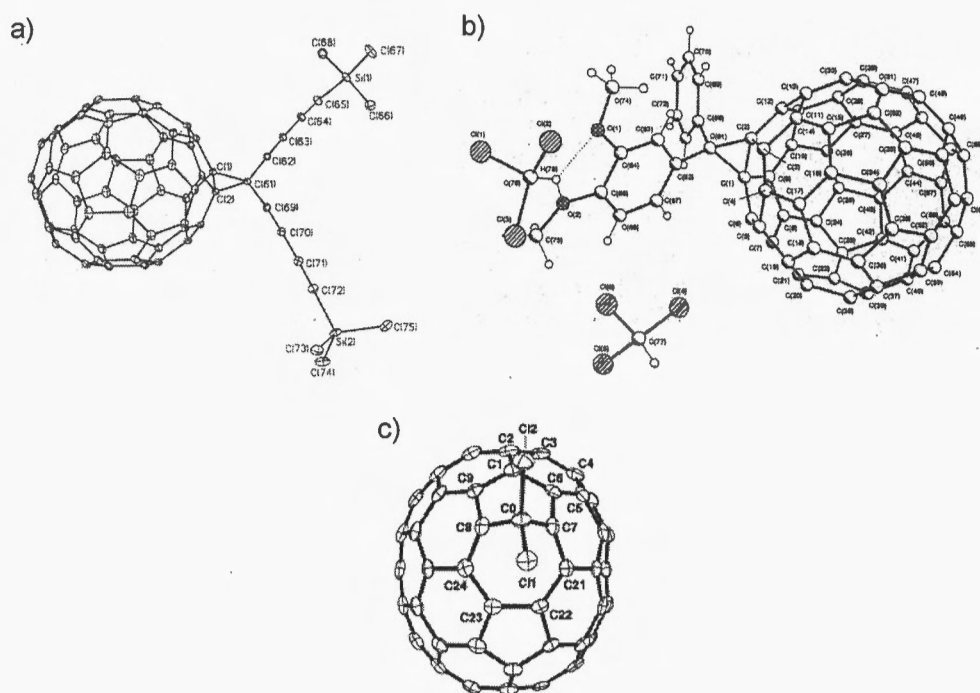
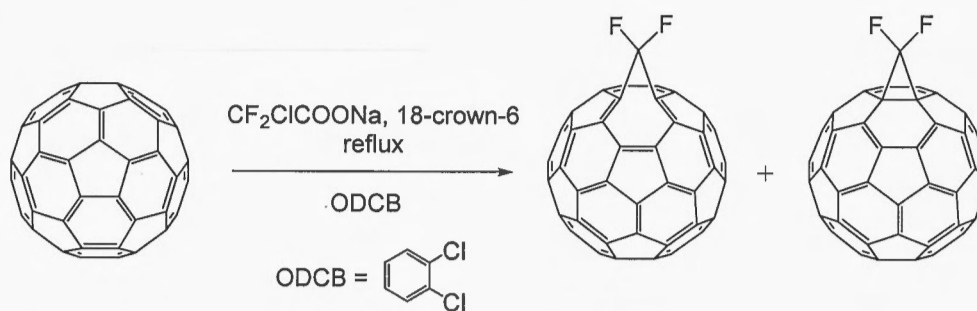


Figure 1-15



Scheme 1-16

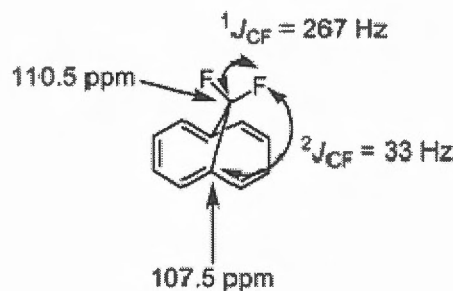
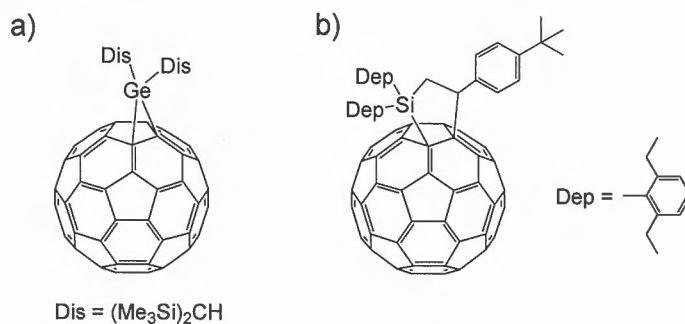


Figure 1-16

As a few rare examples of [5,6]methanofullerene, Kabe and Ando reported that the photolysis of 1,2-digermacyclobutane derivatives bearing bulky bistrimethylsilylmethyl(disyl) groups with C_{60} provided the germylene adducts of C_{60} . The non-equivalence of the two disyl groups at high temperature, as well as the presence of quaternary aliphatic carbon, suggested that the germylene adduct may be a closed [5,6] adduct: a possible first example of a closed [6,5]-bridged fullerene adduct (Scheme 1-17(a)).

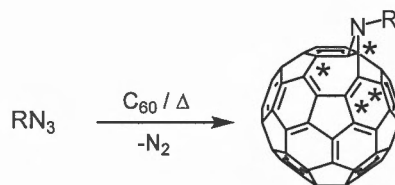


Scheme 1-17

Akasaka also reported that photochemical reactions of C_{60} with siliranes afford adducts of several types as carbosilylated and hydrosilylated C_{60} derivatives. In those, the first example of the crystal structure of a closed 1,2-adduct at the 5,6-ring junction of the C_{60} cage is provided by single-crystal X-ray analysis (Scheme 1-17(b)).

In 1993, Wudl and co-workers reported that the addition of alkyl azides to C_{60} proceeds via intermediate triazoline, which after extrusion of N_2 rearrangement to open 1,6-aza-fulleroid as major monoaddition product (Scheme 1-18).⁸⁷⁾ In order to obtain further information on the structure of azafulleroids, they prepared ^{15}N -labeled alkyl azide and carried out the addition to C_{60} yielding 50% labeling at the azafulleroid nitrogen. The aromatic ^{13}C resonance of azafulleroid at 137 ppm is split by ^{15}N - ^{13}C coupling with $^1J_{CN} = 5.0$ Hz. The methylene resonance at 83 ppm is similarly split ($^1J_{CN} = 7.6$ Hz), which are the resonances of the carbon atoms directly bonded to nitrogen. The two aromatic resonances at 138.43 and 138.32 ppm are broadened and are attributable to the starred 5- and 6-membered-ring carbon atoms (Figure 1-17). These labeling experiments results unambiguously confirmed the open [5,6] structure for

azafulleroid. Although Wudl and co-workers did not assign the structure of intermediate triazoline, later, Hirsch and co-workers confined the X-ray crystal structure of triazoline intermediate (Figure 1-18).⁸⁸⁾ He also showed the thermal decomposition of triazoline to afford a azafulleroid (Scheme 1-19).



R = CH₂OCH₂CH₂SiMe₃, CH₂C₆H₅, CH₂C₆H₄OMe-4, CH₂C₆H₄Br-4

Scheme 1-18

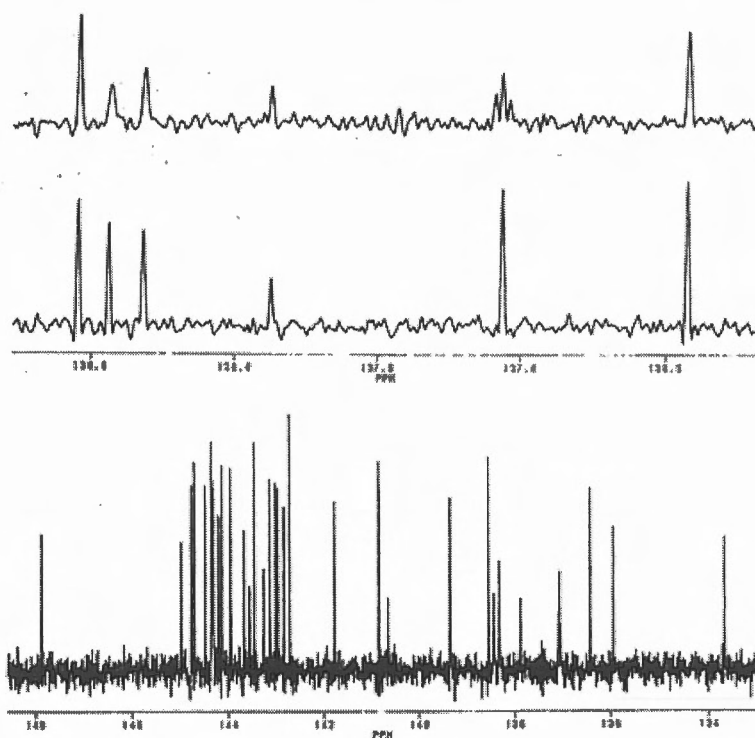
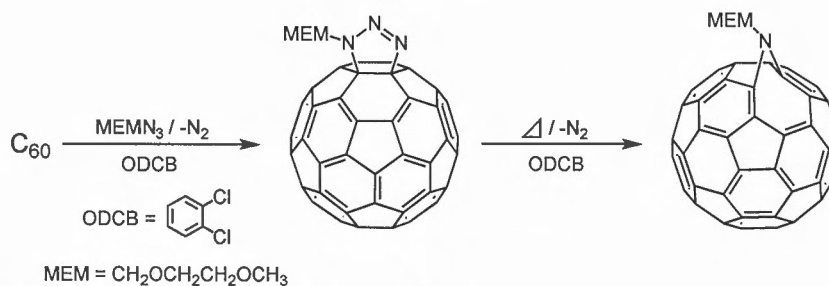


Figure 1-17



Scheme 1-19

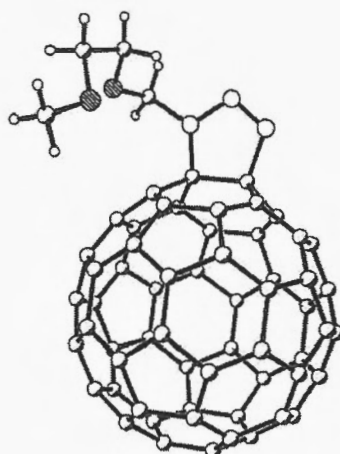
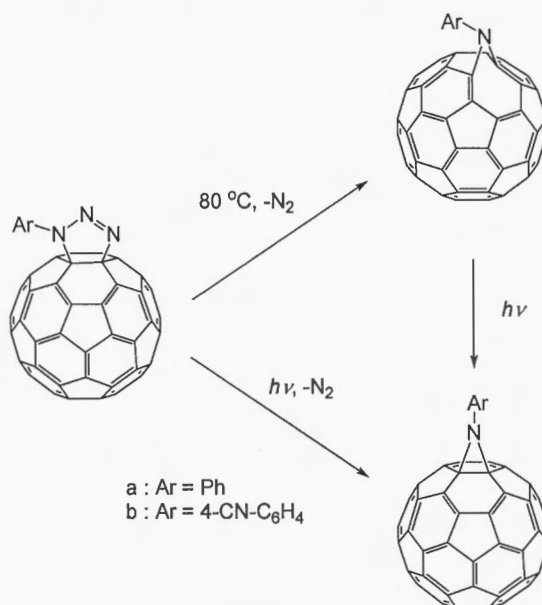


Figure 1-18

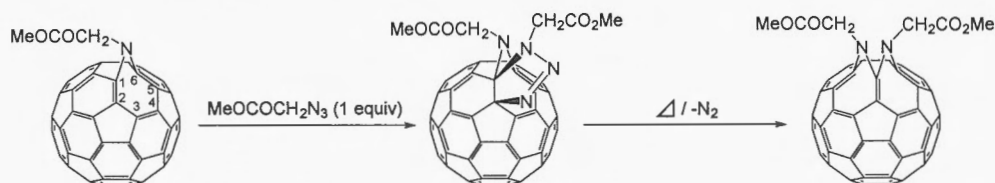
Mattay reported that the reaction of C_{60} with aryl azides leads to isolable triazolinofullerene derivatives. Photolysis of triazolinofullerene selectively yields the aziridinofullerenes. In contrast to the photolysis, the thermolysis affords the azafulleroids as main product. In addition the first photochemically induced rearrangement of azafulleroids (1,6-aza-bridged isomers) to aziridinofullerenes (1,2-aza-bridged isomers) is described (Scheme 1-20).



Scheme 1-20

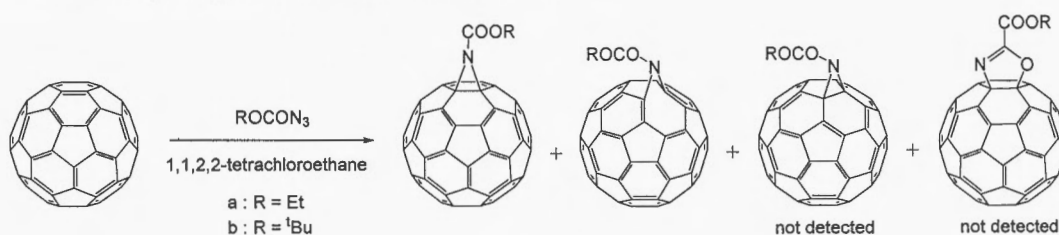
Some reactions of C_{60} with an excess of azide have also been studied. So the reaction with an excess of the azide $\text{MeOCOCH}_2\text{N}_3$ in chlorobenzene at 136°C for 12 h, gives rise to a mixture containing the bisazafulleroid adduct (Scheme 1-21) as the main product (60%) along with the triazoline and aziridine adducts. Triazoline formed by Smith addition of the azide $\text{MeOCOCH}_2\text{N}_3$ to the corresponding azafulleroid give rise to the bisadduct by heating to reflux in toluene and have been proposed as possible intermediates. Bisadduct can be described as a

double azafulleroid with the two nitrogen atoms bonded to the three carbons of two consecutive [5,6] junctions of the same pentagon.



Scheme 1-21

Banks and co-workers claimed that the [5,6] side products obtained by the thermal reaction of the azidoformates N_3CO_2R ($R = Et, ^tBu$ supermesityl) have been assigned as the first examples for closed [5,6] bridged fullerene adducts (Scheme 1-22).^{91,92)}

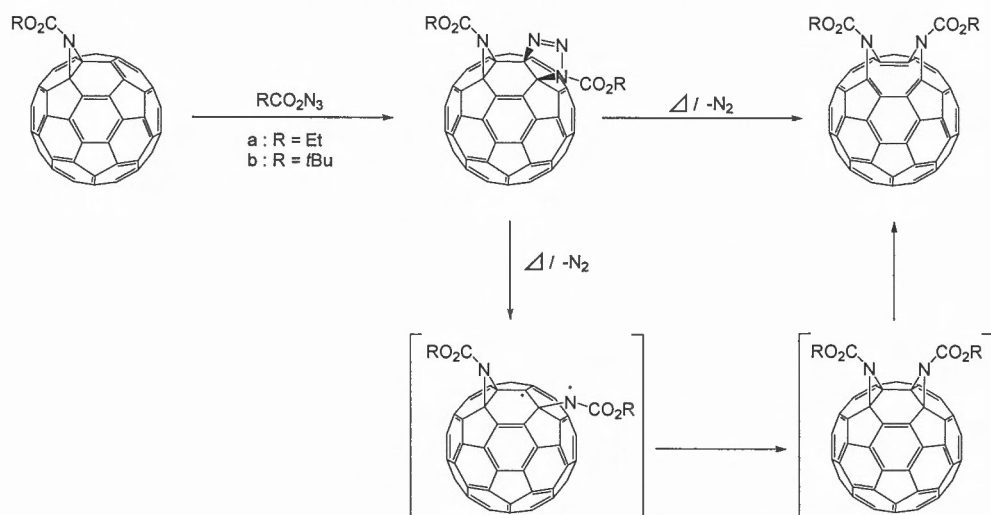


Scheme 1-22

This interpretation was based on the findings that: (i) these compounds are C_s -symmetric (^{13}C NMR); (ii) no 420 nm bands in the UV/Vis spectra characteristic for [6,6] isomers are present and (iii) signals between 80.4 and 83.3 ppm have been observed in ^{13}C NMR spectra, which were attributed to sp^3 carbon atoms of the fullerene core bound to the imino-bridge. With the exception of these signals the reported spectroscopic data are fully consistent with open [5,6] bridged structures. Hirsch and co-workers⁹³⁾ attempted ^{15}N -labeling experiment of Banks's work. The comparison of the ^{13}C NMR spectra of [5,6] NCO_2Et bridged fullerene with those of 100% ^{15}N -labelled one proves unambiguously that the transannular [5,6] bond is open. The $^1J_{C,N}$ coupling of 9.5 Hz at 134 ppm with the sp^2 carbon atoms, C-1 and C'-6 is due to the bridging nitrogen. The doublets at 136 and 134 ppm are caused by $^2J_{C,N}$ couplings with C-2, C-5 and C-7, C-9 respectively (Scheme 1-22). Smith and co-workers also attempted to reproduce Banks's work.⁹⁴⁾ Reaction of ethyl azidoformate (N_3CO_2Et) with C_{60} afforded unreacted C_{60} (40% yield) and three products, the expected [6,6] aziridine (16% yield), oxazoline (17% yield) and the third compound (16% yield), which was the [5,6] annulene rather than the [5,6] aziridine. The 1H NMR spectrum of [5,6] NCO_2Et bridged fullerene was quite similar to that of the [6,6] aziridine. The ^{13}C NMR spectrum contained only a carbonyl resonance, ca. 30 peaks in the sp^2 region, and two sp^3 signals corresponding to the ethyl carbons. Importantly, the reported resonance at 80 ppm was not present, a discrepancy they cannot account for. The reaction of *tert*-butyl azidoformate with C_{60} afforded two products. For [6,6] aziridine the major product (8% yield) as reported, the methyl carbons resonated at 28 ppm. The sp^2 region of the ^{13}C NMR spectrum

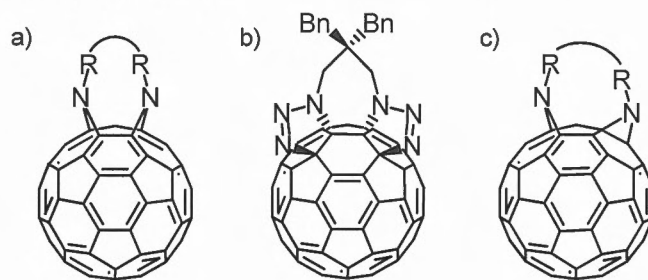
consisted of 15 peaks for the fullerene cage and a carbonyl signal, indicative of C_{2V} symmetry. Two additional singlets at 81 and 84 ppm were assigned to the *tert*-butyl quaternary carbon and the sp^3 carbons of the aziridine ring, respectively. Banks and co-workers reported only one peak, at 83 ppm. A resonance at 30 ppm, assigned by Banks to the *tert*-butyl quaternary carbon, did not appear in their spectrum and apparently should be attributed to an impurity. They also note that the published assignment for this signal is inconsistent with the ^{13}C chemical shifts for several Boc-protected amines. The ^{13}C NMR spectrum of the minor product (2% yield) contained 30 resonances in the sp^2 region, indicative of C_s symmetry, along with sp^3 *tert*-butyl peaks at 18 (CH_3) and 83 (quaternary C). As before, no aziridine carbons were present. In their conclusion, detailed spectroscopic analysis demonstrates that the [5,6] aziridines reportedly formed in nitrene additions to [60] fullerene should be reformulated as the isomeric [5,6] aza-bridged annulenes.

Hirsch et al. isolated another bisadduct which can be described as a double azafulleroid with both nitrogen atoms bonded to four carbons of two alternate [6,6] junctions of a hexagon (Scheme 1-23).^{95,96} These adducts have been prepared regioselectively from the reaction of the aziridine adducts $C_{60}NCO_2R$ ($R = Et, tBu$) with two equivalents of the corresponding azide at $60^\circ C$ in 1-chloronaphthalene and ulterior heating in toluene reflux, and are the major products of the reaction of C_{60} with two equivalents of azide in 1-chloronaphthalene at $60^\circ C$ followed by heating in toluene reflux. On the other hand, the reaction of C_{60} with two equivalents of EtO_2CN_3 in the conditions of formation of the nitrene intermediate gives rise to a mixture of isomers consisting of the bisdiaziridine (21%) and other seven different bisaziridine adducts, all components of which could be separated by HPLC and characterized.

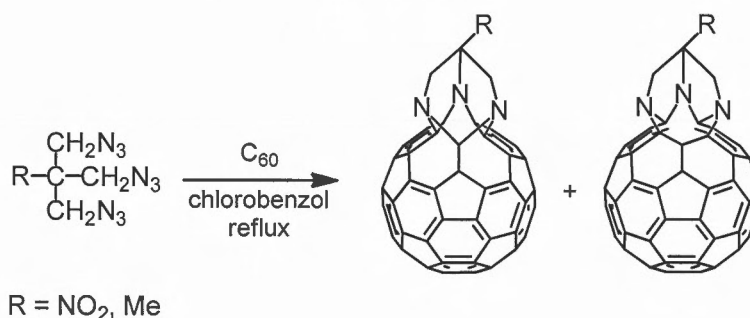


Scheme 1-23

Reactions of C_{60} with diazides have also been studied. So the reaction with $N_3(CH_2)_nN_3$ ($n = 2, 3$) or $N_3C(CO_2Et)_2N_3$ gives a new type of open bisadduct (Scheme 1-24(a)), in which the two nitrogen atoms are bonded to four carbons of alternate [5,6] junctions of a pentagon.^{97,98} A mixture of bisadducts of types (see Scheme 1-23 and Scheme 1-24(a)), together with a bistriazoline adduct of type (see Scheme 1-24(b)), is formed by reaction of C_{60} and 2,2-dibenzyl-1,3-diazopropane in refluxing chlorobenzene for 8 h.⁹⁹ Chiral bisazafulleroids are also formed in the reactions of C_{60} and the C_2 chiral 1,4-*tert*-alkoxy-2,3-bisazidobutanes.¹⁰⁰ Recently the photochemical rearrangement of a new bisazafulleroid of type (see Scheme 1-24(a)) to give an aziridinofullerene of type (see Scheme 1-24(c)) has been shown.¹⁰¹ However, reactions with bisazides tethered by polyglycol or polyglycol diacetate chains give rise to bisazafulleroid of type (see Scheme 1-21).^{102,103} Another two types of trisaza-bridged [60] fullerooids have been synthesized (Scheme 1-25).¹⁰⁴ By means of spectroscopic data, they have been shown to be tris[5,6] opened aza-bridged adducts with substituent on the same five-membered ring with C_s symmetry.



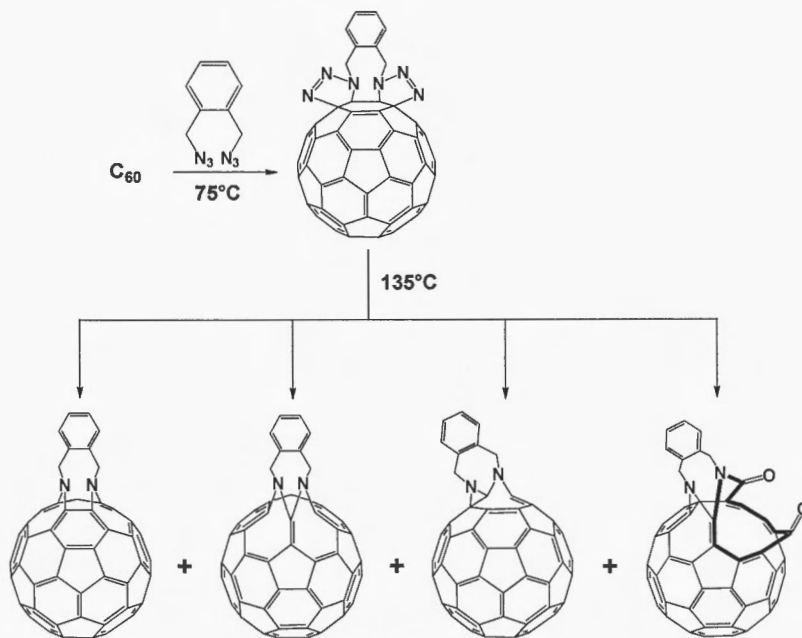
Scheme 1-24



Scheme 1-25

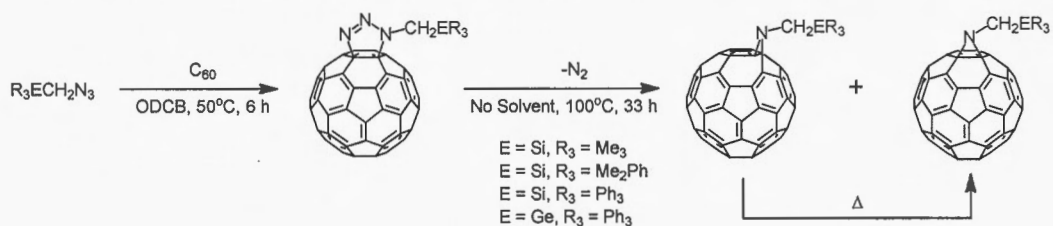
Labile bis-triazoline adducts of C_{60} are supposed to be the precursors of bis-azafulleroids, but the formation mechanism is still unclear because of the incomplete isolation of the thermolized products and the lack of X-ray structures. Finally, Lu et al. reported a rigid-tethered reagent 1,2-bis(azidomethyl)benzene was used to regioselectively synthesize the labile 1,2,3,4-bis(triazolino)[60]-fullerene (Scheme 1-26), the structure of which was determined by single-crystal X-ray crystallography. Further its thermolysis produces four products, which were all characterized by X-ray crystallography. Although two products have traditional

bis-azafulleroid structures, as proposed previously, two remaining products show unprecedented structures with either the coexistence of [5,6]-open and [6,6]-closed patterns or an oxidized structure with an 11-membered ring on the cage.



Scheme 1-26

Hachiya and Kabe reported that addition of silyl and germylmethyl azides to fullerene C_{60} at 50°C through [2+3] cycloaddition led to the formation of the triazoline adducts. Subsequently, heating it at 100°C in the solid state, caused N_2 extrusion producing two different isomers, [5,6]-azafulleroid and [6,6]-aziridinofullerene. The X-ray structures of azafulleroid and aziridinofullerene were firstly confirmed (Scheme 1-27, Figure 1-19). As mentioned below, Akasaka et al. independently reported the X-ray structures of azafulleroid and aziridinofullerene formed by the reaction of sulfilimine with C_{60} (Figure 1-20).¹⁰⁷⁾



Scheme 1-27

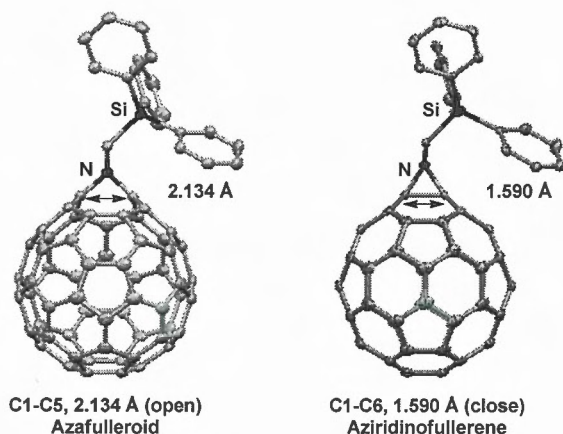
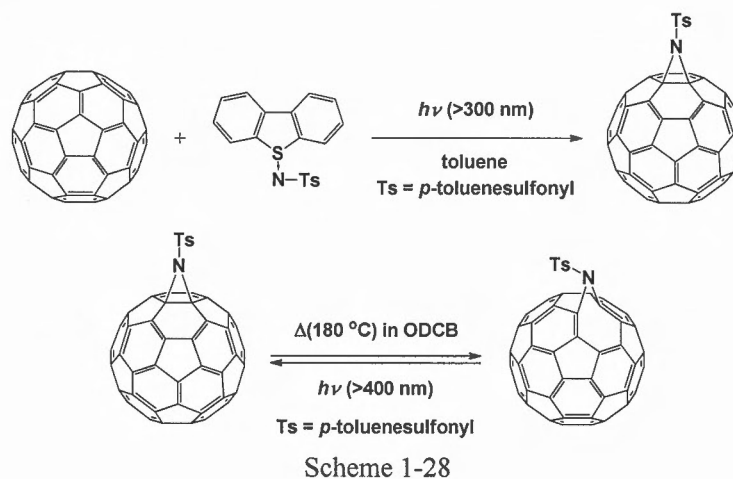


Figure 1-19

Once the valence isomeric preferences of the [5,6] and [6,6] isomers of the methanofullerenes had been established experimentally, the attention turned to the interrelationship between the two isomers. Several groups had reported that the [5,6] open isomer was the kinetic product of the addition of diazo compounds to C_{60} and that, in some cases, it could be isomerized thermally to the [6,6] closed isomer. In contrast, Akasaka et al. reported that in the case of *N*-tolyl substituent ($R = SO_2Tol$) the [6,6] closed isomer thermally rearranged to [5,6] open isomer (Scheme 1-28).¹⁰⁷⁾ Furthermore, by Minakata et al, it is reported two sulfonyl substituted isomers selectively prepared using chloramine-T, phase-transform-catalyst and molecular sieve (Scheme 1-29).¹⁰⁸⁾



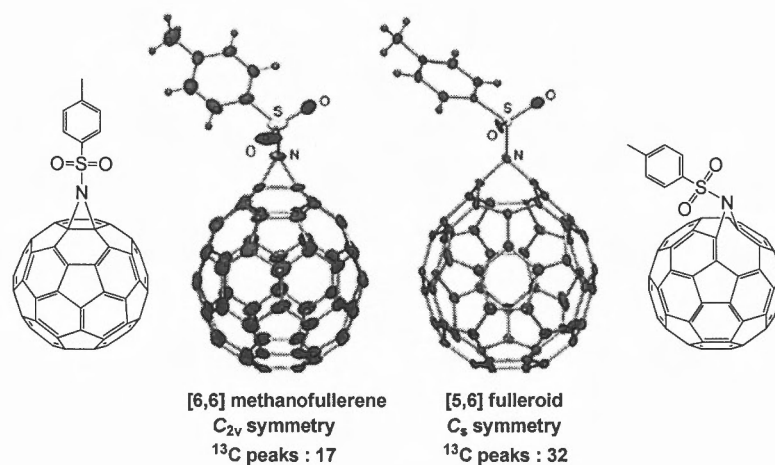
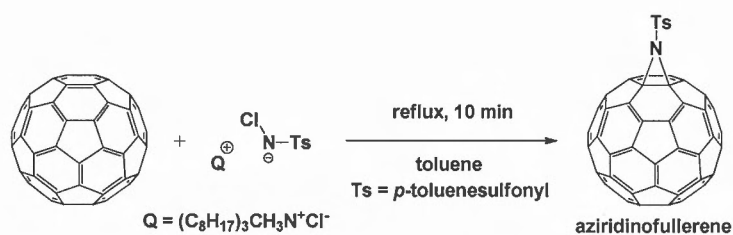
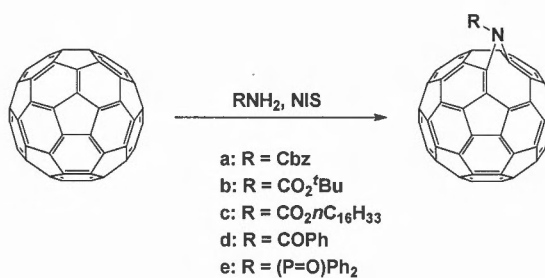


Figure 1-20

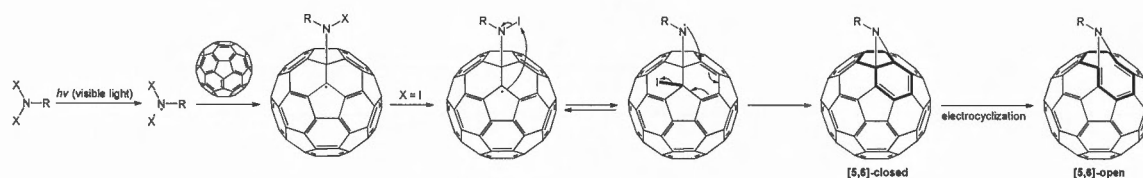
They have also developed highly selective methods for the synthesis of azafulleroids and aziridinofullerenes under mild conditions by using easily handled sulfonamide and *N,N*-dihaloamides as the key chemical species. The reactions tolerated various amide functionalities and allowed isomeric iminofullerenes to be obtained in high yields (Scheme 1-29, 1-30, 1-31).^{109,110)}



Scheme 1-29



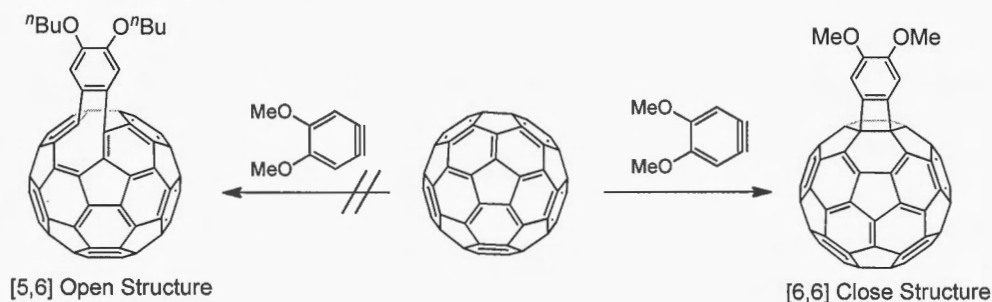
Scheme 1-30



Scheme 1-31

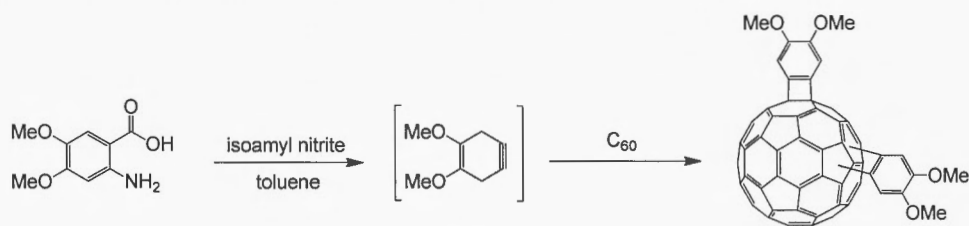
1.2.3 Chemical modification of C₆₀ with Benzyne.

Despite the fact that benzyne typically reacts with polycyclic aromatic compounds by [4+2] cycloaddition, the cycloaddition of benzyne with C₆₀ favorably occurs at 6,6-ring junctions, resulting in a [6,6]-closed adduct in which benzyne adds across one of the interpentagonal bonds (forming a cyclobutene in the process (Scheme 1-32). One reason for this type of reactivity is certainly due to the fact that in a hypothetical [4+2] adduct one unfavorable [5,6]-double bond in the lowest energy valence bond (VB) structure is required. As a result, the synthesis of [5,6]-isomers has hitherto proven to be essentially unobserved.



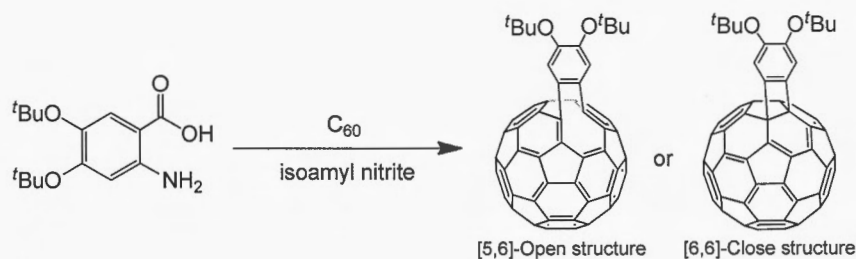
Scheme 1-32

Nishimura et al. reported that the [2+2] cycloaddition between [60]fullerene and benzyne generated from 4,5-dimethoxyanthranilic acid afforded bisadducts along with the monoadduct. All of the eight possible regioisomers were first isolated by HPLC and then characterized on the basis of MS, NMR, UV-vis, and CD spectroscopies. On the basis of the peak area ratio in the GPC chromatogram and in HPLC, the regioisomeric ratio of *trans*-1, *trans*-2, *trans*-3, *trans*-4, *cis*-3, *cis*-2, and *cis*-1 was finally determined as 1:12:15:10:25:3:14:20 (Scheme 1-33).¹¹¹⁾



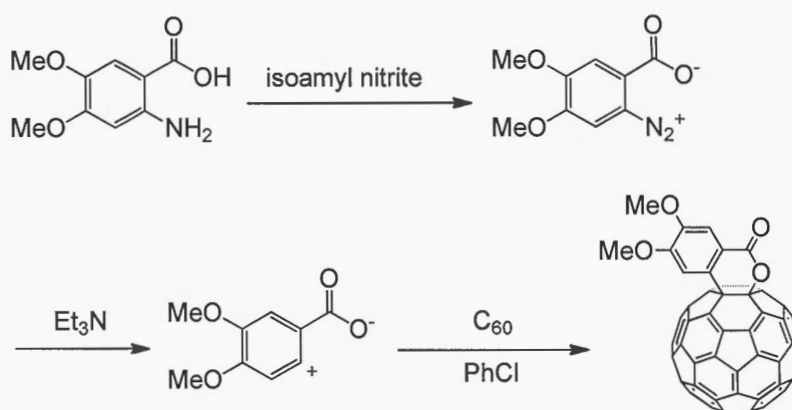
Scheme 1-33

However, Yang et al. reported a reaction of C₆₀ with in situ generated benzyne from 2-amino-4,5-dibutoxybenzoic acid, which affords one monoadduct identified as a [5,6]-open annulene adduct. The structure of [5,6]-open isomer has been characterized by ¹H NMR and ¹³C NMR spectra, which are supported by additional evidence such as UV-vis spectroscopy and electrochemical behavior.¹¹²⁾ Nakamura and Kabe followed their experiment and temporarily assigned the [5,6] closed products (Scheme 1-34).¹¹³⁾



Scheme 1-34

Further surprising were the different products reportedly obtained from same reactants with amine: Wang and coworkers isolated the [6,6] closed adduct via betaine intermediate (Scheme 1-35).¹¹⁴⁾



Scheme 1-35

That is the reaction of [60]fullerene with anthranilic acids and isoamyl nitrite in the presence of triethylamine afforded [60]fullerene-fused δ -lactones, which would be difficult to be prepared by other known methods; The organic base played a key role in the formation of betaines rather than aryne intermediates from the in situ generated unsubstituted and substituted benzenediazonium-2-carboxylates. The reaction of betaines with C₆₀ represents the first example of their cycloaddition to a C=C carbon-carbon unsaturated bond.

1.3 Open-cage and encapsulated fullerene.

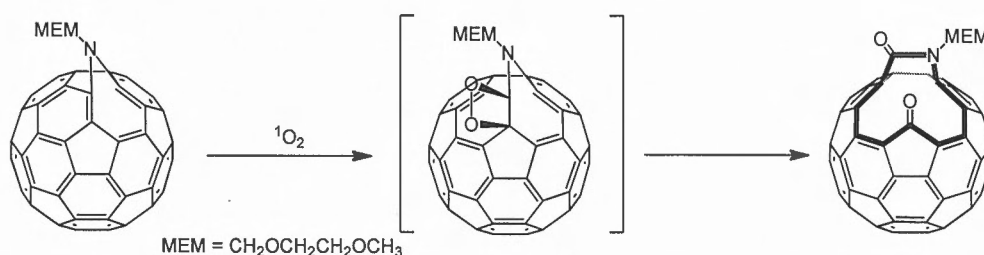
1.3.1 Syntheses of open-cage fullerenes

Endohedral fullerenes, which encapsulate atom(s) or small molecule(s) within the spherical carbon cage, have attracted much attention from viewpoints of not only fundamental curiosity but also applied studies because of their unique electronic structures resulting from the interaction between the fullerene π -system and incorporated species.

Endohedral fullerenes are currently prepared by one of the following physical methods: (a) co-vaporization of carbon and metal atoms in an arc by using graphite rods doped with the metal oxides or carbides; (b) high-pressure/high-temperature treatment of the pure fullerenes with

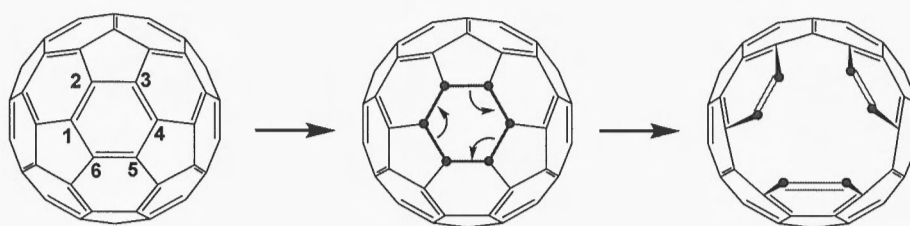
noble gases or nitrogen; (c) by using beams of fast ions or atoms; or (d) by using the recoil energy from nuclear processes to shoot atoms inside the fullerene cage. The above techniques lack efficiency and manageability, as isolation and purification of the endohedral complexes from the produced soot demand exhausting and tedious procedures, and the isolated yields for pure endohedral fullerenes are up to only 1%. A totally different pathway to endohedral fullerenes uses organic reactions that initially provoke σ - and π -bond scission on the fullerene framework, and finally reform the cleaved bonds to afford the intact fullerene i.e. so-called “molecular surgery” approach.

Rubin proposed this a concept to realize endohedral fullerenes with the use of organic reactions, that is, “molecular surgery”.^{115,116} This approach consist of a series of steps, which are (1) “incision” of the fullerene cage to form an opening on the surface, (2) insertion of some small atom(s) or molecular(s) through the opening, and (3) “suture” of the opening to reproduce the fullerene cage while retaining the guest species. Wudl and co-workers has succeeded, developing the first controlled opening of the fullerene cage (Scheme 1-36). They accomplished this using simple reagents. C_{60} was first treated with an organic azide to yield an azafulleroid, in which one carbon-carbon bond has been cleaved and replaced with a nitrogen bridge. The C=C bonds adjacent to this nitrogen atom are much more reactive than other C=C bonds of C_{60} . Taking advantage of this, Wudl and co-workers used a reaction with singlet oxygen to cleave one of these activated C=C bonds, producing an 11-membered ketolactam a fullerene with a hole. It was isolated in pure form in about 70% yield (Scheme 1-36). They gave their JACS paper an unusual title “There Is a Hole in My Bucky”. The reaction probably proceeds in a [2+2] addition mode via the dioxetane derivative, which could not be isolated. Wudl and co-worker reported, for the first time, two-step reactions to create an 11-membered ring opening on the C_{60} cage to give compound. Unfortunately, however, the opening was found to be not large enough even for the smallest atom, helium, to pass through.



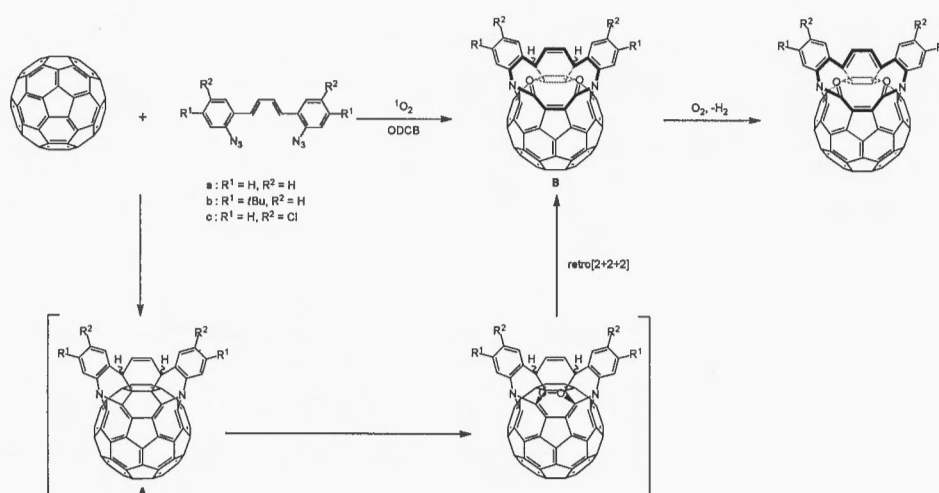
Scheme 1-36

Rubin proposed a strategy toward “incising” a fullerene cage through saturation of three adjacent C=C double bonds within one hexagonal ring. The subsequent [2+2+2] cycloreversion of the planarized cyclohexane ring was expected to give a fullerene derivative with such a large opening as a 15-membered ring (Scheme 1-37).



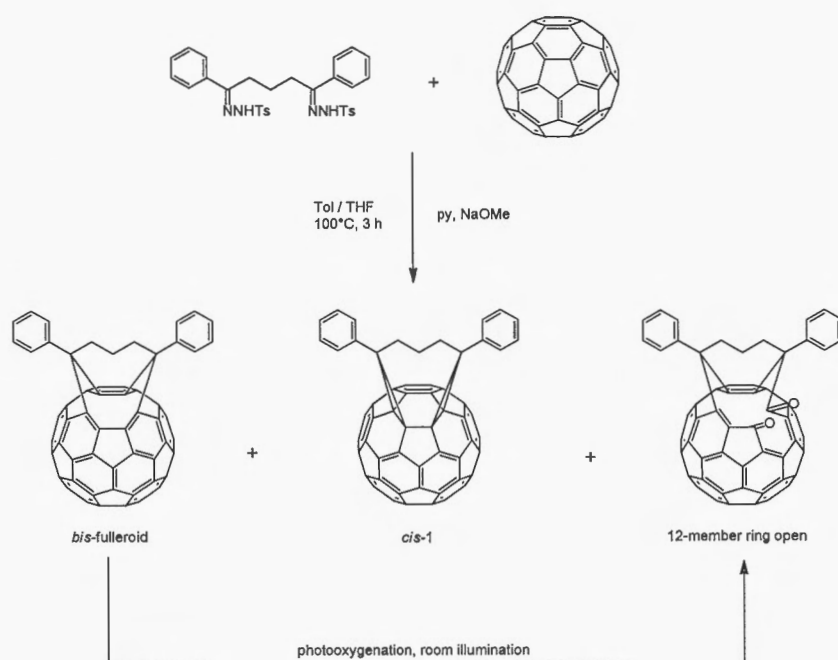
Scheme 1-37

Rubin and co-workers firstly succeeded in the formation of a large orifice in the C_{60} core. A thermal reaction of C_{60} with butadiene derivatives having two azide groups was conducted (Scheme 1-38).¹¹⁸⁾ This reaction was intended to proceed via initial addition of butadiene (involving both a [4+2] cycloaddition and two 1,3-dipolar additions) to form bisfulleroid A. However, the obtained product was instead bislactam B having a 14-membered ring opening produced through a series of reactions involving rearrangements, extrusion of two N_2 molecules, and addition of an O_2 molecular followed by dehydrogenation. The synthesis of bislactam B is of considerable significance because the size of the opening was proved to be large enough for the first time for insertion of the smallest gaseous species such as a 3He atom or a H_2 molecular.



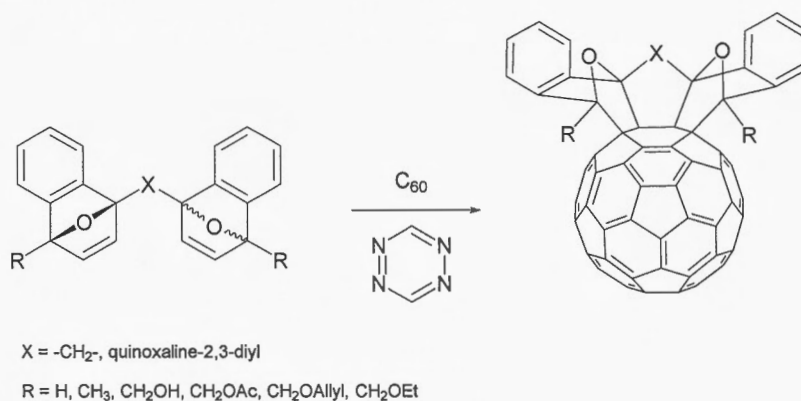
Scheme 1-38

Recently Olmstead, Wudl and Echegoyen reported that new double addition products of both C_{60} and C_{70} have been prepared with both additions occurring within one six-membered ring of the fullerene through the use of 1,3-dibenzoylpropane bis-p-toluenesulfonyl hydrazone as the addend precursor. When the addition occurs at two [6,6] ring junctions within a hexagon, bisadducts with mirror symmetry have been obtained for C_{60} (Scheme 1-39).¹¹⁹⁾ When the addition occurs at two [5,6] ring junctions of C_{60} , a symmetrical bisfulleroid is formed. This adduct readily undergoes photo-oxygenation and ring opening to yield a fullerene with a 12-membered hole in the cage.



Scheme 1-39

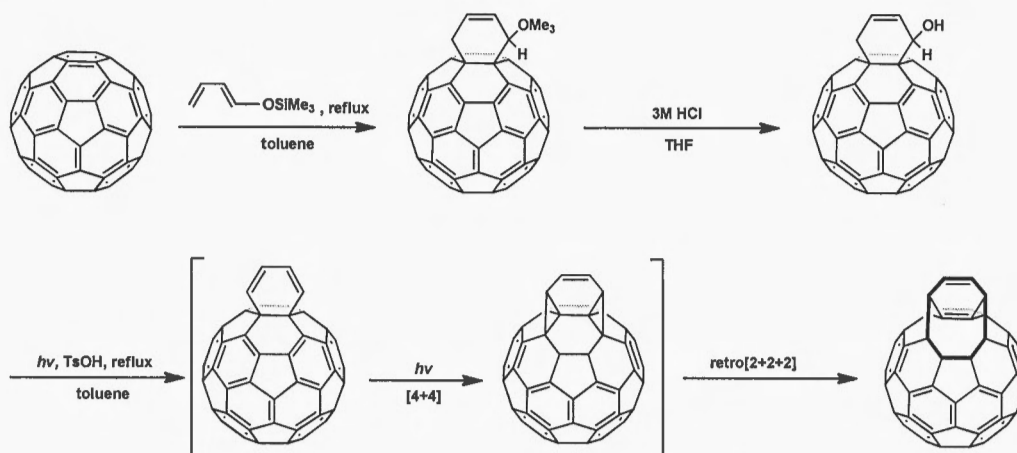
In a quest to form wider openings within the cage of the fullerene C_{60} through controlled bond-breaking reactions, Rubin continued to examine the double saturation of adjacent C=C bonds within a six-membered ring of C_{60} . He investigated the double Diels–Alder cycloaddition of two tethered isobenzofurans to the fullerene C_{60} . Rubin continued to examine in order to afford *cis*-1 adducts in good yields. However triple saturation of adjacent C=C bonds within a six-membered ring was not succeeded so far (Scheme 1-40).^{120,121)}



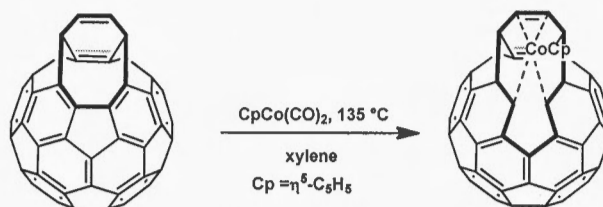
Scheme 1-40

Rubin and co-workers have discovered a versatile method leading to a bisfulleroid which is looked upon as an open-cage fullerene with an 8-membered ring orifice (Scheme 1-41). They demonstrated that when a 1,3-cyclohexadiene moiety is fused to C_{60} , a photochemical intramolecular [4+4] cycloaddition followed by a retro [2+2+2] reaction can cause the formation of an 8-membered ring orifice on the C_{60} cage.¹²²⁾ Rubin and co-workers developed a

straightforward synthesis bypassing the need to isolate the oxygen-sensitive diene. Addition of a 2-fold excess of 1-((trimethylsilyl)oxy)-1,3-butadiene to C_{60} (toluene, reflux) afforded the silyl ether which was usually not isolated. Acidic aqueous workup furnished the allylic alcohol in up to gram quantities, which was simply purified by filtration through a pad of silica gel with toluene. Photolysis (sunlamp) under reflux and acidic conditions (TsOH) afforded good yields of the bisfulleroid (Scheme 1-41). The 8-membered ring formed by the ethylene bridge, the two methano bridgeheads, and the 1,2,3,4-diene moiety of bisfulleroid strongly resembles the COD ligand (COD = 1,5-cyclooctadiene) in its geometry. Thus, the reaction of bisfulleroid with $CpCo(CO)_2$ successfully afforded a new stable complex (Scheme 1-42). The crystal structure of complex showed that the ethylene bridge has indeed acted as an effective η^2 -handle to the metal (Figure 1-21). The C-C bond within the five-membered ring adjacent to the bis-methano[12]annulene ring of bisfulleroid has been broken by oxidative insertion of the cobalt. Thus, cobalt atom was ideally located above a 15-membered ring orifice, but the insertion of this metal atom into C_{60} cage through the orifice was not possible even by application of such high pressure as 40,000 atm in a solid state.



Scheme 1-41



Scheme 1-42

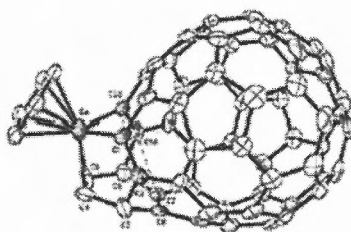
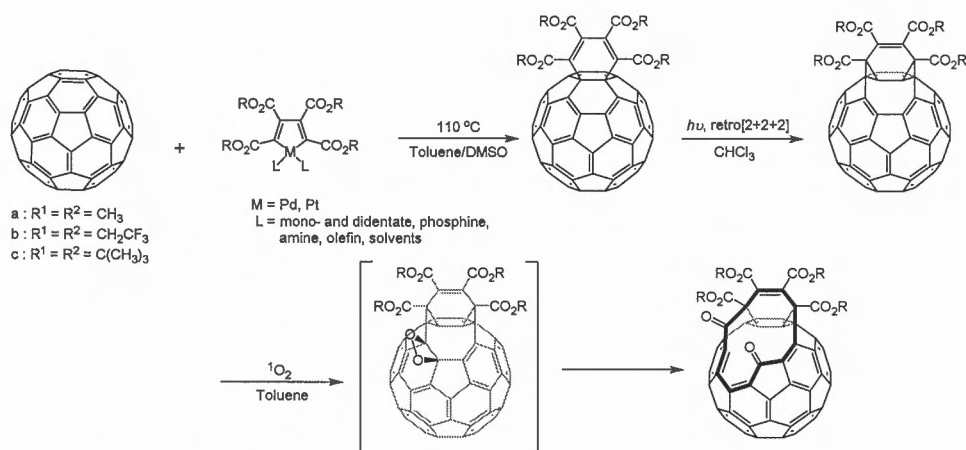


Figure 1-21

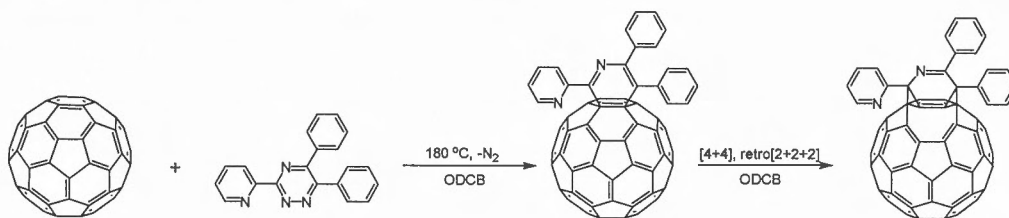
Iwamatsu and co-workers reported another reaction pathway of bisfulleroid and open-cage fullerene, metallacyclopentadiene ($M = \text{Pd}, \text{Pt}$; $L = \text{mono- and didentate, phosphine, amine, olefin}$; solvents, $R = \text{CH}_3, \text{CH}_2\text{CF}_3, \text{C}(\text{CH}_3)_3$), which are prepared from Pd and Pt complex of dibenzylidenacetone (dba), reacted with C_{60} in toluene at 110°C to give butadiene fullerenes as exclusive products in high to moderate yields. The photorearrangement of tubatylene fullerenes easily occurred to give bisfulleroid in almost quantitative yields (98% and 95%, respectively), when solutions of butadiene fullerenes in a toluene or chloroform were irradiated with a room lamp (30 W fluorescent lamp) at 25°C for 10 h.¹²³⁾ Since bisfulleroid derivative has the same 60π structure as C_{60} , bisfulleroid is a good agent for generation of $^1\text{O}_2$ like C_{60} . Indeed, irradiation of chloroform or toluene solutions of bisfulleroid with white visible light in the presence of atmospheric oxygen at 30°C afforded open-cage fullerene in 95% yield (Scheme 1-43). The opening of diketone was greatly enlarged as reported by Iwamatsu and co-workers.¹²⁴⁾



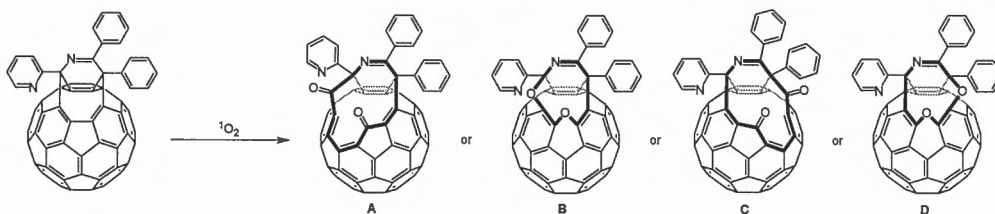
Scheme 1-43

The open-cage fullerene with a large ring opening is quite attractive as novel host molecule. However, from viewpoint of “molecule surgery operation” these compound have a definite drawback that the restoration of such a severely ruptured π -system to the original structure of C_{60} seems almost impossible by means of organic synthetic procedure. Komatsu and co-workers attempted the reaction of C_{60} with 4,6-dimethyl-1,2,3-triazine at 180°C , and obtained a C_{60} derivative with an 8-membered ring opening, which was further enlarged to a 12-membered ring

by photochemical oxidation.¹²⁵⁾ However, because of the low yield (7%) and extreme instability of the first obtained product, they decided to search for a better reaction. Komatsu and co-workers next examined a reaction of C_{60} with 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine in the hope of introducing a nitrogen atom at the rim of the hole, which was expected to be advantageous for further functionalization of the product. In addition, the aromatic substituents are favorable for enhancement of the solubility of the C_{60} derivatives to be formed. When an equimolar mixture of C_{60} and the 1,2,4-triazine was heated at 180°C in ODCB, there was obtained the expected bisfulleroid in 50% yield together with unchanged C_{60} recovered in 41% (Scheme 1-44).¹²⁵⁾ The mechanism for this reaction is considered to be essentially the same as that for the formation of bisfulleroid in Scheme 1-41, that is, by (i) [4+2] cycloaddition of C_{60} with the 3,6-positions of the triazine, (ii) extrusion of nitrogen molecular, (iii) intramolecular formal [4+4] reaction, and (iv) retro [2+2+2] reaction. In addition to the full spectroscopic data, the structure of bisfulleroid was unambiguously determined by X-ray crystallography, which is noticed that the bridge-head double bond on the rim of the orifice is considerably twisted with a dihedral angle being 39°. These facts imply the high reactivity of these double bonds at the rim, which is advantageous for the further ring enlargement reaction as will be expected. Actually the enlargement of an 8-membered ring hole on C_{60} in bisfulleroid by air-oxidation under irradiation of visible light proceeded smoothly to give four isomers of ring opened diketones A, B, C and D in good total yield (Scheme 1-45).¹²⁵⁾ The isomer A is energetically most stable, which was isolated by column chromatography.¹²⁵⁾



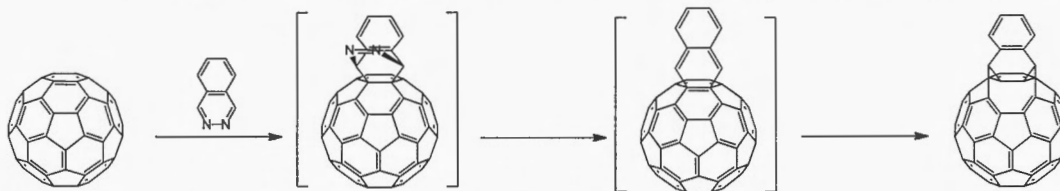
Scheme 1-44



Scheme 1-45

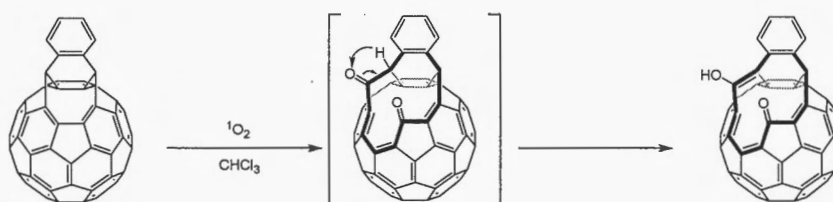
The reaction of C_{60} with phthalazine, i.e., 2,3-diazanaphthalene gave an open-cage benzofullerene derivative when the starting materials were heated at 255°C in a solution in 1-chloronaphthalene.¹²⁶⁾ These reactions are considered to proceed by the first [4+2] reaction between the starting materials and the following nitrogen extrusion to give orthoquinodimethane

intermediates. The highly reactive butadiene unit of orthoquinodimethane structure undergoes the intramolecular formal [4+4] reaction with the fullerene diene system to give bisfulleroid via the retro [2+2+2] reaction of the second intermediate in the liquid phase reaction (Scheme 1-46).



Scheme 1-46

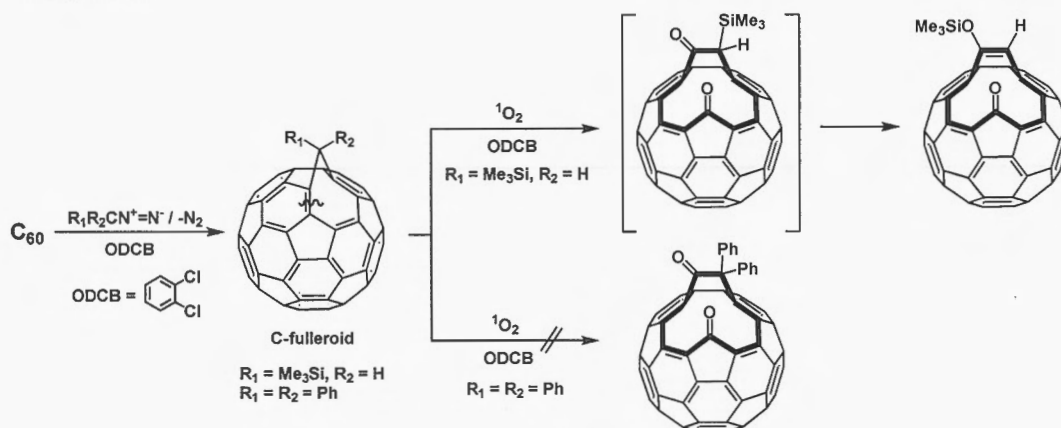
The reaction of this bisfulleroid with oxygen was conducted in a solution of air-saturated benzene under irradiation of room light at room temperature for 3 days. The product, which was more polar than the starting material, was isolated in 32% yield as a brown powder by column chromatography over silica gel. The molecular formula of this product was determined as $C_{68}H_6O_2$ by high-resolution mass spectroscopy, indicating that the product was formed by addition of O_2 to the bisfulleroid. The structure of this product was shown to be not keto-form but enol-form as described below. The 1H NMR exhibited four multiplets at δ 8.01, 7.94, 7.86, and 7.74 and two singlets at δ 6.98 and 6.79. The singlet at δ 6.98 disappeared upon addition of D_2O demonstrating that the product has an acidic proton. The ^{13}C NMR spectrum displayed one signal corresponding to a carbonyl carbon at δ 193.67, one signal corresponding to an sp^3 carbon at 47.82 and 66 signals corresponding to sp^2 carbons at δ 148.67–120.20, indicating that the product has the C_1 symmetry. The IR spectrum showed a strong band at 1706 cm^{-1} corresponding to a carbonyl group and a weak band at 3379 cm^{-1} corresponding to a hydroxy group. These spectra are in good agreement with the structure of enol-form (Scheme 1-47).¹²⁷⁾



Scheme 1-47

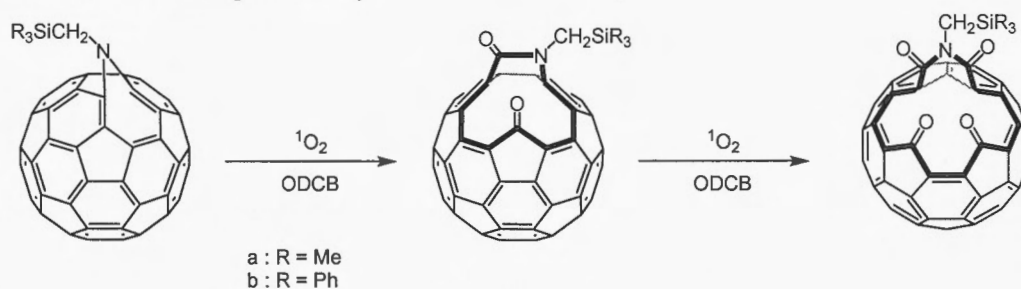
Hachiya and Kabe reported the first study dealing with the self photooxygenation of silyl fulleroids quite recently.¹²⁸⁾ Specifically, the addition of silyl substituted diazomethanes to C_{60} proceeds in a diastereoselective fashion to give silyl fulleroids, with the silyl groups located above a five-membered ring (Scheme 1-48). Self photooxygenation of silyl fulleroid was carried out in CS_2 at $-60\text{ }^\circ\text{C}$ affording the silyl enol ether derivatives, after 1,3-silyl migration of the intermediate diketone derivatives (Scheme 1-48). The latter is formed after a [2+2] cycloaddition of silyl fulleroid with 1O_2 , followed by ring opening of the resulting dioxetane. In contrast, it was also reported that the C-fulleroid with diphenyl substituent did not undergo 1O_2

oxygenation.



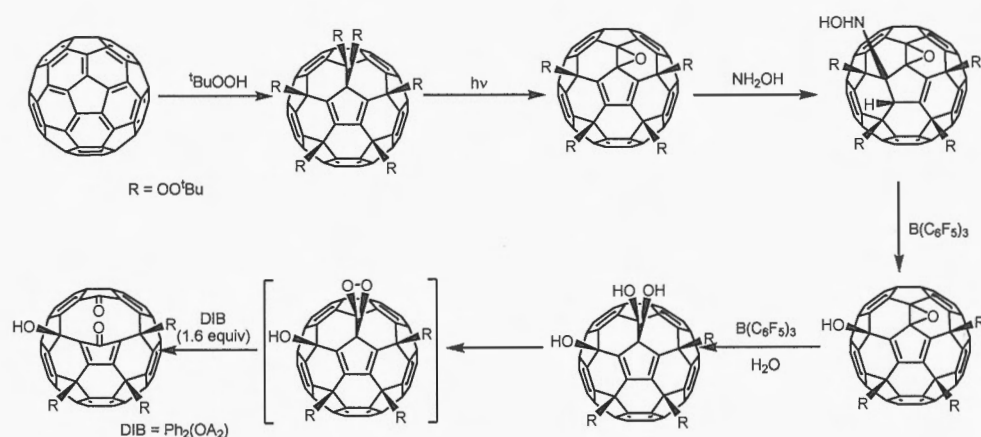
Scheme 1-48

Quite recently, Kabe and Hachiya reported the double photooxygenation of azafulleroids for the first time. Specifically, silyl-modified azafulleroids were oxidized to diketo imides, upon prolonged irradiation in the presence of oxygen (Scheme 1-49).¹²⁹⁾ A stepwise addition of 1O_2 to azafulleroid took place, affording ketolactam bearing an 11-membered ring orifice as the major product, along with diketo imide containing a 15-membered ring opening. The structures of both open-cage fullerenes were assigned on the basis of its 1H and ^{13}C NMR spectra, as well as via MALDI-TOF mass spectrometry.



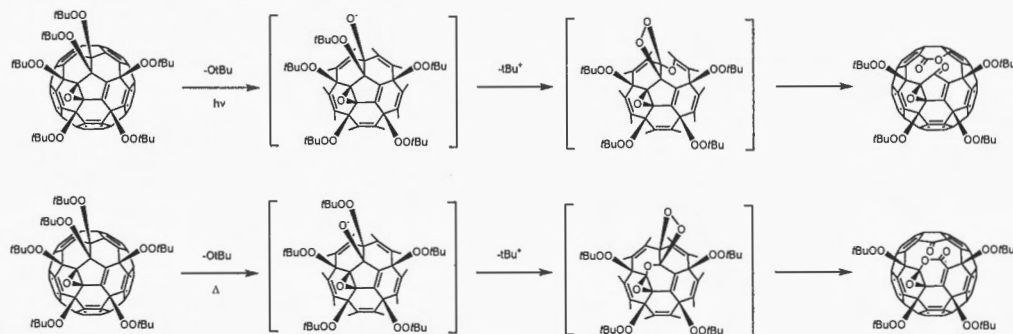
Scheme 1-49

Gan, Zhang and co-workers have reported the synthesis of fullerene mixed peroxides, derived from the addition of *tert*-butyl peroxy radicals to C_{60} . Subsequent studies on the reactivity of these oxygen-rich compounds revealed that they can be transformed into open-cage derivatives. The *tert*-butyl peroxy groups directly attached to the fullerene skeleton serve as excellent oxygen sources for the formation of hydroxyl and carbonyl groups. Open-cage diketone derivative was synthesized from intermediate of fullerene mixed peroxide following a four-step route shown in Scheme 1-50. The epoxy ring is hydrolysed in the presence of $B(C_6F_5)_3$ to the vicinal fullerendiols, and, subsequently, vicinal diol is oxidized by (diacetoxy)iodobenzene $PhI(OAc)_2$ (DIB) to form the expected fullerendione in good yield. Later on, a series of similar DIB-induced oxidation reactions of alike fullerendiols resulted in the formation of a family of open-cage diketone derivatives.¹³⁰⁾



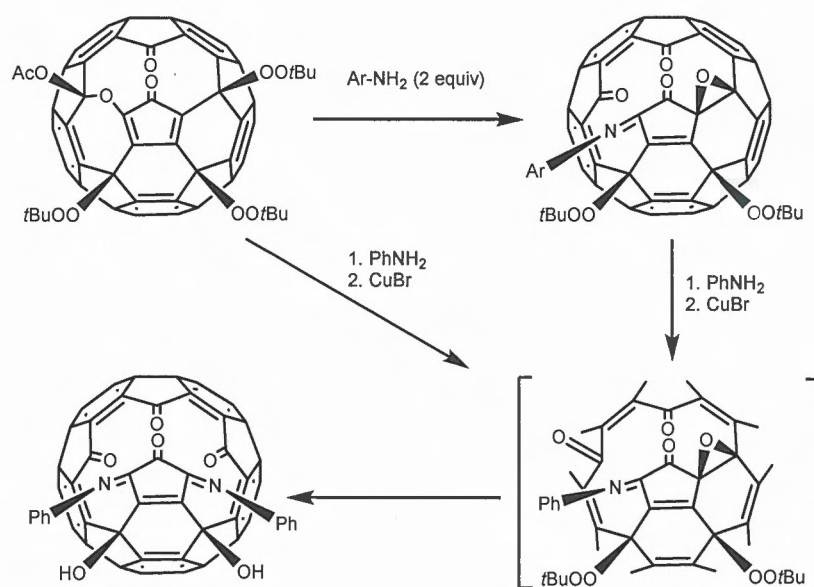
Scheme 1-50

Gan and co-workers reported that cage-opened compound was isolated as the major product after visible light irradiation of the hexa-adduct (Scheme 1-51). The proposed mechanism for this reaction is shown in Scheme 1-51. Homolytic cleavage of the O–O peroxo bond on the central pentagon with sequential loss of a *tert*-butoxy radical from hexa-adduct forms an epoxide on the same pentagon. Next, homolytic cleavage of a C–O bond gives dioxetane intermediate. Ring opening of the dioxetane moiety of intermediate results in the final open-cage product.¹³¹⁾ This rearrangement is analogous to that for the formation of the *N*-MEMketolactam from intermediate reported by Wudl shown in Scheme 1-36. The reactivity of hexa-adduct^{132,133)} was examined under thermal conditions as well. Heating a solution in chlorobenzene at 100 °C promotes homolysis of the O–O bond on the central pentagon, eventually providing the same open-cage fullerene as final products.



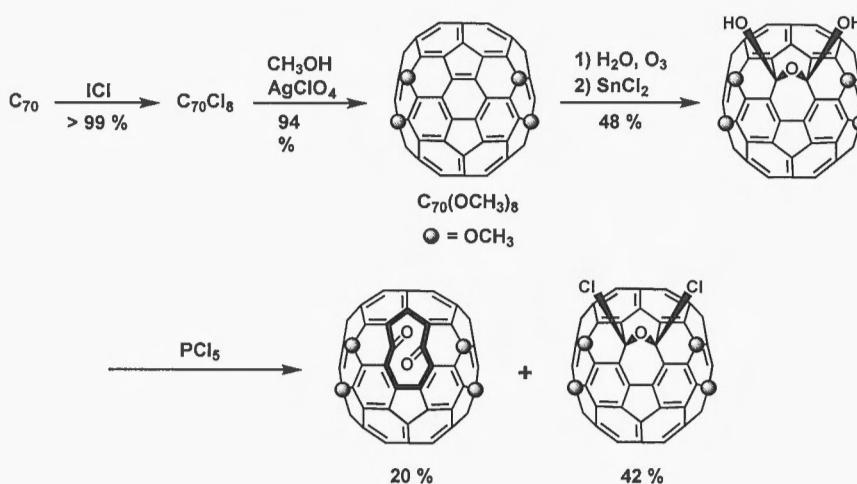
Scheme 1-51

Later on, diketone derivative was reacted with anilines (ArNH₂) to form open-cage adducts (Scheme 1-52).¹³⁴⁾ In the latter, all three *tert*-butoxyl groups are removed, whereas, in the former, one of the *tert*-butylperoxo groups remains. This group can be efficiently reduced to the hydroxyl group with CuBr. The structure of compounds was unambiguously elucidated by single-crystal X-ray analysis. It possesses an 18-membered-ring orifice where the central pentagon is completely lifted up from the cage surface. The opening is wide enough to allow water penetration (see next section).



Scheme 1-52

The unique double bond at the equatorial 5,6-junction in C₇₀X₈ (X=Cl, CF₃) was the most reactive double bond for certain reactions. In 2017, to cleave this double bond and open a small orifice of C₇₀X₈ (X = Cl, CF₃), Gan et al. prepared the vicinal diol derivative by treating C₇₀(OCH₃)₈ with *m*CPBA to form compound with an epoxy moiety, followed by hydrolysis in the presence of B(C₆F₅)₃ (Scheme 1-53). Unlike analogous reactions with C₆₀ diol derivatives, oxidation of the vicinal diol moiety with PhI(OOCF₃)₂ led to compound with diketone moiety. The expected diketone product could not be detected following this procedure. Except oxidation reaction with ¹O₂ and diol oxidation with B(C₆F₅)₃, Gan et al. tested other oxidation conditions to make open-cage compounds from C₇₀(OCH₃)₈. The classical oxidants KMnO₄, Pb(OAc)₄, and HIO₄ did not give any isolable product. However, ozonation of C₇₀(OCH₃)₈ followed by reduction with SnCl₂ gave compound with bishemiacetal moiety in improved yield (Scheme 1-53).¹³⁵⁾ Dehydration of bishemiacetal with PCl₅ eventually led to formation of the diketone. The diketone could be converted into bishemiacetal even in the CDCl₃ solution with trace amounts of water for NMR spectroscopy upon standing for a few days at RT. The dichloro derivative was also formed through an apparent S_N1 replacement process.

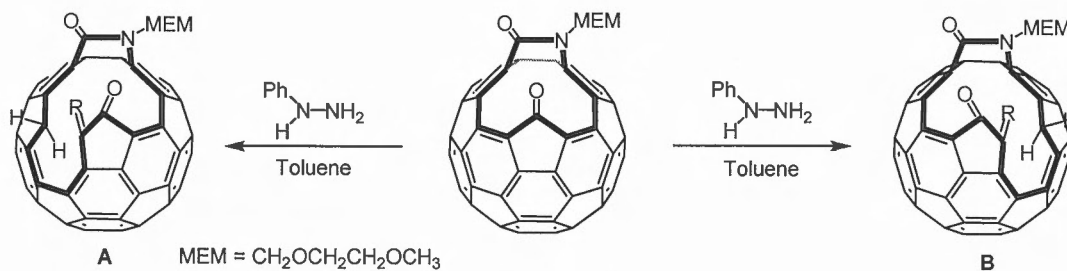


Scheme 1-53

1.3.2 Reaction of open-cage fullerene.

A cage scission via hydroamination reaction, that is the migrative addition reaction between *N*-MEM-ketolactam and phenylhydrazines (Scheme 1-54), was reported.¹³⁶⁾ In this work, Iwamatsu and co-workers proposed open-cage fullerenes (A), bearing a 15-membered-ring orifice on the fullerene framework, as the cage enlargement products. In a more detailed study published one year later, concerning the same hydroamination reaction, Orfanopoulos and coworkers synthesized and characterized open-cage adducts (B) (Scheme 1-54), pointing out that the assumed structural assignment by Iwamatsu and co-workers is incorrect. Their structural assignment was based on the results of 1H NMR, ^{13}C NMR, and nuclear Overhauser effect (NOE) difference experiments as well as MS, FT-IR, and UV-vis spectroscopy. In this regard, Orfanopoulos and coworkers found that the ketone ^{13}C NMR absorption is upfield shifted from 198.5 ppm in starting material to around δ 188 ppm in adducts (B), while the lactam ^{13}C chemical shift change is insignificant. This change in the ketone carbonyl environment was also confirmed by IR spectroscopy, with the $C=O$ absorption shifting from 1727 cm^{-1} to near 1670 cm^{-1} . The shift of the lactam carbonyl position is again insignificant. As inferred from these observations, the bond scission to provide the products (A or B) occurs at one of the two double bonds, (left and right), next to the ketone group, shown in Scheme 1-54. Subsequently, by combining NOE enhancement measurements with theoretical calculations, Orfanopoulos and coworkers concluded that double bond was the one that had been cleaved and, therefore, arrived at the structures (B) presented in Scheme 1-54.¹³⁷⁾ Although the assignment of both carbon atoms C_a and C_b (Figure 1-22) is quite difficult even in starting material, comparison between ^{13}C - 1H coupled and selectively decoupled ^{13}C spectra (by irradiating one proton at a time) of structure (B) also leads to the conclusion that double bond (right) is the one that reacts. In particular, the carbon atom which absorbs at 138.51 ppm (C_a) is coupled both with protons H_a and H_b and with H_c and H_d (Figure 1-23). Taking into account that coupling between a carbon

atom and a proton can be observed only for carbon atoms that are no more than three bonds away from a specific proton, the proposed structures (B) are the only ones possible. If this were not the case and reaction had occurred at double bond (left), the H_a and H_b protons would have been four bonds away from carbon C_b and no coupling between them would have been observed.



Scheme 1-54

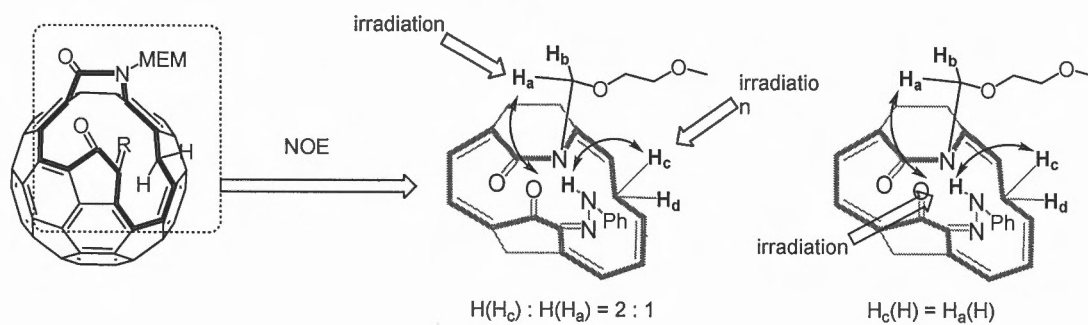
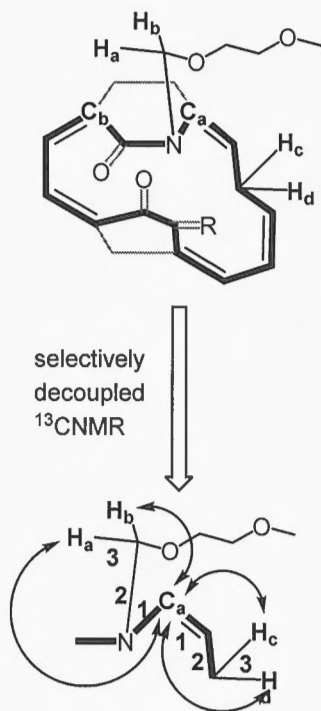


Figure 1-22

Structure of Orfanopoulos (B)



Structure of Murata (A)

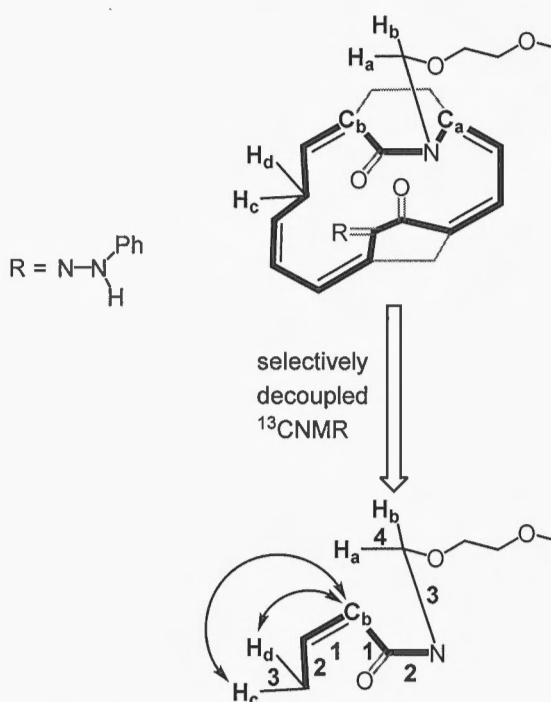
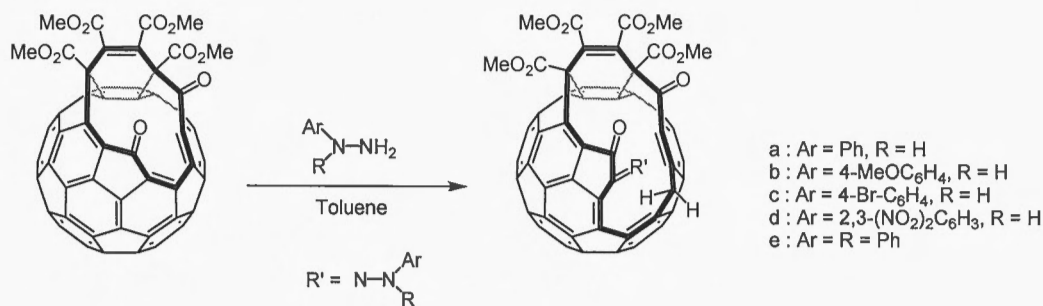


Figure 1-23

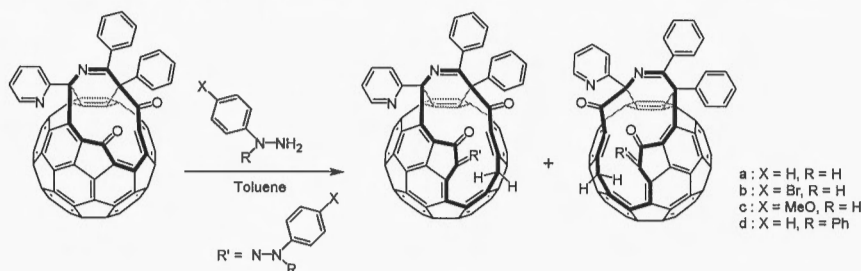
A regioselective addition reaction between the α,β -unsaturated carbonyl structure of the open-cage fullerene adduct and aromatic hydrazines (Scheme 1-55) was reported by Iwamatsu and Murata in 2003.^{138,139} The reaction proceeds with migration of two hydrogen atoms from the hydrazine to the fullerene framework, affording open-cage adducts in 50–89% yield. The enlarged open-cage fullerenes, bearing a methylene carbon along their orifice, contain a 16-membered-ring opening.



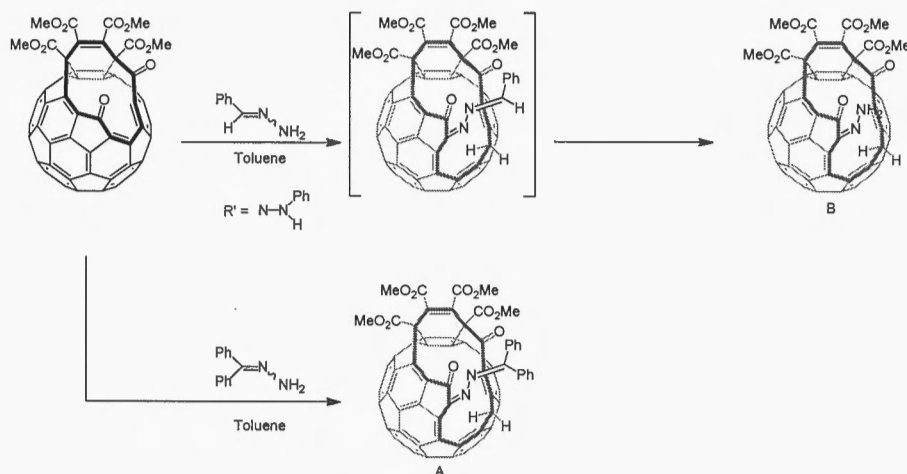
Scheme 1-55

More recently, Murata and Komatsu reported that isomeric diketone open-cage derivatives (Scheme 1-56) were also found to be reactive towards aromatic hydrazines and hydrazones.¹⁴⁰ This derivative possess the characteristic α,β -unsaturated carbonyl structure along their rim; therefore, expansion of the 12-membered ring orifice to a 16-membered one was realized in the

same manner as discussed above. Cage-opened fullerene adducts were isolated in moderate to excellent yields. Besides the previously mentioned reaction with aromatic hydrazines (Scheme 1-55), the orifice on the fullerene framework of open-cage diketone derivative was also regioselectively enlarged by its reaction with aromatic hydrazones (Scheme 1-57).¹⁴¹⁾ In this fashion, fullerene adducts A and B were obtained in 44% and 57% yield respectively. The formation of adduct B was proposed to proceed upon hydrolysis of the intermediate.

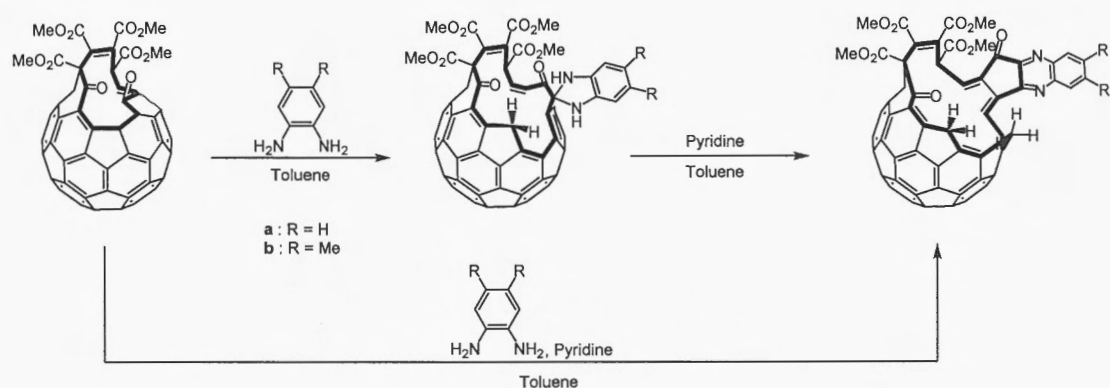


Scheme 1-56

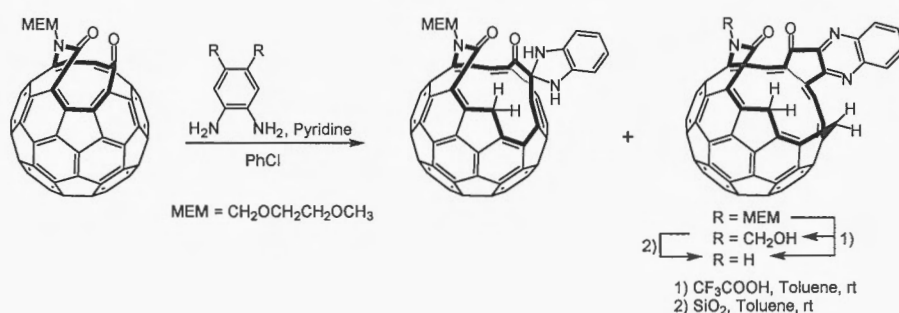


Scheme 1-57

In 2004, Iwamatsu et al. reported another reaction sequence that led to fullerene adducts bearing 19- and 20-membered-ring orifices, the largest openings constructed thus far on the fullerene framework.¹⁴²⁾ Specifically, the bowl-shaped fullerene adducts (Scheme 1-58) were prepared by regioselective, sequential cage-scission reactions of the open-cage fullerene adduct with 1,2-phenylenediamine and 4,5-dimethyl-1,2-phenylenediamine, in the presence of pyridine. Fullerene adducts have a 20-membered-ring orifice on the fullerene shell and were prepared in 52 and 60% yield respectively. When the same reactions were carried out at room temperature in the absence of pyridine, open-cage adducts (Scheme 1-58), containing a 16-membered-ring orifice on the fullerene shell, were obtained in high yield (85% and 74%, respectively). Quite similarly, open-cage adducts (Scheme 1-59) were prepared by regioselective, sequential carbon-carbon bond scissions via its reaction with phenylene diamine.¹⁴³⁾ The MEM group in was subsequently removed, by treatment with trifluoroacetic acid.

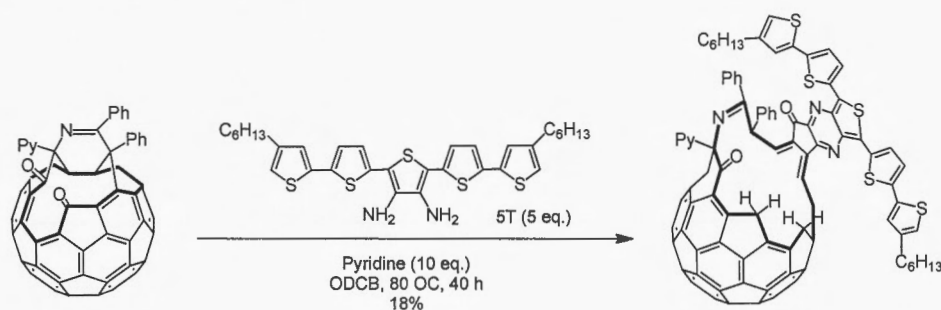


Scheme 1-58



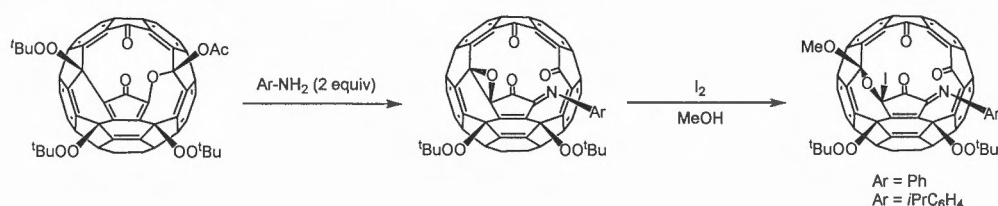
Scheme 1-59

Iwamatsu et al. reported the synthesis of 20-membered ring open-cage fullerenes through a novel ring-enlargement reaction between skeleton-modified fullerenes and orthosubstituted aromatic diamines. Inspired by this work, Ding et al. designed two ortho-diamino-containing oligothiophene chromophores 3T and 5T (Scheme 1-60).¹⁴⁴ 3T and 5T were prepared through straightforward methods including Stille coupling, reduction, and bromination reactions with 2,5-dibromo-3,4-dinitrothiophene as the starting material. The skeleton-modified fullerene was pre-prepared according to Murata's open-cage process. Treatment of it with 3T (or 5T) and pyridine at 80 °C afforded the expected orifice-enlarged product, OC₆₀-3T, in 50% yield (18% yield for OC₆₀-5T). Through this reaction, the systems of oligothiophene and fullerene are completely fused to each other by a conjugated pyrazine bridge.

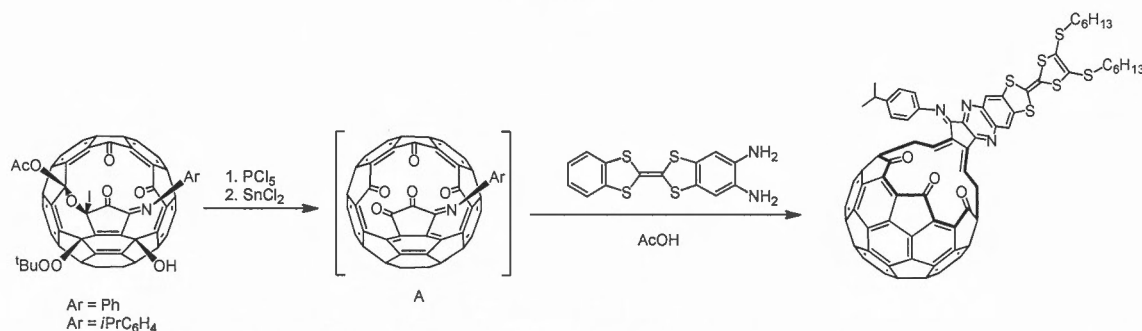


Scheme 1-60

Gan also reported the synthesis of π -extended open-cage fullerene derivatives with donor chromophores such as TTF connected through a similar quinoxaline junction.¹⁴⁵⁾ Open-cage compounds were prepared as they have previously reported. To remove the two *tert*-butyl peroxy groups in compounds, they were reduced with cuprous bromide (Scheme 1-61 and Scheme 1-62). Sequential treatment with PCl_5 and SnCl_2 resulted in formation of compound **A** through reductive aromatization and opening of the iodo acetal moiety. It was not possible to purify the intermediate product of the PCl_5 reaction and compound **A**. The crude product **A** was used directly to react with the *o*-diaminoaromatic compounds. Monoadducts were obtained for the bulky *o*-diaminoaromatic compounds.



Scheme 1-61

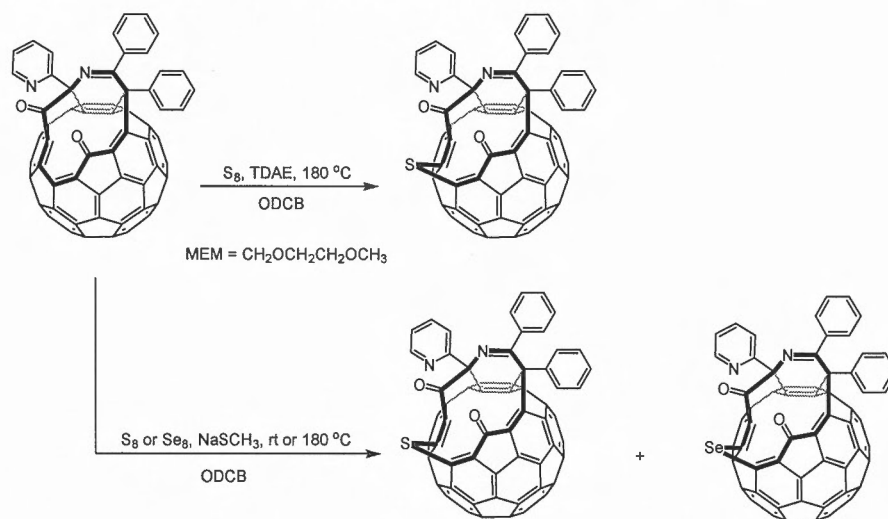


Scheme 1-62

A sulfur atom insertion at the rim of the orifice of an open-cage fullerene derivative, which is an approach based on the fact that sulfur atoms can be inserted into activated carbon-carbon single bonds, was reported for the first time by Komatsu and co-workers in 2003.¹²⁸⁾ Thus, heating of open-cage fullerene, which has a 12-membered-ring orifice on the fullerene framework, together with S_8 in the presence of tetrakis(dimethylamino)ethylene (TDAE) afforded product (Scheme 1-63), bearing an enlarged 13-membered-ring orifice, in 77% yield. TDAE was proposed either to activate open-cage fullerene by an electron transfer or to lead to an intermediate complex that renders the electrophilic addition of elemental sulfur to more feasible. The sulfur atom insertion at the rim of the orifice of open-cage fullerene makes the cage opening rather circular, as shown by its single-crystal X-ray structure, increasing the possibility for the encapsulation of small molecules or atoms in the interior of the fullerene cage (*vide infra*).

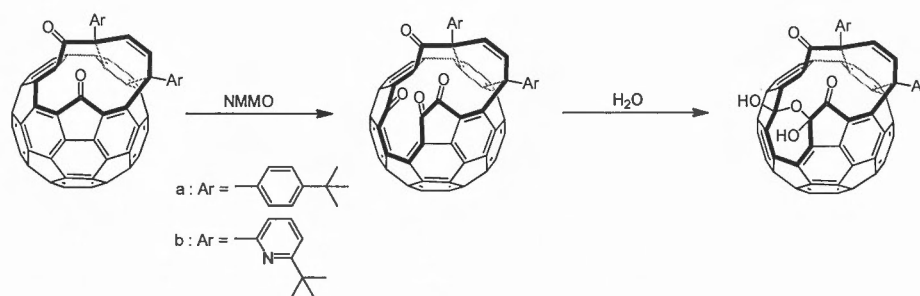
An alternative synthetic route to cage-opened derivative was later on proposed by the same

research group. When open-cage fullerene was stirred with elemental sulfur at ambient temperature, in the presence of 2.2 equivalents of sodium methylthiolate as a reducing agent, the same product was readily formed in 80% yield (Scheme 1-63). The latter method was also successfully applied for the insertion of a selenium atom at the rim of the aperture. Thus, heating a mixture of open-cage fullerene and elemental selenium in the presence of sodium methylthiolate in ODCB, resulted in the formation of open-cage fullerene.

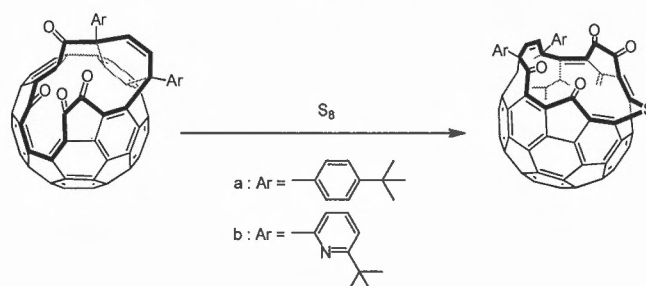


Scheme 1-63

Murata et al. reported that applying their previous synthetic route, diketones were synthesized in 29 and 43% isolated yields, respectively, from the reaction of C₆₀ with pyridazine derivatives followed by photochemical cleavage of one of the C=C double bonds on the rim of the opening on intermediates (Scheme 1-64). *N*-Methylmorpholine *N*-oxide (NMMO) is known as a nucleophilic oxidant, and they found that the reaction of open-cage fullerenes with 2.3 equivalents of NMMO in wet tetrahydrofuran (THF) at room temperature led to the synthesis of bishemiketals (Scheme 1-64), respectively, in good yields after purification with silica gel chromatography.¹⁴⁶⁾ The structure of it determined by single crystal X-ray analysis shows that the opening is constructed by the 13-membered ring containing two hemiacetal carbons, in addition to two carbonyl carbons. This molecule can be considered as the hydrate of tetraketone having the 16-membered-ring opening with four carbonyl carbons. Because wet THF was used in this reaction, a water molecule attacked one of the carbonyl carbons. When the hydrate was heated at reflux temperature in toluene for 30 min, complete transformation of bishemiketal was observed and a new species, probably tetraketone, was detected with high-performance liquid chromatography (HPLC) (Buckyprep, toluene) analysis. However, because this compound quickly went back to hydrate at room temperature, characterization of tetraketone was not achieved yet.



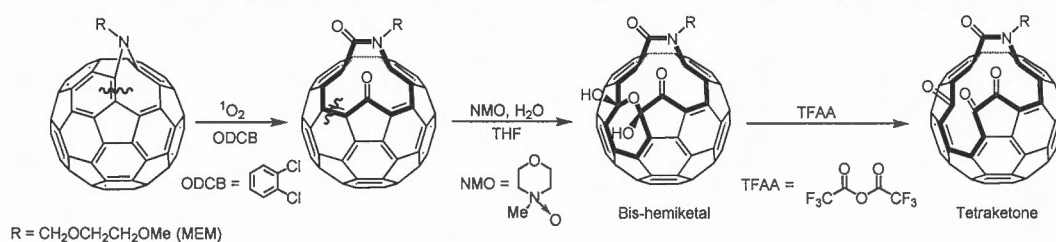
Scheme 1-64



Scheme 1-65

Similar to Scheme 1-63, the reaction of tetraketone with elemental sulfur in the presence of TDAE afforded novel open-cage C_{60} derivatives (Scheme 1-65).¹⁴⁷⁾ The structures of it was determined by single crystal X-ray analyses which showed the encapsulation of a water molecule inside the fullerenes.

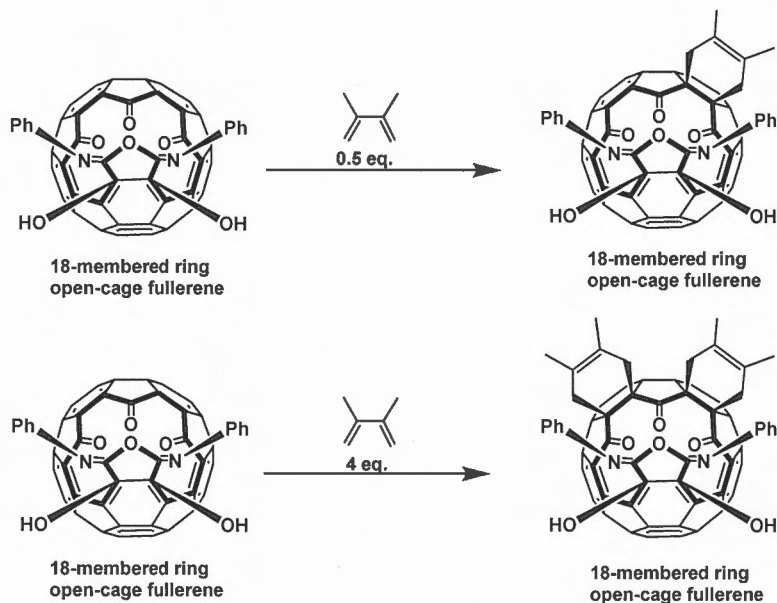
This reaction was applied to MEM-ketolactam open-cage fullerenes by the same researchers (Scheme 1-66).¹⁴⁸⁾ They synthesized a novel open-cage fullerene derivative having a 12-membered ring opening as well as a 15-membered ring opening. With regard to 12-membered ring opening, the structure was clearly determined by X-ray analysis.



Scheme 1-66

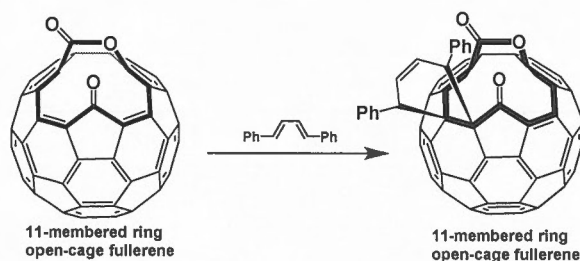
Gan et al. firstly reported the Diels-Alder reaction of open-cage fullerene with 1,3-butadienes.¹⁴⁹⁾ Addition of a large excess of 2,3-dimethylbutadiene resulted in a complex mixture of multi-addition products. Mono adduct could be obtained in good yield by using only 0.5 equiv. of the diene. To form the bis adduct selectively, they added 4 equiv. of 2,3-dimethylbutadiene and followed the progress of the reaction by TLC (Scheme 1-67). Mono adduct could be detected as intermediate. Other products with three or more diene addends were obtained upon prolonging the reaction time. The DA reaction of open-cage fullerene is quite sensitive to steric

and electronic factors, as for reactions of classical organic compounds. The bulky 1,4-diphenylbitadiene gave only mono adduct even though an excess amount of the diene (50 equiv.) and a higher temperature (100 °C) were used.



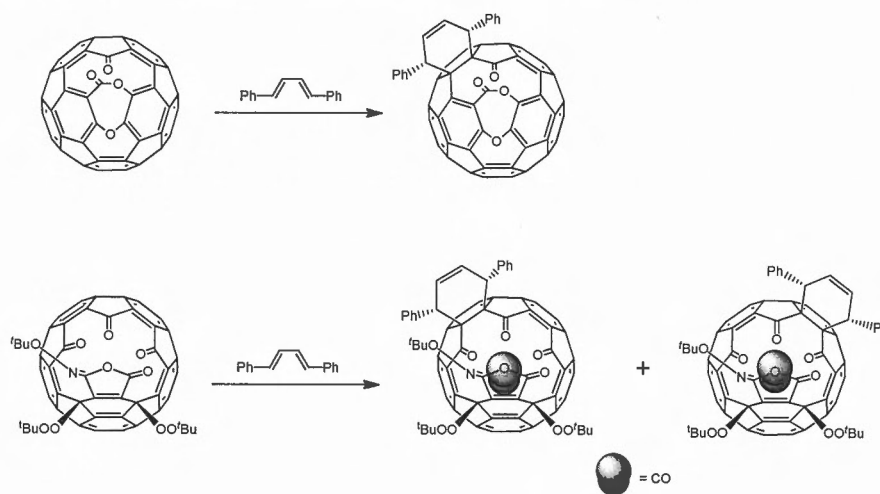
Scheme 1-67

Furthermore, Gan et al. synthesized keto-lactone open-cage fullerenes (Scheme 1-68).¹⁵⁰⁾ Locations of the keto and lactone moieties in the compound are analogous to the first open-cage derivative reported by Wudl et al. in which the keto and lactam forms an 11-membered orifice. To test the effect of the carbonyl groups on the fullerene cage, they treated it with 1,4-diphenylbutadiene to obtain the Diels-Alder adduct (Scheme 1-68). Regioselectivity of the addition is in good agreement with the electron-withdrawing effect of the carbonyl groups. The keto and lactone carbonyl carbons of the adduct appear at 196.9 and 162.0 ppm, respectively, both of which are slightly shifted downfield compared to the starting compounds. The carbonyl stretching bands of the adduct on the IR spectrum appear at 1784 and 1727 cm^{-1} , which are smaller than those of the starting compound. Single crystal X-ray diffraction structure of adduct was obtained in which the fullerene-fused cyclohexene adopts a boat conformation with the two phenyl groups in the equatorial positions.



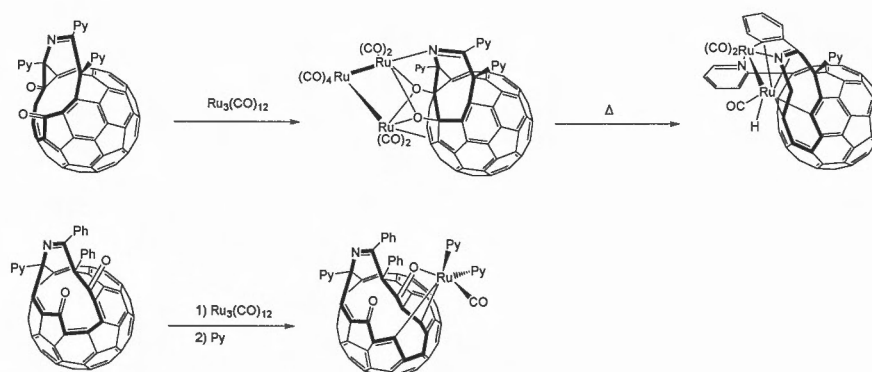
Scheme 1-68

They also converted another open-cage compound into the Diels–Alder derivative (Scheme 1-69).¹⁵¹⁾ The reaction was almost quantitative based on converted starting material. The excellent regioselectivity should be due to the strong electron-withdrawing effects of the ketone and lactone carbonyl groups. The *endo* isomer was obtained exclusively as in most Diels–Alder reactions. The X-ray diffraction analysis confirmed the structure proposed above. The open-cage fullerenes with a CO molecule trapped in the cavity was isolated. Spectroscopic data of it are in agreement with the CO-trapped structure. Conclusive structural assignment of it came from the single-crystal X-ray diffraction structure of its Diels–Alder derivative (Scheme 1-69).¹⁵²⁾ Two regioisomers were obtained from the addition of 1,4-diphenyl butadiene to it. Steric hindrance favors the less crowded product keto-lactone open-cage fullerenes.



Scheme 1-69

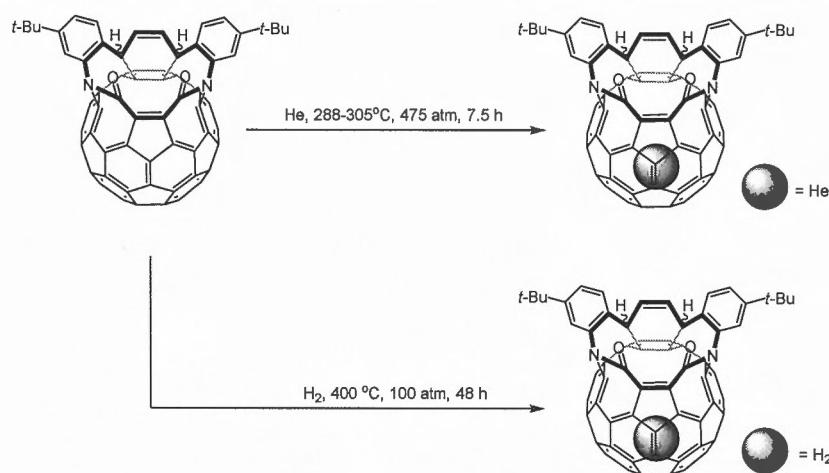
Yeh et al. reported that solid-state pyrolysis of Murata and Komatsu's open-cage fullerenes at 350 °C produces the diruthenium complex $\text{HRu}_2(\text{CO})_3(\mu, \eta^7\text{-C}_{63}\text{N}(\text{Py})(\text{Ph})(\text{C}_6\text{H}_4))$, with one Ru atom being inserted into the fullerene cage to generate an 11-membered ring. On the other hand, the reaction of isomeric open-cage fullerenes and $\text{Ru}_3(\text{CO})_{12}$ in refluxing chlorobenzene, following by extraction with pyridine, produces the mononuclear complex $\text{Ru}(\text{CO})(\text{Py})_2(\eta^3\text{-C}_{63}\text{NO}_2(\text{Py})(\text{Ph})_2)$, and the orifice becomes a 15-membered ring (Scheme 1-70).^{153,154)} It is important to notice that the orifice of isomeric Ru-complex traverses 6.60 Å, which is close to the diameter of C_{60} (7.1 Å).



Scheme 1-70

1.3.3 Syntheses of encapsulated fullerenes.

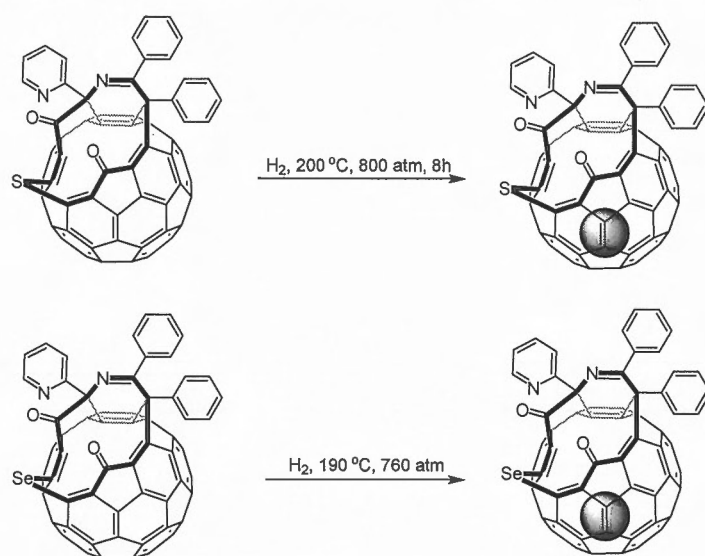
There are several review articles concerning to open-cage fullerenes and encapsulated fullerenes so far.^{115,116,155-158)} The first successful gas encapsulation into an open-cage fullerene derivative was reported in 2001 by Rubin et al.¹⁵⁹⁾ In that work, helium and molecular hydrogen were inserted into the fullerene bislactam derivative (Scheme 1-71), though in very low incorporation fraction. By treating a crystalline powder of derived from bisazide open-cage fullerene with 475 atm of ^3He gas at 288-305 °C for 7.5 h, a ^3He atom was incorporated at an occupation level of 1.5%. A H_2 molecular was also introduced at an occupation level of 5% under the conditions of 100 atm of H_2 gas at 400 °C for 48 h. A highly shielded ^1H NMR signal for the encapsulated H_2 was observed as -5.43 ppm. Unfortunately, since the content of He and H_2 was very low, the information obtained for these endohedral fullerene derivatives is quite limited.



Scheme 1-71

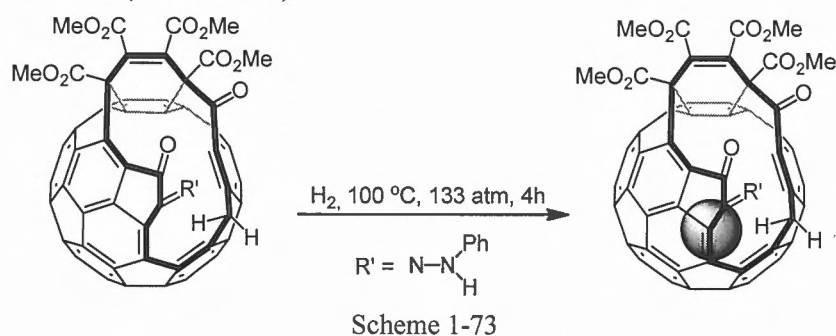
Two years later, Komatsu and co-workers reported their success in incorporating a H_2 molecule into thio-aza open-cage fullerene derivative (Scheme 1-72) that bears a 13-membered-ring orifice on the fullerene framework, at a 100% encapsulation ratio.^{160,161)} Note that thio-aza

open-cage fullerene has an orifice of 5.64 and 3.75 Å along the long and the short axis respectively. According to theoretical calculations at the B3LYP/3-21G level of theory using the 6-31G** basis set, the energies required for He and H₂ insertion into Rubin's open-cage fullerenes (Scheme 1-71) were predicted to be 24.5 and 41.4 kcal mol⁻¹ respectively, whereas the corresponding calculated encapsulation energies for thio-aza open-cage fullerene are 18.9 and 30.1 kcal mol⁻¹, respectively. The encapsulation of H₂ gas into thio-aza open-cage fullerene was accomplished in an autoclave at an applied H₂ pressure of 800 atm, upon 8 hours of heating at 200 °C, while hydrogen encapsulation, affording H₂-encapsulated fullerene (Scheme 1-72), was confirmed by its ¹H NMR spectrum, where encapsulated hydrogen appears at δ -7.25 ppm as a single peak. Moreover, the encapsulation rate was found to be highly dependent on the applied H₂ pressure, affording 90 and 51% incorporation yields under 560 and 180 atm respectively. A single crystal of H₂-encapsulated fullerene was also studied by X-ray diffraction with synchrotron radiation. As inferred from that study, the environment of the encapsulated H₂, which is found to be located at the center of the fullerene cage, is similar to that of the H₂ molecule incorporated in H₂ in H₂@C₆₀ mentioned later and, furthermore, there is no appreciable charge transfer between the encapsulated H₂ and the cage. Selenium bearing cage-opened adduct (Scheme 1-72), possesses an opening slightly larger than that of thio-aza open-cage fullerene. This fact permitted 100% encapsulation of molecular hydrogen inside under milder conditions than those reported for thio-aza open-cage fullerene, *i.e.*, under a pressure of 760 atm and at a temperature of 190 °C. The molecular H₂ that is incorporated in selenium analogue resonates as a single peak at δ -7.10 ppm in the ¹H NMR spectrum of the complex. More interestingly, the rate for hydrogen release was calculated and found to be nearly three times faster than its sulfur analogue, as expected from the orifice-size enlargement.



Scheme 1-72

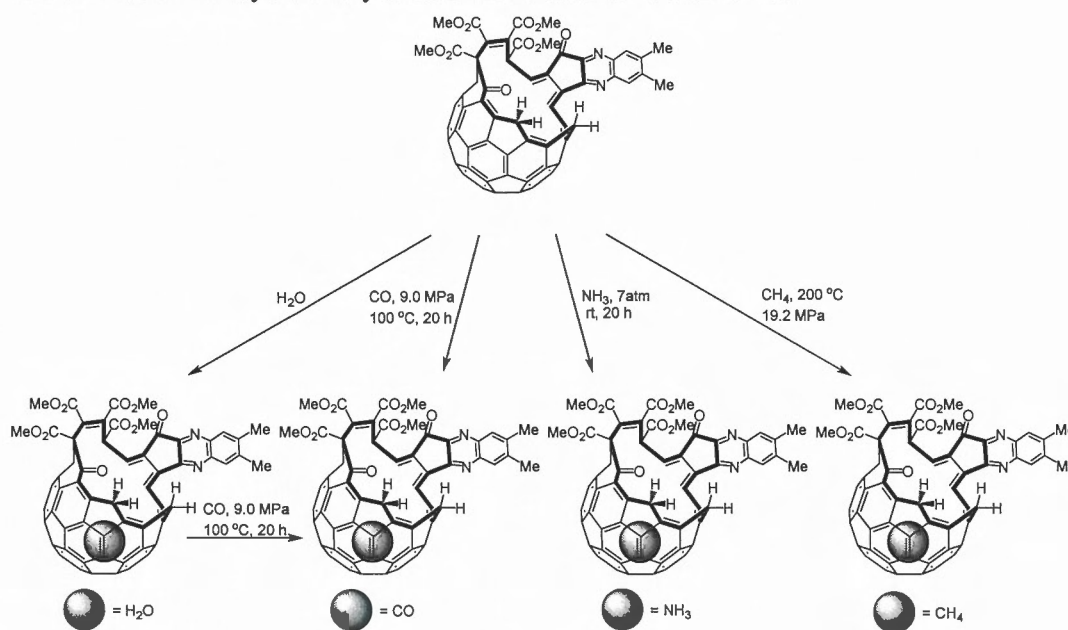
Later on, Iwamatsu, Murata et al. reported the encapsulation of molecular hydrogen into open-cage fullerene derivatives (Scheme 1-73), achieving up to 83% incorporation yield, by applying a H_2 pressure of 6–135 atm at 100 °C.¹⁶²⁾ The encapsulated H_2 was found to be released by heating and the activation energy barriers for this process were determined to be 22–24 kcal mol⁻¹. In that same work, the encapsulation of molecular hydrogen into open-cage fullerene derivatives (Scheme 1-54 and Scheme 1-58) was also attempted, though unsuccessfully, most probably due to the small size of the orifice of the former (which does not allow hydrogen penetration) and the too expanded size of the orifice of the latter (which does not suppress rapid hydrogen escape). When a solution of this open-cage fullerene in 1,1,2,2-tetrachloroethane- d_2 (TCE- d_2) was heated under 133 atm of H_2 gas at 100 °C for 4 h, encapsulation of a H_2 molecule took place to give H_2 -encapsulated fullerene at an occupation level of 62%. Since the activation barrier for the escape of encapsulated H_2 is only 23.7 kcal mol⁻¹ reflecting the large opening of it, release of the H_2 molecule gradually occurred even at room temperature with a half-life of roughly one month (Scheme 1-73).



Although until then the species encapsulated in the open-cage fullerenes had been limited to a He atom or a H_2 molecule, significant progress was made by Iwamatsu and co-workers in 2004 with the creation of a huge opening on the C_{60} cage.¹⁶⁶⁾ The opening was greatly enlarged by the reaction with 1,2-phenylenediamine derivative affording a bowl-shaped compound with a 20-membered ring opening. The size of the opening was calculated to be 6.5 Å for a longer axis and 4.2 Å for a shorter axis (B3LYP/6-31G* level).

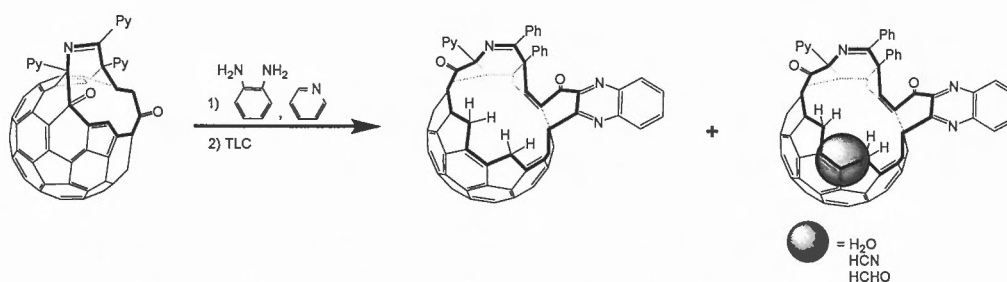
Surprisingly, upon ^1H NMR measurement of bowl-shaped compound in TCE- d_2 , a sharp singlet signal was observed at such a high field as -11.4 ppm even without any intentional procedure for guest incorporation. This signal was assigned to an H_2O molecule encapsulated in bowl-shaped compound based on the results of a D_2O exchange experiment together with elemental analysis. Encapsulation and release of the H_2O molecule in bowl-shaped compound is in equilibrium in TCE- d_2 , as demonstrated by variable-temperature NMR measurements. They showed the occupation level of the H_2O molecule to reach 75% at ambient temperature while it decreased at higher temperatures. Furthermore, it was demonstrated that the bowl-shaped compound is able to incorporate a CO molecule within the cage (Scheme 1-74). Upon heating a

solution in TCE- d_2 under 89 atm of CO gas at 100 °C for 20 h, replacement of the H₂O molecule inside by a CO molecule took place to give CO-encapsulated fullerene at an occupation level of 84%. The ¹³C NMR signal of the encapsulated CO was observed as 174.3 ppm in TCE- d_2 , which is 10 ppm upfield shifted relative to a signal of dissolved CO gas (184.6 ppm in CDCl₃). The IR spectrum of CO-encapsulated fullerene exhibited two absorptions at 2125 and 2112 cm⁻¹ indicating that there exist two orientations in the encapsulated CO molecule on the time scale on the IR measurement. When it was kept in a solution of CDCl₃ in the presence of water at 40 °C, the encapsulated CO molecule was gradually released from the cage with concomitant formation of H₂O-encapsulated fullerene instead. This result indicates that the encapsulation of an H₂O molecule is thermodynamically more favored than of a CO molecule.



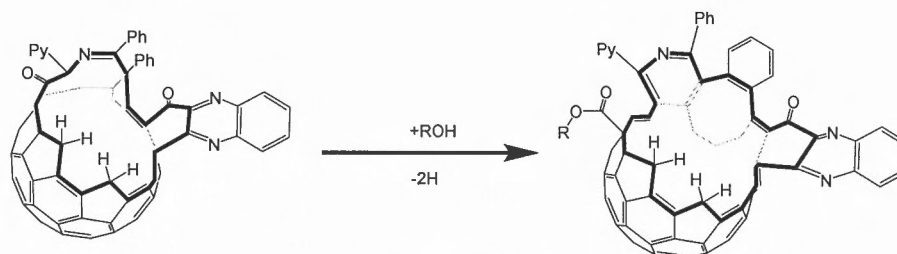
Scheme 1-74

Yeh et al. reported that reaction of open-cage fullerene with *o*-phenylenediamine and pyridine produces a mixture of C₆₃H₄NO₂(Ph)₂(Py)(N₂C₆H₄) and its H₂O encapsulated fullerenes (Scheme 1-75).¹⁶⁶ This compound is a new open-cage fullerene containing a 20-membered heterocyclic orifice, which has been fully characterized by NMR spectroscopy, high-resolution mass spectrometry, and X-ray crystallography. The elliptical orifice spans 7.45 Å along the major axis and 5.62 Å along the minor axis, which is large enough to trap water and small organic molecules. Thus, heating a mixture of it with hydrogen cyanide and formaldehyde in chlorobenzene affords HCN- and H₂CO-encapsulated fullerenes, respectively (Scheme 1-75). The ¹H NMR spectroscopy reveals substantial upfield shifts for the endohedral species (δ = -1.30 to -11.30 ppm), owing to the strong shielding effect of the fullerene cage.



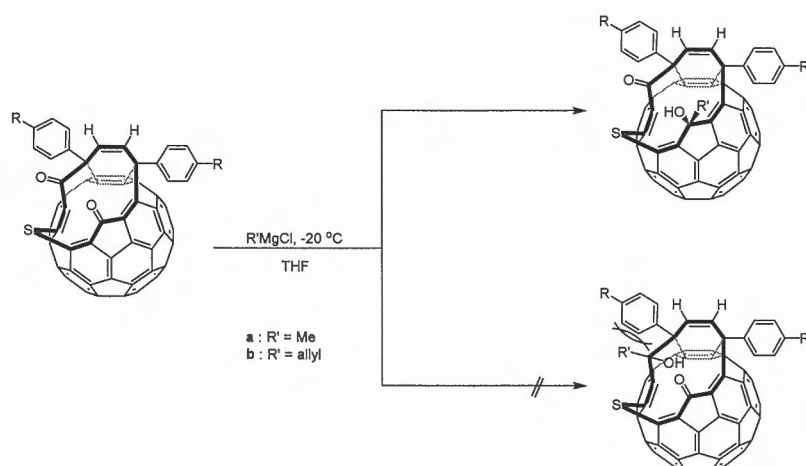
Scheme 1-75

Furthermore, Yeh et al. reported that treatment of this open-cage fullerene $C_{63}H_4NO_2(Ph)_2(Py)(N_2C_6H_4)$ with methanol at 150 °C results in an orifice-enlargement reaction to give $C_{69}H_8NO(CO_2Me)(Ph)(Py)(N_2C_6H_4)$ (Scheme 1-76).¹⁶⁷⁾ The overall yield from C_{60} is 6.1% (four steps). This orifice-enlargement compound contains a 24-membered elliptic orifice that spans 8.45 Å along the major axis and 6.37 Å along the minor axis. The skeleton of it resembles the hypothetical $C_{60}H_{10}$ (5,5)-carbon nanotube endcap. The cup-shaped structure is able to include water, hydrogen cyanide, and acetylene, respectively. The molecular structures of H₂O- and HCN-encapsulated fullerenes have been determined by X-ray crystallography. The ¹H NMR spectra reveal substantial upfield shifts for the endohedral species, such as $\delta = -10.30$ (for H₂O), -2.74 and -14.26 (for C₂H₂), and -1.22 ppm (for HCN), owing to the strong shielding effects of the fullerene cage.

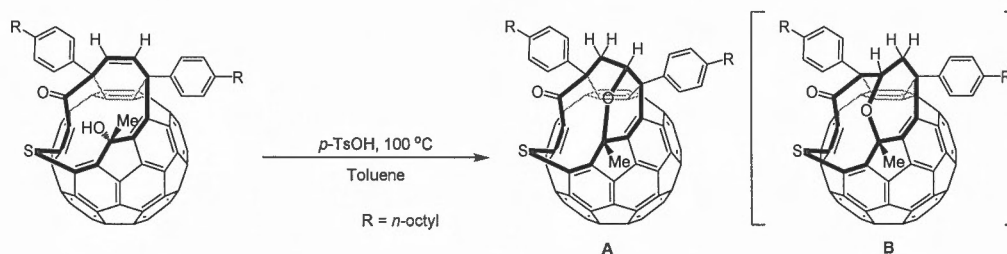


Scheme 1-76

Murata and Komatsu reported that 1,2-Addition of methyl and octyl Grignard reagents to a cage-opened fullerene derivatives selectively proceeded at -20 °C in THF at one of the two carbonyl groups (Scheme 1-77).¹⁶⁸⁾ Under acidic conditions, the resulting alcohol underwent a transannular cyclization (Scheme 1-78).¹⁶⁸⁾ Two diastereomers (**A** and **B**) were expected to be formed **A** was selectively obtained due to thermodynamically more stable than **B**. This is a technique that allowed the entrapment of guest molecules inside a fullerene cage at a greater percentage.



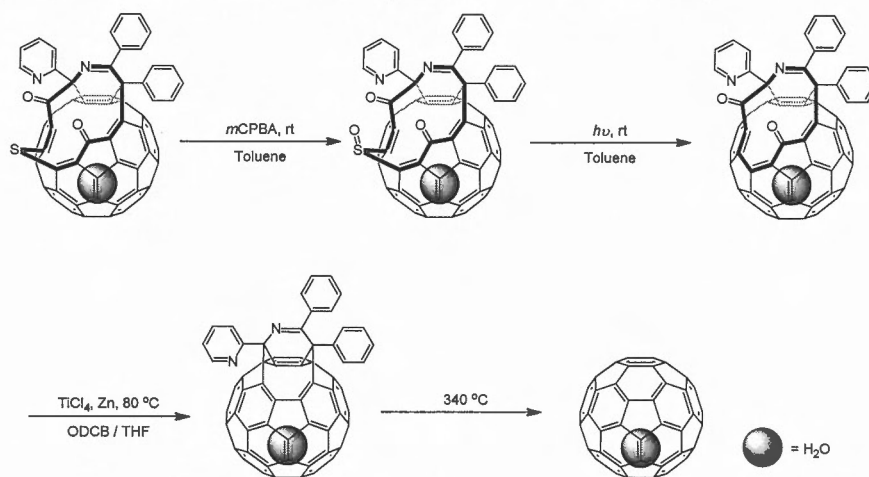
Scheme 1-77



Scheme 1-78

Insertion of a hydrogen molecule into Murata and Komatsu's open-cage fullerene was conducted simply by applying high pressure of hydrogen gas (800 atm) to the powdery sample of it heated at 200 °C in an autoclave for 8 h. There is no change or decomposition observed in the recovered sample, and it exhibited ^1H and ^{13}C NMR spectra which are the same as those of itself except a sharp singlet signal appearing at -7.25 ppm in ^1H NMR. This signal is assigned to the hydrogen molecule encapsulated in the fullerene cage, which is known to exert a strong shielding effect. The integrated intensity of this signal corresponded to 2.00 H, thus indicating that 100 % encapsulation was attained to give the endohedral open-cage fullerene derivative (Scheme 1-78).¹⁶⁹⁾ Although H_2 -encapsulated fullerene was quite stable at room temperature under air or under vacuum, it slowly released hydrogen when heated in an ODCB solution at 160 °C to 190 °C. The rate of release followed the first-order kinetics. The activation energy for release of the encapsulated hydrogen was found to be 34.3 kcal mol⁻¹, which is in fairly good agreement with the calculated value, 28.7 kcal mol⁻¹. The identity of it was confirmed also by MALDI-TOF mass spectrometry, which exhibited a clear molecular ion peak for it. When MALDI-TOF mass spectroscopy was conducted under enhanced laser power on the compound encapsulating hydrogen, they observed a molecular ion peak for $\text{H}_2@\text{C}_{60}$ at a mass to charge ratio (m/z) of 722. This result suggested that H_2 -encapsulated open-cage fullerene could be a precursor for $\text{H}_2@\text{C}_{60}$ in an actual chemical transformation.

Murata and Komatsu finally reported the synthesis of 100 % pure $\text{H}_2@\text{C}_{60}$ (Scheme 1-79). The first step involved the oxidation of the sulfide unit ($-\text{S}-$) to a sulfoxide unit ($>\text{S}=\text{O}$). The resulting $>\text{S}=\text{O}$ unit was removed by a photochemical reaction. Thus, in the next step, two carbonyl groups were reductively coupled by the use of $\text{Ti}(0)$ at 80°C to give H_2 -encapsulated fullerenes with an 8-membered ring orifice (Scheme 1-78). At each process in these three steps, complete retention of encapsulated H_2 was confirmed by observing the characteristically upfield shifted NMR signal of the incorporated H_2 . The integrated signal intensity exactly corresponded to $2.00 \pm 0.05\text{H}$. Finally, complete closure of the orifice was achieved by heating powdery H_2 -encapsulated in a glass tube at 340°C for 2 h under vacuum. The desired product $\text{H}_2@\text{C}_{60}$ was obtained in 67% yield by passing a carbon disulfide solution of the crude product through a silica gel column. Thus, $\text{H}_2@\text{C}_{60}$ was synthesized in a total yield of 22%. The ^1H NMR signal for the encapsulated hydrogen of $\text{H}_2@\text{C}_{60}$ in $\text{ODCB}-d_4$ was observed at -1.44 ppm, which is 5.98 ppm upfield shifted relative to the signal of dissolved free hydrogen.



Scheme 1-79

In 2011, Murata et al. prepared $\text{H}_2\text{O}@\text{C}_{60}$ according to “Molecular surgery” method (Scheme 1-80).¹⁷⁰⁾ When bishemiketal was refluxed in wet toluene and the resulting product was analyzed by ^1H nuclear magnetic resonance (NMR), an H_2O molecule encapsulated inside was detected in 8% yield by comparison of the integrated peak areas. The encapsulation ratio is apparently lower than the reported values by Iwamatsu et al. (75%) and by Gan and coworkers (88%), reflecting the smaller size of the opening on tetraketone than those on their compounds. However, quantitative encapsulation of an H_2O molecule inside bishemiketal was achieved when this process was conducted under the high pressure of 9000 atm at 120°C for 36 hours. The high pressure is critical; only 40% encapsulation was observed under 5000 atm under the similar conditions. The formation of H_2O -encapsulated bishemiketal can be explained by the dynamic control of the opening size. Elimination of a water molecule from it generates tetraketone. The insertion of an H_2O molecule into tetraketone takes place through the 16-membered-ring