Chem. Rev. **2006,** *106,* 5049–5135

Structural Aspects of Fullerene Chemistry—A Journey through Fullerene Chirality

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Received April 7, 2006

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10.1021/cr0505371 CCC: $59.00

1. Introduction

The discovery of the fullerenes, the first molecular allotropes of carbon, in the gas phase in 1985[1] and the equally remarkable discovery of their synthesis in macroscopic amounts by arc vaporization of graphite in 1990[2] have profoundly influenced all aspects of contemporary chemistry. Functionalization of the carbon spheres led to a plethora of unprecedented new molecular structures and shapes that are continuously investigated for their fundamental physicochemical properties and their reactivity, as well as for applications in advanced materials. After the isolation and structural characterization of the first chiral fullerene, C_{76}-D_2, in 1991,[3] it rapidly became clear that fullerene chemistry would also require writing a new chapter in stereochemistry. This is exactly the aim of the present review, which provides an overview of the different aspects of fullerene chirality that have been identified and investigated during the past 15 years.[4] It becomes immediately apparent to the reader that writing about fullerene chirality is very much equal to undertaking a journey into fascinating three-dimensional molecular architecture.

Carlo Thilgen was born in Luxembourg-City in 1961 and studied chemistry at the University of Bonn (1980–1987). He carried out his doctoral thesis on the synthesis of macrocyclic diarylpolyene-type cyclophanes under the supervision of Prof. Fritz Vögtle and was awarded his Ph.D. degree in 1990. During postdoctoral studies with Prof. François Diederich at UCLA and ETH Zürich (1990–1992), he worked on chiral cleft-type receptors for molecular recognition through hydrogen bonding and on the isolation of new fullerenes beyond C_{60} and C_{70}. From there, he became a lecturer at the Laboratory of Organic Chemistry in the Department of Chemistry and Applied Biosciences at ETH Zürich. His research interests are in the area of fullerene chemistry with particular focus on structural aspects such as chirality.

François Diederich, born in the Grand-Duchy of Luxemburg (1952), studied chemistry at the University of Heidelberg (1971–1977). He joined the group of Prof. Heinz A. Staab for his diploma and doctoral thesis, which he completed in 1979 with the synthesis of kekulene. Following postdoctoral studies with Prof. Orville L. Chapman at UCLA (1979–1981), he returned to Heidelberg for his Habilitation at the Max-Planck-Institut für Medizinische Forschung (1981–1985). Subsequently, he joined the Faculty in the Department of Chemistry and Biochemistry at UCLA where he moved up the ranks to become Full Professor of Organic and Bioorganic Chemistry in 1989. In 1992, he joined the Laboratory of Organic Chemistry in the Department of Chemistry and Applied Biosciences at the ETH Zürich. His research interests, documented in more than 480 publications, span from medicinal chemistry, with a focus on molecular recognition studies, to dendritic mimics of globular proteins, and to advanced fullerene and acetylene-based materials with novel optoelectronic properties.

The present review focuses on the chirality of soluble fullerenes and their derivatives and does not cover the chirality of carbon nanotubes, which is associated with

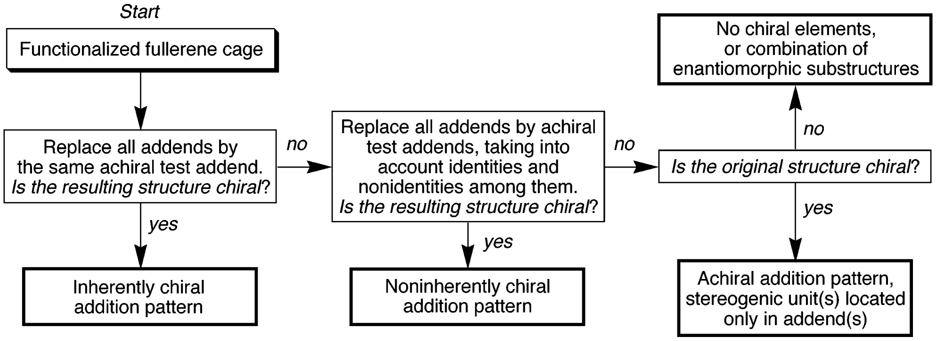


Figure 1. Flowchart for the identification of different types of fullerene chirality by a stepwise, formal substitution test.

special electronic properties of these insoluble polymeric allotropes.[5,6] It covers chiral carbon cages beyond C_{60} and C_{70} that have been isolated and characterized experimentally or confidently identified. The major part describes derivatives of C_{60} and C_{70} with a chiral functionalization pattern, that is, having stereogenic elements located in their cores, which are achiral in the pristine fullerenes. Specific investigations on the chirality of fullerene derivatives with a chiral addition pattern are discussed in depth. To provide an overview of the amazing structural diversity and the many aspects of fullerene chirality, the review also analyzes the numerous chiral structures that have been reported without their chirality having been studied. It includes a number of achiral derivatives that should also be discussed to complete the picture of the chemistry in question. As to the fullerene derivatives that have their stereogenic elements, resulting either from newly generated stereogenic centers during the functionalization of the fullerene or from attachment of chiral residues to the latter, located exclusively in the addends, their number is legion and their presentation would go beyond the scope of the present review. In many cases also, the chirality of these compounds was neither investigated nor mentioned in the corresponding reports.

Regarding the specification of the configuration of chiral fullerenes and fullerene derivatives, the present review uses exclusively the stereodescriptors and fullerene C-atom numberings recommended by the IUPAC (International Union of Pure and Applied Chemistry), which are presented in the next section.

2. Specification of the Configuration of Chiral Fullerenes and of Fullerene Derivatives with a Chiral Functionalization Pattern

2.1. Classification of Fullerene Chirality

Only 1−2 years after C_{60} and C_{70} had become available in macroscopic amounts by arc vaporization of graphite,[2] chromatographic workup of fullerene soot extract led to the isolation and characterization of the first chiral carbon cages, D_2-symmetric C_{76}[3,7] and D_3-symmetric C_{78}.[8−10] According to the structural principles of fullerenes C_{2n},[11−13] the number of allowed constitutional isomers increases dramatically with increasing cage size and so does the number of chiral representatives, which amounts, for example, to 1 out of 5 C_{78} isomers, 2 out of 7 C_{80} isomers, 3 out of 9 C_{82} isomers, 10 out of 24 C_{84} isomers, 14 out of 19 C_{86} isomers, and 21 out of 35 C_{88} isomers.[14] Similarly, a considerable fraction of the enormous amount of fullerene derivatives isolated and characterized during the last 15 years[15−19] is chiral,[4,20−23] even if the compounds have been prepared from the achiral parent fullerenes C_{60} and C_{70}. The first enantiomerically pure fullerene derivative was a glycoconjugate of C_{60} having stereogenic elements (centers) located exclusively in the addend (residue added to the fullerene cage).[24,25] On the other hand, a great deal of chiral fullerene derivatives are neither derived from chiral carbon cages nor characterized by stereogenic elements in the added groups (addends); instead their chirality results from the geometric arrangement of addends, substituting heteroatoms, or even missing carbon atoms (norfullerenes), on the surface of the spheroid. Such an arrangement is termed a *chiral addition pattern* or, more generally, a *chiral functionalization pattern*.

Depending on the origin of their chirality, chiral fullerene derivatives can be classified as follows (Figure 1):[26]

1. Derivatives of achiral parent fullerenes in which the derivatization creates a chiral functionalization pattern on the fullerene skeleton, irrespective of the addends being identical or different; they have an *inherently chiral functionalization pattern*. The derivatives of chiral parent fullerenes have an inherently chiral functionalization pattern per se.
2. Derivatives of achiral parent fullerenes in which a chiral functionalization pattern is due exclusively to nonidentities among addends; they have a *noninherently chiral functionalization pattern*. This situation is related to that of a stereogenic center with tetrahedral bonding geometry, in which case the nonidentity of all substituents is a prerequisite for chirality.
3. Derivatives of achiral parent fullerenes in which the addition of chiral residues does not create a chiral addition pattern on the fullerene surface; they have their chiral elements located exclusively in the addends.

In case the addends of derivatives belonging to classes 1 or 2 are chiral, their stereogenic elements are superposed to a chiral addition pattern. The latter is either inherently or noninherently chiral; both types mutually exclude each other in a given fullerene unit.

The type of functionalization pattern (inherently chiral, noninherently chiral, or achiral) can easily be determined by application of a formal substitution test to the fullerene unit under scrutiny (Figure 1). It consists of a three-step procedure including (a) the replacement of *all* addends by *the same achiral* test addend, (b) the replacement of *identical*/*nonidentical* original addends by *identical*/*nonidentical achiral* test-addends, and (c) the consideration of the original molecule. After each step, the resulting structure of increasing complexity is checked for chirality; as soon as it is found, the type of chirality is identified.

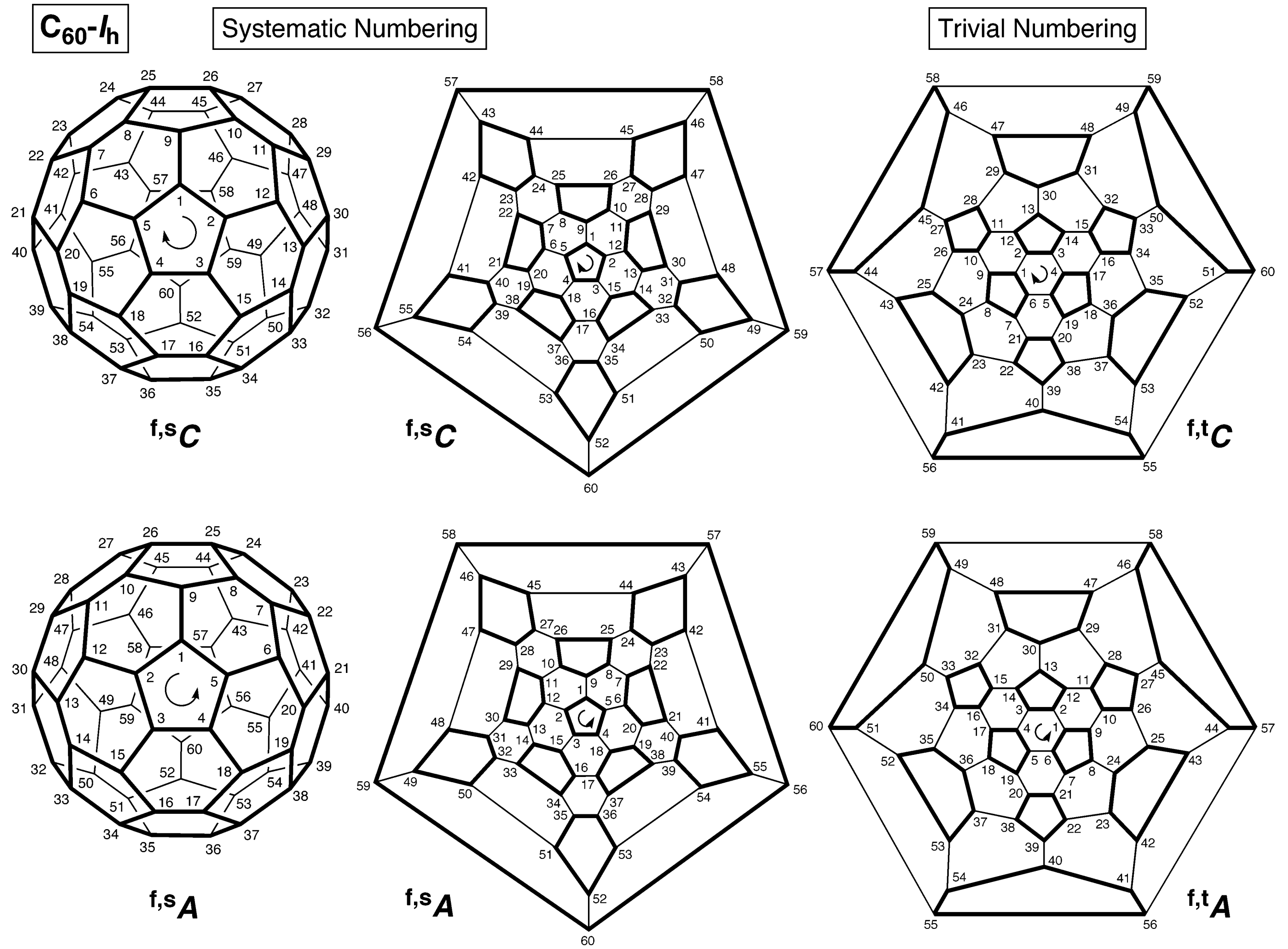


Figure 2. Three-dimensional and Schlegel[37] diagrams of C_{60}-I_h with enantiomeric (top and bottom) numbering schemes: left and center, systematic numbering recommended by IUPAC;[29,34] right, trivial numbering.[32,36] Arrows indicate the direction of the numbering commencement.

2.2. The Stereodescriptor System

Two main motivations led to the proposal of a new stereodescriptor system for the specification of the configuration of chiral fullerenes and fullerene derivatives with a chiral functionalization pattern:[26] (i) chiral parent fullerenes do not include any stereogenic center or other obvious stereogenic element to be specified by the CIP (Cahn, Ingold, Prelog) system;[27,28] (ii) the configuration of fullerene derivatives with a chiral functionalization pattern could, in principle, be described by indicating the absolute configuration (*R* or *S*) for each stereogenic center of the molecule according to the CIP system. For stereogenic centers that are part of a fullerene cage, however, this operation is usually lengthy and unintuitive due to the highly branched carbon framework and may require the development of complex hierarchic digraphs,[28] with differences in CIP priorities becoming apparent only at high generations of connected atoms, if the addends are separated by many fullerene core atoms.[26] For multifunctionalized fullerenes, the operation would have to be repeated for all stereogenic centers that are not related by a symmetry operation and, thus, result in a multitude of stereodescriptors. Furthermore, the configuration of individual cage atoms of common fullerene derivatives can, in general, not be inverted independently of the others, and therefore, it makes sense to consider them as an ensemble or, in other words, the chiral fullerene cage as a single stereogenic unit. The conceivable situation of addends located on the inside of the cage could still be described by using additional stereodescriptors such as *in* and *out*.[29]

The proposed descriptor system,[26,30] the use of which is now recommended by IUPAC,[29,31] is based on the fact that the numbering schemes (pathways following the sequence of numbered atoms) devised for fullerenes[29,32−34] are helical, that is, chiral, and thus constitute a convenient reference for the differentiation between the enantiomers of chiral parent fullerenes and of fullerene derivatives having a chiral functionalization pattern. A single descriptor is sufficient to specify the configuration of an entire chiral fullerene unit, regardless of the degree of functionalization or skeletal replacement.

Whereas two isometric, mirror-symmetric numbering schemes can be applied to an achiral parent fullerene, for example, C_{60}-I_h and C_{70}-D_{5h} (Figures 2 and 3), only one such scheme is associable with a given enantiomer of an inherently chiral carbon cage[26,29,30,33,34] and, consequently, with all its derivatives.[26,29,30,34] The mirror image numbering scheme must be applied to the other optical antipode (Figure 4). Similarly, for a specific enantiomer of a fullerene derivative resulting from an inherently chiral functionalization pattern generated on an achiral parent carbon cage, there is a unique and preferred helical numbering path leading to the lowest set of locants[35] for the addends (Figure 5). Because each of

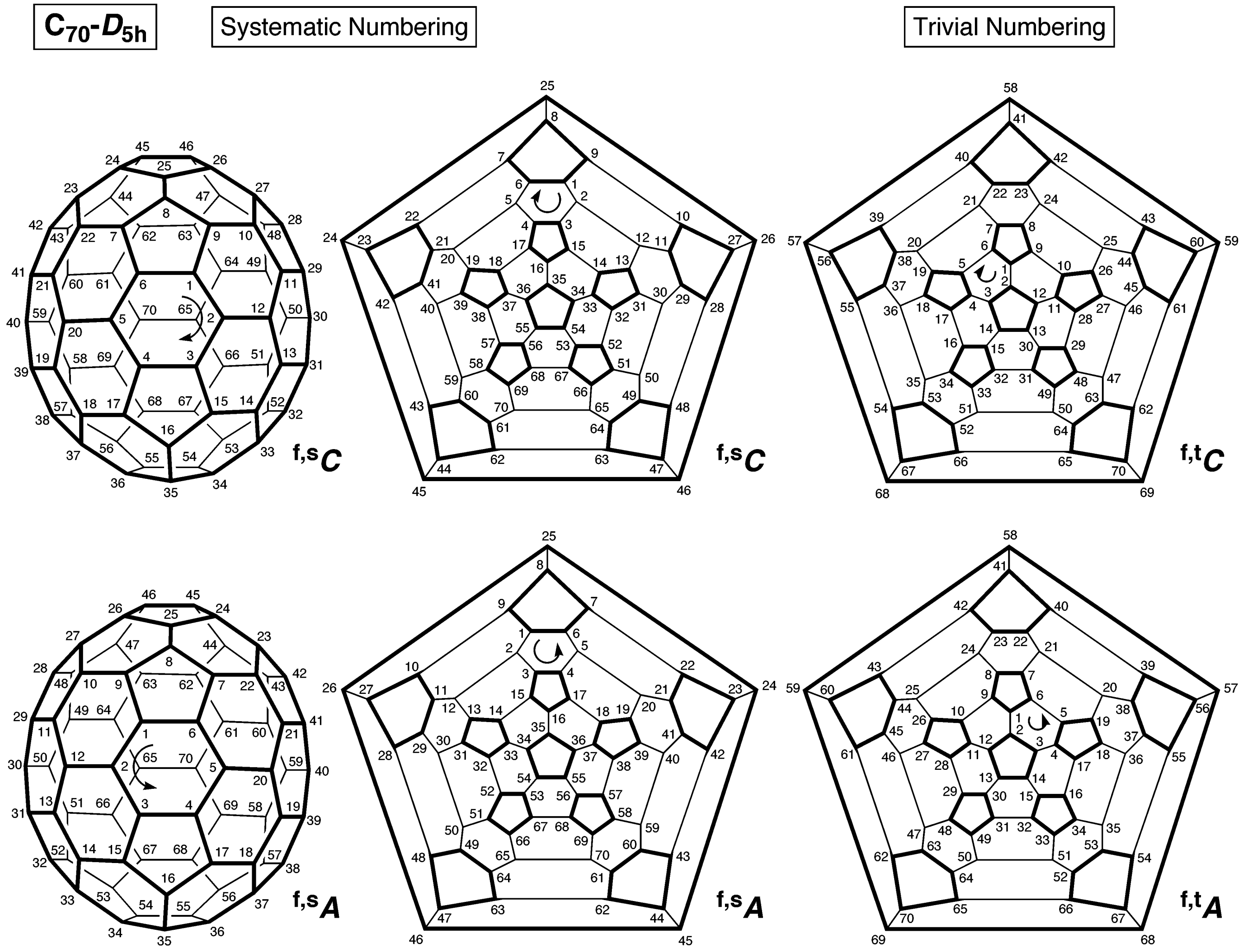


Figure 3. Three-dimensional and Schlegel[37] diagrams of C_{70}-D_{5h} with enantiomeric (top and bottom) numbering schemes: left and center, systematic numbering recommended by IUPAC;[29,34] right, trivial numbering.[32,36] Arrows indicate the direction of the numbering commencement.

two mirror-symmetric numberings can be associated only with a single enantiomer, a description of the handedness of the used numbering scheme is sufficient to specify the absolute configuration of a fullerene unit.[26,29,30] This principle is valid for any helical numbering pathway.

Historically, different numbering schemes have been proposed,[29,32−34,36] and are in use for commonly accessible fullerenes. The system initially proposed by Taylor,[32,36] based on low atom numbers for bonds with a high reactivity, is accepted as "trivial numbering" for C_{60} and C_{70} (Figures 2 and 3, right).[29,34] A systematic procedure for numbering fullerenes and related structures using symmetry elements as references was recently recommended by the IUPAC.[29,34] In any case, the correct interpretation of a stereodescriptor based on vertex numbering requires a reference to the used system.

To assign a descriptor to a chiral fullerene unit, the viewer, looking from the outside of the cage at the polygon in which the numbering starts,[37] traces a path from atom C(1) to C(2) to C(3), which are never aligned in a fullerene structure. If this path describes a clockwise direction, the configuration is specified by the descriptor ($^{\mathrm{f},x}C$), where the superscript "f" indicates that the descriptor refers to a fullerene and the superscript "x" is either "s" for the systematic numbering[29,34] ($^{\mathrm{f,s}}C$) or "t" for the trivial numbering[32,36] ($^{\mathrm{f,t}}C$) (formerly denoted simply as ($^{\mathrm{f}}C$)[26,30]).[29,34] If the path from C(1) to C(2) to C(3) describes an anticlockwise direction, the descriptor is ($^{\mathrm{f},x}A$).

In the case of a noninherently chiral functionalization pattern, CIP priorities[27,28] are attributed to the addends (in the way they are to the ligands of a stereogenic center), and the handedness of the preferred numbering helix is chosen such that, at the first point of difference, the lowest cage atom number is allocated to the addition site bearing the addend of highest CIP priority. Finally, the configuration of chiral elements that are located exclusively in the addend(s) is described by the classical stereodescriptors,[27,28] for example, (*R*)/(*S*) or (*M*)/(*P*).

The nomenclature of isolated and characterized chiral fullerene derivatives has proven the versatility of the present descriptor system.[4,16,20−22,26,29,34] It is easily applicable "by hand", even if simple computation further facilitates its handling.[38] The dependence of a numbering scheme to be specified may be considered as a disadvantage from a more fundamental viewpoint, but the general use of these schemes by people working in the field makes them a rather convenient tool. Nonetheless, alternative systems have been reported in the literature: a nomenclature system for C_{60} derivatives that is based on edge labeling of the icosahedron was proposed also for the configurational description of chiral molecules, but it has not become widely accepted.[39] Another method for the structural description of chiral fullerene

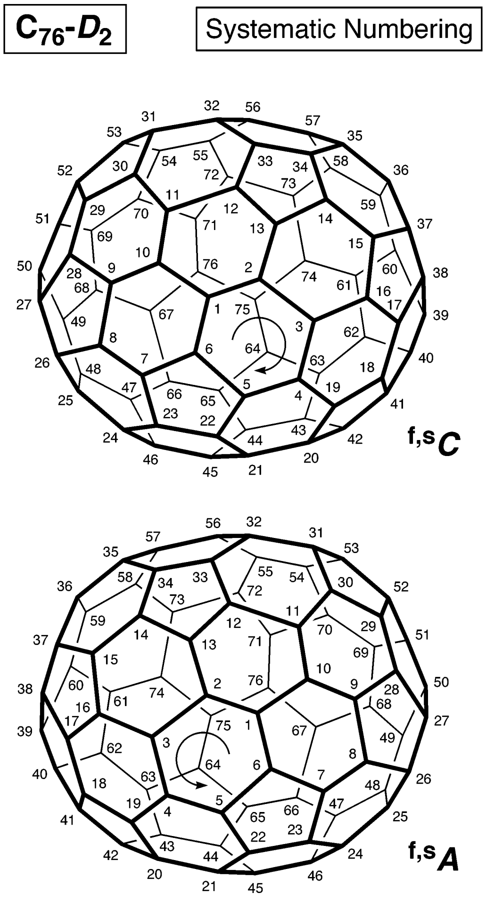


Figure 4. Three-dimensional diagrams of C_{76}-D_2 with enantiomeric (top and bottom) systematic numbering schemes.[29,34] Arrows indicate the direction of the numbering commencement. In all cases of inherently chiral fullerenes, the same numbering applies to a given enantiomer of the parent cage and to all its derivatives.

derivatives using a bond-labeling algorithm eventually relies on the helicity of the fullerene numbering schemes as well.[40] Two fundamentally different approaches that do not depend on vertex labeling of polyhedra were taken by Rassat, Fowler, and co-workers:[41,42] they suggested an extension of the CIP system to chiral parent fullerenes that invokes the development of rooted trees for each stereogenic center and leads, ultimately, to a multitude of (*R*)/(*S*) descriptors.[41] The second method is a graph-theoretical procedure consisting in the diagonalization of the adjacency matrix of the molecule, followed by the use of the resulting “topological coordinates”, together with the eigenvectors of the adjacency matrix, in the calculation of formal rotational strengths of HOMO−LUMO transitions within the framework of Hückel theory.[42] The signs of these quantities are uniquely related to the identity of the constructed enantiomer and can, therefore, be used as stereodescriptors. Whereas this conceptually interesting approach conveniently leads to a single descriptor per molecule, its application normally requires the use of computational methods.

2.3. Examples for the Configurational Description of Fullerene Derivatives with a Chiral Functionalization Pattern

2.3.1. Inherently Chiral Fullerenes and Their Derivatives

A given enantiomer of a chiral parent fullerene and all its adducts (derivatives) are associated with the same representative out of two mirror-symmetric, isometric numbering schemes (Figure 4). Therefore, the descriptor (^{f,s}*C*) or (^{f,s}*A*) specifying the absolute configuration of such compounds depends only on the parent carbon cage, regardless of the number and arrangement of addends.

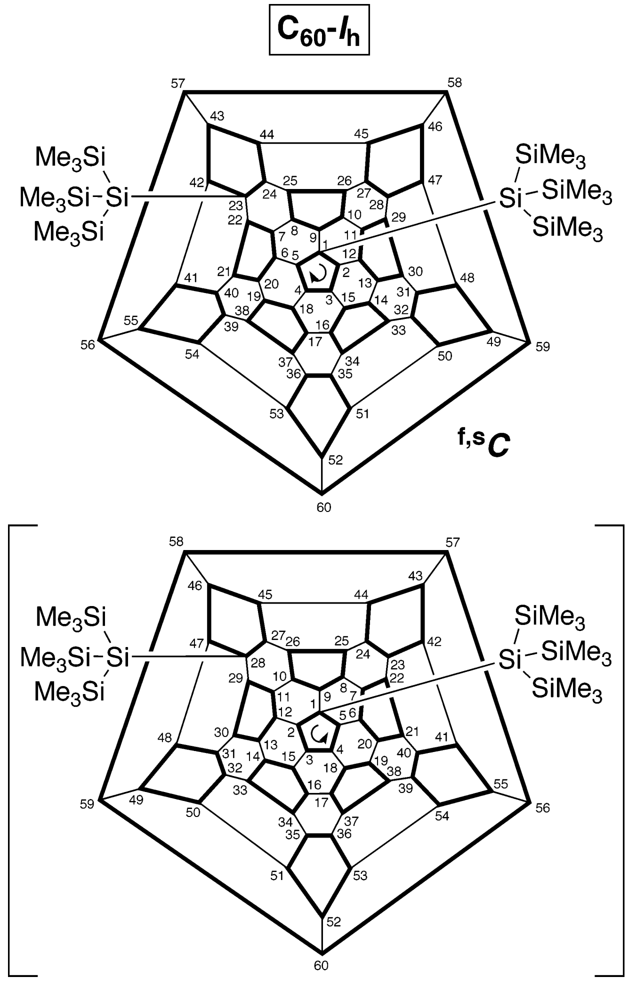


Figure 5. Schlegel diagram[37] (top) of (^{f,s}*C*)-1,23-bis[1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl]-1,23-dihydro(C_{60}-I_h)[5,6]-fullerene; application of the anticlockwise numbering scheme of C_{60} to the same enantiomer (bottom) would afford “1,28” as lowest set of locants, which is higher than the above set “1,23” and, therefore, in disaccord with IUPAC conventions.[29,34,35]

2.3.2. Achiral Parent Fullerenes with an Inherently Chiral Functionalization Pattern

The C-atom numbering of an achiral fullerene can, in principle, be achieved with either of two mirror-symmetric numbering schemes (cf. Figures 2 and 3). For a specific enantiomer of its derivatives with an inherently chiral functionalization pattern, however, only one of the two numbering schemes leads to the lowest set of locants for the addends and is, therefore, preferred (Figure 5).

2.3.3. Achiral Parent Fullerenes with a Noninherently Chiral Functionalization Pattern

In the case of a noninherently chiral functionalization pattern, the symmetric arrangement of addends on an achiral fullerene spheroid allows no distinction between enantiomers based on the above criteria: the same lowest set of locants is obtained with both mirror-symmetric numbering schemes. To discriminate between the two cases, a ranking of addends or substituting skeletal atoms is established on the basis of structural differences among them.[43] This is achieved most conveniently by application of the CIP system, which allows a hierarchic ordering of residues differing in constitution or configuration.[27,28] For the fullerene derivatives considered in this section, heteroatoms or isotopes that substitute skeletal carbon atoms and addends are treated alike, starting the atom-by-atom comparison of these substructures according to the CIP rules at the functionalized cage atom and then progressively moving away from the core until a priority difference is identified.[44] Of the two mirror-symmetric numbering schemes leading to the same lowest set of locants, the one assigning a lower locant to an atom or group of higher CIP ranking at the first point of difference is preferred and confers its descriptor to the enantiomer in question (Figure 6).

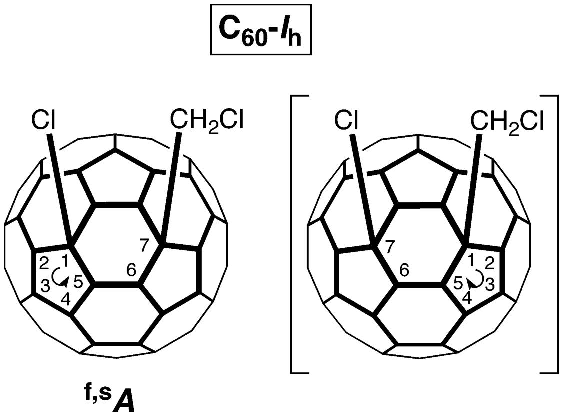


Figure 6. ($^{f,s}A$)-1-Chloro-7-chloromethyl-1,7-dihydro(C_{60}-I_h)[5,6]fullerene (left). This structure has a noninherently chiral addition pattern, and the anticlockwise numbering allocates the lowest locant (“1”) to the addend of highest CIP priority (Cl). Application of the clockwise numbering (left) leads to the same overall set of locants (“1,7”), but it associates the lowest locant (“1”) to the addend of lower CIP priority (CH_2Cl), which is in disaccord with IUPAC conventions.[29,34]

2.3.4. Superposition of Stereogenic Elements in a Fullerene Derivative

The addition of chiral residues to an achiral fullerene does not necessarily lead to a chiral addition pattern. In such a case, only the configuration of the stereogenic element(s) in the addend(s) is specified by CIP stereodescriptors.[27,28] If, on the other hand, a chiral functionalization pattern is superposed to chiral addends, the configuration of both types of stereogenic elements has to be indicated for a full stereodescription of the structure (Figure 7).

3. Inherently Chiral Fullerenes

3.1. The Higher Fullerenes

The isolation and characterization of the first higher fullerene beyond C_{70},[45,46] C_{76}-D_2, which was achieved by Diederich, Whetten, and co-workers only about a year after fullerenes became available in isolable quantities, provided the first example of a chiral carbon cage, thereby initiating the study of the many aspects of fullerene chirality.[3,7] Its D_2-symmetric structure (Figures 4 and 8) had been predicted by Manolopoulos[12] to be the only closed-shell isomer of [76]fullerene obeying the IPR (isolated pentagon rule),[1,47,48] that is, including no edge-sharing pentagons.

The structure was confirmed by its 1D ^{13}C NMR spectrum, which consists of 19 lines of equal intensity.[3,49] Achiba et al. later determined the carbon atom connectivity by 2D ^{13}C NMR INADEQUATE (incredible natural abundance double quantum transfer experiment) analysis performed on a ^{13}C-enriched sample.[50] They found that the observed chemical shifts correlate with the curvature of the spheroid, the more strongly pyramidalized carbon atoms being shifted toward lower magnetic field.

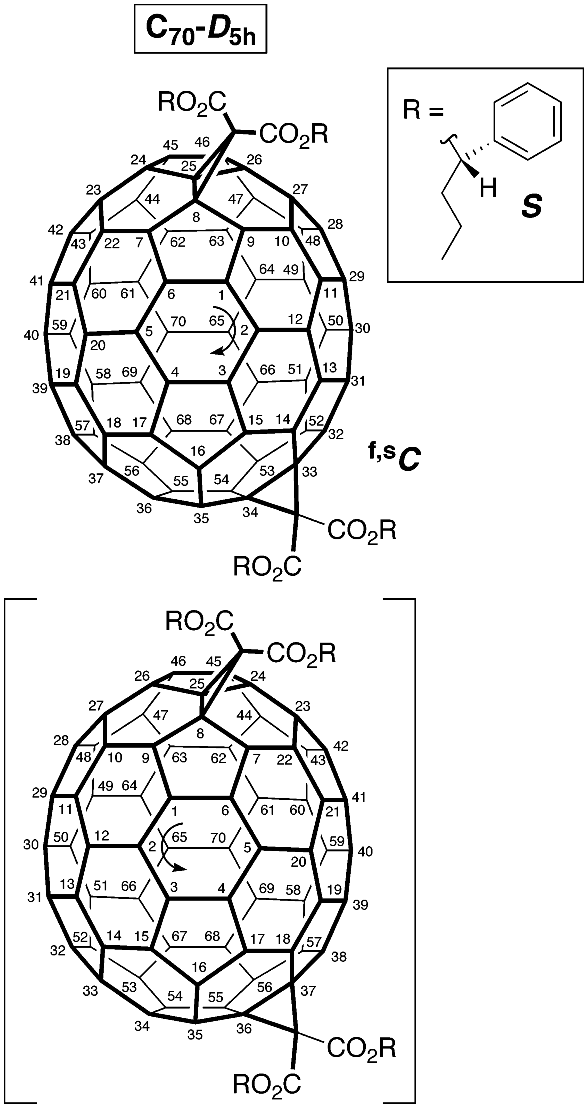
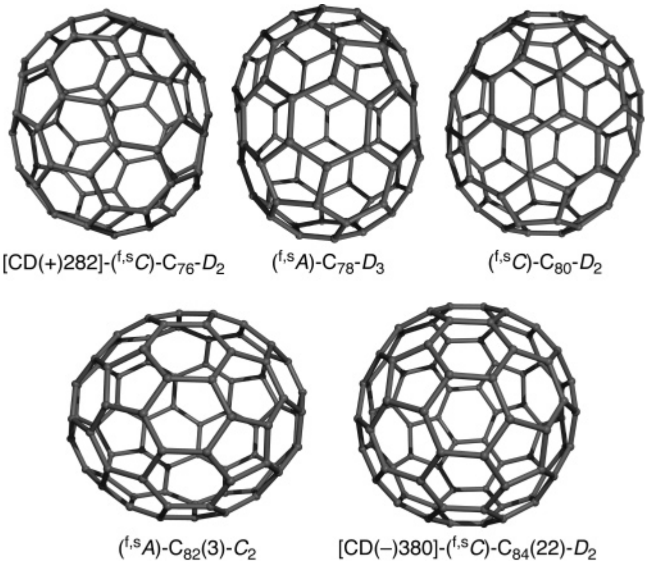


Figure 7. Tetrakis[(1*S*)-1-phenylbutyl] ($^{f,s}C$)-3′*H*,3″*H*-dicyclopropa[8,25:33,34](C_{70}-$D_{5h(6)}$)[5,6]fullerene-3′,3′,3″,3″-tetracarboxylate (top).[840] This structure combines an inherently chiral addition pattern of C_{70} with stereogenic centers in the ester residues, and the two types of stereogenic elements are specified independently of each other. Application of the anticlockwise numbering scheme (bottom) of C_{70} to the same enantiomer would afford “8,25:36,37” as lowest set of locants, which is higher than the above set “8,25:33,34” and, therefore, in disaccord with IUPAC conventions.[29,34,35]

The structure of C_{76}-D_2 was further supported by X-ray crystallography of the van der Waals compound [(±)-C_{76}-D_2]$(S_8)_6$,[51] but there was pronounced disorder in the measured crystal containing both enantiomers of C_{76}, and despite further efforts, resolution at the atomic level has not been achieved so far.[52,53]

Among the five possible IPR-satisfying structures of C_{78}, a single one, C_{78}-D_3 (common notation “78:1”[14] or “C_{78}(1)-D_3”), is chiral (Figure 8).[13,14] This isomer was first isolated and unambiguously assigned[8] by its 13 ^{13}C NMR lines of equal intensity[8−10,49] as minor component next to C_{78}(2)-C_{2v},



[CD(+)282]-($^{f,s}C$)-C_{76}-D_2 ($^{f,s}A$)-C_{78}-D_3 ($^{f,s}C$)-C_{80}-D_2

($^{f,s}A$)-C_{82}(3)-C_2 [CD(−)380]-($^{f,s}C$)-C_{84}(22)-D_2

Figure 8. A selection of inherently chiral fullerenes for which certain or confident structural assignments have been possible. All structures are viewed along a C_2 axis, and the stereodescriptors of the represented enantiomers are given. In the case of the enantiomerically resolved C_{76}-D_2 and C_{84}(22)-D_2, the sign of a characteristic experimental CD band is indicated. The numbers in parentheses correspond to the isomer designations in ref 14.

obtained by HPLC (high performance liquid chromatography) purification of the higher fullerene fraction of soot extract. Depending on the conditions of soot production, these two allotropes may be accompanied by another achiral isomer, C_{78}(3)-C_{2v} (sometimes referred to as C_{78}-C_{2v}').[9,49,54] Calculation of the ^{13}C NMR chemical shifts employing the GIAO (gauge-independent atomic orbital) method at the B3LYP/6-31G* level of theory showed a good agreement with the experimental data measured for C_{76} and the various C_{78} isomers.[55]

Due to a very low abundance in fullerene soot, it took several years for the next higher fullerene, C_{80}, to be isolated and characterized by ^{13}C NMR spectroscopy.[56] The measured resonances were consistent with 20 groups of four symmetry-equivalent carbon atoms, and in combination with theoretical calculations on structures and energies of the seven IPR-conforming isomers,[14,57] a D_2-symmetric structure was proposed for the isolated allotrope (Figure 8). This assignment was confirmed by calculation of the ^{13}C NMR chemical shifts employing the GIAO method.[55] The electronic circular dichroism spectrum was calculated and should allow the assignment of absolute configurations to the enantiomers,[58] but no experimental data are available so far. A second, even less abundant, light green (CS_2 solution) [80]fullerene isomer was prepared and isolated by Shinohara and co-workers using multistage HPLC. Based on its characteristic ^{13}C NMR spectrum, it was identified unambiguously as achiral C_{80}-D_{5d}.[59]

A chiral isomer of C_2-symmetry (41 ^{13}C NMR resonances) has been shown to be the major component in the C_{82} fraction of fullerene soot.[9,50] Because there are three structures with this symmetry among the IPR-conforming [82]fullerene isomers, an assignment seemed difficult at first, but theoretical ^{13}C NMR spectra calculated by density functional theory, in conjunction with stability considerations, have identified the isolated allotrope as C_{82}(3)-C_2 (Figure 8).[60]

Due to its relatively large abundance in fullerene soot as well as its structural (isomeric) diversity, C_{84} is one of the most interesting higher fullerenes. Early ^{13}C NMR studies revealed the presence of two major isomers of D_2- and D_{2d}-symmetry in a ∼2:1 ratio.[9,45,46,49] In conjunction with theoretical calculations, the structures of C_{84}(22)-D_2 [61] (Figure 8) and C_{84}(23)-D_{2d} were confidently proposed for the major isomers. A first unequivocal experimental assignment of the observed C_{84}(23)-D_{2d} to one out of the 24 IPR-conforming isomers was accomplished when Balch et al. solved the X-ray crystal structure of $[Ir(CO)Cl(PPh_3)_2(\eta^2\text{-}C_{84}(23)\text{-}D_{2d})]\cdot 4C_6H_6$, obtained by selective crystallization from a solution containing both C_{84}(22)-D_2 and C_{84}(23)-D_{2d}.[62] Four years later, Shinohara et al. were able to separate the two major C_{84} isomers by multistage recycling HPLC and recorded the ^{13}C NMR spectrum of each allotrope.[63,64] Eleven carbon resonances (one of intensity 4, 10 of intensity 8) allowed an unambiguous assignment of the achiral isomer as C_{84}(23)-D_{2d}, thus confirming the crystallographic results. As to the D_2-symmetric isomer, the 21 measured resonances are in accord with all four D_2-symmetric IPR-conforming isomers and a secure assignment to the C_{84}(22)-D_2 structure was possible only through 2D ^{13}C NMR spectroscopy.[50]

Another purification technique, involving a separation of functionalized C_{84} derivatives and a reversion of the latter to the parent fullerenes, was presented shortly afterward. In this experiment, Diederich and co-workers were able to isolate another CD (circular dichroism)-silent and therefore achiral C_{84} isomer, but due to the small available amounts, UV and electrochemical data only were recorded.[65] More importantly, the applied strategy allowed the resolution of the optical antipodes of C_{84}(22)-D_2 (see section 3.2).[65] In a related approach, Saunders and co-workers took advantage of the known[66] reversible addition of 9,10-dimethylanthracene (DMA) to fullerenes, in combination with the facilitated chromatographic purification of the intermediate adducts, to enrich certain allotropes, in particular C_{84}(22)-D_2, of a higher fullerene fraction labeled with incarcerated ^{3}He (for incarceranes of higher fullerenes, see section 3.3).[67] The dissociation constants of the DMA adducts of the various C_{2n} allotropes and even of isomeric cages differed considerably, with the derivatives of C_{76} and C_{78} appearing not to dissociate at all, even in the presence of dimethyl acetylenedicarboxylate, which irreversibly reacts with 9,10-dimethylanthracene.

First indications for the presence of a number of minor isomers in the C_{84} fraction had been obtained relatively early by Taylor et al.[49] This observation was confirmed by Saunders and co-workers who measured possibly up to nine ^{3}He NMR resonances for i^3HeC_{84} (C_{84} with endohedrally *incarcerated* ^{3}He, also denoted as $^3He@C_{84}$)[29] obtained from high-pressure helium capture by a C_{84} sample.[68] Further investigations showed that the carbon cages can encapsulate even two ^{3}He atoms and the according $i^3He_2C_{2n}$ fraction increased with increasing cage size. A first attempt to structurally assign minor C_{84} isomers was made by Taylor and co-workers through ^{13}C NMR analysis of different chromatographically purified fractions.[69] Shinohara, Achiba, and co-workers finally succeeded in isolating a number of minor C_{84} isomers from material accumulated during extensive HPLC purification of endohedral metallofullerenes.[70,71] ^{13}C NMR spectroscopic analysis showed the isolated isomers to have C_s(a)-, C_s(b)-, C_2-, D_2(II)-, and D_{2d}(I)-symmetries and a mixed fraction[72,73] to consist of D_{3d}- and D_6-symmetric cages. An as yet unobserved C_2-symmetric [84]fullerene isomer was obtained by multistage HPLC purification of soot produced by direct current arc discharge using Dy_2O_3/graphite composite rods.[74] Modeling of the ^{13}C NMR shifts of all C_{84} isomers by the IGLO−DFTB (individual gauge for local orbitals−density functional tight binding)[75] or the GIAO method at the B3LYP/6-31G* level of theory[76,77] support the assignment of the main C_{84} isomers and, in some cases, give good hints at the structures of isolated minor isomers.

Enriched samples of fullerenes with more than 84 C-atoms were obtained as early as 1991.[7,49,78] Purification efforts by Achiba, Miyake, and co-workers resulted in ^{13}C NMR data of fullerenes such as C_{86}, C_{88}, C_{90}, C_{92}, and C_{94}.[50,79,80] Comparison of the experimental spectra of two C_s- and three C_2-symmetric isomers of C_{86} and C_{88} to those calculated using the GIAO method, in combination with energetic considerations, prompted Sun and Kertesz to identify the following structures: $C_{86}(16)$-C_s,[61] $C_{86}(17)$-C_2, $C_{88}(7)$-C_2, $C_{88}(17)$-C_s, and $C_{88}(33)$-C_2.[81,82] By multistage recycling HPLC purification of the extract of soot obtained by DC arc discharge of dysprosium/graphite composite rods, Shinohara, Prato, and co-workers obtained two [92]fullerene fractions.[83] Whereas one of them was a mixture of several isomers, the other one consisted of a pure C_2-symmetric isomer (one out of 16 C_2-symmetric structures out of altogether 86 IPR-conforming C_{92} allotropes)[14] as revealed by ^{13}C NMR spectroscopy. Interestingly, encapsulation of a Dy atom in the C_{92}-C_2 or $C_{82}(9)$-C_{2v} cages leads to an enhancement of the second hyperpolarizability whereas incorporation of a second one results in a decrease.[84]

Higher fullerenes can be transformed into smaller cages, a process known since the early days of fullerene research to occur under the conditions of mass spectrometry by progressive ejection of C_2 fragments from the cages.[85] Cross and Saunders have investigated the transmutation of fullerenes by subliming them into a stream of Ar passed through an oven at ∼1000 °C. They found that C_{76}, C_{78}, and C_{84}−but neither C_{60} nor C_{70} (1110 °C)−readily lose carbon atoms to form smaller fullerenes.[86] In the case of C_{78}, some isomerization was also seen. About a decade earlier, Hawkins and Meyer studied the possible racemization of C_{76}-D_2 and $C_{84}(22)$-D_2 (the enantiomers of the latter can, in principle, be interconverted by two Stone−Wales pyracylene rearrangements[87,88] via the achiral $C_{84}(23)$-D_{2d}).[89] But neither heating (600/700 °C) nor irradiation ($\lambda = 193$ nm) led to a significant loss of optical activity in samples of enantiomerically enriched cages. This showed that the activation barrier for a Stone−Wales rearrangement amounts to ≥ 83 kcal mol^{-1}. On the other hand, the observation of spectrally broad transient spectra of higher fullerenes (C_{76}, C_{84}, C_{86}, C_{90}) after excitation at 388 nm was considered as evidence for photoisomerization.[90]

Unlike the achiral carbon compounds C_{122}, C_{121},[91−94] and C_{120},[95,96] consisting of two C_{60}-cages[97] interconnected by two, one, and zero carbon atoms, respectively, a chiral allotrope, C_{119}, was isolated in the form of a ^{13}C-enriched sample from the thermolysis of $C_{120}O$.[98] Krätschmer and co-workers proposed a C_2-symmetric, peanut-shaped structure consisting of two fullerene-like C_{58} units bridged by three C(sp^3)-atoms,[98] a structure supported by computation of its ^{13}C NMR spectrum.[93,99]

At the end of this section on chiral carbon allotropes, it should be mentioned that most carbon nanotubes, which in their idealized single-walled form can be considered as extremely large and oblong fullerenes, are chiral. In fact, the central part represents a graphite lattice that is rolled up into a cylinder, a "process" that does not necessarily have to occur parallel or perpendicular to opposite edges of the constituting hexagons. Any intermediate orientation leads to an arrangement of the honeycomb lattice in which the tube walls can be considered as interlocking helical strands of edge-sharing hexagons winding around the axis of the tube (Figure 9).[5,6,100−104] The discovery of helical carbon nanotubes by Iijima et al. in the early 1990s[105,106] was later confirmed by STM (scanning tunneling microscopy) images of single nanotube surfaces resolved at the atomic level.[107−109] The helicity of nanotubes is of prime importance for potential technological applications, as it is closely related to electronic structure and properties.[110,111]

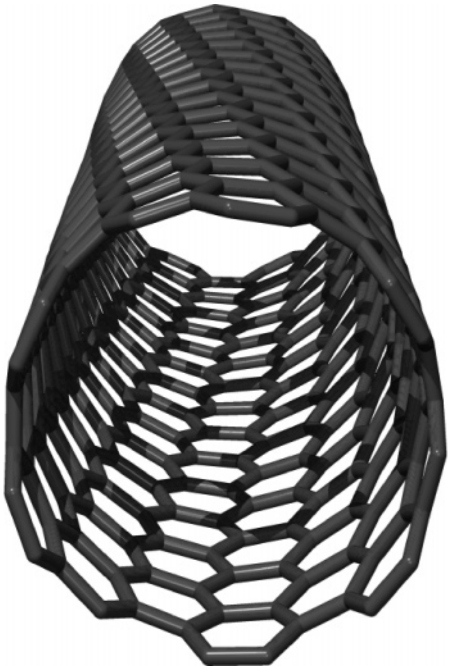


Figure 9. Chiral (9,6)-SWNT (single-walled carbon nanotube). The pair of integers (9,6) defines the roll-up vector, which describes the orientation of the furled graphite sheet in relation to the axis of the tube. Except for the vectors (*n*,*n*) and (*n*,0), which correspond to the so-called "armchair" and "zig-zag" tubes, respectively, all SWNTs are chiral.[5,6,100,102] The multiple-helical arrangement of zig-zag chains of carbon atoms becomes nicely apparent in the perspective view.

3.2. Resolution of Chiral Fullerenes and Configurational Assignments

In 1993, Hawkins and Meyer effected a kinetic resolution of C_{76}-D_2 by asymmetric Sharpless osmylation of the racemic fullerene, using OsO_4 complexes with an enantiomerically pure ligand derived from a cinchona alkaloid (Figure 10).[112] Incomplete osmylation of (±)-C_{76} afforded enantiomerically enriched unreacted [76]fullerene and a diastereoisomerically enriched osmate complex. Removal of the addend from the latter with $SnCl_2$ yielded C_{76} enriched in the other enantiomer. When a pseudoenantiomeric ligand was used in the osmylation of (±)-C_{76}, the opposite optical antipodes of the carbon cage were enriched in the starting material and the product (Figure 10). With enriched samples of both C_{76} enantiomers in hands, Hawkins and Meyer recorded the first CD spectra of the chiral carbon allotrope.[112] Application of the same kinetic resolution procedure to C_{78} and to C_{84}

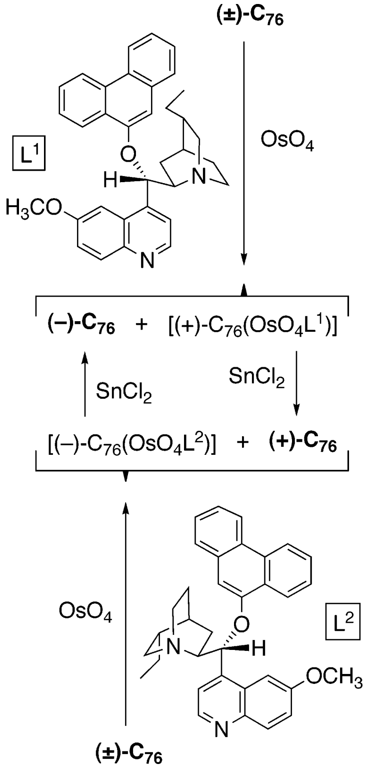


Figure 10. Kinetic resolution of (±)-C_{76}-D_2 by reaction of the fullerene with enantiomerically pure, pseudoenantiomeric OsO_4 complexes and regeneration of the pristine carbon cages by reduction of the adducts with $SnCl_2$.[112]

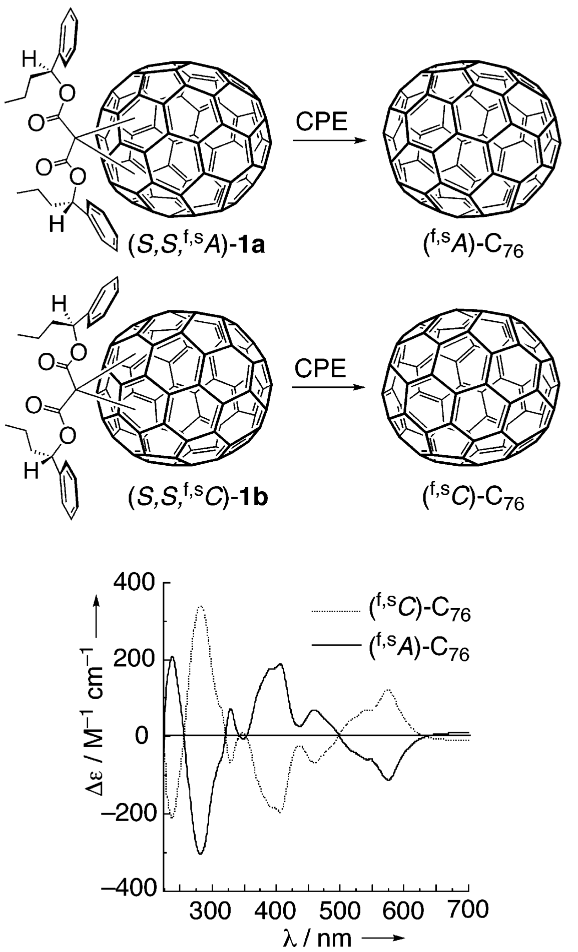


Figure 11. Last step of a resolution procedure for C_{76}-D_2 (top), electrochemical retro-Bingel reaction with two separated diastereoisomeric adducts having enantiomeric carbon cages, and CD spectra (CH_2Cl_2) and configurational assignment (bottom) of the enantiomers of [76]fullerene.[114]

afforded the respective data for the optical antipodes of C_{78}-D_3 and $C_{84}(22)$-D_2.[89]

The Cotton effects in the CD spectra reported by Hawkins and Meyer[112] for C_{76} were significantly smaller ($\Delta\epsilon \leq 32$ M^{-1} cm^{-1}) than those measured by Diederich and co-workers for a number of optically pure, covalent derivatives of this fullerene ($\Delta\epsilon \leq 250$ M^{-1} cm^{-1}) (see sections 3.4.1 and 3.4.2).[113] To reinvestigate the chiroptical properties of enantiomerically pure [76]fullerene, a resolution using the so-called Bingel/retro-Bingel approach was carried out.[114] This separation procedure consists of three steps, starting with the cyclopropanation of a fullerene mixture with 2-halomalonates (Bingel reaction).[115] The fullerene-derived esters are generally easier to separate than the unfunctionalized carbon cages, and once this is achieved, the Bingel addends are removed by exhaustive constant potential electrolysis (CPE) at a potential situated, in general, slightly below the second reduction potential of the adduct (electrochemical retro-Bingel reaction[116]), under regeneration of the pristine fullerene.[114,117−119] In summary, the method involves a reversible functionalization of fullerenes including a facilitated separation of the intermediate covalent derivatives. Pure C_{76} enantiomers were thus obtained by electrochemical retro-Bingel reaction[116] with each of $(S,S,{}^{f,s}A)$-**1a** and $(S,S,{}^{f,s}C)$-**1b** (Figure 11), two diastereoisomeric mono-adducts of C_{76}-D_2 with enantiomeric carbon cores, prepared by Bingel reaction of (±)-C_{76}-D_2 with bis((*S*)-1-phenylbutyl) 2-bromomalonate.[113] The CD spectra of the separately generated optical antipodes of C_{76}-D_2 (Figure 11) displayed the expected mirror image shapes with band positions in full agreement with those of Hawkins and Meyer[112] but with Cotton effects that are about an order of magnitude larger ($\Delta\epsilon \leq 320$ M^{-1} cm^{-1}). The latter figures are in good agreement with those measured for optically pure C_{76} derivatives[113] and with calculated values.[120−122]

Taking into account the roundish shape of pristine carbon cages and the lack of functional groups, the direct chromatographic resolution of fullerene enantiomers on a chiral stationary phase (CSP) appears as a difficult enterprise. It was finally achieved, though, for C_{76} by Okamoto and co-workers through recycling HPLC on amylose tris[(3,5-dimethylphenyl)carbamate] with hexane/$CHCl_3$ 80:20 as an eluent.[123]

Bingel cyclopropanation of the C_{84} fraction of fullerene soot (main constituents: $C_{84}(22)$-D_2 and $C_{84}(23)$-D_{2d}) with optically pure bis[(*S*)-1-phenylbutyl] 2-bromomalonate afforded a series of mono- and bis-adducts, among which was a pair of C_2-symmetric bis-adducts ($(S,S,S,S,{}^{f,s}A)$-**2a** and $(S,S,S,S,{}^{f,s}C)$-**2b**, Figure 12)[124] featuring mirror-image CD spectra with relatively large Cotton effects.[65] Such spectra are characteristic of diastereoisomers with enantiomeric carbon cores, for which the chiroptical contributions of the inherently chiral fullerene chromophores dominate those of the chiral addends by far.[4] Besides, the UV/vis spectra differed considerably from those of $C_{84}(23)$-D_{2d} derivatives, which pointed at the presence of $C_{84}(22)$-D_2 adducts. Electrolysis of the separated diastereoisomers $(S,S,S,S,{}^{f,s}A)$-**2a** and $(S,S,S,S,{}^{f,s}C)$-**2b** under retro-Bingel conditions[116] afforded the enantiomers of pristine $C_{84}(22)$-D_2. Their mirror image CD spectra (Figure 12) correspond nicely to those

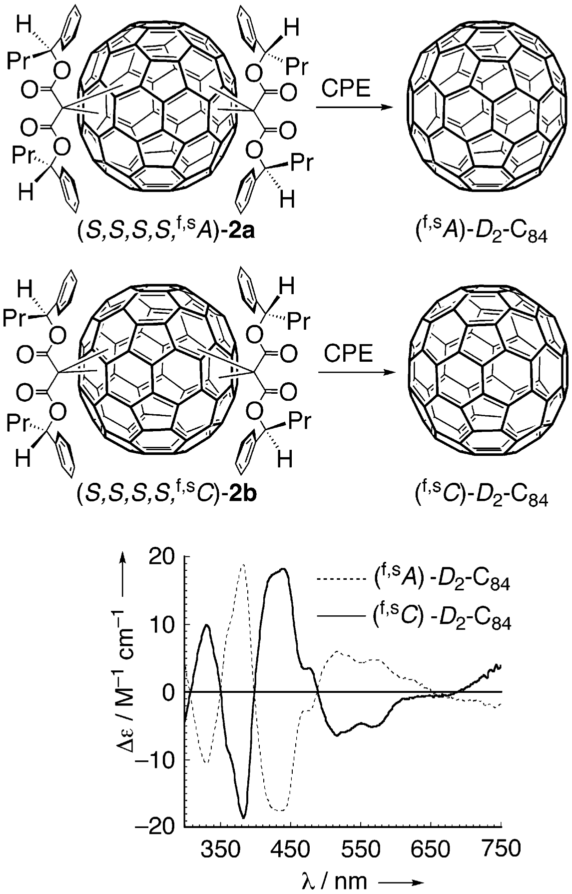


Figure 12. Last step of a resolution procedure for $C_{84}(22)$-D_2 (top), electrochemical retro-Bingel reaction with two separated diastereoisomeric bis-adducts having enantiomeric carbon cages, and CD spectra (CH_2Cl_2) and configurational assignment (bottom) of the enantiomers of $C_{84}(22)$-D_2.[65]

reported by Hawkins et al. for samples obtained by kinetic resolution via asymmetric osmylation (vide supra).[89]

Theoretical calculation of the CD spectra of C_{76}-D_2 [120,121] by the π-electron SCF−CI−DV MO (self-consistent field−configuration interaction−dipole velocity molecular orbital) method[121,125,126] and comparison with the experimental data[112,114] allowed the assignment of absolute configurations to the isolated enantiomers of [76]fullerene, which can be denominated as [CD(−)282]-($^{f,s}A$)-C_{76}-D_2 and [CD(+)282]-($^{f,s}C$)-C_{76}-D_2 (Figures 8 and 11).[121] The absolute configuration of [76]fullerene was also determined as $(+)_{589}$-($^{f,s}C$)-C_{76} by comparison of the experimental and predicted optical rotatory dispersion (ORD) patterns.[127] The experimental ORD pattern was derived from the experimental electronic circular dichroism (ECD) spectrum using the Kramers−Kronig (KK) transform.

The CD spectrum of $C_{84}(22)$-D_2 has been simulated by Furche and Ahlrichs using TDDFT (time-dependent density functional theory),[122] a technique that allows large-scale and often quantitative simulation of absorption and CD spectra and, as opposed to semiempirical methods,[128] is accurate enough to determine the absolute configuration of fullerenes. The theoreticians found a surprisingly good qualitative agreement between the experimental data[65] and the calculations,[122] and the enantiomers of $C_{84}(22)$-D_2 can now be addressed as [CD(+)380]-($^{f,s}A$)-C_{84}-D_2 and [CD(−)380]-($^{f,s}C$)-C_{84}-D_2 (Figures 8 and 12).[124] As to the calculated intensities, they differ from the experimental measurements[65,89] by roughly an order of magnitude, a discrepancy that still needs to be resolved.

3.3. Endohedral Derivatives of Higher Fullerenes

3.3.1. Nonmetal Incarceranes

As a consequence of their cage structure, C_{60} and higher fullerenes can incarcerate metal atoms (section 3.3.2), noble gases,[67,68,129−138] and other nonmetal atoms such as nitrogen or phosphorus.[139−145] Compounds with incarcerated ^{3}He have been used, in particular, to investigate the composition,[67,68,134] separation,[67] and transmutation[86] of higher fullerene samples (see also section 3.1) and to probe the magnetic field[146,147] inside anions of the larger[148,149] and the two smaller (C_{60} and C_{70})[150−153] carbon cages.

3.3.2. Metal Incarceranes

The first fullerenes with entrapped metals (endohedral metallofullerenes) were identified[154] and isolated[155] very shortly after the discovery of the empty carbon cages.[1] Since then, the field has developed explosively, driven by the structural novelty and the interesting electronic properties that hold great promise for materials and biomedical applications.[155−165] But despite the plethora of species generated, complete structural elucidation of single species has remained relatively rare due to problems such as low solubility/extractability, low stability under ambient conditions (oxygen, moisture), or tedious separation from other cage homologues and isomers. In addition, the paramagnetism of many endohedral metallofullerenes hampers NMR spectroscopic analysis and, even if this is not the case, the obtained symmetry information alone is relatively unmeaningful because the metal-filled cages observe the IPR "rule" less strictly than the empty counterparts.

A non-IPR structure is found, for example, in $i(Sc_3N)$-C_{68}-D_3 (IUPAC notation[29] for the commonly used $Sc_3N@C_{68}$), a member of a family of nonclassical endohedral metallofullerenes, $i(REM_xSc_{(3-x)}N)C_{68}$ (where REM = rare-earth metal and $x = 0-2$), prepared by the Krätschmer−Huffmann arc method[2] from graphite rods doped with a mixture of scandium and rare-earth metal (REM) oxide in a dynamic atmosphere of He and N_2.[166,167] The incarcerane $i(Sc_3N)C_{68}$ consists of a planar, D_{3h}-symmetric Sc_3N unit encased in a D_3-symmetric C_{68} cage for which the spiral algorithm[14] finds 6332 distinct isomers made up of pentagons and hexagons. Of these, only 11 isomers with 3-fold symmetry are consistent with the single symmetric line and the 12 singlets (11 of intensity 3, one of intensity 1) in the measured ^{45}Sc and ^{13}C NMR spectra, respectively. On the basis of density-functional calculations, which nicely reflect the finding that each pentalene unit (pair of fused pentagons) in a neutral fullerene accounts for an energy penalty of ca. 70−90 kJ mol^{-1},[168] one (isomer no. 6140) out of two structures with a minimum of three such units was proposed for $i(Sc_3N)C_{68}$-D_3 (Figure 13).[166] This prediction was confirmed by X-ray crystallography of $i(Sc_3N)C_{68}\cdot[Ni^{II}(OEP)]\cdot 2C_6H_6$ (OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato(2−)), which showed also that the principal scandium sites are the bulges (locations of maximum curvature) created by the pentalene units.[167] A computational study on relative energies of isomers, geometric data, and the ^{13}C NMR pattern provided further insight into structural details.[169]

A confident structural assignment was possible for iLa_2C_{72} a "filled" counterpart of the "missing" empty cage C_{72}.[170]

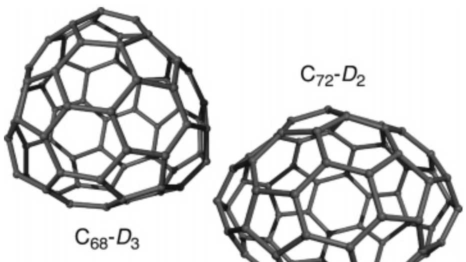


Figure 13. Cage structures of i(Sc$_3$N)C$_{68}$-D_3 (isomer no. 6140, viewed along the C_3 axis), and iLa$_2$C$_{72}$-D_2 (isomer no. 10611, viewed along a C_2 axis). The structures do not obey the isolated pentagon rule (IPR) and contain three (C$_{68}$) and two (C$_{72}$) pentalene units (lying in the "plane of the paper"), which lead to bulges in the spheroids.[166]

Nuclear magnetic resonance analysis revealed a single broad ^{139}La resonance at −575.6 ppm, indicating two geometrically equivalent lanthanum atoms, and 18 ^{13}C NMR signals of equal intensity in a diamagnetic chemical shift range between 130 and 160 ppm. The latter are in contradiction with the only IPR-conforming D_{6d}-symmetric structure of C$_{72}$,[14] and this is further corroborated by a low-field resonance at 158.1 ppm, which is typical for pentagon−pentagon fusion sites. Of a total of 11 189 non-IPR isomers of C$_{72}$ with pentagonal and hexagonal faces,[171] 24 D_2-symmetric structures satisfy the observed NMR spectra, and two of these include a minimum of only two pentalene units. Based on a comparison between UV/vis/NIR absorption onset and calculated HOMO−LUMO gaps as well as isomer stabilities, structure no. 10 611 (Figure 13) was finally assigned to the isolated iLa$_2$C$_{72}$.[170]

Multistage HPLC was used by Kodama et al. to isolate three isomers of iTmC$_{82}$.[172] Although these divalent metallofullerenes (iTm^{2+}C$_{82}^{2-}$) are paramagnetic, no unpaired electron resides on the cages, and ^{13}C NMR spectroscopy allowed the determination of the molecular symmetries as C_s, C_2, and C_{2v}. Whereas the cages of the former two could not be unambiguously assigned to specific IPR-conforming [82]fullerene structures, that of the last isomer corresponds to the single C_{2v}-symmetric isomer,[172] which was also identified[173] in the long-known iLaC$_{82}$.[155] The latter incarcerane is a trivalent metallofullerene (iLa^{3+}C$_{82}^{3-}$) with an unpaired electron on the carbon shell, which impedes ^{13}C NMR measurements, a problem that was elegantly circumvented by Akasaka et al. by recording the resonances of the electrochemically generated monoanion.[173] C_2-Symmetry was also found for an isomer of iCaC$_{82}$ by ^{13}C NMR and ultraviolet photoelectron spectroscopy, but again no specific cage assignment was possible.[174,175]

Despite the difficulties in the isolation, purification, and structural elucidation of endohedral metallofullerenes, a remarkable number of structures have recently been identified with certainty or great confidence. Among these incarceranes, most of which are achiral, should be mentioned iSc$_2$(C$_{66}$-C_{2v}) (non-IPR cage),[176,177] iCa(C$_{74}$-D_{3h}),[178] iLa$_2$(C$_{78}$(5)-D_{3h}),[179] i(Sc$_3$N)(C$_{78}$(5)-D_{3h}),[180] titanium carbide incarcerane i(Ti$_2$C$_2$)(C$_{78}$-D_{3h})[181] (previously assigned as iTi$_2$(C$_{80}$-I_h)[182]), iTi$_2$(C$_{80}$-D_{5h}),[182] i(Sc$_3$N)(C$_{80}$-D_{5h}),[183,184] i(Dy$_3$N)(C$_{80}$-D_{5h}),[185] i(Tm$_3$N)(C$_{80}$-D_{5h}),[186] iLa$_2$(C$_{80}$-I_h),[187,188] i(Sc$_3$N)(C$_{80}$-I_h),[184,189] i(ErSc$_2$N)(C$_{80}$-I_h),[190] i(Gd$_3$N)(C$_{80}$-I_h),[191] i(Tb$_3$N)(C$_{80}$-I_h) and i(Ho$_3$N)(C$_{80}$-I_h),[192] i(Dy$_3$N)(C$_{80}$-I_h),[185] i(Tm$_3$N)(C$_{80}$-I_h),[186] i(Lu$_3$N)(C$_{80}$-I_h),[193] i(Sc$_3$C$_2$)(C$_{80}$-I_h)[194] (scandium carbide incarcerane; this structure was previously interpreted as iSc$_3$(C$_{82}$(7)-C_{3v})[195]), iY(C$_{82}$-C_{2v}),[196] iLa(C$_{82}$-C_{2v}),[173,197] iPr(C$_{82}$-C_{2v}),[198] iDy(C$_{82}$-C_{2v}),[199] iTm(C$_{82}$-C_{2v}),[172] iCa(C$_{82}$-C_{2v}),[200] iLa(C$_{82}$(6)-C_s),[201] iEr$_2$(C$_{82}$(6)-C_s),[202] iEr$_2$(C$_{82}$(8)-C_{3v}),[203] iY$_2$(C$_{82}$(8)-C_{3v}), i(Y$_2$C$_2$)(C$_{82}$-C_{2v}),[204] i(Y$_2$C$_2$)(C$_{82}$(8)-C_{3v}),[204] iSc$_2$(C$_{84}$(23)-D_{2d}),[205,206] and i(Sc$_2$C$_2$)(C$_{84}$(23)-D_{2d}).[207] A major advance in the purification of the trimetallic nitride incarceranes has recently been reported by Dorn, Gibson, and co-workers: it makes these compounds available in multimilligram quantities and takes advantage of their extraordinary kinetic stability as compared with other fullerenes in Diels−Alder reactions with a cyclopentadiene-functionalized resin.[208] The thermodynamic stability of the known incarceranes of this type is related to the six electrons transferred to the carbon cage, which is described by the ionic model i(Met$_3$N^{6+})C$_{2n}^{6-}$ (Met = metal). In fact, the empty cages of all known trimetallic nitride endohedral fullerene complexes (C$_{68}$(6140)-D_3, C$_{78}$(5)-D_{3h}, C$_{80}$(6)-D_{5h}, and C$_{80}$(7)-I_h) have a (LUMO + 3)−(LUMO + 4) gap larger than 1 eV, which corresponds to a large HOMO−LUMO gap in the incarcerane.[209] The only notable exception to this correlation is buckminsterfullerene itself, which is too small to accommodate a trimetallic nitride cluster, although it meets the electronic criterion.

3.3.3. Derivatives of Metal Incarceranes

After some exploratory work on the chemistry of endohedral metallofullerenes had been carried out around the mid-1990s,[158,161,210] activity in this field seems to have rekindled for the last two years. In most cases, however, complete structural elucidation was not possible, even if single products were isolated.

Photoinduced addition of 1,1,2,2-tetramesityl-1,2-disilirane or a related digermirane[211] to endohedral metallofullerenes such as iLaC$_{82}$, iGdC$_{82}$, iLa$_2$C$_{80}$, iSc$_2$C$_{84}$, and i(Sc$_3$N)(C$_{80}$-I_h) yielded isomeric mixtures of mono-adducts.[212−216] In contrast to the empty cages, most of the endohedral metallofullerenes (but not i(Sc$_3$N)(C$_{80}$-I_h))[216] also react thermally with the disilirane reagent. This reactivity seems to be related to the stronger electron acceptor as well as the stronger electron donor properties of the metal incarceranes when compared with the empty cages.[158] Very recently, full structural elucidation was possible for the mono-adduct obtained by heating iCe$_2$(C$_{80}$-I_h) with 1,1,2,2-tetrakis(2,4,6-trimethylphenyl)-1,2-disilirane at 80 °C in toluene.[217] The C_2-symmetric product (±)-**3** (Figure 14), easily isolated by HPLC, was analyzed by means of MS and ^{1}H and ^{13}C NMR spectroscopy (ROESY [rotating frame overhauser enhancement spectroscopy] and HMBC [heteronuclear multiple bond correlation]), as well as by X-ray crystallography. The silanomethanosilano addend is bridging the diametrically opposed positions C(1) and C(7)[34] of a six-membered ring of the fullerene, both bridgeheads being 665[218] atoms. This results in an inherently chiral functionalization pattern on the highly symmetric carbon cage. Interestingly, the free random motion of the two Ce atoms, which occurs in pristine iCe$_2$(C$_{80}$-I_h), is frozen in specific positions by the exohedral functionalization.

The first structurally characterized derivative of an endohedral metallofullerene was obtained by Diels−Alder addition of 4,5-dimethoxy-o-quinodimethane to i(Sc$_3$N)(C$_{80}$-I_h). X-ray crystallography revealed that addition had occurred across a 6−5 bond of the C$_{80}$-I_h cage and that the Sc$_3$N unit

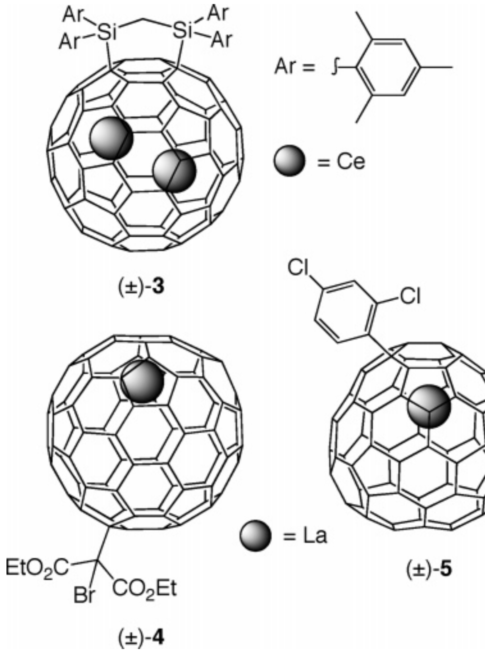


Figure 14. Chiral metallofullerene derivatives resulting from the reaction of *i*Ce_2(C_{80}-I_h) with 1,1,2,2-tetrakis(2,4,6-trimethylphenyl)-1,2-disilirane ((±)-**3**; view along a C_2 axis of the parent fullerene for which the plane of the paper represents a mirror plane—note that the addend is lying "in front" of this plane), of *i*La(C_{82}-C_{2v}) with diethyl bromomalonate in the presence of DBU ((±)-**4**; the plane of the paper represents one mirror plane of the parent fullerene, and the "bottom" bond is bisected by the other), and of *i*La(C_{74}-D_{3h}) with 1,2,4-trichlorobenzene at reflux temperature ((±)-**5**; view along the C_3 axis of the parent fullerene for which the plane of the paper represents a mirror plane—note that the addend is lying "in front" of this plane). The structures have been elucidated by X-ray crystallography.[217,231,233] Double bonds are omitted for clarity.

of the C_s-symmetric molecule was located away from the addition site.[219,220] A bis-adduct of *i*(Gd_3N)(C_{80}-I_h) was isolated from its reaction with an excess of the above diene.[221] Incarceranes *i*(Sc_3N)(C_{80}-I_h) and *i*(Er_3N)(C_{80}-I_h) underwent also [3 + 2] cycloaddition with C_{2v}-symmetric azomethine ylides to afford achiral mono-adducts by addition across the 5−6 bond.[222,223] Conversely, addition of *N*-ethylazomethine ylide to *i*(Y_3N)(C_{80}-I_h) gave exclusively the 6−6 regioisomer (C_s-symmetric), showing a strong dependence of the exohedral functionalization mode on the encaged metal cluster.[224] Cylopropanation with diethyl bromomalonate occurred in the same manner, whereas it completely failed with *i*(Sc_3N)(C_{80}-I_h).[224] Both the C_{2v}-symmetric 6−6 and the C_s-symmetric 6−5 adducts were obtained by reaction of *i*La_2(C_{80}-I_h) with the azomethine ylide generated by thermal CO_2 extrusion from *N*-trityl-1,3-oxazolidin-5-one. As shown by X-ray crystallography, the two La atoms are fixed in the 6−6 adduct, unlike the random circulation of the metals in *i*La_2(C_{80}-I_h).[225] Mono-, bis-, and even higher dihydropyrrolofullerenes were obtained from *i*GdC_{82}[226] and *i*LaC_{82}.[227] Cycloaddition between the latter and cyclopentadiene yielded a single mono-adduct regioisomer, which underwent the retro-reaction much more easily than the corresponding derivative of C_{60}.[228] A regioselective reaction was observed upon irradiation of solutions of *i*La(C_{82}-C_{2v})[229] or *i*(Sc_3C_2)(C_{80}-I_h)[194] in the presence of spiro[3*H*-diazirine-adamantane]. In both cases, the intermediately formed adamantylidene carbene adds to a 6−6 bond of the fullerene cage, and X-ray crystallographic analysis points at 6−6 open adduct structures. Reaction of a metallofullerene sample of enriched *i*YC_{82} (paramagnetic) with CF_3CO_2Ag at 10^{-6} Torr and 400 °C yielded two stable isomers of diamagnetic *i*$YC_{82}(CF_3)_5$ as main products displaying five ^{19}F NMR resonances each.[230] Based on a combination of 2D ^{19}F NMR spectroscopy, stability considerations as obtained from DFT calculations using C_{82}-C_{2v} as parent fullerene model, and the knowledge of the course of the corresponding reaction with C_{60} (cf. section 4.11.2), Kareev, Boltalina, and co-workers proposed an addition pattern with 1,4-relationships between nearest trifluoromethyl neighbors across four contiguous six-membered rings of the fullerene. A diamagnetic, C_1-symmetric adduct with one singly bonded addend was obtained as the main product from the reaction of *i*LaC_{82} with diethyl bromomalonate in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene).[231] Aside from the 81 ^{13}C NMR resonances in the C(sp^2) spectral region, the structure of (±)-**4** (Figure 14) was unequivocally unveiled by X-ray crystallography, showing the $CBr(CO_2Et)_2$ addend to be attached to the core C-atom that adjoins to the C−C unit bisected by the two mirror planes of *i*La(C_{82}-C_{2v}). In fact, this is the atom with the highest Mulliken charge density and the second-largest local strain as indicated by π-orbital axis vector (POAV)[232] analysis.[231] The La ion, on the other hand, occupies a localized site remote from the addend. Differential pulse voltammetry (DPV) and UV/vis/NIR spectroscopy show the closed-shell adduct (±)-**4** to have a considerably larger HOMO−LUMO gap than the open-shell *i*La(C_{82}-C_{2v}).[231]

Another chiral metallofullerene derivative with a single functionalized C-atom was obtained by surprise during the extraction of soot containing La-incarceranes with 1,2,4-trichlorobenzene.[233] The fraction attributed to *i*LaC_{82} was EPR (electron paramagnetic resonance)-silent, although La-monometallofullerenes are known as open-shell structures due to the transfer of three electrons from the endohedral atom to the cage. ^1H and ^{13}C NMR, 2D NMR (HMQC [heteronuclear multiple quantum coherence] and HMBC), and UV/vis spectroscopies pointed at the presence of three C_1-symmetric structures with the same fullerene cage and three isomeric dichlorophenyl groups. X-ray crystallography of one isomer unambiguously revealed a derivative of *i*La(C_{74}-D_{3h}) ((±)-**5**, Figure 14) in which a single cage carbon atom is attached to a 2,4-dichlorophenyl ring. The latter must originate from the solvent by loss of a chlorine atom, and a radical addition mode is supported by calculations showing that ca. 50% of the spin density of *i*La(C_{74}-D_{3h}) is confined to three cage positions including the actually functionalized C-atom. This leads to an unseen functionalization pattern in the lanthano[74]fullerene derivative (±)-**5**, which has a closed-shell electronic structure.[233]

3.4. Covalent Derivatives of Higher Fullerenes

Due to the low abundance of the larger carbon cages in fullerene soot, as well as the tediousness of their chromatographic isolation, they have been derivatized much less in comparison to buckminsterfullerene.[4,16,20,21] But the lower symmetry of most of the accessible higher homologues of C_{60} and C_{70} and, *a fortiori*, the inherent chirality of representatives such as C_{76}-D_2, C_{78}-D_3, and C_{84}(22)-D_2 is at the origin of a large fraction of chiral compounds among the isolated and characterized derivatives.

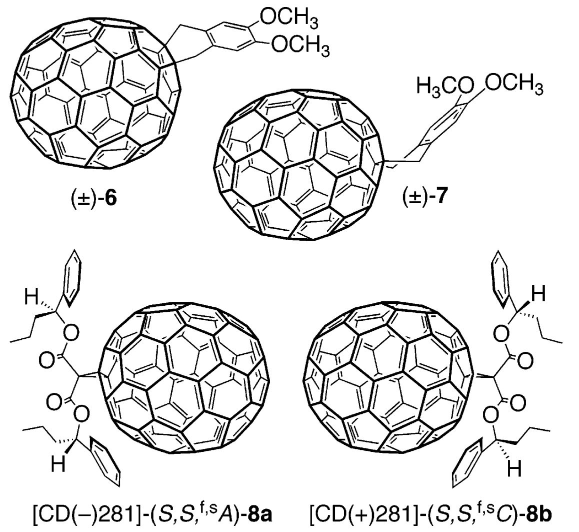


Figure 15. Confidently assigned mono-adducts of C_{76}-D_2: two constitutionally isomeric Diels−Alder adducts ((±)-**6** and (±)-**7**)[234] and a diastereoisomeric pair of Bingel adducts ((*S*,*S*,^{f,s}*A*)-**8a** and (*S*,*S*,^{f,s}*C*)-**8b**).[113] The absolute configuration of the latter was assigned by comparison of the CD spectra to those of the optical antipodes of the parent fullerene (cf. Figure 11).

3.4.1. o-Quinodimethane Adducts of C_{76}

The addition of 3,4-dimethoxy-*o*-quinodimethane to racemic C_{76}-D_2 yielded at least six constitutionally isomeric 6−6 adducts (these result from addition across the fusion site of two six-membered rings).[234] The major product was isolated in pure form and assigned the C_1-symmetric C(25)−C(26)-adduct structure (±)-**6** (Figure 15, for the IUPAC numbering of C_{76}, see Figure 4) based on a combination of ^{1}H NMR spectroscopic analysis and the assumption of a high reactivity of bonds located in regions of strong spheroid curvature. In addition, a C_2-symmetric mono-adduct, isolated in a mixture with two other C_1-symmetric isomers, was assigned the structure of the apical C(27)−C(50)-adduct (±)-**7**.[234] The addition patterns of (±)-**6** and (±)-**7** involve the most pyramidalized C-atoms of C_{76}-D_2 and correspond to the regioisomers proposed by Hawkins et al. for the main products of the osmylation reaction.[112]

3.4.2. Nucleophilic Cyclopropanation of C_{76}-D_2, C_{78}-D_3, and C_{84}

Bingel cyclopropanation[115] of racemic C_{76}-D_2 with bis-[(*S*)-1-phenylbutyl] 2-bromomalonate yielded mainly six mono-adducts, which were isolated by HPLC to afford the first optically pure adducts of an inherently chiral fullerene. UV/vis, CD, and ^{13}C NMR spectra showed distinct similarities pairwise, thus allowing facile identification of the three constitutionally isomeric pairs of diastereoisomers, namely, two of C_1- and one (**8a**/**8b**, Figure 15) of C_2-symmetry.[113] The CD spectra[113] displayed pronounced Cotton effects with $\Delta\epsilon$ values up to 250 M^{-1} cm^{-1}, which is comparable to those of the pure enantiomers of the parent C_{76}-D_2 [114] (see Figure 11). Pronounced similarity, with regard to band positions and shape, of the CD spectra of diastereoisomers **8a** and **8b** on one hand and those of the pure optical antipodes of [76]-fullerene on the other allows a configurational assignment of these mono-adducts as [CD(+)-281]-(*S*,*S*,^{f,s}*C*)-**8a** and [CD-(−)-281]-(*S*,*S*,^{f,s}*A*)-**8b** (Figure 15).

Bingel reaction of a 3:1 isomeric mixture of $C_{78}(2)$-C_{2v} and C_{78}-D_3 with diethyl 2-bromomalonate yielded, among others, three isomeric tris-adducts that displayed a higher symmetry than C_1 and could, therefore, be unambiguously assigned to their respective parent [78]fullerene isomers.[235] By comparison of the UV/vis and ^{13}C NMR spectra of a C_2-symmetric tris-adduct of $C_{78}(2)$-C_{2v} to those of the obtained bis-adducts, three possible structures ((±)-**9**, Figure 16) were proposed for a C_1-symmetric bis-adduct, which was identified as a precursor to tris-adduct (±)-**10**. Both (±)-**9** and (±)-**10** have an inherently chiral functionalization pattern, but they are derived from achiral $C_{78}(2)$-C_{2v}. For symmetry reasons, a common addend position in the two adducts must be the bond C(73)−C(78) (Figure 16; for the atom numbering see ref 34) bisected by the 2-fold symmetry axis of the parent fullerene. Based on π-bond order considerations[32] and steric effects, the second ((±)-**9**) and symmetry-related third ((±)-**10**) addends are most likely located at one out of three positions within the six-membered ring indicated in Figure 16.[235]

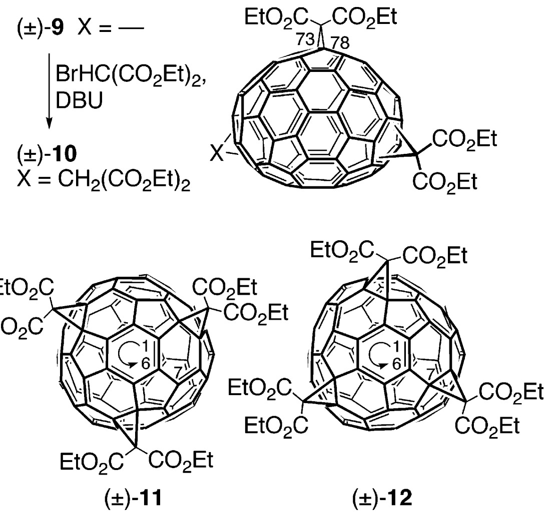
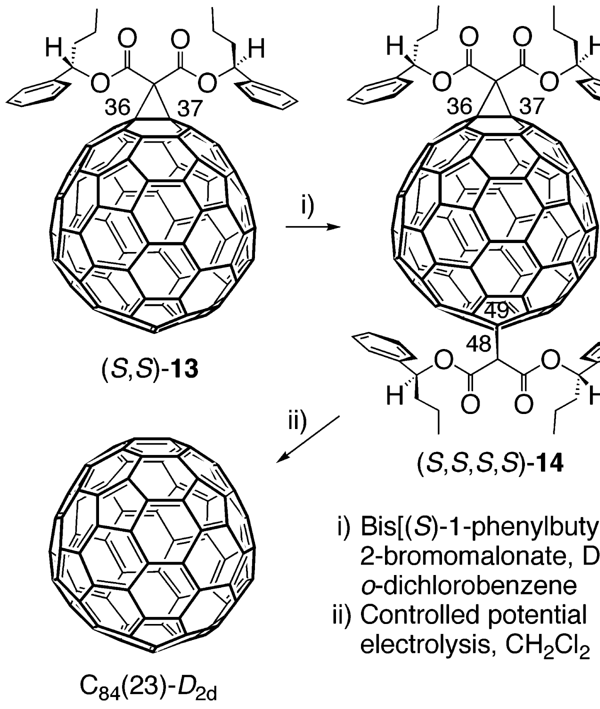


Figure 16. Structures proposed for a tris-adduct of $C_{78}(2)$-C_{2v} (the "top" addend is lying on the C_2 symmetry axis) and its bis-adduct precursor (top)[235] and two constitutionally isomeric arrangements (bottom) proposed as possible structures for a tris-adduct of C_{78}-D_3.[235]

A pure, C_3-symmetric Bingel-type tris-adduct of C_{78}-D_3 was proposed to have either of two constitutionally isomeric structures, (±)-**11** or (±)-**12** (Figure 16), each of which is distinguished by three homotopic addends showing the same pairwise local arrangement that corresponds to the *equatorial* relationship in C_{60} (cf. section 4.1 and Figure 19).[235] According to π-bond order considerations,[32] (±)-**12** should be formed preferentially.

As part of our program on the isolation and characterization of constitutional and configurational isomers of higher fullerenes by use of the Bingel/retro-Bingel strategy, the C_{84} fraction of fullerene soot was subjected to the cyclopropanation with optically pure, C_2-symmetric bis[(*S*)-1-phenylbutyl] malonate (cf. section 3.2).[65] Two chiral mono-adducts and four chiral bis-adducts could be isolated in a pure state and characterized. The combined information from ^{1}H and ^{13}C NMR, CD, and UV/vis spectroscopy allowed the structural assignment of a C_2-symmetric mono- ((*S*,*S*)-**13**, Scheme 1) and a D_2-symmetric bis-adduct ((*S*,*S*,*S*,*S*)-**14**) of $C_{84}(23)$-D_{2d}. Both derivatives display weak Cotton effects ($\Delta\epsilon \leq 3$ M^{-1} cm^{-1}), which is typical for an achiral fullerene with stereogenic centers in the addend(s). In addition, scrutiny of the structures resulting from addition of a C_2-symmetric residue to one of the 10 most curved bonds of

Scheme 1. Transformation of a Monoadduct of $C_{84}(23)$-D_{2d} ((*S*,*S*)-13) into Bis-Adduct (*S*,*S*,*S*,*S*)-14 and Release of the Parent Fullerene from the Latter by Electrochemical Retro-Bingel Reaction[65]



C_{84}-D_{2d} left (*S*,*S*)-**13** as the only possible structure for the C_2-symmetric mono-adduct. This regioisomer corresponds to that of the previously reported complex $[Ir(CO)Cl(PPh_3)_2\{\eta^2\text{-}(C_{84}\text{-}D_{2d})\}]\cdot 4\ C_6H_6$ and results from addition across the bond C(36)−C(37) (Scheme 1, for the atom numbering of $C_{84}(23)$-D_{2d}, see also ref 34).[62] As to the D_2-symmetric bis-adduct, which afforded C_{84}-D_{2d} in the electrochemical retro-Bingel reaction,[114] it had to be a derivative of that fullerene with an achiral functionalization pattern (weak Cotton effects, vide supra). In combination with the NMR data, this unambiguously supports the assignment as C(36)−C(37): C(48)−C(49) (Scheme 1) bis-adduct (*S*,*S*,*S*,*S*)-**14**, which must be formed by further functionalization of (*S*,*S*)-**13**.[65]

Two C_2-symmetric bis-adducts, obtained by Bingel reaction with an isomeric [84]fullerene mixture, were identified as diastereoisomers with enantiomeric $C_{84}(22)$-D_2 cages ((*S*,*S*,*S*,*S*,^{f,s}*A*)-**2a** and (*S*,*S*,*S*,*S*,^{f,s}*C*)-**2b** [six possible constitutions], Figure 12).[65] Each one was subjected to the electrochemical retro-Bingel reaction[114,116] to separately afford the enantiomers of $C_{84}(22)$-D_2 (see section 3.2). In addition, constant potential electrolysis with two other products, a C_1-symmetric mono-adduct and a C_1-symmetric bis-adduct, yielded a novel, CD-silent C_{84} isomer.[65]

3.4.3. Fluorination of Higher Fullerenes

One of the more intensely studied reactions on higher fullerenes is their fluorination,[236,237] starting either from pure fullerenes or from mixtures[238,239] and using various fluorinating agents such as K_2PtF_6, MnF_3, or CeF_4.[240−242] As can be imagined, mixtures of fluorofullerenes exhibiting various degrees of fluorination, $C_{2n}F_{2m}$, are generally formed. Among the (partially) purified compounds, $C_{76}F_{32}$, $C_{76}F_{36}$, $C_{76}F_{38}$ (main isomer of C_1-symmetry), $C_{76}F_{40}$ (five isomers, one of C_2-symmetry), $C_{76}F_{42}$, $C_{76}F_{44}$, $C_{78}F_{38}$, $C_{78}F_{42}$,[240] $C_{82}F_{44}$, $C_{84}F_{40}$ (two isomers), and $C_{84}F_{44}$ [241] may be mentioned. Regarding the chirality of incompletely separated or purified derivatives of higher fullerenes, not much experimental information is available, but it goes without saying that all derivatives of the inherently chiral fullerenes are chiral. In some cases, symmetries could be determined by NMR spectroscopy even if full structural elucidation was impossible. For a considerable number of species, however, only the chemical composition is known.

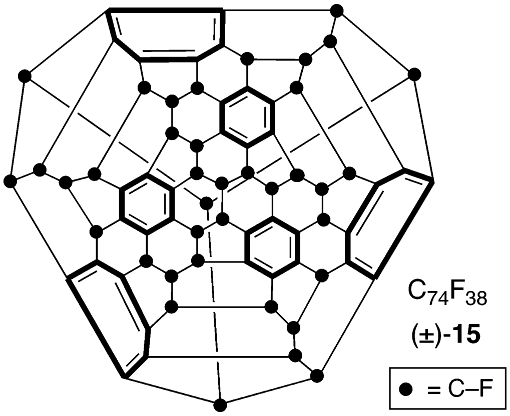


Figure 17. Schlegel-like diagram of $C_{74}F_{38}$, a D_3-symmetric derivative of C_{74}-D_{3h} (viewed along the C_3 axis).[243] The benzenoid substructures of the residual π-chromophore are highlighted in bold. Nonbenzenoid double bonds are omitted for clarity. The interrupted lines represent bonds on the backside of the flattened diagram.

The first structurally characterized fluorinated higher fullerene, D_3-symmetric $C_{74}F_{38}$ ((±)-**15**, Figure 17) was isolated by Boltalina, Strauss, and co-workers from the high-temperature fluorination of a C_{74}-enriched soot sublimate with K_2PtF_6.[243] It represents also the first structurally characterized exohedral derivative of a small band gap fullerene, thus providing direct experimental support for the single IPR-conforming C_{74}-D_{3h} structure, pure samples of which were first reported in 1998.[244] The structural elucidation of air-stable octatriacontafluoro[74]fullerene ((±)-**15**) was mainly based on a combination of 1D and 2D ^{19}F NMR spectroscopy and energetic considerations. The inherently chiral functionalization pattern of $C_{74}F_{38}$ is distinguished by six isolated, stabilizing benzenoid rings as well as by a contiguous pattern of adjacent fluorine-bearing atoms, features that it shares to various extents, for example, with $C_{60}F_{18}$ and $C_{60}F_{36}$ (see section 4.11.1).

A 1:1 mixture of two fluorinated cages, $C_{84}F_{40}$ and $C_{84}F_{44}$ ((±)-**16** and (±)-**17**, Figure 18), was isolated from fluorination of [84]fullerene with MnF_3 or CoF_3 at 500 °C. The information from 1D and 2D ^{19}F NMR spectroscopy in conjunction with the large available body of knowledge on fluorofullerenes (see sections 4.11.1 and 4.11.3) indicated both (±)-**16** and (±)-**17** to be derived from $C_{84}(22)$-D_2 and to have a C_2-symmetric cuboid shape with benzenoid rings on four of the six sides. The two remaining faces include naphthalene substructures in $C_{84}F_{40}$ and two offset benzene-type rings in $C_{84}F_{44}$.[245] The isolated aromatic patches of $C_{84}F_{40}$ are the largest, in terms of number and size, found in any fullerene derivative so far.[246]

In this context of halogenated higher fullerenes, the recently reported preparation and crystal structure of achiral $C_{78}Br_{18}$ is worth mentioning.[247] The high molecular symmetry (D_{3h}) observed in the crystals resulted from a statistical ordering of octadecabromo derivatives of $C_{78}(2)$-C_{2v} and C_{78}-(3)-C_{2v}.[247,248] The presence of a possible bromination product of C_{78}-D_3 was excluded by the authors.

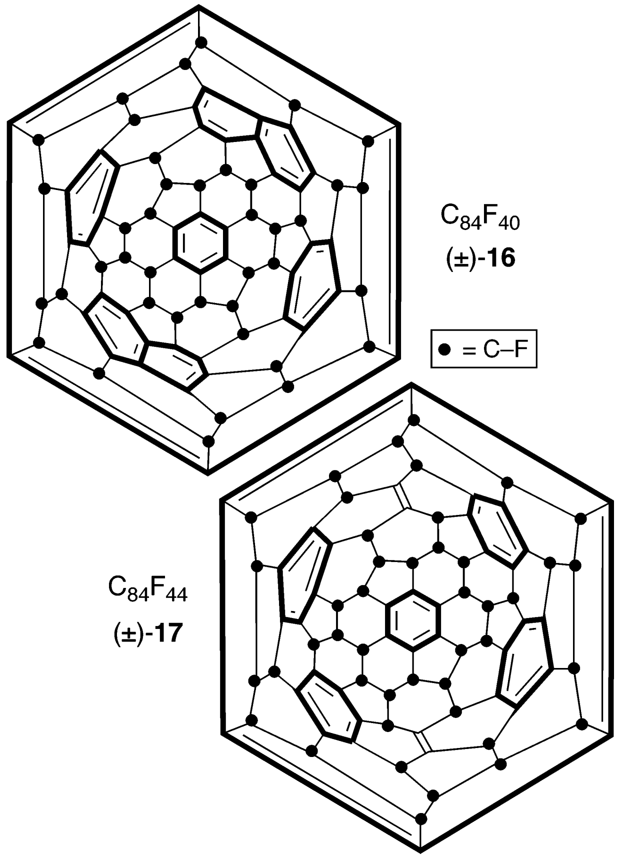


Figure 18. Schlegel diagrams of two C_2-symmetric fluorinated derivatives of $C_{84}(22)$-D_2, $C_{84}F_{40}$ ((±)-**16**) and $C_{84}F_{44}$ ((±)-**17**), both viewed along the C_2-axis.[245] The aromatic substructures of the residual π-chromophores are highlighted in bold.

3.4.4. Silylation of Higher Fullerenes

Silylation of higher fullerenes was carried out by photochemical reaction of 1,1,2,2-tetramesityldisilirane with C_{76}, C_{78} (mixture of C_{78}-C_{2v} and C_{78}-D_3), and C_{84}-D_2 to afford isomeric mixtures of mono-adducts.[249,250] A remarkable selectivity was observed for [78]fullerene, in which case only the C_{2v}-symmetric isomer reacted.[250] Among the multitude of mono-adducts, which are assumed to be fullerene-fused 1,3-disilolanes, several could be isolated by HPLC and further analyzed. Whereas most are C_1-symmetric and precise structural proposals are impossible, a C_2-symmetric derivative of C_{84}-D_2 may be the result of addition across the C(36)−C(37) bond (cf. Scheme 1).[249]

3.4.5. Further Reactions with Higher Fullerenes

Adducts of osmium tetroxide have been prepared by Hawkins and co-workers as intermediates in the kinetic resolution of C_{76}-D_2,[89,112] C_{78}-D_3, and C_{84}-D_2 [89] (see section 3.2).

A pure C_2-symmetric derivative $C_{76}Me_2O$ was isolated from the reaction of C_{76} with Al/Ni in the presence of NaOH, followed by quenching of the intermediate anions with MeI.[251] The compound was proposed to be an oxahomo[76]fullerene derivative with an oxygen atom inserted between the two methylated positions C(25) and C(26) (for the IUPAC numbering of C_{76} see Figure 4). In addition, the reaction afforded a C_2-symmetric dioxide, $C_{76}Me_4O_2$, as well as methylated and methylenated[252] products.[251] Oxygenation of higher fullerenes can also be effected by ozonation.[253] The methylation of [84]fullerene afforded various $C_{84}Me_2$ adducts.[251]

Hydrogenation of a mixture of higher fullerenes with Zn/concentrated HCl in toluene yielded hydrofullerene mixtures $C_{2n}H_{2m}$ with $C_{76}H_{46-50}$, $C_{78}H_{36-48}$, and $C_{84}H_{48-52}$ as the most prominent species.[254] A notable feature of this reaction is a substantial cage breakdown of the higher fullerenes, mainly to $C_{60}H_{36}$ and $C_{70}H_{2x}$ ($x = 18-20$).

Photochemically generated phosphoryl radicals ($(i\text{-PrO})_2OP^\bullet$) were added to C_{76}-D_2 to give seven out of the nineteen possible chiral mono-adduct regioisomers. On removing the irradiation source, one radical dimerized whereas six persisted in solution.[255]

4. C_{60} Derivatives with an Inherently Chiral Functionalization Pattern

4.1. Common Patterns of Twofold Addition to C_{60}

As a result of their construction principle,[11−14] IPR-conforming fullerenes[1,47,48] have two types of bonds, that is, 6−6 bonds and 6−5 bonds (common edge between two hexagons and between a pentagon and a hexagon, respectively). The most common monofunctionalization pattern of C_{60}-I_h results from 1,2-addition of divalent addends across the 6−6 bond C(1)−C(9) (cf. Figure 2), which has the highest double bond character.[15,18,19,256] Certain primary adducts, such as fullerene-fused pyrazolines and triazolines, can rearrange to homofullerenes[29] with structurally modified cores resulting from insertion of an extra CH_2 group or a heteroatom into a 6−5 junction (between cage atoms C(1) and C(2), cf. Figure 2), affording a so-called "6−5 open" structure (cf. section 4.9).[15,18,19,256] With C_{2v}- or C_s-symmetric divalent addends (and also, as observed in practice for 6−6 adducts, with two achiral[257] monovalent addends), both functionalization patterns translate into achiral molecules because the 6−5 bond is bisected by a mirror plane of the C_{60} core, as is the 6−6 bond, which, in addition, is lying on another mirror plane. Other reactions, such as chlorination, bromination, trifluoromethylation, and a number of nucleophilic additions that are followed by quenching with an electrophile, occur mostly as intrahexagonal 1,4-additions to positions C(1) and C(7) (cf. Figure 2) to avoid steric congestion between eclipsed, vicinal monovalent addends.[15,18,19,256] For nonidentical groups,[258] the resulting functionalization pattern is noninherently chiral (cf. section 6). Very bulky groups, finally, can lead to a 1,6-addition mode across two hexagons with attachment of the addends to C(1) and C(23) of the cage (cf. Figure 2), an arrangement that corresponds to an inherently chiral functionalization pattern.

For reasons of clarity, the general discussion of bis-adducts will be limited to the addition of C_{2v}-symmetric divalent residues to 6−6 bonds, all 30 of which are identical in icosahedral C_{60}. Functionalization of one of them lowers the symmetry of the derivatized carbon cage to C_{2v}, thereby eliminating the equivalence of the remaining 6−6 bonds. As a result, addition of a second, identical group can, in principle, lead to eight different bis-adduct regioisomers. They can be designated in an intuitive way by indication of the relative arrangement of addends, as proposed by Hirsch and co-workers (Figure 19):[259] the two groups can be located in the same hemisphere (*cis*) or in opposite hemispheres (*trans*) of the carbon cage and, in addition, there is a borderline case, which is termed *equatorial* or simply *e*. There are three possible arrangements for two addends within a hemisphere (*cis*-1, *cis*-2, and *cis*-3) and four of them

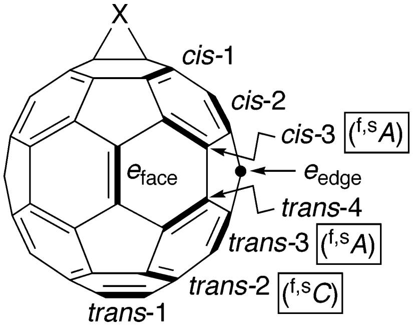


Figure 19. The possible [60]fullerene bis-adduct isomers and the stereodescriptors for the highlighted inherently chiral addition patterns. If both addends are identical and C_{2v}-symmetric, the addition patterns *cis*-1, *cis*-2, *e*, and *trans*-4 are C_s-symmetric, *cis*-3, *trans*-3, and *trans*-2 are C_2-symmetric, and *trans*-1 is D_{2h}-symmetric.

involving both hemispheres (*trans*-1, *trans*-2, *trans*-3, and *trans*-4) (Figure 19). If two different, C_{2v}-symmetric addends are considered, the structural degeneracy of *e* arrangements vanishes due to the heterotopicity of the concerned bonds, and the second addend can occupy two different *e* sites in relation to the first. In fact, considering the frequent case of rings fused to the fullerene core and looking from one of them at the other, either the edge or the face of the distal cycle is seen, and accordingly, the position of the viewer is described as e_edge or e_face (Figure 19).[260] The resulting possibility of two different achiral *e* functionalization patterns leads to a total of nine potential constitutional bis-adduct isomers.

The number of bis-adducts further increases if stereoisomers are taken into account. In fact, the *cis*-3, *trans*-3, and *trans*-2 addition patterns are inherently chiral[4,20,21,26] and represent stereogenic units, the configuration of which can be specified by the descriptors $^{f,s}C$ and $^{f,s}A$ (see section 2).[26,29] Other addition patterns (*cis*-1, *cis*-2, and *trans*-4) become chiral only with two different addends: they are termed noninherently chiral. As to the remaining patterns, *trans*-1 bis-adducts are always achiral unless the addends include appropriate stereogenic elements. In the case of *e* bis-adducts with two C_s-symmetric methano type addends, that is, carrying two different substituents at the bridging atom, the methano C-atom in e_face position is a stereogenic center but the addition pattern remains achiral. In other cases of *e* bis-adducts with identical or different C_s-symmetric addends, the addition pattern becomes noninherently chiral without new stereogenic centers appearing in the addends.

4.2. Bis-Adducts Resulting from Addition of Untethered Reagents

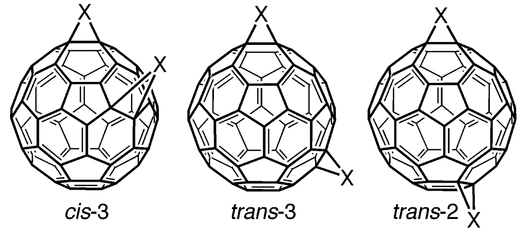
The first systematic study of the regiochemistry of double addition to C_{60} was carried out in 1992 by Hawkins et al., who reacted the fullerene with OsO_4 and isolated *e* and *trans*-3 bisosmates.[261] Asymmetric double osmylation using ligands derived from dihydroquinine or dihydroquinidine afforded nonracemic *trans*-3 and *trans*-2 bis-adducts. Subsequent exchange of the ligands for achiral pyridine and purification enabled them to record the first CD spectra of [60]fullerene bis-adducts **18** and **19** (Figure 20) with an inherently chiral functionalization pattern, that is, with a chiral fullerene-derived π-chromophore.[262]

4.2.1. Methanofullerene Derivatives

Seven out of the eight possible dicyclopropa[60]fullerene tetracarboxylates were isolated by Hirsch and co-workers from stepwise double Bingel addition to C_{60}.[259] This reaction, which is one of the most versatile in fullerene chemistry, consists of the addition of 2-halomalonate anions across a 6−6 bond of the spheroid under formation of methanofullerene derivatives.[115,263] The structures of the isolated bismethanofullerenes were assigned based on ^{1}H NMR data in combination with the HPLC elution order; they included (±)-**20** (*cis*-3), (±)-**21** (*trans*-3), and (±)-**22** (*trans*-2) as derivatives with an inherently chiral functionalization pattern (Figure 20). In 2003, the enantiomers of (±)-**21** and (±)-**22** were separated by Nishimura and co-workers, using chiral stationary phases based on cellulose or amylose carbamate.[264] Absolute configurations could be assigned through comparison of the CD spectra to those of previously separated enantiomers of *trans*-3 and *trans*-2 methano[60]fullerene derivatives,[265] the CD spectra of which had been calculated.[266] Such assignments are admissible for fullerene derivatives with an inherently chiral π-system because the main contributions to the Cotton effects originate from the fullerene chromophore, that is, the functionalization pattern, and only to a minor extent from the addends, as first noted by Diederich and co-workers in reports on stereoisomerically pure C_{70} derivatives.[30,267] As to pure enantiomers of *cis*-3 bismethano[60]fullerene derivatives, they were obtained either stereoselectively via tether-directed remote functionalization[268−270] (cf. section 4.4.1) or through chromatographic resolution ($C_{60}[C(p\text{-}C_6H_4OCH_3)_2]_2$),[271] and their configuration was also assigned by comparison between experimental and theoretical CD spectra.[121]

The most abundantly formed products in the above reaction were the *e* and *trans*-3 ((±)-**21**) isomers, and the regioselectivity of the kinetically controlled nucleophilic cyclopropanation was accounted for by enhanced coefficients of low-lying unoccupied orbitals, in the mono-adduct, at the positions of preferred second addition.[40,272] The absence of the *cis*-1 adduct (cf. Figure 19) in the product mixture, despite being favored electronically, was ascribed to steric hindrance between addends in such close proximity. This conclusion was supported by the preferential formation of the *cis*-1 isomer of $C_{60}[C(CO_2Et)_2](NCO_2Et)$, the epimino addend of which has a reduced steric requirement in comparison to the Bingel addends.[273] Similarly, double nitrene addition by reaction of C_{60} with ethyl azidoformate, under thermal conditions, yielded eight regioisomeric bisepimino[60]fullerenes[274] including the C_2-symmetric *cis*-3 ((±)-**23**), *trans*-3 ((±)-**24**), and *trans*-2 ((±)-**25**) adducts as fullerene derivatives with an inherently chiral addition pattern (Figure 20). Due to the lesser steric requirement of ethoxycarbonylimino- in comparison to bis(ethoxycarbonyl)methano addends, the corresponding *cis*-1 isomer (C_s-symmetric) was obtained as a major product in this reaction. It was the first fullerene derivative with open 6−6 junctions, resulting from valence isomerization in the doubly functionalized six-membered ring.[274]

Pure *trans*-3 ((±)-**21**) and *e* Bingel-type bis-adducts were used to study the chemical retro-Bingel reaction with amalgamated Mg in THF, affording a mixture of the mono-adduct and C_{60}.[275] Pure C_{60} was obtained by reductive electrolysis of spiromethanofullerenes (±)-**26**−(±)-**28**, isolated next to the achiral *cis*-2 and *e* isomers from the thermal reaction of 2-diazoindane-2,3-dione with C_{60}.[276] Interestingly,



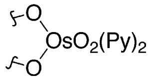
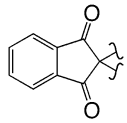
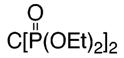
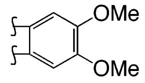
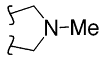
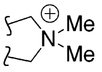
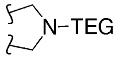
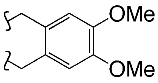
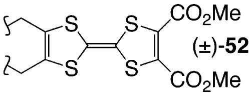
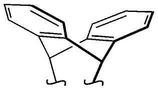
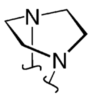
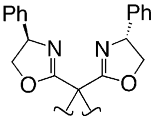
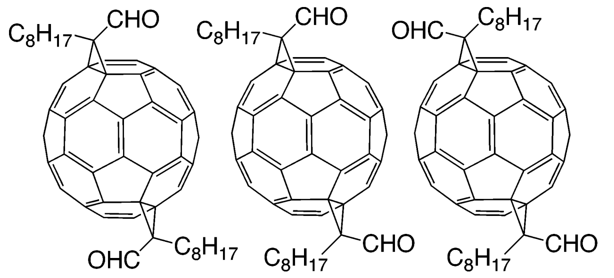
X =	*cis*-3	*trans*-3	*trans*-2
		**18**	**19**
$C(CO_2Et)_2$	(±)-**20**	(±)-**21**	(±)-**22**
NCO_2Et	(±)-**23**	(±)-**24**	(±)-**25**
	(±)-**26**	(±)-**27**	(±)-**28**
$C(CO_2H)_2$	(±)-**29**	(±)-**30**	(±)-**31**
$C(p\text{-}C_6H_4NMe_2)_2$			(±)-**32**
 $C[P(O)(OEt)_2]_2$		(±)-**33**	(±)-**34**
	(±)-**36**	(±)-**37**	(±)-**38**
	(±)-**39**	(±)-**40**	(±)-**41**
	($^{f,s}A$)-**42**/ ($^{f,s}C$)-**42**	($^{f,s}A$)-**43**/ ($^{f,s}C$)-**43**	($^{f,s}A$)-**44**/ ($^{f,s}C$)-**44**
	(±)-**45**	(±)-**46**	(±)-**47**
	TEG = $(CH_2CH_2O)_3CH_3$		
	(±)-**48**	(±)-**49**	(±)-**50**
	(±)-**52**	(±)-**53**	(±)-**51**
	(±)-**54**	(±)-**55**	(±)-**56**
			(±)-**58**
	(*R*,*R*,*R*,*R*,^{f}C)-**128a**/ (*R*,*R*,*R*,*R*,^{f}A)-**128b**	(*R*,*R*,*R*,*R*,^{f}C)-**129a**/ (*R*,*R*,*R*,*R*,^{f}A)-**129b**	

Figure 20. Bis-adducts of C_{60} with an inherently chiral addition pattern. A single enantiomer only is shown for each regioisomer. Osmates **18** and **19** are nonracemic, but the configuration is unassigned.

constant potential electrolysis of the corresponding mono-adduct in THF with discharge of 1.8 electrons per molecule, followed by reoxidation, afforded a sizable amount of bis-adducts, which must be generated by addend transfer between fullerenes.[277] The resulting regioisomer distribution deviates significantly from that of the direct chemical synthesis. An unexpected electrochemically induced regioisomerization, the so-called walk-on-the-sphere rearrangement of different $C_{60}[C(CO_2Et)_2]_2$ bis-adducts by migration of the methano addends on the C_{60}-surface was observed by Echegoyen, Diederich, and co-workers in the course of nonexhaustive constant potential electrolysis of the tetraesters.[278] Bis-adduct regioisomers have been studied by ^{3}He NMR spectroscopy of the corresponding ^{3}He-incarceranes,[279,280] revealing strong and specific shieldings for each compound, and computation of the corresponding ^{3}He chemical shifts can serve as a tool in isomer identification.[281] Photophysical properties such as the quantum yield of singlet oxygen production of tetraesters (±)-**20**−(±)-**22**, as well as of the corresponding carboxylic acids ((±)-**29**−(±)-**31**), showed a clear dependence on the addition pattern.[282] Tetra-acids (±)-**30** and (±)-**31** also proved to be effective in the inhibition of glutathione reductase.[283] Ground- and excited-state electron transfers from the dimethylaniline moiety to the fullerene were observed for a series of mono- to tris-adducts, including *trans*-2 dicyclopropafullerene (±)-**32**.[284]

Bismethano[60]fullerene-derived tetraphosphonates have been synthesized in a Bingel-type reaction with C_{60} and tetraethyl bromomethylenediphosphonate. Five regioisomers could be isolated and characterized by MALDI-TOF MS (matrix-assisted laser-desorption time-of-flight mass spectrometry) and $^{31}P\{^1H\}$ and ^{13}C NMR spectroscopy as *trans*-1, *trans*-2 ((±)-**33**), *trans*-3 ((±)-**34)**, *trans*-4, and *e* bis-adducts (Figure 20).[285] Cleavage of the ester groups of (±)-**33** and (±)-**34** and of the *e* bis-adduct by treatment with trimethylsilyl iodide and water afforded the corresponding tetraphosphonic acids, promising compounds for the selective targeting of mineralized bone tissue. A tetraphosphonate of the above type (unidentified regioisomer) and a mixed dicarboxylate−diphosphonate (unidentified regioisomer) were obtained in a modified Bingel reaction[286] from C_{60} and tetraethyl methylenediphosphonate or ethyl 2-(diethoxyphosphoryl)acetate, respectively.[287] The tetraphosphonate, in particular, showed photoinduced cytotoxicity toward HeLa cells with an IC_{50} value of 1.3 μM. Dumbbell-type C_1-linked difullerenes $HC_{60}-C[PO(OEt)_2]_2-C_{60}H$ and $[PO(OEt)_2]_2$-$CC_{60}-C[PO(OEt)_2]_2-C_{60}C[PO(OEt)_2]_2$ were prepared in high yield by reaction of C_{60} and [bis(diethoxyphosphoryl)]-methano[60]fullerene, respectively, with various tetraethyl [(cycloalkyl)amino]methylenediphosphonate anions.[288] Studies on the addition of diisopropoxyphosphoryl radicals to fullerene derivatives[289,290] such as (±)-**33** and (±)-**34** showed that the number of stable fullerene-derived radicals is dependent on the starting regioisomer.[291] The behavior of various diethoxyphosphoryl-substituted methanofullerenes under the conditions of the electrochemical retro-Bingel reaction was studied by Diederich, Echegoyen, and co-workers.[118]

Very recently, Saigo and co-workers reported the first systematic investigation of the regio- and stereochemistry of bis-adducts with C_s-symmetric methano addends, that is, carrying two different substituents (e.g., (±)-**35a**−**c**, Figure 21).[292] They were obtained from the reaction of [60]fullerene with 2.5 equiv of the sulfonium ylide prepared from treatment of 2-bromodecanal with dimethyl sulfide and subsequent deprotonation. Fourteen pure products were isolated out of 22 possible isomers (enantiomeric pairs being counted as one) resulting from the combination of eight different addition patterns (see Figure 19) and the diastereoisomerism



(±)-35a (*in*,*in trans*-3) **(±)-35b** (*in*,*out trans*-3) **(±)-35c** (*out*,*out trans*-3)

Figure 21. Juxtaposition of the *in*,*in*-, *in*,*out*-, and *out*,*out*-stereoisomers of *trans*-3 regioisomer (±)-**35a**−**c**.[292] The descriptors *in* and *out* refer to the relative orientation of nonidentical substituents at the methano-C-atoms, "*in*,*in*" meaning that given substituents (the formyl groups, in the present case) point toward each other, "*out*,*out*" that they point away from each other, and "*in*,*out*" describes the remaining arrangement. This constitutes an extension of the usage of *in* and *out* to describe relative configurations at bridgeheads of macrobicyclic systems.

related to the relative orientation of the aldehyde functions at the two methano bridges: two diastereoisomers exist for each of the *trans*-1 and *e* regioisomers, and three of them (*in*,*in*; *in*,*out*; *out*,*out*) for the remaining six addition patterns. Figure 21 shows the diastereoisomers identified for the inherently chiral *trans*-3 dialdehyde (±)-**35a**−**c**. Interestingly, neither *cis*-1 nor *cis*-3 isomers were detected in the reaction mixture. Whereas the absence of the former is understandable for steric reasons, that of the latter is rather surprising, particularly if one considers that a minor *trans*-1 isomer, which is the least likely to form on statistical and electronic grounds,[40,259,272,273] was isolated. Whereas regioisomers were assigned by comparison of the UV/vis spectra to those of the corresponding Bingel adducts,[259] the assignment of *in*,*out* isomers was based on ^{1}H NMR spectroscopy (i.e., symmetry considerations), a correlation between chromatographic elution order and calculated dipole moments, and the (dis-)ability of forming a macrocyclic diimine by reaction with butane-1,4-diamine or heptane-1,7-diamine. Molecular modeling predicted this reaction, which can be considered as the reverse of removing a spacer after a template-directed macrocyclization (cf. sections 4.3 and 4.4), to be possible only for certain combinations of addition pattern and formyl group orientation.[292]

4.2.2. Bis-Adducts from [2 + 2] Cycloaddition

[2 + 2] Cycloaddition between C_{60} and 4,5-dimethoxybenzyne, generated from 4,5-dimethoxyanthranilic acid and isoamyl nitrite in refluxing toluene, afforded all eight bis-adducts, including the *cis*-1 regioisomer. They were separated chromatographically and assigned on the basis of MS, ^{1}H and ^{13}C NMR, and UV/vis spectroscopy, in conjunction with the chromatographic elution order.[293] The formation of ca. 20% of *cis*-1 regioisomer strongly contrasts the reaction of C_{60} with 2-halomalonates[259,273] (cf. section 4.2.1) or azomethine ylides[294,295] (cf. section 4.2.3.1) and was ascribed to a reduced steric requirement of the *o*-phenylene addend in comparison to the other mentioned cases.[293] Interestingly, the resolution of the C_2-symmetric *cis*-3 ((±)-**36**), *trans*-3 ((±)-**37**), and *trans*-2 ((±)-**38**) isomers (Figure 20) on a CHIRALPAK AD column was used as a tool in the structural assignments (identification of chiral vs achiral regioisomers).

4.2.3. Bis-Adducts from [3 + 2] Cycloaddition

4.2.3.1. Addition of Azomethine Ylides. Since the early days of fullerene chemistry, the 1,3-dipolar cycloaddition of azomethine ylides to C_{60} has been one of the most widely used reactions for its derivatization.[296−298] Yet, it was only in 1996 that the distribution of bis-adduct regioisomers of 1-methyl-1*H*-dihydropyrrolo-fused [60]fullerenes (e.g. (±)-**39**−(±)-**41**, Figure 20) was systematically investigated,[294] and some of the six isolated compounds could only be definitively assigned by transient excited triplet state EPR spectroscopy.[299] Saunders, Schuster, and co-workers studied the identification of regioisomers resulting from 2-fold addition of azomethine ylides or malonates to C_{60} by ^{3}He NMR spectroscopy of the corresponding noble gas incarceranes.[279] Although the absolute chemical shifts differ in both adduct series, ^{3}He NMR spectroscopy revealed a significant yet not perfect correlation between relative shifts and addition patterns. Thus, *trans* regioisomers tend to have their ^{3}He resonances downfield from those of *cis* adducts.

All eight bis-adducts, including the *cis*-1 isomer and the chiral derivatives (±)-**39**−(±)-**41** were recently prepared and isolated by Nishimura and co-workers,[300] as well as by Prato and co-workers,[301] so that all their N−CH_3 ^{1}H NMR resonances are now known. The Nishimura group was also able to separate the enantiomers of the *cis*-3 ((±)-**39**), *trans*-3 ((±)-**40**), and *trans*-2 ((±)-**41**) isomers on an amylose carbamate-derived chiral stationary phase. Absolute configurations were easily assigned by comparison of the CD spectra to those of the previously assigned benzyne adducts having the same residual fullerene π-chromophore.[293] The resolved enantiomers were then treated with an excess of methyl iodide to afford the corresponding quaternary ammonium salts **42**−**44** (Figure 20) with $^{f,s}A$- and $^{f,s}C$-configuration. They were tested for their potential as noncovalent macromolecular helicity-inducers for poly(phenylacetylene) substituted with a sodium ethyl phosphonate group at every aromatic nucleus. Only the *trans*-3 bis-adducts $^{f,s}C$- and $^{f,s}A$-**43** led to a characteristic induced CD in the UV/vis region due to predominant one-handed helix induction in the polymer backbone.[300]

Eight regioisomeric bis-adducts, including the chiral derivatives (±)-**45**−(±)-**47** (Figure 20), were isolated and characterized by Prato and co-workers as N-substituted derivatives bearing residues derived from triethylene glycol (TEG) monomethyl ether, which leads to an increased solubility in comparison to the *N*-methyl relatives.[295] Similarly to other cases, the isomers were identified by a combination of HPLC elution order and various spectroscopies, including HMQC and HMBC NMR techniques. Unlike other reactions,[274,293] the [3 + 2] cycloaddition of TEG-derived azomethine ylides afforded only minor amounts of *cis*-1 bis-adduct.[295] Looking at the entire regioisomer distribution, which matches that of the *N*-methyl series[300] (vide supra) pretty well, it can be said that the bis-addition of azomethine ylides is much less selective than the double Bingel addition, which may be related to the high reactivity of the 1,3-dipoles when compared with the nucleophilic malonate anions (Bingel reaction).

A cyclovoltammetric study of the TEG-derived series and the corresponding dications obtained by quaternization of the pyrrolidine nitrogen atoms with methyl iodide revealed a strong dependence of the electrochemical properties, in particular of the potential separation between second and third reduction, on the addition pattern.[302] Also, the diammonium ions exhibit a strong enhancement of the electron-attracting properties, in such a way that the *trans*-1 and *trans*-2 regioisomers belong to the strongest reversible electron acceptors among oligoadducts of C_{60}. The strong electron-accepting properties of the related bis(*N*,*N*-dimethylpyrrolidinium) salts (e.g., **42**−**44**) were confirmed in radical- and light-induced reduction studies in aqueous solution.[303] Further chemical modifications of this versatile class of C_{60}-derived pyrrolidines has led to some of the most water-soluble fullerene compounds.[304] A variety of regioisomers of the neutral and cationic members of the family has been studied by techniques such as pulse radiolysis, laser flash photolysis,[305,306] and EPR spectroscopy.[307−309] Electrostatic interactions between fulleropyrrolidinium ions and CdTe nanoparticles, carrying different carboxylic acids as surface stabilizers, were taken advantage of in the construction of nanocomposites that hold promise for photovoltaic applications.[310,311] They are also a key component of a biosensor for the amperometric detection of glutathione by acting as a redox mediator between the electrode and the enzyme glutathione reductase.[312] Finally, this class of compounds was used to study anti-HIV (human immunodeficiency virus) activity and the inhibition of RNA-dependent RNA polymerase of the hepatitis C virus.[313,314]

4.2.3.2. Addition of Nitrile Oxides. When the symmetry of the addend in a [3 + 2] cycloaddition is reduced from C_{2v} to C_s, the number of possible bis-adduct regioisomers increases from eight to 22. Such a case occurs in the 1,3-dipolar cycloaddition of 2,4,6-trimethoxybenzonitrile oxide to C_{60}, leading to bisisoxazolo[60]fullerenes.[315] Counting not only regioisomers but also stereoisomers, a total of 36 products may be formed, and among these, 28 have a functionalization pattern that is either inherently or noninherently chiral. ^{1}H and ^{13}C NMR spectroscopy of different HPLC fractions isolated by Irngartinger and Fettel from the above reaction revealed the presence of 16 constitutional isomers. Similarly, two bisisoxazoline fractions were obtained as isomeric mixtures from addition of (diisopropoxyphosphoryl)methanenitrile oxide to C_{60}.[316] Based on the calculation of relative stabilities by semiempirical methods and estimation of dipoles according to the vector-additive scheme, in combination with HPLC retention times, the two possible *e* structures (two constitutional isomers with a noninherently chiral functionalization pattern, cf. section 6.2) as well as *trans*-3 and *trans*-4 bis-adducts were proposed to be formed preferentially.[317]

4.2.3.3. Addition of a Thiocarbonyl Ylide. Regioisomeric mixtures of bis(2,5-dihydrothieno)[60]fullerenes were obtained by [3 + 2] cycloaddition between the fullerene and the thiocarbonyl ylide generated from bis[(trimethylsilyl)methyl] sulfoxide by sila-Pummerer rearrangement.[318] Oxidation with MCPBA (*meta*-chloroperbenzoic acid) afforded the corresponding bissulfoxides, which were used for pharmacological testing.

4.2.4. Bis-Adducts from [4 + 2] Cycloaddition

The Diels−Alder reaction between C_{60} and 4,5-dimethoxy-*o*-quinodimethane[319,320] was investigated systematically by Nishimura and co-workers.[321] All bis-adducts (e.g., (±)-**48**−(±)-**50**, Figure 20) except for the *cis*-1 regioisomer could be isolated and characterized by FAB (fast atom bombardment)-MS, ^{1}H and ^{13}C NMR, or UV/vis spectroscopy or a combination of these. In addition, partial optical resolution was achieved for the C_2-symmetric *trans*-3 ((±)-**49**) and *trans*-2 ((±)-**50**) isomers, and the respective CD spectra were recorded.

A family of triads including a [60]fullerene unit attached to two addends derived from TTF (tetrathiafulvalene) were prepared[322] by heating the fullerene in chlorobenzene with a TTF-fused 2,5-dihydrothiophene-1,1-dioxide as diene precursor.[323,324] A number of bis-adducts were isolated and identified by HMBC NMR (*e*, *trans*-2 ((±)-**51**, Figure 20))[323] or reliably assigned (*cis*-3 ((±)-**52**), *trans*-3 ((±)-**53**)) using, in particular, the information from computed heats of formation, dipole moments, and chromatographic elution order.[324] It was also found that the structured EPR signals arising from the coupling of the unpaired electron of reductively generated "TTF−$C_{60}^{\bullet -}$−TTF" with the hydrogen atoms of the methylene linkers show a strong dependence on the addition pattern of the measured bis-adduct.

Five regioisomeric bis-adducts were obtained from Diels−Alder addition of a second anthracene moiety to the corresponding mono-adduct of C_{60}.[325] Structures, for example, C_2-symmetric (±)-**54**−(±)-**56**, were determined by spectroscopic or crystallographic means or both. The regioselectivity of this reaction differs from that of others in that no *cis* isomers were formed at all. The bis-adducts decompose only slowly in solution at room temperature, with loss of one and eventually two anthracene units. They feature both concave and convex surface areas and pack with (partial) recognition of the shape-complementary subunits in the crystalline state.[325−329] Equilibria of the reversible Diels−Alder addition of 9,10-dimethylanthracene (DMA) to C_{60} and C_{70} have been studied by Wang, Saunders, and Cross.[330] The ^{3}He NMR resonances of the corresponding ^{3}He incarceranes measured in the reaction mixtures allowed the determination of the number of addends for each species and conclusions on the number of isomers formed: one mono-adduct, six bis-adducts, eleven tris-adducts, and ten tetrakis-adducts were observed in the case of C_{60} and one mono-adduct and three bis-adducts in the case of C_{70}. In addition, equilibrium constants as well as ΔG-, ΔH-, and ΔS-values were determined for these reactions. It should also be mentioned that the reversible addition of DMA was first used by Hirsch and co-workers in the synthetic chemistry of C_{60} as a template method to activate *e* double bonds for subsequent additions, thereby leading eventually to the regioselective formation of a pseudo-octahedral arrangement of six addends.[66,331]

Complete absence of *cis* isomers, possibly due to steric effects, was also observed in the Bingel addition of diethyl 2-bromomalonate with the interesting fullerene dimer C_{120}, easily prepared by solid-state reaction of C_{60}[332] in the presence of various promoters, using a high-speed vibration milling technique.[95,96,333] The ratio of the remaining adducts, that is, e_{face}, e_{edge}, *trans*-4, *trans*-3 ((±)-**57**, Figure 22), and *trans*-2 regioisomers (traces of the *trans*-1 isomer were detected but not isolated), pretty much resembled the product distribution of the double Bingel reaction with C_{60}.[334] When the reaction was carried out with C_{120} having a ^{3}He atom encapsulated in one of the two cages, a pair of ^{3}He NMR resonances was observed for each addition pattern: one resonance of each pair corresponded to a doubly functionalized ^{3}He-containing cage, the other to a molecule with a doubly functionalized empty cage. Equal signal intensities for each pair pointed at identical reactivities for filled and empty cage.[334]

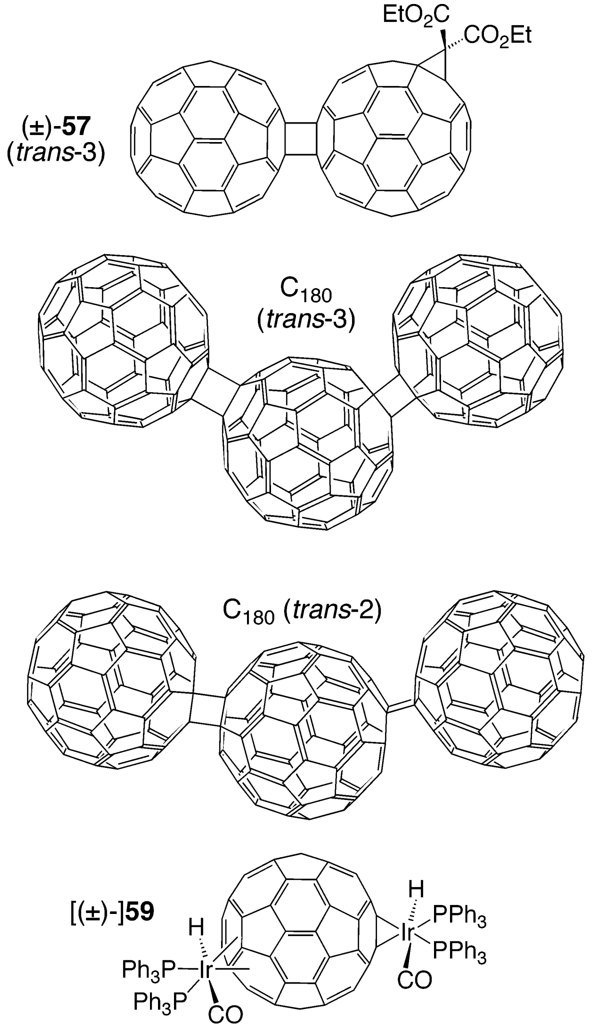


Figure 22. One ((±)-**57**) out of several regioisomers obtained by Bingel cyclopropanation of fullerene dimer C_{120},[334] two fullerene trimers (C_{180}) in which the central C_{60}-unit has a noninherently chiral addition pattern,[335] and regioisomeric mixture of diiridium complexes of C_{60} ([(±)-]**59**)[343] bonded in a μ-η^2:η^2 mode.[344]

The use of 4-aminopyridine as catalyst in the high-speed vibration milling treatment of hexacontacarbon (C_{60}) afforded not only the fullerene dimer (C_{120}) but also a series of isomeric trimers (C_{180}), which were identified, ultimately, by scanning tunneling microscopy (STM). They included the chiral *trans*-3 and *trans*-2 (Figure 22), as well as the achiral *e* and *trans*-4, adducts as acyclic trimers, in addition to the cyclic *cis*-2,*cis*-2,*cis*-2 $(C_{60})_3$.[335]

4.2.5. Various Bis-Adducts and Investigations

The chromatographic resolution of *trans*-3 and *trans*-2 bis-adducts resulting from double Bingel ((±)-**21** and (±)-**22**, Figure 20), benzyne ((±)-**37** and (±)-**38**), azomethine ylide ((±)-**40** and (±)-**41**), and Diels−Alder addition ((±)-**49** and (±)-**50**) to C_{60} was systematically investigated by Nishimura and co-workers using chiral stationary phases based on amylose or cellulose carbamates.[264] The CD spectra of all $[n + 2]$ cycloadducts ($n = 2-4$) with the same residual fullerene π-chromophore were very similar, irrespective of the particular addend,[264] thus confirming previous observations (cf. sections 4.2.1 and 5.6).[30,265−267] Small deviations from this near-superimposability were observed, however, between the spectra of $[n + 2]$ cycloadducts ($n = 2-4$) and those of bismethano[60]fullerenes: they were ascribed to the stronger perturbation of the fullerene π-system by the strain associated with the three-membered rings or by Walsh-type $\sigma-\pi$ interactions in cyclopropafullerenes.[264,336] The absolute configuration of all isolated enantiomers could be assigned by simple comparison of their CD spectra to those of previously assigned C_{60} derivatives with the same addition patterns.

A variety of mixed *trans*-3 [60]fullerene bis-adducts carrying one bis(ethoxycarbonyl)methano group next to an addend resulting from benzyne, azomethine ylide, or Diels−Alder addition were prepared in two-step reactions. Exhaustive electrolysis at the potential of the second fullerene-centered reduction resulted in the selective removal of the Bingel addend, thereby opening up the possibility of using the latter as a temporary protecting and directing group.[117]

The addition of diamines to C_{60} with concomitant oxidation (dehydrogenation) affords cyclic 1,4-diamines with the fullerene being fused to the bond C(2)−C(3) of the heterocycle.[337] Kampe and Egger conducted the first systematic investigations on the reaction of piperazine or *N*,*N*′-dimethylethylene-1,2-diamine with C_{60} and made a number of structural proposals for the obtained bis-adduct regioisomers.[338,339] When reinvestigating the addition of piperazine to C_{60}, Balch et al. isolated the mono-adduct and six bis-adducts.[340,341] X-ray crystal structures were determined for the former as well as the bis-adduct regioisomers *cis*-2, *e*, and *trans*-2 ((±)-**58**, Figure 20).

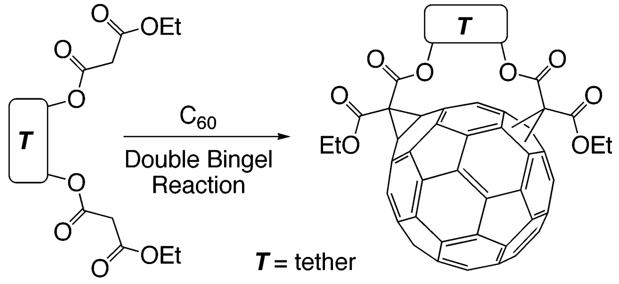
The recently discovered oxahomo[60]fullerene (5−6 open oxidoannulene structure), generated by photolysis of the ozonide $C_{60}O_3$, was found to undergo facile dimerization to $C_{120}O_2$.[342] ^{13}C NMR spectroscopic analysis, in combination with ab initio quantum computations and HPLC retention behavior, prompted the authors to propose a C_2-symmetric structure consisting of a formal [2 + 2] fullerene dimer in which each C_{60} cage retains the oxahomo substructure next to the cyclobuta-fusion site. This dimer of homochiral moieties, which display an inherently chiral functionalization pattern, undergoes photodissociation from the triplet state to regenerate the oxahomo[60]fullerene monomers.

A complex mixture of regio- and stereoisomers can arise from bimetallic complexes such as [(±)-]**59**[343] (Figure 22), even if one assumes that the metal binds exclusively in an η^2-fashion to the 6−6 bonds of the fullerene and that the hydrido and carbonyl ligands adopt a *trans* arrangement at the iridium center.[344] Analysis of 15 well-defined $^{1}H\{^{31}P\}$ NMR resonances by a combinatorial approach points at the presence of at least five regioisomers of the type [(±)-]**59**.

4.3. Nondiastereoselective Tether-Directed Multifunctionalization of C_{60}

Due to the intrinsic reactivity of fullerene derivatives, many multiaddition patterns are not available by simple consecutive additions.[18,256] In the quest for a rational approach to the regioselective and, possibly, stereoselective multifunctionalization of C_{60} and other fullerenes, Diederich and co-workers successfully applied the concept of tether-directed remote functionalization[345] to the chemistry of the carbon molecules in 1994.[346] It consists of the attachment to the spheroids of an anchor carrying a reactive group at the end of a tether; conformational preferences of the latter and steric constraints then allow the reactive group to attack, in the ideal case, a single specific position within the molecular conjugate, thereby affording a well-defined bis-adduct.[22,347−350] In a simplified version, the fullerene is treated with a multifunctional reagent in which two or several reactive groups are interconnected by a spacer; in such one-pot multistage additions, each addend already in place on the fullerene acts as an anchor for the remaining reactive groups (Scheme 2).

Scheme 2. General Scheme for the Tether-Directed Double Bingel Reaction of C_{60} with Bismalonates (Bingel Macrocyclization)



4.3.1. Tether-Directed Double Bingel Additions

Dibenzo crown ethers have been employed as extended templates to access *trans*-bis-adducts of C_{60}. Addition of a bismalonate with an *anti*-disubstituted dibenzo[18]crown-6 spacer (substitution at positions 2 and 13 of the dibenzo-fused heterocycle, Figure 23, cf. also Scheme 22) afforded *out*,*out*[351] *trans*-1 bismethanofullerene (±)-**60** (Figure 23) together with a minor amount of *out*,*out* *trans*-2 isomer (±)-**61**.[352] Addition of KPF_6 to the reaction mixture led to an enhanced yield (50%) and regioselectivity (only *trans*-1) through an additional template effect that originates from the complexation of K^+ ions by the ionophore, thereby reducing its conformational flexibility.[353] Although the *trans*-1 addition pattern of (±)-**60** is D_{2h}-symmetric and the crown ether-derived bismalonate reagent is achiral, the product of the double Bingel addition to C_{60} is a racemate. The chirality of the C_2-symmetric bis-adduct results from the restricted conformational mobility of the crown ether fixed in close proximity to the fullerene sphere to which it can expose only a single face and, in conjunction with the substitution pattern of the dibenzo-fused heterocycle, constitutes an element of "planar" chirality. The C_2-symmetric *out*,*out* *trans*-2 adducts, on the other hand, have an inherently chiral addition pattern. In combination with the "planar" chirality resulting from the bridged *anti*-disubstituted crown ether moiety, this can lead to the appearance of two diastereoisomeric pairs of enantiomers ((±)-**61a**/**b**, Figure 23). At 393 K, the rotation of the crown ether around its "arms" becomes fast (in the *trans*-2 bis-adducts, the distance to the fullerene surface is larger than that in *trans*-1 ((±)-**60**), which leads to fast interconversion of diastereoisomers within each of the pairs (*P*,*P*,$^{\mathrm{f,s}}C$)-**61a**/(*M*,*M*,$^{\mathrm{f,s}}C$)-**61b**, and (*M*,*M*,$^{\mathrm{f,s}}A$)-**61a**/(*P*,*P*,$^{\mathrm{f,s}}A$)-**61b**). Reaction of an isomeric tether derived from *syn*-disubstituted dibenzo[18]crown-6 (substitution at positions 2 and 14 of the dibenzo-fused heterocycle, Figure 23) regioselectively afforded *trans*-3 bis-adduct (±)-**62**. According to variable-temperature NMR measurements, this bis-adduct represents an *in*,*out*-bridged dicyclopropafullerene in which the *syn*-disubstituted crown ether moiety does not represent an element of "planar" chirality.

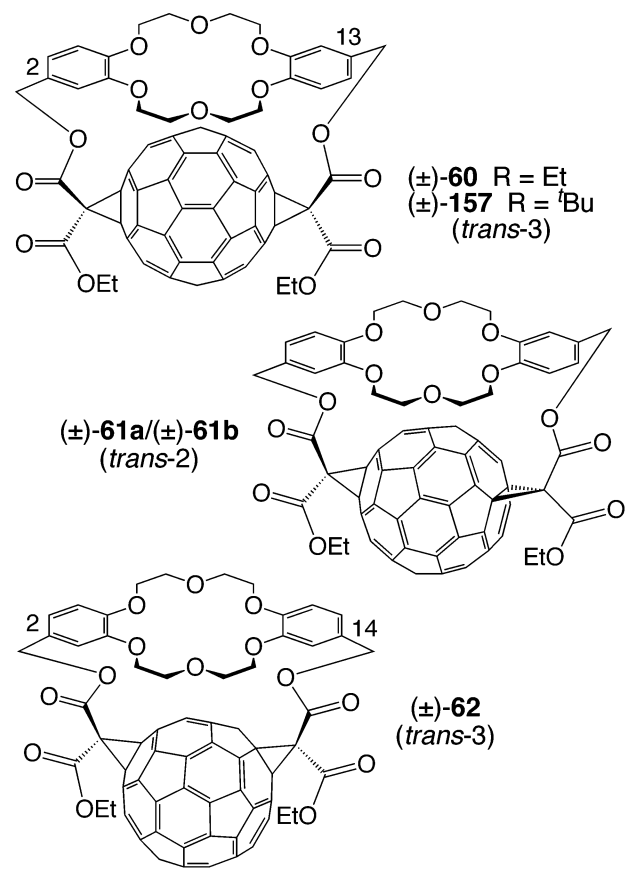


Figure 23. Fullerene−ionophore conjugates with an inherently chiral addition pattern ((±)-**61a/b** and (±)-**62**) and/or a "planar-chiral" crown ether ((±)-**60**, (±)-**157**, and (±)-**61a/b**).[352,353]

Molecular dyads combining the strongly electron-accepting C_{60} and a variety of porphyrin derivatives as electron donors have been prepared and investigated in recent years as model systems mimicking natural photosynthetic reaction centers.[354−358] Use of the porphyrin unit as a spacer in the tether-directed remote functionalization leads to bridged structures, thus allowing for a precise control of the relative orientation of the components, which has a crucial influence on the photophysical and electron-transfer properties of such dyads. Following this concept, the *trans*-1 bis-adduct **63** (Figure 24) was obtained regioselectively by Bingel reaction with a porphyrin−bismalonate conjugate.[359,360] Interestingly, double Bingel reaction with a similar bismalonate comprising an elongated tether afforded exclusively *trans*-2 bis-adduct (±)-**64** with a shorter distance between the addends.[361] When the two malonate-bearing residues were attached to the alternative pair of *meso*-positions of the porphyrin, *e* bis-adduct (±)-**65** was obtained regioselectively.[362] Although its functionalization pattern is achiral, the racemate originates from the methano C-atom in e_{face} position, which represents a stereogenic center generated in the course of the addition. Photophysical properties, in particular the photoinduced electron transfer in metal-free and metal-containing *trans*-1,[360,363,364] *trans*-2,[363−369] and *e*[370,371] dyads of the above types, were extensively studied by different groups.

Good regioselectivities in tether-directed multifunctionalizations are generally achieved with rigid tethers. Hirsch and co-workers suggested an interesting alternative concept using flexible cyclo-oligomalonates,[372,373] an approach that was successfully employed for the regioselective one-pot synthesis of bis- to tetrakis-adducts of C_{60}. The regioselectivity of these reactions is governed by the even distribution of strain within the macrocycle, and the specific addition pattern of the products depends on the length of the spacers. Cyclobis- and -oligomalonates containing identical alkane-

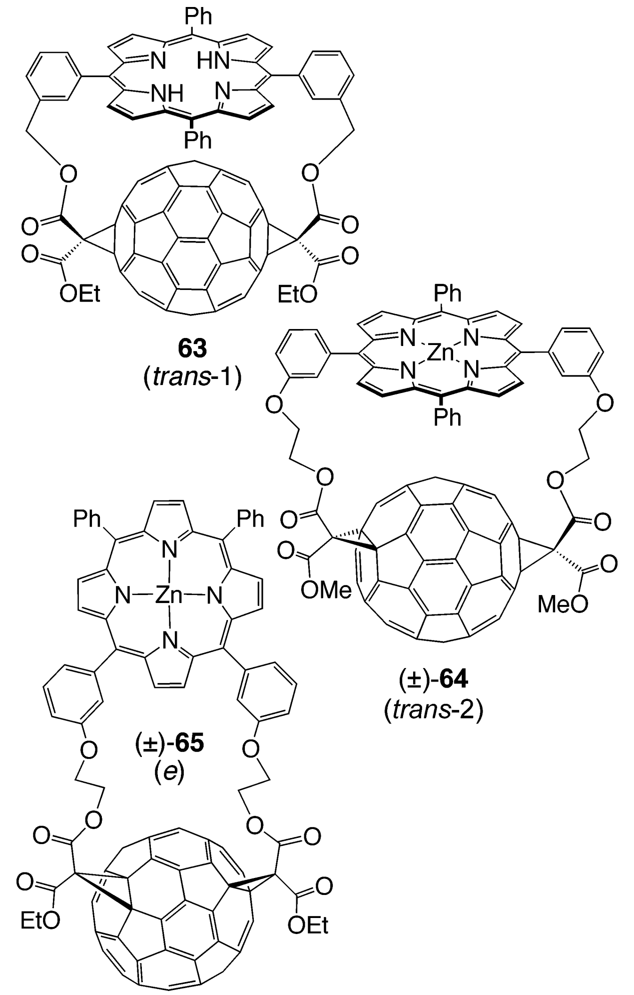


Figure 24. Fullerene–porphyrin conjugates with an achiral addition pattern (**63**),[359,360] an inherently chiral addition pattern ((±)-**64**),[361] or a stereogenic center at the e_{face} methano-C-atom ((±)-**65**).[362]

α,ω-diyl spacers selectively form bis- and oligoadducts (see also sections 4.7 and 4.8) of C_{60} with rotational symmetry. Thus, reaction of buckminsterfullerene with a cyclobismalonate containing two dodecamethylene chains afforded C_2-symmetric *trans*-3 bis-adduct (±)-**66** (Figure 25), and the larger hexadecamethylene-based cyclobismalonate gave a 55:45 mixture of C_2-symmetric *trans*-3 ((±)-**67**) and D_{2h}-symmetric *trans*-1 bis-adducts.[372] On the other hand, when cyclo-oligomalonates with unequal spacers are used, C_s-symmetric addition patterns are preferred, for example, in a *cis*-2 bis-adduct including a tetra- and an octamethylene residue or in *e* bis-adduct (±)-**68** with an octa- and a tetradecamethylene chain. It should be noted that the latter tetraester combines an achiral functionalization pattern with a newly formed stereogenic center in e_{face} position.[372] Similar results were obtained by Wilson and co-workers upon switching from oligo(methylene glycol)- to oligo(ethylene glycol)-type cyclo-oligomalonates, although selectivities may change due to different conformational preferences of the two kinds of tethers.[374] These authors reported the formation of *cis*-3 bis-adducts ((±)-**69** and (±)-**70**) from both 3,6-dioxaoctane-1,8-diyl- and 3,6,9-trioxaundecane-1,11-diyl-based cyclobismalonates, the latter affording also the *e* bis-adduct (±)-**71**.

In some cases, very simple structural units were quite efficient in the regioselective tether-directed Bingel macrocyclization. Thus, a bismalonate featuring a plain ethane-1,2-diyl tether afforded *cis*-3 bis-adduct (±)-**72** (Figure 26) along with a similar amount of the corresponding mono-adduct.[270] Double Bingel reaction of a bismalonate tethered by the 1,10-phenanthroline-2,9-dimethylene moiety yielded bismethanofullerene derivative (±)-**73** with an *e* addition pattern, together with the corresponding *trans*-4 isomer.[269] Further *e* regioisomers were obtained with bismalonates[268,269,375] or bis-β-ketoesters[376] including, as spacers, a *p*-xylylene, a 9,9′-spirobifluorene-2,2′-dimethylene ((±)-**74**),[269] or a rather flexible *o*-phenylenediamine-derived unit ((±)-**75**).[377] On the other hand, *o*- and *m*-xylylene spacers afforded exclusively achiral *cis*-2 bis-adducts of C_{60}.[269,378] Macrocyclization with a rather large tether derived from 2,9-diphenyl-1,10-phenanthroline gave two diastereoisomeric bis-adducts, (±)-**76** and (±)-**77** in 20% and 5% yield, respectively. The absorption spectra of both compounds are nearly identical and consistent with the *trans*-3 addition pattern. The NMR spectra, however, are very different and reveal C_1 symmetry for (±)-**76**, while (±)-**77** is C_2-symmetric. Based on these considerations, (±)-**76** and (±)-**77** were identified as *in,out* and *in,in* diastereoisomers,[351] respectively.[269] The same *in,out* isomerism was also observed for C_1-symmetric *trans*-3 bis-adduct (±)-**78** including a (diethylene glycol)-derived biscarbazole unit as tether and generated next to the corresponding *e* isomer.[379] A rather unselective Bingel macrocyclization occurred with the anthracene-derived tether of (±)-**79**. Careful examination of spectroscopic data and calculations led to the assignment of the chiral *cis*-3 ((±)-**79**), *trans*-3, and *e* isomers, formed in addition to the corresponding mono-adduct and a bis-fullerene derivative.[380] Various macrocyclic dyads, comprising a [60]fullerene and a π-extended tetrathiafulvalene

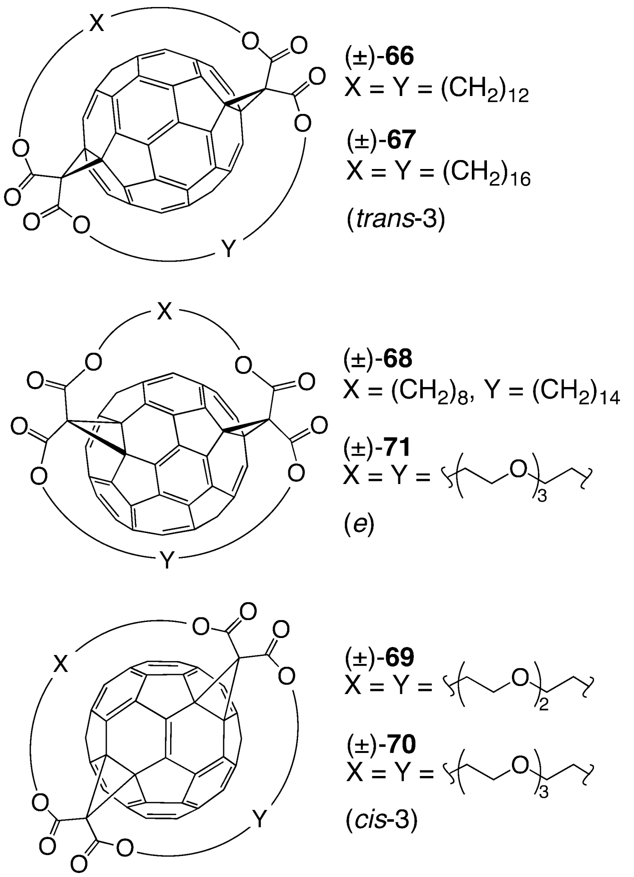
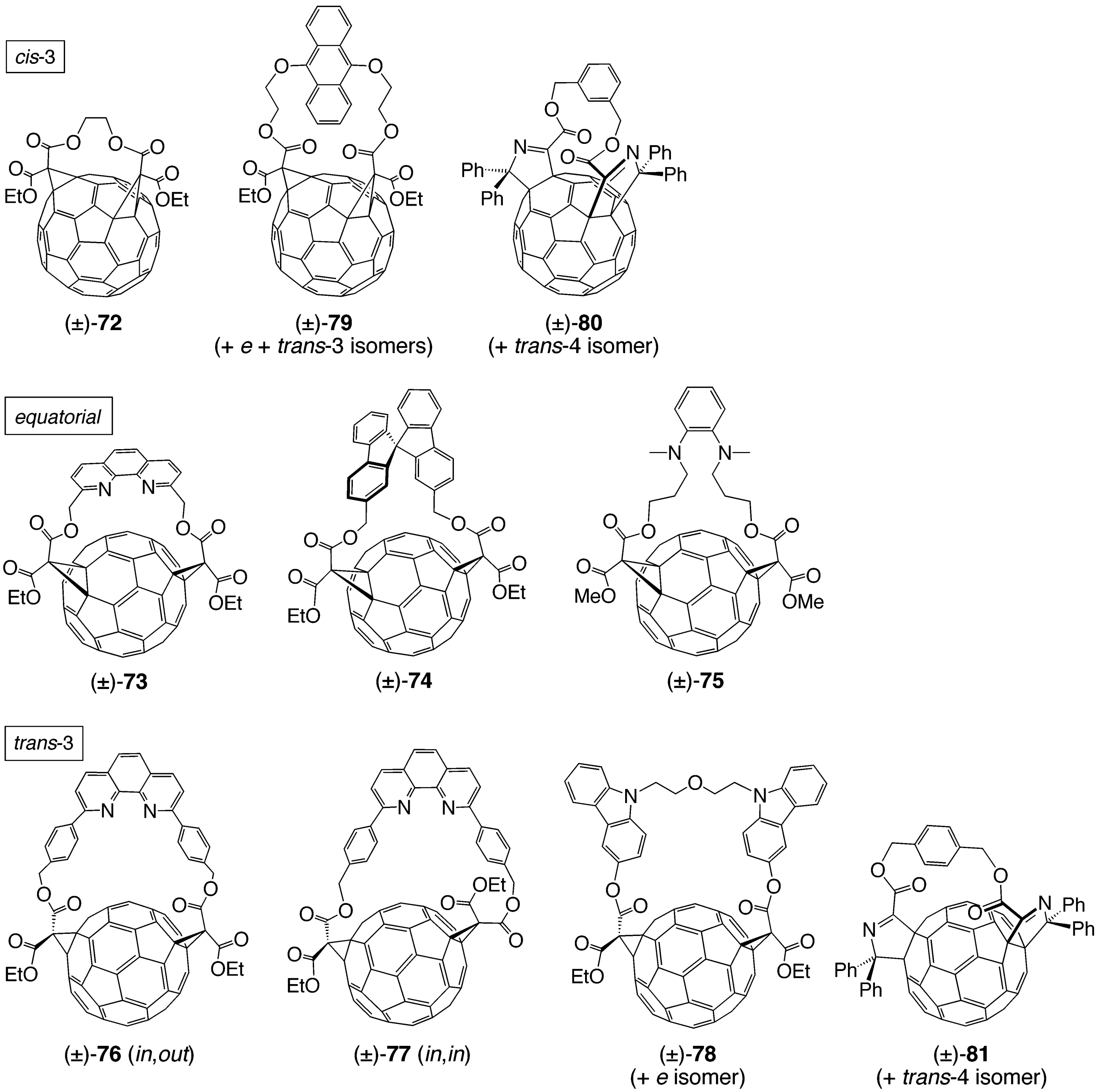


Figure 25. Dicyclopropa[60]fullerenes with an inherently chiral addition pattern formed by addition of macrocyclic bismalonates.[372]



(±)-**72**

(±)-**79** (+ *e* + *trans*-3 isomers)

(±)-**80** (+ *trans*-4 isomer)

(±)-**73**

(±)-**74**

(±)-**75**

(±)-**76** (*in*,*out*)

(±)-**77** (*in*,*in*)

(±)-**78** (+ *e* isomer)

(±)-**81** (+ *trans*-4 isomer)

Figure 26. Chiral bis-adducts obtained in various tether-directed Bingel macrocyclizations.

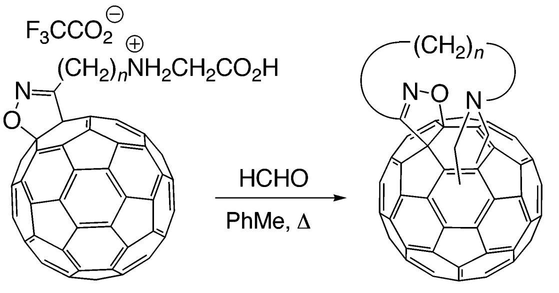
(exTTF) unit,[381] were prepared and subjected to electrochemical and photophysical studies.[382] Complex NMR spectra did not allow unambiguous structural assignments for these compounds, but in one case, semiempirical calculations showed the *cis*-3 or *trans*-3 isomers to be lowest in energy.

An interesting course is taken by the addition of *N*-(diphenylmethylene)glycine esters ($Ph_2C{=}NCH_2CO_2R$) to C_{60} under Bingel conditions. As found recently by INADEQUATE NMR studies on ^{13}C-enriched material, the products of this reaction are 2′*H*-pyrrolo[3′,4′:1,9](C_{60}-I_h)-[5,6]fullerene derivatives[383] and not dicyclopropafullerenes as originally[384−386] assumed. Use of bifunctional reagents tethered with *m*- and *p*-xylylene spacers afforded *cis*-3 ((±)-**80**)/*trans*-4 and *trans*-3 ((±)-**81**)/*trans*-4 bis-adduct mixtures, respectively.[383−386] Reductive ring opening of the pyrrolofullerenes with $NaBH_3CN/BF_3{\cdot}Et_2O$ provides a convenient access to fullerenyl-substituted glycinates.[383,385,386]

4.3.2. Tether-Directed [3 + 2] Cycloaddition

In a systematic study, Prato and co-workers examined the regioselectivity of the intramolecular attack of azomethine ylides tethered through oligomethylene chains $(CH_2)_n$ ($n = 3{-}5$) to a C_{60}-fused isoxazoline anchor (Scheme 3).[387,388] Structure elucidations for the C_1-symmetric products were complicated by the fact that the C_s-symmetry of the isoxazoline ring leads to a doubling of the number of conceivable regioisomeric *cis*-type bis-adducts. As often done in such cases, assignments were based on spectroscopic methods in combination with a computational study on the relative stabilities of the various isomers. Tri- and tetramethylene tethers afforded *cis*-1 bis-adducts (±)-**82** and (±)-**83** (pyr-

Scheme 3. Regioselective Intramolecular [3 + 2] Cycloaddition of an Azomethine Ylide Generated at the End of a Tether, Which Is Attached to a [60]Fullerene-Fused Isoxazoline Anchor[387,388] [a]



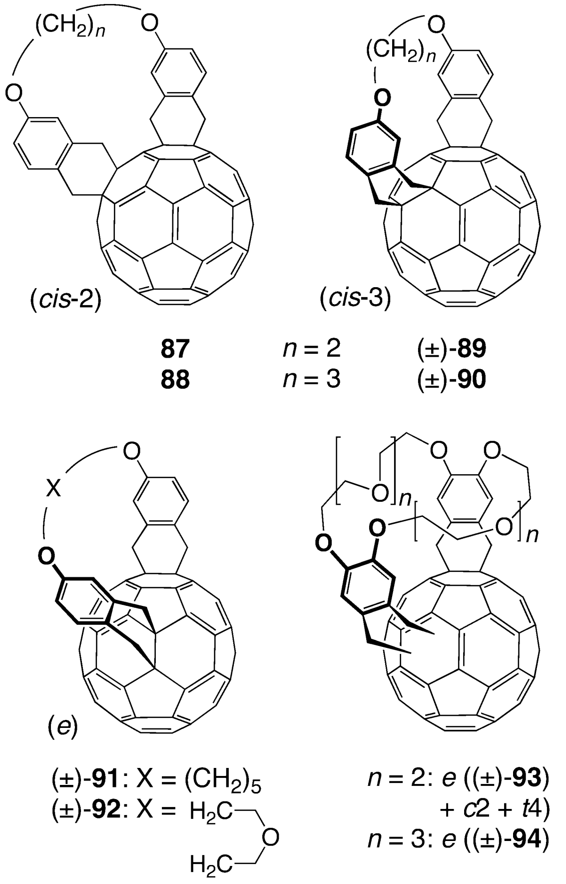
n = 3: (±)-**82** (*cis*-1, C=N-sided)
n = 4: (±)-**83** (*cis*-1, C=N-sided)
n = 5: (±)-**84** (*cis*-1, N–O-sided)
n = 5: (±)-**85** (*cis*-3, C=N-sided)
n = 5: (±)-**86** (*cis*-2, C=N-sided)

[a] In addition to the relative position of the addends, their relative orientation is specified by indication of the dihydroisoxazole portion that is closest to the pyrrolidine ring.

rolidine ring adjacent to isoxazoline-C), respectively, as sole isolated products (Scheme 3). The longer pentamethylene spacer, on the other hand, afforded a mixture of three regioisomeric bis-adducts assigned as (±)-**84** (*cis*-1 isomer with pyrrolidine ring adjacent to isoxazoline-O), (±)-**85** (*cis*-3 isomer with pyrrolidine ring adjacent to isoxazoline-C), and (±)-**86** (minor, tentatively assigned *cis*-2 isomer with pyrrolidine ring near isoxazoline-C). From a synthetic viewpoint, it is interesting to mention that the fullerene-fused isoxazoline heterocycles can be removed by treatment with Mo(CO)$_6$, thus affording *N*-cyanoalkyl-substituted pyrrolo[60]fullerenes. The N,O-heterocycles may, therefore, be used as directing and protecting groups in fullerene chemistry.

4.3.3. Tether-Directed [4 + 2] Cycloaddition

Nishimura and co-workers investigated the regioselectivity of the Diels–Alder addition to C$_{60}$ of two *o*-quinodimethane entities generated in situ from bis(bromomethyl)arene precursors, attached via ether linkages to $(CH_2)_n$ tethers (n = 2–5).[350] Even if the *cis*-1 as well as all *trans*, bis-adducts were excluded for steric reasons, the macrocyclization could lead to eight constitutional isomers due to the addends being C_s-symmetric.[389,390] Assignments were based on a combination of NMR spectroscopy (symmetries), MM2 calculations (steric energies), UV/vis spectroscopy (comparison of typical fingerprints to those of known bis-adducts with the same residual fullerene π-chromophore), and chromatographic separability on a chiral stationary phase (proof of chirality). Figure 27 shows the regioisomers obtained as a function of the number (n) of methylene groups in the tether.[389,390] The shorter spacers (n = 2, 3) afforded a mixture of C_s-symmetric *cis*-2 (**87**, **88**) and C_2-symmetric *cis*-3 ((±)-**89**, (±)-**90**) isomers with the ether oxygen atoms pointing toward each other. In the case of n = 5, the only isolated bis-adduct was the *e* regioisomer (±)-**91**, the chirality of which is not associated with stereogenic centers outside of the fullerene sphere (cf. *e*-bis-adducts of Figure 26) but with a noninherently chiral addition pattern related to the asymmetric substitution of the e_{edge} addend (for details, see section 6.2).[391] The chiral *cis*-3 ((±)-**89** and (±)-**90**) and *e* ((±)-**91**) bis-adducts, as well as the bisphenols resulting from removal of the tethers by cleavage of the ether linkages,[392] were successfully resolved[389,393] by HPLC on silica gel coated with cellulose tris(3,5-dimethylphenyl carbamate).[394] When the pentane-1,5-diyl tether in the precursor to (±)-**91** was exchanged for a 3-oxapentane-1,5-diyl analogue, the *e* regioisomer (±)-**92** was accompanied by a minor amount of *cis*-2 bis-adduct.[395]



87 n = 2 (±)-**89**
88 n = 3 (±)-**90**

(±)-**91**: X = $(CH_2)_5$
(±)-**92**: X = H_2C–O–H_2C

n = 2: *e* ((±)-**93**) + *c*2 + *t*4)
n = 3: *e* ((±)-**94**)

Figure 27. Products of regioselective double Diels–Alder additions of singly or doubly tethered *o*-quinodimethane moieties to C$_{60}$. Whereas the *cis*-3 adducts have an inherently chiral functionalization pattern, that of the *e* adducts is noninherently chiral.

To enhance the regioselectivity of the addition and also to confer ionophoric properties to the fullerene adducts, the *o*-quinodimethane precursors were interconnected by an additional chain in the form of tetrakis(bromomethyl)-dibenzocrown ethers.[395,396] Fullerene–crown ether conjugates (±)-**93** and (±)-**94** (Figure 27) were the only chiral minor regioisomers formed in this reaction next to the C_s-symmetric *cis*-2 and *trans*-4 bis-adducts (for further details, see section 6.2).

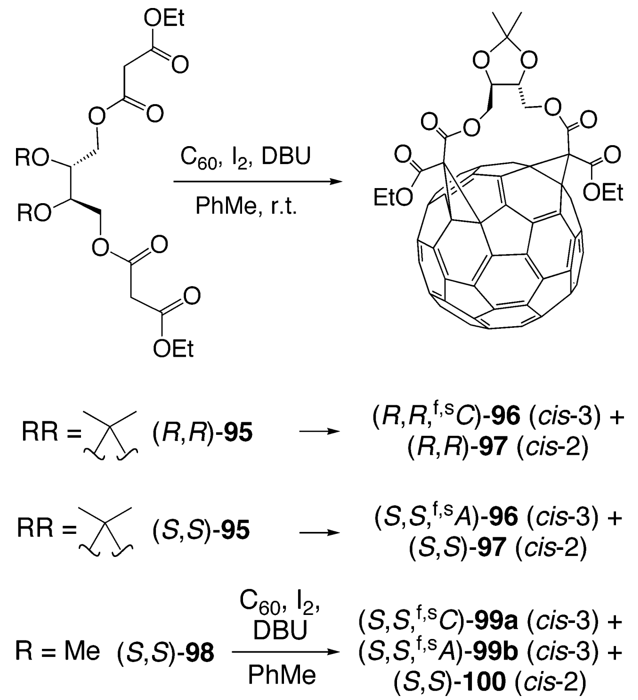
4.4. Nonracemic Bis-Adducts Resulting from Diastereoselective Tether-Directed Multiple Functionalization

4.4.1. Diastereoselective Generation of cis-3 Bis-Adducts

The stereoselective generation of fullerene derivatives by use of chiral, enantiopure tethers is a topic of high interest. The first attempts in this direction were based on spacers derived from easily available enantiopure threitol,[268,269] a tether that, in the meantime, has proven to be a versatile chiral auxiliary in fullerene chemistry.[4,22]

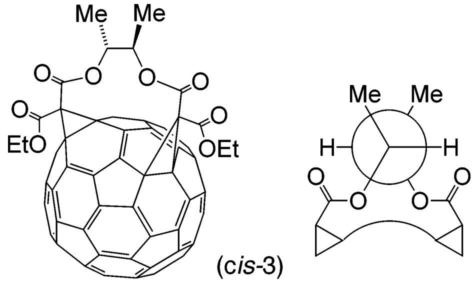
Bingel reaction between C$_{60}$ and either (*R*,*R*)-**95** or (*S*,*S*)-**95** afforded the enantiomeric *cis*-3 bis-adducts $(R,R,{}^{f,s}C)$-

Scheme 4. Diastereoselective Biscyclopropanation of C_{60} Using Enantiomerically Pure Bismalonates Derived from Threitol



96[397] and (*S*,*S*,^{f,s}*A*)-**96** (Scheme 4), respectively, with de ≥ 96%, as minor products besides the corresponding *cis*-2 bis-adducts (*R*,*R*)-**97** and (*S*,*S*)-**97**, the addition pattern of which is achiral.[268,269] Removal of the chiral tethers from (*R*,*R*,^{f,s}*C*)-**96** and (*S*,*S*,^{f,s}*A*)-**96** by transesterification with ethanol yielded tetraethyl esters (^{f,s}*C*)-**20** and (^{f,s}*A*)-**20** (Figure 20), respectively, as pure enantiomers exhibiting strong CD bands between 250 and 750 nm with $\Delta\epsilon$ values approaching 150 M^{-1} cm^{-1}. Such strong Cotton effects are typical for the chiral π-chromophores of fullerene derivatives with an inherently chiral addition pattern.[4,20−22] Comparison with CD spectra calculated by the π-electron SCF−CI−DV MO (self-consistent field−configuration interaction−dipole velocity molecular orbital) method[125,126,398] allowed an assignment of their absolute configurations as [CD(−)488]-(^{f,s}*C*)-**20** and [CD(+)488]-(^{f,s}*A*)-**20**.[121] Bis-adducts derived from (*S*,*S*,^{f,s}*A*)-**96**, having the diol moiety in the tether deprotected and bearing long aliphatic chains in the outer ester groups, have been shown to form stable Langmuir films at the air−water interface.[399,400] It should also be mentioned that chiral exciton coupling between two fullerene chromophores was observed for the first time in the CD spectrum of a Bingel-type adduct in which two methano[60]fullerenes are interconnected by the tether unit of (*R*,*R*)-**95**.[270]

The open-chain L-threitol-derived tether of bis-malonate (*S*,*S*)-**98** afforded the diastereoisomeric *cis*-3 bis-adducts (*S*,*S*,^{f,s}*A*)-**99a** and (*S*,*S*,^{f,s}*C*)-**99b** (Scheme 4), as minor products next to *cis*-2 bis-adduct (*S*,*S*)-**100**, in a 5:2 ratio which reflects a relatively poor diastereoselectivity.[401] The higher conformational flexibility of (*S*,*S*)-**98**, associated with the lack of cyclic acetal function in comparison to (*S*,*S*)-**95**, seems to be responsible for the lower diastereoselectivity observed in the formation of *cis*-3 bis-adducts (*S*,*S*,^{f,s}*A*)-**99a** and (*S*,*S*,^{f,s}*C*)-**99b**. A configurational assignment as [CD(−)281]-(*S*,*S*,^{f,s}*C*)-**99a** and [CD(+)281]-(*S*,*S*,^{f,s}*A*)-**99b**, based on a conformational analysis relying on the determination of ^3J(H,H) coupling constants for the central CH(OMe)−CH(OMe) unit of (*S*,*S*)-**95**,[401] is in agreement with the above assignments[121] for **20** and **96**.



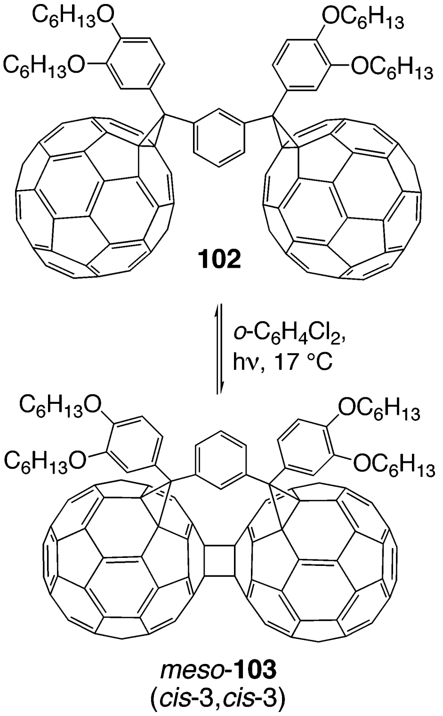
(*R*,*R*,^{f,s}*A*)-**101**
(*S*,*S*,^{f,s}*C*)-**101**

Figure 28. Bis-adduct (*R*,*R*,^{f,s}*C*)-**101**, diastereoselectively synthesized by Bingel macrocyclization of C_{60} with (*R*,*R*)-butane-2,3-diyl bismalonate (left) and Newman projection of the preferred tether conformation (right). The (*S*,*S*)-configured bismalonate similarly afforded bis-adduct (*S*,*S*,^{f,s}*A*)-**101**.[270]

The importance of the conformational homogeneity of chiral tethers for achieving a high diastereoselectivity in multifunctionalizations of fullerenes is also nicely illustrated by a systematic study on Bingel additions, to C_{60}, of enantiopure bismalonates derived from 1,2-disubstituted ethylene glycol.[270] Excellent regio- and diastereoselectivity was achieved with diethyl (*R*,*R*)- and (*S*,*S*)-butane-2,3-diyl bismalonates, affording *cis*-3 bis-adducts (*R*,*R*,^{f,s}*A*)-**101** (Figure 28) and (*S*,*S*,^{f,s}*C*)-**101**, respectively, with de > 97%. According to semiempirical calculations, the substituents of the ethylene tether fragment of (*R*,*R*,^{f,s}*A*)-**101** adopt a staggered conformation with gauche relationships between the two methyl as well as between the two ester groups and an antiperiplanar (*ap*) arrangement of the H-atoms (Figure 28, Newman projection). Fixation of the ethylene unit of the tether in this favorable conformation by incorporation in a bismalonate derived from *trans*-cyclohexane-1,2-diol even led to an increased yield of the exclusively and diastereoselectively generated *cis*-3 regioisomer upon reaction with C_{60}. Conversely, when the ethane-1,2-diyl bismalonate moiety is locked in an unproductive conformation, for example, in tethers derived from *trans*-cyclopentane-1,2-diol, or *exo,cis*- and *exo,trans*-norbornane-2,3-diol, Bingel macrocyclization with C_{60} failed. As to the unobserved (*R*,*R*,^{f,s}*C*)-**101** diastereoisomer, the computations anticipated gauche relationships between the ester groups, as well as between the H-atoms, and an *ap* arrangement for the methyl residues. The coupling constant $^3J(H,H) = 7.9$ Hz measured for the vicinal protons of the glycolic fragment clearly indicates an *ap* relationship, which corresponds to the most stable conformer of (*R*,*R*,^{f,s}*A*)-**101**.[270] This result is in accord with the near-identity of the CD spectra of (*R*,*R*,^{f,s}*A*)-**101** and (*S*,*S*,^{f,s}*A*)-**20**, which reflects their matching chiral π-chromophores.[121] It was further corroborated by the work of Harada and co-workers who determined the X-ray crystal structure of [CD(+)280]-(*R*,*R*,^{f,s}*A*)-**101**, using the known configuration of the tether as an internal reference.[402] With this ultimate experimental proof for the structure of (*R*,*R*,^{f,s}*A*)-**101**, its CD data can serve as reference for further configurational assignments of *cis*-3 bis-adducts of C_{60}.

Knol and Hummelen reported the first controlled intramolecular photodimerization of two methanofullerene moieties held in close proximity by the *m*-phenylene spacer in **102** (Scheme 5).[403] When the C_{2v}-symmetric molecule was irradiated with a 150-W sodium flood lamp, a clean steady-

Scheme 5. Photochemical Equilibrium between Bis(methanofullerene) 102 and *meso*-103, Which Results from Intramolecular [2 + 2] Cycloaddition between the Two Fullerene Moieties[403]



state mixture of **102** (ca. 40%) and C_s-symmetric **103** with a cyclobutabis(cyclopropafullerene) structure resulted, each fullerene cage displaying a *cis*-3 addition pattern. Interestingly, the steric requirements for the photodimerization enforce opposite configurations of the inherently chiral *cis*-3 addition patterns of the interconnected fullerenes, thus leading diastereoselectively to the *meso* form **103**.

An early step toward regio- and diastereoselective bisfunctionalization of buckminsterfullerene was taken by Nakamura and co-workers, testing the [3 + 2] cycloaddition with thethered nucleophilic vinylcarbenes.[404,405] The reactive groups were generated under thermal conditions from cyclopropenone acetals with which they are in equilibrium. The observed product distribution as a function of the length of the oligomethylene tether was the following: $(CH_2)_3 \rightarrow$ *cis*-1 and *cis*-2, $(CH_2)_4 \rightarrow$ *cis*-1, and $(CH_2)_6 \rightarrow$ *cis*-3 ((±)-**104**, Figure 29). Due to the low symmetry (C_s) of the addends, the number of theoretically possible bis-adduct isomers increases from eight (for C_{2v}-symmetric addends) to 36.[406] Nevertheless, a single constitutional isomer was formed for each addition pattern, the double bonds of the two fullerene-fused pentagons being oriented toward each other. Reduction of the enantiomeric diones obtained from (±)-**104** by acetal cleavage and subsequent esterification of the diols with (*S*)-2-methoxy-2-phenylacetic acid allowed the separation of the diastereoisomeric esters, that is, of *cis*-3 bis-adducts of C_{60} with enantiomeric addition patterns.[407] Subsequent regeneration of the alcohol functions was achieved by reduction of the esters with DIBAL-H (diisobutylaluminum hydride).

The use of nonracemic tethers, made up of a C_6-chain including an acetal of a nonracemic vicinal diol unit, resulted in the formation of diastereoisomerically pure *cis*-3 bis-adducts.[404,405,407] For example, a tether derived from D-mannitol induced the ($^{f,s}C$)-configuration of the *cis*-3 addition pattern in C_2-symmetric (−)-**105**, which is characterized by a very large optical rotation ($[\alpha]_D = -1665°$, $c = 0.01$, $CHCl_3$, 28 °C).[408] The configurational assignment took into account a molecular mechanics analysis, which showed the ($^{f,s}C$)-structure to be more stable by 0.41 kcal mol^{-1} than the ($^{f,s}A$)-diastereoisomer. In addition, the CD spectrum of (R,R,R,R,$^{f,s}C$)-**105** displays a strong positive Cotton effect in the region between 210 and 230 nm, which was also observed for a simpler analog[407] and for *cis*-3 dicyclopropa[60]fullerene derivatives with previously assigned ($^{f,s}C$)-configuration.[121,270]

Tetra-ammonium ion (±)-**106**, prepared in a four-step transformation from (±)-**104**, proved to be a potent gene transfection vector. Together with a related, enantiopure fullerene-based vector,[408] it has an efficiency that is comparable to commercial lipofection agents.[409,410] It binds reversibly to duplex DNA, leading to its condensation, delivery of the complex into mammalian cells through phagocytosis, and the transient expression of the released DNA in the target cell. The aggregation process between (±)-**106** and DNA, studied by static and dynamic light scattering, showed a fractal behavior.[411]

Shinkai and co-workers studied the regio-and diastereoselective Diels−Alder addition to C_{60} of saccharide-derived arylboronates carrying bromomethyl groups as *o*-quinodimethane precursors on the aromatic nucleus.[412−414] The most thoroughly investigated tethers, L- and D-threitol, afforded ca. 72:28 and 28:72 mixtures, respectively, of *cis*-3 bis(boronic acid)s ($^{f,s}C$)-**107** and ($^{f,s}A$)-**107** (Scheme 6) after removal of the templates and regeneration of the boronic acid functions.[412,414] Regioisomer assignments are based mainly on symmetry considerations (^1H and ^{13}C NMR) and UV/vis fingerprints of the 5,5-dimethyl-1,3,2-dioxaborinanes (Scheme 6) prepared after removal of the sugar templates.[414] Also, oxidation of the dioxaborinanes with H_2O_2 afforded the corresponding bisphenols, the spectral data of which could be directly compared with those of the bisphenols prepared in a different way by Nishimura and co-workers (cf. section 4.3.3).[389] The absolute configuration of the enantiomers of **107** was assigned by comparison of their CD spectra to those of [CD(−)488]-($^{f,s}C$)-**20** and [CD(+)488]-

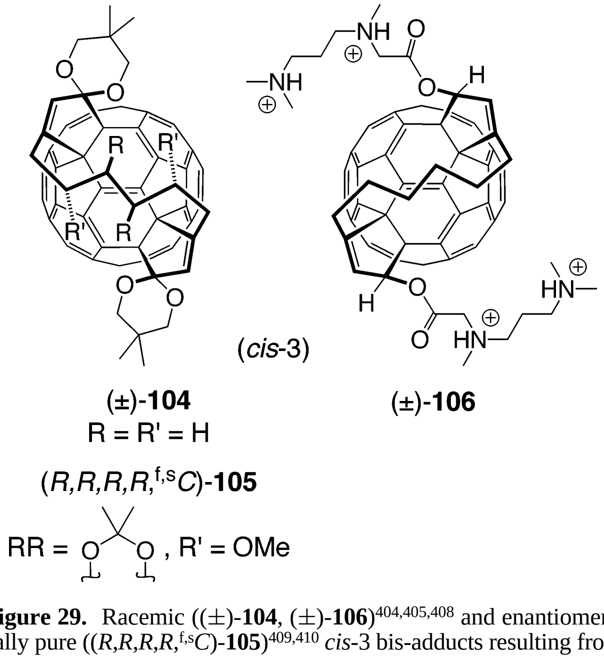
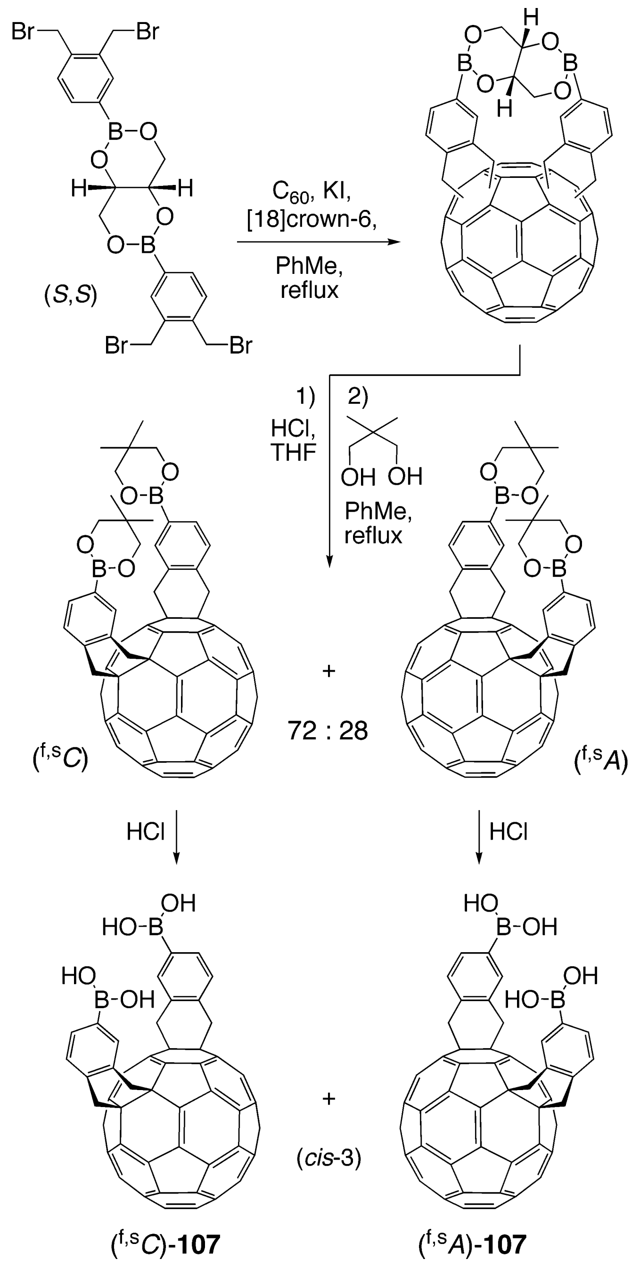


Figure 29. Racemic ((±)-**104**, (±)-**106**)[404,405,408] and enantiomerically pure ((R,R,R,R,$^{f,s}C$)-**105**)[409,410] *cis*-3 bis-adducts resulting from [3 + 2] cycloaddition of appropriately tethered vinylcarbenes to C_{60}.

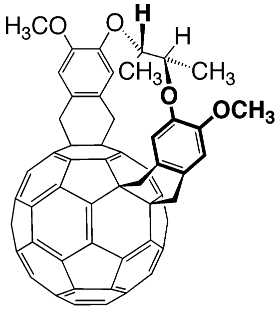
Scheme 6. Regio- and Diastereoselective Double Diels−Alder Addition to C_{60} Using an L-Threitol Derivative as Imprinting Template[412,414]



($^{f,s}A$)-**20** (Figure 20).[121] Competitive complexation studies indicated that L-threitol-imprinted boronic acid ($^{f,s}C$)-**107** and D-threitol-imprinted ($^{f,s}A$)-**107** preferentially rebind their original templates with up to 48% de, and the entire process can be considered as a molecular imprinting technique using C_{60} as a soluble nanosize matrix.[413]

When Nishimura and co-workers used an (*S*,*S*)-configured tether prepared stereospecifically from enantiopure commercial (*R*,*R*)-butane-2,3-diol (cf. supra), Diels−Alder addition to C_{60} afforded *cis*-3 bis-adduct **108** (Figure 30) as a minor product next to the corresponding *cis*-2 isomer.[393] A tentative configurational assignment based on ^{1}H NMR spectroscopic analysis and computer modeling,[393] was later revised as (*S*,*S*,$^{f,s}A$)-**108**.[350,402]

The exploration of other regio- and diastereoselective double Diels−Alder additions to C_{60} of bis(*o*-quinodimethane)-type esters derived from a number of cholates or from



(*S*,*S*,$^{f,s}A$)-**108**
(*cis*-3)

Figure 30. Bis-adduct (*S*,*S*,$^{f,s}A$)-**108**, diastereoselectively synthesized by double Diels−Alder addition using an enantiomerically pure tether.[393,402]

(2*R*,3*R*)-butane-2,3-diol (cf. supra) showed various regio- and diastereoselectivities.[415]

4.4.2. Diastereoselective Generation of e Bis-Adducts

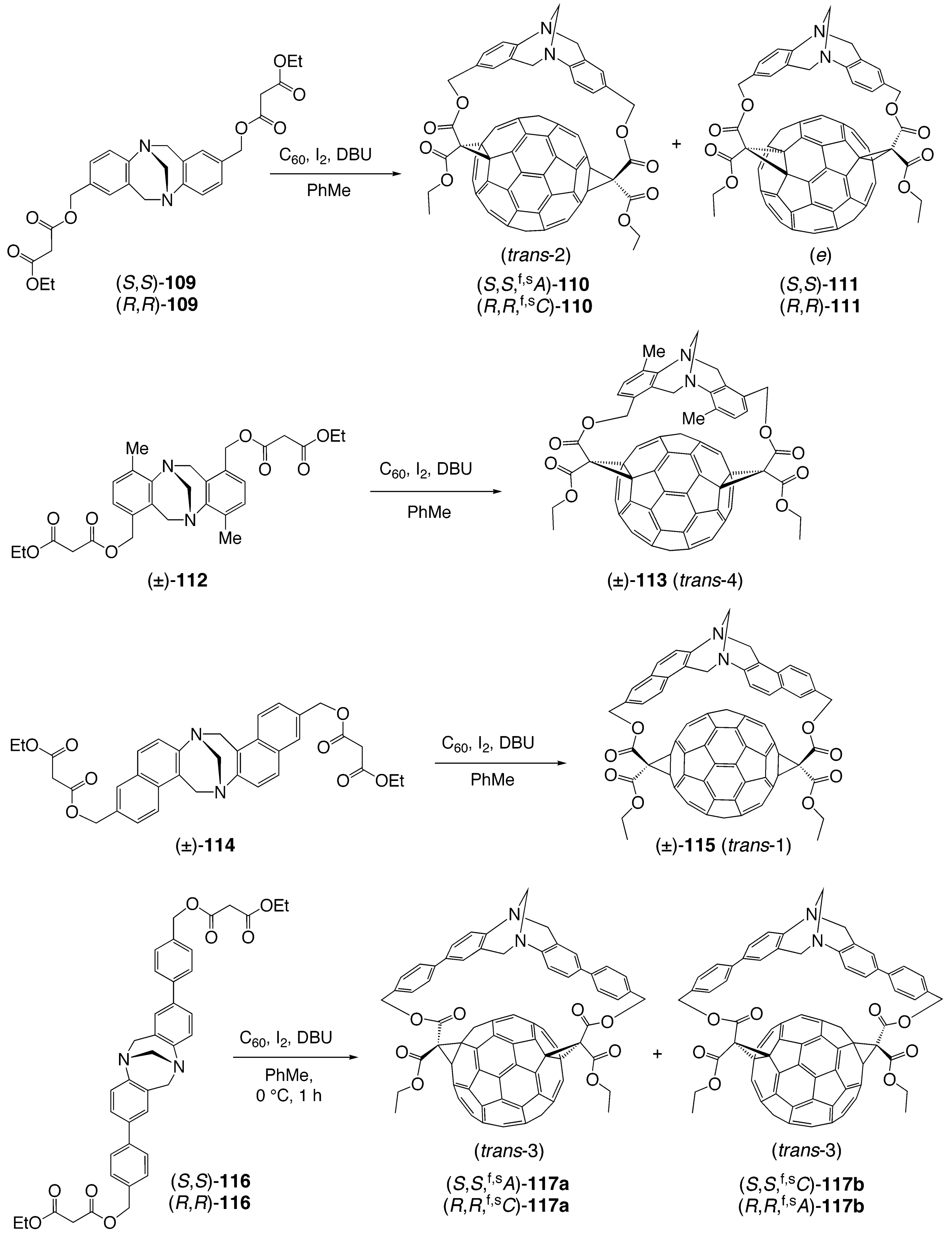
Reports on the diastereoselective tether-directed generation of *e* bis-adducts having either a noninherently chiral functionalization pattern or a newly generated stereogenic center at the bridge in e_{face} position are still rare. In the former category, a certain diastereoselectivity in the [4 + 2] cycloaddition of *o*-quinodimethane groups appended to a hyodeoxycholate should be mentioned.[415] As to the latter, a nonracemic 9,9′-spirobifluorene-2,2′-diyl tether enforces a specific configuration of **74** (Figure 26) when the corresponding bismalonate is added to C_{60}.[269] A comparison between the CD spectra of the enantiomers of **74** and those of the starting spirobifluorene−bismalonate conjugate indicates a strong electronic coupling between the fullerene and spirobifluorene chromophores.

4.4.3. Diastereoselective Generation of trans Bis-Adducts

The regio- and stereoselective targeting of the inherently chiral *trans*-2 and *trans*-3 addition patterns, which span both hemispheres of C_{60}, posed a great challenge since it requires large and conformationally constrained chiral tethers. Derivatives of the C_2-symmetric Tröger base were envisaged as suitable spacers: they are distinguished by rigidity and a folded geometry with nearly orthogonal aromatic rings as prominent structural features.

Thus, in the double Bingel cyclopropanation of C_{60} with enantiomerically pure bismalonates (*S*,*S*)-**109** and (*R*,*R*)-**109** (Scheme 7), bis-adducts (*S*,*S*,$^{f,s}A$)-**110** and (*R*,*R*,$^{f,s}C$)-**110**, respectively, were obtained with complete diastereoselectivity, next to minor amounts of *e* isomers (*S*,*S*)-**111** and (*R*,*R*)-**111**.[416,417] Addition patterns were determined by means of UV/vis and NMR spectroscopy. In the region between 400 and 800 nm, the electronic absorption spectra of dicyclopropa[60]fullerenes are mainly determined by the structure of the fullerene π-chromophore and can, therefore, be used as fingerprints for the corresponding addition patterns.[266] The absolute configurations of (*S*,*S*,$^{f,s}A$)-**110** and (*R*,*R*,$^{f,s}C$)-**110**, as well as of the enantiomers discussed below, were established by comparison of their CD spectra with those of previously assigned enantiomerically pure derivatives of C_{60} with the same functionalization pattern.[264,266] Under the assumption that the thermodynamic stability of such bis-adducts is reflected in the transition state of the second cyclopropanation, the calculated difference $\Delta\Delta H =$

Scheme 7. Regio- and Diastereoselective Bingel Macrocyclizations between [60]Fullerene and Enantiomerically Pure Bismalonates Derived from Different Tröger Bases[416,417]



(*trans*-2)
(*S*,*S*,$^{\mathrm{f,s}}$*A*)-**110**
(*R*,*R*,$^{\mathrm{f,s}}$*C*)-**110**

(*e*)
(*S*,*S*)-**111**
(*R*,*R*)-**111**

(*S*,*S*)-**109**
(*R*,*R*)-**109**

(±)-**112**

(±)-**113** (*trans*-4)

(±)-**114**

(±)-**115** (*trans*-1)

(*S*,*S*)-**116**
(*R*,*R*)-**116**

(*trans*-3)
(*S*,*S*,$^{\mathrm{f,s}}$*A*)-**117a**
(*R*,*R*,$^{\mathrm{f,s}}$*C*)-**117a**

(*trans*-3)
(*S*,*S*,$^{\mathrm{f,s}}$*C*)-**117b**
(*R*,*R*,$^{\mathrm{f,s}}$*A*)-**117b**

29.4 kcal mol^{-1} (PM3) in favor of the actually formed (*S*,*S*,$^{\mathrm{f,s}}$*A*)-**110** over the hypothetical (*S*,*S*,$^{\mathrm{f,s}}$*C*)-configured diastereoisomer rationalizes the experimental observation very well.

Variation of the geometry of the tether by attachment of the malonate residues to a different position of the Tröger base core ((±)-**112**) afforded exclusively *trans*-4 regioisomer (±)-**113** upon reaction with C_{60}.[416,417]

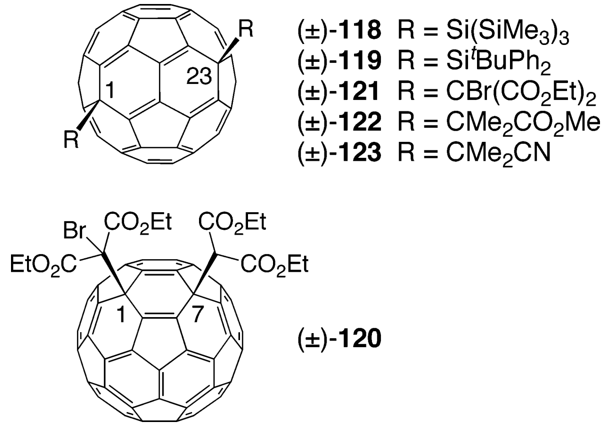
On the other hand, the switching from an aniline- to a naphthyl-2-amine-derived Tröger base (bismalonate (±)-**114**) led to the completely regioselective and high-yielding formation of *trans*-1 bis-adduct (±)-**115**.[417] X-ray analysis of (±)-**115** showed the used crystal to contain only the (*R*,*R*)-configured enantiomer: this seems to be the first case of spontaneous resolution of a racemic fullerene derivative.

In an attempt to achieve also the inherently chiral *trans*-3 functionalization pattern, bismalonates (*S*,*S*)-**116** and (*R*,*R*)-**116** with an extended Tröger base core were added to C_{60}. The reaction was completely regioselective, affording only the targeted *trans*-3 addition pattern but in the form of a pair of C_1-symmetric *in*,*out*[351] diastereoisomers, namely, (*S*,*S*,^{f,s}*A*)-**117a** and (*S*,*S*,^{f,s}*C*)-**117b** from (*S*,*S*)-**116**, and (*R*,*R*,^{f,s}*C*)-**117a** and (*R*,*R*,^{f,s}*A*)-**117b** from (*R*,*R*)-**116**.[417] Whereas the CD spectra of enantiomers, prepared in separate syntheses as described, are exact mirror images, those of diastereoisomers show some deviation from this relationship due to the superposition of the Cotton effects originating from the fullerene and the Tröger base chromophores and a possible coupling between them.

These asymmetric syntheses allowed the first stereoselective targeting of the inherently chiral *trans*-2 and *trans*-3 addition patterns of buckminsterfullerene. Tröger type bases with different angles between the planes of the arene rings as well as representatives derived from thiophene and benzothiophene were successfully used by Saigo and co-workers in a further study on the regio- and stereocontrolled addition of accordingly tethered bismalonates to C_{60}.[418]

4.5. C(1),C(23)-Adducts

Two hydrogen atoms prefer addition across a 6−6 double bond of C_{60} over other addition modes.[419] However, as addends become bulkier and eclipsing vicinal interactions stronger, C(1),C(7)-addition (the corresponding products are also called 1,4-adducts because the addends are separated by three bonds) is increasingly favored. The rather rare inherently chiral C(1),C(23)-functionalization pattern of 1,6-adducts (see Figure 31) was observed for the first time by Ando and co-workers upon addition of very bulky silyllithium or germyllithium reagents: treatment of C_{60} with $(Me_3Si)_3SiLi$, followed by quenching with EtOH, gave the 1,6-adduct (±)-**118** (Figure 31) as sole product and its C_2-symmetric structure was confirmed by X-ray crystallography.[420,421] Some of the silyllithium reagents yielded 1,4-adducts next to the 1,6-adducts. The latter were also obtained by photochemical addition of disilanes to C_{60}, a reaction proceeding probably via silyl radicals.[422,423] Irradiation of a 1:1 solution of C_{60} and the disilane $(^tBuPh_2Si)_2$ in benzene with a low-pressure mercury arc lamp thus gave high yields of the 1,6-adduct (±)-**119**, a reaction that is suppressed if the radiation energy is insufficient ($\lambda > 300$ nm) to cleave the Si−Si bond or in the presence of radical scavengers such as cumene or CCl_4.[424] The C(1),C(23) positional relationship between pairs of addends appears also in three structures proposed by Akasaka and co-workers for tetrakis-adducts isolated as main products under similar conditions, but using a 2:3 ratio of C_{60} and disilane.[425]



(±)-**118** R = $Si(SiMe_3)_3$
(±)-**119** R = Si^tBuPh_2
(±)-**121** R = $CBr(CO_2Et)_2$
(±)-**122** R = CMe_2CO_2Me
(±)-**123** R = CMe_2CN

(±)-**120**

Figure 31. Variety of C(1),C(23)-adducts (1,6-adducts) with an inherently chiral functionalization pattern, and C(1),C(7)-adduct (1,4-adduct) (±)-**120**, formed together with (±)-**121** and having a noninherently chiral functionalization pattern.

When buckminsterfullerene was treated with diethyl bromomalonate and manganese(III) acetate dihydrate in refluxing chlorobenzene, the isolated product did not include a cyclopropafullerene but consisted of a mixture of C_1-symmetric 1,4-adduct (±)-**120** and C_2-symmetric 1,6-adduct (±)-**121** (Figure 31).[426] This reaction is also thought to proceed via radical intermediates generated from the active methylene compounds under the action of $Mn(OAc)_3{\cdot}2\,H_2O$. Interestingly, when unbrominated malonates were used as starting materials, mono- and dimeric 1,4-adducts (see section 6.1) were the only products.

A preference for the C(1),C(23)-addition pattern in certain radical reactions is further illustrated by the thermal decomposition of dimethyl azo(bisisobutyrate) in a C_{60}-containing solution.[427] 2D INADEQUATE ^{13}C NMR spectroscopy allowed the identification of one product as (±)-**122** (Figure 31), formed next to the achiral 1,4-adduct. The related reaction of azobis(isobutyronitrile) (AIBN) with [60]fullerene afforded also the C(1),C(9)-isomer (1,2-adduct) in addition to the C(1),C(7)- (1,4-adduct) and C(1),C(23)-isomers (1,6-adduct (±)-**123**).[428]

4.6. Tris-Adducts Resulting from Addition of Untethered Reagents

Further cyclopropanation of *e*- and *trans*-3 ((±)-**21**, Figure 20) bis[bis(ethoxycarbonyl)methano][60]fullerenes leads to the tris-adducts (±)-**124** and (±)-**125**, respectively (Figure 32).[40,259] Whereas all pairs of addends in C_3-symmetric (±)-**124** and in the corresponding ^3He incarcerane[279] are distinguished by an *e*-relationship (*e*,*e*,*e* addition pattern), the arrangement is *trans*-3,*trans*-3,*trans*-3 in D_3-symmetric (±)-**125**. The enantiomers of both tris-adducts, (±)-**124** and (±)-**125**, have been resolved by HPLC on a chiral (*R*,*R*)-Whelk-O1 phase, and their CD spectra have been recorded.[271] Resolution of the *trans*-3,*trans*-3,*trans*-3 adduct (±)-**125** was achieved on the chiral stationary phase (*R*)-(−)-TAPA (2-(2,4,5,7-tetranitro-9-fluorenylidenaminoxy)propionic acid).[429] Treatment of (±)-**124** with NaH, followed by acidic workup yielded the hexa-acid (±)-**126** as a water-soluble fullerene derivative.[430] Both the *e*,*e*,*e* ((±)-**126**) and *trans*-3,*trans*-3,*trans*-3 ((±)-**127**) hexa-acids, combining the radical-scavenging ability of fullerenes with the water solubility of oligo(carboxylic acid)s, were proven to have potent antioxidant, neuroprotective,[431,432] and other interesting biological activities.[433,434] Semiempirical calculations suggest that the attack of a hydroxy radical at the first-encountered double bond of the hexa-acids is followed by its migration to the

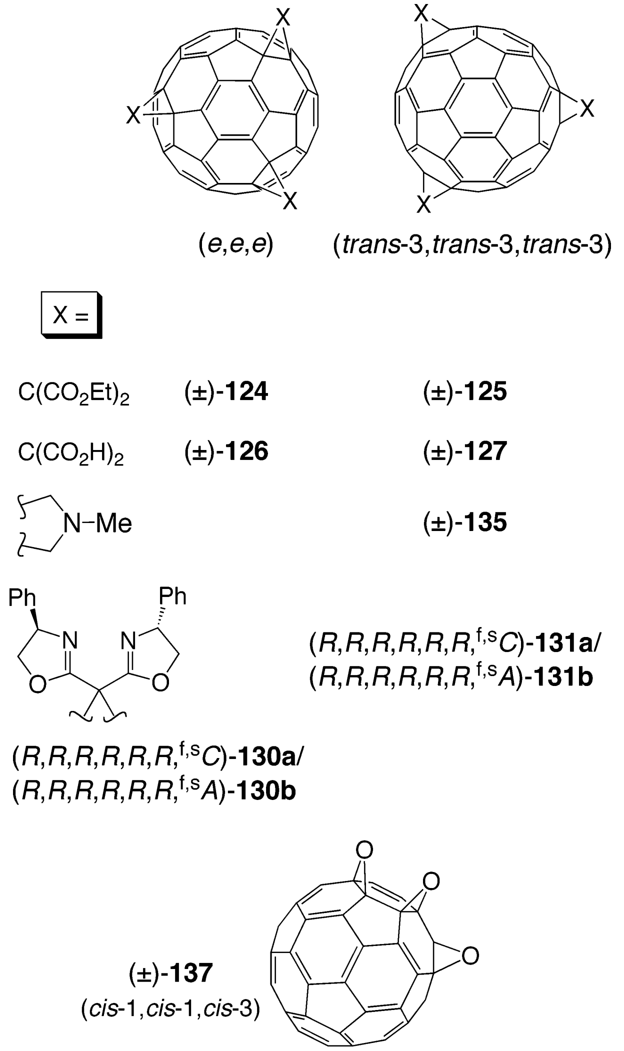


Figure 32. Tris-adducts of C_{60} with the inherently chiral *e*,*e*,*e*; *trans*-3,*trans*-3,*trans*-3; and *cis*-1,*cis*-1,*cis*-3 addition patterns.

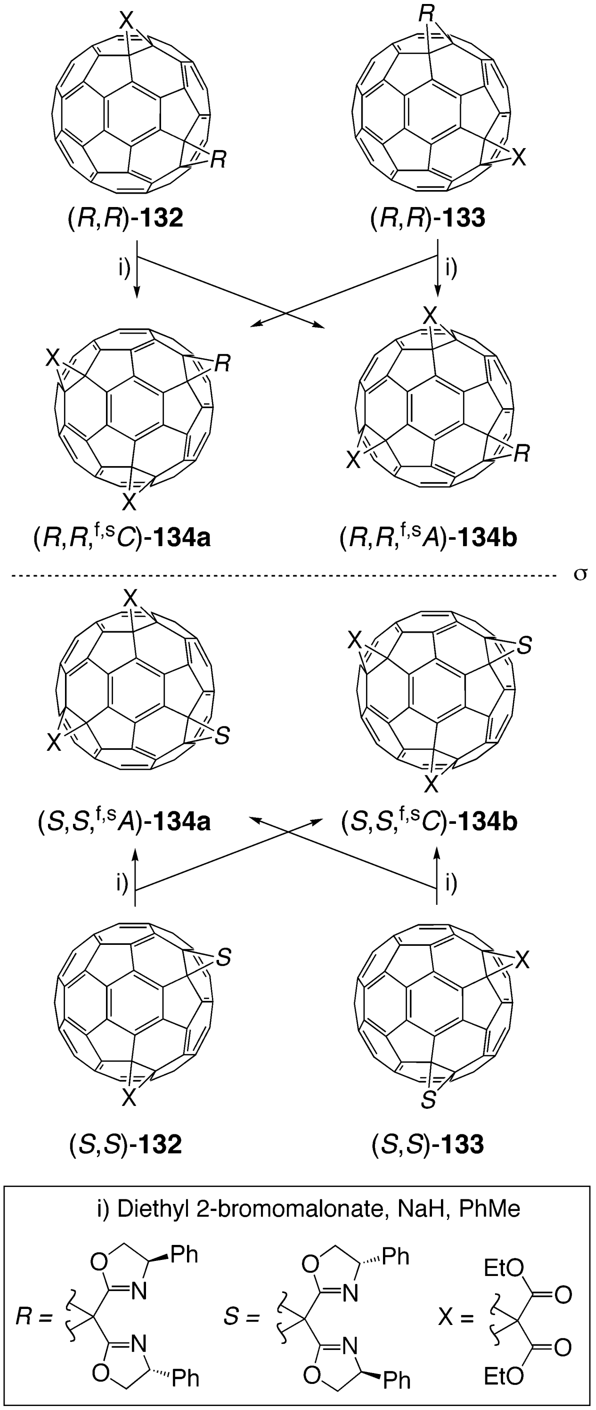
position with the highest Coulson free valence index.[435] Changes of photophysical and electron-transfer properties as a function of the number and arrangement of addends have been studied, among others, with a variety of compounds including several of the above adducts as well as with *trans*-3,*trans*-3,*trans*-3 tris{bis[4-(dimethylamino)-phenyl]methano}[60]fullerene.[282,284,436,437] A “Teflon ponytail” fullerene derivative, the hexakis[$(CH_2)_3(CF_2)_7CF_3$] ester of (±)-**126**, shows excellent solubility in perfluorinated solvents while maintaining its sensitizing ability for singlet oxygen generation in fluorous phases, thereby manifesting potential with regard to biphasic systems and photobiology.[438,439]

Of the remaining 44 regioisomeric tris-adducts of C_{60}, five diethyl malonate-derived Bingel-type adducts with the following, mostly inherently chiral, addition patterns have been isolated and characterized: C_1-symmetric *e*,*t*4,*t*3 (“*t*” stands for “*trans*-” in this short notation); C_1-symmetric *e*,*t*4,*t*2; C_1-symmetric *e*,*t*3,*t*2; C_2-symmetric *t*4,*t*4,*t*2; C_s-symmetric *t*4,*t*4,*t*3.[266] Electrochemical studies in CH_2Cl_2 showed that two-electron constant potential electrolysis (CPE) with each of the seven tris[bis(ethoxycarbonyl)methano][60]fullerene isomers (including (±)-**124** and (±)-**125**) leads to a competition between retro-Bingel reaction and isomerization reactions with preferential loss of 1−2 addends.[440] These results contrast those obtained with a series of bis-adducts, where two-electron CPE mainly resulted in isomerization.[278] PM3 and AM1 computational studies suggest that the experimental finding of different regioselectivities taking effect in malonate additions to the neutral (uncharged) precursors and in rearrangements of electrochemically generated dianions is related to a switching from kinetic to thermodynamic control.[440] On the other hand, systematic application of the electrochemical retro-Bingel reaction to tetrakis-, pentakis-, and hexakis-adducts of C_{60} (all bis(ethoxycarbonyl)methano addends were believed to occupy positions belonging to a pseudo-octahedral, T_h-symmetric subset of formal double bonds of buckminsterfullerene, cf. section 6.8 and Figures 66 and 67) at potentials ∼100 mV more negative than the second reduction potential produced tris-adducts in ca. 30% yield. The major products had the addition patterns *e*,*t*4,*t*2 and *e*,*t*4,*t*3, whereas *e*,*e*,*e* and *t*3,*t*3,*t*3 were generated in relatively small amounts.[441]

Making use of a strategy similar to that applied by Diederich and co-workers to chiral derivatives of C_{70} (section 5.6),[30,267] Djojo and Hirsch reported facile access to enantiomerically pure bis- and tris-adducts of C_{60} with an inherently chiral functionalization pattern.[265] By stepwise modified Bingel reactions[268,331,442] using optically pure methylenebis(oxazoline)s derived, for example, from (*R*)-phenylalanine, they obtained, among other regioisomers, bis-adducts (*R*,*R*,*R*,*R*,$^{f,s}C$)-**128a**/(*R*,*R*,*R*,*R*,$^{f,s}A$)-**128b**, and (*R*,*R*,*R*,*R*,$^{f,s}C$)-**129a**/(*R*,*R*,*R*,*R*,$^{f,s}A$)-**129b** (Figure 20) as well as tris-adducts (*R*,*R*,*R*,*R*,*R*,*R*,$^{f,s}C$)-**130a**/(*R*,*R*,*R*,*R*,*R*,*R*,$^{f,s}A$)-**130b** and (*R*,*R*,*R*,*R*,*R*,*R*,$^{f,s}C$)-**131a**/(*R*,*R*,*R*,*R*,*R*,*R*,$^{f,s}A$)-**131b** (Figure 32), as diastereoisomeric pairs in which the (*R*,*R*)-configured heterocycles are combined with inherently chiral addition patterns of either $^{f,s}C$- or $^{f,s}A$-configuration.[265] For each diastereoisomeric pair (**128a**/**128b**, **129a**/**129b**, and **130a**/**130b**), the CD spectra are nearly mirror-image shaped, which clearly proves the opposite configuration of the addition patterns and also the predominant chiroptical contribution of the residual fullerene π-chromophores in comparison to that of the addends.[30,265,267]

The generation of an *e*,*e*,*e* tris-adduct from an achiral *e* bis-adduct can occur by functionalization of either of two enantiotopic double bonds and, consequently, the two resulting addition patterns are enantiomeric. Taking advantage of this fact, Djojo and Hirsch subjected each of the two constitutional isomers (*R*,*R*)-**132** and (*R*,*R*)-**133** (Scheme 8), which differ in having their malonate and methylenebis-(isoxazoline) addends swapped between the heterotopic e_{edge} and e_{face} positions, to diethyl bromomalonate addition. The combination of the (*R*,*R*)-configured addend already in place and the newly generated, inherently chiral *e*,*e*,*e* addition pattern afforded a pair of diastereoisomers, (*R*,*R*,$^{f,s}C$)-**134a** and (*R*,*R*,$^{f,s}A$)-**134b**, which could be purified by chromatography on an achiral stationary phase. Similarly, starting from the according (*S*,*S*)-configured bis-adducts (*S*,*S*)-**132** and (*S*,*S*)-**133**, the diastereoisomeric *e*,*e*,*e* tris-adducts (*S*,*S*,$^{f,s}A$)-**134a** and (*S*,*S*,$^{f,s}C$)-**134b** could be isolated. As evidenced by their stereodescriptors, the four stereoisomeric tris-adducts include two diastereoisomeric pairs of enantiomers ((*R*,*R*,$^{f,s}C$)-**134a**/(*S*,*S*,$^{f,s}A$)-**134a** and (*R*,*R*,$^{f,s}A$)-**134b**/(*S*,*S*,$^{f,s}C$)-**134b**). Comparisons among the CD spectra of stereoisomers belonging to the series **128a/b**−**131a/b** (Figures 20 and 32) and **134a/b** (Scheme 8) show that compounds having addition patterns of matching constitution and configuration give rise to (nearly) identical Cotton effects, irrespective of the constitution or configuration of the addends. The absolute config-

Scheme 8. Access to Diastereoisomeric Tris-Adducts of C_{60} with Mirror-Image *e,e,e* Addition Patterns, Starting from *e*-Bis-Adducts with an Achiral Addition Pattern and Enantiomerically Pure Addends of Identical Configuration[a]



[a] Separation of the diastereoisomers and repetition of the procedure with enantiomerically pure bis-adducts of opposite configuration affords, in total, four pure stereoisomers consisting of two pairs of enantiomers ((*R*,*R*,^{f,s}*C*)-**134a**/(*S*,*S*,^{f,s}*A*)-**134a** and (*R*,*R*,^{f,s}*A*)-**134b**/(*S*,*S*,^{f,s}*C*)-**134b**)).[266]

uration of the addition patterns of isoxazolinyl-persubstituted *trans*-2 and *trans*-3 dicyclopropa[60]fullerenes, as well as of an *e*,*e*,*e* tricyclopropa[60]fullerene could be assigned by calculation of the CD spectra of the corresponding unsubstituted methanofullerene isomers.[266]

After reacting buckminsterfullerene with an excess of *N*-methyl azomethine ylide, Prato and co-workers were able to isolate a number of tris-adducts next to the entire series of eight [60]fullerene-fused bispyrrolidines (e.g., (±)-**39**−(±)-**41**, Figure 20).[301] Preparation of the tris-adducts by introduction of the third addend on each previously isolated bis-adduct facilitated assignments, which were made for the following nine tris-adducts: *c*2,*e*,*t*2 ("*c*" and "*t*" stand for "*cis*-" and "*trans*-", respectively, in this short notation); *c*2,*t*4,*t*2; *c*2,*t*3,*t*2; *e*,*t*4,*t*3; *e*,*t*4,*t*2; *e*,*t*3,*t*2; *t*4,*t*4,*t*2; *t*4,*t*3,*t*3; and *t*3,*t*3,*t*3 ((±)-**135**, Figure 32). It should be mentioned that a related, D_3-symmetric hexakis-adduct combining two *t*3,*t*3,*t*3 patterns ((±)-**136**, Figure 35) had previously been reported by Rubin, Garcia-Garibay, and co-workers (cf. section 4.8).[443] In comparison to the 3-fold Bingel addition, the 1,3-dipolar cycloaddition of azomethine ylides presents a remarkably lower regioselectivity, and the three above functionalization patterns that include a *cis* relationship had never been observed before.[301]

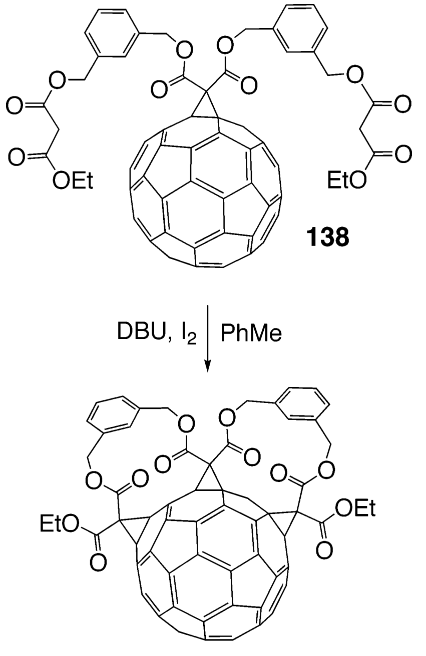
Epoxidation of buckminsterfullerene can be brought about by a variety of oxidizing agents such as oxygen under irradiation,[444,445] *m*-chloroperbenzoic acid,[446−448] or 1,1-dimethyldioxirane.[449] In the resulting mono-adduct, C_{2v}-symmetric oxireno[2′,3′:1,9](C_{60}-I_h)[5,6]fullerene, an O atom bridges a closed 6−6 bond. $C_{60}O$ was also obtained by oxidation of C_{60} with PhIO in the presence of a chemical cytochrome P450 model system, in addition to the C_s-symmetric *cis*-1 bis-adduct and a triepoxy fraction containing two components.[450] Both tris-adducts can also be obtained by epoxidation of *cis*-1 $C_{60}O_2$, and in combination with a ^{13}C NMR spectroscopic analysis, they were assigned as C_s-symmetric *cis*-1,*cis*-1,*cis*-2 adduct (not shown) and C_2-symmetric *cis*-1,*cis*-1,*cis*-3 adduct (±)-**137** (Figure 32).[450] The above bis- and tris-adduct isomers were also found upon oxidation of C_{60} with methyl(trifluoromethyl)dioxirane, a mild and high-conversion method for the epoxidation of fullerenes.[451] The C_{3v}-symmetric *cis*-1,*cis*-1,*cis*-1 adduct structure (not shown) was finally proposed for a third regioisomer, isolated beside the other two from the reaction of C_{60} with *m*-chloroperbenzoic acid.[452]

4.7. Tris-Adducts Resulting from Tether-Directed Remote Functionalization

Similar to the selective targeting of specific fullerene bis-adducts, the tether-directed multifunctionalization constitutes an effective means of controlling the regio- and stereochemistry in tris-addition reactions.[22,347−349] In the early applications of this methodology[345] to fullerene chemistry, Diederich and co-workers used a sequence of a Bingel and a double Diels−Alder reaction to attach a total of three addends to the fullerene spheroid.[22] All these adducts were based on an *e*,*e*,*trans*-1 addition pattern and, therefore, achiral. The first chiral tris-adduct was obtained in a so-called clipping reaction by double intramolecular Bingel reaction of mono-adduct **138** (Scheme 9).[269] Assuming that both *m*-xylylene tethers enforce the expected *cis*-2 functionalization pattern (cf. section 4.8 and Scheme 12), the C_2-symmetry of (±)-**139** strongly suggested the presence of an inherently chiral *cis*-2,*cis*-2,*trans*-3 adduct.

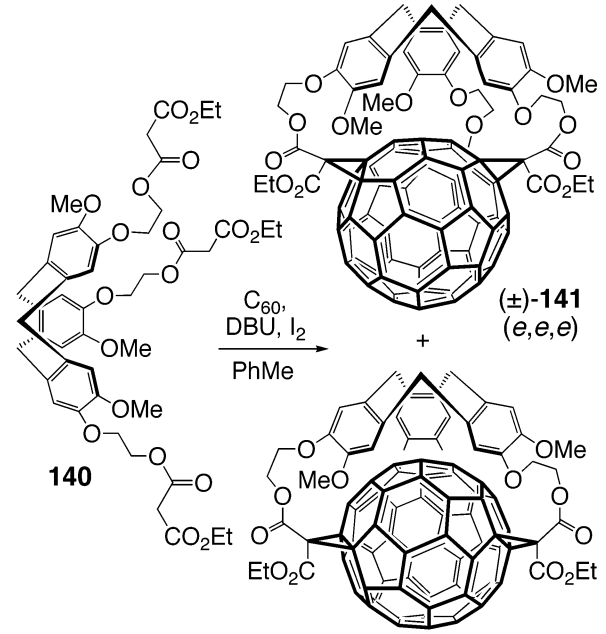
The first direct 3-fold Bingel macrocyclization was realized by addition to C_{60} of tripodal trismalonate (±)-**140** in which three propanedioate moieties are attached to a chiral CTV (cyclotriveratrylene) core (Scheme 10).[453] The two racemic tris-adducts isolated from this reaction were assigned as *e*,*e*,*e* and *trans*-3,*trans*-3,*trans*-3 regioisomers (±)-**141** and (±)-**142**, respectively. Both structures present an interesting superposition of inherently chiral fullerene addition pattern

Scheme 9. Synthesis of a *cis*-2,*cis*-2,*trans*-3 Tris-Adduct of C_{60} by One-Pot Double Bingel Macrocyclization[269]



(±)-**139**
(*cis*-2,*cis*-2,*trans*-3)

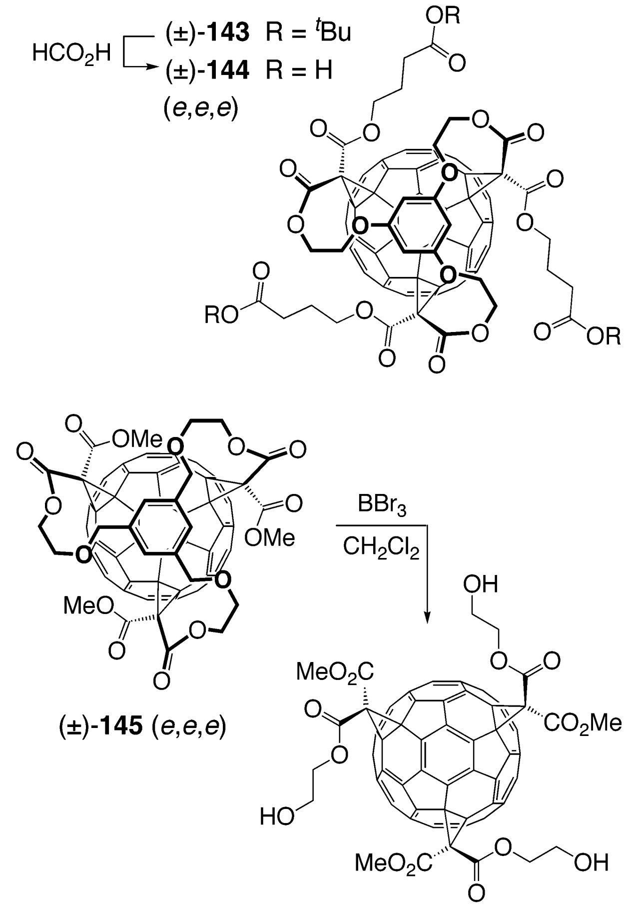
Scheme 10. Products of the First One-Pot Direct Addition of a Trismalonate to C_{60}, Combining an Inherently Chiral Fullerene Addition Pattern with a Chiral Conformer of an Appropriately Substituted Cyclotriveratrylene (CTV)[453,455]



(±)-**142**
(*trans*-3,*trans*-3,*trans*-3)

(possible configurations $^{\mathrm{f,s}}C$ and $^{\mathrm{f,s}}A$) and a conformationally chiral CTV unit (possible configurations *P* and *M*),[454] which can lead to a total of four stereoisomers (two pairs of enantiomers) for each regioisomer. Intriguingly, a detailed mathematical analysis revealed that the corresponding topological stereoisomers, besides being topologically chiral, amount to four in the case of the *e,e,e* tris-adduct but only to two in that of the *trans*-3,*trans*-3,*trans*-3 isomer.[455] In fact, whereas each of the theoretically possible four "classical" *e,e,e* stereoisomers ((P,$^{\mathrm{f,s}}A$)-**141**, (M,$^{\mathrm{f,s}}C$)-**141**, (M,$^{\mathrm{f,s}}A$)-**141**, and (P,$^{\mathrm{f,s}}C$)-**141**) corresponds to a unique topological stereoisomer, the stereoisomers of the *trans*-3,*trans*-3,*trans*-3 tris-adduct are interconvertible pairwise ((P,$^{\mathrm{f,s}}A$)-**142** ⇆ (M,$^{\mathrm{f,s}}A$)-**142**, and (M,$^{\mathrm{f,s}}C$)-**142** ⇆ (P,$^{\mathrm{f,s}}C$)-**142**) by a continuous deformation of the structure making the C_{60} sphere formally pass through the nine-membered ring of the CTV unit. This is a consequence of the fact that the median plane including the addends cuts the carbon sphere into unequal fractions in the former ((±)-**141**) but into equal halves in the latter ((±)-**142**) structure.

Scheme 11. One-Pot Direct Addition of Tripodal Malonates to C_{60} and Selective Deprotection of the Tris-Adducts by Removal of the Terminal Groups ((±)-143 → (±)-144) or the Polar Cap ((±)-145 → (±)-146)[456]



(±)-**146** (*e,e,e*)

Easily accessible and tunable D_{3h}-symmetric tripodal trismalonates have been used by Hirsch and co-workers for the synthesis of C_3-symmetric *e,e,e* tris-adducts of C_{60} displaying distinct polar and equatorial addend zones that may be selectively deprotected.[456] Addition of a trismalonate with a phloroglucinol-derived focal point to C_{60} under modified Bingel conditions[286] afforded *e,e,e* tris-adduct (±)-**143** (Scheme 11) with complete regioselectivity. Subsequent elimination of the *tert*-butyl ester groups with formic acid gave triacid (±)-**144**. An extended tether core derived from 1,3,5-tris(hydroxymethyl)benzene again induced an *e,e,e* addition pattern in (±)-**145** but with a lower regioselectivity. On the other hand, the polar "cap" of this addend could be conveniently removed by treatment with BBr_3 under formation of triol (±)-**146**.[456]

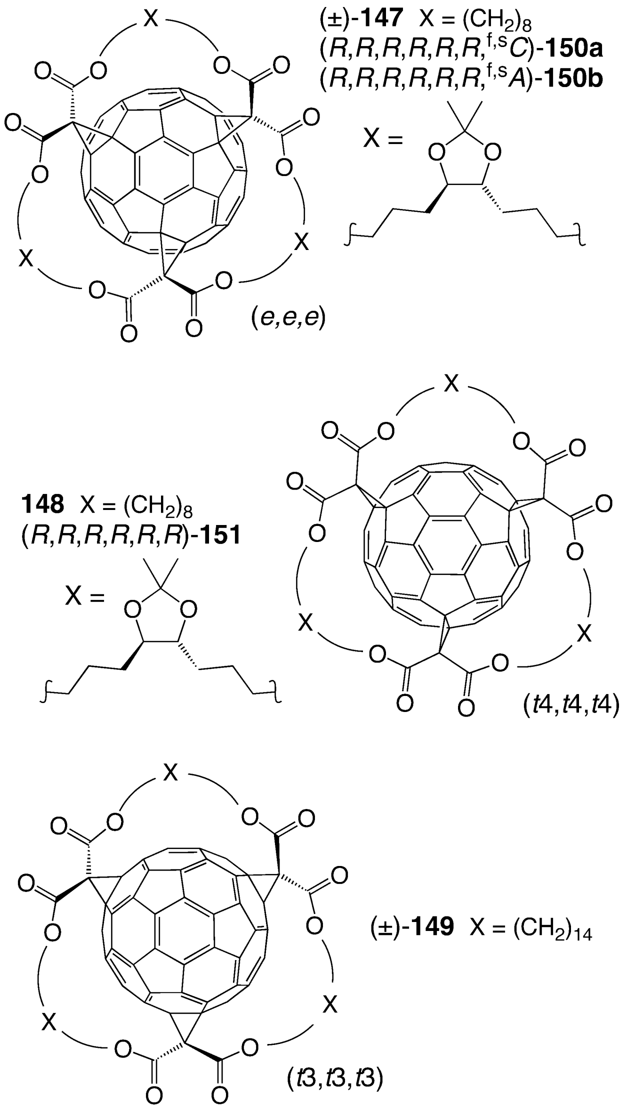


Figure 33. Tris-adducts with 3-fold symmetry, obtained by regio- ((±)-**147**, **148**, (±)-**149**,[372] (*R,R,R,R,R,R*)-**151**)[457] and diastereoselective ((*R,R,R,R,R,R*,^{f,s}*C*)-**150a**, (*R,R,R,R,R,R*,^{f,s}*A*)-**150b**)[457] addition of cyclotrimalonates to C_{60}.

The cyclo-oligomalonate methodology (cf. section 4.3.1 and Figure 25), consisting of a one-pot multiple cyclopropanation with macrocyclic oligo(alkane-α,*ω*-diyl) oligomalonates, was also successfully applied by Hirsch and co-workers to the synthesis of tris-adducts of C_{60} with 3-fold symmetry.[372] When the reaction was carried out with tris(octamethylene) cyclotrimalonate, C_3-symmetric *e,e,e* isomer (±)-**147** (Figure 33) was formed in 94% relative yield next to 6% **148** with a hitherto unknown achiral *trans*-4,*trans*-4,*trans*-4 addition pattern. In combination with subsequent saponification of (±)-**147**, this regioselective synthesis provides a valuable access to the water-soluble hexa-acid (±)-**126** (Figure 32) used in many studies on biological and pharmacological properties of fullerene derivatives.[431,432,434] Wilson and co-workers reproduced the triple addition of tris(octamethylene) cyclotrimalonate using i^3HeC_{60} instead of pristine C_{60} as a starting material.[374] The *e,e,e* functionalization pattern of the noble gas incarcerane of (±)-**147** was confirmed by a single ^{3}He NMR resonance at −12.085 ppm.[279] Replacement of the octane-1,8-diyl residues of the reagent by oligo(ethylene glycol)-type 3,6-dioxaoctane-1,8-diyl fragments afforded a single tris-adduct, the addition pattern of which was tentatively assigned as *cis*-3,*cis*-3,*trans*-4.[374] Extension of the alcohol part of the cyclotrimalonate to a tetradecane-1,14-diyl moiety led to the isolation of D_3-symmetric *trans*-3,*trans*-3,*trans*-3 adduct (±)-**149** as sole isomer in 30% yield.[372]

By switching from achiral to enantiopure cyclo-oligomalonates derived from 3,4-*O*-isopropylidene-D-mannitol, Chronakis and Hirsch turned the above approach into a tether-directed regio- and diastereoselective tris-functionalization method.[373,457] Reaction of the corresponding cyclotrimalonate with C_{60} in the presence of iodine and DBU afforded three tris-adducts ((*R,R,R,R,R,R*,^{f,s}*C*)-**150a** (74%), (*R,R,R,R,R,R*,^{f,s}*A*)-**150b** (21%), and (*R,R,R,R,R,R*)-**151**; ratio ≈ 28:7:1; Figure 33), which could be isolated by chromatography on SiO_2. ^{1}H and ^{13}C NMR as well as UV/vis spectroscopy proved the cherry-red (*R,R,R,R,R,R*,^{f,s}*C*)-**150a** and (*R,R,R,R,R,R*,^{f,s}*A*)-**150b** to be diastereoisomers with opposite configurations of their inherently chiral *e,e,e* functionalization pattern. This steric relationship is also reflected by the mirror-image appearance of the CD spectra, and the comparison with those of previously assigned pure enantiomers with the same residual fullerene *π*-chromophore[265,266,271] actually allowed configurational assignments as (*R,R,R,R,R,R*,^{f,s}*C*)-**150a** ($[\alpha]_D = -1389°$) and (*R,R,R,R,R,R*,^{f,s}*A*)-**150b** ($[\alpha]_D = +1275°$).[457] As to the olive-green, minor isomer (*R,R,R,R,R,R*)-**151**, it was identified as C_3-symmetric structure with the C_{3v}-symmetric *trans*-4,*trans*-4,*trans*-4 addition pattern.

4.8. C_{60} Derivatives with More than Three Divalent Addends

The use of tetrakis(octamethylene) cyclotetramalonate in the tether-directed multifunctionalization of C_{60} cannot afford an addition pattern with 4-fold symmetry due to incompatibility with the structure of C_{60}-I_h. Instead, Hirsch and co-workers isolated two tetrakis-adducts, a major product with C_1 symmetry and a minor product with C_2-symmetry.[372] Comparison of the UV/vis data of the former with those of simple diethyl malonate adducts[272] led to its assignment as *e,e,e,e,e,trans*-1 (C(1),C(9):C(16),C(17):C(21),C(40):C(30),C(31))-tetrakis-adduct (±)-**152** (Figure 34; for the numbering of C_{60}, see Figure 2). This addition pattern was also obtained by Diederich and co-workers for a different achiral tetrakis-adduct in early applications of the tether-directed functionalization methodology to fullerene chemistry.[22,346,458] In fact, the functionalization pattern of C_1-symmetric (±)-**152** is C_s-symmetric and the chirality is related to the different orientations of the ester groups at the addend positioned doubly e_{face} and singly e_{edge} in relation to its neighbors ("front" position in structure (±)-**152**, Figure 34), together with the resulting twist in the connected octamethylene chains. As to the C_2-symmetric regioisomer, a detailed analysis of all possibilities, excluding the presence of *cis* interrelationships between addends, which would lead to a rather uneven distribution of strain in the octane-1,8-diyl chains, suggested a C(1),C(9):C(16),C(17):C(41),C(42):C(49),C(59)-tetrakis-adduct structure (±)-**153** (for the numbering of C_{60}, see Figure 2).[372] A C_2-symmetric tetrakis-adduct was also obtained from the Bingel addition of two didodecyl cyclobismalonate macrocycles. Taking into account the preference of a single such cycle for the *trans*-3 addition pattern, the only reasonable structure with the observed symmetry appears to be (±)-**154**. Interestingly, its addition pattern is a substructure of that of a hexakis-adduct

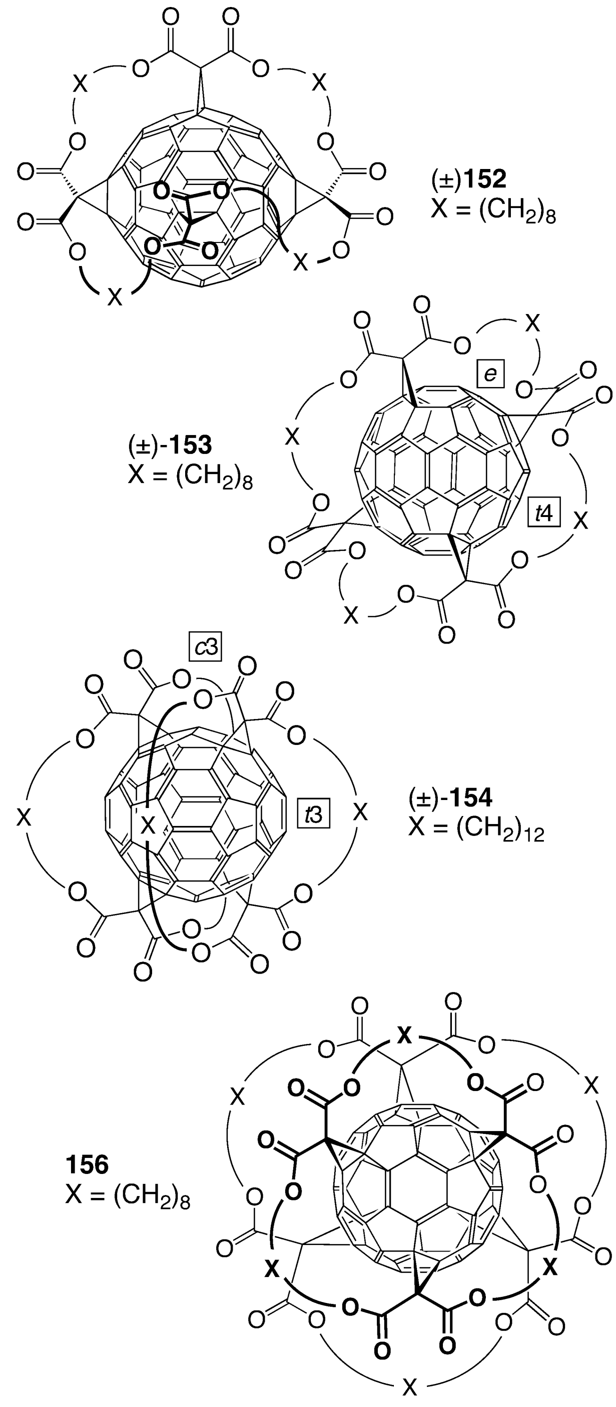
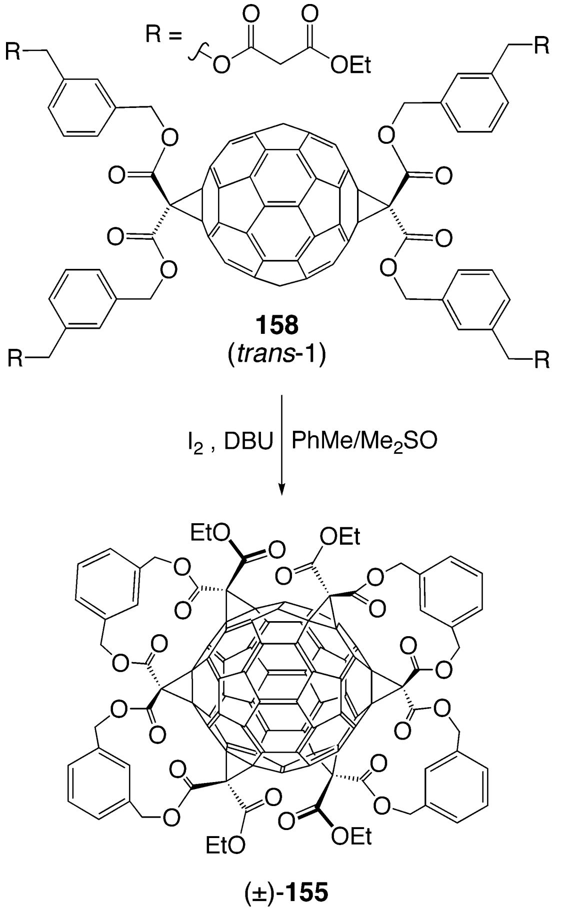


Figure 34. Chiral tetrakis-adducts of C_{60} resulting from addition to hexacontacarbon of a tetrakismalonate (→ (±)-**152** and (±)-**153**) or of two bismalonates (→ (±)-**154**), and achiral hexakis-adduct resulting from addition of two trismalonates (→ **156**).[372] For some pairs of addends, the positional relationship is indicated in square boxes.

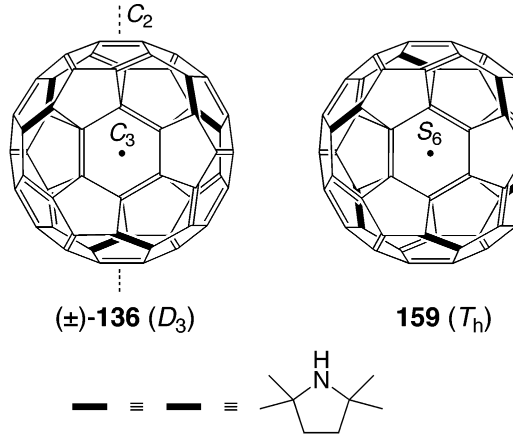
prepared by the Diederich group ((±)-**155**, Scheme 12).[459,460] Reaction of *e*,*e*,*e* tris-adduct (±)-**147** (Figure 33) with another molecule of tris(octamethylene) cyclotrimalonate, afforded an achiral hexakis-adduct, **156**, in which all six positions within a pseudo-octahedral set of 6−6 bonds of C_{60} are occupied (combination of two enantiomorphic *e*,*e*,*e* subpatterns.[372] However, as a consequence of the embedding of the 12 ester groups in two trismalonate macrocycles, the T_h-symmetry of the addition pattern is reduced to overall S_6 molecular symmetry (see also below, Figure 35, and section 6.8).

Scheme 12. One-Pot Fourfold Bingel Transformation of *trans*-1 Bis-Adduct 158 into D_2-Symmetric Hexakis-Adduct (±)-155 with a Double-Helical, Inherently Chiral Addition Pattern[459,460]



Crown ether−fullerene conjugate (±)-**157** (Figure 23) was used as a key intermediate on the way to the corresponding *trans*-1 dicyclopropafullerene−tetracarboxylic acid by cleavage of the *tert*-butyl ester groups and the crown ether template under acidic conditions.[459,460] Further chemical transformation over several steps afforded *trans*-1 bis-adduct **158** (Scheme 12) with four pendant malonate groups, which were subsequently reacted with the fullerene core in two double tether-directed remote Bingel macrocyclizations that had previously been described as "clipping reactions"[269] and given access to tris- and tetrakis-adducts of C_{60} (e.g., (±)-**139**, Scheme 9). The only product of this highly regioselective, 4-fold addition was the shiny red, D_2-symmetric hexakis-adduct (±)-**155** (C(1),C(9):C(3),C(15):C(22),C(23):C(34),C(35):C(43),C(57):C(49),C(59)-adduct; for the numbering of C_{60}, see Figure 2), in which the four newly introduced homotopic addends occupy the same positions as in C_2-symmetric tetrakis-adduct (±)-**154** (Figure 34). X-ray crystallography of (±)-**155** confirmed the two homotopic groups of three tethered cyclopropane rings to be arranged in a double-helical fashion with the axis of the helix passing through the unfunctionalized poles of the carbon sphere. The two 6−6 bonds bisected by this axis are the most accessible ones in the remaining fullerene π-system, and they readily undergo further Bingel addition under formation of orange-yellow heptakis- and octakis-adducts with C_2 and D_2-symmetry, respectively.[459,460]

A rarely observed, inherently chiral functionalization pattern was identified by Rubin, Garcia-Garibay, and co-

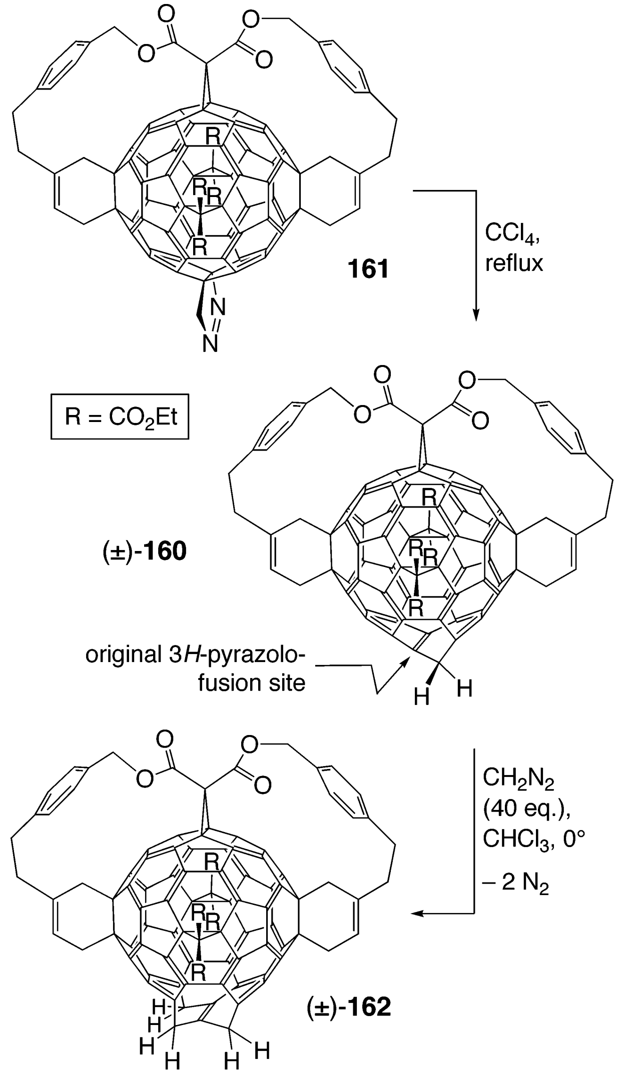


(±)-**136** (D_3) **159** (T_h)

Figure 35. Two constitutional isomers (D_3-symmetric (±)-**136** and T_h-symmetric **159**) resulting from 6-fold [3 + 2] cycloaddition of tetramethylazomethine ylide to C_{60}.[443] For reasons of clarity, the addends are simply represented by the functionalized bonds (in bold); some symmetry elements are indicated.

workers in hexakis-(2,2,5,5-tetramethyl-1*H*-dihydropyrrolo)-fused [60]fullerene (±)-**136** (Figure 35), resulting from 6-fold [3 + 2] cycloaddition between C_{60} and the corresponding sterically congested azomethine ylide.[443] Whereas the Bingel reaction, through an increasing selectivity for e_{face} double bonds in every step of a multiaddition, preferentially yields a T_h-symmetric hexakis-adduct with a pseudo-octahedral arrangement of addends on the carbon cage, the large steric bias of the tetramethylazomethine ylide appears to be responsible for the formation of D_3-symmetric (±)-**136** as the major hexakis-adduct besides T_h-symmetric **159**. Both structures were substantiated by X-ray crystallography, and the compounds exhibit a strong fluorescence, which is unusual for fullerenes[461] and most of their derivatives. Photophysical properties of hexakis-adducts of these types as well as of a possible S_6-symmetric congener were investigated in a theoretical study, which confirmed the experimental observations and showed a clear dependence of the $S_0 \rightarrow S_1$ transition on the addition pattern.[462] When the addition patterns of hexakis-adducts (±)-**136** and **159** are compared, it strikes that both are made up of two sets of *e*,*e*,*e* substructures (cf. also **156**, Figure 34). But whereas D_3-symmetric (±)-**136** combines two homochiral patterns, those of T_h-symmetric **159** are heterochiral. As to the resulting molecules, they are constitutional isomers, not diastereoisomers, because the relative arrangement of both *e*,*e*,*e* subsets is not the same in both structures. In fact, the relationship between nearest neighbors of different *e*,*e*,*e* sets is *e* in T_h-symmetric **159**, whereas it is *cis*-3 in D_3-symmetric (±)-**136**.

Scheme 13. Chiral Mono- ((±)-160) and Trihomofullerene ((±)-162), Produced by Thermal Extrusion of Dinitrogen from the Appropriate Pyrazolofullerene Precursors[463,464]



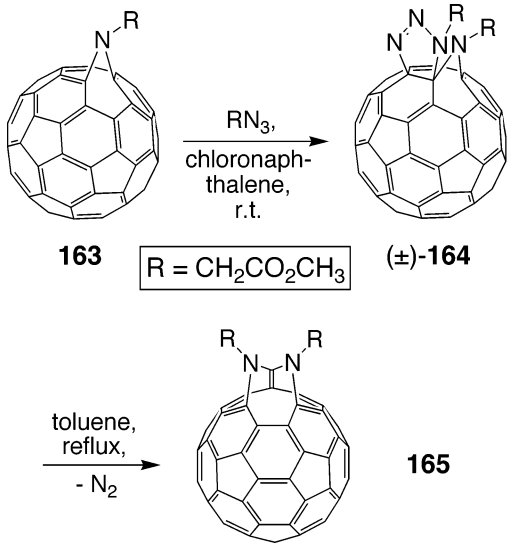
A C_1-symmetric homofullerene derivative, (±)-**160** (Scheme 13), was obtained by thermal extrusion of dinitrogen from pyrazolofullerene **161**, product of the [3 + 2] cycloaddition between the according pentakis-adduct precursor and diazomethane.[463,464] Thermolysis was proposed to occur as an eight-electron orbital-symmetry-controlled $[2\pi_s + 2\pi_s + 2\sigma_s + 2\sigma_a]$ process.[463−465] It leads to an intermediate norcaradiene substructure that cycloreverts to the cycloheptatriene unit of homofullerene derivative (±)-**160**. Further addition of diazomethane provided di- and trihomofullerene (C_1-symmetric (±)-**162**) derivatives in which all inserted CH_2 groups are connected to the same central double bond. However, complete isolation of the latter from the residual fullerene π-system by introduction of a fourth methylene group failed, presumably for steric reasons. No cyclopropane substructures were produced in this rearrangement in the absence of light.[463,464] A C_1-symmetric addition pattern analogue of (±)-**160** with an azahomofullerene substructure was obtained by Hirsch and co-workers as a side product of the nitrogen extrusion from a C_{60} derivative bearing five Bingel-type addends and a fused triazoline in a pseudo-octahedral arrangement.[466]

4.9. Cage-Opened Derivatives of C_{60}

Addition of azides or nitrenes to fullerenes, in combination with various follow-up reactions, has led to a diversity of core-modified structures and ultimately to the synthesis of azafullerenes.[467,468] A large fraction of the molecules with modified cages are chiral and although the relation between their structure and that of the parent fullerenes is not always directly apparent, many of them can be considered in a broader sense as fullerene derivatives with an inherently chiral functionalization pattern.

Hirsch and co-workers found that the reaction of ethyl azidoacetate with azahomofullerene **163** afforded a single bis-adduct regioisomer, C_1-symmetric (±)-**164** (Scheme 14).[469] It results from formal nitrogen insertion into a 6−5

Scheme 14. Regioselective Addition of Ethyl Azidoacetate to Azahomo[60]fullerene Derivative 163 and Subsequent Extrusion of Dinitrogen from the Adduct (±)-164 under Formation of Diazadihomofullerene 165[469]

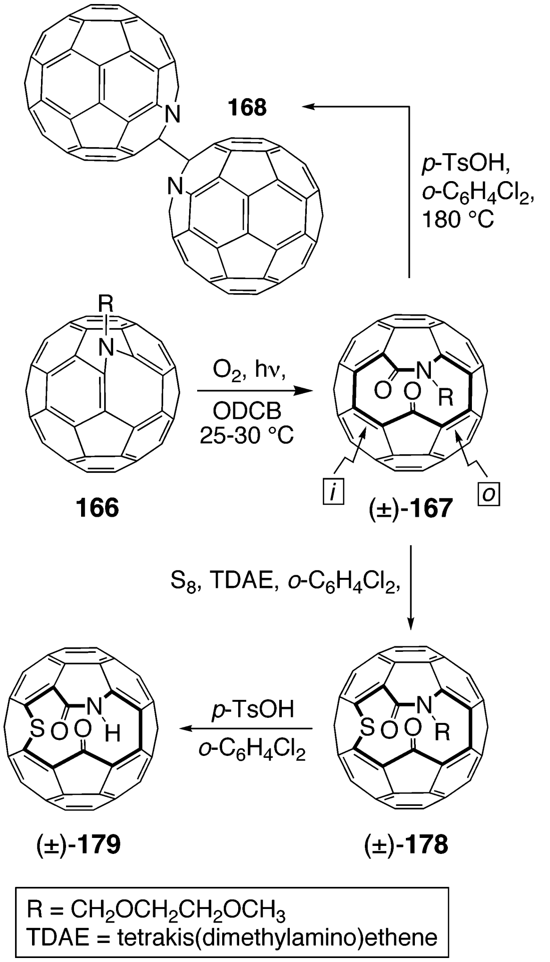


bond and fusion of a triazoline heterocycle to an adjacent enamine-type 6−6 bond. Even at room temperature, (±)-**164** slowly rearranges, under loss of dinitrogen, to C_s-symmetric **165** as the main product.[469]

In a series of pioneering investigations,[467] Wudl, Hummelen, and co-workers found evidence for the *N*-MEM (*N*-methoxymethyl)-protected azahomo[60]fullerene **166** (Scheme 15) to undergo autosensitized photo-oxygenation in the form of a [2 + 2] cycloaddition of singlet oxygen to one of its electron-rich enamine bonds (cf. transformation **163** → (±)-**164**, Scheme 14). This reaction is followed by cleavage of the 1,2-dioxetane intermediate (not shown), which generates the two carbonyl groups of ketolactam (±)-**167**, the first cage-opened fullerene.[470] Under wet-chemical conditions promoting processes observed in the gas phase,[471] acid-induced loss of 2-methoxyethanol from (±)-**167** triggered a sequence that ultimately afforded C_s-symmetric 9,9′-bi-1-aza(C_{60}-I_h)[5,6]fullerene **168**.[471,472] The conjectured reaction mechanism involves a rearrangement of the carbenium ion generated from (±)-**167** and subsequent extrusion of formaldehyde and carbon monoxide to afford azonia[60]fullerene (not shown) as an important intermediate.[471] The latter is reduced to the azafullerenyl radical (not shown), which dimerizes to **168**[471,472] or reacts further to give the monomeric 2*H*-1-aza(C_{60}-I_h)[5,6]fullerene (not shown).[473] Racemic ketolactam (±)-**167** with its "chiral orifice" was resolved into the enantiomers (80% and 92% ee) by HPLC on a Pirkle-type chiral stationary phase.[474] The measured Cotton effects were relatively weak with $\Delta\epsilon$ values ≤ 29 M^{-1} cm^{-1}. It should be mentioned that Hirsch and co-workers opened another synthetic avenue to azafullerenes, starting from *N*-MEM-protected diazadihomofullerenes of type **165** (Scheme 14).[468,475−477]

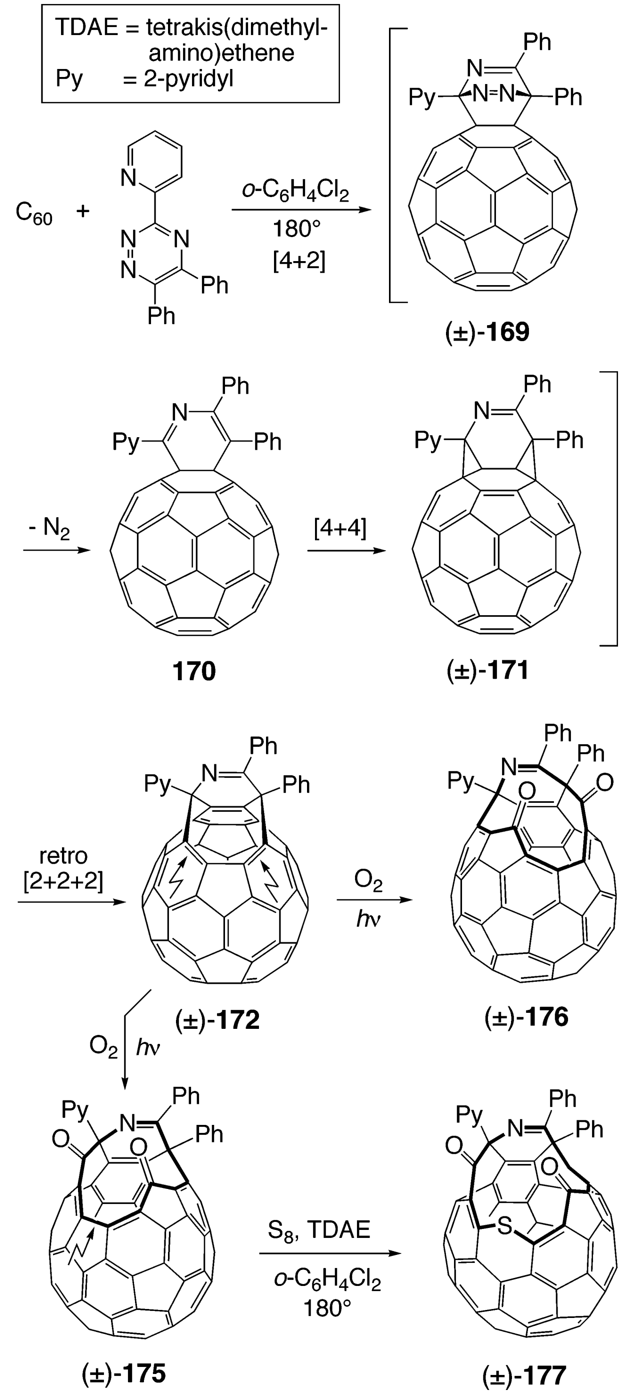
Many of the recent cage-opening reactions[478,479] start with an interesting sequence of cycloadditions and cycloreversions, following a general scheme first elaborated by Rubin and co-workers.[480−484] It is illustrated by the reaction of 5,6-diphenyl-3-(pyridin-2-yl)-1,2,4-triazine with C_{60}, reported by Komatsu and co-workers and rationalized by initial [4 + 2] cycloaddition (→ (±)-**169**, Scheme 16) followed by dinitrogen extrusion (→ **170**), intramolecular formal [4 + 4] cycloaddition (→ (±)-**171**), and retro-[2 + 2 + 2] ring opening of the resulting dicyclopropafullerene (→ (±)-**172**).[485] From a related reaction between 4,6-dimethyl-1,2,3-triazine and C_{60}, the same group had isolated the chiral ketone (±)-**173**[486] (Figure 36) and elucidated its structure with the help of the available data on the desmethyl analogue (±)-**174**, prepared by Qian et al.[482] from the silylenol ether of a fullerene-fused cyclohex-2-enone[487] and further oxidized to the 1,2-diketone as intermediate on the way to the nonclassical fullerene C_{62}-C_{2v}, which includes a four-membered ring surrounded by four hexagons.[482] The distorted double bonds at the rim of (±)-**172** (Scheme 16, bonds marked by zigzag arrows) selectively react with singlet oxygen generated in situ by irradiation with visible light. [2 + 2] Cycloaddition to either of these double bonds with high HOMO coefficients leads to a 1,2-dioxetane intermediate, which cycloreverts under enlargement of the orifice to afford (±)-**175** and (±)-**176**.[485,488] As demonstrated by measured redox potentials and calculated LUMO levels, these compounds are good electron acceptors, and this allowed a further enlargement of the rim to a 13-membered cycle by insertion of a sulfur atom into the central bond of the hexa-2,4-diene-1,6-dione structure

Scheme 15. First Controlled Opening of the [60]Fullerene Cage (→ (±)-167) by Self-Sensitized Photo-oxygenation of an Azahomofullerene Derivative (166)[470] **and Subsequent Acid-Induced Formation of 9,9′-Bi-1-aza(C_{60}-I_h)[5,6]fullerene (168)**[471a]



[a] Further enlargement of the orifice of (±)-**167** was brought about by sulfur insertion into its rim (→ (±)-**178**), followed by deprotection of the N-atom (→ (±)-**179**).[496] The zigzag arrows ((±)-**167**) point at the cleavage sites proposed by Orfanopoulos (o)[508] and Iwamatsu (i)[506] for the reaction with arylhydrazones (vide infra).

Scheme 16. [60]Fullerene Cage-Opening Strategy of Komatsu and Co-workers[a]



[a] Zigzag arrows indicate bonds broken in the next step.[478]

(→ (±)-**177**) through reaction of (±)-**175** with S_8 in the presence of the activating π-donor tetrakis(dimethylamino)ethene (TDAE).[485] Treatment of solid (±)-**177** with hydrogen at 200 °C and 800 atm for 8 h led to 100% capture of H_2 inside the cavity of the host.[489] Synchrotron X-ray crystallography and MEM (maximum entropy method) analysis[490] showed the guest, which resonates at −7.25 ppm (^{1}H NMR) with respect to TMS (tetramethylsilane), to be located at the center of the cage.[489,491] From the rate of hydrogen release between 160 and 190 °C, the activation energy, E_a, was determined[489] to be 34.3 kcal mol^{-1}, which compares with 22.8 kcal mol^{-1} measured for the escape of ^{3}He from (±)-**177**.[492] The described approach was turned into a true molecular "surgical" method when the Komatsu group showed that complete cage reclosure to iH_2C_{60} is possible, not only under mass-spectrometric but also under wet-chemical conditions. In fact, the sulfur can be photoextruded after oxidation of (±)-**177** with MCPBA to the corresponding sulfoxide, and further suturing is possible by intramolecular McMurry reaction involving the two keto functions (→ (±)-iH_2**172**). Restoration of the I_h-symmetric cage was achieved, finally, by heating of a powder of (±)-iH_2**172** at 340 °C in a glass tube under vacuum, supposedly taking place under extrusion of picolinonitrile and tolane. The obtained iH_2C_{60} shows an ^{1}H NMR resonance at −1.44 ppm, which is 5.98 ppm upfield from dissolved H_2.[493] It should also be mentioned that the supramolecular assembly and electrochemical response of (±)-**177** was studied after deposition on zinc octaethylporphyrin (OEP)-covered gold surfaces.[494,495]

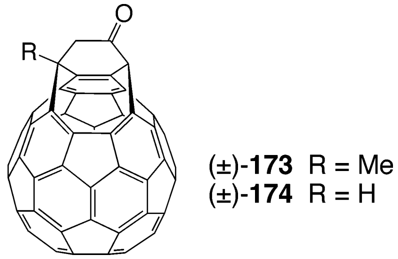
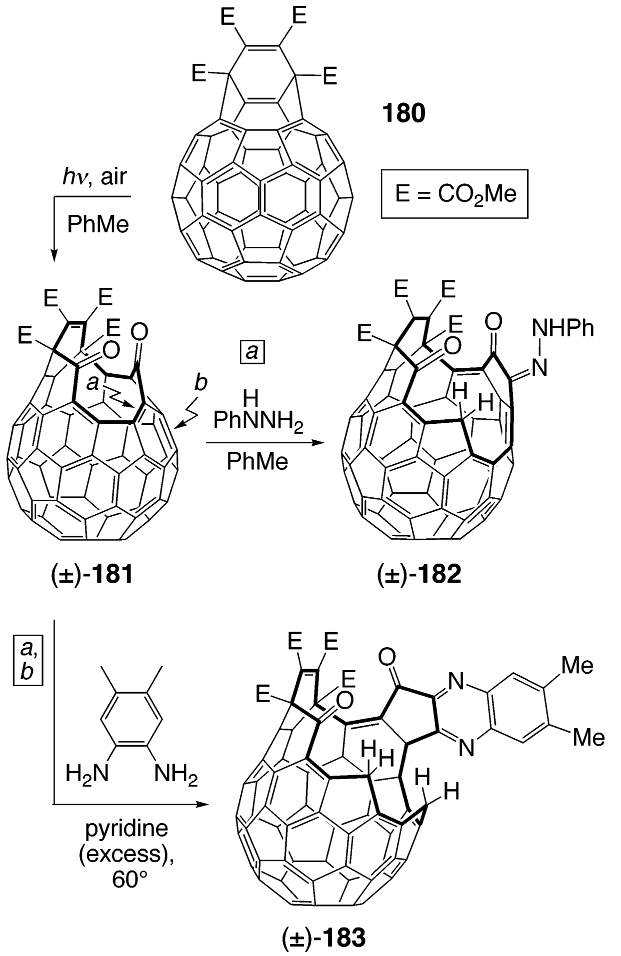


Figure 36. "Open-cage" fullerene derivatives (±)-**173**[486] and (±)-**174**[482] with an eight-membered ring as orifice.

After relating the hexa-2,4-diene-1,6-dione substructure of (±)-**175** (Scheme 16) to that of ketolactam (±)-**167** (Scheme 15), Vougioukalakis, Prassides, and Orfanopoulos successfully applied the sulfur insertion method reported by Komatsu and co-workers (vide supra)[485] to the latter compound, thereby enlarging its orifice to the 12-membered ring of (±)-**178** (Scheme 15).[496] Removal of the MEM group, unexpectedly, did not lead to the corresponding thiahomo-analogue of **168** but simply to N-deprotection and formation of (±)-**179**, the first open-cage derivative without organic residue at the rim.

The largest hole in the shell of buckminsterfullerene, so far, was excised by Iwamatsu, Murata, and co-workers.[479] It starts with a sequence that is related to methods used by the Rubin[480,482−484] and Komatsu groups (vide supra and Scheme 16)[478] and leads to a dihomo[60]fullerene derivative such as **180** (Scheme 17). The latter was obtained quantitatively by irradiation of the benzo[60]fullerene-tetraester precursor (cf. transformation of **170** into (±)-**172**, Scheme 16) prepared by thermal reaction of the fullerene with a palladacyclopentadiene-2,3,4,5-tetracarboxylate.[497] An interesting finding in the corresponding reaction with the tetra-*tert*-butyl ester analogue of the palladacycle was the formation, next to the bishomofullerene (^{t}Bu-analogue of **180**), of 24% of bismethanofullerene (cf. (±)-**171**, Scheme 16) in addition to small amounts of an unsymmetric derivative including both a homo- and a methano-substructure.[498,499] It was suggested to be generated in a di-π-methane-type rearrangement[500] of the benzo[60]fullerene-tetra-*tert*-butylester precursor, a reaction that may compete with the alternative [4 + 4]/retro-[2 + 2 + 2] sequence (vide supra and Scheme 16). Dihomofullerene **180** with its buckminsterfullerene-like 60 π-electron system is a good sensitizer for the photogeneration of $^1O_2$,[461,501] and similarly to **166** (Scheme 15) and (±)-**172** (Scheme 16), the double bond with the largest HOMO coefficient, adjacent to the homo C-atom, underwent photo-

Scheme 17. [60]Fullerene Cage-Opening Strategy of Iwamatsu, Murata, and Co-workers[479a]



[a] Zigzag arrows ((±)-**181**) indicate bonds broken in steps *a* and *b* ((±)-**181** → (±)-**182** and (±)-**181** → (±)-**183**).

oxygenative cleavage under formation of diketone (±)-**181** (Scheme 17).[502]

It was found that the orifice of (±)-**181** with its 12-membered ring could be further enlarged by an unusual reaction with phenylhydrazine. ^{1}H NMR spectroscopy of the product revealed a pair of doublets corresponding to a CH$_2$ group, and a detailed analysis including INADEQUATE, HMBC, and ^{15}N NMR, led to the assignment as (±)-**182** with a rim made up of a 16-membered ring, which results from formal double bond scission (bond marked *a* in (±)-**181**) at one of the enone substructures under generation of a methylene group at one end and a hydrazone function at the other end.[503] The same type of transformation took place with hydrazones, the mechanism still being unclear at this point.[504] The widening of the hole was even taken a step further by reaction of (±)-**181** with *o*-diaminoarenes, for example, 1,2-diamino-4,5-dimethylbenzene. In comparison to the formation of (±)-**182**, the diamine led to the disruption of another double bond (marked *b* in (±)-**181**), which newly appears at the rim as a consequence of the first scission (bond marked *a* in (±)-**181**), thus affording (±)-**183** with a 20-membered ring aperture and a quinoxaline "flap" resulting from incorporation of the reagent into the molecular framework.[505] It contains the largest orifice among all open-cage fullerene derivatives known to date.[478,479]

In addition, Iwamatsu and co-workers applied the "phenylhydrazine" as well as the "*o*-phenylenediamine" routes successfully to ketolactam (±)-**167** (Scheme 15).[506,507] The reaction of (±)-**167** with arylhydrazines was also investigated by Orfanopoulos and co-workers,[508] but the two groups reached different conclusions regarding the actual reaction site in the 11-membered ring and put forward isomeric product structures: whereas the latter team claims scission of the enone structure on the side of the amide-N (marked "o" in (±)-**167**),[508] the former proposes cleavage of the enone closer to the amide-C=O (marked "i" in (±)-**167**).[506]

The large orifice in (±)-**182** (Scheme 17) allows H$_2$ to get in but also to escape relatively easily (estimated activation energy 22−24 kcal mol^{-1}).[509] In (±)-**183**, the opening is even too large to suppress rapid escape of hydrogen. In both cases, the CH$_2$ groups make the rim more flexible and probably facilitate passage of a guest. On the other hand, (±)-**183** spontaneously encapsulates a molecule of water, manifesting itself by a ^{1}H NMR resonance at −11.3 ppm, the intensity of which decreases with increasing temperature and instantaneously disappears upon addition of D$_2$O.[505] The smaller hole in a related compound, prepared by reaction of (±)-**167** (Scheme 15) with *o*-phenylenediamine, makes encapsulation and escape of H$_2$O more difficult, in such a way that the water complex could be detected by ESI (electrospray ionization)-MS.[507]

4.10. Hydrofullerenes

In the hydrogenation of C$_{60}$,[510] 1,2-addition is generally preferred over 1,4-addition or other functionalization modes, despite eclipsing interactions between the vicinal hydrogen atoms.[18,511,512] In 1993, Cahill and co-workers prepared the simplest homolog, C_{2v}-symmetric 1,9-dihydro(C$_{60}$-I_h)[5,6]fullerene as one out of 23 conceivable isomers[419,513] by hydroboration of C$_{60}$ and subsequent hydrolysis.[514] The hydrocarbon exhibits a remarkable acidity (pK_a^1 = 4.7, pK_a^2 = 16, DMSO)[515] and a sharp ^{1}H NMR resonance at 5.9 ppm (toluene-d_8).[514]

Six C$_{60}$H$_4$ regioisomers, on the other hand, were found in the reaction of C$_{60}$H$_2$ with BH$_3$•THF.[516] Of these, the C_s-symmetric and thermodynamically most stable *cis*-1 adduct[517] (1,2,9,12-tetrahydro(C$_{60}$-I_h)[5,6]fullerene, for the numbering of C$_{60}$, see Figure 2) was isolated and characterized.[516] It is also the main product of the reduction of C$_{60}$ with diimide[518,519] or anhydrous hydrazine.[520] In addition, a clear-cut and a confident ^{1}H NMR structural assignment was possible for the C_s-symmetric *e* and the D_{2h}-symmetric *trans*-1 adducts, respectively.[516] Of the remaining three unassigned tetrahydro[60]fullerenes, at least one must have an inherently chiral addition pattern, that is, *cis*-3, *trans*-2, or *trans*-3; among these, the latter appears to be energetically favored based on ab initio calculations.[516]

Meier and co-workers reported the reaction of C$_{60}$ with reducing metals in the presence of a proton source.[511,512,521,522] Reduction with the Zn(Cu) couple produced C$_{60}$H$_2$, C$_{60}$H$_4$, and C$_{60}$H$_6$ in a limited number of isomers, presumably under kinetic control.[522] Although the regioisomeric composition of the C$_{60}$H$_4$ fraction differed from that obtained by hydroboration (vide supra),[522,523] the two major products were assigned as the achiral *e* isomer and the C_2-symmetric *trans*-3 adduct (±)-**184** (Figure 37).[522]

Two C$_{60}$H$_6$ isomers have been isolated in a 6:1 ratio when Zn(Cu) was used as reducing agent. The cranberry-colored solution of the major isomer showed a single ^{1}H NMR and 10 ^{13}C NMR resonances, which, together with the 1,2-addition mode confirmed by coupling constant analysis, led

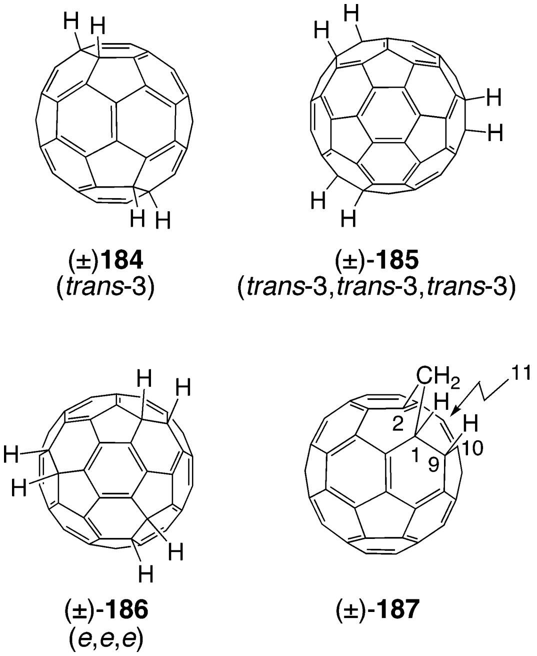


Figure 37. Major products of the reduction of C_{60} ((±)-**184**−(±)-**186**)[522] and of 1,9-dihydro-1a*H*-1(2)a-homo(C_{60}-I_h)[5,6]fullerene ((±)-**187**)[528] with Zn(Cu) in the presence of a proton source.

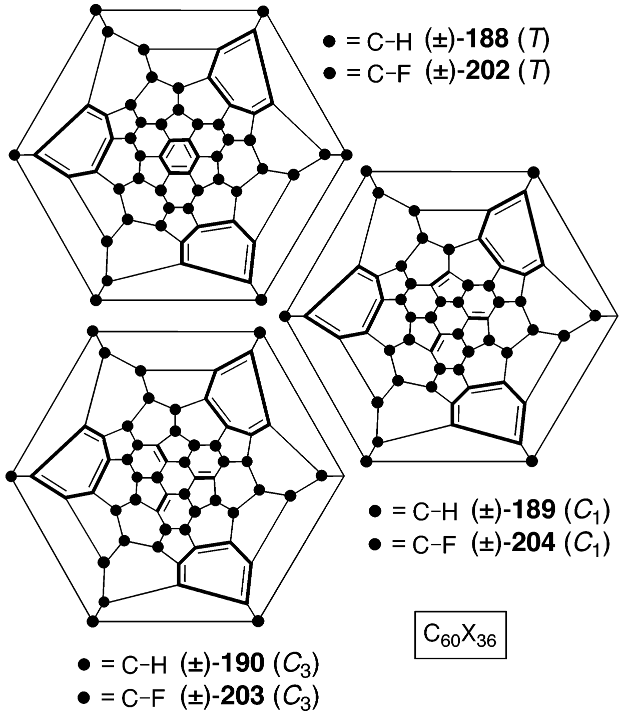


Figure 38. Schlegel diagrams of hexatriacontahydro- ((±)-**188**−(±)-**190**)[536,538,539,546] and hexatriacontafluoro[60]fullerenes ((±)-**202**−(±)-**204**)[542,546,585−587] with inherently chiral addition patterns.

to the assignment as D_3-symmetric *trans*-3,*trans*-3,*trans*-3 adduct (±)-**185**.[521,522] The other highly symmetric molecule (minor isomer) was identified as C_3-symmetric *e*,*e*,*e* tris-adduct (±)-**186**.[522] Both (±)-**185** and (±)-**186** are kinetic products derived from *trans*-3- and *e* $C_{60}H_4$, respectively. Neither the tetra- nor the hexahydro[60]fullerene isomers were interconvertible under the conditions of their formation, and attempts to isomerize (±)-**185** with Pd/C or Pt/C resulted in dehydrogenation rather than isomerization.[522] When the reduction was carried out with i^3HeC_{60}, a ^3He NMR signal at −14.24 ppm pointed at the formation of a third isomer next to *trans*-3,*trans*-3,*trans*-3 $i^3He(C_{60}H_6)$ (−15.31 ppm) and *e*,*e*,*e* $i^3He(C_{60}H_6)$ (−16.35 ppm).[524] The hydrofullerenes $C_{60}H_6$ ((±)-**185**) and $C_{60}H_2$ have been prepared in ^{13}C-enriched form, and 2D INADEQUATE NMR spectra allowed an unambiguous and a nearly unambiguous assignment, respectively, of all carbon resonances.[525]

Reaction of homo[60]fullerene, $C_{61}H_2$,[526,527] with Zn(Cu) afforded two major $C_{61}H_4$ isomers, which were identified by detailed ^1H and ^{13}C NMR spectroscopic analysis as C_1-symmetric 1,9-dihydro-1a*H*-1(2)a-homo(C_{60}-I_h)[5,6]fullerene ((±)-**187**, Figure 37) and C_s-symmetric 10,11-dihydro-1a*H*-1(2)a-homo[60]fullerene.[528] The inherently chiral functionalization pattern of the thermodynamic product, (±)-**187**, corresponds to that generated in the reaction of azahomo[60]fullerene derivatives with azides[469] (cf. Scheme 14) or in the primary addition of singlet oxygen to homo-[478,479] and azahomofullerenes[470] (cf. Schemes 15 and 16). The high reactivity of fullerene double bonds that are adjacent to a homo C-atom was attributed to π-orbital misalignment and the resulting strain.[528−530]

Polyhydro[60]fullerenes[512] can be conveniently prepared from C_{60} by various methods such as the Birch−Hückel reduction ($Li/NH_3/^tBuOH$),[531,532] the reaction with Zn/HCl,[519,533,534] or transfer hydrogenation with 9,10-dihydroanthracene.[535−538] A major product found in these reactions is $C_{60}H_{36}$, commonly accompanied by $C_{60}H_{18}$, and these compounds were among the first fullerene derivatives reported in the literature.[531] The structure of the latter was elucidated by Taylor and co-workers who showed that the molecule has a C_{3v}-symmetric crown shape, the addition pattern of which can be considered as a substructure of (±)-**188** (vide infra and Figure 38).[539] As to hexatriacontahydro[60]fullerene, structural elucidation was difficult due to facile oxidative degradation and the formation of different isomers. The recognition of parallels between hydrogenation and fluorination (cf. section 4.11.1) of fullerenes provided a valuable additional handle for structural elucidation.[540−542] Combining that information with an analysis of the ^1H NMR multiplet patterns and coupling constants, Taylor and co-workers concluded on the chiral *T*-symmetric structure (±)-**188** (Figure 38) for $C_{60}H_{36}$,[539] an assignment that received further support from X-ray spectroscopic[543] and neutron diffraction[544] data. Inspired by the observation of two close-lying ^3He NMR resonances measured for $i^3He(C_{60}H_{36})$[545] and by the structural elucidation of $C_{60}F_{36}$ (cf. section 4.11.1), Taylor, Saunders, and co-workers proposed the presence of a second, C_3-symmetric isomer for $C_{60}H_{36}$.[546] A major breakthrough was achieved by Billups and co-workers upon HPLC purification of the hydrofullerenes prepared by transfer hydrogenation of C_{60} and of its ^3He incarcerane.[536] The combined information from ^1H, ^{13}C, and ^3He NMR analysis showed their main isomers to have C_1- and C_3-symmetries. By 2D ^1H NMR spectroscopy, Gakh et al. were finally able to conclusively elucidate the suggested[536] molecular structures of C_1-(±)-**189**, C_3-(±)-**190**, and *T*-(±)-**188**, obtained in the approximate ratio 16:7:1 by transfer hydrogenation of C_{60}.[538] Aromatic delocalization in the benzenoid rings of the $C_{60}H_{36}$ isomers compensates for the destabilization arising from eclipsing interactions, which are particularly important in fully hydrogenated six-membered rings (cf. section 4.11.1).[539]

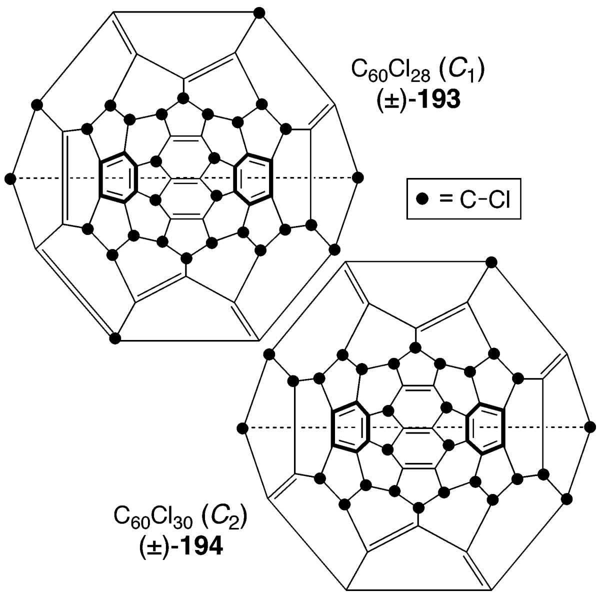


Figure 39. Schlegel-type diagrams of C_1-symmetric $C_{60}Cl_{28}$ and of C_2-symmetric $C_{60}Cl_{30}$.[553] Each of the dashed lines represents a bond on the backside of the flattened structural representations. The C_2 symmetry axis of (±)-**194** passes through the center of the diagram.

4.11. Halogenofullerenes

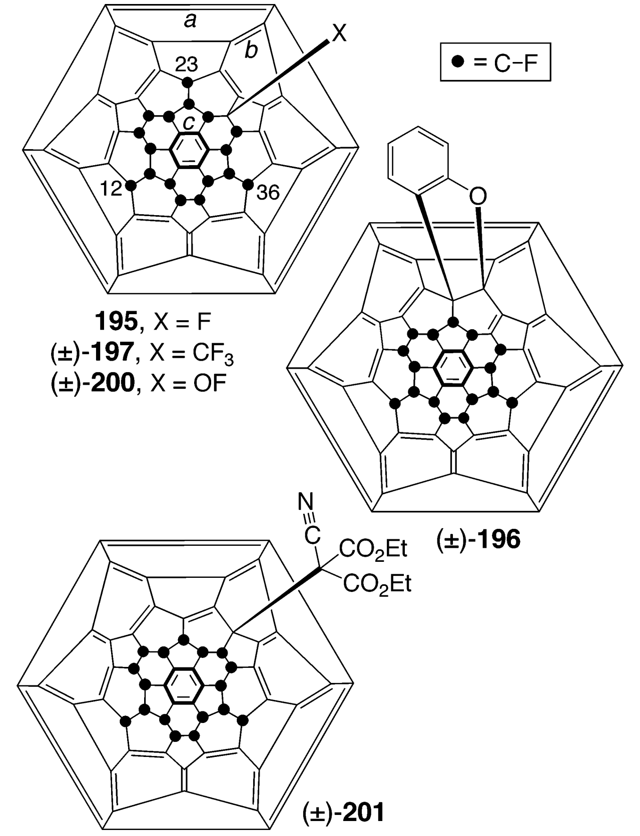
The highest possible degree of halogenation for fullerenes varies greatly with the halogen involved: whereas fluorination with different reagents and under different conditions leads to a large variety of fluorofullerenes, only a moderate number of chloro- and bromofullerenes is known, and iodination of the carbon cages does not take place at all. On the other hand, the bromides have a particularly high tendency to crystallize, which has made several X-ray crystal structures available.[248] Most of the bromides have structures with relatively high symmetry and are achiral, for example $C_{60}Br_6$-C_s (**191**, see Figure 68) and the isomorphous $C_{60}Cl_6$-C_s [547,548] (**192**), which will be discussed in more detail in section 6.9. The same is true for $C_{60}Br_8$ with molecular C_{2v}-symmetry, whereas the according chloro derivative has not been isolated.[548,549] The molecular structure of $C_{60}Br_{24}$-T_h was among the first multiadduct structures elucidated:[548−550] it is isomorphous with $C_{60}Cl_{24}$, and includes 18 isolated double bonds but no vicinal halogen atoms.[551,552] The next higher chlorofullerene with established structure, $C_{60}Cl_{28}$, is chiral and has C_1-symmetry ((±)-**193**, Figure 39). It is closely related to $C_{60}Cl_{30}$-C_2 ((±)-**194**), the additional two chlorine atoms of the latter being positioned in such a way that a "pseudo-C_2 axis" ((±)-**193**) is turned into a real one ((±)-**194**).[553] Both structures are characterized by two chains of C(sp^3)−Cl groups and two nonparallel benzenoid rings, which compensate for the considerable number of destabilizing eclipsing interactions. The two multiadducts can be transformed into each other by addition of two Cl atoms to $C_{60}Cl_{28}$-C_1 or by thermal decomposition of $C_{60}Cl_{30}$-C_2.[248] Another $C_{60}Cl_{30}$ isomer has D_{3d}-symmetry and the shape of a drum with two planar, parallel benzenoid rings at the top and the bottom and an 18-π-electron all-*trans* annulene at the center of the cylindrical part.[552,553] This "trannulene"[554−556] substructure is completely isolated from the aromatic rings by two [C(sp^3)Cl]$_{15}$ macrocycles. It should also be mentioned that a highly symmetric chloride, $C_{50}Cl_{10}$-D_{5h}, formally a derivative of (C_{50}-D_{5h})[5,6]fullerene with five equatorial ClC(sp^3)−C(sp^3)Cl groups as pentagon−pentagon fusion sites, has been isolated from soot generated in a modified arc discharge in the presence of CCl_4 vapor.[557]

4.11.1. Fluorofullerenes

An impressive number of fluorofullerenes have been prepared, isolated, and structurally characterized by taking advantage, among others, of similarities in the course of polyfluorination and polyhydrogenation, in addition to key information from ^{19}F NMR spectroscopy and X-ray crystallography.[18,236,237,558] Fluorofullerenes have been prepared by direct reaction of fullerenes with F_2, with noble gas fluorides, and, in a more selective and versatile manner, with various metal fluorides.[18,236,237,558−561] Except for T_h-symmetric $C_{60}F_{24}$[562] and, to a certain degree, $C_{60}F_8$-C_s,[563,564] all known fluorofullerenes $C_{60}F_{2n}$ are characterized by a contiguous fluorination pattern resulting from consecutive 1,2-additions across 6−6 bonds. Such motifs are ascribed to sequential bond activation resulting from increased localization of double bonds adjacent to addends already in place.[546] Another important characteristic, common to highly fluorinated or hydrogenated [60]fullerenes, is the generation of isolated and flattened benzenoid substructures, the aromaticity of which is enhanced relative to the fullerene precursor and acts as a counterbalance for a considerable number of unfavorable eclipsing 1,2-interactions. Facile fluorine migration ("fluorine dance") during high-temperature fluorination often leads to a preponderance of the thermodynamically most stable isomer(s) in an equilibrium mixture.[565] This also provides an explanation for the remarkable selectivity observed for high degrees of fluorination. Fluorofullerenes are generally stable when exposed to air and light, but they are sensitive toward hydrolysis.

Most $C_{60}F_{2n}$ species have highly symmetric structures and, with the exception of 1,2,7,8,9,12-hexafluoro-1,2,7,8,9,12-hexahydro(C_{60}-I_h)[5,6]fullerene ($C_{60}F_6$-C_2 with an S-shaped functionalization pattern across three adjacent 6−6 bonds; for the numbering of C_{60}, see Figure 2),[563] all known representatives up to $C_{60}F_{24}$-T_h (isomorphous with the corresponding chloro- and bromofullerenes, see section 4.11)[562] are achiral. They include $C_{60}F_2$-C_{2v},[566] $C_{60}F_4$-C_s, and $C_{60}F_8$-C_s,[563,564] for which confident NMR spectroscopy-based structural proposals have been made, as well as $C_{60}F_{16}$-C_s,[567] $C_{60}F_{18}$-C_{3v} (**195**, Figure 40),[568−571] and $C_{60}F_{20}$-D_{5d}.[572]

Lemon-yellow $C_{60}F_{18}$ (**195**) is formed as a single isomer and was shown by 2D COSY ^{19}F NMR spectroscopy to be isomorphous with the C_{3v}-symmetric $C_{60}H_{18}$.[568] The structure was confirmed by X-ray crystallography, which nicely showed a turtle-like overall shape and the first-observed truly benzenoid substructure at the center of the flattened "bottom", which is isolated from the remaining fullerene π-chromophore by a macroring of C−F groups.[571] $C_{60}F_{18}$ undergoes [4 + 2] cycloaddition with anthracene[573,574] and [3 + 2] cycloaddition with the azomethine ylide generated from sarcosine and formaldehyde[575] to yield the products from addition across bond *a* (C_s-symmetric; see Schlegel diagram of **195**, Figure 40) and across bond *b* (C_1-symmetric). The latter adduct, in the case of anthracene, is less stable and rearranges to the former by "ring walking". Electrophilic substitution of phenol by $C_{60}F_{18}$ occurs both *ortho* and *para* to the OH group. The primary adduct of the former substitution mode undergoes 1,3-fluorine migration, followed by HF elimination between the relocated F atom and the acidic OH proton, to afford C_1-symmetric benzo[*b*]furano-



195, X = F
(±)-**197**, X = CF3
(±)-**200**, X = OF

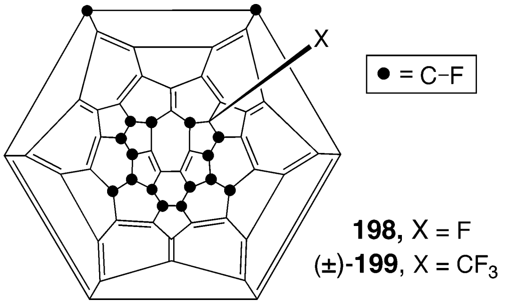
(±)-**196**

(±)-**201**

Figure 40. Octadecafluoro[60]fullerene, $C_{60}F_{18}$-C_{3v} (**195**),[568,571] and a variety of chiral derivatives thereof.

fused hexadecafluoro[60]fullerene (±)-**196** (Figure 40).[576] Various trifluoromethyl-fluorofullerenes accompany $C_{60}F_{18}$ in its preparation; they originate from addition of trifluoromethyl radicals or insertion of CF_2 carbenes into C−F bonds. The X-ray crystal structure of $C_{60}F_{17}CF_3$ shows a major C_s-symmetric isomer in which one of the three “outer”, most accessible F atoms (e.g., C(12)−F, see Schlegel diagram of **195**) has been replaced by a CF_3 group and a minor C_1-symmetric isomer (±)-**197** with a noninherently chiral functionalization pattern (cf. section 6).[577] Insertion of another CF_2 group into the existing CF_3 group of the former leads to an adduct with a CF_2CF_3 group.[577] Variable temperature ^{19}F NMR spectra of the mixture $C_{60}F_{17}CF_3$-C_s/$C_{60}F_{17}CF_3$-C_1 ((±)-**197**) show that fullerene derivatives with adjacent F and CF_3 groups exhibit slow conformational exchange due to hindered rotation of the trifluoromethyl addend at −40 ± 10 °C.[578]

Derivatives of a new parent “quasi-fullerene” with a seven-membered ring, C_{58}, were formed by fluorination of C_{60} with mixed cesium/lead oxyfluorides at 550 °C.[579] ^{19}F NMR spectroscopy was the main tool used to deduce the structures of $C_{58}F_{18}$-C_s (**198**) and $C_{58}F_{17}CF_3$-C_1 ((±)-**199**) (Figure 41). Fluorofullerene **198** can be formally derived from $C_{60}F_{18}$-C_{3v} (**195**, Figure 40) by removal of a C−C unit (6−5 fusion site marked “*c*” in structure **195**, Figure 40) of the central benzenoid ring, thereby leading to the seven-membered ring, and concomitant migration of the nearby on-σ-plane F-atoms to a position that can be considered as *equatorial* in relation to their original location. Trifluoromethyl derivative (±)-**199** (Figure 41) is derived in an analogous way from $C_{60}F_{17}$-CF_3-C_1 ((±)-**197**, Figure 40). The strain related to the seven-membered rings in **198** and (±)-**199** is mitigated by the sp^3-hybridization of a number of C-atoms as a consequence of their bonding to fluorine.[579]



198, X = F
(±)-**199**, X = CF3

Figure 41. “Quasi-fullerenes” $C_{58}F_{18}$-C_s (**198**) and $C_{58}F_{17}CF_3$-C_1 ((±)-**199**) including a heptagon in their cage.[579]

Oxygen insertion into a C−F bond of $C_{60}F_{18}$ afforded the first fluoroxy-fluorofullerene, $C_{60}F_{17}OF$ ((±)-**200**, Figure 40, noninherently chiral addition pattern).[580] A corresponding fluoroxy derivative was also obtained[581] from “triumphene”, $C_{60}F_{15}Ph_3$, the C_{3v}-symmetric product of the Friedel−Crafts reaction between $C_{60}F_{18}$ (**195**) and benzene, which takes place under replacement of its three most accessible F atoms attached to C(12), C(23), and C(36).[582] UV-irradiation of a toluene solution of $C_{60}F_{18}$ in air led to the isolation of the first oxahomo-fluorofullerenol $C_{60}F_{17}O(OH)$.[580] It is produced by S_N2' substitution of F−C(23) by OH, followed by oxygen insertion into a 6−5 bond (α,β to the OH group), giving a C_1-symmetric motif. The same S_N2' substitution with the anion of diethyl 2-cyanomalonate as a nucleophile (without concomitant oxygen insertion) afforded the chiral adduct $C_{60}F_{17}[C(CN)(CO_2Et)_2]$ ((±)-**201**, Figure 40),[583] whereas the sterically more congested bromomalonates lead to so-called trannulenes[556] by three successive S_N2'' (extended S_N2') substitutions (vide infra).

Pyrolysis of $C_{60}F_{18}$-C_{3v} (**195**) affords $C_{60}F_{16}$-C_s, possibly by removal of two F-atoms lying on one of the symmetry planes of the former, and it seems to be also an intermediate on the way to octadecafluorofullerene **195** in the fluorination of C_{60} with K_2PtF_6.[567]

$C_{60}F_{20}$-D_{5d} has a completely different structure with an undulated macrocycle of C−F groups (single ^{19}F NMR resonance) at the equator, which completely separates two polar corannulene-type π-systems from each other.[572]

A greater number of chiral fluorofullerene structures is found among the highly fluorinated derivatives of C_{60}. $C_{60}F_{36}$ has been prepared by fluorination of C_{60} with various metal fluorides,[236,558] and three chiral isomers, displaying *T*-, C_3- (major isomer obtained from reaction of C_{60} with MnF_3),[542,584] and C_1-symmetries, have finally been isolated and characterized. The similarity between the ^{3}He NMR spectra of the fluoro derivatives $i^3He(C_{60}F_{18})$ and $i^3He(C_{60}F_{36})$ on one hand and those of the corresponding polyhydro[60]fullerenes[545,546] (cf. section 4.10) on the other suggested isomorphous compounds in both series.[546] Constitutionally homogeneous material was first obtained when cream-colored $C_{60}F_{36}$ was separated into two chiral isomers, one of C_3- and one of *T*-symmetry (ratio ≈ 10:1).[565,584] Whereas the *T*-symmetric structure (±)-**202** (Figure 38) was established by a combination of ^{19}F NMR and ^{13}C NMR spectroscopy,[542] the structural elucidation of C_3-symmetric $C_{60}F_{36}$ ((±)-**203**) was based on a detailed 2D COSY ^{19}F NMR analysis in conjunction with calculations on the relative stabilities of different isomers and a theoretical prediction of the ^{3}He NMR shifts of different $i^3He(C_{60}F_{36})$ isomers.[546,585] A few years later, a third,

C_1-symmetric isomer of $C_{60}F_{36}$ ((±)-**204**) was isolated from the fluorination of C_{60} with MnF_3/K_2NiF_6 at 480 °C.[586] The assignments of the C_1-[586] and the T-symmetric[587] isomers have been confirmed by X-ray crystallography. The structure of $C_{60}F_{36}$-T deviates strongly from sphericity and displays four flat faces with isolated benzenoid[588] rings. The other two $C_{60}F_{36}$ isomers ((±)-**203** and (±)-**204**) are related to the latter ((±)-**202**) by 1,3-shifts of fluorine affecting one of the aromatic substructures and leaving three of them intact. $C_{60}F_{36}$-C_1 was found to rearrange within a few days to $C_{60}F_{36}$-C_3 (toluene/$CDCl_3$, room temperature) as a result of a unique 1,3-shift of fluorine.[589] On standing in organic solvents containing traces of water, the C_3- ((±)-**203**) and C_1-symmetric ((±)-**204**) isomers of $C_{36}F_{36}$ slowly convert to two C_1-symmetric isomers of fluorofullerenol $C_{60}F_{35}OH$.[590] This reaction provided the first truly proven example for a fullerene derivative undergoing an S_N2'-type reaction.

A C_1-symmetric structure with three benzenoid rings and an isoindole substructure has been conjectured for $C_{59}NF_{33}$, a product obtained from fluorination of $(C_{59}N)_2$ (**168**, Scheme 15) with MnF_3.[236]

Fluorination of [60]fullerene with MnF_3/K_2NiF_6 at 485 °C afforded minor amounts of $C_{60}F_{38}$-C_1, the proposed structure of which is based on detailed spectroscopic analysis.[591] It is characterized by addition of two F-atoms to one of the isolated double bonds of $C_{60}F_{36}$ (cf. Figure 38) and concomitant double bond isomerization, which leads to the loss of one benzenoid ring. This is probably the consequence of a strain relief associated with the disappearance of a nearly planar hexagon, outweighing the aromatic stabilization at this point.

White $C_{60}F_{48}$, which forms colored charge-transfer complexes in aromatic solvents, represents the highest observed level of fluorination with a well-defined closed fullerene cage.[592] It was actually the first highly fluorinated [60]fullerene derivative to be structurally elucidated in 1994 by Gakh, Tuinman, and co-workers.[593] The obtained product generates eight ^{19}F NMR resonances of equal intensity and proved to have largely a single constitution.[593] 2D COSY ^{19}F NMR analysis allowed a unique structural assignment for $C_{60}F_{48}$ as energetically low-lying[594] D_3-symmetric (±)-**205** (Figure 42), a structure that was confirmed by Boltalina and co-workers[239] and later through X-ray crystallography by Troyanov, Neretin, and co-workers[595,596] to be made up of two identically functionalized, C_3-symmetric fullerene hemispheres. Careful examination of low-intensity ^{19}F NMR signals also suggested the presence of a minor, S_6-symmetric $C_{60}F_{48}$ isomer (**206**).[593] Despite identical and enantiomeric double bond arrangements in the two hemispheres of $C_{60}F_{48}$-D_3 ((±)-**205**) and $C_{60}F_{48}$-S_6 (**206**), respectively, the octatetracontafluorofullerenes are constitutional isomers and, therefore, do not represent a *d*,*l*/*meso* ensemble of stereoisomers. A similar relationship exists between hexakis-adduct structures (±)-**136** and **159**[443] (Figure 35) combining two C_{60}-hemispheres with an *e*,*e*,*e* addition pattern each. The structure of $C_{60}F_{48}$ was also studied in the gas phase by electron diffraction on a sample evaporated at 360 °C.[597]

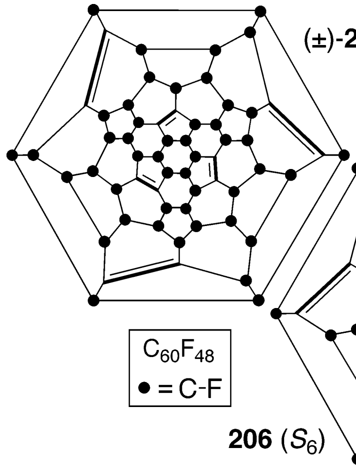


Figure 42. Schlegel diagrams of a chiral (D_3-symmetric)[239,593,595,596] and an achiral (S_6-symmetric)[593] isomer of $C_{60}F_{48}$.

4.11.2. Trifluoromethylated [60]Fullerenes

The direct, pyrolytic trifluoromethylation of fullerenes with CF_3CO_2Ag[598] generates a large diversity of derivatives $C_{60}(CF_3)_{2n}$ (n = 1−7), often in the form of regioisomeric mixtures.[599] The low symmetry of many of the isolated compounds, for example, $C_{60}(CF_3)_4$-C_1,[600,601] $C_{60}(CF_3)_4$-C_s,[601] or $C_{60}(CF_3)_6$-C_1,[600,601] makes definite, solely NMR-based structural assignments difficult. Based on ^{19}F NMR spectra, it was proposed that some compounds feature addition patterns with contiguous CF_3 groups.[599,600] But other investigations,[599,601] including a number of recent X-ray crystallographic characterizations, for example, of $C_{60}(CF_3)_8$,[602] $C_{60}(CF_3)_{10}$,[603−606] and $C_{60}(CF_3)_{12}$,[607] as well as $C_{60}(CF_2CF_3)_6$ and $C_{60}(CF_2CF_3)_8$,[608] showed that isolated perfluoroalkyl groups are a more typical feature of this class of fullerene derivatives. The most stable isomer of $C_{60}(CF_3)_2$-C_s was shown to have the structure of a 1,4-adduct.[601,609] An improvement in the selectivity of fullerene trifluoromethylation consists of the reaction of the carbon cages with trifluoroiodomethane[610] at 460 °C. One out of three isomers of the predominant product of this reaction, $C_{60}(CF_3)_{10}$, was isolated and structurally assigned by X-ray crystallography as C_1-symmetric (±)-**207** (Figure 43).[603,604] Its functionalization pattern is distinguished by isolated CF_3 groups

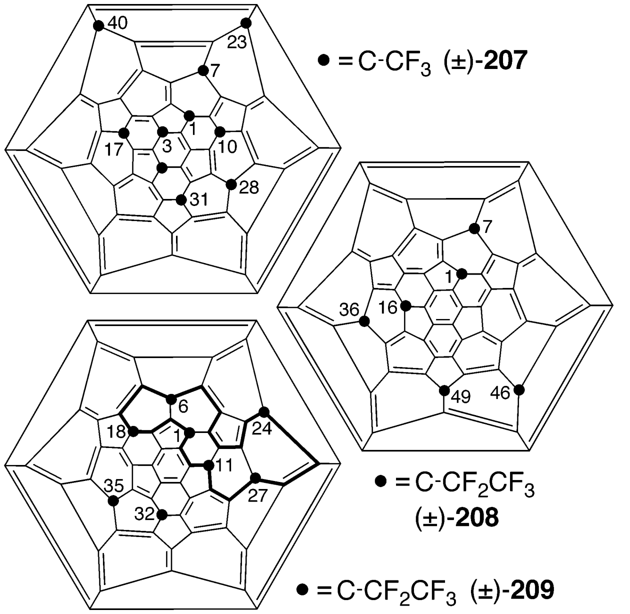


Figure 43. Schlegel diagrams of 1,3,7,10,14,17,23,28,31,40-decakis(trifluoromethyl)-1,3,7,10,14,17,23,28,31,40-decahydro(C_{60}-I_h)[5,6]fullerene ((±)-**207**),[603,604] 1,7,16,36,46,49-hexakis(pentafluoroethyl)-1,7,16,36,46,49-hexahydro(C_{60}-I_h)[5,6]fullerene ((±)-**208**),[608] and 1,6,11,18,24,27,32,35-octakis(pentafluoroethyl)-1,6,11,18,24,27,32,35-octahydro(C_{60}-I_h)[5,6]fullerene ((±)-**209**).[608]

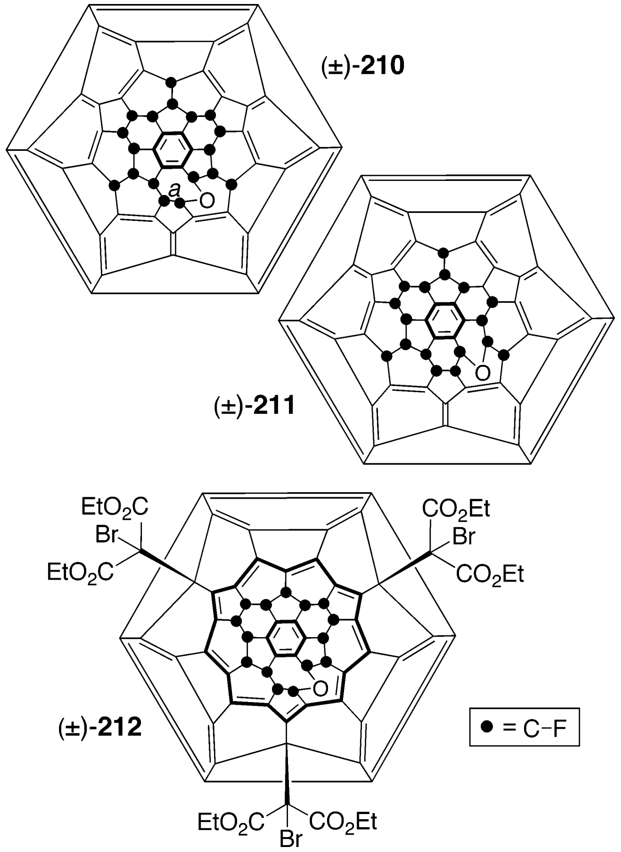


Figure 44. Chiral fluoro-oxahomofullerene derivatives. Bond "*a*" in (±)-**210** corresponds to the oxygen insertion site of an isomeric, C_s-symmetric structure. The 18-π-electron *trans*-annulene perimeter of (±)-**212** is marked in bold.

exhibiting 1,3- or 1,4-relationships between nearest neighbors. Very recently, two C_1-symmetric isomers of $C_{60}(C_2F_5)_6$ ((±)-**208**) and $C_{60}(C_2F_5)_8$ ((±)-**209**) could be isolated from the cold zone condensate of the reaction between buckminsterfullerene and C_2F_5I gas.[608] X-ray crystallography showed that hexakis-adduct (±)-**208** contains three isolated 1,4-difunctionalized hexagons, which represents an unprecedented $C_{60}X_6$ addition pattern (cf. section 6.9). As to octakis-adduct (±)-**209**, its addition pattern includes a substructure of the same kind, in addition to a "*para-para-para-meta-para*"-functionalized ribbon of edge-sharing hexagons. Other isomers of $C_{60}(C_2F_5)_6$ were present in the product mixture but have not been purified so far.

4.11.3. Fluoro-oxahomofullerenes

One of the byproducts of $C_{60}F_{18}$-C_{3v} formation (**195**, Figure 40), $C_{60}F_{18}O$-C_s, was shown by X-ray crystallography not to have the previously postulated epoxy[611] but an oxahomofullerene structure; actually the first of its kind.[612] It results from insertion of oxygen, probably originating from dioxygen or water,[558] into the longest and weakest C(F)−C(F) bond ("*a*" in the isomeric structure (±)-**210**, Figure 44). Similar insertion into the next longest bonds yielded two C_1-symmetric isomers, (±)-**210** and (±)-**211**.[613] S_N2' nucleophilic substitution of three fluorine atoms of $C_{60}F_{18}O$-C_s or of (±)-**210** by the anions generated from diethyl bromomalonate and DBU led to [18]trannulenes (e.g., (±)-**212** from (±)-**210**) with an intact oxahomofullerene substructure.[614] In these [60]fullerene derivatives, an aromatic all-*trans* [18]-annulene system (marked in bold in structure (±)-**212**) with small bond length alternation is responsible for the emerald-green color.[554−556] Among the seven isolated isomers of bis(oxahomo)fullerenes $C_{60}F_{18}O_2$, 1D and 2D ^{19}F NMR spectroscopy, in combination with the consideration of heats of formation, led to structural proposals for one C_s- and three C_1-symmetric structures.[615] They result from oxygen insertion into different bonds of the types that reacted in the formation of (±)-**210** and (±)-**211**. Among the oxahomofullerenes with a lower degree of fluorination, $C_{60}F_6O$-C_1 was proposed as a chiral structure next to $C_{60}F_2O$-C_{2v},[563] $C_{60}F_4O$-C_s, and $C_{60}F_8O$-C_s.[236,616]

5. C_{70} Derivatives with an Inherently Chiral Functionalization Pattern

5.1. The Most Common Chiral Addition Patterns of Mono-Adducts of C_{70}

C_{60} and the empty higher fullerenes[16,21] show a similar general behavior in addition reactions.[15,17−19] But whereas C_{60}-I_h is distinguished by 30 identical 6−6 bonds, C_{70}-D_{5h} features four different types of them, which leads to a higher number of possible adduct isomers. This number increases further if one includes the four different 6−5 bonds of C_{70}, which contrast a single such type in buckminsterfullerene. Nevertheless, [70]fullerene and other higher fullerenes show a remarkable selectivity in the formation of mono- and multiadducts.[16,21] In C_{70}-D_{5h}, the first addition often takes place, with decreasing preference, at the 6−6 bonds C(8)−C(25) and C(7)−C(22) (for the numbering of C_{70}, see Figures 3 and 45), to a lesser extent at the 6−6 bond C(1)−C(2), and in some rare instances at the 6−5 bond C(1)−C(6). In addition and similarly to C_{60}, certain primary adducts, including fullerene-fused pyrazolines and triazolines, can rearrange to homo[70]fullerenes with insertion of the extra

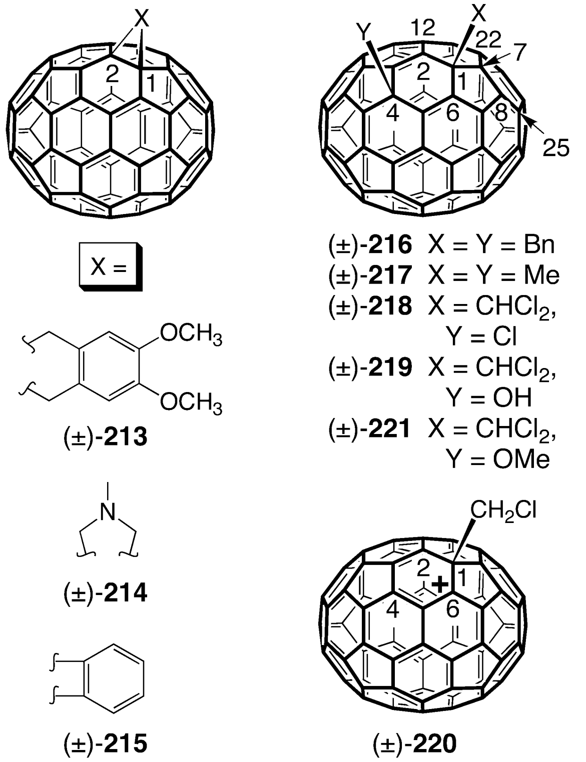


Figure 45. C_{70} derivatives with an inherently chiral functionalization pattern: C(1)−C(2)-mono-adducts (left), C(1),C(4)-adducts (top right), and cation (±)-**220**.[631]

atom into the 6−5 junction between C(24) and C(25) or between C(7) and C(8) (for the numbering of C_{70}, see Figures 3 and 45).

For reasons of clarity, the following general considerations on chiral addition patterns of C_{70} are limited to the most common mono-adduct types with C_{2v}- or C_s-symmetric addends. Chiral functionalization patterns of multiadducts, on the other hand, will be discussed in the following sections for specific examples. Established inherently chiral mono-functionalization patterns result from addition across the bond C(1)−C(2) or from insertion between C(7) and C(8) (for the numbering of C_{70}, see Figure 3). A noninherently chiral addition pattern has been realized with C_s-symmetric cycles fused to C(7)−C(22). The most common C(8)−C(25)-addition pattern, on the other hand, is achiral with both types of addends because the functionalized bond lies on a mirror plane of the parent fullerene. However, C_s-symmetric addends can lead to constitutional isomers, in this case.

5.2. C(1)–C(2)-Mono-Adducts of C_{70}

The regiochemistry of single and double additions of OsO_4 to C_{70} was explored by Hawkins et al. in 1993.[617] A major and a minor mono-adduct were identified as C_s-symmetric C(8)−C(25)- and C(7)−C(22)- isomers (for the numbering of C_{70}, see Figures 3 and 45), respectively. Further osmylation of the mono-adducts afforded a total of nine compounds, but no structural assignments were made.

The C_1-symmetric C(1)−C(2)-functionalized derivatives of C_{70} (Figure 45) are the only 6−6 mono-adducts with an inherently chiral functionalization pattern. Just a few such compounds have been isolated, mostly as minor products formed next to the achiral C(8)−C(25)- and C(7)−C(22)-adducts. This low frequency may seem surprising, given the occurrence of 20 C(1)−C(2)-type bonds in C_{70}, but it is ascribed to their low reactivity.[16,21] The first observed case ((±)-**213**, Figure 45) was detected by Diederich and co-workers in an investigation on the regioselectivity of the Diels−Alder addition of 4,5-dimethoxy-*o*-quinodimethane to C_{70} and C_{76}.[234] Another C(1)−C(2)-adduct, (±)-**214**, was isolated as a minor product from the [3 + 2] cycloaddition of *N*-methylazomethine ylide to C_{70}.[294,618] The isomeric assignment was based on ^{1}H NMR spectroscopy showing the presence of two different methylene groups with two different H-atoms each. The same compound ((±)-**214**) was formed next to the C(7)−C(22)- and the C(8)−C(25)-adducts (16:36:47 ratio) when [70]fullerene was reacted with *N*-methyl glycine and paraformaldehyde in a high-speed vibration mill (HSVM) in the absence of solvent.[619] Conversely, under microwave irradiation, C(1)−C(2)-adduct (±)-**214** was not formed at all, regardless of irradiation power or solvent, and moreover, the C(7)−C(22)- isomer was found to predominate at high microwave power over the C(8)−C(25)-adduct.[620,621] The inherently chiral C(1)−C(2)-addition pattern was finally observed in one ((±)-**215**) of the minor mono-adduct isomers resulting from [2 + 2] cycloaddition of benzyne to C_{70}.[622,623] It was accompanied by the common C(8)−C(25)- and C(7)−C(22)-adducts, as well as by an unusual isomer resulting from addition across the 6−5 bond C(1)−C(6).[622]

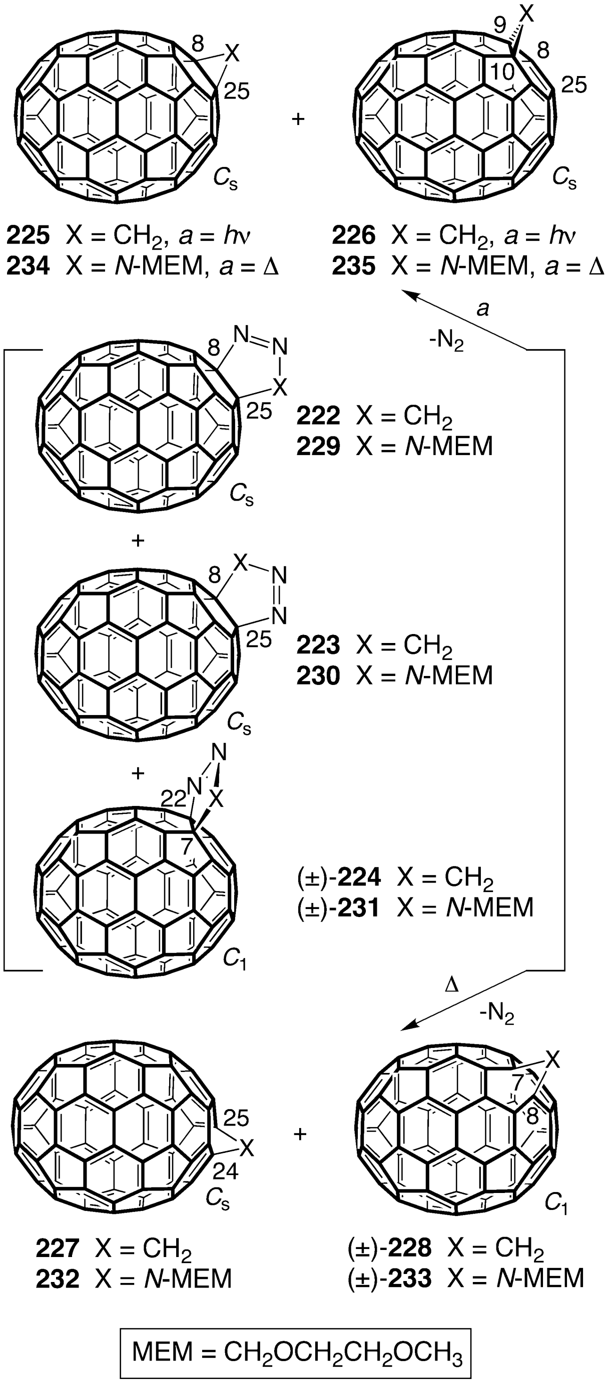
5.3. C(1),C(4)-Adducts of C_{70}

C_2-symmetric C(1),C(4)-adducts of C_{70} have been obtained with identical monovalent addends. Generation of $C_{70}{}^{2-}$ by deprotonation of 8,25-dihydro(C_{70}-D_{5h})[5,6]fullerene with TBAH (tetrabutylammonium hydroxide) in the presence of benzyl bromide afforded several $C_{70}Bn_2$ isomers.[624] Minor products isolated from this mixture were the 8,25-dibenzyl-8,25-dihydro(C_{70}-D_{5h})[5,6]fullerene and a C_2- or C_s-symmetric adduct, the structure of which could not be elucidated. The main product was assigned by Meier and co-workers, using INADEQUATE ^{13}C NMR spectroscopy of ^{13}C-enriched material, as C_2-symmetric (±)-**216** (Figure 45), which had already been postulated as product of the benzylation of electrochemically generated $C_{70}{}^{2-}$.[625] The transequatorial C(1),C(4)-addition mode was rationalized by the high density of the SOMO (singly occupied molecular orbital), which is likely to be involved in the irreversible C−C bond formation, and the significant charge concentration of $BnC_{70}{}^-$ at C(4).[624] Careful control of the amount of base in the above reaction allows for regioselective deprotonation of $C_{70}H_2$ at C(8), and subsequent alkylation affords 8-benzyl-8,25-dihydro(C_{70}-D_{5h})[5,6]fullerene (for the numbering of C_{70}, see Figure 45).[626] This method is complementary to the monoalkylation at C(25) of C_{70} by reaction of the fullerene with Zn and methyl bromoacetate (see section 7.1 and Figure 69).[627]

The photochemical addition of 1,1,2,2-tetramesityl-1,2-disilirane afforded an adduct for which the unparalleled addition across the equatorial bond C(2)−C(12) (cf. Figure 45) was proposed.[628] This addition pattern is achiral, and the chirality was ascribed to conformational effects related to the bulky mesityl substituents. In any case, the biphenyl-like bond C(2)−C(12) is expected to be rather unreactive, and transequatorial 1,4-addition, resulting in the inherently chiral C(1),C(4)-functionalization pattern (cf. Figure 45), was put forward as an alternative.[623] This addition pattern was also proposed for the reassigned $C_{70}Ph_2$, as well as for $C_{70}Me_2$ ((±)-**217**), formed together with $C_{70}Me_{2n}$ ($n = 2-5$) by reduction of C_{70} with Al/Ni alloy in NaOH/dioxane/THF, followed by alkylation with MeI.[629] $C_{70}Me_{10}$-C_s is isomorphous with $C_{70}Cl_{10}$ [630] (see section 5.13) with all addends located on an equatorial belt, and the methylation patterns of the lower homologues are C_s-symmetric substructures thereof. A second methylation manifold is operative in the reaction of C_{70} with Li, followed by quenching with MeI. It afforded the “polar”, achiral C(8),C(25)- and C(7),C(22)-bis-adducts (cf. Figure 45) in addition to more highly functionalized derivatives with up to 26 methyl groups.[629]

A C_1-symmetric C(1),C(4)-adduct of C_{70}, (±)-**218**, was isolated as major product from the reaction of the fullerene with chloroform in the presence of the Lewis acid $AlCl_3$.[631] As opposed to nucleophilic additions or cycloadditions in which fullerene carbon atoms C(25) and C(8) react preferentially, electrophilic attack under Friedel−Crafts conditions is selective for C(1), an observation that is consistent with the large HOMO coefficient at this atom. Chromatographic purification of (±)-**218** over wet silica gel produced the corresponding alcohol (±)-**219**, which, upon treatment with CF_3SO_3H, gave a reddish-brown solution of C_1-symmetric cation (±)-**220**.[631] It is stable at room temperature for over a week, and its structure was confirmed by NMR spectroscopic analysis and DFT calculations. Quenching of the acidic solution with methanol yielded a single fullerenyl methyl ether regioisomer (±)-**221**. It is sterically favored[632−635] among the products that result from attack of the nucleophile at one of the three atoms of cation (±)-**220** exhibiting the highest LUMO coefficients, that is, C(2), C(4), and C(6)

Scheme 18. Primary Adducts Resulting from 1,3-Dipolar Cycloaddition of Diazomethane or Azides to C_{70} (Center) and Thermal or Photochemical Extrusion of N_2 from These under Formation of 6−6 Closed (Top) or 6−5 Open (Bottom) Structures



(Figure 45). Solvolysis rate measurements showed (±)-**220** to have a thermodynamic stability similar to $[Cl_2HC{-}C_{60}]^+$ or the *tert*-butyl[636] cation.[631]

5.4. Homo[70]fullerenes, Aza- and Oxahomo[70]fullerenes, and Open-Cage Derivatives of C_{70}

Homo-[527,637,638] and azahomo[70]fullerenes[467,468,639−642] have been intensively studied, not only for their formation in [3 + 2] cycloaddition/N_2-extrusion sequences (Scheme 18) but also for their further transformation into a number of interesting compounds, such as open-cage derivatives of C_{70} and aza[70]fullerenes (Scheme 19). Whereas all the opened cages produced along the aza[70]fullerene route are inherently chiral, this is the case also for one of the azahomofullerene regioisomers (vide infra). As to the primary [3 + 2] cycloadducts, they include achiral isomers as well as a regioisomer with a noninherently chiral addition pattern (Scheme 18).

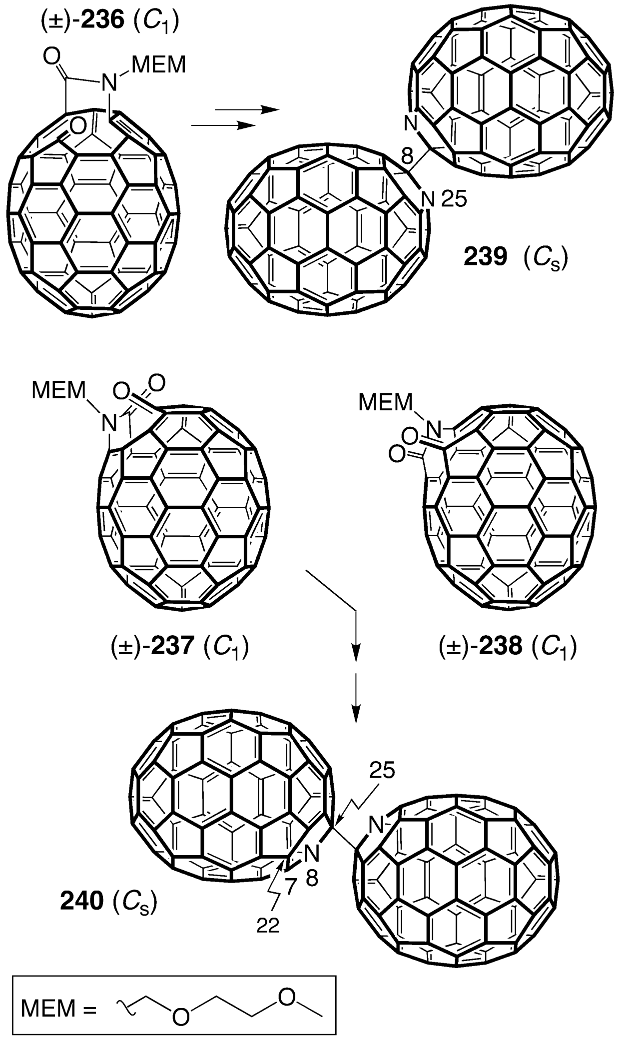
The [3 + 2] cycloaddition of diazoalkanes to 6−6 bonds was among the first reactions carried out with buckminsterfullerene;[526] it affords isolable 3′*H*-pyrazolofullerenes as primary adducts. Whereas the photoinduced extrusion of N_2 from the fused heterocycles yields cyclopropafullerenes, the thermal process affords homofullerenes with a methylene group inserted in the junction between a six- and a five-membered ring (cf. Scheme 13).[15,16,18,256]

Because diazomethane can adopt two different orientations in relation to all bonds not lying on the equator of C_{70}, two constitutionally isomeric pyrazolofullerenes, **222** and **223** (Scheme 18), arise from addition to C(8)−C(25). In addition, the racemate of a third regioisomer, (±)-**224**, which displays a noninherently chiral addition pattern, results from cycloaddition across C(7)−C(22).[527,638] Irradiation of **222**−(±)-**224** yielded methanofullerenes **225** and **226** next to minor amounts of **227**, whereas thermolysis of the same mixture gave homofullerenes **227** and C_1-symmetric (±)-**228**.[527,638] Homofullerenes retain the basic electronic structure of the parent fullerenes due to strong homoaromatic interaction, and the perturbation of the π-system is minimal.[637,643] Homo[70]fullerenes **227** and (±)-**228**, each of which has a proton located atop a pentagon and a hexagon, were therefore used to probe the local aromaticity of individual rings in the neutral as well as in the hexa-anionic state of the fullerene, to rationalize the aromatic behavior[146,147] of C_{70} and C_{70}^{6-}.[152,153] Similar to C_{60}^{6-},[644] the extra electrons of C_{70}^{6-} are mainly located in the five-membered rings, rendering them diatropic. But as opposed to hexa-anionic buckminsterfullerene, the distribution in C_{70}^{6-} is uneven with the highest charge density located at the pole of the ovoid cage.[152,153] Endohedral ^{3}He incarceranes of the $C_{71}H_2$ isomers **225**−(±)-**228** have been prepared in order to study the effect of the functionalization of the carbon spheroid on the ^{3}He NMR shift.[637]

In analogy to the reaction of C_{70} with diazomethane, the 1,3-dipolar cycloaddition with alkyl azides afforded three constitutionally isomeric 3′-alkyl-3′*H*-triazolo[70]fullerenes (**229**−(±)-**231**, Scheme 18).[467,468,639,640] Thermal elimination of N_2 from the fullerene-fused triazoles preferentially yielded azahomofullerenes (**232** and (±)-**233**) as compared with azireno[70]fullerenes (**234** and **235**).[639,640]

After the first azafullerene had been successfully prepared by Wudl and co-workers in its dimeric form $(C_{59}N)_2$ (**168**, Scheme 15) from *N*-MEM ([2-(methoxy)ethoxy]methyl)-protected azahomo[60]fullerene (**166**) via the open-cage derivative (±)-**167**,[470,471] the established methodology (cf. section 4.9) was also applied to azahomo[70]fullerenes.[467,468,640,641] Self-sensitized photo-oxygenation of **232** and (±)-**233** (Scheme 18) thus led to the open-cage ketolactams (±)-**236**, and a mixture of (±)-**237** and (±)-**238**, respectively (Scheme 19). Treatment of (±)-**236** with acid further transformed the C_1-symmetric "opened cage" into isomerically pure, C_s-symmetric 8,8′-bi-25-aza(C_{70}-D_{5h})[5,6]fullerene (**239**). Ketolactam (±)-**237** similarly gave the C_s-symmetric 25,25′-bi-8-aza(C_{70}-D_{5h})[5,6]fullerene (**240**).[467,468] When (±)-**238** was treated under the same conditions,[467] the intermediate radicals, which dimerize to azafullerenes in the

Scheme 19. Three Chiral "Holey" C_{70}-Cages ((±)-236−(±)-238) and Transformation of Two of Them into Dimeric Aza[70]fullerenes ((±)-239 and (±)-240)[467,468,640] [a]



[a] The third ketolactam ((±)-**238**) appears to afford *meso*-22,22′-bi-7-aza(C_{70}-D_{5h})[5,6]fullerene rather than the alternative *d,l*-racemate.[645]

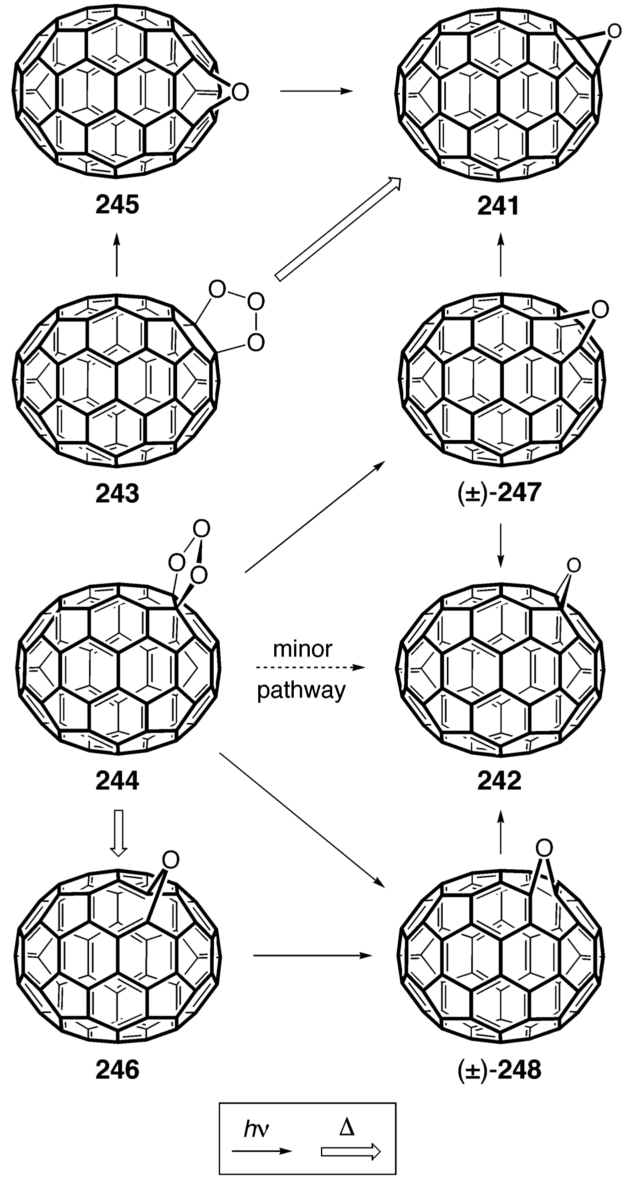
last step of an entire reaction cascade, are chiral. The combination of homo- and heterochiral radicals can consequently afford three stereoisomers of 22,22′-bi-7-aza(C_{70}-D_{5h})[5,6]fullerene (not shown; for the numbering, cf. **240**), namely, a C_2-symmetric *d,l*-pair and a C_s-symmetric *meso* form. Isolation of this $(C_{69}N)_2$-regioisomer at the end of a reaction sequence distinguished by an improved yield of ketolactam precursor (±)-**238** points at the exclusive formation of the *meso* isomer.[645]

Hirsch and co-workers made heterofullerenes accessible by a different route involving, in the case of $(C_{59}N)_2$, intermediates of type **165** (Scheme 14) with acid-labile substituents at the nitrogen atoms.[468,475,476] Application of their approach to the according derivatives of C_{70} actually afforded aza[70]fullerene dimers **239** and **240** (Scheme 19) for the first time.[468,476] In this context, it may also be mentioned that singly bonded, functionalized C_{70} dimers have been detected as anionic intermediates in the electrochemical retro-Bingel reaction[117] of methanofullerene-carboxylates.[118]

5.5. Oxahomo- and Epoxy[70]fullerenes

$C_{70}O$, reported in 1991 by Diederich and co-workers, was one of the first known derivatives of [70]fullerene.[7] Subsequent synthetic, spectroscopic, and crystallographic investigations by the groups of Smith,[646] Taylor,[647] and Balch[648] provided structural details of two $C_{70}O$ regioisomers with epoxy bridges across C(8)−C(25) (**241**, Scheme 20) and C(7)−C(22) (**242**). A more recent study by Heymann, Bachilo, and Weisman extended the picture of the [70]-fullerene−oxygen system, accounting for interconversions among various species.[649] Ozonation of C_{70} in the dark, by passing a stream of O_2/O_3 through a solution of the fullerene in toluene or *o*-xylene, produced the rather unstable C_s-symmetric ozonides **243** and **244** as primary adducts. Whereas the thermolytic decay of the former (**243**) led to epoxide **241**, oxahomofullerene **245** was formed under irradiation. In the case of ozonide **244**, thermolysis gave another oxahomofullerene (**246**), and photolysis resulted in a mixture of further oxahomofullerenes (±)-**247** and (±)-**248**, in addition to minor amounts of epoxide **242**. Whereas both oxirane rings are fused to 6−6 bonds of the cage, the oxahomofullerenes result from insertion of an oxygen atom

Scheme 20. Photochemical and Thermal Conversions of Ozonides 243 and 244 into Oxahomo[70]fullerenes ((±)-245−(±)-248) or Epoxides 241 and 242[649] [a]



[a] The epoxides are the endpoints of all transformations.

into 6−5 bonds. In cases where the latter are not orthogonal to the *C*$_5$-symmetry axis of the parent spheroid, the according oxahomofullerenes are chiral (*C*$_1$-symmetric (±)-**247** and (±)-**248**). Interestingly, all oxahomo[70]fullerenes eventually photoisomerize to the epoxides (**245** and (±)-**247** → **241**; **246**−**248** → **242**).[649]

5.6. Bingel Addition of Untethered Malonates to C$_{70}$

The highly selective Bingel reaction[115] shows a pronounced preference for the C(8)−C(25) bond of C$_{70}$.[30,115] Subsequent addition of another malonate equivalent to the according mono-adduct[30,263,267] takes place at one of the five bonds C(16)−C(35), C(33)−C(34), C(36)−C(37), C(53)−C(54), or C(55)−C(56) (for the numbering of C$_{70}$, see Figure 3) radiating from the polar pentagon of the opposite hemisphere.

In the case of achiral, *C*$_{2v}$-symmetric diethyl malonate addends, three constitutionally isomeric bis(methano)-fullerenes are formed,[30,263,267] namely, *C*$_{2v}$-symmetric **249** (Figure 46) and *C*$_2$-symmetric (±)-**250** and (±)-**251**, the latter two having an inherently chiral addition pattern.[30,267] When viewed along the *C*$_5$ axis of the parent fullerene, the three regioisomers can be represented as simplified Newman projections displaying only the polar pentagons (inner pentagon = proximal pentagon) and the functionalized bonds, which appear as clockface and watchhands, respectively (Figure 46). According to this metaphor, the structures are designated as “twelve o’clock” (**249**), “two o’clock” ((±)-**250**), and “five o’clock” ((±)-**251**) regioisomers.

Double addition of enantiomerically pure bis[(*S*)-1-phenylbutyl] 2-bromomalonate to C$_{70}$ leads to a combination of the stereogenic elements of the addend (stereogenic centers) and, in the occurrence, of the fullerene cage (inherently chiral functionalization pattern). This results in a total of five optically active isomers, namely, *C*$_2$-symmetric (*S*,*S*,*S*,*S*)-**252**, in addition to two regioisomers occurring as pairs of *C*$_2$-symmetric diastereoisomers ((*S*,*S*,*S*,*S*,$^{\text{f,s}}$*A*)-**253a**/(*S*,*S*,*S*,*S*,$^{\text{f,s}}$*C*)-**253b**) and ((*S*,*S*,*S*,*S*,$^{\text{f,s}}$*A*)-**254a**/(*S*,*S*,*S*,*S*,$^{\text{f,s}}$*C*)-**254b**) (Figure 46).[30] Because there is no enantiomeric relationship among any of these five chiral C$_{70}$ derivatives, they could all be isolated by HPLC on plain silica gel, and the same was true for the five products (*R*,*R*,*R*,*R*)-**252**, (*R*,*R*,*R*,*R*,$^{\text{f,s}}$*C*)-**253a**/(*R*,*R*,*R*,*R*,$^{\text{f,s}}$*A*)-**253b**, and (*R*,*R*,*R*,*R*,$^{\text{f,s}}$*C*)-**254a**/(*R*,*R*,*R*,*R*,$^{\text{f,s}}$*A*)-**254b** resulting from cyclopropanation of C$_{70}$ with the corresponding bis[(*R*)-1-phenylbutyl] 2-bromomalonate.[267] From the two reactions, a total of 10 optically active Bingel-type bis-adducts were isolated, and they can be grouped into five pairs of enantiomers: one with stereogenic centers in the addends only ((+)- and (−)-**252**) and four with both an inherently chiral fullerene functionalization pattern and chiral ester residues ((+)- and (−)-**253a**, (+)- and (−)-**253b**, (+)- and (−)-**254a**, and (+)- and (−)-**254b**).

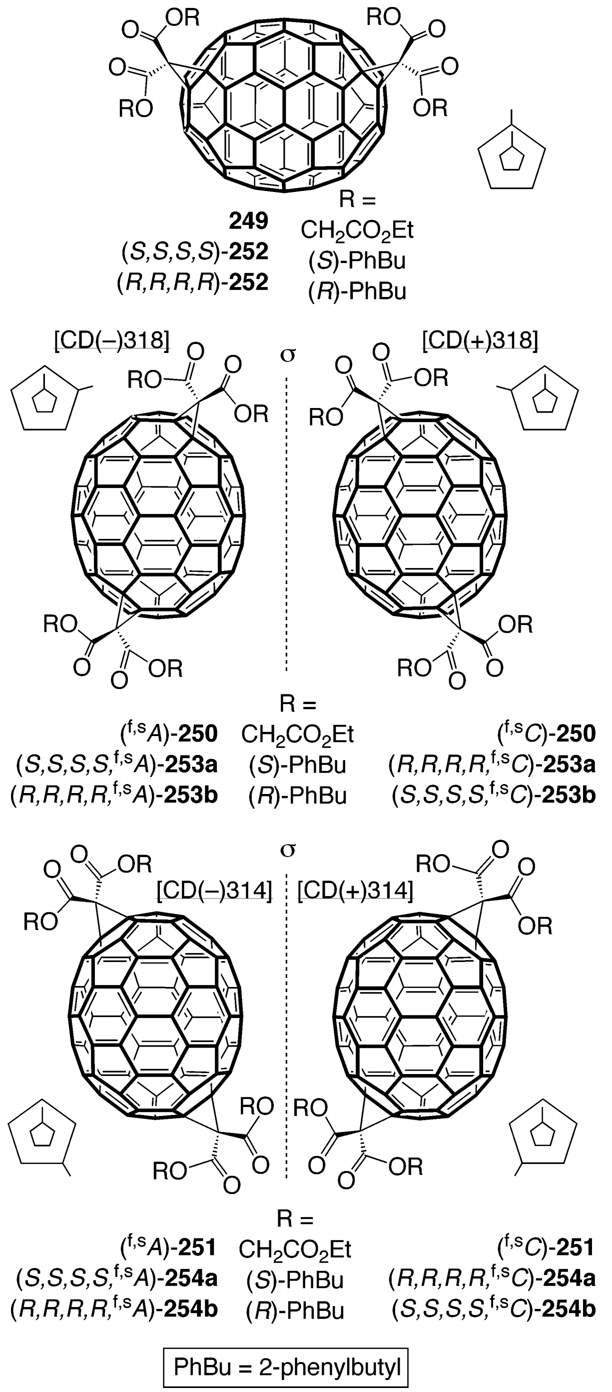


Figure 46. Bis-adducts of C$_{70}$ resulting from two consecutive Bingel additions.[30,263,267] Whereas the “twelve o’clock” regioisomer (top, cf. Newman-type projection with two concentric pentagons − further explanations are given in the main text) has an achiral addition pattern, those of the “two o’clock” (center, main product) and “five o’clock” (bottom, minor product) regioisomers are inherently chiral, which leads to racemates and pairs of diastereoisomers if achiral and enantiopure malonates, respectively, are used in the cyclopropanation reaction. Separate syntheses of the (*R*)- and (*S*)-series makes all 10 stereoisomers, which include five pairs of enantiomers, easily available as pure compounds.

The chiral *π*-chromophores of fullerene derivatives with inherently chiral addition patterns manifest themselves by intense bands in the circular dichroism (CD) spectra (cf. Figure 48), in contrast to simple perturbation of achiral fullerene chromophores by chiral addends. Furthermore, it turned out that matching fullerene functionalization patterns lead to practically identical CD curves, irrespective of the structure of the addends, as long as the latter do not give rise to strong Cotton effects of their own or interact strongly with the *π*-system of the fullerene.[4] Based on these findings, the comparison between the calculated CD spectrum of the dimethyl ester analogue of (*S*,*S*,*S*,*S*,$^{\text{f,s}}$*C*)-**253b** and the experimental data allowed assignments of absolute configurations in the “**253** series” as [CD(−)318]-(*S*,*S*,*S*,*S*,$^{\text{f,s}}$*A*)-**253a** and [CD(+)318]-(*S*,*S*,*S*,*S*,$^{\text{f,s}}$*C*)-**253b**.[121] Due to the negligible contribution of the stereogenic centers of the ester residues to the Cotton effects, [CD(−)318]-(*R*,*R*,*R*,*R*,$^{\text{f,s}}$*A*)-**253b** and [CD(+)318]-(*R*,*R*,*R*,*R*,$^{\text{f,s}}$*C*)-**253a** were assigned by the same

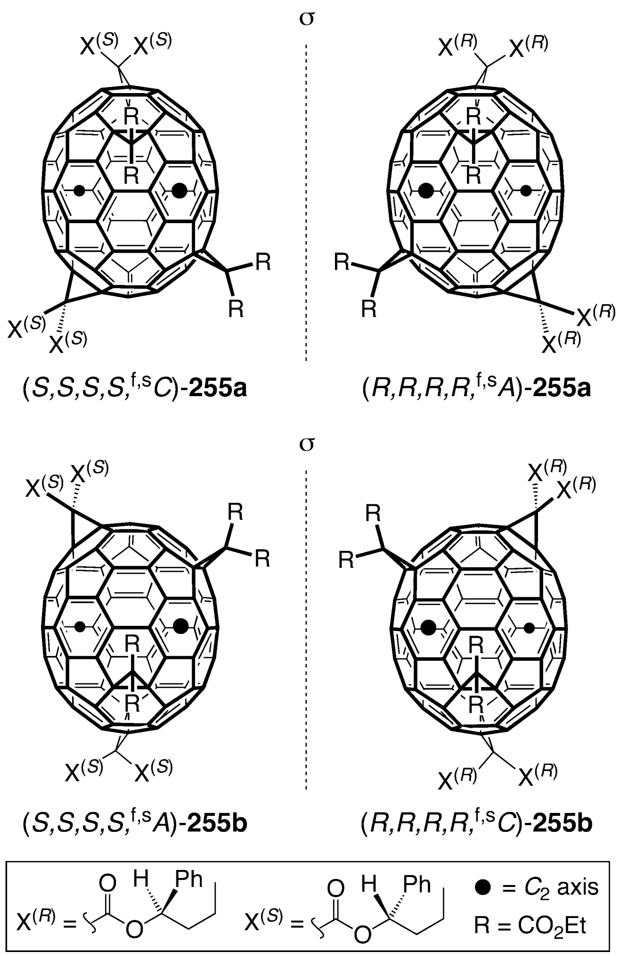
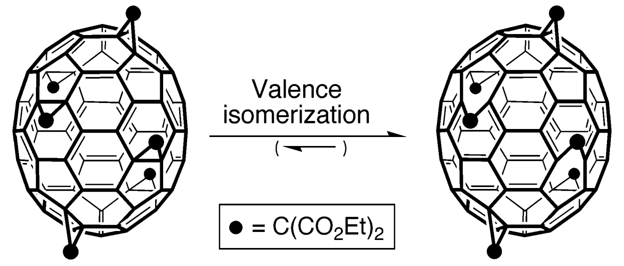


Figure 47. Stereoisomeric tetrakis-adducts of C_{70} prepared by diethyl malonate addition to each of the bis-adducts (*S*,*S*,*S*,*S*,^{f,s}*C*)-**253b**, (*R*,*R*,*R*,*R*,^{f,s}*A*)-**253b**, (*S*,*S*,*S*,*S*,^{f,s}*A*)-**253a**, and (*R*,*R*,*R*,*R*,^{f,s}*C*)-**253a** (Figure 46).[267] The black dots represent intersections of the 2-fold symmetry axis with the fullerene cage.

token. On the basis of very similar CD bands (positions and signs), the following assignments were also made with confidence: [CD(−)314]-(*S*,*S*,*S*,*S*,^{f,s}*A*)-**254a**, [CD(+)314]-(*S*,*S*,*S*,*S*,^{f,s}*C*)-**254b**, [CD(−)314]-(*R*,*R*,*R*,*R*,^{f,s}*A*)-**254b**, and [CD-(+)314]-(*R*,*R*,*R*,*R*,^{f,s}*C*)-**254a**.[267]

To explore the regiochemistry of the formation of higher Bingel-type adducts and also the impact of a higher functionalization degree on the Cotton effects of the fullerene π-chromophore, bis-adducts of C_{70} were subjected to further cyclopropanation. Tetrakis-adduct formation occurred with pronounced regioselectivity:[30,267] addition of diethyl 2-bromomalonate to **249** (Figure 46) afforded the C_{2v}-symmetric 7,22:17,18:46,47:53,54-tetrakis-adduct (for the numbering of C_{70}, see Figure 3), and a C_2-symmetric tetrakis-adduct was obtained from bis-adduct (±)-**250** (Figure 46).[267] The inherently chiral addition pattern of the latter tetrakis-adduct is the same as that of the four stereoisomers (*S*,*S*,*S*,*S*,^{f,s}*C*)-**255a**, (*R*,*R*,*R*,*R*,^{f,s}*A*)-**255a**, (*S*,*S*,*S*,*S*,^{f,s}*A*)-**255b**, and (*R*,*R*,*R*,*R*,^{f,s}*C*)-**255b** (Figure 47), obtained in separate reactions from bis-adducts (*S*,*S*,*S*,*S*,^{f,s}*C*)-**253b**, (*R*,*R*,*R*,*R*,^{f,s}*A*)-**253b**, (*S*,*S*,*S*,*S*,^{f,s}*A*)-**253a**, and (*R*,*R*,*R*,*R*,^{f,s}*C*)-**253a** (Figure 46), respectively.[267] CD spectroscopy revealed that the bands of bis- and derived tetrakis-adducts are similar in shape and sign below ~400 nm, but the agreement is less good in the longer wavelength region, which may represent a fingerprint of the specific addition pattern.[267]

Scheme 21. Primary Adduct (left) Resulting from Sixfold Bingel Cyclopropanation of C_{70} and Valence Isomerization to (±)-256 under Formation of Two Homo[70]fullerene Substructures[267] [a]



(±)-**256**

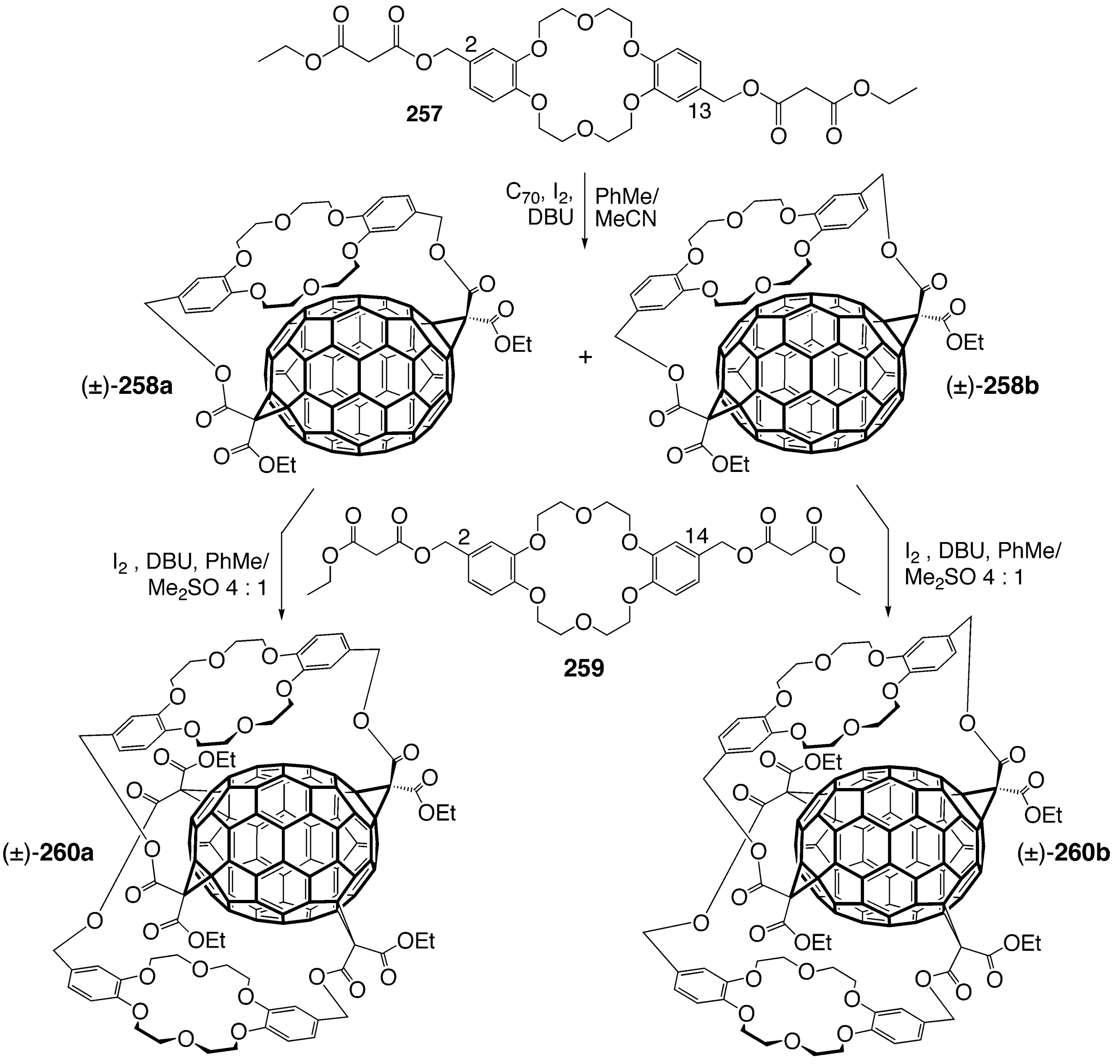
[a] The C_2-symmetric molecule is viewed along the symmetry axis.

The polar solvent dimethyl sulfoxide leads to an enhanced reactivity for the Bingel reaction, and hexakis- to octakis-adducts were formed by addition of diethyl 2-bromomalonate to **249** and (±)-**250** (Figure 46) via the intermediacy of tetrakis-adducts with the addition pattern of (+)/(−)-**255a/b** (Figure 47).[267] Substantial regioselectivity was observed up to the stage of hexakis-adducts, but it became strongly reduced at higher degrees of functionalization. Starting from bis-adduct (±)-**250** (Figure 46), the singular hexakis-adduct (±)-**256** (Scheme 21) was isolated as a major product. Its structure could be confidently elucidated by a combination of ^{13}C NMR spectroscopic analysis, steric considerations, known reactivity patterns of C_{70},[16,21] and ab initio calculation of frontier orbital (LUMO and LUMO + 1) coefficients, which can be correlated[40,272,273] to the sites of preferred nucleophilic attack.[267] C_2-symmetric (±)-**256** includes four cyclopropafullerene units in the polar regions besides two homofullerene substructures near the equator.[267] The latter are the result of malonate additions to 6−5 bonds with enhanced LUMO coefficients and subsequent valence isomerization.

5.7. Bingel Addition of Achiral Tethered Malonates to C_{70}

Dibenzo[18]crown-6-derived bismalonates were successfully used not only for the regioselective bisfunctionalization of C_{60} (cf. section 4.3.1 and Figure 23) but also in the first tether-directed remote functionalization of C_{70}.[650−652] Macrocyclization of this fullerene with bismalonate **257**, derived from *anti*-disubstituted dibenzo[18]crown-6 (substitution at positions 2 and 13 of the dibenzo-fused heterocycle, Scheme 22), afforded four stereoisomers, namely, racemates (±)-**258a** and (±)-**258b** (ratio ca. 1:1.7), with complete regioselectivity.[650,652] The identity of C_2-symmetric (±)-**258a** was established by X-ray crystallography. The chirality of the [70]fullerene−crown ether conjugates ensues from a combination of inherently chiral fullerene addition pattern and “planar” chiral unit represented by the *anti*-disubstituted crown ether with restricted conformational mobility. Interestingly, the “five o’clock” addition pattern (cf. Figure 46) of (±)-**258a** and (±)-**258b** corresponds to the least favored product of two independent diethyl malonate additions to C_{70}, the major product displaying the “two o’clock” addition pattern.[30,263,267] A notable template effect was observed when the synthesis of (±)-**258a** and (±)-**258b** was carried out in the presence of KPF_6: whereas the regioselectivity remained unaffected, the diastereoselectivity (ratio (±)-**258a**: (±)-**258b** ≈ 1.3:1) was shifted in favor of the former.[650,652]

Scheme 22. Sequential Functionalization of C_{70} with Crown Ether−Bismalonate Conjugates Having *anti*- and *syn*-Geometries[650−652] [a]



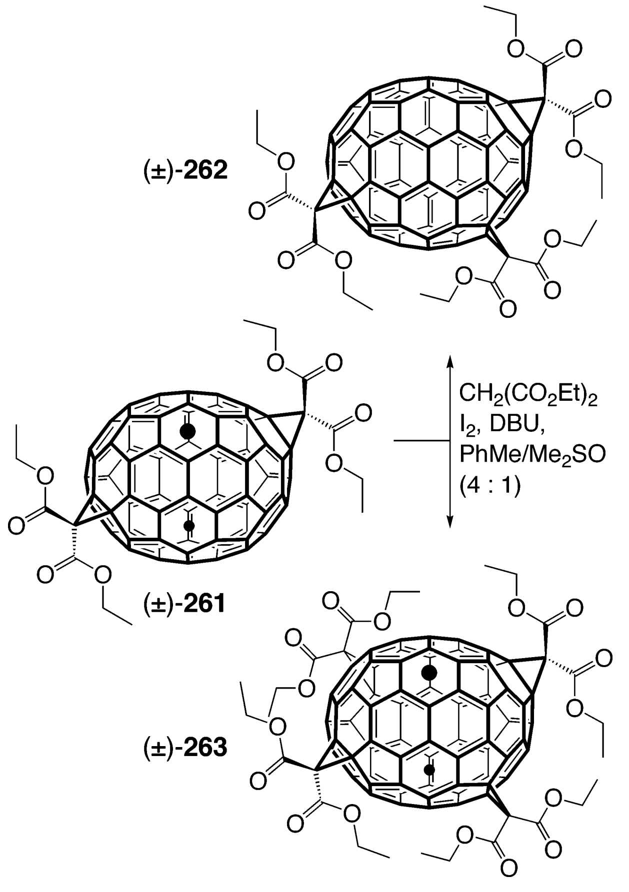
[a] The resulting bis- and tetrakis-adducts have inherently chiral addition patterns, which are superposed to the chirality of the *anti*-disubstituted dibenzo[18]crown-6 unit with restricted conformational mobility in close proximity to the fullerene spheroid.

Reaction of bis-adduct (±)-**258a** with a second equivalent of tethered bismalonate **257** led to an inseparable mixture of four products. However, when bis-adducts (±)-**258a** and (±)-**258b** were allowed to individually react with *syn*-disubstituted dibenzo[18]crown-6 derivative **259** (substitution at positions 2 and 14 of the dibenzo-fused heterocycle, Scheme 22), C_1-symmetric tetrakis-adducts (±)-**260a** and (±)-**260b**, respectively, with C_{70} sandwiched between two crown ethers, were obtained regio- and stereoselectively.[651,652] It should be pointed out that the *syn* substitution pattern of **259** avoids the introduction of another planar chiral unit. Besides, the switching from bismalonate **257** to **259** in the Bingel reaction with pristine C_{70} led to a complete change in regioselectivity, generating the achiral "twelve o'clock" and the inherently chiral "two o'clock" addition patterns in a ~1:1 ratio.[652]

Although the conformation of the bridging crown ethers in conjugates (±)-**258a/b** and (±)-**260a/b** is not particularly favorable for strong association with metal ions such as K^+ or Na^+, complexation was demonstrated with the help of ion-selective electrodes and by significant anodic shifts of the first reduction potentials (CV).[651,652]

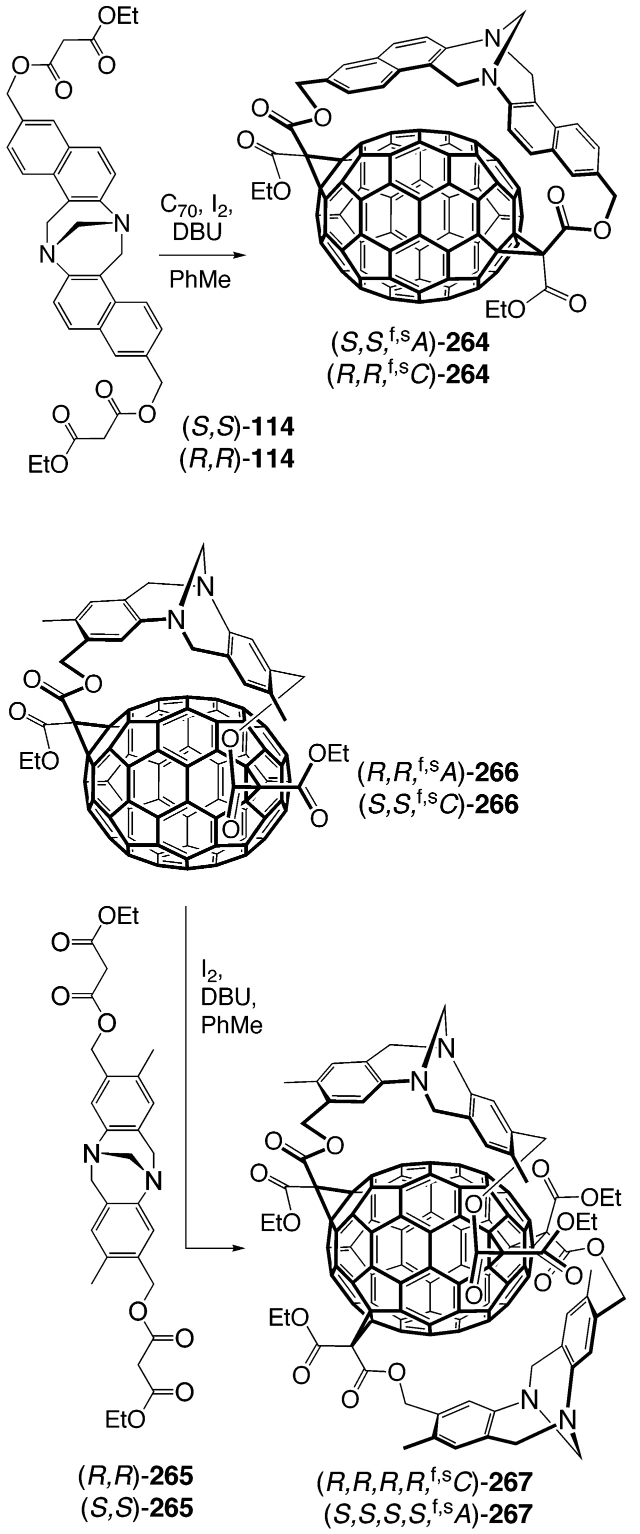
Transesterification of the mixture (±)-**258a/b** (Scheme 22) provided, for the first time, good access to the "five o'clock" bis-adduct (±)-**261** (Scheme 23). When the latter was reacted under modified Bingel conditions (I_2, DBU, PhMe/Me_2SO 4:1) with 1 and 3 equiv of diethyl malonate, C_1-symmetric tris-adduct (±)-**262** and C_2-symmetric tetrakis-adduct (±)-**263**, respectively, were obtained as sole isolable products.[652] These structures were confidently assigned on the basis of NMR data, predictions from density-functional theory (DFT), and the information from known[30,267] Bingel-type tris- and tetrakis-adducts, for example, (+)/(−)-**255a/b** (Figure 47) with a related addition pattern. In fact, two addends located within a hemisphere of any of these tris- and tetrakiscyclopropafullerenes always adopt the same arrangement, which corresponds to *equatorial* in C_{60}. The difference between (±)-**262** and (±)-**263** on one hand and the previously reported compounds ((+)/(−)-**255a/b**, Figure 47) on the other hand[30,267] resides in the relative orientation of the functionalized

Scheme 23. Transformation of C_2-Symmetric Bis-Adduct (±)-261 of C_{70}, Obtained by Transesterification of (±)-258a/b (Scheme 22), into C_1-symmetric Tris-Adduct ((±)-262) and C_2-Symmetric Tetrakis-Adduct ((±)-263)[652] [a]



[a] The black dots represent intersections of the twofold symmetry axis with the fullerene cage.

Scheme 24. Regio- and Diastereoselective Single (→ (*S*,*S*,^{f,s}*A*)-264 and (*R*,*R*,^{f,s}*C*)-264; → (*S*,*S*,^{f,s}*C*)-266 and (*R*,*R*,^{f,s}*A*)-266) and Double (→ (*S*,*S*,*S*,*S*,^{f,s}*A*)-267 and (*R*,*R*,*R*,*R*,^{f,s}*C*)-267) Additions to C_{70} of Two Bismalonates Derived from the Tröger Base[653] [a]



[a] The chiral spacers of (*S*,*S*)-**265** and (*R*,*R*)-**265** induce an unprecedented motif of double addition to C_{70}.

hemispheres that are combined in a molecule: whereas the polar addends of (±)-**262** and (±)-**263** (Scheme 23) define a "five o'clock" pattern, their arrangement corresponds to "two o'clock" in the other cases.

5.8. Diastereoselective Tether-Directed Multifunctionalization of C_{70} with Enantiopure Bismalonates

Very recently, the Diederich group reported the first regio- and diastereoselective tether-directed multifunctionalization of C_{70}, using bismalonates derived from the Tröger base, which had already proven very successful in similar reactions with C_{60} [416,417] (cf. section 4.4.3).[653] Although the synthesis of bis- and tetrakis-adducts was first tested with racemic tethers, the discussion will be limited to the synthesis of the enantiomerically pure products, starting from optically pure Tröger bases.

Complete regio- and diastereoselectivity was observed in the Bingel macrocyclization of C_{70} with bismalonates (*S*,*S*)-**114** and (*R*,*R*)-**114** (Scheme 24; cf. also Scheme 7), yielding bis-adducts (*S*,*S*,^{f,s}*A*)-**264** and (*R*,*R*,^{f,s}*C*)-**264**, respectively.[653] Their "five o'clock" functionalization pattern (cf. Figure 46) was clearly established by comparison of the UV/vis spectra to those of previously assigned members[30,267,652] of this regioisomer family, and the diastereoselectivity was nicely reflected by the mirror-image CD spectra of (*S*,*S*,^{f,s}*A*)-**264** and (*R*,*R*,^{f,s}*C*)-**264,** which closely resemble those of (*R*,*R*,*R*,*R*,^{f,s}*A*)-**254b** and (*S*,*S*,*S*,*S*,^{f,s}*C*)-**254b** (Figure 46),[267] respectively, the absolute configurations of which had previously been assigned (cf. section 5.6). Intriguingly, ^1H and ^{13}C NMR spectra revealed C_1-symmetry for (±)-**264** although both the fullerene addition pattern and the Tröger base are C_2-symmetric. Possible explanations for this observation are the presence of an *in,out*-isomer[351] or a misalignment between the C_2-axes of the two substructures.

Reaction of C_{70} with bismalonates (*S*,*S*)-**265** and (*R*,*R*)-**265**, on the other hand, afforded the bridged dicyclopropa[70]fullerenes (*S*,*S*,$^{\mathrm{f,s}}C$)-**266** and (*R*,*R*,$^{\mathrm{f,s}}A$)-**266**, respectively, again with perfect regio- and diastereoselectivity.[653] The configurational assignment of C_1-symmetric (±)-**266** was not straightforward because its addition pattern had not been observed so far. A key experiment for the structural elucidation was the addition of another equivalent of bismalonates (*S*,*S*)-**265** and (*R*,*R*)-**265** to dicyclopropafullerenes (*S*,*S*,$^{\mathrm{f,s}}C$)-**266** and (*R*,*R*,$^{\mathrm{f,s}}A$)-**266**, respectively.[653] Such an application of two sequential tether-directed remote bisfunctionalizations to the preparation of enantiomerically pure tetrakis-adducts had not been reported, and it diastereoselectively afforded (*S*,*S*,*S*,*S*,$^{\mathrm{f,s}}A$)-**267** and (*R*,*R*,*R*,*R*,$^{\mathrm{f,s}}C$)-**267** (note that the stereodescriptor for the fullerene addition pattern is formally inverted on the transition from the bis- to the corresponding tetrakis-adducts). The UV/vis spectrum of (±)-**267** is in good agreement with that of a previously reported tetracyclopropafullerene (octaethyl ester analogue of (±)-**255a**, Figure 47),[30,267] suggesting identical addition patterns, an assignment that was further corroborated by molecular modeling. The absolute configurations of (*S*,*S*,*S*,*S*,$^{\mathrm{f,s}}A$)-**267** and (*R*,*R*,*R*,*R*,$^{\mathrm{f,s}}C$)-**267** (Scheme 24) could also be assigned by matching their CD spectra (Figure 48) with those of the previously assigned (*R*,*R*,*R*,*R*,$^{\mathrm{f,s}}A$)-**255a** and (*S*,*S*,*S*,*S*,$^{\mathrm{f,s}}C$)-**255a** (Figure 47), displaying addition patterns with the same constitution and configuration. As to the configurational assignments of (*S*,*S*,$^{\mathrm{f,s}}C$)-**266** and (*R*,*R*,$^{\mathrm{f,s}}A$)-**266**, they rely on molecular mechanics-based calculations of heats of formation for geometry-optimized structures, assuming that the thermodynamic stability of the bis-adduct is reflected in the transition state of the second cyclopropanation, which determines the absolute configuration of the addition pattern.

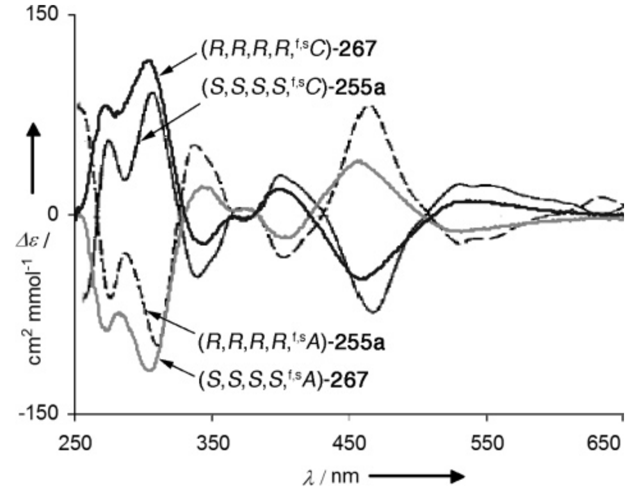


Figure 48. Superposition of the CD spectra of [70]fullerene tetrakis-adducts (*S*,*S*,*S*,*S*,$^{\mathrm{f,s}}A$)-**267**, (*R*,*R*,*R*,*R*,$^{\mathrm{f,s}}C$)-**267** (Scheme 24),[653] (*S*,*S*,*S*,*S*,$^{\mathrm{f,s}}A$)-**255a**, and (*R*,*R*,*R*,*R*,$^{\mathrm{f,s}}C$)-**255a**[267] (Figure 47). All four tetrakis-adducts have the same addition pattern, and the absolute configuration of the former compounds could be assigned by comparison of their spectra to those of the latter, which have known absolute configurations.

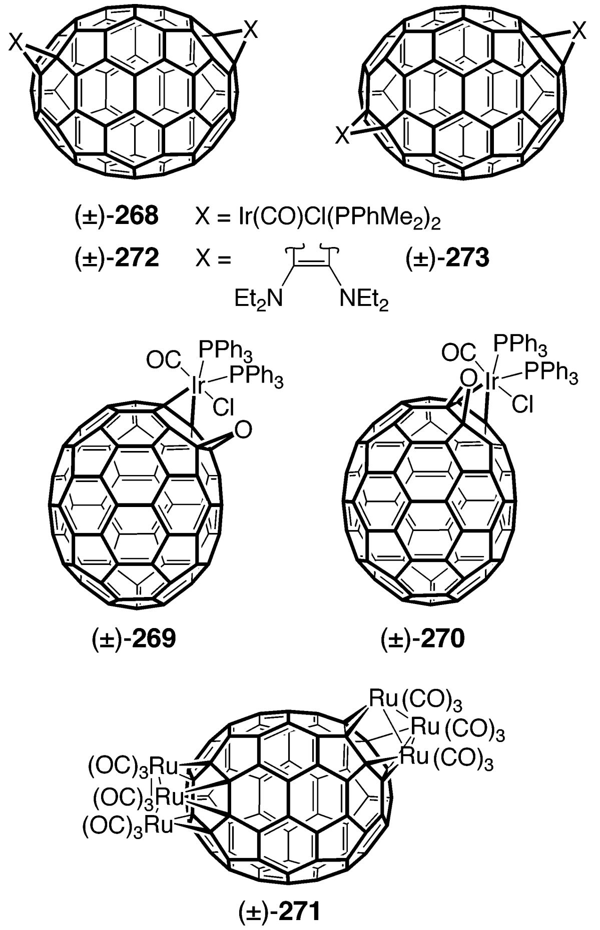


Figure 49. Transition metal complexes of C_{70} and biscyclobuta[70]fullerenes with chiral addition patterns.

5.9. Transition Metal Complexes of C_{70}

Transition metal complexes with fullerenes as ligands[654] typically show reversible, thermodynamically controlled association. A high selectivity for η^2-complexation by Ir and Pt at the most curved polar 6−6 bonds is encountered in mono-[655,656] and multiadducts of C_{70}.[657−659] Accordingly, C_2-symmetric "two o'clock" adduct (±)-**268** (Figure 49) was obtained as a crystalline bis-adduct from the reaction of C_{70} with [Ir(CO)Cl(PPhMe$_2$)$_2$].[657] The photochemical reaction of C_{70} with Mo(CO)$_3$ and 1,2-bis(diphenylphosphino)benzene (dppb) in chlorobenzene at room temperature yielded, besides a mixture of stereoisomeric mono-adducts, a single bis-adduct isomer *mer*-[{Mo(CO)$_3$(dppb)}$_2$(μ-η^2:η^2-C_{70})]. The C_2-symmetric compound has the two metal atoms bonded to 6−6 bonds near the two poles of the fullerene, but in the absence of an X-ray crystal structure, the addition pattern ("two o'clock" or "five o'clock") remains unelucidated.[660] The same accounts for the corresponding tungsten (*mer*-[{W(CO)$_3$(dppf)}$_2$(μ-η^2:η^2-C_{70})][661] [dppf = 1,1′-bis(diphenylphosphino)ferrocene]) and chromium (*mer*-[{Cr(CO)$_3$(dppb)}$_2$(μ-η^2:η^2-C_{70})])[660] complexes, the latter being the first organochromium derivative of [70]fullerene.

Overlaying a solution of epoxy[70]fullerene isomers oxireno[2′,3′:7,22]- (**242**, Scheme 20) and oxireno[2′,3′:8,25](C_{70}-D_{5h})[5,6]fullerene (**241**, Scheme 20)[646,647] in benzene with a solution of [Ir(CO)Cl(PPh$_3$)$_2$] in chloroform afforded the regioisomeric [Ir(CO)Cl(PPh$_3$)$_2$(η^2-C_{70}O)] complexes (±)-**269** and (±)-**270** (Figure 49), respectively.[648] In both structures, the transition metal and the epoxy bridge are located within the same six-membered ring, which abuts on the polar pentagon, an arrangement that leads to an inherently chiral functionalization pattern in (±)-**269** and a noninherently chiral functionalization pattern in (±)-**270**.[648]

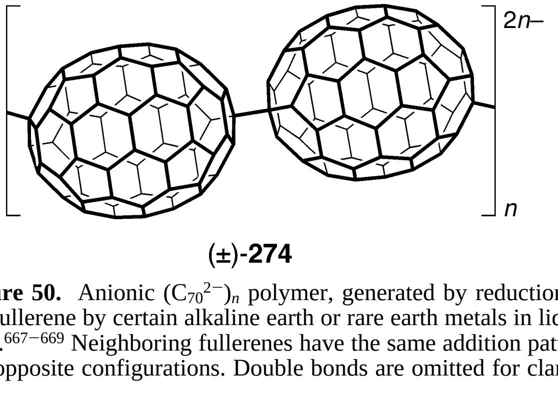
[$Ru_3(CO)_9$] clusters bind in a μ_3-η^2:η^2:η^2-fashion to arenes, C_{60},[662] and C_{70}.[659] In the latter case, they add preferentially to the near-polar hexagon, which displays the most marked bond alternation and includes the most pyramidalized C-atoms.[659] Addition of two [$Ru_3(CO)_9$] clusters at opposite poles of C_{70} afforded the chiral bis-adduct [$\{Ru_3(CO)_9\}_2$-(μ_6-η^2:η^2:η^2:η^2:η^2:η^2-C_{70})] for which three constitutional isomers (one of C_{2v}-symmetry and two of C_2-symmetry) are conceivable, similar to the "twelve o'clock", "two o'clock", and "five o'clock" addition patterns (cf. section 5.6). Of the three isomers formed, the major one corresponds to (±)-**271** (Figure 49) as shown by X-ray crystallographic analysis.[659]

5.10. Biscyclobuta[70]fullerenes

Zhang and Foote reported the thermal [2 + 2] cycloaddition between electron-rich bis(diethylamino)acetylene and C_{70}.[663] Double addition yielded two products, tentatively assigned as "two o'clock" and "five o'clock" regioisomers (±)-**272** and (±)-**273** (Figure 49). The "twelve o'clock" isomer was not observed, which points at a higher selectivity as compared with the Bingel reaction (cf. section 5.6). Self-sensitized photo-oxygenation of a mixture of (±)-**272** and (±)-**273**, molecules that include both a photosensitizer moiety (= tetrahydrofullerene)[664] and an easily photo-oxidizable group (= enediamine), afforded the "two o'clock" tetrakis-(carboxamide).[663]

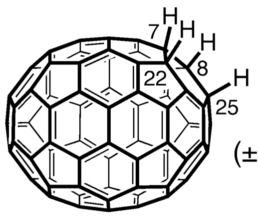
5.11. Polymeric Di- and Trianions of C_{70}

Unlike the pressure treatment of polycrystalline C_{70} at 1 GPa and 200 °C, which, by [2 + 2] cycloaddition between the C(8)−C(25) bonds, led to the C_{2h}-symmetric dimer cyclobuta[1″,2″:8,25;3″,4″:8′,25′]di(C_{70}-D_{5h})[5,6]-fullerene[665,666] (for a more complete picture of the dimerization of C_{70}, see section 7.2 and Figure 70; for the numbering of C_{70}, see Figure 3), the reduction of the fullerene with alkaline earth (Ca, Sr, Ba) or rare earth (Eu, Yb) metals in liquid ammonia afforded the first linear $(C_{70}^{2-})_n$ polymer.[667,668] For all metal ions under investigation, the fulleride substructure is the same, as exemplified by the X-ray crystal structures of $[Ba(NH_3)_9]C_{70}\cdot 7NH_3$ [667] or $[Sr(NH_3)_8]C_{70}\cdot 3NH_3$ in which all cage atoms could be refined.[668] The point symmetry of the fullerene units in the linear, polymeric fulleride chains ((±)-**274**, Figure 50) is reduced from D_{5h} (neutral C_{70}) to C_2, and the spheroids are interconnected by single bonds through atoms C(24) and C(35), which are located at opposite poles. This leads to a functionalization pattern with a geometry resembling the "two o'clock" arrangement, and the fullerene cages in the polymer chain show alternating configurations in such a way that the macromolecule can be considered as *meso* compound. A similar structure is found in the trianionic $(C_{70}^{3-})_n$ fulleride chains of $[Sr(NH_3)_8]_3(C_{70})_2\cdot 19NH_3$, obtained from the reduction of C_{70} with strontium in a 2:3 ratio.[669] It should also be mentioned that the dimeric $(C_{70}^{-})_2$ with two monofunctionalized C_{70} cages interconnected through atoms C(24) and C(24′) is achiral.[670]

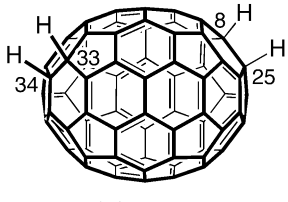


(±)-**274**

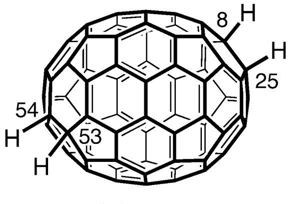
Figure 50. Anionic $(C_{70}^{2-})_n$ polymer, generated by reduction of the fullerene by certain alkaline earth or rare earth metals in liquid NH_3.[667−669] Neighboring fullerenes have the same addition pattern but opposite configurations. Double bonds are omitted for clarity.



(±)-**275**



(±)-**276**



(±)-**277**

Figure 51. Three tetrahydro[70]fullerenes with an inherently chiral addition pattern.

5.12. Hydro[70]fullerenes

Two C_s-symmetric $C_{70}H_2$ isomers out of 143 conceivable structures[671] have been isolated and characterized, that is, 8,25-dihydro(C_{70}-D_{5h})[5,6]fullerene and 7,22-dihydro(C_{70}-D_{5h})[5,6]fullerene (for the numbering of C_{70}, see Figure 3).[518,672,673]

Several chiral hydro[70]fullerene structures occur, on the other hand, among the $C_{70}H_4$ isomers. Of the two constitutional tetrahydro[70]fullerenes obtained in the reduction of C_{70} with diimide, one is C_s-symmetric (8,23,24,25-tetrahydro-(C_{70}-D_{5h})[5,6]fullerene) and the other one C_1-symmetric ((±)-7,8,22,25-tetrahydro(C_{70}-D_{5h})[5,6]fullerene, (±)-**275**, Figure 51).[518]

Reduction of C_{70} with Zn(Cu) in the presence of a proton source[512] gives completely different results. Among the products, a major and a minor $C_{70}H_4$ isomer were isolated and assigned by ^1H-coupled ^{13}C NMR spectroscopy as (±)-8,25,33,34-tetrahydro(C_{70}-D_{5h})[5,6]fullerene ("two o'clock" isomer (±)-**276**) and (±)-8,25,53,54-tetrahydro(C_{70}-D_{5h})[5,6]-fullerene ("five o'clock" isomer (±)-**277**), respectively.[511,673] The difference in the product composition as compared with diimide reduction was explained by the preferred charge distribution in the intermediate fulleride ions, which are protonated irreversibly under kinetic control.[673]

Another manifold of the Zn(Cu) reduction leads to a higher degree of hydrogenation and completely different functionalization patterns in C_s-symmetric $C_{70}H_8$ (isomorphous with $C_{70}Ph_8$ [674] and $C_{70}(OO^tBu)_8$ (**278**, see Figure 55[675])[511,673] and in the major C_s-symmetric isomer of $C_{70}H_{10}$ (isomorphous with $C_{70}Cl_{10}$,[630] cf. section 5.13),[676] both of which have the hydrogen atoms added in a zigzag fashion around the equator of C_{70} with the addition pattern of the former being a substructure of the latter. The functionalization of the

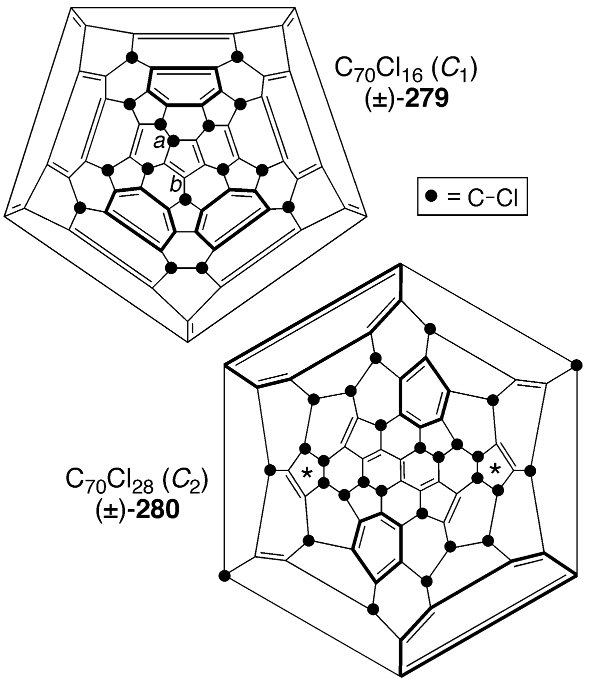


Figure 52. Chiral polychloro[70]fullerenes. The upper left panel shows the C_1-symmetric isomer of $C_{70}Cl_{16}$ ((±)-**279**).[679] It is related to a known C_s-symmetric isomer by formal shift of one Cl-atom from position *a* to position *b* within the polar pentagon. The lower right panel shows the C_2-symmetric isomer of $C_{70}Cl_{28}$ ((±)-**280**).[680] To emphasize the molecular symmetry, the unusual Schlegel-type representation of [70]fullerene is projected along the C_2 axis, which passes through one of the equatorial bonds (center of diagram) and the diametrically opposed hexagon. The polar pentagons of the fullerene are marked by asterisks. In both structures, benzenoid rings isolated from the remainder of the π-system are highlighted in bold.

equatorial belt manifests itself by the strong upfield ^3He NMR shift (−17.17 ppm for $C_{70}H_{10}$) of the corresponding ^3He incarceranes, which have been studied along with those of di- and tetrahydro[70]fullerenes.[281,524]

Various highly hydrogenated species such as $C_{70}H_{2n}$ ($n = 18-23$) have been prepared, but conclusive structural assignments are lacking so far.[18,512]

5.13. Halogeno[70]fullerenes

The only structurally characterized bromo[70]fullerene is $C_{70}Br_{10}$, prepared by bromination of C_{70} in neat Br_2, *o*-dichlorobenzene, or CS_2.[677] The C_s-symmetric molecule is isomorphous with $C_{70}Cl_{10}$,[630] as well as with $C_{70}H_{10}$,[676] $C_{70}Ph_{10}$,[674,678] and $C_{70}Me_{10}$.[629] These structures are characterized by 10 addends on the equatorial belt of C_{70} with a single 1,2- and nine 1,4-relationships between nearest neighbors. In fact, chloro- and bromofullerenes show a tendency to avoid 1,2-contacts, if possible, whereas such eclipsing arrangements are frequently found in fluorofullerenes with their typical contiguous addition patterns.[248]

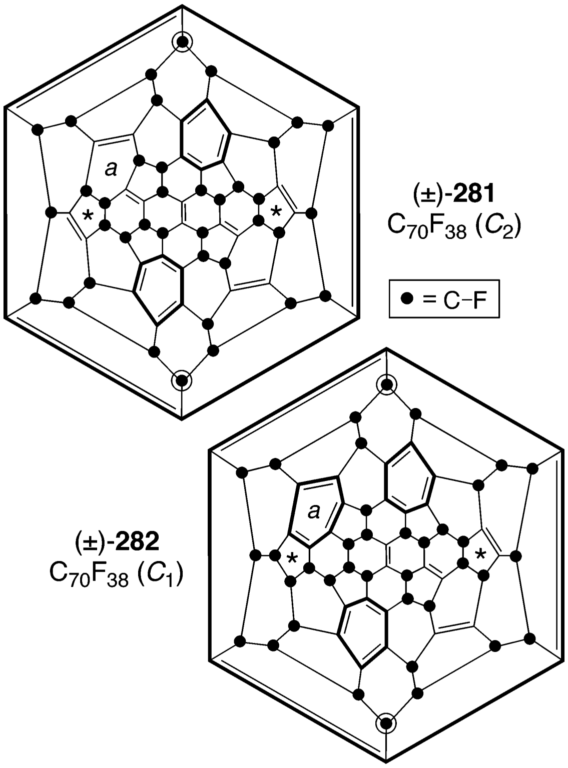
The next higher polychloro[70]fullerene, $C_{70}Cl_{16}$, was obtained in an attempt to brominate C_{70} with Br_2 in $TiCl_4$.[679] It is composed of two isomers, one having C_1-symmetry ((±)-**279**, Figure 52) and the other one C_s-symmetry (ratio 4:3), as revealed by X-ray crystallography. Their structures can be depicted as combining the equatorial, C_s-symmetric "Cl_{10}" belt of $C_{70}Cl_{10}$ (vide supra) with the polar, C_s-symmetric "Cl_6" cap of $C_{60}Cl_6$ (see section 6.9.1 and Figure 68). The two isomers of $C_{70}Cl_{16}$ differ in the relative orientation of "Cl_6" cap and "Cl_{10}" belt or, in other words, the position of a single Cl atom, which belongs to the polar pentagon. It occupies position *a* in the C_1-symmetric regioisomer (±)-**279** and position *b* in $C_{70}Cl_{16}$-C_s (Figure 52).

Chlorination of [70]fullerene with $SbCl_5$, VCl_4, or PCl_5 in sealed glass ampules at elevated temperature yields $C_{70}Cl_{28}$, which can also be obtained by treating $C_{70}Br_{10}$ with $SbCl_5$.[680] It displays crystallographically imposed C_2-symmetry, which is most probably the result of a superposition of two orientations of a C_1-symmetric isomer and two C_2-symmetric isomers (one of these, (±)-**280**, is shown in Figure 52). All three isomers include four benzenoid rings, which, in contrast to $C_{60}F_{18}$ [571] (**195**, Figure 40) or $C_{60}F_{36}$ [587] ((±)-**202**−(±)-**204**, Figure 38), exhibit perceptible deviation from planarity. Nevertheless, they are likely to counterbalance the considerable number of 1,2-interactions between contiguous chlorine atoms. The addition patterns of the three $C_{70}Cl_{28}$ isomers differ only in the positions of one or two chlorine atoms.

In comparison to bromo- and chloro[70]fullerenes, fluorinated derivatives have been obtained in an enormous variety. Forty-nine fluoro- and oxygenated fluoro[70]fullerenes have thus been isolated by HPLC from the fluorination of the fullerene with MnF_3 at 450 °C.[681] As demonstrated by 1D and, when quantities permitted, 2D ^{19}F NMR spectroscopy, many of these compounds have low symmetry, and conclusive structural elucidation must rely on X-ray crystallographic analysis. Crystal structures have recently been determined for a C_2- and a C_1-symmetric isomer of $C_{70}F_{38}$, isolated next to six other C_1-symmetric congeners and five C_1-symmetric $C_{70}F_{40}$ species. The main isomer, $C_{70}F_{38}$-C_2 ((±)-**281**, Figure 53), is distinguished by three benzenoid rings, in addition to seven isolated double bonds and, a first-time undisputed observation for C_{70}, two addends located exactly on the equator of the carbon spheroid.[682] The second, dominant member of the $C_{70}F_{38}$-C_1 family, (±)-**282**, displays four benzenoid substructures, four isolated double bonds, and again two fluorine atoms exactly on the equator.[683] The destabilization resulting from the latter feature is counterbalanced by the aromatic patches, which may also be an important characteristic of hydro[70]fullerenes $C_{70}H_{36}$ and $C_{70}H_{38}$.[533] Regioisomers (±)-**281** and (±)-**282** are related by three 1,3-shifts of fluorine atoms affecting one of the benzenoid rings. These shifts parallel the relationships among the *T*-, C_3-, and C_1-symmetric isomers of $C_{60}F_{36}$ (cf. section 4.11.1 and Figure 38). The $C_{70}F_{38}$ isomers do not contain the motif of $C_{70}Cl_{10}$, [630] which means that the two types of halogeno[70]fullerenes must be generated by different pathways.[682,683]

5.14. Trifluoromethylated [70]Fullerenes

Trifluoromethylation of C_{70} by thermolysis of CF_3CO_2Ag results in a vast range of adducts with up to 12 CF_3 groups.[684,685] No single derivative seems to be dominant, pointing at a kinetic control of the reaction. ^{19}F NMR spectroscopy showed most trifluoromethylated [70]fullerenes to have low or no symmetry. Furthermore, it was proposed that some of the obtained compounds have contiguous arrangements of CF_3 groups, which appear to add across 6−6 bonds as well as 6−5 bonds.[600,684] Trifluoromethylation of C_{70} with gaseous CF_3I at 470 °C appears to be more selective, yielding a single, C_1-symmetric $C_{70}(CF_3)_{10}$ isomer ((±)-**284**, Figure 54) as the main product.[603] Whereas its structure could not be definitively assigned by 1D- or 2D-COSY ^{19}F NMR spectroscopy, X-ray crystallography showed that it includes

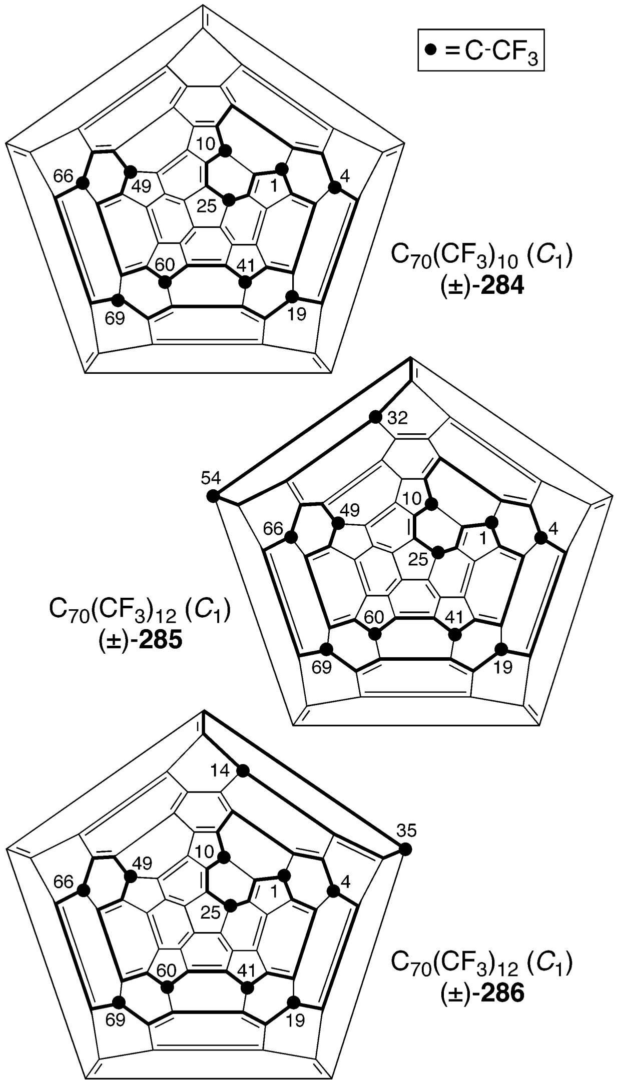


(±)-281
$C_{70}F_{38}$ (C_2)

(±)-282
$C_{70}F_{38}$ (C_1)

Figure 53. Chiral octatriacontafluoro[70]fullerenes. The C_1-symmetric isomer of $C_{70}F_{38}$ ((±)-**282**)[683] is related to the C_2-symmetric isomer (±)-**281**[682] by formal displacement of three F-atoms from ring *a*, thereby making it aromatic. To emphasize the molecular symmetry, the unusual Schlegel-type representation of [70]fullerene is projected along the C_2 axis of (±)-**281**, which passes through one of the equatorial bonds (center of diagram) and the diametrically opposed hexagon. The polar pentagons of the fullerene are marked by asterisks and the on-equator C−F groups are circled. In both structures, benzenoid rings isolated from the remainder of the π-system (three in (±)-**281**, four in (±)-**282**) are highlighted in bold.

a “*para-para-para-para-para-para-para-meta-para*”-functionalized ribbon of edge-sharing hexagons (also denoted as p^7mp).[686] Formal removal of two CF_3 groups from the terminal hexagon of the ribbon leads to a p^7 pattern in $C_{70}(CF_3)_8$-C_s.[687] Such addition patterns with trifluoromethyl groups arranged on 1,4- and 1,3-bisfunctionalized hexagons, which can be isolated but mostly form a ribbon through edge-sharing, appears to be typical for $C_{2n}(CF_3)_{2m}$ structures. The addition pattern of decakis-adduct (±)-**284** clearly differs from that of most other known $C_{70}X_{10}$ compounds prepared at relatively low temperature, for example, $C_{70}H_{10}$,[676] $C_{70}Cl_{10}$,[630] $C_{70}Br_{10}$,[677] $C_{70}Me_{10}$,[629] $C_{70}Ph_{10}$,[674,678] or $C_{70}Ph_9$-OH[688] ((±)-**283**, Figure 71), which are distinguished by a closed “p^9o” (o = *ortho*) loop. The high-temperature trifluoromethylation may, therefore, reveal aspects of thermodynamically vs kinetically controlled multiaddition reactions. A p^7mp pattern (vide supra) was also seen, next to an isolated 1,4-bisfunctionalized hexagon, in the X-ray crystal structures of two C_1-symmetric isomers of $C_{70}(CF_3)_{12}$ ((±)-**285** and (±)-**286**); it may represent a particularly stable feature in trifluoromethylated [70]fullerenes with more than eight addends.[689,690] Very recently, molecular structures have been determined by single-crystal X-ray crystallography for $C_{70}(CF_3)_{14}$, $C_{70}(CF_3)_{16}$,[691] and four isomers of $C_{70}(CF_3)_{18}$,[692] all prepared by reaction of C_{70} with CF_3I.



$C_{70}(CF_3)_{10}$ (C_1)
(±)-**284**

$C_{70}(CF_3)_{12}$ (C_1)
(±)-**285**

$C_{70}(CF_3)_{12}$ (C_1)
(±)-**286**

Figure 54. Schlegel diagrams of C_1-symmetric trifluoromethylated [70]fullerenes: 1,4,10,19,25,41,49,60,66,69-decakis(trifluoromethyl)-1,4,10,19,25,41,49,60,66,69-decahydro(C_{70}-D_{5h})[5,6]fullerene ((±)-**284**);[603] 1,4,10,19,25,32,41,49,54,60,66,69-dodecakis(trifluoromethyl)-1,4,10,19,25,32,41,49,54,60,66,69-dodecahydro(C_{70}-D_{5h})-[5,6]fullerene ((±)-**285**); and 1,4,10,14,19,25,35,41,49,60,66,69-dodecakis(trifluoromethyl)-1,4,10,14,19,25,35,41,49,60,66,69-dodecahydro(C_{70}-D_{5h})[5,6]fullerene ((±)-**286**).[689,690] Ribbons of contiguous functionalized hexagons as well as isolated such features are marked in bold.

5.15. Addition of *tert*-Butylperoxy Radicals to C_{70}

Five regioisomeric mono-adducts can be generated by attack of a radical to each of the five types of C-atoms of C_{70}. If a radical adds to C(1) or C(7), which do not lie on a mirror plane of the fullerene, the resulting $RC_{70}^\bullet$ species is C_1-symmetric (for the numbering of C_{70}, see Figure 3). By means of ESR spectroscopy, three regioisomers were detected in the addition of alkyl, trichloromethyl,[693,694] methylsulfanyl,[695] or dimethoxyphosphoryl,[693] up to four for hydro, aryl, or pentafluoroethyl,[694,696−698] and all five for methoxy[695] and trifluoromethyl[698] radicals. Whereas the chiral adducts may be recognized spectroscopically by their symmetry, exact structural assignments are difficult.

Well-defined products, on the other hand, have been obtained by Gan and co-workers in a systematic study on the multiaddition of *tert*-butylperoxy radicals to C_{70} (for related reactions with C_{60}, see section 6.9.3).[675,699] Reaction

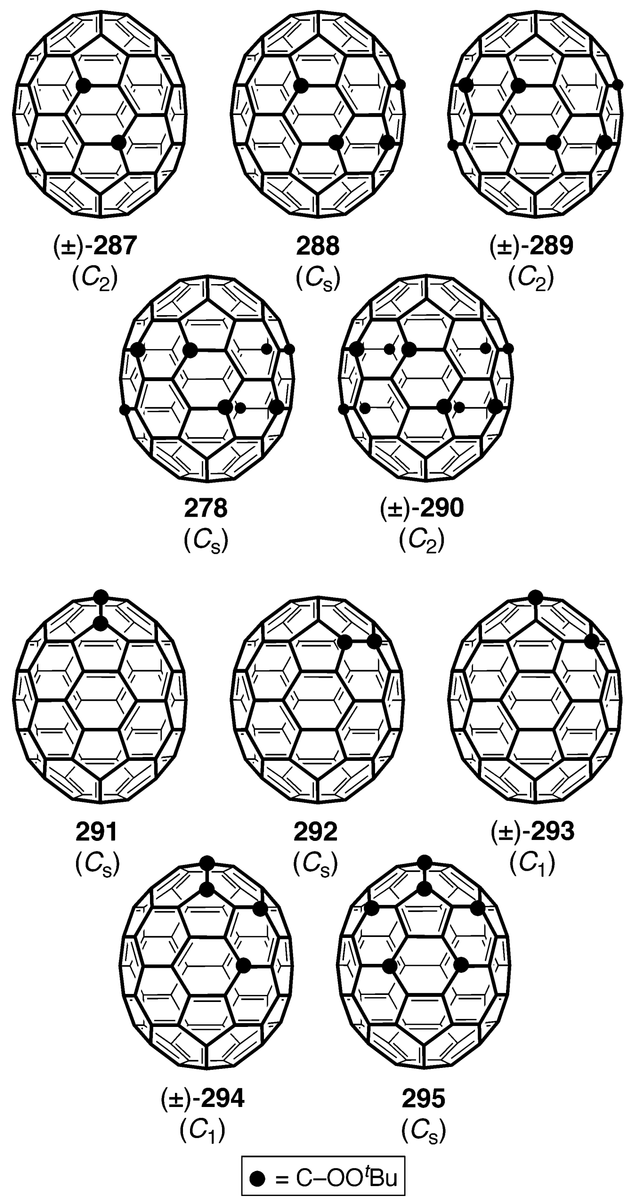
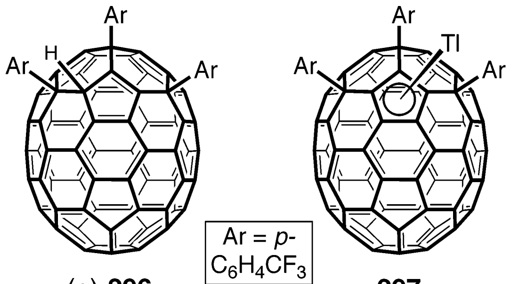


Figure 55. Two series of five characterized products, formed via two manifolds in the addition of *tert*-butylperoxy radicals to C_{70}.[675,699]



(±)-**296** **297**

Figure 56. Incomplete "cyclopentadiene addition mode" observed in the reaction of C_{70} with ArMgBr/CuBr·SMe$_2$, followed by protonation (→ (±)-**296**),[702] and complex **297** prepared by deprotonation of (±)-**296** with TlOEt.[704]

of a solution of the fullerene in benzene with an excess of *tert*-butylhydroperoxide in the presence of catalytic amounts of $(NH_4)_2Ce(NO_3)_6$ (CAN)[675] afforded a mixture of adducts $C_{70}(OO^tBu)_{2n}$ ($n = 1-5$), some of which were composed of several isomers. All of them were isolated and structurally assigned by a combination of NMR spectroscopy and chemical correlation experiments, which unveiled two formation manifolds.[675] The first one leads to derivatives with all addends located on an equatorial belt of [70]fullerene. They include $C_{70}(OO^tBu)_2$ (C_2-symmetric (±)-**287**, Figure 55), $C_{70}(OO^tBu)_4$ (C_s-symmetric **288**), $C_{70}(OO^tBu)_6$ (C_2-symmetric (±)-**289**), $C_{70}(OO^tBu)_8$ (C_s-symmetric **278**), and $C_{70}(OO^tBu)_{10}$ (C_2-symmetric (±)-**290**). The lower adducts are obviously intermediates on the way to $C_{70}(OO^tBu)_{10}$ because the addition pattern of the latter includes the others as substructures. Interestingly, $C_{70}(OO^tBu)_8$ (**278**) is isomorphous with $C_{70}Ph_8$,[674] and $C_{70}H_8$.[511,673] However, addition of two further residues takes a different course in the *tert*-butylperoxylation as compared with decahydrogenation,[676] -chlorination,[630] or -bromination.[677] In fact, the last two residues in the formation of C_s-symmetric $C_{70}H_{10}$ and $C_{70}Cl_{10}$ add in a 1,2-fashion across a near-equatorial 6−5 bond (cf. addition pattern of (±)-**283**, Figure 71), whereas the larger *tert*-butylperoxy radicals prefer transequatorial 1,4-addition. This leads to an unprecedented C_2-symmetric addition pattern with only 1,4-relationships between nearest neighbors in an equatorial zigzag ribbon of contiguous hexagons (p^9 ribbon). The second manifold is based on the "cyclopentadiene addition mode", which is well-known in the chemistry of C_{60} (cf. section 6.9). Interestingly however, the cyclopentadiene structure does not form at the pole of C_{70} but on its side. The products isolated and characterized in this series include $C_{70}(OO^tBu)_2$ (three regioisomers: C_s-symmetric **291**, Figure 55; C_s-symmetric **292**; and C_1-symmetric (±)-**293**), $C_{70}(OO^tBu)_4$ (C_1-symmetric (±)-**294**), and $C_{70}(OO^tBu)_6$ (C_s-symmetric **295**), the latter displaying the full "cyclopentadiene pattern".[675]

5.16. Arylcuprate Addition to C_{70}

An addition style that is formally similar to the above-described lateral "cyclopentadiene mode" (section 5.15) occurs in the reaction of C_{70} with aryl Grignard reagents in the presence of CuBr·SMe$_2$.[700] Indeed, whereas the according addition to C_{60} leads to the full "cyclopentadiene pattern" (see section 6.9.2),[700,701] the reaction with C_{70} stops at the tris-addition stage, and subsequent protonation affords C_1-symmetric adducts such as (±)-**296** (Figure 56).[702] A reason for the completely regioselective reaction not to proceed any further may be that the two C(sp^2) atoms expected to receive the fourth and the fifth addend are located in the relatively flat equatorial region, thus resisting rehybridization to C(sp^3) atoms.[703] Another notable feature of this reaction is the practically quantitative conversion, which is rather exceptional in fullerene chemistry.[704] Compound (±)-**296** is readily deprotonated with alkoxides to afford the corresponding metal complexes, for example, [K(η^5-$C_{70}Ar_3$)] or the deep red [Tl(η^5-$C_{70}Ar_3$)] (**297**). X-ray crystallographic analysis of the latter showed that the organometallic compound is distinguished by a thallium−(η^5-indenyl) substructure with the metal being equidistant from all three aryl groups and bonded to the pentagon flanked by the three sp^3-hybridized carbon atoms.[704] Also, the crystal structure of dark brown [Rh(η^5-$C_{70}Ph_3$)(η^2:η^2-cod)] (cod = cyclo-octa-1,5-diene), prepared by metathesis of [K(η^5-$C_{70}Ph_3$)] with [RhCl(cod)], evidences a great similarity between the considered substructure of the fullerene complex and [Rh(η^5-indene)-(cod)].[705]

6. C_{60} Derivatives with a Noninherently Chiral Functionalization Pattern

6.1. Mono- and Dimeric C(1),C(7)-Adducts of C_{60}

6.1.1. Anionic Approach

The introduction of bulky groups into C_{60} often occurs as intrahexagonal 1,4-addition with functionalization of positions C(1) and C(7) (for the numbering of C_{60}, see Figure 2).[15,18,256] If the addends are homomorphic and achiral, such a [60]fullerene derivative is C_s-symmetric. Structurally different groups, on the other hand, cannot be reflected into each other by a mirror plane, and the symmetry of such an adduct is reduced to C_1. Nonidentity of the addends is, therefore, a conditio sine qua non for chirality, and the corresponding addition pattern is termed "noninherently chiral". It is easily recognized with the substitution test delineated in Figure 1.

By addition of organolithium or Grignard reagents to C_{60}, followed by in-situ protonation, Hirsch et al. isolated isomerically pure 1,4-adducts with the general formula $RC_{60}H$.[706,707] On the other hand, by protonation of the isolated salt $Li(^{t}BuC_{60})\cdot 4CH_3CN$, Fagan et al. obtained the C_s-symmetric C(1),C(9)-isomer (1,2-adduct) as well as the C_1-symmetric C(1),C(7)-isomer (1,4-adduct (±)-**298**, Figure 57), the latter slowly rearranging to the thermodynamically more stable 1,2-adduct.[708−710] In fact, whereas 1,2-addition preserves the favorable π-electron system of C_{60} to a large extent, the generally lower thermodynamic stability of 1,4-adducts can be ascribed to the unavoidable introduction of an intrapentagonal double bond, entailing an energetic penalty of ~8.5 kcal mol^{-1}.[419,711] However, this unfavorable electronic effect can be counterbalanced by the lack of steric interactions that would exist between eclipsing vicinal addends, particularly if they are bulky. The 1,4-addition pattern was thus proposed for some of the products isolated from the reaction of buckminsterfullerene with sterically demanding silyl-lithium reagents, for example, $^{t}Bu_2(4\text{-}MeC_6H_4)SiLi$ or $^{t}Bu(4\text{-}MeC_6H_4)_2SiLi$, followed by quenching with ethanol.[421] A diagnostic feature of 1,4-adducts is a UV/vis band around 445 nm[633,710,712,713] contrasting with the characteristic absorption of 1,2-adducts at ~430 nm.[15,714]

Kitagawa, Takeuchi, and co-workers found that the reaction of $^{t}BuC_{60}^{-}$, in THF/MeCN, with stabilized, aromatic tropylium or cyclopropenylium ions led do immediate disappearance of the dark green color of the fullerenide ion, which was consumed under formation of covalent adducts (±)-**299**, (±)-**300**, and (±)-**301a/b** (four stereoisomers composed of two racemates).[632,635,715] In contrast to the rapid isomerization of 1-*tert*-butyl-1,7-dihydro(C_{60}-I_h)[5,6]fullerene ((±)-**298**), (±)-**299** does not rearrange, even at 75 °C in $CDCl_3$, to the C(1),C(9)-adduct. A notable feature of (±)-**299**, (±)-**300**,[634] and similar[633] systems is their partial dissociation in the dipolar aprotic solvent DMSO, giving greenish-yellow solutions of fullerenide and arenylium ions.[632,635,715] The unusual heterolytic bond cleavage in these reversibly dissociative systems appears to be facilitated not only by the formation of stabilized ions but also by steric repulsion between the bulky groups attached to the fullerene. Switching to the 1,2,3-tris(guaiazulen-3-yl)cylopropenylium ion with further delocalization and stabilization of the positive charge led to a completely dissociated pure hydrocarbon salt, which could be precipitated as a dark reddish-brown powder.[716]

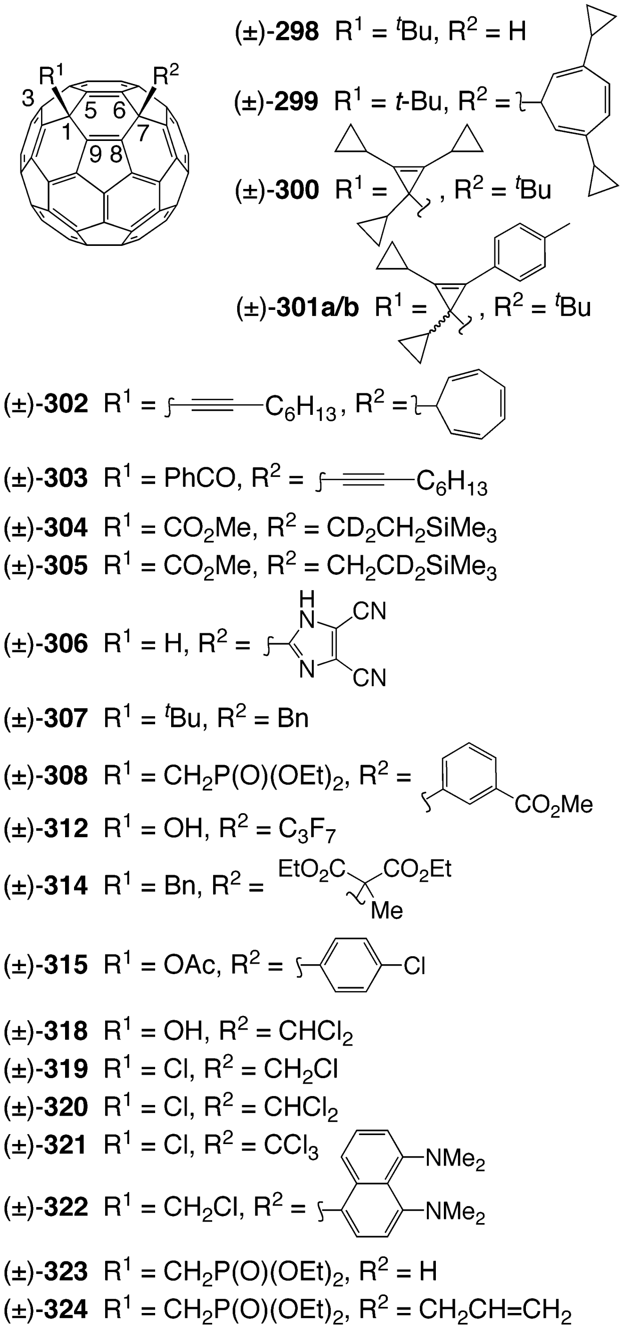


Figure 57. C_1-symmetric 1,4-adducts of C_{60} (addition of monovalent addends to cage atoms C(1) and C(7)), the simplest and most common derivatives with a noninherently chiral functionalization pattern.

The dependence of the addition mode (1,2- vs 1,4-) on both organic addends becomes nicely apparent when the above examples are compared with the reaction of the tropylium ion with $CH_3(CH_2)_5C{\equiv}C{-}C_{60}^{-}$, affording a mixture of 1,2- and 1,4-adducts ((±)-**302**).[717] Conversely, (±)-**303** was obtained as sole product by benzoylation of the same octynylfullerenide ion.[717]

Reaction of C_{60} with 1-methoxy-1-[1,1-dideuterio-2-(trimethylsilyl)ethoxy]carbene afforded a mixture of 1,4-adducts (±)-**304** and (±)-**305**, in addition to the corresponding 1,2-adducts, instead of the anticipated methanofullerene (the same result was obtained,[713] the necessary changes having been made, with the unlabeled carbene).[718] Complete scrambling of the CD_2 group in the products strongly insinuates the involvement of a silacyclopropyl cation and a (methoxycarbonyl)fullerenide as crucial intermediates.[718]

Addition to C_{60} of the electrophilic species generated by thermal dinitrogen extrusion from 2-diazo-4,5-dicyanoimidazole was completely selective in affording 1,4-adduct (±)-**306** with an aromatic heterocycle rather than a spiroanellated derivative combining a 2*H*-imidazole and a methano- or homofullerene moiety.[719]

Kinetic studies by Fukuzumi, Kadish, and co-workers suggest that the formation of fullerene adducts R_2C_{60} or $RC_{60}R'$ (e.g., (±)-**307**) by reaction of $C_{60}{}^{2-}$ with alkyl halides in acetonitrile occurs in two steps, starting with an electron transfer, which leads to the organofullerenide $RC_{60}{}^{-}$, followed by a nucleophilic substitution (S_N2) of the second halide molecule by $RC_{60}{}^{-}$.[710,720,721] The combination of fast SET (single electron transfer) and slower S_N2 reaction was exploited systematically by Cousseau and co-workers for the one-pot synthesis of 1,4-adducts $RC_{60}R'$ with two different addends (e.g., (±)-**308**).[722] Protonation of the intermediate $RC_{60}{}^{-}$ species, on the other hand, provides facile access to 1,2-adducts of type $RC_{60}H$. By deprotonation (KO^{t}Bu) and subsequent alkylation, these can again be transformed into 1,4-adducts $RC_{60}R'$.[722]

6.1.2. Radical Approach

As early as 1991, it was found that alkyl radicals react easily with buckminsterfullerene to give adducts R_nC_{60}.[723] A remarkable feature of the ESR signals observed for $RC_{60}{}^{\bullet}$ species was a dramatic and reversible increase in intensity with rising temperature.[610,724] Such a behavior is characteristic for an equilibrium between a radical and its dimer. An observed correlation between the position of the dimerization equilibrium and the steric requirement of the residue R suggested the interfullerene bond to be formed in close proximity to the addend. Of the three carbon atoms, C(9), C(7), and C(5) (for the numbering of C_{60}, see Figures 57 and 2), showing the highest spin density,[725] C(7) is the only one allowing bonding to another carbon cage on steric grounds, and structure **309a** (Figure 58) was proposed for the dimer ^{t}Bu$C_{60}C_{60}{}^t$Bu.[708,724]

As a consequence of their structure with two interconnected fullerene cages,[97] each of which displays a noninherently chiral addition pattern, 7,7′-disubstituted 7*H*,7′*H*-1,1′-bi(C_{60}-I_h)[5,6]fullerenes can give rise to three stereoisomers, namely, a *d*,*l*-pair of enantiomers (e.g., (±)-**309b**) containing either two ^{f,s}*A*- or two ^{f,s}*C*-configured spheroids and a *meso* form (e.g., **309a**) combining an ^{f,s}*A*- and an ^{f,s}*C*-configured cage.[4,20] Although many of the early reports on 7,7′-disubstituted 7*H*,7′*H*-1,1′-bi(C_{60}-I_h)[5,6]fullerenes do not include any information on the obtained stereoisomer(s), both the *meso*- and the *d*,*l*-form have been observed in a number of cases although no separation has been achieved so far. Despite the apparent similarity of the two diastereoisomeric forms, the chiral isomers (±)-**310b** have been calculated (PM3) to be more stable than their *meso* counterpart **310a** by 1.42 kcal mol^{-1}.[726] As to the preferred conformation resulting from rotation around the interfullerene pivot bond, molecular mechanics calculations predicted those with *syn*-oriented addends to be more stable than those with an *anti* arrangement.[727] Based on data from dilution experiments, the interfullerene bond enthalpy in (^{t}BuC_{60})$_2$ (**309a**/(±)-**309b**) was estimated to be 22.1 kcal mol^{-1}.[724] Comparison of the integrated ESR signal intensity for **310a**/(±)-**310b** (*o*-dichlorobenzene solution) to that of a standard reference allowed the determination of the dissociation constant for the equilibrium between dimer and monomer, and the corresponding free energy of dissociation Δ*G* at 300 K was estimated to be 13 kcal mol^{-1}. The temperature dependence of the ESR signal intensity in the temperature range between 380 and 420 K afforded an enthalpy of dissociation $\Delta H° = 17.0$ kcal mol^{-1}.[726]

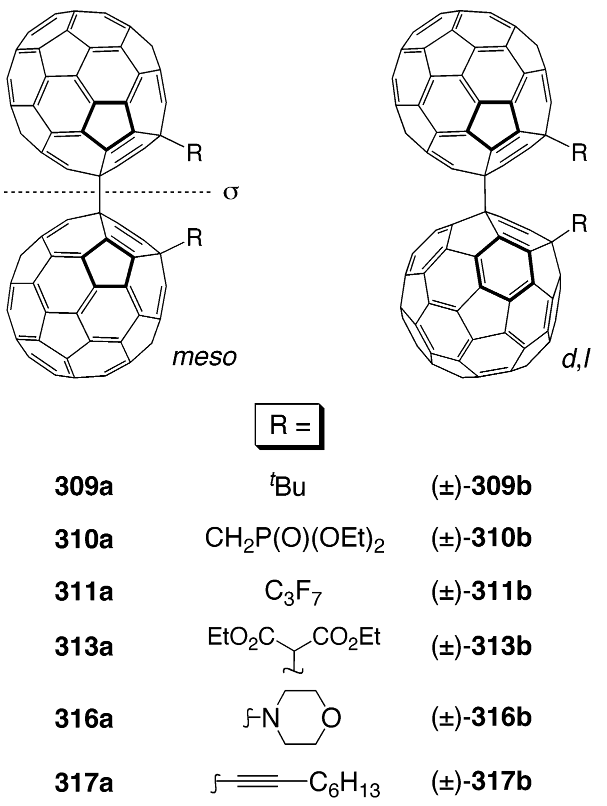


Figure 58. "Dimeric" 1,4-adducts of C_{60} (7,7′-disubstituted 7*H*,7′*H*-1,1′-bi(C_{60}-I_h)[5,6]fullerenes) in which each spheroid is distinguished by a noninherently chiral addition pattern. Each of these derivatives can in principle occur in the form of three stereoisomers: whereas the combination of homochiral moieties can lead to a *d*,*l*-pair of enantiomers, that of heterochiral cages gives rise to a *meso* form. The highlighted polygons (bold) help to recognize the presence (*meso* form) or the absence (*d*,*l*-pair) of a mirror plane.

7,7′-Bis(perfluoroalkyl)-7*H*,7′*H*-1,1′-bi(C_{60}-I_h)[5,6]fullerenes containing trifluoromethyl,[712,728] pentafluoroethyl,[610] or heptafluoropropyl (**311a**/(±)-**311b**)[712,728] addends were obtained by reaction of C_{60} with perfluoroalkanoyl peroxides as a byproduct in the synthesis of monomeric fullerenol (±)-**312** (Figure 57). Bifullerenes with perfluoroalkyl side chains can also be prepared by photoirradiation of a solution of C_{60} and a perfluoroalkyl iodide,[610] possibly in the presence of a hexa-alkyldistannane.[729] Treatment of solutions of bifullerenes **309a**/(±)-**309b**[708] or **311a**/(±)-**311b**[728] (Figure 58) with Bu_3SnH afforded monomeric adducts $RC_{60}H$ by reduction of the $RC_{60}{}^{\bullet}$ species, which are in equilibrium with the starting dimers. Yoshida et al. have also isolated "mixed dumbbells" with different perfluoroalkyl side chains in the two fullerene moieties.[729] Such compounds can be formulated as two diastereoisomeric pairs of enantiomers, which may be considered as *erythro* and *threo* forms.

The propensity of $RC_{60}{}^{\bullet}$ intermediates to dimerize manifested itself also in the reaction between buckminsterfullerene and the radicals generated from activated methylene compounds by treatment with manganese(III) acetate dihydrate, studied by Wang and co-workers. Thus, when C_{60} was treated for 20 min with diethyl malonate and $Mn(OAc)_3{\cdot}2H_2O$ in refluxing chlorobenzene, *meso*-**313a** and (±)-**313b** were obtained in a 1.7:1 ratio.[426] Extension of the reaction time to 1 h afforded a monomeric, C_s-symmetric [60]fullerene derivative with two malonate residues attached to C(1) and C(7). This compound is also formed, next to C_{60}, by simple heating of a solution of the bifullerene mixture **313a**/(±)-**313b**, an observation that suggests a disproportionation of the monomeric $(EtO_2C)_2CC_{60}^{\bullet}$, which is in equilibrium with the bifullerene. Treatment of C_{60} with bromomalonate and manganese(III) acetate, on the other hand, afforded (±)-**120** and (±)-**121** (Figure 31), and the reaction with ethyl cyanoacetate or malononitrile gave the corresponding methano[60]fullerenes.[426] When [60]fullerene was reacted with diethyl 2-methylmalonate and $Mn(OAc)_3{\cdot}2H_2O$ in toluene (noninert solvent in the present case), (±)-**314** (Figure 57) was the main product.[730,731] Replacement of the unsubstituted malonate in the above reaction (solvent, chlorobenzene) by β-diketones or β-ketoesters led to intramolecular cyclization of the primary adduct under formation of substituted furano[60]fullerenes,[731] also obtained in reactions mediated by piperidine[732,733] or another base, for example, by Na_2CO_3 under high-speed vibration milling[332] conditions.[733] Oxidation of 1-aryl-1,9-dihydro(C_{60}-I_h)[5,6]fullerenes with $Mn(OAc)_3{\cdot}2H_2O$ in refluxing chlorobenzene affords a monomeric 1,4-adduct (e.g., (±)-**315**; Figure 57).[734] The $ArC_{60}H$ starting materials can be prepared by treatment of C_{60} with arylhydrazine hydrochlorides in the presence of oxygen, which seems to play a key role in the generation of aryl radicals from arylhydrazines. Combining this sequence in a two-step one-pot reaction makes fullerenyl acetate (±)-**315** directly accessible from C_{60}.

Reaction of C_{60} with an excess of morpholine under aerobic conditions afforded bifullerenes **316a**/(±)-**316b** as main products precipitating from a benzene solution containing, among others, a multiadduct with four morpholine residues and an epoxy bridge as a result of the so-called “cyclopentadiene” addition mode (cf. section 6.9).[735]

Radical dimerization under formation of 7,7′-disubstituted 7,7′-dihydro-1,1′-bi(C_{60}-I_h)[5,6]fullerenes occurs not only in reactions implying the addition of radicals to C_{60} but also upon oxidation of RC_{60}^- ions.[708] Thus, when $CH_3(CH_2)_5C{\equiv}C{-}C_{60}^-$ was oxidized with iodine in THF, an immediate color change from dark green to brown accompanied the formation of **317a**/(±)-**317b**.[717] Bifullerenes **310a**/(±)-**310b** were elegantly synthesized in a one-pot reaction starting from [60]fullerene, which was reduced to the dark red C_{60}^{2-} by treatment with NaSMe. Addition of an excess of diethyl iodomethylphosphonate made the solution turn dark green, indicating the formation of monoanionic $[(EtO)_2(O)PCH_2]C_{60}^-$. The bulkiness of the phosphonate group prevented further alkylation of the monoanion, which was transformed into the mixture **310a**/(±)-**310b** by treatment with iodine.[726] A single crystal, containing a disordered mixture of the *meso*- and *rac*-forms, provided the first X-ray crystal structure of such a singly bonded [60]fullerene dimer. It showed the interfullerene pivot bond to be longer (157.6(6) pm) than a typical $C(sp^3){-}C(sp^3)$ bond (154 pm).[726] Chemical reduction of **310a**/(±)-**310b** generated the $[(EtO)_2(O)PCH_2]C_{60}^-$ ion as a final reduction product, in accord with its irreversible CV. Photoexcitation of the bifullerene in the absence of an electron donor yielded free radicals $[(EtO)_2(O)PCH_2]C_{60}^{\bullet}$.[736]

7,7′-Disubstituted 7,7′-dihydro-1,1′-bi(C_{60}-I_h)[5,6]fullerenes were finally observed, besides the monomeric species, among the products isolated after addition of certain silyl-lithium reagents to C_{60} and subsequent quenching with ethanol.[421]

6.1.3. Cationic Approach

Well-defined fullerenols are convenient starting materials for the generation of fullerenylium ions RC_{60}^+ by dissolution in strong, non-oxidizing acids.[715] Treatment of (±)-**318** (Figure 57) with F_3CSO_3H thus gives stable, reddish-purple solutions of the corresponding cations.[737] In addition to the delocalization of the positive charge, the coordination of a Cl atom of the addend R to the cationic center (C(9) of the fullerene), suggested in the case of $Cl_2HC{-}C_{60}^+$ by its shielding (^{13}C NMR, 175.6 vs 211.8 ppm[738] for the trityl cation) and by J_{C-H} coupling constant analysis, seems to play a crucial role in the formation of chloroalkyl-fullerenylium ions. Quenching of acidic solutions of such cations with methanol led to the regioselective bonding of a methoxy group to form C_1-symmetric C(1),C(7)-adducts $RC_{60}OMe$.[737]

Monofunctionalized fullerenylium ions open up a general access route to 1,4-adducts of C_{60}. A second way to generate RC_{60}^+ species[715] consists of the addition of an electrophile to C_{60}. In the “simplest” case, the electrophile is the proton of a superacid with a nonnucleophilic conjugate base, as nicely shown by Reed and co-workers through preparation of $[HC_{60}]^+[CB_{11}H_6Cl_6]^-$ in which the carborane anion is exceptionally inert.[739] Controlled addition of carbon electrophiles was first achieved by $AlCl_3$-promoted reactions of C_{60} with the solvents CH_2Cl_2, $CHCl_3$, or CCl_4, affording (±)-**319**, (±)-**320**, and (±)-**321**, respectively.[737] Whereas (±)-**320** and (±)-**321** were obtained as pure regioisomers, the smaller chloromethyl addend afforded about equal amounts of (±)-**319** and the corresponding 1,2-adduct.[636] The importance of the stabilizing interaction between the chlorine atoms of the halomethyl addends and the neighboring cationic center of the fullerenylium ion is evidenced by the unsuccessful addition of ^tBuCl, ^iPrCl, or MeI under similar conditions.[715] Thermodynamic stabilities of RC_{60}^+ ions were determined based on the activation free energies of the S_N1-solvolysis of (±)-**319**−(±)-**321** in a 1:9 mixture of highly ionizing 2,2,2-trifluoroethanol and anisole, in which the fullerene derivatives are moderately soluble. Whereas NMR studies of (±)-**320** have shown that most of the positive charge of the fullerenylium ions is located on cage atom C(9), the S_N1 solvolysis afforded only 1-chloroalkyl-7-(1,1,1-trifluoroethoxy)- and 1-chloroalkyl-7-(4-methoxyphenyl)-1,7-dihydro(C_{60}-I_h)[5,6]fullerenes as products, probably for steric reasons. The kinetic studies indicated that the stability of RC_{60}^+ is similar to that of the *tert*-butyl cation, a rather surprising fact in light of the electronegative nature of [60]fullerene.[636] It should also be mentioned that chloride (±)-**320** is readily hydrolyzed to fullerenol (±)-**318**.[737]

1-Chloro-7-chloroalkyl-1,7-dihydro(C_{60}-I_h)[5,6]fullerenes (±)-**319**−(±)-**321** were found to undergo nucleophilic substitution with the proton sponge 1,8-bis(dimethylamino)naphthalene under formation, for example, of (±)-**322**.[740] An $S_{RN}1$ mechanism, initiated by a single electron transfer (SET) from the electron-rich proton sponge to fullerene derivatives (±)-**319**−(±)-**321** was proposed for this reaction on grounds of the enhanced rates as compared to the S_N1 reaction of the same chlorides with anisole. The involvement of free radicals in the reaction was further corroborated by the formation of minor amounts of bifullerenes $RC_{60}-C_{60}R$.[740] The electronic structure and charge-transfer properties of dyad (±)-**322**, in which donor and acceptor are directly connected, were studied in detail.[741,742]

Komatsu and co-workers recently discovered a third access door to fullerenylium ions (RC_{60}^+) from 1-substituted 1,9-dihydro(C_{60}-I_h)[5,6]fullerenes ($RC_{60}H$) such as (±)-**323**.[743] Addition of the latter to H_2SO_4, under aerobic conditions, immediately made the solution turn reddish-purple, which is the characteristic color[715] of monofunctionalized fullerenylium ions. Alternatively, the cation was generated from bifullerene **310a**/(±)-**310b** (Figure 58) by the same treatment. The ^{13}C NMR shift of the cationic center C(9) (174.67 ppm vs 175.6 ppm for $Cl_2HC-C_{60}^+$), in combination with an observed coupling of C(9) with phosphorus indicated an intramolecular stabilizing interaction with the lone pair of a protonated phosphoryl O-atom, in the assumed species $(EtO)_2(OH)P^+CH_2-C_{60}^+$.[743] The mechanism proposed for the generation of this species, which requires the presence of an oxidizing acid, starts with removal of one electron from (±)-**323** (Figure 57) to give the radical cation (±)-$\mathbf{323}^{\bullet+}$, followed by proton release from the fullerene cage under formation of fullerenyl radical $(EtO)_2(O)PCH_2-C_{60}^\bullet$, which is supposed to be in equilibrium with bifullerenes **310a**/(±)-**310b** (Figure 58). Further one-electron oxidation of $(EtO)_2(O)PCH_2-C_{60}^\bullet$ should finally lead to the fullerenylium ion, which can be generated alternatively, in CH_2Cl_2, by oxidation of monomeric **323** or the more reactive dimeric **310a**/(±)-**310b** with a triarylammoniumyl species such as $(2,4\text{-}Br_2C_6H_3)_3N^{\bullet+}SbF_6^-(HSbF_6)_{0.5}$. Quenching of the fullerenylium cation with allyltrimethylsilane, 1,1,1-trifluoroethanol, or benzene afforded (±)-**324** (Figure 57) and the corresponding trifluoroethoxy or phenyl derivatives, respectively.[743]

6.2. Equatorial Bis-Adducts with a Noninherently Chiral Functionalization Pattern

Nishimura and co-workers investigated the regioselectivity of the Diels−Alder addition to C_{60} of two *o*-quinodimethane entities that were either singly or doubly interconnected by tethers of various length (see also section 4.3.3).[350] For the simple pentamethylene and 3-oxapentane-1,5-diyl tethers, *e* bis-adducts (±)-**91**[389,390] and (±)-**92**[395] (Figure 27) were obtained as the only and the main product, respectively. Their chirality is associated with a noninherently chiral addition pattern originating from the unsymmetric substitution of the e_{edge} addend, which makes the corresponding points of attachment on the fullerene heterotopic. In the doubly tethered series, only the larger *o*-quinodimethanes based on the dibenzo[24]crown-8 and dibenzo[30]crown-10 ethers were flexible enough to afford small amounts of *e* bis-adducts (±)-**93** and (±)-**94** (Figure 27).[396] Again, the noninherently chiral functionalization pattern is related to the heterotopicity of the C-atoms of the e_{edge} bond, which is made plausible by their extra-cage connections to constitutionally different C-atoms of the e_{face} bond of the fullerene.

6.3. Bis-Adducts with *cis*-1, *cis*-2, and *trans*-4 Addition Patterns

6.3.1. cis-1 Bis-Adducts with Untethered Addends

The addition patterns of *cis*-1, *cis*-2, and *trans*-4 bis-adducts are either achiral (C_s-symmetric) or, if the mirror symmetry of the basic pattern is broken by nonidentical residues in appropriate positions, noninherently chiral. Whereas noninherently chiral *cis*-2 and *trans*-4 addition patterns remain very rare (vide infra), the *cis*-1 addition pattern, which represents one of the electronically preferred arrangements for nonbulky addends,[273] occurs in a large diversity of chiral C_{60} derivatives. A particularity of the *cis*-1 pattern is the proximity of the four involved reaction sites, C(1), C(2), C(9), and C(12) (Figure 59), allowing for the introduction of short bridges between addends, which corresponds to a multiple anellation of the fullerene.

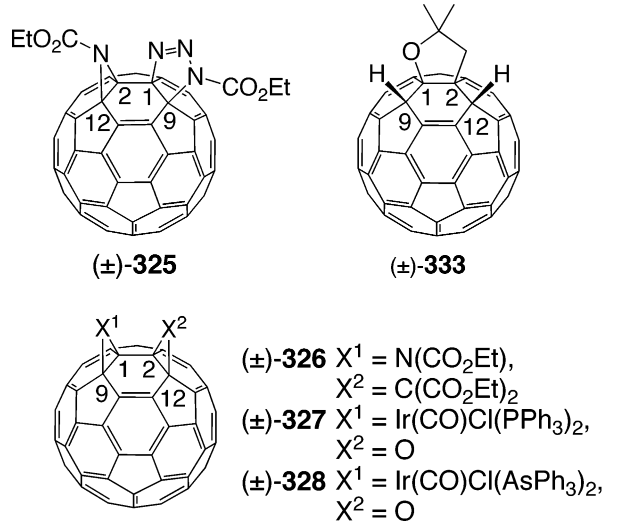


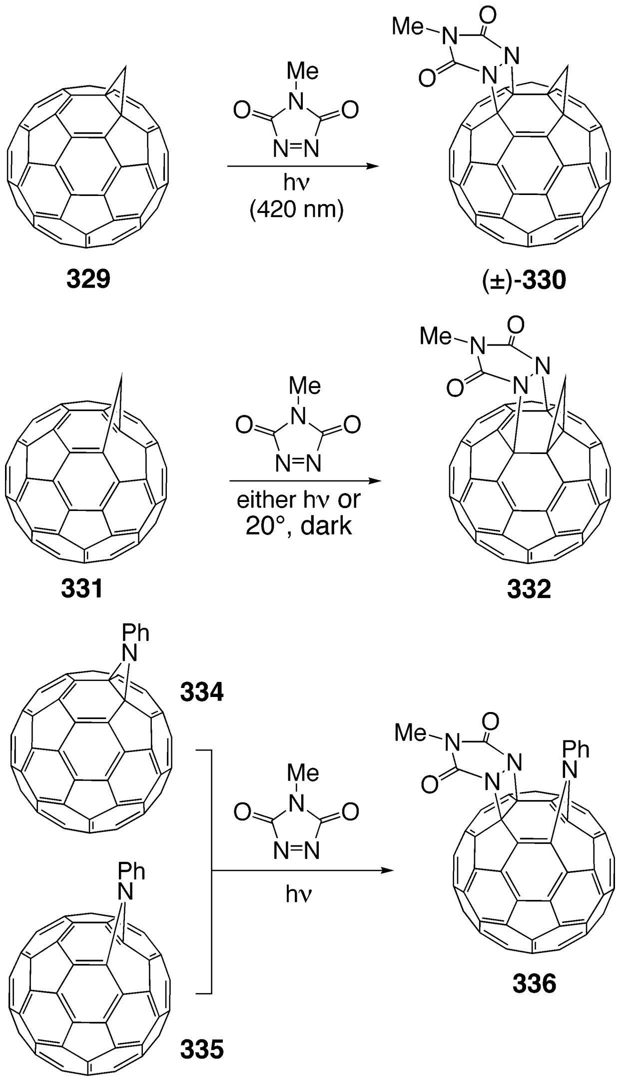
Figure 59. C_{60} derivatives with a noninherently chiral *cis*-1 addition pattern.

An early reported *cis*-1 bis-adduct of C_{60} with a noninherently chiral functionalization pattern was (±)-**325** (Figure 59), prepared by addition of ethyl azidoformate to ethyl 1′*H*-azireno[2′,3′:1,9](C_{60}-I_h)[5,6]fullerene-1′-carboxylate.[274] The lower steric demand of the *N*-monosubstituted aziridine ring, as compared with a methano bridge with two carboxylate substituents, allowed also the realization of a *cis*-1 addition pattern in the mixed azireno-cyclopropa-[60]fullerene (±)-**326**. Its *cis*-1 addition pattern was unambiguously proven by ^{13}C NMR spectroscopy using ^{15}N-labeled material,[273] and HPLC on the Whelk-O1 chiral stationary phase allowed the separation of its enantiomers.[271]

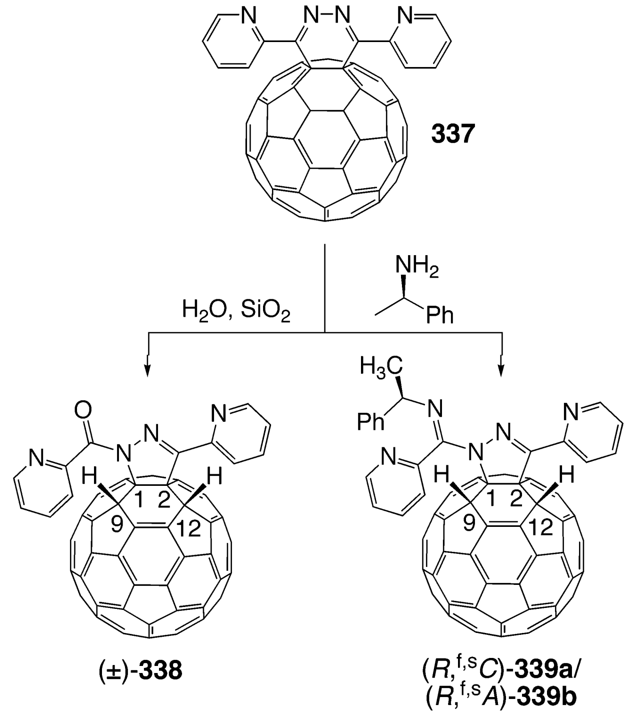
Noninherently chiral *cis*-1 addition patterns were also found in iridium complexes of $C_{60}O$.[446,448] Whereas some deoxygenation, presumably by PPh_3, appears to have occurred in $[Ir(CO)Cl(PPh_3)_2(\eta^2\text{-}C_{60}O)]\cdot 0.53CHCl_3\cdot 4.47C_6H_6$ ((±)-**327**, Figure 59),[446] the X-ray crystal structure of $[Ir(CO)Cl(AsPh_3)_2(\eta^2\text{-}C_{60}O)]\cdot 0.18CHCl_3\cdot 4.82C_6H_6$ ((±)-**328**), which contains an arsine instead of a phosphine ligand, shows a greater degree of disorder with respect to the position of the oxirane ring.[448] Nevertheless, the major oxygen occupancies indicate bonding of both addends to the same hexagon.

4-Methyl-1,2,4-triazoline-3,5-dione (NMTAD) is a potent dienophile in Diels−Alder reactions, but it reacts also with alkenes in a photoinduced [2 + 2] cycloaddition. The latter reaction mode occurs with C(1)−C(9)-functionalized adducts of C_{60} such as cyclopropafullerene (**329**, Scheme 25), under formation of C_1-symmetric *cis*-1 bis-adduct (±)-**330**.[744] Interestingly, homo[60]fullerene (**331**) behaves quite differently and undergoes either a photoinduced [2 + 2 + 2] cycloaddition or a thermal reaction with NMTAD, both leading to the unusual C_s-symmetric **332** in which the heterocycle bridges the functionalized hexagon of the C(1),C(2),C(9),C(12)-adduct in a 1,4-fashion, and the cyclopropane ring is anellated to a 6−5 bond of the fullerene (cf. structure (±)-**333**, Figure 59). Yet another reaction course

Scheme 25. Various Products Resulting from Photochemical or Thermal Addition of 4-Methyl-1,2,4-triazoline-3,5-dione (NMTAD) to Cyclopropa- (329), Homo- (331), Azireno- (334), and Azahomo[60]fullerene (335)[744]



Scheme 26. Chiral *cis*-1 Bis-Adducts Resulting from Reaction of Pyridazino[60]fullerene (337) with Water (→ (±)-338)[746,747] or (*R*)-2-Phenylethylamine (→ (*R*,^{f,s}*C*)-339a/ (*R*,^{f,s}*A*)-339b)[746] [a]



[a] Due to the combination of the (*R*)-configured stereogenic center originating from the amine and the newly generated, noninherently chiral fullerene addition pattern, pyrazolo[60]fullerene, (*R*,^{f,s}*C*)-**339a**/(*R*,^{f,s}*A*)-**339b**, is a mixture of two diastereoisomers.

is observed in the photocycloaddition of NMTAD to azirenofullerene **334** and azahomofullerene **335**, which both afford a C_s-symmetric azahomofullerene derivative **336**, again having a rather unusual functionalization pattern. Based on further experimental observations, Mattay and co-workers proposed the formation of **336** to occur by a [2 + 2] cycloaddition to a *cis*-1 double bond of **334**, followed and, in the case of **335**, also preceded by a rearrangement between azireno- and azahomofullerene structures.[744]

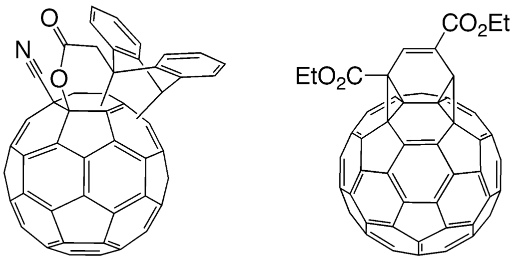
A C_1-symmetric C(1),C(2),C(9),C(12)-adduct with an oxolane ring fused to the 6−5 bond C(1)−C(2) ((±)-**333**, Figure 59) has been obtained as a minor product from the reaction between *tert*-butyl alcohol and $C_{60}^{\bullet+}$, generated by irradiation in the presence of the PET (photoinduced electron transfer)-sensitizer 2,4,6-triphenylpyrylium tetrafluoroborate.[745]

Another class of adducts with a similar addition pattern was reported independently by the groups of Miller, Balch,[746] and Komatsu.[747] In both cases, compounds were obtained from the same precursor **337** (Scheme 26), prepared by a combination of Diels−Alder addition and dinitrogen extrusion, starting from 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine and C_{60}, which were reacted either in refluxing toluene[746] or by high-speed vibration milling[332] of the solid compounds.[747] Pyridazinofullerene **337** is isolable but highly reactive toward nucleophiles bearing protic H-atoms. By reaction with water or with (*R*)-2-phenylethylamine, it thus underwent an unusual rearrangement affording (±)-**338**[746,747] or the diastereoisomeric mixture (*R*,^{f,s}*C*)-**339a**/(*R*,^{f,s}*A*)-**339b**,[746] respectively. In both cases, X-ray crystallography was necessary for complete structural elucidation including the position of the fullerene-bonded hydrogen atoms, in particular.

6.3.2. cis-1 Bis-Adducts as Multianellated [60]Fullerenes

In a systematic study, Prato and co-workers examined the regioselectivity of the intramolecular attack of azomethine ylides tethered through oligomethylene chains $(CH_2)_n$ (n = 3−5) to a [60]fullerene-fused isoxazoline (see also section 4.3.2).[387,388] The combination of C_{2v}-symmetric pyrrolidine and C_s-symmetric isoxazoline rings leads to a high number of conceivable regioisomeric *cis* type bis-adducts; with the tri- and tetramethylene tethers, the macrocyclization reaction was highly selective, affording *cis*-1 bis-adducts (±)-**82** and (±)-**83** (Scheme 3, pyrrolidine rings in both cases adjacent to isoxazoline-C), respectively, as sole isolated products. The longer pentamethylene spacer, on the other hand, afforded the alternative *cis*-1 isomer ((±)-**84**, pyrrolidine ring adjacent to isoxazoline-O) as main product.

Irngartinger and co-workers discovered that the refluxing, in dioxygen-free toluene, of a [60]fullerenyl ester derived from anthracen-9-ylacetic acid having a cyano group directly attached to the carbon spheroid resulted in an intramolecular Diels−Alder addition of the arene to the fullerene moiety. Of the two conceivable C_1-symmetric *cis*-1 and *cis*-2 bis-adducts, PM3 calculations favor the *cis*-1 structure (±)-**340** (Figure 60) by 3.6 kcal mol^{-1}.[748]



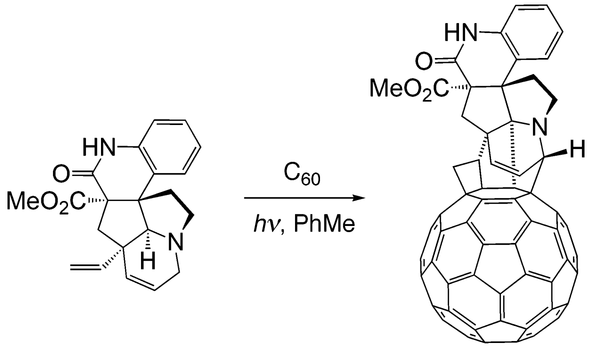
(±)-340 **(±)-341**

Figure 60. Multianellated C_{60} derivatives with a noninherently chiral *cis*-1 addition pattern.

The C_1-symmetric *cis*-1 bis-adduct (±)-**341** (Figure 60) has an additional short bridge between the addends and, similar to (±)-**340**, can be considered as a multianellated fullerene. It was obtained from the reaction between two molecules of ethyl propiolate and C_{60} in the presence of triphenylphosphane.[749] The noninherently chiral addition pattern of (±)-**341** is related to the head-to-tail connectivity of the two propiolate units.

Another multianellated C(1),C(2),C(9),C(12)-adduct of C_{60}, **342** (Scheme 27) including a noninherently chiral addition pattern as well as a multitude of stereogenic centers in the addend moiety, was obtained in a diastereoselective tandem reaction between the alkaloid scandine (**343**) and C_{60}.[750] The sequence includes a photoinduced addition of the tertiary amine subunit of the alkaloid and a [2 + 2] cycloaddition of the pendant vinyl group to the adjacent formal double bond of the fullerene. A second major product (1,2-mono-adduct of C_{60} with a regioisomeric substitution pattern on the amine moiety) was also isolated and characterized in the course of a more detailed investigation on the formation of fullerene-fused pyrrolidines by photoinduced cycloaddition between C_{60} and the tertiary amine substructures of a selection of alkaloids.[751]

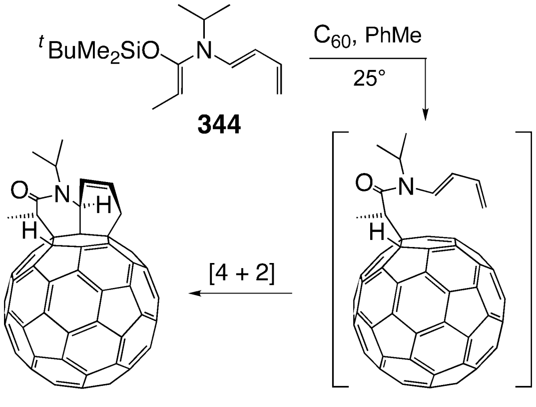
Scheme 27. Diastereoselective Tandem Addition of the Alkaloid Scandine to C_{60} [750,751]



343 **342**

Rubin, Neier, and co-workers investigated the stereoselective addition of a series of electron-rich *N*-buta-1,3-dienyl-*O*-silyl ketene *N*,*O*-acetals (e.g., **344**; Scheme 28) to C_{60}.[752] It takes place as a tandem sequence starting with a nucleophilic Michael-type addition, presumably involving a SET (single electron transfer), followed by a radical recombination. The second step consists of an intramolecular [4 + 2] cycloaddition leading to diastereoisomerically pure *cis*-1 adduct (±)-**345**. The interest in such compounds came from efforts aiming at the functionalization of contiguous reactive centers in C_{60}, possibly leading to a fully saturated, planar cyclohexane substructure prone to spontaneous ring opening in a retro-[2 + 2 + 2] fashion under creation of an orifice delimited by a 15-membered ring.

Scheme 28. Tandem Reaction Consisting of Michael-Type Addition and Diels−Alder Cycloaddition between C_{60} and an *N*-Buta-1,3-dienyl-*O*-silyl Ketene *N*,*O*-Acetal, 344[752] [a]

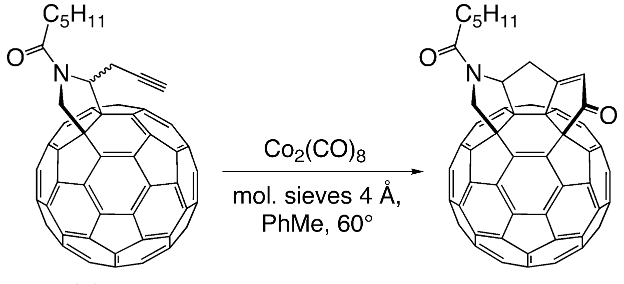


(±)-345

[a] The final product (±)-**345** can be deprotonated with a non-nucleophilic base and the carbon cage subsequently alkylated at the diametrically opposed intrahexagonal position. This transformation leads from a noninherently chiral to an inherently chiral addition pattern.

Martín and co-workers found that the 1,6-enyne systems of fullerene-fused pyrrolidines bearing a propargyl group at C(2) of the pyrrolidine ring (e.g., (±)-**346**; Scheme 29) undergo efficient and regioselective intramolecular Pauson−Khand reaction. The products are rigid [60]fullerene-fused cyclopentenones such as (±)-**347**, with three contiguous five-membered rings anellated in a *cis*-1 fashion to the same hexagon of the fullerene, thus generating a noninherently chiral addition pattern.[753,754] A *gem*-dipropargyl analogue of (±)-**346** even underwent double, albeit low-yielding, Pauson−Khand reaction under formation of a strained C_s-symmetric adduct with five contiguous pentagons anellated to the fullerene.[754]

Scheme 29. Intramolecular Pauson−Khand Reaction of Propargyl-Substituted Fullerene-Fused Pyrrole (±)-346, Affording Adduct (±)-347[753,754] with a Noninherently Chiral Functionalization Pattern Distinguished by the Anellation of Three Contiguous Five-Membered Rings to the Same Hexagon of the Fullerene



(±)-346 **(±)-347**

Furanodi[60]fullerene, $C_{120}O$,[755−757] was prepared by Krätschmer and co-workers in a solid-phase reaction between C_{60} and $C_{60}O$.[758] A byproduct of this reaction is $C_{120}O_2$, of which the authors isolated two HPLC fractions. One of them consisted of two closely related C_1-symmetric isomers, and structure (±)-**348** (Figure 61) with an epoxy bridge in *cis*-1

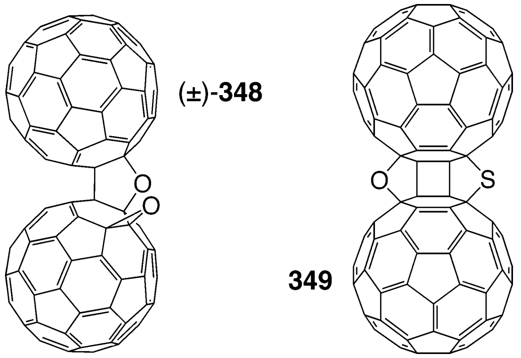


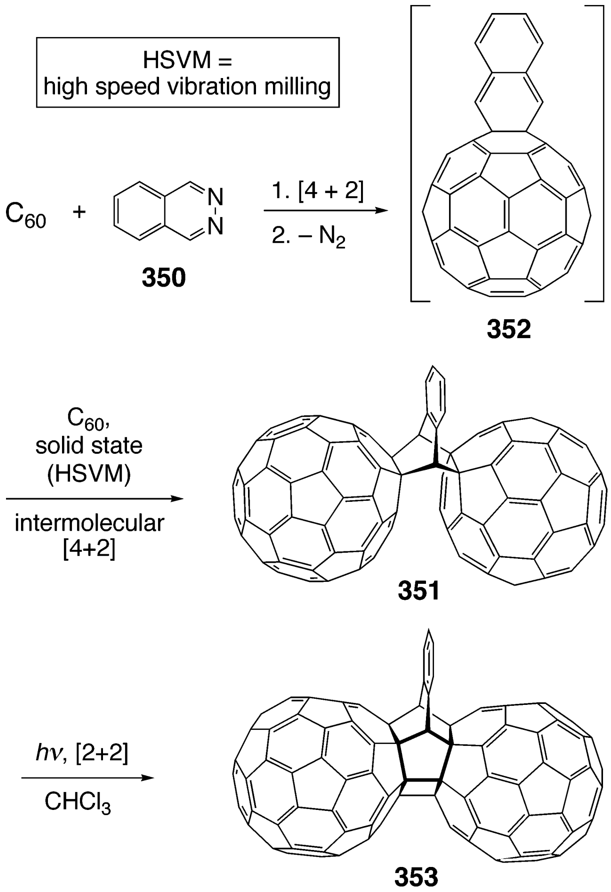
Figure 61. $C_{120}O_2$ ((±)-**348**)[758] and $C_{120}OS$ (**349**)[759] with one and two noninherently chiral *cis*-1 fullerene functionalization patterns, respectively. In **349**, the combination of enantiomorphic fullerene moieties leads on an achiral multianellated system.

position relative to the furano-fusion site in one of the fullerene moieties was proposed for the major component.[758] A constitutionally isomeric structure, having the epoxy bridge located at the remaining *cis*-1 site of the doubly anellated hexagon, was proposed for the minor component.

When $C_{120}O$ was heated with sulfur under Ar at 230 °C, the analytical data for the main product were consistent with C_s-symmetric **349**,[759] which is isomorphous with another C_{2v}-symmetric isomer of $C_{120}O_2$ [758,760] and the C_{2v}-symmetric hydrocarbon $C_{122}H_4$ (= $C_{120}(CH_2)_2$).[761,762] Although the C_{120}-OS molecule is achiral as a whole, the replacement of one oxygen bridge of $C_{120}O_2$-C_{2v} by a sulfur atom leads to a noninherently chiral *cis*-1 addition pattern in each carbon spheroid. The combination of two enantiomorphic such moieties results in the achiral structure **349**.

Komatsu and co-workers discovered that the reaction between C_{60} and phthalazine (**350**, Scheme 30) takes a very different course in solution as compared with the solid state. Whereas the former procedure yielded a dihomofullerene derivative that is structurally related to compounds (±)-**172**−(±)-**174** (Figure 36 and Scheme 16), the reaction of C_{60} with 4 equiv of phthalazine in the solid state under mechanochemical conditions using high-speed vibration milling[332] afforded difullerene derivative **351**, probably by Diels−Alder addition of *o*-quinodimethane intermediate **352** to a second C_{60} molecule.[763] Although this difullerene analogue of triptycene, with two fullerene cages rigidly fixed in close proximity, is stable in the solid state up to 200 °C, irradiation with an incandescent lamp in $CHCl_3$ or heating in *o*-dichlorobenzene gradually transforms it into **353** by intramolecular [2 + 2] cycloaddition. Similar to **349** (Figure 61), the multianellated, C_s-symmetric difullerene **353** combines two carbon spheroids with enantiomorphic, noninherently chiral *cis*-1 functionalization patterns. In contrast to cyclobutadifullerene C_{120} and to fullerene "dimer" **103** (Scheme 5), heating of **353** to 200 °C leads to no appreciable cycloreversion. On the other hand and similar to C_{120}, the cyclobuta-fusion in **353** is readily cleaved upon transfer of one electron as shown by cyclovoltammetry (CV) and differential pulse voltammetry (DPV).[763]

Scheme 30. Course of the Reaction between C_{60} and Phthalazine (350) under High Speed Vibration Milling Conditions[763 a]

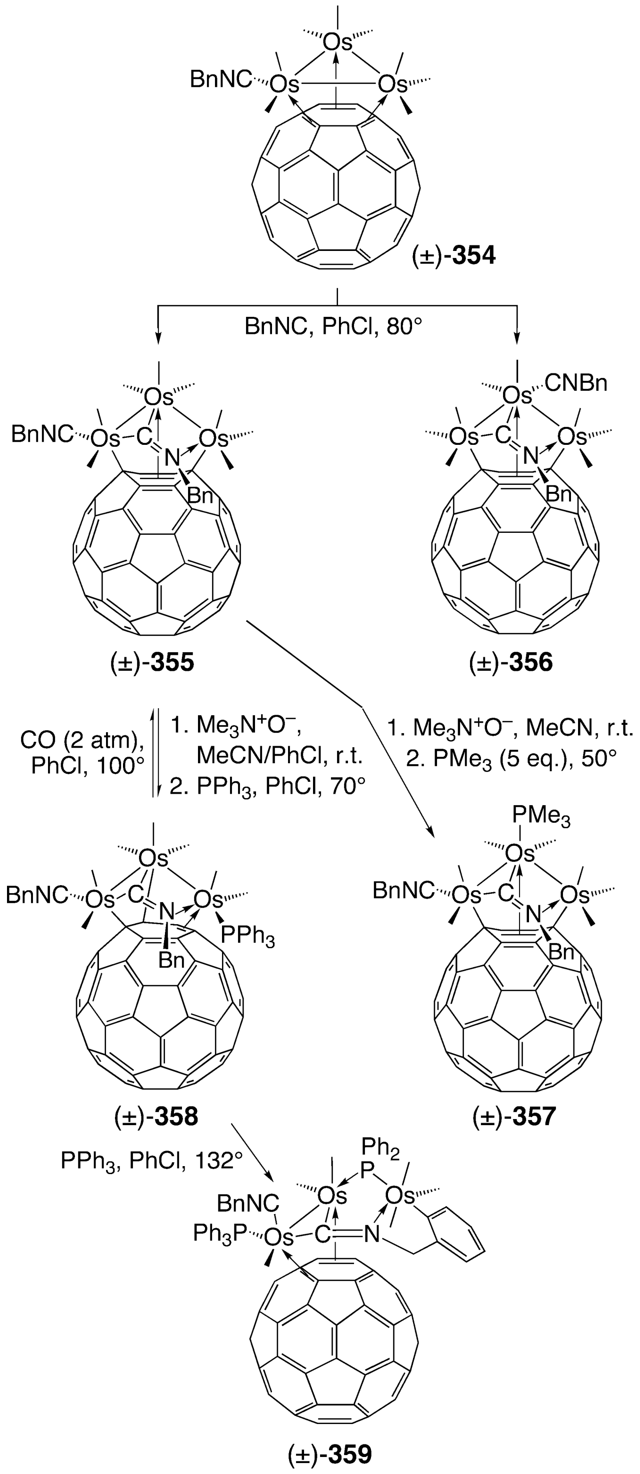


[a] The multianellated fullerene moieties of the achiral product **353** display enantiomorphic noninherently chiral *cis*-1-type functionalization patterns.

6.4. *cis*-1-Type Transition Metal Cluster Complexes of C_{60}

New bonding modes of C_{60}, corresponding to a *cis*-1-type noninherently chiral functionalization pattern involving cage atoms C(1), C(2), C(9), and C(12) (for the numbering of C_{60}, see Figure 2), were discovered by Park and co-workers in their attempts to convert existing bonding patterns of C_{60}−metal cluster complexes into new ones by modifying the coordination sphere of the metal centers.[654,764] By doing so, they discovered that C_{60} can act as a multifunctional ligand exhibiting various π- and σ-bonding modes. Thus, when [$Os_3(CO)_8(CNBn)(\mu_3$-η^2:η^2:η^2-$C_{60})$] ((±)-**354**, Scheme 31, obtained from the reaction between C_{3v}-symmetric [$Os_3(CO)_9(\mu_3$-η^2:η^2:η^2-$C_{60})$] and BnN=PPh_3) was treated with benzyl isonitrile at 80 °C in chlorobenzene, two constitutional isomers of [$Os_3(CO)_8(CNBn)(\mu_3$-CNBn)$(\mu_3$-η^2:η^2:η^2-$C_{60})$], (±)-**355** and (±)-**356**, with one isonitrile ligand inserted into an Os−Os bond were obtained and characterized by X-ray crystallography.[765,766] Adduct (±)-**355** was the first structurally characterized complex exhibiting σ-bonding between the fullerene and a metal center. The coordination of one isonitrile ligand to three Os centers in a four-electron-donor μ_3-η^2(C):η^1(N) mode and the equatorial bonding of another isonitrile to one of the outer Os atoms lead to an unsymmetric trimetallic framework and, thus, to a noninherently chiral fullerene functionalization pattern. The outer Os centers of (±)-**355** and (±)-**356** bind to C(9) and C(12) of the μ_3-η^1:η^2:η^1-C_{60} ligand in a σ-fashion, while π-coordination to C(1) and C(2) is observed for the central Os atom. The functionalized cyclohexa-1,4-diene-type ring of the fullerene thus adopts a boat conformation with the σ-bonded C(sp^3)-atoms located at the bow and stern positions. The thermally (80 °C) noninterconvertible complexes (±)-**355** and (±)-**356** differ only in the coordination site of the terminal isonitrile ligand.[765,766]

Scheme 31. Chemical Transformations between Triosmium Cluster Complexes Bonded in Various Ways to a C_{60} Ligand, Which Displays a Noninherently Chiral C(1),C(2),C(9),C(12)-Addition Pattern[764] [a]



[a] Carbonyl ligands are not shown explicitly but indicated by free valences departing from the metal atoms.

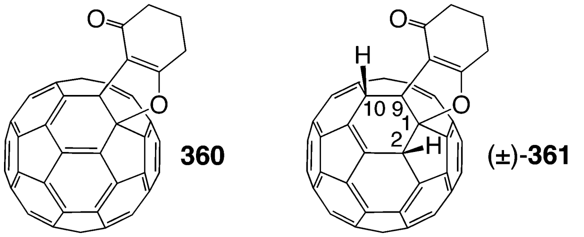


Figure 62. Unusual noninherently chiral functionalization pattern in C(1),C(2),C(9),C(10)-adduct (±)-**361**, formed together with achiral **360** in the photocycloaddition between cyclohexane-1,3-dione and C_{60}.[769]

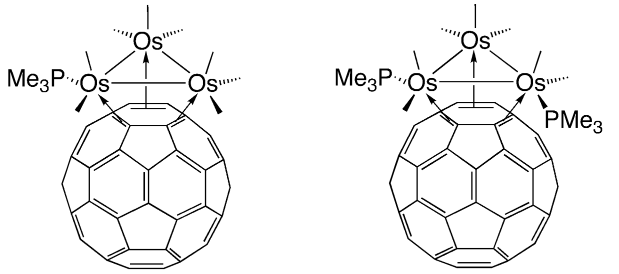
Decarbonylation of (±)-**355** with $Me_3N^+O^-$/MeCN and reaction with PMe_3 afforded $[Os_3(CO)_7(CNBn)(\mu_3\text{-CNBn})(PMe_3)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})]$ ((±)-**357**) with a phosphine ligand substituting an axial CO ligand at the central Os center of (±)-**355** but the bonding mode between osmium cluster and fullerene remaining unchanged.[767] In product (±)-**358**, on the other hand, the bulkier phosphine PPh_3 replaces a carbonyl ligand at an equatorial position of an outer Os atom, and the fullerene ligand has undergone an orbital rearrangement, switching from $\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1$-bonding ((±)-**355**) to $\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^2$-bonding ((±)-**358**).[768] The latter mode again corresponds to a noninherently chiral *cis*-1-type fullerene addition pattern for which X-ray crystallography reveals a cyclohexa-1,3-diene substructure, as opposed to the cyclohexa-1,4-diene boat structure in (±)-**355**. Metal−fullerene back-donation seems to be the cause for the preferred π-type interaction between the fullerene and the Os center bearing the phosphine donor ligand. Stronger heating of (±)-**358** with PPh_3 leads to the formation of (±)-**359** by a series of rearrangements including carbonyl and PPh_3 migration, switching of the terminal isonitrile ligand from an equatorial to an axial position, insertion of a bridging PPh_2 ligand into one of the Os−Os bonds, and orthometalation of the second benzyl isonitrile ligand under formation of a five-membered metallacycle. In this π-type complex, the fullerene adopts a $\mu\text{-}\eta^2{:}\eta^2$-binding mode and its functionalized six-membered ring has regained a cyclohexatriene-like structure, still corresponding to a noninherently chiral *cis*-1 addition pattern.[768]

6.5. C(1),C(2),C(9),C(10)-Adduct of C_{60}

Photocycloaddition between cyclohexane-1,3-dione or related compounds and C_{60} did not give the expected De Mayo type fullerene-fused cyclo-octane-1,4-diones after workup, but a C_s-symmetric (**360**, Figure 62) and a C_1-symmetric ((±)-**361**) compound.[769] The latter could be dehydrogenated to **360**, and its enantiomers separated on an (*S*,*S*)-Whelk-O chiral stationary phase. Whereas the achiral compound (**360**) is a mono-adduct of C_{60}, ^{3}He NMR spectroscopy of the ^{3}He incarcerane of (±)-**361** rather pointed at a bis-adduct structure. Having one 6−6 and two 6−5 junctions within a six-membered ring of the fullerene functionalized, (±)-**361** does not represent a *cis*-1-type adduct of C_{60}, the addition pattern of which extends over two 6−6 and one 6−5 junctions. The unprecedented addition pattern of C(1),C(2),C(9),C(10)-adduct (±)-**361** leads to an intrapentagonal double bond at the unfunctionalized 6−5 junction of the functionalized hexagon.

6.6. *cis*-1,*cis*-1,*cis*-1 Metal Cluster Complexes of C_{60}

Complexes (±)-**362** ($[Os_3(CO)_8(PMe_3)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})]$) and (±)-**363** ($[Os_3(CO)_7(PMe_3)_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})]$) (Figure 63) have been prepared next to a tris(phosphine) substitution product (not shown) by decarbonylation of $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})]$[662] with 3 equiv of $Me_3N^+O^-$ in the presence of an excess of PMe_3.[770−772] As shown by X-ray crystallography, (±)-**363** has two heterotopic equatorial phosphine ligands attached to neighboring Os atoms. This leads to configurational differences at the corresponding metal cen-



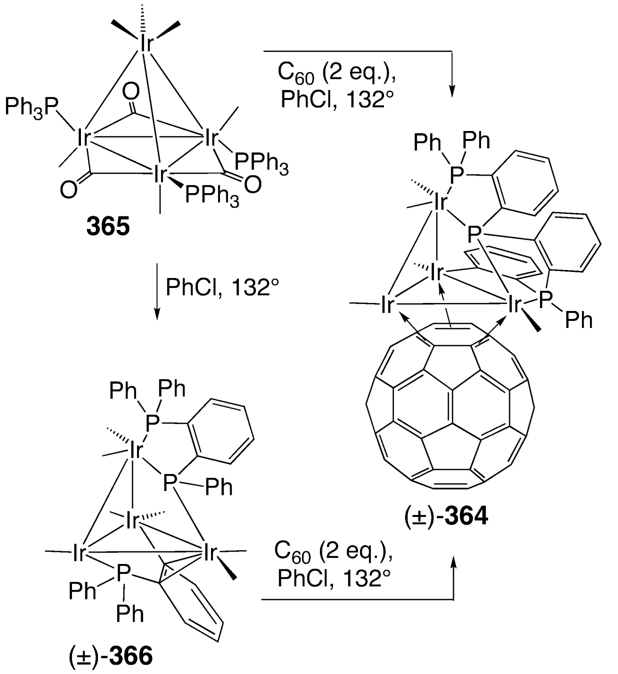
(±)-**362** (±)-**363**

Figure 63. Two triosmium cluster complexes with a [60]fullerene ligand exhibiting a noninherently chiral C(1),C(2),C(9),C(10),C(11),C(12)-addition pattern, which originates from configurational differences at the Os-centers. Carbonyl ligands are not shown explicitly but indicated by free valences departing from the metal atoms.

ters, and in combination with the constitutionally different third center, the three atoms of the Os_3 cluster are nonidentical. As a result, the *cis*-1,*cis*-1,*cis*-1 addition pattern of the $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$-bonded fullerene ligand becomes noninherently chiral. The same is true for (±)-**362**, in which case configurational differences exist between the two Os atoms devoid of phosphine ligands. In the homologous C_3-symmetric tris(phosphine) substitution product (not shown), on the other hand, all centers of the Os_3 cluster are identical, and the addition pattern of the fullerene is achiral. Nevertheless, that complex is chiral as a whole, and its stereogenic elements are restricted to the addend. In solution, temperature-dependent 3-fold rotation of the three nonbridging ligands at each Os center was detected and investigated by ^{13}C and ^{31}P NMR spectroscopy. In a related study, the fluxional behavior (carbonyl site exchange) of the ruthenium cluster complexes $[Ru_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})]$ (Ru/PPh_3-analogue of (±)-**362**), $[Ru_3(CO)_7(PPh_3)_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})]$ (Ru/PPh_3-analogue of (±)-**363**), $[Ru_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{70})]$ (Ru/PPh_3/C_{70}-analogue of (±)-**362** with a single hexagonal fullerene face capped in comparison to (±)-**271**, Figure 49), and $[Ru_3(CO)_7(PPh_3)_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{70})]$ (Ru/PPh_3/C_{70}-analogue (±)-**363**) was probed by Hsu and Shapley using ^{31}P and ^{13}C NMR spectroscopy.[773] A disubstitution product of $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})]$ with two different isonitrile ligands (cf. monosubstitution product (±)-**354**, Scheme 31), one of them carrying a zinc(II)-porphyrin and the other one serving to attach the entire conjugate to an ITO (indium tin oxide) surface, was used by Park and coworkers to build a highly ordered and nearly fully covered SAM (self-assembled monolayer) of a [60]fullerene−metal cluster−porphyrin dyad. Such an assembly, having its zinc(II)-porphyrin units interconnected by DABCO (1,4-diazabicyclo[2.2.2]octane) ligands, exhibited efficient photocurrent generation in a zinc(II)-porphyrin−fullerene/ITO/ascorbic acid/Pt cell.[774]

A noninherently chiral *cis*-1,*cis*-1,*cis*-1 addition pattern, originating from constitutionally different Ir centers in a $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$-bonded C_{60}, is present in cluster complex $[Ir_4(CO)_6\{\mu_3\text{-}PPh_2(o\text{-}C_6H_4)P(o\text{-}C_6H_4)PPh(\eta^1\text{-}o\text{-}C_6H_4)\}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})]$ ((±)-**364**, Scheme 32) with a tetrairidium butterfly framework.[775] It was characterized by X-ray crystallography as an unexpected product of the reaction between the tetrairidium cluster complex $[Ir_4(CO)_9(PPh_3)_3]$ (**365**) and C_{60}, demonstrating, for the first time, the behavior of the latter as a "noninnocent" ligand that induces the chemical transformation of PPh_3 ligands into a P−(C)$_n$−P−(C)$_n$−P species by a series of *ortho*-phosphanation and *ortho*-metalation reactions. Thermolysis of **365** alone in chlorobenzene afforded (±)-**366**, which, upon refluxing with C_{60}, produced (±)-**364**, thereby showing that the former is a reaction intermediate on the way to the latter.[775] Another example for the C_{60}-mediated conversion of two PPh_3 ligands into a diphosphine ligand by successive phosphanation and *ortho*-metalation at an Ir_4 cluster was reported recently.[776] Such transformations may open up a convenient avenue for the synthesis of oligophosphines that are not easily accessible otherwise.

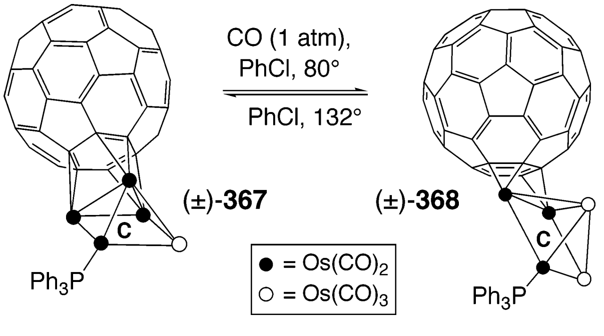
Scheme 32. *ortho*-Phosphanation and *ortho*-Metalation Reactions with PPh_3 Ligands, Induced by the "Noninnocent" $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60}$ Ligand in a Tetrairidium Cluster Complex[775] [a]



[a] Nonbridging carbonyl ligands are not shown explicitly but indicated by free valences departing from the metal atoms.

The carbidopentaosmium cluster complex $[Os_5C(CO)_{11}(PPh_3)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})]$ ((±)-**367**, Scheme 33) features a square-pyramidal metal cluster framework with a carbon atom in its base, attached through one of its triangular faces to a six-membered ring of the fullerene.[777] Its solid-state structure is isomorphous to that of the previously prepared ruthenium analogue $[Ru_5C(CO)_{11}(PPh_3)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})]$,[778,779]

Scheme 33. Interconversion between $[Os_5C(CO)_{11}(PPh_3)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})]$ ((±)-367) and $[Os_5C(CO)_{12}(PPh_3)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_{60})]$ ((±)-368),[777] Two Carbidopentaosmium Cluster Complexes in Which the C_{60} Ligand Exhibits Different Bonding Modes and Noninherently Chiral Addition Patterns



and the noninherently chiral *cis*-1,*cis*-1,*cis*-1 addition pattern of both originates from differences in the ligands bound to the basal Os atoms. In solution, (±)-**367** can be reversibly converted to $[Os_5C(CO)_{12}(PPh_3)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_{60})]$ ((±)-**368**) in an equilibrium that depends on the concentration of carbon monoxide. This transformation is accompanied by a switching in the C_{60}-bonding mode from $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ to $\mu\text{-}\eta^2{:}\eta^2$, a phenomenon observed here for the first time. Intriguingly, at the same time, the fullerene formally rotates by 180° in such a way that the top of the pyramid is located atop a hexagon in (±)-**367** and atop a pentagon in (±)-**368**.[777] The conversion from $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60}$ to $\mu\text{-}\eta^2{:}\eta^2\text{-}C_{60}$ was not detected with a related Ru_5C cluster complex, an observation giving a hint at the stability of the $Ru\cdots(C{=}C^{\text{fullerene}})$ π-interaction versus $Ru\cdots CO$ bonding.[780]

Coordination of a single metal cluster to two C_{60} cages can be realized with a cluster framework that has enough electron-donating ligands to compensate for the electron-withdrawing fullerenes. When the complex $[Rh_6(CO)_{12}(dppm)_2]$ (dppm = bis(diphenylphosphino)methane) with an octahedral hexarhodium cluster framework was reacted with 1.4 equiv of [60]fullerene in chlorobenzene at 120 °C, the color of the solution changed from dark red to green, and the complex $[Rh_6(CO)_9(dppm)_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})]$ ((±)-**369**, Figure 64), in which a triangular face of the Rh_6 octahedron caps a six-membered ring of the fullerene, could be isolated.[781,782] The unsymmetric distribution of the carbonyl and phosphine ligands on the hexarhodium cluster causes the *cis*-1,*cis*-1,*cis*-1 addition pattern of the fullerene to be noninherently chiral. Treatment of (±)-**369** with an excess of C_{60} in refluxing chlorobenzene, followed by treatment with 1 equiv of benzyl isonitrile, gave the first bisfullerene–metal cluster sandwich complex $[Rh_6(CO)_5(dppm)_2(CNBn)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})_2]$ ((±)-**370**) as a green solid.[781,782] The X-ray crystal structure shows that the two $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60}$ ligands are capping triangular faces of the Rh_6 octahedron, one vertex of which is bonded to both carbon cages. Due to the unsymmetric distribution of the nonfullerene ligands (terminal CO, μ_3-CO, and μ_2-dppm) on the cluster framework, the coordination environments of the two carbon cages differ from each other and, in addition, each one displays a noninherently chiral *cis*-1,*cis*-1,*cis*-1 functionalization pattern. It is interesting to note that the six redox waves corresponding to the first three reductions of the two C_{60} units are well separated, thereby reflecting an unusually strong electronic communication through the hexarhodium cluster.[781,782]

A combination of different bonding modes and two noninherently chiral addition patterns, involving a *cis*-1-type C(1),C(2),C(9),C(12)- and a *cis*-1,*cis*-1,*cis*-1-type C(1),C(2),C(9),C(10),C(11),C(12)-functionalization, is found in the complex $[Ir_4(CO)_3(\mu_4\text{-}CH)(PMe_3)_2(\mu\text{-}PMe_2)(CNBn)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_{60})(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}C_{60})]$ ((±)-**371**) in which a tetranuclear Ir_4 cluster is bonded to two C_{60} ligands.[783] The complex was obtained as the major product in the form of a green solid from the reaction of $[Ir_4(CO)_8(PMe_3)_4]$ with 4 equiv of C_{60} in refluxing dichlorobenzene, followed by treatment with benzyl isonitrile. Interesting features revealed by X-ray crystallography are the face capping of the square-planar Ir_4 cluster by a methyne (CH) group, the bridging of two Ir centers by a PMe_2 group, the cyclohexatriene structure in the π-bonded fullerene ($\mu\text{-}\eta^2{:}\eta^2$-fashion), and the cyclohexa-1,3-diene ring in the σ- and π-bonded second fullerene ($\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2$-fashion). The noninherently chiral addition patterns of the fullerene units arise from differences, that is, exchange of a carbonyl for an isonitrile ligand, in the coordination spheres of the two Ir centers that are bonded to only one fullerene. Similar to (±)-**370**, electrochemical studies revealed a notable electronic interaction between the two fullerene ligands in (±)-**371**.

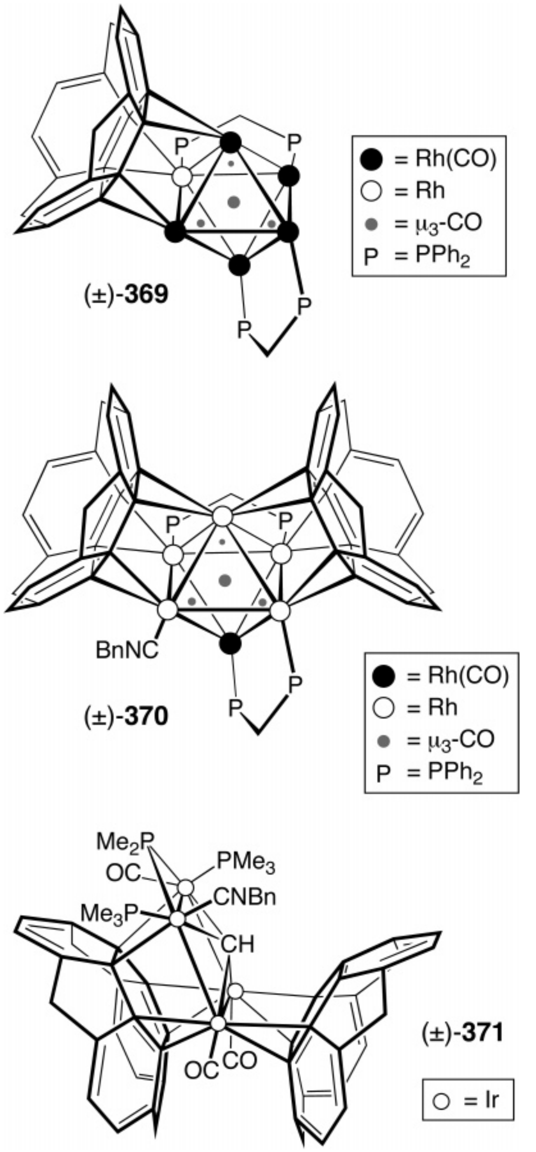
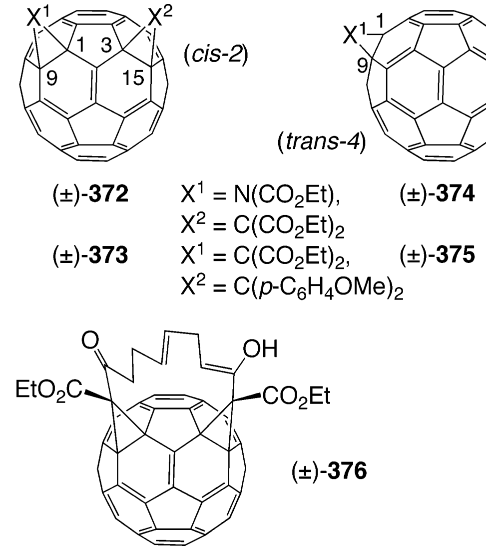


Figure 64. The top figures show complexes including an octahedral hexarhodium cluster framework and one fullerene ($[Rh_6(CO)_9(dppm)_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})]$, (±)-**369**)[781,782] or two fullerene ligands ($[Rh_6(CO)_5(dppm)_2(CNBn)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{60})_2]$, (±)-**370**).[781,782] The *cis*-1,*cis*-1,*cis*-1 addition pattern of each fullerene is noninherently chiral due to the unsymmetric distribution of the other ligands around the hexarhodium cluster. Triply bridging carbonyl ligands (μ_3-CO) cap the triangular cluster surfaces that have their center marked by a gray dot. The bottom figure shows a square-planar tetrairidium cluster framework in the complex $[Ir_4(CO)_3(\mu_4\text{-}CH)(PMe_3)_2(\mu\text{-}PMe_2)(CNBn)(\mu\text{-}\eta^2{:}\eta^2\text{-}C_{60})(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-}C_{60})]$ ((±)-**371**)[783] including two fullerenes, each of which displays its own binding mode and a noninherently chiral addition pattern resulting from the unsymmetric distribution of the ligands at the σ-bonded Ir centers. For reasons of space, all fullerenes are reduced to sumanene-type fragments.

6.7. Bis-Adducts with *cis*-2 and *trans*-4 Addition Patterns

Studying the regiochemistry of double addition to C_{60}, Hirsch and co-workers synthesized a series of bis-adducts



(±)-**372** $X^1 = N(CO_2Et)$, (±)-**374**
$X^2 = C(CO_2Et)_2$
(±)-**373** $X^1 = C(CO_2Et)_2$, (±)-**375**
$X^2 = C(p\text{-}C_6H_4OMe)_2$

(±)-**376**

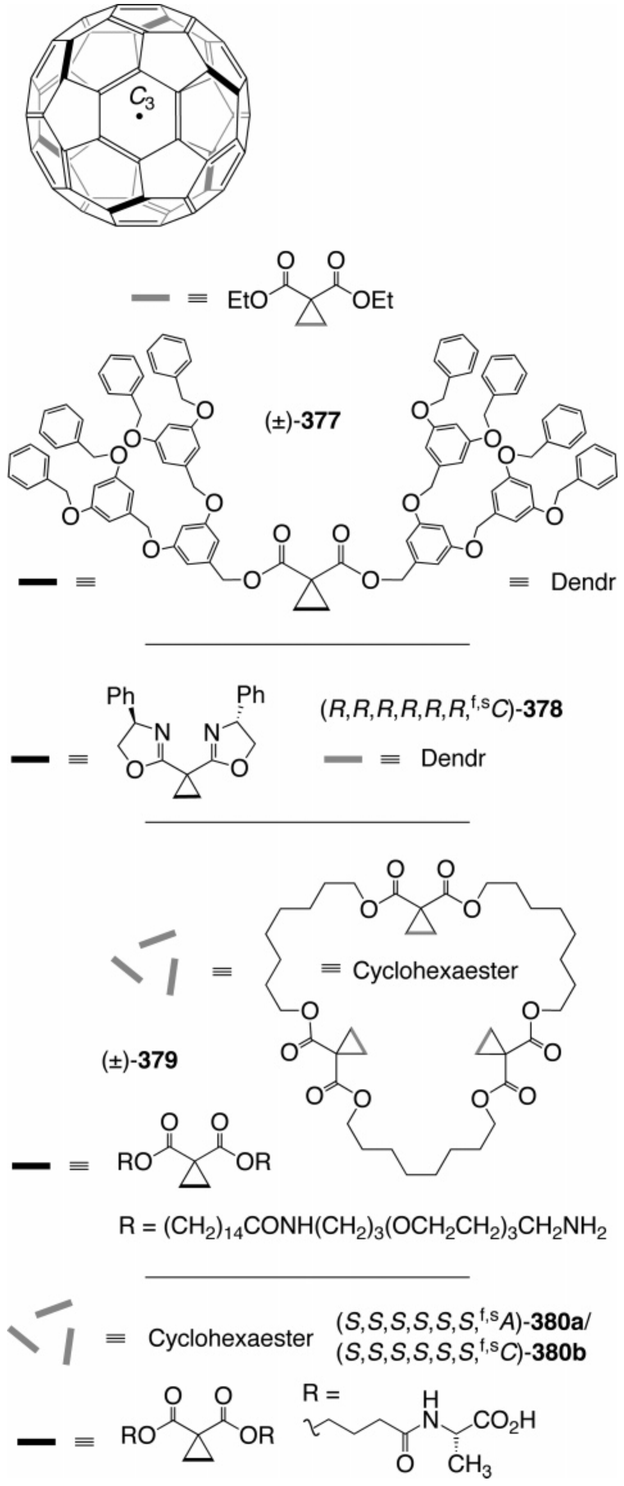
Figure 65. Bis-adducts of C_{60} with noninherently chiral *cis*-2 and *trans*-4 addition patterns.

with two different addends.[273] As a consequence of this nonidentity, the otherwise C_s-symmetric *cis*-2 and *trans*-4 addition patterns become noninherently chiral, for example, in C_1-symmetric C(1)−C(9):C(3)−C(15)-adducts (±)-**372** and (±)-**373** and in C(1)−C(9):C(32)−C(33)-adducts (±)-**374** and (±)-**375** (Figure 65). It is interesting to note in this context that *e* bis-adducts with different C_{2v}-symmetric addends are achiral but can occur as two constitutional isomers as a result of the heterotopicity of the e_{edge} and e_{face} positions.[260] A *cis*-2 bis-adduct with an unsymmetric tether, giving rise to a noninherently chiral addition pattern and two stereogenic methano C-atom centers ((±)-**376**) was reported by Nierengarten et al.[376]

6.8. Mixed Hexakis-Adducts of C_{60} with an Underlying Pseudo-Octahedral Addition Pattern

6.8.1. Hexakis-Adducts of C_{60} with Two Types of Addends Grouped in e,e,e-Subpatterns

Hirsch and co-workers reported a number of [60]fullerene hexakis-adducts that are distinguished by a pseudo-octahedral arrangement of two types of addends on the carbon sphere.[784,785] If these addends are grouped in two sets defining oppositely configured *e*,*e*,*e* patterns in antipodal hemispheres, the underlying overall addition pattern, which is achiral (T_h-symmetric) for identical addends, becomes C_3-symmetric and noninherently chiral. The reported examples include the dendronized fullerene (±)-**377** (Figure 66), obtained from C_3-symmetric *e*,*e*,*e* tris-adduct (±)-**124** (Figure 32) by 9,10-dimethylanthracene (DMA)-template-mediated[66] cyclopropanation with 2-bromomalonate-containing Fréchet-type dendritic ester residues.[786] This approach was also applied to the synthesis of (*R*,*R*,*R*,*R*,*R*,*R*,$^{\text{f,s}}$*C*)-**378** (Figure 66) which was regio- and diastereoselectively obtained from (*R*,*R*,*R*,*R*,*R*,*R*,$^{\text{f,s}}$*A*)-**130b** (Figure 32), in complete analogy to the preparation of the other three stereoisomers resulting from the different combinations of fullerene addition pattern and side chain configuration.[787] A variety of hexakis-adducts was synthesized from (±)-**147** (Figure 33), itself obtained by Bingel reaction between C_{60} and tris(octamethylene) cyclotrimalonate.[788] DMA-mediated completion of the pseudo-octahedral addition pattern of (±)-**147** using polar malonates featuring amino- (e.g., → (±)-**379**, Figure 66) or carboxy- (e.g., → (*S*,*S*,*S*,*S*,*S*,*S*,$^{\text{f,s}}$*A*)-**380a**/(*S*,*S*,*S*,*S*,*S*,*S*,$^{\text{f,s}}$*C*)-**380b**) termini afforded amphiphilic fullerene derivatives, which can be charged by up to 6-fold protonation or deprotonation. The amphiphiles carrying six charges are highly soluble in water and revealed pH-dependent aggregation in first studies.[788]



(±)-**377**

(*R*,*R*,*R*,*R*,*R*,*R*,$^{\text{f,s}}$*C*)-**378**

(±)-**379**

$R = (CH_2)_{14}CONH(CH_2)_3(OCH_2CH_2)_3CH_2NH_2$

(*S*,*S*,*S*,*S*,*S*,*S*,$^{\text{f,s}}$*A*)-**380a**/
(*S*,*S*,*S*,*S*,*S*,*S*,$^{\text{f,s}}$*C*)-**380b**

R =

Figure 66. Hexakis-adducts of C_{60} with a noninherently chiral addition pattern originating from superposition of two *e*,*e*,*e*-subpatterns with different addends. Compounds (*R*,*R*,*R*,*R*,*R*,*R*,$^{\text{f,s}}$*C*)-**378**[787] and (*S*,*S*,*S*,*S*,*S*,*S*,$^{\text{f,s}}$*A*)-**380a**/(*S*,*S*,*S*,*S*,*S*,*S*,$^{\text{f,s}}$*C*)-**380b**[788] include stereogenic centers in addition to their chiral addition pattern. The C_3 symmetry axis is indicated in the general structure (top).

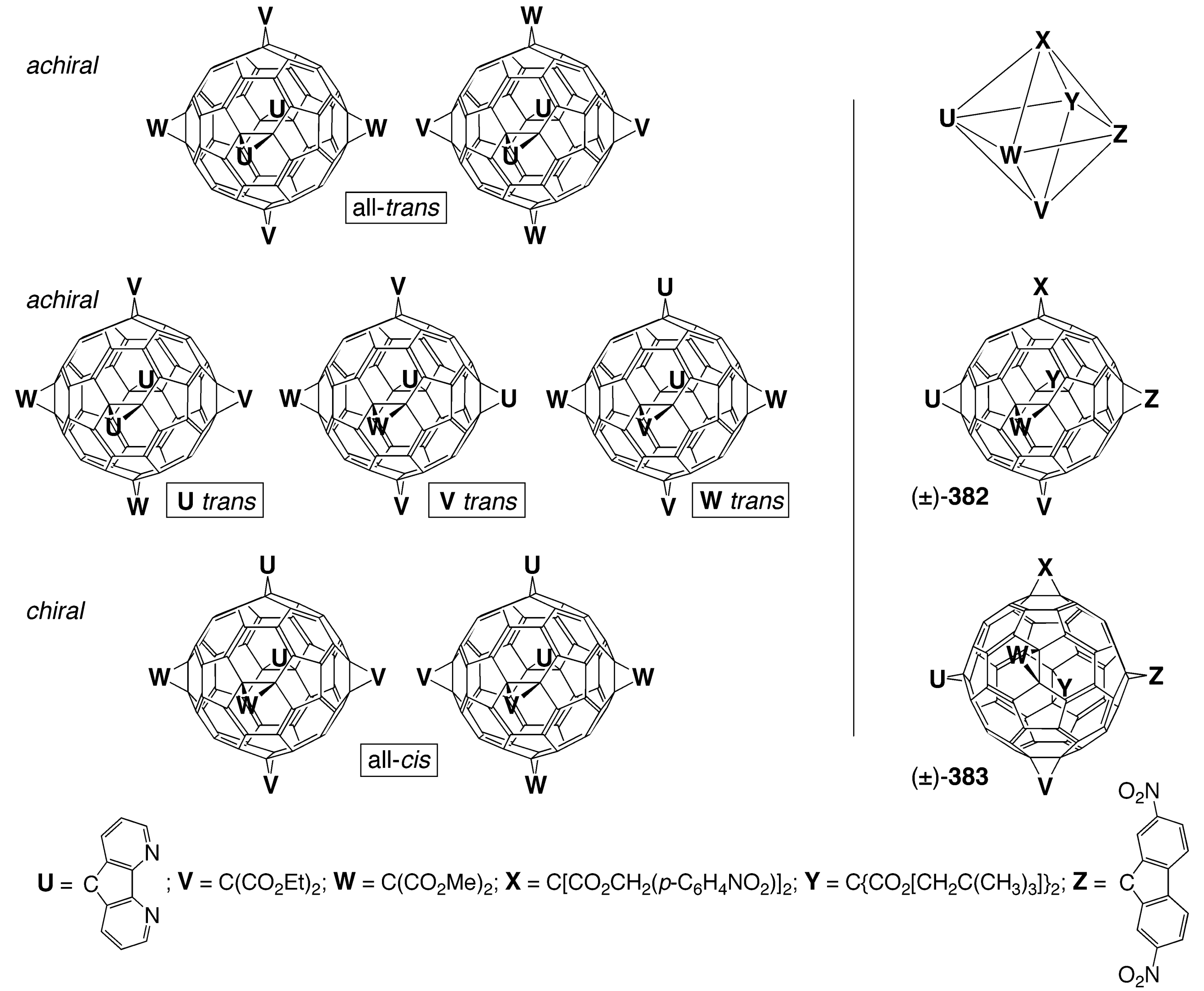


Figure 67. On the left are the seven $U_2V_2W_2(C_{60})$ regioisomers in which a pseudo-octahedral bond set is functionalized. The two all-*cis* isomers have a noninherently chiral addition pattern. On the right are two UVWXYZ(C_{60}) regioisomers ((±)-**382** and (±)-**383**)[791] in which each addend has the same nearest neighbors but with inverted e_{face} and e_{edge} relationships. Both constitutional isomers have a noninherently chiral addition pattern.

6.8.2. Full Control of Addend Permutation at a Pseudo-Octahedral Bond Set

Six double bonds of C_{60}-I_h, with four *e* and one *trans*-1 inter-relationships each, have their centers located at the vertices of a regular octahedron (Figure 67). If the geometry of these bonds as well as their orientation in space are taken into account, the O_h-symmetry of the regular octahedron is reduced to T_h, and the corresponding spatial arrangement is often termed “pseudo-octahedral”. It is characterized by a center of symmetry, and the corresponding hexakis-adducts with C_{2v}-symmetric addends can only be chiral if some of them are nonidentical and disposed in such a way that they lead to a noninherently chiral functionalization pattern. If one considers the addition of three different pairs of C_{2v}-symmetric addends (2 U, 2 V, 2 W) to C_{60}, seven diastereoisomers can be formed (Figure 67, left) as compared with only five possible diastereoisomeric complexes resulting from the octahedral coordination of pairwise identical monodentate ligands to a transition metal (in the latter case, there is only a single all-*trans* and a single all-*cis* isomer).[789] As soon as there is a *trans*-1 relationship between two identical addends, this arrangement, together with the C_{2v}-symmetry of all addends, leads to a mirror plane as symmetry element and, therefore, to an achiral hexakis-adduct. Solely all-*cis* arrangements lack second-order symmetry elements, and the corresponding two constitutional isomers are chiral.

The entire library of seven isomers was prepared by Qian and Rubin in an elegant parallel synthesis starting from the bridged *trans*-1 bis-adduct **381** (see Scheme 40) as a strategically protected and activated building block.[789] Two $V_2W(C_{60})$ and two $VW_2(C_{60})$ tris-adducts (all achiral) with an *e*,*e*,*trans*-1 functionalization pattern were prepared as key intermediates of these syntheses.[790] Partial regioselectivity, possibly determined by an interplay between electronic and steric effects, in the functionalization of the remaining three fullerene bonds within the considered pseudo-octahedral set allowed the synthesis of the seven $U_2V_2W_2(C_{60})$ isomers to be completed (Figure 67, left).

Complete command of addend permutation at all six positions made pure UVWXYZ(C_{60}) regioisomers (±)-**382** and (±)-**383** accessible in separate syntheses (Figure 67, right).[791] The exquisite control of the regiochemistry around the T_h-symmetric “coordination core” of C_{60} was achieved in the synthesis of (±)-**383** by (i) sequential Bingel additions of three different addends (V, W, X) to the *trans*-1 intermediate **381** (see Scheme 40), (ii) elimination of the

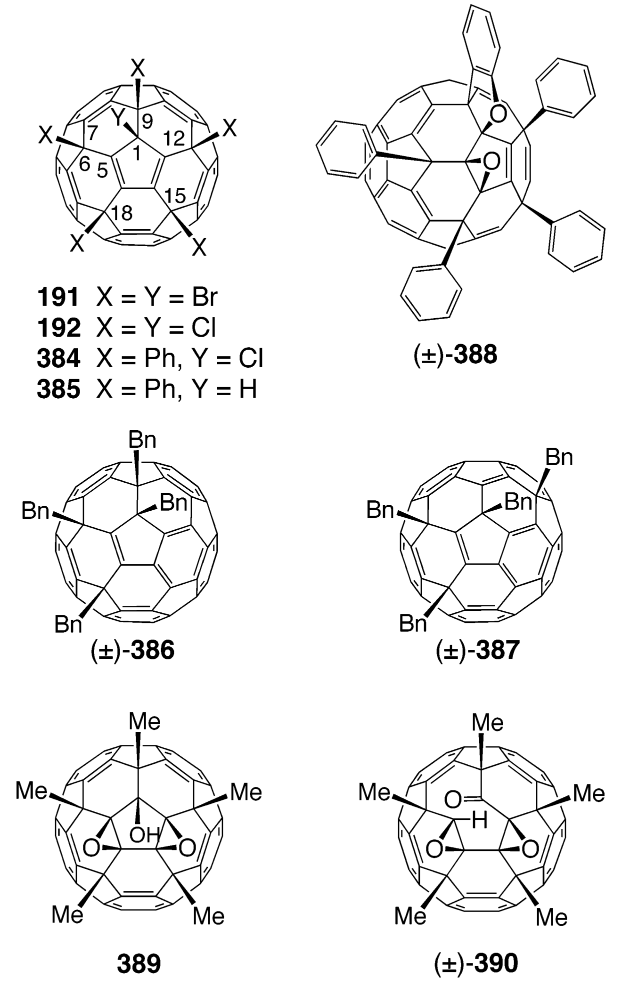


Figure 68. Hexahalogeno[60]fullerenes $C_{60}Br_6$ (**191**)[792] and C_{60}-Cl_6 (**192**),[519,547] paradigmatic examples for products of "cyclopentadiene addition mode" reactions and other fullerene derivatives with a related addition pattern.

tolanediacetic acid template, which made a sterically blocked reactive bond within the considered pseudo-octahedral set accessible, (iii) addition of the fourth malonate (Y), (iv) removal of the fullerene-fused cyclohexadiene rings in a Diels−Alder/retro-Diels−Alder sequence, and (v) consecutive addition of addends U and Z to the regenerated fullerene double bonds.[791] Specific permutation in the order of attachment of addends V−X, on the other hand, allowed the preparation of the constitutional isomer (±)-**382**.

6.9. The "Cyclopentadiene Addition Mode" Applied to C_{60}

The C(1),C(6),C(9),C(12),C(15),C(18)-addition pattern of C_{60}, nicely illustrated by the crystal structure of $C_{60}Br_6$ (**191**, Figure 68),[792] is typical for certain monovalent addends as they are seen in the reaction of buckminsterfullerene with free radicals,[793,794] iodine chloride,[248,547] bromine,[248,792] amines,[735,795] or specific organocopper[700,701,796] and organolithium reagents.[797] It is characterized by five groups adding in successive 1,4-additions to the outer ends of the radial hexagon−hexagon fusions in a corannulene substructure, the sixth addend being attached to the central pentagon. This results in the formation of a cyclopentadiene substructure that is isolated from the remainder of the fullerene π-chromophore. The basic form of this addition pattern being C_s-symmetric, it can become (noninherently) chiral only if nonidentical addends are placed in appropriate positions. Inherently chiral functionalization patterns are possible, on the other hand, if this "cyclopentadiene addition mode" is incompletely realized.

6.9.1. Derivatives of $C_{60}Cl_6$

The addition pattern of $C_{60}Br_6$ (**191**, Figure 68)[792] occurs also in $C_{60}Cl_6$ (**192**), the main product of the reaction of buckminsterfullerene with ICl,[519,547] which was only recently obtained in high purity thanks to an improved synthesis.[798] Hexachloride **192** is a convenient starting material for the Friedel−Crafts-type arylation of fullerenes, leading to derivatives such as $C_{60}Ph_5Cl$ (**384**), which can be reduced to $C_{60}Ph_5H$ (**385**).[519,799] Phenylation of $C_{60}Cl_6$ also produced 1,7-diphenyl-1,7-dihydro(C_{60}-I_h)[5,6]fullerene and a C_1-symmetric derivative $C_{60}Ph_4$,[800] for which both a C(1),C(6), C(9),C(18)- and a C(1),C(6),C(11),C(18)-adduct structure (cf. addition patterns of (±)-**386** and (±)-**387**) are in accord with spectroscopic data, the latter being preferred on chemical grounds (vide infra).[801] The above phenyl derivatives of C_{60} were also prepared as ^{3}He incarceranes. As a general trend, ^{3}He NMR shows an increased shielding of the entrapped noble gas with increasing degree of functionalization.[802]

Two C_1-symmetric tetrabenzyl derivatives of C_{60}, (±)-**386** and (±)-**387**, were isolated from the products obtained by reaction of the electrosynthetically generated dianion $[(C_6H_5CH_2)_2C_{60}]^{2-}$ with benzyl bromide. X-ray crystallography showed that they have the same inherently chiral addition patterns that had been proposed[800,801] for $C_{60}Ph_4$.[803] ESR spectroscopic studies of the radical anion of 1,6,11,18-$[(C_6H_5CH_2)_4C_{60}]$ ((±)-**387**) pointed at a large splitting of the degenerate t_{1u} orbitals caused by introduction of the four benzyl groups.[804,805]

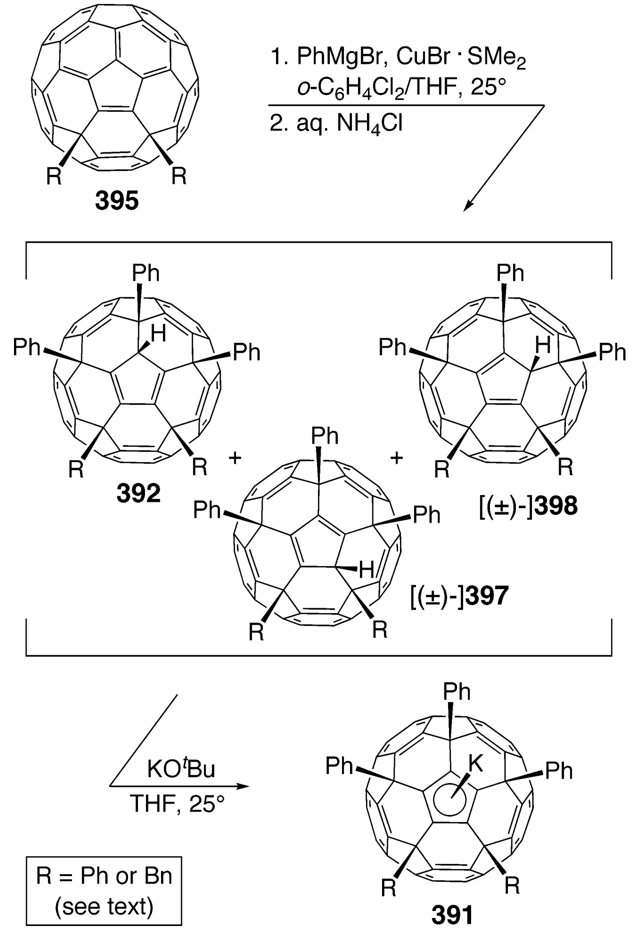
Chiral species appear also to be among the three isomers produced from $C_{60}Ph_5Cl$ by the addition of the radicals generated from $Hg[P(O)(O^iPr)_2]_2$ under UV irradiation.[806]

On exposure to air, $C_{60}Ph_5Cl$ (**384**), $C_{60}Ph_5H$ (**385**), or the corresponding *p*-fluorophenyl derivatives spontaneously undergo replacement of the hydrogen or chlorine attached to C(1) by oxygen, followed by oxidative ring closure at the *ortho* position of the adjacent aryl ring under formation of a fullerene-fused benzo[*b*]furan ring system (cf. (±)-**388**).[801,807] Additional epoxidation of one of the double bonds in the central cyclopentadiene unit leads to a C_1-symmetric product such as (±)-**388**. The propensity of this diene system toward epoxidation has been illustrated by the X-ray crystal structure of C_s-symmetric bisoxirenofullerene **389**, which was produced in the reaction of $C_{60}Cl_6$ with MeLi, followed by hydrolysis.[808,809] Another product, formed in the same reaction, is C_1-symmetric diepoxyketone (±)-**390**, a tautomer of **389** resulting from a 1,3-shift of the hydroxy-H-atom in a cage-opening reaction, which may be driven by strain relief.[810]

6.9.2. Addition of Organocuprates to C_{60}

The high-yielding treatment of C_{60} with organocopper reagents (cf. 1st reaction of Scheme 34) leads to addition of five organic groups to the far ends of the 6−6 bonds radiating from a pentagon, turning the latter into a cyclopentadienyl anion (e.g., anion of **391**, R = Ph, Scheme 34), which, upon protic workup, affords hexakis-adducts such as **392** (R = Ph).[700,701,796,811−813] The anionic cyclopentadienides, besides forming small bilayer vesicles in water,[814] can act as η^5-ligands in a variety of metal complexes (e.g., **391**, R = Ph

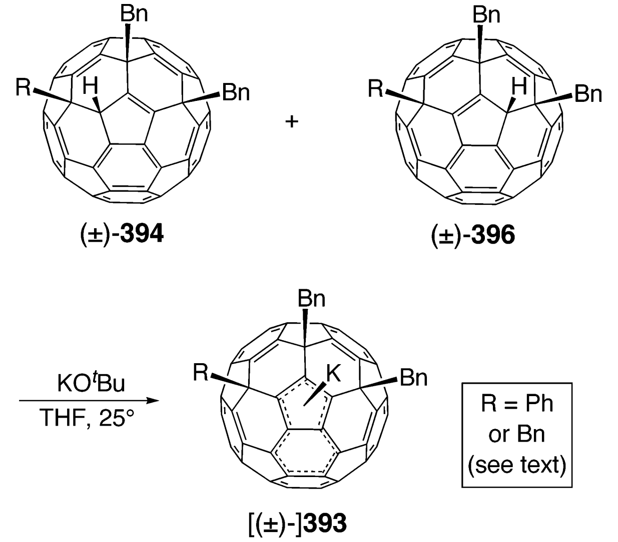
Scheme 34. Organocuprate Addition to a 1,4-Adduct of C_{60} (395), Products (392, [(±)-]397, and [(±)-]398)[343] Resulting from Protonation of the Primary Pentakis-Adduct Anion, and Further Treatment with KO^{t}Bu under Formation of the Cyclopentadienyl-Type Potassium Complex (391)[a]



[a] The direct addition of five identical organic residues to C_{60} (not shown) is also possible and affords achiral products. For the nature of the residue R, see main text.

or Bn).[700,701,796,811−813] If the added residues in such complexes are aryl groups (**391**, R = Ph), they adopt a chiral, propeller-shaped, C_5-symmetric arrangement,[796] whereas they can freely rotate in the protonated species (**392**, R = Ph) unless the addends are sterically demanding such as fluorenyl groups.[797] Interestingly, when a Grignard reagent is added instead of a cuprate to a 1,4-bisaddduct of C_{60}, the reaction stops at the stage of a tris-adduct (e.g., anion of **393**, R = Bn, Scheme 35).[703,705,815] Theoretical calculations have shown that the anionic fragment, in this case, corresponds to an indenyl rather than a cyclopentadienyl or allyl anion,[816] and protonation of the corresponding pentagon takes place in an unsymmetric way, leading to an inherently chiral addition pattern ((±)-**394**, R = Bn) (for similar derivatives of C_{70}, see Figure 56).[703,705,815] The symmetry of the above compounds can also be lowered by introduction of different organic residues. In fact, if a 1,4-adduct such as **395** (R = Bn, Scheme 34) is reacted with an organometallic reagent containing a residue that differs from the addends already in place, mixed tris- and pentakis-adducts result. Among these, the anions of the tris-adducts ((±)-**394** or (±)-**396**, R = Ph, Scheme 35) and two of the three protonated (uncharged) pentakis-adducts ((±)-**397** and (±)-**398**, R = Bn, Scheme 34) have a noninherently chiral functionalization pattern.[705,815] Such patterns occur also in the products of the regioselective hydrogenation of compounds such as (±)-**394** (R = Ph, Scheme 35), mediated by 9,10-dihydroanthracene/[$Re_2(CO)_{10}$].[817] In the presence of water, these reactions occur as transfer hydrogenations and the addition of hydrogen atoms leads to completion of the full "cyclopentadiene-mode" hexakis-addition pattern. Under anhydrous conditions, hydrometalation affords cyclopentadienyl-type η^5-hydrofullerene rhenium complexes. This reaction, which works even with pristine C_{60}, albeit in low yield, is the first method for a completely regiocontrolled delivery of hydrogen atoms to a fullerene.

Scheme 35. Tris-Adducts((±)-394, and (±)-396) Resulting from Addition of Grignard Reagents to 1,4-Adducts of C_{60} in the Absence of Copper, and Treatment with KO^{t}Bu under Formation of an Indenyl-Type Potassium Complex ([(±)-]393)[343] [a]

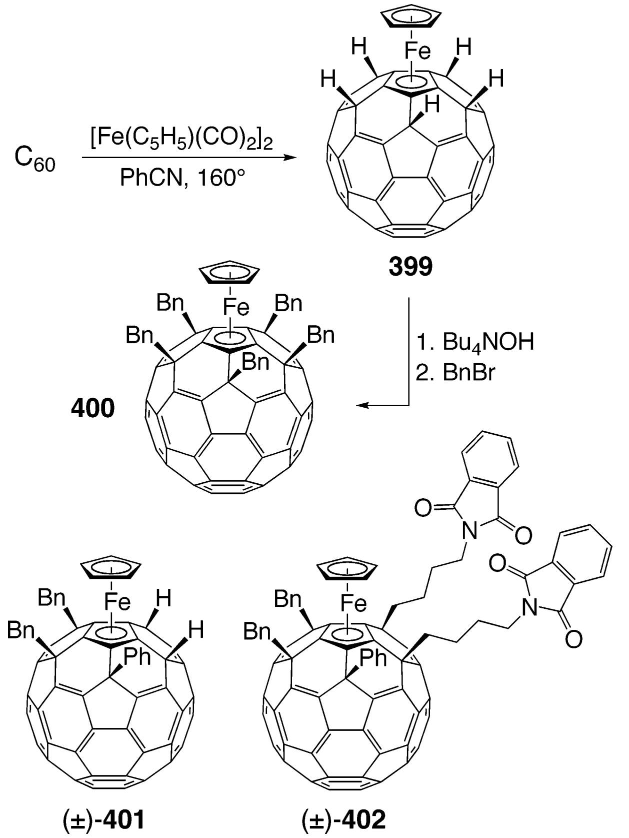


[a] For the nature of the residue R, see main text.

Five H-atoms can also be attached regioselectively to the fullerene cage in the form of the iron(II) complex [$Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_{60}H_5)$] (**399**, Scheme 36) by reaction of hexacontacarbon (C_{60}) with [$Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$.[817] Deprotonation of hydrofullerene complex **399** with Bu_4NOH in PhCN and subsequent alkylation with haloalkanes afforded pentaalkylated products such as **400** with retention of the C_{5v}-symmetric functionalization pattern.[818] Similarly, starting from fullerene derivative (±)-**396**[815] (R = Ph, Scheme 35) and using the appropriate alkylating agent, the first step and both steps of the above procedure lead to hydrofullerene derivatives (±)-**401** and (±)-**402**, respectively, each with a noninherently chiral addition pattern.[818] Related rhenium-carbonyl complexes have been obtained by [$Re_2(CO)_{10}$]-mediated transfer hydrogenation of (±)-**394** or (±)-**396**[815] (R = Ph, Scheme 35) with 9,10-dihydroanthracene (→ [$Re(CO)_3(\eta^5\text{-}C_{60}R_3H_2)$])[817] and subsequent deprotonation/alkylation (→ [$Re(CO)_3(\eta^5\text{-}C_{60}R_2R'_3)$]).[818]

By twofold application of the "cyclopentadiene addition mode" to C_{60}, Nakamura and co-workers were able to access an interesting class of compounds in which opposite corannulene caps are functionalized and the fullerene chromophore is reduced to an equatorial [10]cyclophenacene belt with 40 π-electrons, which represents the shortest version of a (5,5) armchair carbon nanotube (Scheme 37).[819] Starting from pentamethyl-hexahydrofullerene **403**, the acidic hydrogen atom had to be replaced by a protecting and activating cyano

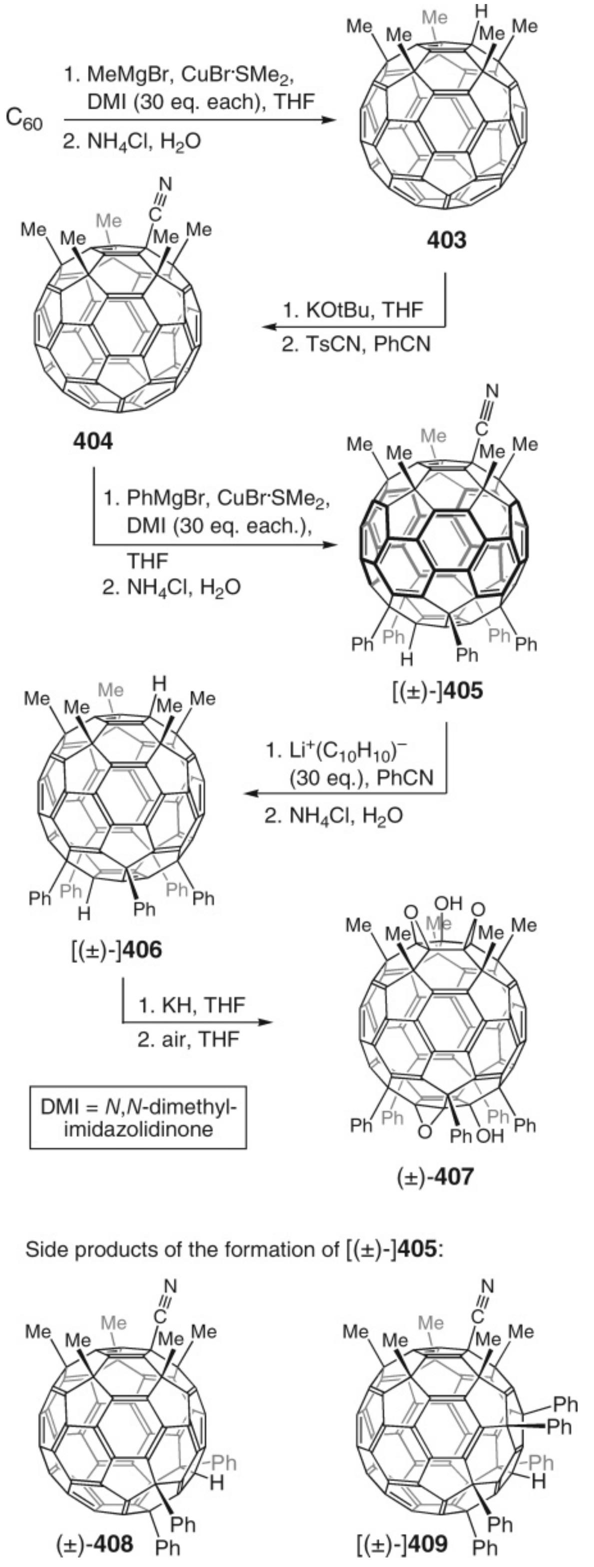
Scheme 36. Preparation of (η^5-Cyclopentadienyl)(η^5-hexahydro[60]fullerenyl)iron Complexes[817,818] [a]



[a] Compounds (±)-**401** and (±)-**402**[818] with mixed addends have a noninherently chiral addition pattern.

group (→ **404**) because homoconjugation between the cyclopentadienide generated from **403** under basic conditions and the bottom 50 π-electrons makes the latter moiety unreactive toward further cuprate addition. After introduction of the nitrile function, the other hemisphere of the cage was pentaphenylated to afford the strongly luminescent [(±)-]**405**[343] (mixture of three isomers differing in the relative orientation of the functionalized polar caps, vide infra)[820] and reductive deprotection with lithium naphthalenide finally yielded hydrocarbon [(±)-]**406** (mixture of three isomers). The closed-shell 40 π-system of the latter was found to be chemically stable. Treatment of [(±)-]**406** with potassium hydride, followed by exposure to molecular oxygen, afforded triepoxydiol (±)-**407**, which gave crystals suitable for X-ray analysis. Whereas the double bonds at the edge of the cyclophenacene belt are short (1.36(2) and 1.37(2) Å), bond lengths in the equatorial region are quite similar (1.43(1) and 1.40(2) Å). Computed nucleus-independent chemical shifts (NICS),[146,821] which are a useful measure for the magnetic shielding by a ring current, support the aromatic character of the belt-shaped π-system of a model compound in which all organic residues have been replaced by H.[819] The peroxygenated pole of (±)-**407** corresponds to diepoxyfullerenol **389** (Figure 68) isolated by Taylor and coworkers from the reaction of $C_{60}Cl_6$ with an excess of MeLi.[808] The noninherently chiral addition pattern of (±)-**407** is related to differences in the addends at the polar pentagons. As to the precursors [(±)-]**405** and [(±)-]**406**, possible chirality depends on the considered isomers, in particular on the relative positions of the two addends H and

Scheme 37. Realization of the "Cyclopentadiene Addition Mode" at Two Poles of C_{60}[819,820] [a]



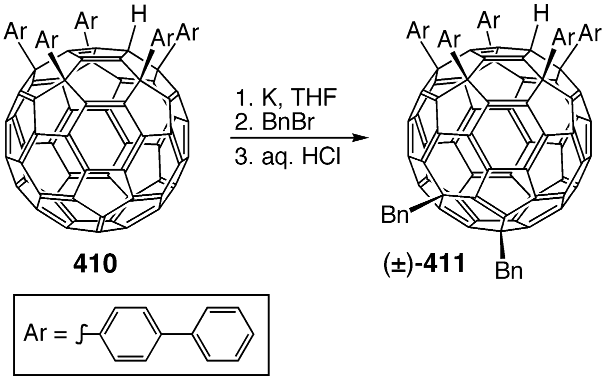
[a] The residual fullerene chromophore is a [10]cyclophenacene belt marked in bold in structure [(±)-]**405**.[343] Compounds [(±)-]**405** and [(±)-]**406** consist of three isomers each, which can be designated as "six o'clock" (achiral), "one o'clock", and "four o'clock" (both with an inherently chiral addition pattern). As to (±)-**407**, its functionalization pattern is (noninherently) chiral, regardless of the relative orientation of the polar pentagons. decakis-adduct (±)-**408** (mixture of five regioisomers) and dodecakis-adduct [(±)-]**409** (mixture of 13 regioisomers) are byproducts of the formation of [(±)-]**405**. They result from partial and complete implementation, respectively, of the "cyclopentadiene addition mode" at the second type of pentaradialene substructure in **404**.

CN: either they define an achiral addition pattern (both addends are bisected by a mirror plane as in the structures shown in Scheme 37; considering a projection along the pseudo-C_5-axis of the functionalized cage, this arrangement may be termed “six o’clock” addition pattern, in analogy to the “twelve o’clock”, “two o’clock”, and “five o’clock” patterns of C_{70}, see section 5.6 and Figure 46), or the addends define an inherently chiral functionalization pattern (the corresponding arrangements can be specified as “one o’clock” and “four o’clock” patterns; the different “times” in comparison to C_{70} result from the fact that the polar pentagons in C_{60} are staggered and not eclipsed).

Side products isolated from the preparation of [(±)-]**405** were the adducts (±)-**408** and [(±)-]**409** (Scheme 37), the latter (constitutional isomer of [(±)-]**405**) being also directly available from the former. The new yellow and luminescent compounds (±)-**408** (5 regioisomers) and [(±)-]**409** (13 regioisomers) result from partial and complete phenylation, respectively, of the second type of intact pentaradialene substructure of the starting material [(±)-]**405**.[820] In the case of [(±)-]**409** with its two fully functionalized pentaradialene units, the isomer in which the cyano group and the hydrogen atom lie in a plane (mirror plane) bisecting both pentaradialenes is achiral, whereas both inherently and noninherently chiral patterns are possible for the remaining isomers. On the other hand, the five regioisomers of the less highly functionalized (±)-**408** have an inherently chiral addition pattern. It should also be mentioned that deprotonation of the cage-bonded H-atoms may result in a raise of molecular symmetry, and a number of X-ray crystal structures of metal complexes as well as of metal-free compounds have substantiated structural assignments in this area of fullerene chemistry.[820]

Three-electron reduction of pentakis(biphenyl) derivative **410** (Scheme 38) with metallic potassium gave a black-green trianion $[K^+(THF)_n]_3[C_{60}Ar_5]^{3-}$.[822] Treatment of the latter with 3.5 equiv of benzyl bromide caused the solution to turn dark red immediately, and protonation with aq HCl afforded the doubly alkylated product (±)-**411**, which has an inherently chiral addition pattern, regardless of the five possible locations for the fullerene-bonded hydrogen. Structural elucidation was greatly facilitated by a deprotonation/palladation sequence affording a single C_1-symmetric regioisomer of the complex $[Pd\{\eta^5\text{-}C_{60}(\text{biphenylyl})_5Bn_2\}\{\eta^3\text{-}(2\text{-methylallyl})\}]$. Treatment of (±)-**411** with BnMgCl, on the other hand, gave an addition-pattern analogue of (±)-**408** (Scheme 37), which could be deprotonated in two steps with KH to the C_s-symmetric cyclopentadienyl/indenyl-type dianion.[822]

Scheme 38. Double Benzylation of 410 via the Intermediacy of the Trianionic Species $[K^+(thf)_n]_3[C_{60}Ar_5]^{3-}$ [822]



Mixtures of isomers have been observed for complexes of the type $[M(\eta^2\text{-}C_{60}Ar_5H)(PPh_3)_2]$ (M = Pd, Pt), prepared under thermodynamic conditions from the corresponding fullerene hexakis-adducts $C_{60}Ar_5H$ and $[M(PPh_3)_4]$.[823] The addition pattern of all chiral regioisomers is inherently chiral.

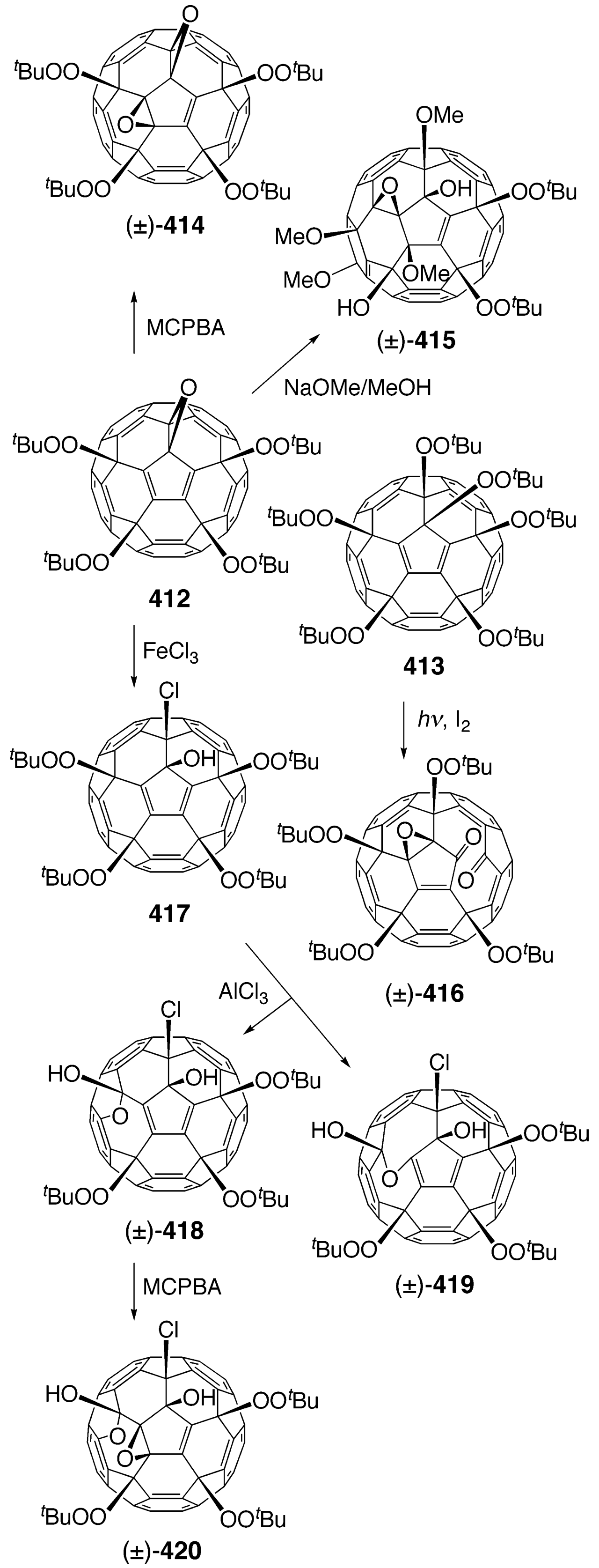
6.9.3. Addition of tert-Butylperoxy Radicals to C_{60}

Fullerenes react easily with a large variety of radicals to form mono-adducts or multiadducts (see also section 6.1).[18,723,824] Multiaddition of radicals to C_{60} preferentially follows the “cyclopentadiene mode” characterized by stabilized allyl- and cyclopentadienyl-type radicals at the tris- and pentakis-adduct stage, respectively. This addition mode is further promoted by the removal of an unfavorable intrapentagonal fullerene double bond on the transition from bis- to tris- and from tetrakis- to pentakis-adduct, as well as by the reduced steric interference between addends in a 1,4-arrangement. The addition of *tert*-butylperoxy radicals to buckminsterfullerene and follow-up reactions were extensively investigated by Gan, Zhang, Chen, and co-workers.[825,826] The broad variety of identified products includes achiral structures, as well as molecules with an inherently or a noninherently chiral addition pattern, and also [60]-fullerene derivatives with a modified core.

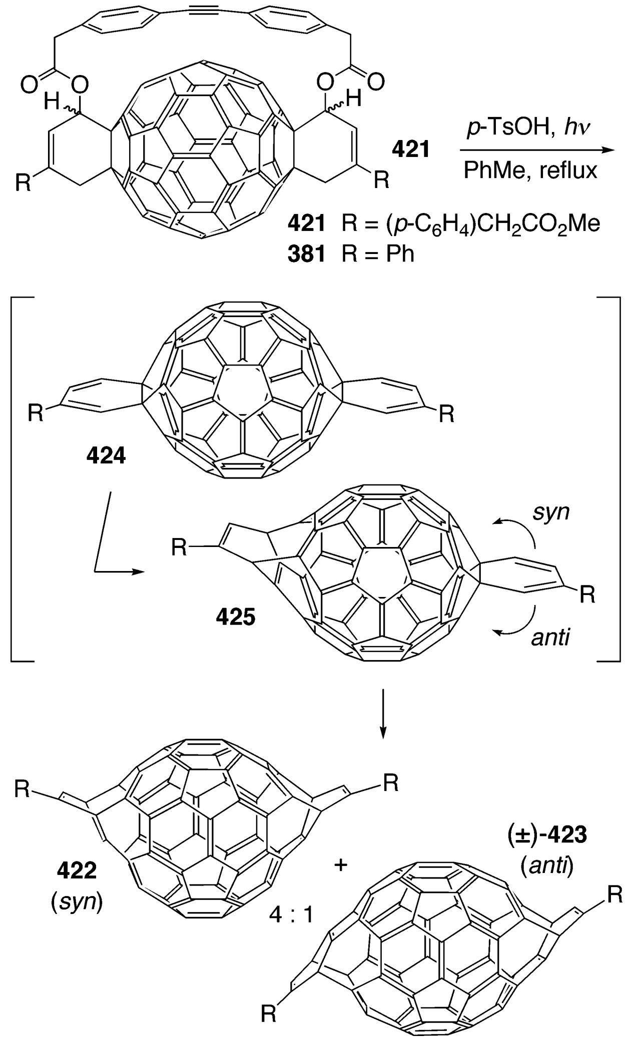
Achiral adducts **412** and **413** (Scheme 39) were the main products of the reaction between C_{60} and *tert*-butyl hydroperoxide, catalyzed by $Ru(PPh_3)_3Cl_2$ and $(NH_4)_2Ce(NO_3)_6$ (CAN), respectively, in the dark.[825] A key factor determining the product selectivity appears to be the concentration of *tert*-butylperoxy radicals, which can vary as a function of the used catalyst: high levels lead to efficient trapping of the fullerene radical intermediates before O−O bond breakage takes place under formation of an epoxy bridge. Treatment of **412** with MCPBA afforded diepoxide (±)-**414** with a noninherently chiral addition pattern, which is isomorphous with that of epoxide (±)-**388**[801,807] (Figure 68). As opposed to acid-catalyzed oxirane ring opening, the nucleophilic addition of NaOMe in MeOH to a compound such as **412** is a complex reaction leading not only to epoxide ring opening but also to attack of carbanionic fullerene intermediates at the peroxy functions under generation of new epoxy structures. One of the products isolated from this reaction is (±)-**415**, which provided crystals suitable for X-ray analysis.[825] Irradiation of **413** by visible light in the presence of iodine afforded a C_1-symmetric cage-opened compound, proposed to have structure (±)-**416** and to result from cleavage of a dioxetane intermediate. Such a step is reminiscent of the first fullerene bond scission reported by Wudl and co-workers (section 4.9 and Scheme 15).[470]

Treatment of **412** with anhydrous $FeCl_3$ in benzene cleanly afforded chlorohydrin **417**.[826] Exposure of the latter to the Lewis acid $AlCl_3$ led to heterolysis of a peroxy group, and a subsequent rearrangement, possibly related to the key step of the Hock reaction, afforded oxahomo[60]fullerene derivatives (±)-**418** and (±)-**419**. In pure dichloromethane, (±)-**418** with the oxygen atom inserted in a 5−6 bond is the main product of this reaction. Addition of diethyl ether reverses the regioselectivity in favor of (±)-**419** having the homo atom inserted in a 6−6 bond. Interestingly, the latter compound is inert toward reaction with MCPBA, but in (±)-**418**, one of the “cyclopentadiene” double bonds is epoxidized by the peracid, leading to (±)-**420**, which has been charac-

Scheme 39. Products Resulting from "Cyclopentadiene Mode" Addition of *tert*-Butylperoxy Radicals to C_{60} (412 and 413) and Transformation into Further Oxygenated Derivatives with Complex Functionalization Patterns[825,826]



Scheme 40. Regioselective Synthesis of Tetrahomo[60]fullerenes 422 and (±)-423,[481,483] **the Latter Structure Displaying a Noninherently Chiral Substitution Pattern**



terized by X-ray crystallography. It reveals intermolecular hydrogen bonding between the hemiacetal-type OH group and a peroxy function of a neighboring molecule, as well as intramolecular hydrogen bonding between the second OH group of the molecule and the closest peroxy addend.[826]

6.10. Substituted Tetrahomo[60]fullerene

The simplest ring enlargement in a fullerene, without creating a real orifice in the cage structure, consists of the insertion of an extra atom (group) into a formal single bond of the fullerene under generation of a homofullerene. Chiral structures can result from insertion of atoms or groups into appropriately located bonds of the parent fullerene. In addition and as opposed to fullerene core atoms, homo carbon atoms are tetracoordinate, thereby offering further possibilities for the generation of chiral structures. Bis-adduct **421** (Scheme 40) was obtained next to the corresponding *trans*-2 regioisomer in the Diels−Alder addition to C_{60} of a bisdiene designed to target the *trans*-1 addition pattern and generated in situ by cycloreversion of the cyclobutene moieties of an appropriate precursor.[483,790] Acid-catalyzed removal of the tolane−diacetic acid tether under irradiation afforded the two constitutionally isomeric tetrahomofullerenes **422** and (±)-**423** (ratio 4:1) in which homoconjugative bridges have been inserted into four 6−5 bonds of the fullerene.[481,483] Whereas C_s-symmetric **422** is achiral, C_2-symmetric (±)-**423** represents a structurally modified fullerene with a noninherently chiral substitution pattern. In fact, the chirality is due neither to the integration of the homo atoms into the cage nor to their pairwise interconnection by etheno bridges, but to the presence of different substituents (H and (p-C_6H_4)CH_2CO_2-Me) in the latter or, in other words, different substitution of the two homo atoms in each hemisphere. The one-pot multistep reaction proceeds by a sequence of intramolecular, photochemically promoted [4 + 4] and retro-[2 + 2 + 2] rearrangements of the intermediately formed dibenzofullerenes **424** and **425**.[480]

7. C_{70} Derivatives with a Noninherently Chiral Functionalization Pattern

In C_{70}, all additions of C_s-symmetric addends across a bond that is perpendicular to the C_5-symmetry axis of the parent fullerene lead to noninherently chiral functionalization patterns. Taking into account bond reactivities, the C(7)−C(22) bond is the most important to be considered in this context (see Figure 69).[4,16,21]

Some C_{70} derivatives with a noninherently chiral addition pattern, for example, [Ir(CO)Cl$(PPh_3)_2$(η^2-C_{70}O)]-isomer (±)-**270** (Figure 49) or pyrazolo[70]fullerene (±)-**224** and triazolo[70]fullerene (±)-**231** (Scheme 18), have already been discussed in the context of chemically related compounds with an inherently chiral functionalization pattern. Also, it may be worth mentioning that no derivatives with a noninherently chiral addition pattern are known so far of the fullerenes beyond C_{70}, the chemistry of which is still hardly explored (cf. sections 3.3.3 and 3.4).[16,18,21]

7.1. C(7)−C(22)-Adducts of C_{70}

Independent studies by Meier et al.[827] and Irngartinger et al.[828] have shown that isonitrile oxides add to the same bonds (C(8)−C(25) and C(7)−C(22), see Figure 69) of C_{70} as diazomethane or alkyl azides (cf. section 5.4 and Figure 49), albeit with lower regioselectivity. Thus, the addition of 2,4,6-trimethoxybenzonitrile oxide across C(8)−C(25) gave rise to similar amounts of two C_s-symmetric constitutional isomers that can be distinguished by the orientation of the CNO group (**426** and **427**, Figure 69), whereas the C(7)−C(22)-adduct (±)-**428** is a racemic mixture of C_1-symmetric enantiomers with a noninherently chiral functionalization pattern. Similarly, trimethoxystyryl-substituted isoxazolo[70]fullerenes **429**, **430**, and (±)-**431** were obtained by addition of the vinylogous isonitrile oxide to C_{70}.[829] While the first reduction potentials of the latter three regioisomers do not differ significantly from each other and from that of C_{70}, they exhibit clear differences in their UV/vis absorption and fluorescence spectra.

The same types of regioisomers (**432**, **433**, and (±)-**434**) resulted from [3 + 2] cycloaddition to C_{70} of a dipolar trimethylenemethane derivative[830] generated by thermolytic ring opening of a methylidenecyclopropanone acetal.[831] Rearrangement of the primary adducts and hydrolysis of the intermediates yielded a pair of enantiomers with a stereogenic center in the addend ((±)-**435**),[832] together with a pair of achiral *cis*/*trans* isomers (**436** and **437**; *cis* and *trans* with respect to the fullerene-fused cyclopentane ring).

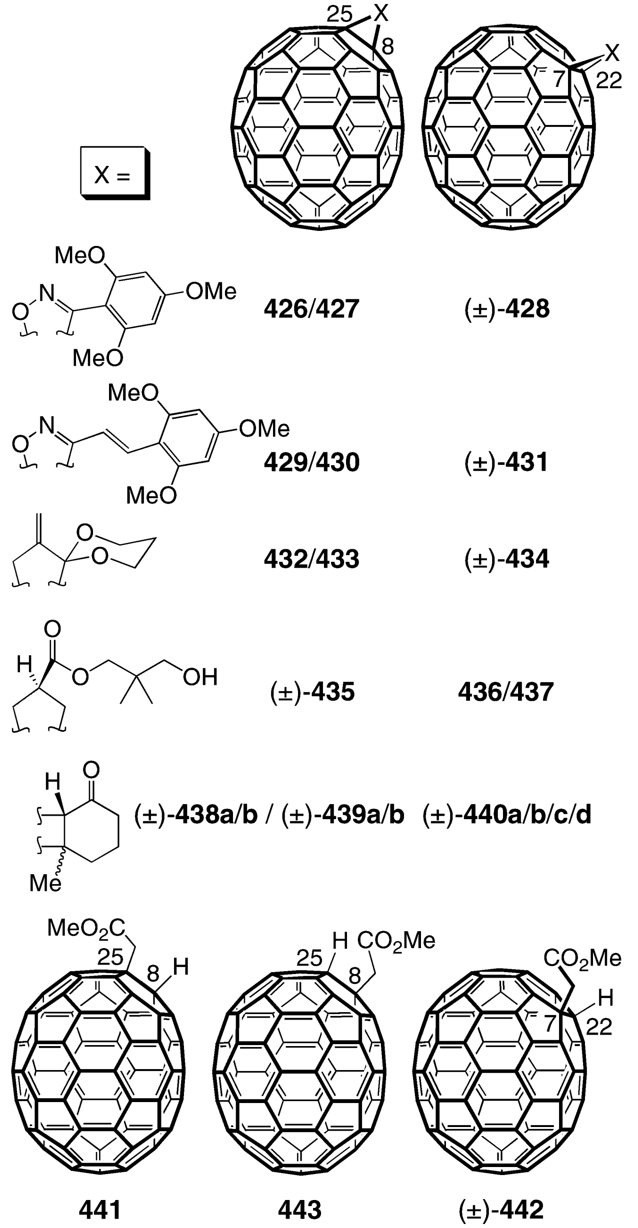


Figure 69. C_{70} adducts with a noninherently chiral functionalization pattern resulting from addition of C_s-symmetric addends across C(7)−C(22). Also shown are the C(8)−C(25)-adducts formed in the same syntheses.

α,β-Unsaturated ketones can be added to fullerenes in a photochemical reaction that is likely to involve the enones in their triplet excited state and the carbon cages in their ground state and to proceed via triplet 1,4-biradical intermediates.[833] The compounds added to C_{60} include cyclohex-2-enone,[833,834] substituted and anellated cyclohex-2-enones,[834−836] and cyclohept-2-enone.[833] Diastereoisomeric adducts with *cis*- and *trans*-fused rings could be distinguished in a number of cases by ^{3}He NMR spectroscopy of the corresponding noble gas incarceranes.[134,833] It is interesting to note that the resolution, on a chiral (*S*,*S*)-Whelk-O stationary phase, of the *cis*- and *trans* racemates obtained by addition of 3-methylcyclohex-2-enone to C_{60} was the first chromatographic separation of enantiomeric fullerene derivatives.[835]

Addition of the same enone to C_{70} and to i^3HeC_{70} afforded eight different products, taking into account constitutional isomers and diastereoisomers ((±)-**438a**/**b**−(±)-**440a**/**b**/**c**/**d**, Figure 69).[837] An interesting analytical tool, besides ^{1}H, ^{13}C, and ^{3}He NMR spectroscopy, was the acid-catalyzed isomerization of the *trans*-fused cyclohexanones to the more stable *cis*-compounds, which allowed a correlation of epimeric products and, at the same time, reduced the number of species in the product mixture. Separation and spectroscopic analysis finally led to the following conclusions: addition of 3-methylcyclohex-2-enone to the bond C(8)−C(25) affords two constitutional isomers (the carbonyl group can point toward either the pole or the equator ((±)-**438a/b** and (±)-**439a/b**), each of which is composed of two diastereoisomeric pairs of enantiomers (a *cis* and a *trans* racemate [*cis* and *trans* with respect to the fusion of six- and four-membered ring]). Addition also takes place at the C(7)−C(22) bond, which leads to four diastereoisomers characterized by *cis*/*trans*-relationships with respect to the substituents of the newly formed cyclobutane ring ((±)-**440a/b/c/d**−C_{70}-pole, Me-group, and methine-H-atom *cis*; C_{70}-pole and Me-group *cis*; C_{70}-pole and methine-H-atom *cis*; C_{70}-pole and cyclohexanone unit *cis*). Whereas the former addition pattern (C(8)−C(25)) is achiral and the stereogenic centers of the corresponding products reside entirely in the addends, the latter (C(7)−C(22)) is noninherently chiral due to the unsymmetric nature of the fused six-membered ring, and each of the four mentioned diastereoisomers occurs as a racemate. Spectroscopic analysis showed a rather strong bias with respect to the different addition modes, leading to a product distribution (±)-**438a/b**/**440a/b/c/d**/(±)-**439a/b** ≈ 66:34: <1.[837]

Wang and Meier developed a simple solution-phase procedure for the monoalkylation of C_{60} and C_{70}, proceeding through electron-transfer reaction between the fullerene and zinc in the presence of an alkyl halide.[627] Alkylation of C_{70} under these conditions with methyl 2-bromoacetate afforded a ca. 9:1 mixture of methyl 8,25-dihydro(C_{70}-D_{5h})[5,6]-fulleren-25-yl acetate (**441**) and methyl 7,22-dihydro(C_{70}-D_{5h})[5,6]fulleren-7-yl acetate ((±)-**442**). Interestingly, the regioisomeric adduct methyl 8,25-dihydro(C_{70}-D_{5h})[5,6]-fulleren-8-yl acetate (**443**) was absent from the product mixture. On the other hand, **443** was the only product (besides a trace of **441**) when C_{70}^{2-}, generated by deprotonation of 8,25-dihydro(C_{70}-D_{5h})[5,6]fullerene with tetrabutylammonium hydroxide in PhCN, was alkylated with methyl 2-bromoacetate.[626] The isomers **441** and **443** can be distinguished by the ^{1}H NMR downfield-shift experienced by protons in the polar region of the fullerene. Substitution of bromoacetate by benzyl bromide resulted in rapid dibenzylation (formation of (±)-**216**, Figure 45, as a major isomer), unless the amount of base is carefully controlled, in which case monobenzylation occurs preferentially at C(8).

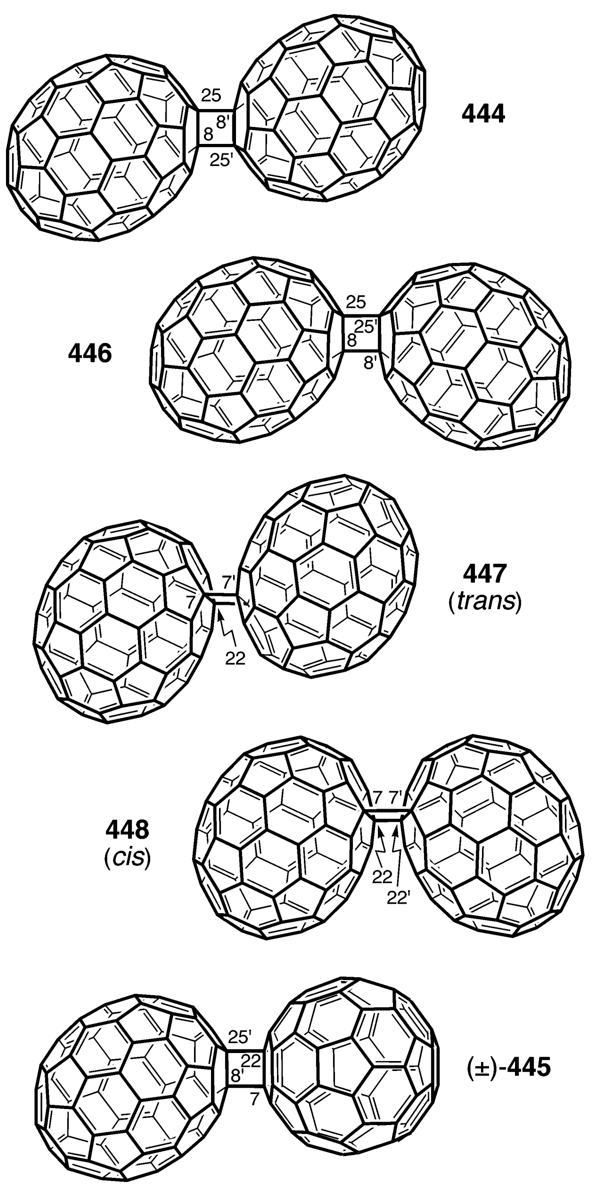


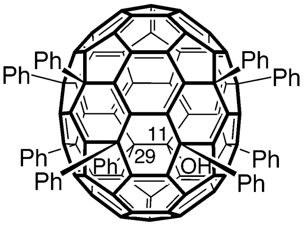
Figure 70. The five cyclobutadi(C_{70}-D_{5h})[5,6]fullerenes that result from formal [2 + 2] dimerization involving the reactive bonds C(8)−C(25) and C(7)−C(22).[838] Dimer (±)-**445** represents the only chiral structure and its C(7)−C(22)-fused fullerene unit displays a noninherently chiral addition pattern.

7.2. Cyclobutadi(C_{70}-D_{5h})[5,6]fullerenes

By grinding C_{70} together with K_2CO_3 in a mortar for 15 min and subsequent multistage HPL-chromatographic separation, Shinohara and co-workers were able to prepare and isolate five regioisomeric cyclobutadi(C_{70}-D_{5h})[5,6]fullerenes, **444**−(±)-**448** (Figure 70) in a 0.5:0.2:0.8:1.0:0.5 ratio.[838] They represent all possible $(C_{70})_2$ combinations that result from formal [2 + 2] dimerization involving the reactive bonds C(8)−C(25) and C(7)−C(22): C_{2h}-symmetric **444** (interfullerene bonds C(8)−C(25′) and C(25)−C(8′)), C_{2v}-symmetric **446** (interfullerene bonds C(8)−C(8′) and C(25)−C(25′), C_{2h}-symmetric **447** (interfullerene bonds C(7)−C(7′) and C(22)−C(22′), *trans*-configured cyclobutane ring), C_{2v}-symmetric **448** (interfullerene bonds C(7)−C(7′) and C(22)−C(22′), *cis*-configured cyclobutane ring), and C_1-symmetric (±)-**445** (interfullerene bonds C(7)−C(8′) and C(22)−C(25′)). In the latter dimer, the C(7)−C(22)-functionalized fullerene has a noninherently chiral functionalization pattern because the connected C-atoms of the second fullerene, C(8′) and C(25′), are heterotopic. Application of the same procedure to C_{60} and to an equimolar mixture of C_{60} and C_{70} afforded the homodimer $(C_{60})_2$ and the heterodimer [(C_{60})-(C_{70})], respectively. The latter was accompanied by the former but not by C_{140}. [2 + 2] Dimerization of C_{70} was also brought about by pressure treatment of the fullerene (1 GPa, 200 °C, 30 min), and Lebedkin and co-workers proposed the C_{2h}-symmetric structure **444** for the sole isomer isolated from their material.[666]

7.3. Furanodi(C_{70}-D_{5h})[5,6]fullerenes

Additional arrangements are possible if two molecules of C_{70} are fused through the C(8)−C(25) or C(7)−C(22) bonds not to a D_{4h}-symmetric cyclobutane (vide supra) but to a C_{2v}-symmetric furan ring. Three out of seven possible $C_{140}O$ regioisomers were isolated and characterized by Tohji and co-workers from the material obtained by hydrothermal



(±)-283

Figure 71. Decakis-adduct of C_{70} with a noninherently chiral functionalization pattern resulting from unsymmetric addition of OH and Ph across the 6−5 bond C(11)−C(29).[688]

treatment (aq NaOH, 100 °C, 12 h) of mixed $C_{70}/C_{70}O$ powder.[839] Based on ^{13}C NMR spectroscopy (symmetry information) in combination with calculated Mulliken charges for the starting epoxide (reactivity against nucleophiles), the structures furano[2″,3″:8,25;4″,5″:25′,8′]di(C_{70}-D_{5h})[5,6]-fullerene and furano[2″,3″:8,25;4″,5″:8′,25′]di(C_{70}-D_{5h})[5,6]-fullerene (for the numbering of C_{70}, see Figures 3 and 70) were proposed for one out of two C_{2v}-symmetric and one out of two C_s-symmetric regioisomers, respectively. As to the third isomer (one out of two C_1-symmetric structures), the assignment proved to be more difficult in the absence of a ^{13}C NMR spectrum with good signal-to-noise ratio. In any case, one fullerene moiety should be fused to the heterocycle through its C(7)−C(22) bond and have a noninherently chiral addition pattern in which one of the atoms in question is directly connected to the second fullerene and the other one to the intercage oxygen bridge.

7.4. Decakis-Adduct of C_{70}

Fullerenol $C_{70}Ph_9OH$ ((±)-**283**, Figure 71) is a byproduct of the Friedel−Crafts alkylation of benzene with $C_{70}Cl_{10}$ (cf. section 5.13), affording $C_{70}Ph_{10}$ as main product via the intermediacy of $C_{70}Ph_8$.[688] The noninherently chiral functionalization pattern of the C_1-symmetric (±)-**283** can be ascribed to the functionalization of the bond C(11)−C(29) by two different residues (OH and Ph). In $C_{70}Ph_8$, this site remains an intact 6−5 double bond,[674] whereas its functionalization by formal addition of Cl and Ph leads to the C_s-symmetric $C_{70}Cl_{10}$ [630] and $C_{70}Ph_{10}$,[674] respectively.

8. Concluding Remarks

Fifteen years after the isolation and characterization of the first chiral fullerene, C_{76}-D_2, and a year less after the preparation of the first enantiomerically pure derivative of C_{60} in the form of a spiro-linked C-glycoside, the number of reported chiral fullerene derivatives and their diversity is gargantuan. This is true for compounds in which the chiral elements are exclusively located in the addends (not discussed in the present review) and also for fullerene derivatives with a chiral functionalization pattern, a fact that is not surprising if one thinks of a fullerene as a “superatom” to which a large number of addends can be attached with a great variety of bonding geometries. The structural elucidation of such complex fullerene derivatives is not easy if different addend arrangements can lead to given molecular symmetry, C_1-symmetry in particular. Invaluable analytical tools in such cases are 2D NMR techniques and X-ray crystallography, which have allowed the elucidation of an impressive number of intricate structures since 2000 when fullerene chirality was comprehensively reviewed the last time. Significant progress was achieved in the areas of halogenofullerenes (fluorofullerenes, in particular), hydrofullerenes, transition metal cluster complexes with fullerene ligands, cage-opened fullerenes, and reactions related to the so-called “cyclopentadiene addition mode”. Impressive accomplishments were also made in the field of endohedral metallofullerenes where a considerable number of compounds could be isolated and structurally elucidated despite the notorious experimental difficulties concerning the stability of the compounds under ambient conditions and their solubility or the fact that the larger cages can in principle occur as a number of different isomers, some even having the same symmetry. Also, the first pure exhohedrally functionalized endohedral metallofullerenes could be isolated and their structures unambiguously identified. As to the empty higher fullerenes, only a few new structures have been found in recent years, and the exploration of the chemistry of fullerenes such as C_{76}, C_{78}, and C_{84} stagnated due to the still laborious production and isolation of the pure allotropes. Hopefully, more selective manufacturing procedures and improved separation protocols will eliminate this obstacle in the future.

It has to be mentioned also that, contrasting the abundance of fascinating chiral structures in fullerene chemistry, relatively few studies have dealt explicitly with chirality in the form of stereoselective syntheses, the isolation of pure enantiomers, or the investigation of chiroptical properties. Certain chiral addition patterns of C_{60} and C_{70}, for example, inherently chiral patterns with three and more addends and most noninherently chiral patterns, need further and more systematic exploration, and truly templated stereoselective synthesis is still in its infancy. Regarding application-related work, few investigations have been carried out on enantiomerically pure material so far.

Finally, the assignment of absolute configurations to isolated enantiomers of chiral fullerenes or fullerene derivatives with a chiral functionalization pattern has become much easier in recent years thanks to methodological improvements in the calculation of CD spectra and also to the considerable body of experimental data available for C_{60} and C_{70} derivatives with two and, in a few cases, three addends.

9. Acknowledgments

The authors thank their co-workers, whose names appear in the references, for their valuable contributions. Continuing support of fullerene research by the Swiss National Science Foundation is gratefully acknowledged.

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(840) Although the parenthetic subscript “6” is part of the full IUPAC name of C_{70}-$D_{5h(6)}$ (it serves to distinguish this constitutional isomer from a conceivable one that has been described in the literature),[29] it will generally be omitted in this review because only a single isomer of C_{70} has been observed and isolated so far.

CR0505371