[2] L. Pasteur, "*Researches on the Molecular Asymmetry (sic) of Natural Organic Products*" ("Recherches sur la Dissymmetric Moleculaire des Produits Organiques Naturels") *Alembic Club Reprint*, *No. 14* (Ed.: W. F. Clay), Edinburgh, UK, **1860**.

[3] A monolayer film on a mica plate shows a two-dimensional conglomerate: C. J. Echardt, N. M. Peachy, D. R. Swanson, J. M. Takacs, M. A. Khan, X. Gong, J.-H. Kim, J. Wang, R. A. Uphaus, *Nature* **1993**, *362*, 614–616; P. Nassoy, M. Goldmann, O. Bouloussa, F. Rondelez, *Phys. Rev. Lett.* **1995**, *75*, 457–460; H. Möhwald, A. Dietrich, C. Bohm, G. Brezenski, *Mol. Membr. Biol.* **1995**, *12*, 29–38. A similar two-dimensional conglomerate has been observed with a racemic liquid crystalline substance, however, on a crystalline graphite surface rather than in a fluid smectic phase: F. Stevens, D. J. Dyer, D. M. Walba, *Angew. Chem.* **1996**, *108*, 955–957; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 900–901. Leading references on spontaneous separation of enantiomers in crystals: I. Kuzmenko, I. Weissbuch, E. Gurovich, L. Leiserowitz, M. Lahav, *Chirality* **1998**, *10*, 415; I. Weissbuch, M. Berfeld, W. Bouwman, K. Kjaer, J. Als-Nielsen, M. Lahav, L. Leiserowitz, *J. Am. Chem. Soc.* **1997**, *119*, 933–942.

[4] R. Noyori, M. Kitamura, *Angew. Chem.* **1991**, *103*, 34–55; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 49–69.

[5] E. L. Eliel, S. H. Wilen, *Stereochemistry of Organic Compounds*, Wiley, New York, **1994**, chap. 6.

[6] R. B. Meyer, L. Lieber, L. Strzelcki, P. Keller, *J. Phys.* **1975**, *36*, L69–L71.

[7] A. D. L. Chandani, E. Gorecka, Y. Ouchi, H. Takezoe, A. Fukuda, *Jpn. J. Appl. Phys.* **1989**, *28*, L1265–L1268.

[8] A. D. L. Chandani, T. Hagiwara, Y. Suzuki, Y. Ouchi, H. Takezoe, A. Fukuda, *Jpn. J. Appl. Phys.* **1988**, *27*, L729–L732.

[9] Y. Suzuki, T. Hagiwara, I. Kawamura, N. Okamura, T. Kitazume, M. Kakimoto, Y. Imai, Y. Ouchi, H. Takezoe, A. Fukuda, *Liq. Cryst.* **1989**, *6*, 167–174.

[10] A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikawa, H. Takezoe, *J. Mater. Chem.* **1994**, *4*, 997–1016.

[11] K. Mikami, T. Yajima. M. Terada, Y. Suzuki, I. Kobayashi, *Chem. Commun.* **1997**, 57–58.

[12] K. Miyasato, S. Abe, H. Takezoe, A. Fukuda, E. Kuze, *Jpn. J. Appl. Phys.* **1983**, *22*, L661–L663.

[13] E. Gorecka, M. Glogarova, L. Lejeck, H. Sverenyak, *Phys. Rev. Lett.* **1995**, *75*, 4047–4050.

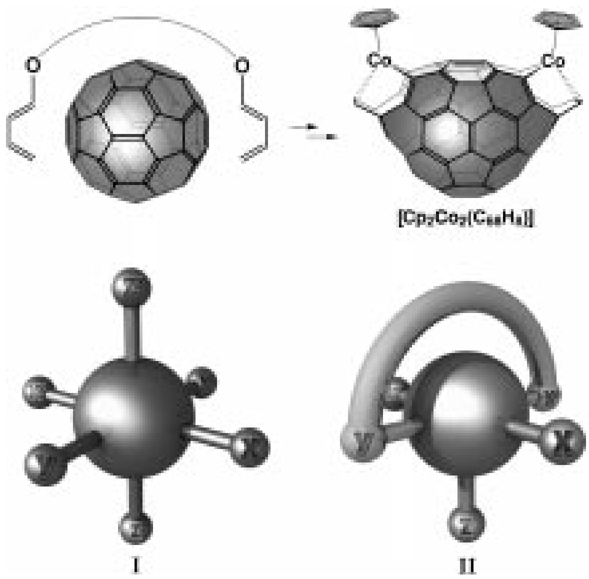
[14] M. Glogarova, E. Gorecka, L. Lejeck, H. Sverenyak, *Mol. Cryst. Liq. Cryst.* **1997**, *301*, 325–336.

[15] K. Mikami, T. Yajima, M. Terada, S. Kawauchi, Y. Suzuki, I. Kobayashi, *Chem. Lett.* **1996**, 861–862.

Towards Sixfold Functionalization of Buckminsterfullerene (C_{60}) at Fully Addressable Octahedral Sites**

Wenyuan Qian and Yves Rubin*

In the context of our fullerene opening strategies,[1] a relatively efficient method of functionalizing the opposite double bonds of C_{60} (*trans*-1 positions) by a twofold Diels–Alder reaction was required as a way to access the bis-cobalt complex $[Cp_2Co_2(C_{68}H_8)]$. Within a broader context we have been interested in the development of selective C_{60}-functionalization reactions that provide access to unusual multifunctional molecules with spatially defined addends.[1–5] Most current methods are confronted with the formation of regioisomeric by-products, coupled with the difficulty of maintaining stereochemical control throughout the addition steps. Hence, methods providing complete control of the degree and regiochemistry of additions on C_{60}, as well as the type of addends, are still needed for the construction of highly organized three-dimensional scaffolds (for example, **I**, where X, X′, Y, Y′, Z, Z′ are all different groups). The method reported here gives rapid access to a variety of multiple adducts in high yields from a tethered *trans*-1 bisadduct **3a** (see Scheme 1). Bisadduct **3a** has temporary directing moieties that address reactants to only three sequential sites of an octahedral scaffold by exploiting steric and electronic effects (**II**, addends X, Z, X′). The trisadducts **5a**, **b** and **13**, and the



---

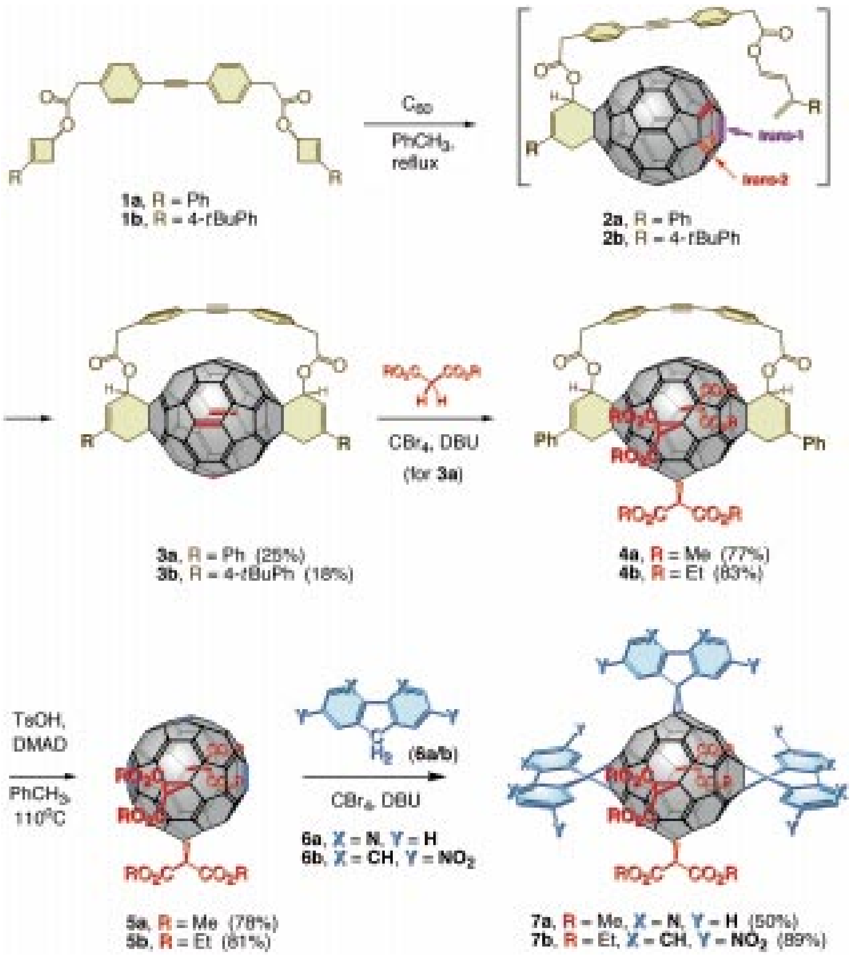
[*] Prof. Y. Rubin, W. Qian
Department of Chemistry and Biochemistry
University of California, Los Angeles
Los Angeles, CA 90095-1569 (USA)
Fax: (+1) 310-206-7649
E-mail: rubin@chem.ucla.edu

[**] This work was supported by a National Science Foundation young investigator award (CHE-9457693).

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

mixed hexaadducts **7a**,**b** with unique and otherwise inaccessible addition patterns can thus be obtained (Schemes 1, 3, and 4).

The selective formation of *trans*-1 bisadducts such as compounds **3a**,**b** has been challenging because this regioisomer is the least likely to form on statistical and electronic grounds.[3b, 4] A remarkable topochemically controlled solid-state disproportionation of the C_{60} monoanthracene adduct to the *trans*-1 bisadduct has allowed selective placement of four malonate moieties around the equator of C_{60}.[5] However, the generality of this method is limited by the anthracene addends and their relatively facile loss under thermal conditions. Recently, a bisaddition with a dibenzocrown ether bismalonate tether has provided access to *trans*-1 bisadducts,[6a] while a similar porphyrin bismalonate gives exclusive *trans*-2 addition.[6b] The approach reported herein provides *trans*-1 Diels–Alder bisadducts **3a**,**b** with relatively good selectivity by using the designed tethered bisdiene **1a** (Scheme 1). For successful formation of these bisadducts, the tether in intermediates **2a**,**b** has to favor the second intramolecular [4+2] cycloaddition at the *trans*-1 position over attack at any nearby double bonds, including the four closely positioned *trans*-2 hydrogen bonds. Under the high temperature conditions necessary for these Diels–Alder reactions (≥100 °C) one has to expect a large number of unproductive rotamers to be significantly populated, which requires a substantial energy difference between the desired and undesired transition states (T.S.).[7]



Scheme 1. Formation of the tris- and hexaadducts **5a**,**b** and **7a**,**b**. DMAD = dimethyl acetylenedicarboxylate.

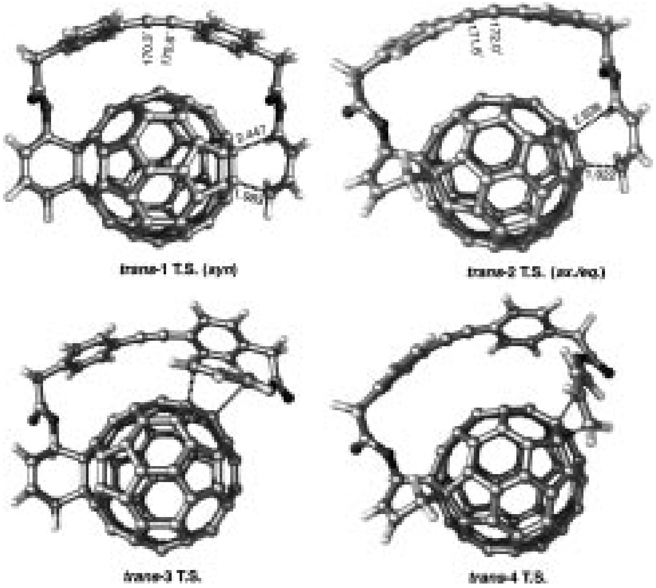
The tether in **1a**, **b** was designed by computational modeling at the AM1 semi-empirical level taking into account its synthetic accessibility.[8] Our initial choice was made by considering approximated T.S. geometries,[9] which favored the *trans*-1 bisadduct by 2.1 kcal mol^{-1}. The fact that the tether is longer than it needs to be to reach the *trans*-1 site was deemed beneficial to avoid those C=C bonds on the "upper" hemisphere of C_{60} that are positioned closer to the first addition site (*e*, *trans*-3, *trans*-4). However, as can be seen from the T.S. geometries in Table 1, this tether lengthening has the effect of significantly bending the alkyne and aromatic moieties for both *trans*-1 and *trans*-2 approaches. The fact that the latter is somewhat less strained constitutes a likely source of lower selectivity by favoring the *trans*-2 approach.

To gain further insight into the selectivity of this reaction fully optimized transition states of the most favorable regio/stereoisomers were obtained. As seen in Table 1 the *trans*-1 product has now a T.S. energy 1.3 kcal mol^{-1} higher than that of the *trans*-2 product. Interestingly, the crude experimental mixture contains a 1:1.5–2 ratio of the *trans*-1 to *trans*-2 regioisomeric diastereomers as found by HPLC,[10] which is in line with these calculations. The *trans*-3, *trans*-4, and *e* regioisomers are not detected experimentally and are found to be 3–10 kcal mol^{-1} higher in energy. Interestingly also is that the relative product energies give similar trends as the T.S. energies and appear to be good predictors of selectivity.[4b]

The tethered biscyclobutene precursors **1a** and **1b** were prepared from the corresponding cyclobutenols and the tethered dicarboxylic acid.[10] The twofold Diels–Alder cycloaddition of **1a** to C_{60} was carried out in toluene under high dilution conditions. Analysis[10] of the crude cyclization mixture by HPLC (hexane/toluene, 30/70) allowed assignments of addition patterns, which showed that the first two main bands contain the expected *rac* and *meso* diastereomers of the bisadduct **3a** in a 1:1 ratio, with both having UV/Vis absorption spectra characteristic of the *trans*-1 bisaddition pattern.[2a, 4c, 10] Four other diastereomers with the *trans*-2 pattern are also present but with no other detectable regioisomers. The least polar *trans-1* bisadduct mixture **3a** was isolated in 25 % yield (up to 0.5 g scale) from the *trans*-2 diastereomeric mixture (~40 %) by flash chromatography (SiO_2, hexane/toluene, 1/4).

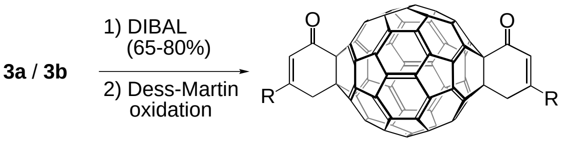
To fully confirm the *trans*-1 regiochemistry of fraction **3a** the two stereocenters were eliminated (Scheme 2). Deprotection with diisobutylaluminum hydride (DIBAL) gave the inseparable diastereomeric diols very cleanly, which were

Table 1. Constrained or fully optimized AM1 geometries and energies for the transition states and products of the second Diels–Alder step (**2c** and **3c**).



	trans-1	*trans*-2	*trans*-3	*trans*-4	*e* (*edge*)
T.S.	961.2[a,b]	959.9[a,b]	968.8[b]	964.1[b]	970.8[b]
	(rel. 0)	(−1.3)	(+7.6)	(+2.9)	(+9.6)
product	902.7	902.1	911.1	903.9	913.8
	(rel. 0)	(−0.6)	(+8.4)	(+1.2)	(+11.1)

[a] Fully optimized T.S. structures. [b] Constrained bond distances of 2.50 Å (proximal diene C atom) and 1.95 Å (distal C atom); these constrains are based on distances obtained from the fully optimized transition state of the 1-formyloxybutadiene monoadduct, and gave practically identical energies in the *trans*-1 and *trans*-2 approaches relative to the fully optimized T.S. energies.



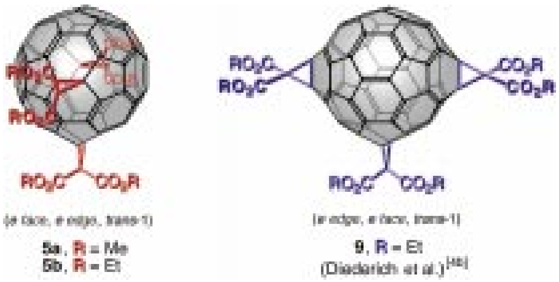
8a, R = Ph (30%)
8b, R = 4-*t*BuPh (91%)

Scheme 2. Increasing the symmetry of the tethered bisadducts **3a** and **3b** by enone formation (**8a**,**b**).

oxidized to the poorly soluble C_{2v}-symmetric bisenone **8a**. For the latter reason the more soluble *tert*-butyl-substituted bisenone **8b** was also prepared by using the above procedures. Its C_{2v} symmetry was confirmed by the presence of 22 signals for sp^2 carbons and 5 for sp^3 carbons in the ^{13}C NMR spectrum, while there are 5 sets of protons in the ^{1}H NMR spectrum.[10]

The *trans*-1 bisadduct **3a** represents a strategically protected octahedral building block (**II**). Not only are the two opposite poles of C_{60} blocked covalently by the cyclohexene addends, but several double bonds around its longitude, including one of the reactive equatorial edge positions (*e-edge*), are noncovalently masked by the tether that spans the two poles. The remaining three *e*-positions are strongly activated toward subsequent nucleophilic additions thanks to the additive directing effects of both *trans*-1 addends.[3–5] However, as will be seen below, each of these three *e*-positions can be addressed exclusively in a sequential manner (*e-face*, *e-edge*, and finally *e′-face*), which primes this system for fully directed hexasubstitutions.

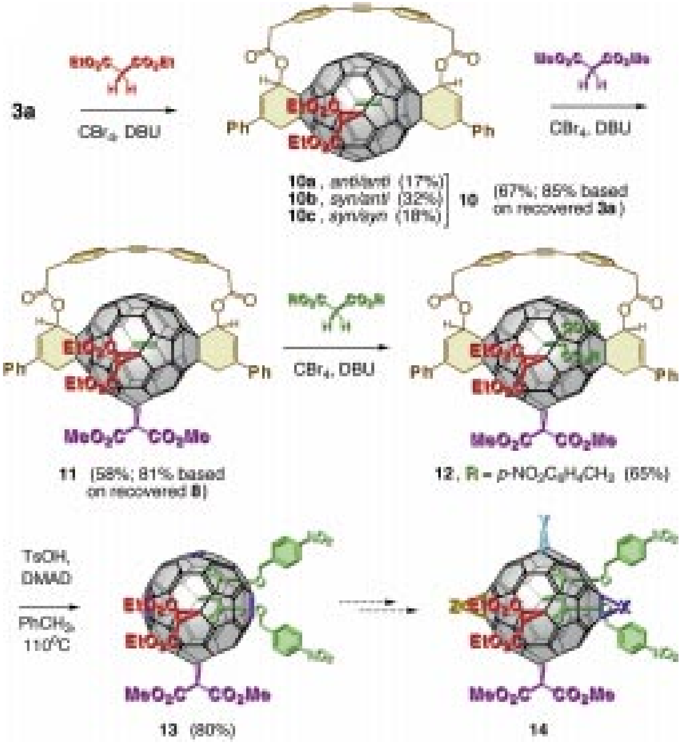
Sequential bromomalonate additions on **3a** allowed a demonstration of the potential of this approach; the full scope of compatible reagents needs to be studied (see Schemes 1, 3, and 4). Both methyl and ethyl esters were used, the former for crucial simplification of the ^{1}H NMR spectra to allow unequivocal structural assignments,[10] and the latter to give products of much higher solubility. The reaction of **3a** with either malonate under in situ bromination conditions (CBr_4, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), toluene, 25 °C)[11] smoothly afforded the mixed pentakisadducts **4a** and **4b** as orange solids (Scheme 1). The trisadducts **5a** and **5b** were obtained by the one-pot elimination/Diels–Alder/retro-Diels–Alder procedure developed in our group ($MeO_2C{-}C{\equiv}C{-}CO_2Me$, $H_3CC_6H_4SO_3$ (TsOH), toluene, reflux)[12] to remove the "masking" moiety on **4a** and **4b**. The C_{2v} symmetry of these two unknown trisadducts (**5a**,**b**) was confirmed by their simple ^{1}H NMR spectra, which displayed three sets of alkyl signals in a 1:1:1 ratio. It is interesting to note that this set of trismalonate regioisomers has a different topology (*e-face*, *e-edge*, *trans*-1) over that obtained by Diederich et al. (**9**, *e-edge*, *e-face*, *trans*-1; Scheme 3).[4b] Both products (**5a**, **b** and **9**) result from trisaddition by the same addends onto three out of the four *e*-positions along the equatorial belt of C_{60}, and neither of them can be obtained by trivial methods.



Scheme 3. Topological isomerism between the trisadducts **5a**,**b** and **9**.

The facile accessibility of trisadducts **5a** and **5b** offered an opportunity to generate unprecedented heterohexaadducts by attaching different sets of addends to the remaining three *e*-positions of the carbon cage (Scheme 1). The rigid addends 4,5-diazafluorene (**6a**) and 2,7-dinitrofluorene (**6b**) were of interest either for their metal complexing ability,[13] potentially leading to 3-dimensional nanostructures,[14] or their electron-withdrawing homoconjugative effect on the fullerene π system.[15] Both compounds added surprisingly fast and with exquisite selectivity under the in situ bromination/nucleophilic addition conditions used for the malonates.[11] Indeed, the mixed hexaadducts **7a** or **7b** were formed almost instantaneously at 25 °C when trisadducts **5a** or **5b** were treated with 3.3 equivalents of 4,5-diazafluorene (**6a**) or 2,7-dinitrofluorene (**6b**) in the presence of CBr_4 (3.3 equiv) and DBU (6.7 equiv) in toluene. Both 4,5-diazafluorene and 2,7-dinitrofluorene offer higher versatility than the corresponding diazomethanes[15] and follow the characteristic selectivity of malonate additions. Furthermore, as addends, they confer unusually bright visible fluorescence (orange-red) to the fullerene core, a property recently found for two hexapyrrolidines.[2a]

In the formation of trisadducts **4a** or **4b** it was initially observed that each addition step proceeds in a very clean, sequential manner (spot-to-spot conversion by TLC and ^{1}H NMR spectroscopy on the crude products). Increasing the proportions of reagents gave only the next higher adduct up to the trisadducts **4a** or **4b** without any other regioisomers. Forcing conditions did not give a tetramalonate product, which shows that the tether bridge is held rigidly in place by the two cyclohexene rings and does not allow reaction at the fourth equatorial or any other position. The reactions can be carried out with less than one equivalent of malonate to minimize the formation of the next higher adduct, and allows the easy recovery of the starting materials. Application of these observations enabled the formation of a fully differentiated trisadduct (**13**), which was obtained by stepwise additions of diethyl, dimethyl, and finally bis(*p*-nitrobenzyl)-malonates to the bridged bisadduct **3a** (Scheme 4).



Scheme 4. Sequential formation of the trisadduct **13**.

First, monoaddition of a diethyl bromomalonate moiety to **3a** gave exclusively one regioisomer (**10**). The latter consisted of the three possible diastereomers **10a** – **c**, which were in this instance easily separated by column chromatography (CH_2Cl_2, SiO_2). The ^{1}H and ^{13}C NMR spectra of **10a** – **c**[10] indicate that they have C_s (**10a**), C_1 (**10b**), and C_s (**10c**) symmetry. The two C_s-symmetric *meso* isomers (**10a**, *anti/anti*; **10c**, *syn/syn*) elute first and last, respectively, and are compatible only with the monoaddition pattern shown in Scheme 4. Their tentative relative stereochemical assignment is based on the fact that **10a** should have the lowest polarity since it has its tethered ester carbonyl groups pointing away from the malonate units (AM1). The C_1 symmetry of **10b** precludes its unequivocal regiochemical assignment at this stage, but as will be seen below it gives compound **13** as the only possible final structure and the addition pattern follows that of **10a** and **10c**. Additionally, the AM1 calculated frontier orbitals of **3a** have the highest LUMO coefficients at the position being attacked in the malonate additions.[10]

The second malonate addition to the main isomer **10b** also proceeded very cleanly to give only the tetrakisadduct **11** besides starting material and a small amount of the next higher adduct. Final addition of the benzylic bromomalonate to **11** gave the pentaadduct **12**, from which removal of the tether afforded the trisadduct **13** as a single isomer in good overall yield. The structure of compound **13** can be deduced directly from its ^{1}H NMR spectrum: with two sets of ethoxy signals, one for the methoxy groups, and two sets of benzylic signals, only structure **13** is possible since the addition pattern is the same as that of **5a** (their UV/Vis spectra are identical).[10]

Preliminary results from the addition of dimethyl malonate indicate (^{1}H NMR) that the fourth most reactive octahedral position of **13** is that indicated by the symmetrically disposed addends X or Z (X or Z = $C(CO_2Me)_2$) in compound **14**, as is expected from the high yield obtained for **11** and other reactivity studies.[3–5, 16] The fifth and sixth additions (X/Y or Y/Z) are unlikely to be regioselective,[3–5] unless steric hindrance or tether-directed additions are used. Following this precept the preparation of isomers having three pairwise addends with topologies similar to those of octahedral metal complexes bearing bidentate ligands (for example, $[Ru(bpy)_3]$, bpy = bipyridine) is currently under way. The potential of such work lies in the construction of various nanosized 3-D superstructures (boxes, cubes, etc.) based on metal complexation of the diazafluorenyl or similar moieties.[13, 14]

Received: March 1, 1999 [Z 13091 IE]
German version: *Angew. Chem.* **1999**, *111*, 2504 – 2508

Keywords: cycloadditions · Diels – Alder reactions · diimines · fullerenes · semiempirical calculations

---

[1] a) Y. Rubin, *Top. Curr. Chem.* **1999**, *199*, 67 – 91; b) Y. Rubin, *Chem. Eur. J.* **1997**, *3*, 1009 – 1016.

[2] a) G. Schick, M. Levitus, L. D. Kvetko, B. A. Johnson, I. Lamparth, R. Lunkwitz, B. Ma, S. I. Khan, M. A. Garcia-Garibay, Y. Rubin, *J. Am. Chem. Soc.* **1999**, *121*, 3246 – 3247; b) Y. Rubin, P. S. Ganapathi, A. Franz, Y.-Z. An, W. Qian, R. Neier, *Chem. Eur. J.* **1999**, *5*, in press.

[3] a) P. J. Fagan, J. C. Calabrese, B. Malone, *J. Am. Chem. Soc.* **1991**, *113*, 9408 – 9409; b) A. Hirsch, I. Lamparth, T. Grösser, H. R. Karfunkel, *J. Am. Chem. Soc.* **1994**, *116*, 9385 – 9386; c) I. Lamparth, A. Herzog, A. Hirsch, *Tetrahedron* **1996**, *52*, 5065 – 5075; d) L. Isaacs, F. Diederich, R. F. Haldimann, *Helv. Chim. Acta* **1997**, *80*, 317 – 342.

[4] a) J. F. Nierengarten, T. Habicher, R. Kessinger, F. Cardullo, F. Diederich, V. Gramlich, J. P. Gisselbrecht, C. Boudon, M. Gross, *Helv. Chim. Acta* **1997**, *80*, 2238 – 2276; b) F. Cardullo, P. Seiler, L. Isaacs, J. F. Nierengarten, R. F. Haldimann, F. Diederich, T. Mordasini-Denti, W. Thiel, C. Boudon, J. P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **1997**, *80*, 343 – 371; c) F. Djojo, A. Herzog, I. Lamparth, F. Hampel, A. Hirsch, *Chem. Eur. J.* **1996**, *2*, 1537 – 1547; d) H. Isobe, H. Tokuyama,

M. Sawamura, E. Nakamura, *J. Org. Chem.* **1997**, *62*, 5034–5041; e) M. Taki, S. Sugita, Y. Nakamura, E. Kasashima, E. Yashima, Y. Okamoto, J. Nishimura, *J. Am. Chem. Soc.* **1997**, *119*, 926–932; f) T. Ishii, K. Nakashima, S. Shinkai, *Chem. Commun.* **1998**, 1047–1048.

[5] a) B. Kräutler, T. Müller, J. Maynollo, K. Gruber, C. Kratky, P. Ochsenbein, D. Schwarzenbach, H. B. Bürgi, *Angew. Chem.* **1996**, *108*, 1294–1296; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1204–1206; b) R. Schwenninger, T. Müller, B. Kräutler, *J. Am. Chem. Soc.* **1997**, *119*, 9317–9318.

[6] a) J. P. Bourgeois, L. Echegoyen, M. Fibbioli, E. Pretsch, F. Diederich, *Angew. Chem.* **1998**, *110*, 2203–2207; *Angew. Chem. Int. Ed.* **1998**, *37*, 2118–2121; b) E. Dietel, A. Hirsch, E. Eichhorn, A. Rieker, S. Hackbarth, B. Roder, *Chem. Commun.* **1998**, 1981–1982.

[7] S. H. Friedman, G. L. Kenyon, *J. Am. Chem. Soc.* **1997**, *119*, 447–448.

[8] Semiempirical and molecular mechanics calculations were carried out with Spartan 4.0 (SGI) and MacSpartan Plus (Macintosh) packages, Wavefunction Inc., Irvine, CA 92612.

[9] Approximate transition-state geometries for the second Diels–Alder step were obtained at the AM1 level for several approaches by using multiple starting conformations (Sybyl) and by fixing the distances of the approaching diene and C_{60} carbons to 2.2 Å. The most favorable structure of each set was then optimized according to the legend of Table 1 and confirmed by vibrational analysis (one imaginary frequency for the pathway of addition).

[10] See Supplementary Information.

[11] X. Camps, A. Hirsch, *J. Chem. Soc. Perkin Trans. 1* **1997**, 1595–1596.

[12] Y. Z. An, G. A. Ellis, A. L. Viado, Y. Rubin, *J. Org. Chem.* **1995**, *60*, 6353–6361.

[13] M. Riklin, A. von Zelewsky, *Helv. Chim. Acta* **1996**, *79*, 2176–2179.

[14] J. M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**.

[15] a) M. Eiermann, R. C. Haddon, B. Knight, Q. C. Li, M. Maggini, N. Martin, T. Ohno, M. Prato, T. Suzuki, F. Wudl, *Angew. Chem.* **1995**, *107*, 1733–1735; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1591–1594; b) B. Knight, N. Martin, T. Ohno, E. Orti, C. Rovira, J. Veciana, J. Vidal-Gancedo, P. Viruela, R. Viruela, F. Wudl, *J. Am. Chem. Soc.* **1997**, *119*, 9871–9882.

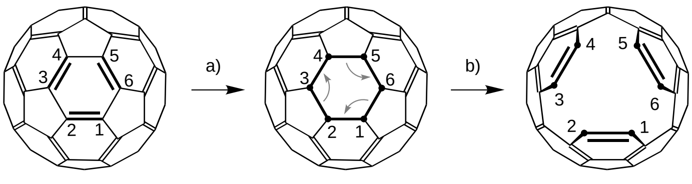
[16] A similar application of the Bingel reactions on compound **3a** gave mono- to hexakisadducts that were used in a recent photophysical study: F. Prat, R. Stackow, R. Bernstein, W. Qian, Y. Rubin, C. S. Foote, *J. Phys. Chem.* **1999**, in press.

Formation of an Effective Opening within the Fullerene Core of C_{60} by an Unusual Reaction Sequence**

Georg Schick, Thibaut Jarrosson, and Yves Rubin*

With the formation of a large orifice in the fullerene shell, the potential arises to introduce practically any atom inside these hollow structures. This constitutes a critical step for the development of a powerful method to produce endohedral fullerene complexes.[1] Thus far, the task of opening an effective aperture on the surface of fullerenes has proven very challenging.[1, 2] Although up to three bonds[2f] are cleaved in current ring-opening reactions, the relative positions of the fullerene carbon atoms are maintained by bridging addends, whose steric requirement can further hinder accessibility of the cavity.

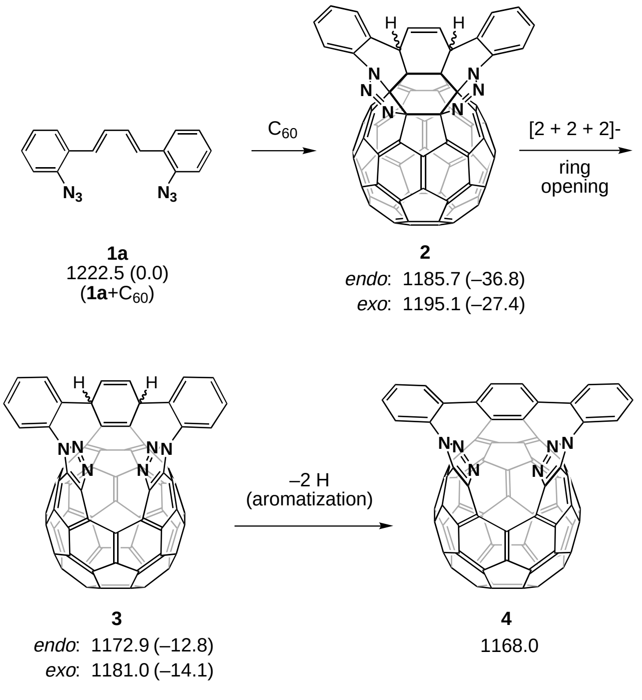
These restrictions can be eliminated by placing three adding groups within a relatively rigid, preorganized reactant such as a macrocycle.[1b] Threefold addition of the reactive moieties to three endocyclic C=C bonds of C_{60} ([6,6] junctions) results in a fully saturated, strained planar cyclohexane moiety (Scheme 1).



Scheme 1. a) Addition of six saturating groups. b) [2+2+2] ring-opening reaction.

This arrangement promotes a facile [2+2+2] ring-opening reaction following a mechanism similar to that of all presently known fullerene ring scission reactions, for example, those leading to [5,6] ring-opened methanofullerenes (fulleroids).[3]

The system chosen for this initial study is based on the relatively rigid diazidobutadiene system **1a** (Scheme 2). Azide and Diels–Alder cycloadditions to C_{60} have been studied extensively.[3–5] Possible side reactions of the fragile triazoline moieties formed by azide additions include the formation of [5,6]-iminofullerenes and/or [6,6]-aziridinofullerenes under loss of N_2.[6] Semiempirical calculations on the



Scheme 2. Conceptual set of reactions at the origin of this work with calculated (AM1) heats of formation [kcal mol^{-1}] (the relative energies at each step are given in parentheses).

---

[*] Prof. Y. Rubin, Dr. G. Schick, T. Jarrosson
Department of Chemistry and Biochemistry
University of California, Los Angeles
Los Angeles, CA 90095-1569 (USA)
Fax: (+1) 310-206-7649
E-mail: rubin@chem.ucla.edu

[**] This work was supported by a National Science Foundation Young Investigator award (CHE-9457693) and the Office of Naval Research (N00014-98-1-0035).

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.