

Chimia 52 (1998) 118–126
 © Neue Schweizerische Chemische Gesellschaft
 ISSN 0009–4293

Functionalization Studies of C₆₀ and Synthetic Approaches to Endohedral Metallofullerenes

Yves Rubin*

Ruzicka Prize Winner 1997

Abstract. Two strategies aimed at the synthesis of endohedral metallofullerenes are presented. They have required the exploration of the surface chemistry of C₆₀ as well as the development of efficient syntheses of highly unsaturated acetylenic cyclophanes. These studies have led to the formation of the largest orifice on the framework of C₆₀ in the form of a cobalt(III) complex having the metal sitting on top of the opening. Further exploitation of the mechanisms involved in the formation of this cavity are discussed. In the second approach to metallofullerenes, highly unsaturated acetylenic cyclophanes have been designed to fold to fullerenes in a series of cascade reactions, either in the gas phase (mass spectroscopy, flash vacuum pyrolysis), or in solution (metal catalysis, radical-anion rearrangements). The origin of this second approach lies in the mechanism of gas-phase coalescence of polyynes during fullerene formation in the graphite evaporation method. Endohedral metal complexes of C₆₀ are expected to have interesting and diverse properties perhaps as rich as those of C₆₀ and other empty fullerenes.

Introduction

When buckminsterfullerene (C₆₀) was discovered in 1985 as an ion in carbon vaporization experiments, no one imagined that this molecule would take such an important role in the chemical sciences within only a few years [1]. Once macroscopic quantities became available, it was soon discovered that the compound has a particularly large array of important physical and chemical properties that have led to some of the most intense investigations in this century. I came in this area while working under Prof. François Diederich as a graduate student at UCLA, where we isolated the first pure samples of C₆₀ and C₇₀ in collaboration with Krätschmer and Huffman [2]. This gave us the unique opportunity to experience the exciting initial steps of this field. Since my appointment at UCLA, we have focused our attention on the surface chemistry of C₆₀ which was just beginning to develop in 1991 under the leadership of Fred Wudl at UC Santa Barbara, California [3].

*Correspondence: Prof. Y. Rubin
 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

Our interest in the reactivity of C₆₀ was first motivated by the challenges of controlling mono- and multiple additions, and exploiting the chemical and physical properties of C₆₀ for physical organic and biological studies. Soon, we also discovered a way to create an opening on C₆₀, which originated the exciting goal of synthesizing endohedral metallofullerenes [4]. The cavity inside C₆₀ is large enough to contain any single atom of the periodic table (Fig. 1). In view of the important proper-



Yves Rubin was born on March 9, 1963 in Yverdon. He received his diploma in chemistry in 1987 from the University of Fribourg with Profs. Albert Gossauer and Alexander von Zelewsky as diploma thesis advisors. From 1987 to 1991, he was a doctoral student with Prof. François Diederich at UCLA, working on synthetic approaches to all-carbon molecules and networks and on the isolation and characterization of the fullerenes C₆₀, C₇₀, and C₈₄. After obtaining his Ph.D. degree, he became a postdoctoral fellow with Prof. Ronald Breslow at Columbia University, working on the development of organic ferromagnets. He won the Saul Winstein Dissertation Award at UCLA and was awarded a Swiss National Foundation Postdoctoral Fellowship. Since July 1992, he is an assistant professor of organic chemistry at UCLA. He is the recipient of an Alfred P. Sloan Research Fellowship (1998), the Ruzicka Prize (1997), an NSF Young Investigator Award (1994), an Arnold and Mabel Beckman Young Investigator Award (1994), and a Camille and Henry Dreyfus New Faculty Award (1994). His research interests are in the total synthesis of C₆₀ and endohedral metallofullerenes as well as in the preparation and study of designed organic materials.

ties displayed by empty C₆₀ and its compounds (e.g., superconductivity, ferromagnetism, nonlinear optical activity, optical limiting), it is not difficult to expect this same highly symmetrical structure containing any of the transition metals to lead to similarly interesting properties [5]. The

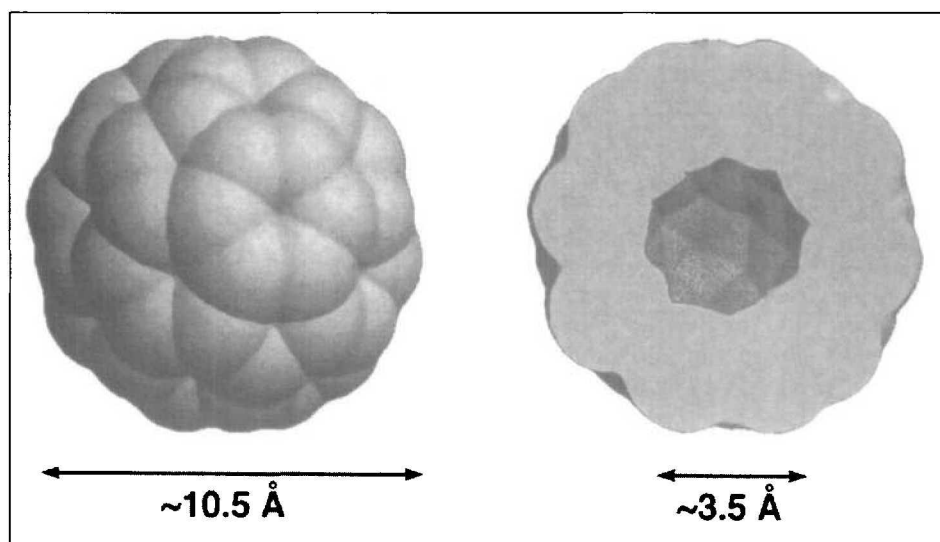


Fig. 1. The hollow cavity within C₆₀

highly variable electronic properties of transition metals undoubtedly will confer their endohedral complexes a rich array of physical properties when they interact with the inside orbital lobes of C_{60} . In this regard, it is particularly interesting to find that a N-atom inside C_{60} ($N@C_{60}$) is completely unbound, despite the highly reactive quartet spin state of this atom [6][7]. On the other hand, known endohedral lanthanide complexes of higher fullerenes have the metal-atom bound to the inside wall of the cage [8], while those of C_{60} have not yet been isolated in pure form because they seem to be too reactive. The reason for these observations is that covalent bonding from inside the cage is highly unfavorable with nitrogen because of the required convex-to-concave distortion of the cage, while the lanthanide metals easily transfer their electrons to the cage making it prone to oxidation. An intermediate situation should be seen with transition metals, where orbital interactions will be 'softer' and charge transfer reversible. Intriguing spin and redox states will most likely result.

Results and Discussion

The chemical reactivity of C_{60} was initially explored using large excesses of reagent because the available amounts of this precious material were very small. This, of course, complicated the characterization of the products because they were formed as a number of multiple adducts and their isomers. By 1992, fullerenes were commercially available – albeit at a hefty cost – in the form of soot containing 5–10% of C_{60} (with an order of magnitude less of C_{70}), and later as the C_{60}/C_{70} extract or 99.5% pure C_{60} . Some part of our work consisted in laboriously isolating pure C_{60} , which made exploring its chemistry quite slow. Nevertheless, it was soon discovered that well-defined single addition products could be generated [9][10], and we concentrated our efforts on the *Diels-Alder* cycloaddition because of the wide variety of dienes available for further functionalizations.

The test case of *Diels-Alder* reactivity consisted in the reaction of diene **1** with C_{60} , which was designed to give, after cheletropic loss of CO, the adduct **2** further stabilized toward retro-*Diels-Alder* reaction by the aromaticity of the benzene ring (Scheme 1) [9]. The possibility of retro-*Diels-Alder* reaction was at the origin of these precautions because the anthracene adduct, and subsequently the cyclopentadiene adduct, were found by

Scheme 1. Formation of the Diels-Alder Adduct **2**

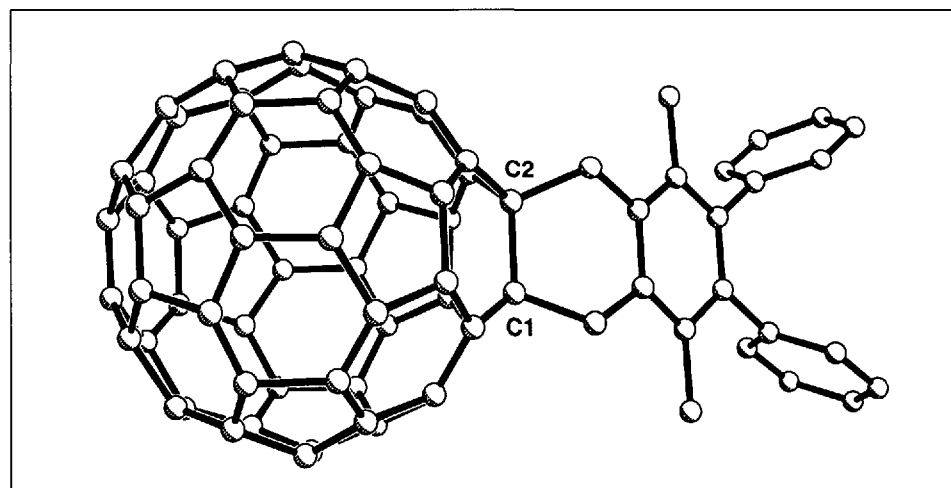
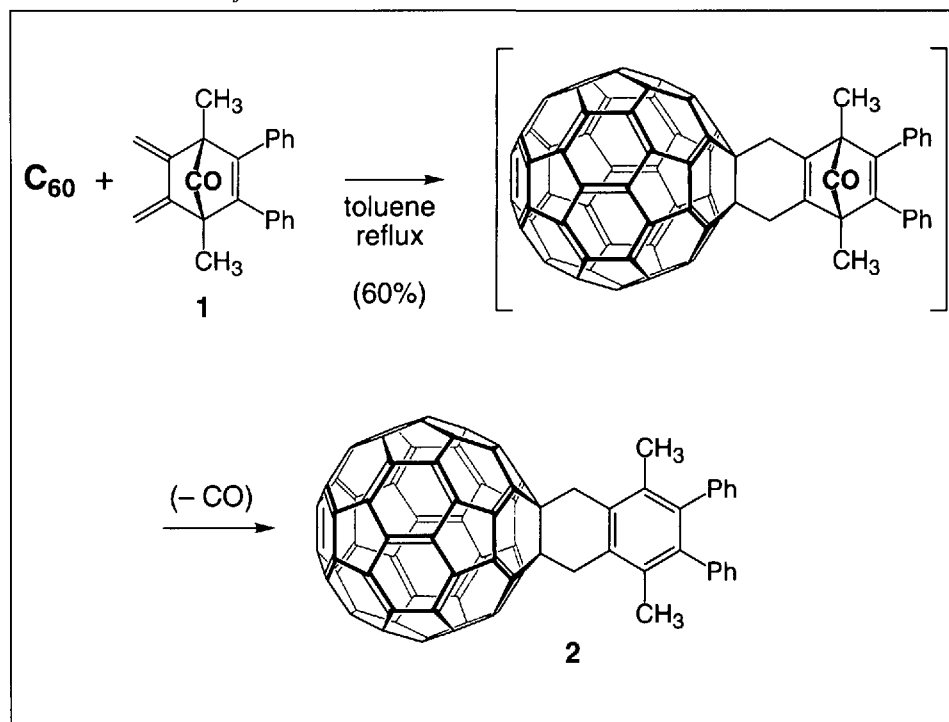
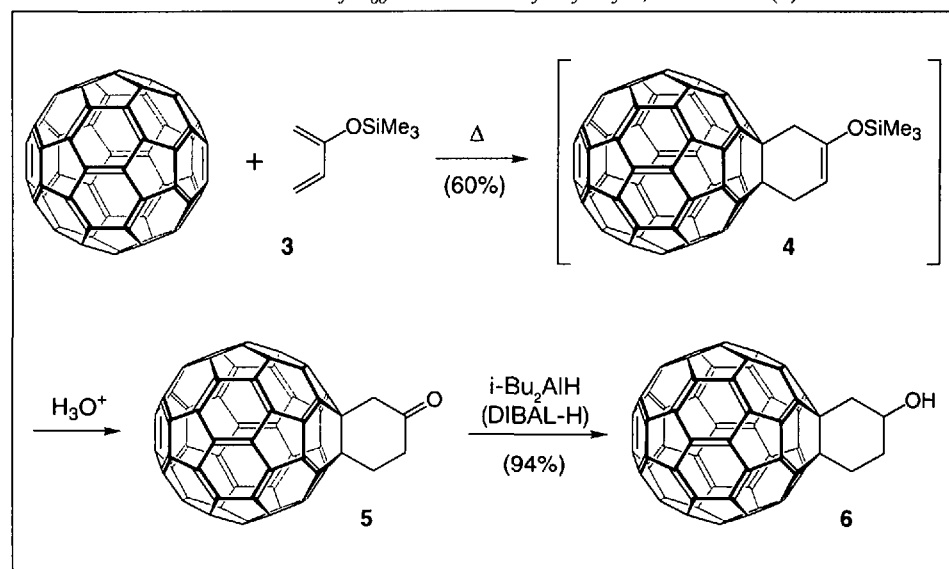


Fig. 2. X-ray structure of Diels-Alder adduct **2**

Scheme 2. Diels-Alder Reaction of C_{60} and 2-Trimethylsilyloxy-1,3-butadiene (**3**)



others to be prone to cycloreversion [11]. Compound **2** permitted its characterization by X-ray crystallography, which confirmed in particular that reaction at the [6,6]-ring junction (*i.e.*, between two 6-membered rings) is preferred (*Fig. 2*). The effect of converting two sp^2 -hybridized C-atoms of a [6,6]-ring junction to the tetrahedral sp^3 -C-atoms C_1 and C_2 introduces some strain in the resulting single bond separating these two atoms, which is expressed by its longer bond length (1.62

Å) compared to a normal C–C bond (1.53 Å). However, the greater strain relief occurring upon converting two pyramidalized sp^2 C-atoms to sp^3 largely compensates for this distortion.

As implied earlier, the structure of the starting diene can be exploited to give products with useful functionalities. *Diels-Alder* cycloaddition of an easily available diene such as **3** afforded the intermediate enol ether **4**, hydrolyzed under the workup conditions to the corre-

sponding ketone **5** (*Scheme 2*). This product can be reduced efficiently to alcohol **6** with diisobutylaluminum hydride (DIBAL-H). Alcohol **6** was subsequently used in several projects, one of them involving the covalent attachment of this 1,2-dihydrofullerene to a single-strand oligonucleotide to effect site-specific DNA modification (*Figs. 3 and 4*).

The C_{60} -linked oligonucleotide **7** induced very efficient and site-selective cleavage of the single-stranded portion of DNA upon visible light irradiation and basic hydrolysis of the modified bases. The mechanism involves primarily single-electron transfer to triplet-excited C_{60} (a strong oxidant) from the closely located guanosines, resulting in further hydrolytic degradation of the oxidized bases. The involvement of singlet oxygen (1O_2) in this strand scission was not implicated, at least to a large degree, because its quenching had little effect on the efficacy of this reaction.

Singlet oxygen is formed by photosensitization whenever solutions of fullerenes and their simple derivatives are left in ambient light and air. This is due to the very efficient formation of the triplet-excited state of the fullerene with visible light. This facile 'self'-sensitization can be used with advantage in the preparation of allylic alcohols derived from cyclohexene-fused fullerenes by ene-reaction (*Scheme 3*) [12]. One of the more relevant examples for this article is the reaction of butadiene **8** ($R_1, R_2, R_3 = H$) with C_{60} and subsequent conversion to allylic alcohol **11** ($R_1, R_2, R_3 = H$). This compound became the key to a surprising development in our work when we found that its elimination product, the cyclohexadiene **12** (*Scheme 4*) [13], rearranges very smoothly upon visible light irradiation to the bismethano-fullerene **13** undergoing spontaneous retro-[2+2+2]-ring opening to the bis-fulleroid **14** [4b]. The interesting structure of **14**, related to the simpler monofulleroids obtained by diazo-compound additions to C_{60} , was yet unknown [10]. It thus became an interesting and ultimately rewarding exercise to obtain an X-ray structure of this framework. After a number of unsuccessful crystallization attempts on **14**, we reasoned that a metal bound at a defined site of this framework would help crystallization. Rather than relying on chance forming $Pt(PR_3)_2$ or $Ir(CO)Cl(PPh_3)_2$ complexes that are known to be fluxionally bonded to fullerenes [14], we considered the alternate possibility of using the unique ethylene bridge of compound **14** to promote initial η^2 -binding at this site. This thinking materialized into

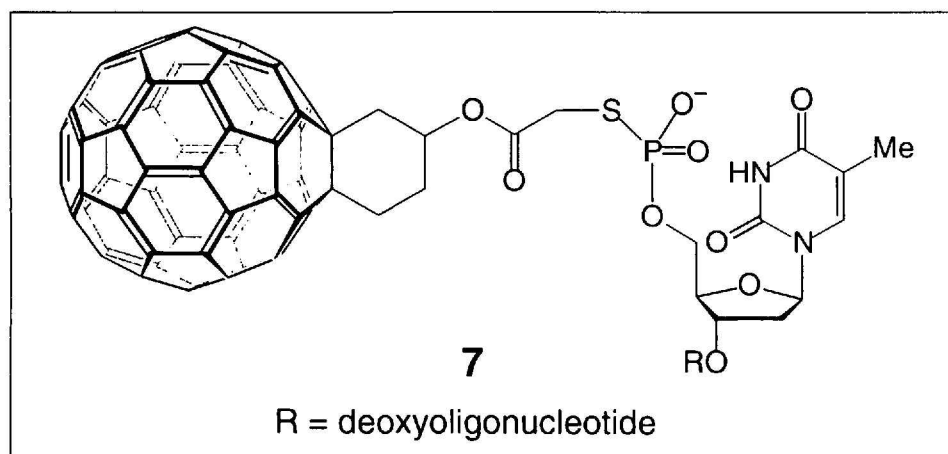


Fig. 3. Structure of the C_{60} -oligonucleotide conjugate **7** based on alcohol **6**

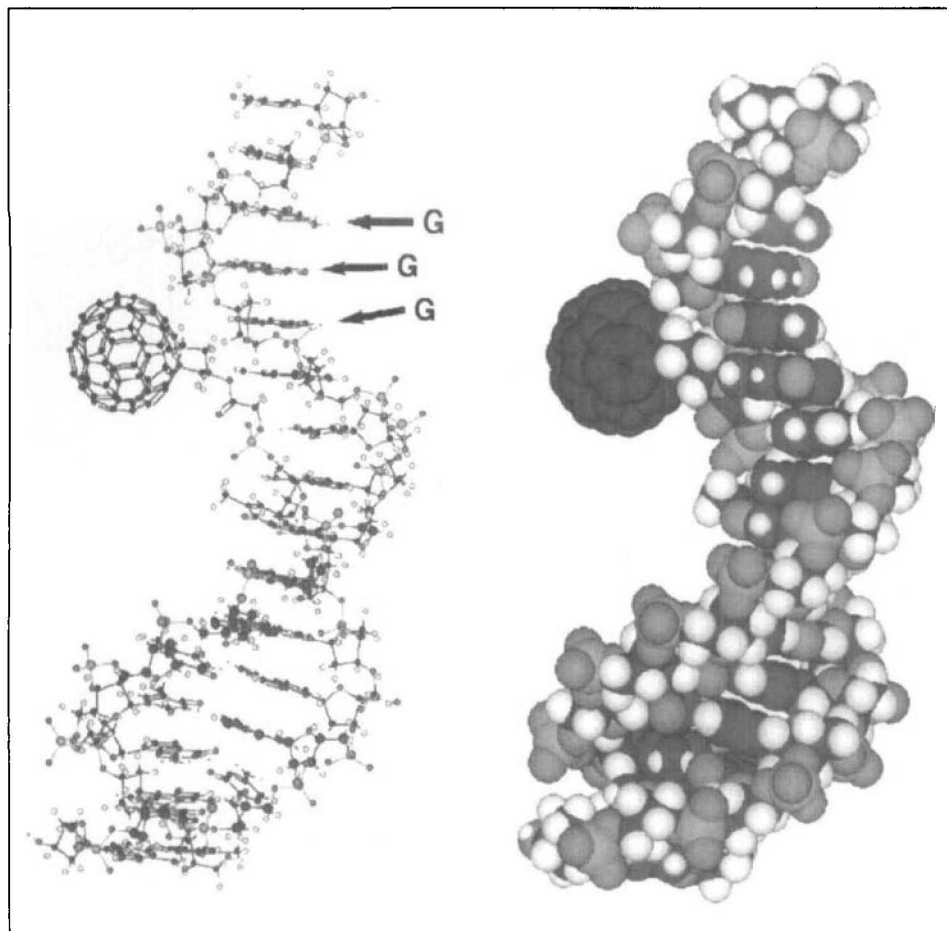


Fig. 4. Ball-and-stick and space-filling representations of a portion of the C_{60} -oligonucleotide conjugate **7** hybridized to a complementary sequence. The three guanosine moieties on the hybridized fragment which are involved in the strand scission by C_{60} are indicated by arrows.

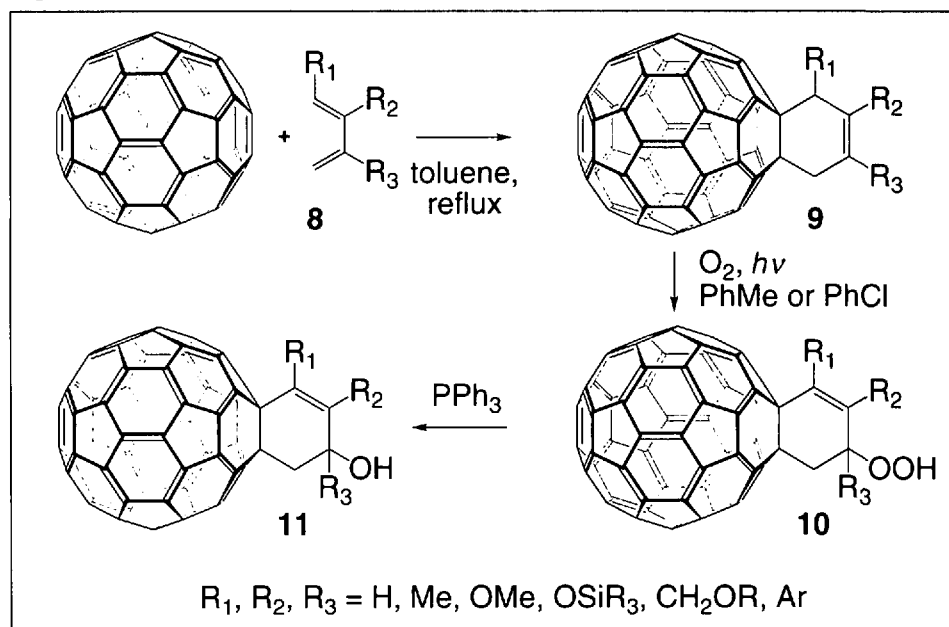
very concrete results upon complexation of dicarbonyl(cyclopentadienyl)cobalt(I) ($\text{CpCo}(\text{CO})_2$) with **14**, which led to the cobalt(III) complex **15a** (Scheme 5).

Complex **15a** is the final product of an overall sequential triple scission of a 6-membered ring on C_{60} affording a 15-membered ring opening, the largest formal opening created so far on a fullerene [4b][15]. Two of the three 5-membered rings surrounding this 6-membered ring open up during the photochemical conversion of intermediate **13** to the bisfulleroid **14**, while the last bond scission occurs during the complexation step with cobalt to afford **15a**. The isoelectronic indenyl complex **15b** can be prepared in the same manner from 1,5-cyclooctadienyl(indenyl)cobalt(I) [16]. This complexation reaction is more efficient than with $\text{CpCo}(\text{CO})_2$, reflected in the higher isolated yield of complex **15b** over **15a**.

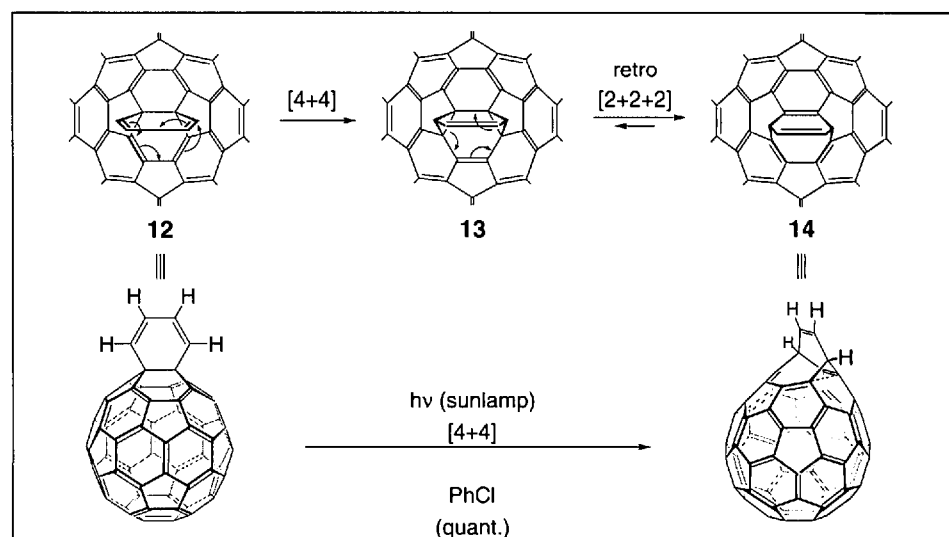
Complex **15a** was characterized by X-ray crystallography (Fig. 5). The Co-atom is ideally seated above the orifice of the cage, but the C_4H_4 bridge ($\text{C}(3')\text{-C}(4')\text{-C}(5')\text{-C}(6')$) constrains its cavity to a large extent. As a result, the C-C distance between the two fullerene C-atoms bonded to cobalt is limited to 2.41 Å. In principle, this distance can be increased by thermal motions, and experiments with this concept in mind have been carried out [4a][17]. However, the combining factors of short C-C distance and a strong bond between the Co-atom and the Cp ring made these attempts unsuccessful. One of the parameters that was easily changed was to turn the Cp ligand into the more labile indenyl ligand in compound **15b**, which underwent facile loss of indene upon heating in the crystalline state as found by DSC and TGA [16]. Unfortunately, loss of indene apparently was also accompanied by rapid solid-state polymerization affording intractable material, even upon examination by laser-desorption mass spectroscopy.

With these observations in mind, we have initiated the synthesis of bis-addition products that are designed to combine a twofold set of reactions leading to complexes **15a** and **15b** [4a]. With the appropriate choice of a bridging moiety embodied in the bis-diene **16**, a 1:2 ratio of the *trans*-1 (i.e., antipodal) bis-adduct **17** was formed that could be separated from other regioisomers. The rearranged products **18a** and **18b** were formed in a manner analogous to the conversion of **11b** to **14** (Schemes 5 and 6). We are currently working on the formation of larger amounts of this material and the formation of its cobalt complexes. It is possible that regioselective dihydroxylation or epoxidation

Scheme 3. Diels-Alder Reaction of C_{60} with Various Dienes and Self-Sensitized Ene-Reaction with $^1\text{O}_2$



Scheme 4. Mechanism of the Conversion of Fullerocyclohexadiene **12** to the Bisfulleroid **14**



Scheme 5. Synthesis of the Cobalt(III) Complexes **15a** and **15b**

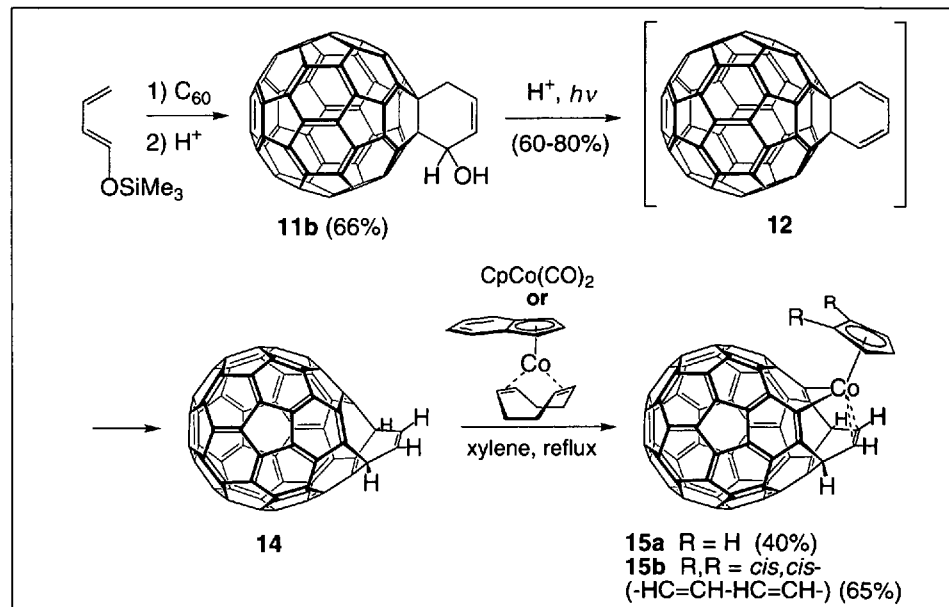
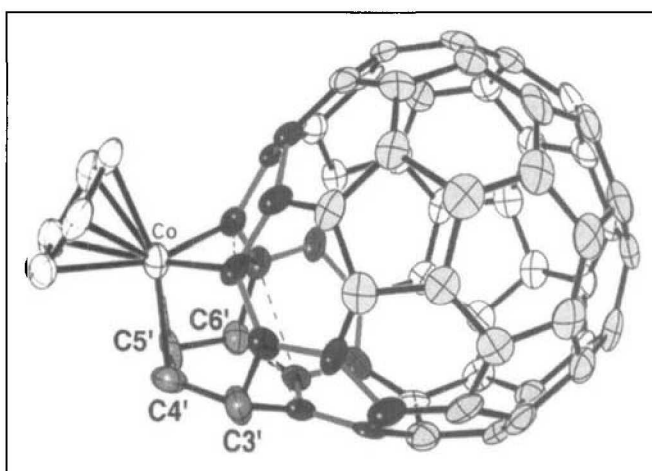
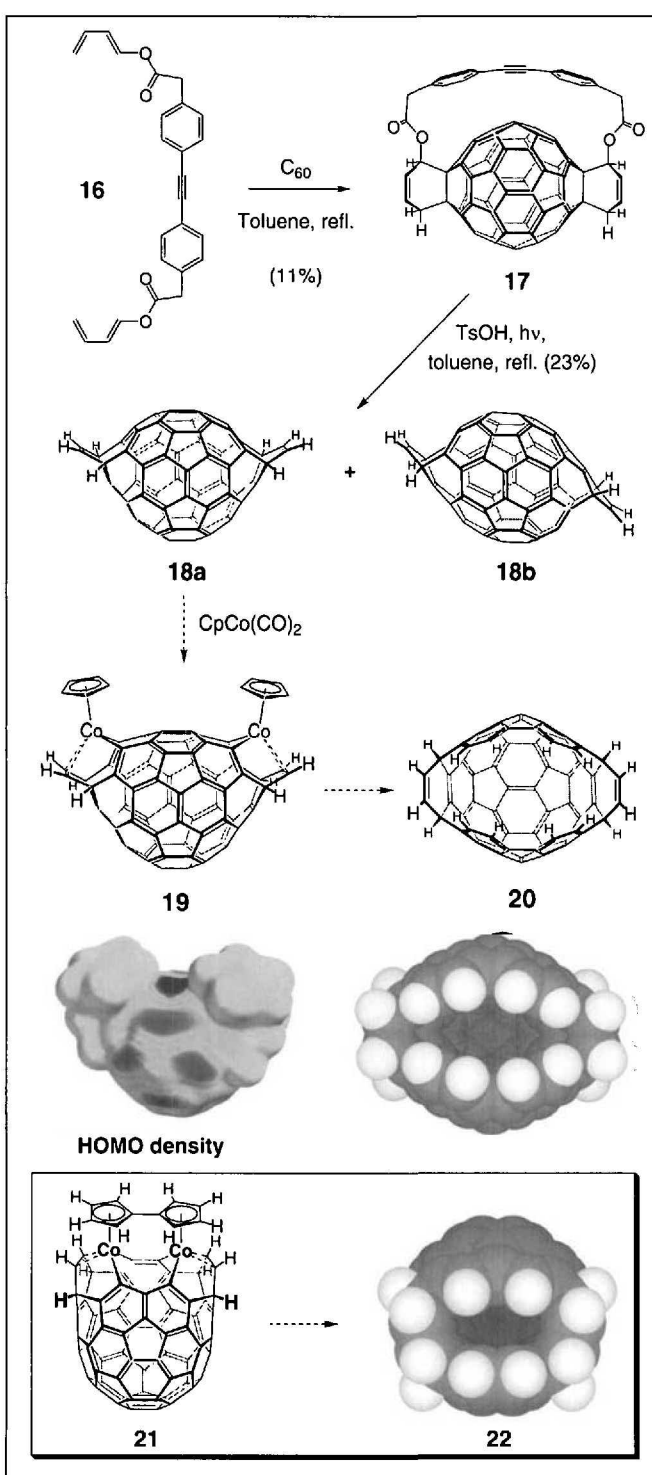


Fig. 5. X-ray structure of complex **15a**. Note that the C-atoms in dark gray denote the 15-membered ring opening formed within the fullerene structure. C-atoms C(3'), C(4'), C(5'), and C(6') are from the original cyclohexadiene ring in compound **12**. The white atoms form the cyclopentadienyl ring.



Scheme 6. Formation of the Bis-Rearrangement Products **18a** and **18b**



reactions will provide access to a 'clam-shell' compound (**20**) after hydrolytic scission of the Co–C bonds in **19**. Most likely, closer reaction centers such as the ones leading to the bis-cobalt complex **21** will constitute a more efficient approach to large cavities on the surface of C_{60} expressed in compound **22**. The formation of **17** can be regarded as a preliminary study of the regioselective double functionalization of C_{60} at remote double bonds, which is in fact the most challenging aspect of this project. Success in this project relies heavily on judicious design of the tether helped by computation [18].

The formation of the first cobalt complex **15a** gave us an important insight into the type of mechanism that should be used in our search for opening strategies. The retro-[2+2+2]-cycloaddition reaction can, in principle, be exploited on a fully saturated six-membered ring of a fullerene derivative represented by the 1,2,3,4,5,6-hexahydro compound **23** (Scheme 7) [4a]. Here, the strain provided by the fullerene cage encourages its expansion to the fragmented six-membered ring of **24**, while the steric hindrance of the six addends on the overcrowded ring with all-eclipsed interactions also favor expansion. The real challenge in this concept is the formation of the desired 1,2,3,4,5,6-hexahydro derivative **23** or alkylated analogs. We are currently developing approaches to such compounds.

In a very different approach to endohedral metallofullerenes, we have initiated the synthesis of highly unsaturated C_{60} cyclophanes (**25–29**) containing a large number of energy-rich sp-hybridized C-atoms in the form of alkynyl linkages to two benzene rings (Fig. 6) [19][20]. The main thinking behind this approach is that similar structures are formed as intermediates in the gas phase during the formation of fullerenes from evaporated carbon [21–24]. Giving a nearly spherical shape to these precursors allows them to form perhaps isolable metal complexes prior to the rearrangement event giving the fullerene framework.

Our first approach to these systems consisted in the formation of tris-linked macrocycles based on the framework of **26**. This system is much easier to access than more compact, hexa-linked systems like **27–29**, because the methodology to generate differentially protected hexaalkynylbenzenes had to be developed [19b] [25]. The model compound **26a** was rapidly assembled in a highly convergent manner from the bromoalkyne **30**, easily accessible from 1,3,5-tribromobenzene (Scheme 8) [19a].

Compound **26a** transpired to be quite an interesting system. It is a helical molecule with D_3 symmetry in its relaxed conformation and has therefore two chiral forms as such. Because of the highly flexible nature of the dienehexayne linkages in **26a** (bending alkynes is much easier than sp^2 - or sp^3 -hybridized C-atoms), its crystallization proved to be very difficult and necessitated eight months of constant trials with freshly prepared crystals. Solving its structure gave us important information on its conformation and packing in the crystal. The two benzene decks of each unit of **26a** are in an offset close contact in the crystal with the closest C–C distance being 3.50 Å, while the energy-minimized structure (PM3) has a much larger distance (5.22 Å; Fig. 7). Accordingly, the benzene rings come into *van-der-Waals* contact in the crystal, which may be due to crystal packing forces or attractive interactions between the two aromatic systems (Fig. 8). The crystal packing structure of **26a** has another interesting aspect: the two enantiomeric conformers pack discriminately to form two interpenetrated columns of isostructural units facing each other. A large portion of space in the middle of these four columns is occupied by the solvent, 1,2-dichlorobenzene. One of the reasons for the difficulty in crystallizing **26a** was that only dichlorobenzene was able to occupy this space efficiently without creating disorder.

Since we had compound **26a** in our hands, it was evident that its coalescence to C_{60} should be attempted. A practical method to test the thermal behavior of compounds under conditions similar to those of flash vacuum pyrolysis lies in laser-desorption mass spectroscopy [21]. However, not unexpectedly, laser-desorption mass-spectroscopic studies of **26a** showed that it does not lose its H-atoms readily, and no ion for C_{60} was observed. The fact that the hydrogens of **26a** are very poor leaving groups is the most likely factor accounting for the lack of dehydrogenation of the parent ion.

Our current outlook on this project consists in the synthesis of the squarate derivative **31** (Scheme 9), whose carbonyl groups constitute excellent leaving groups to form the highly unsaturated macrocycle **25** ($C_{60}H_6$) [21][26]. In fact, all H-atoms of **25** can be potentially replaced by bromine to give **32** ($C_{60}Br_6$) starting from 2,4,6-tribromo-1,3,5-triethynylbenzene (**36b**) whose synthesis is described below.

In our approach to the compact hexalinked macrocycles **27–29**, we have developed a straightforward methodology to

Scheme 7. A Possible Ring-Opening Reaction of $C_{60}H_6$ (**23**) on the Way to Endohedral Metallofullerenes

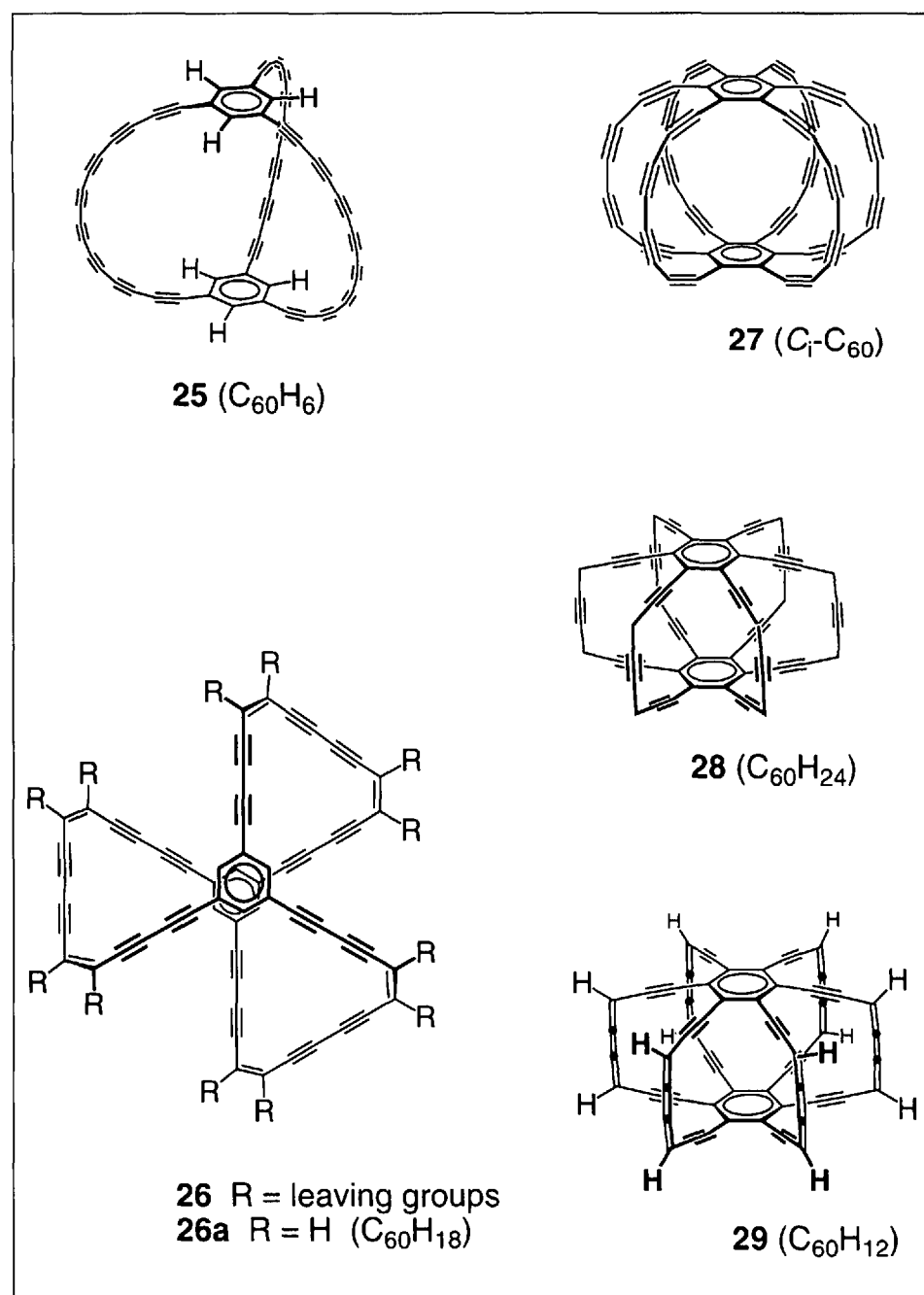
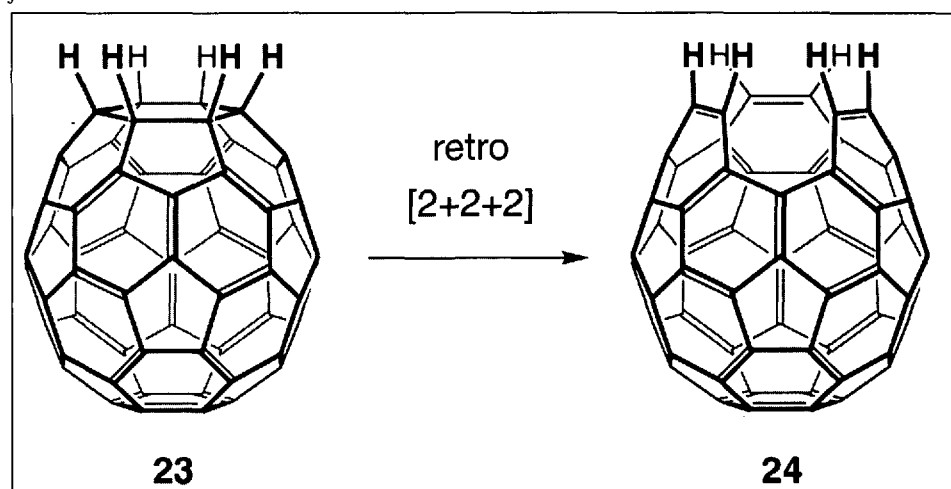
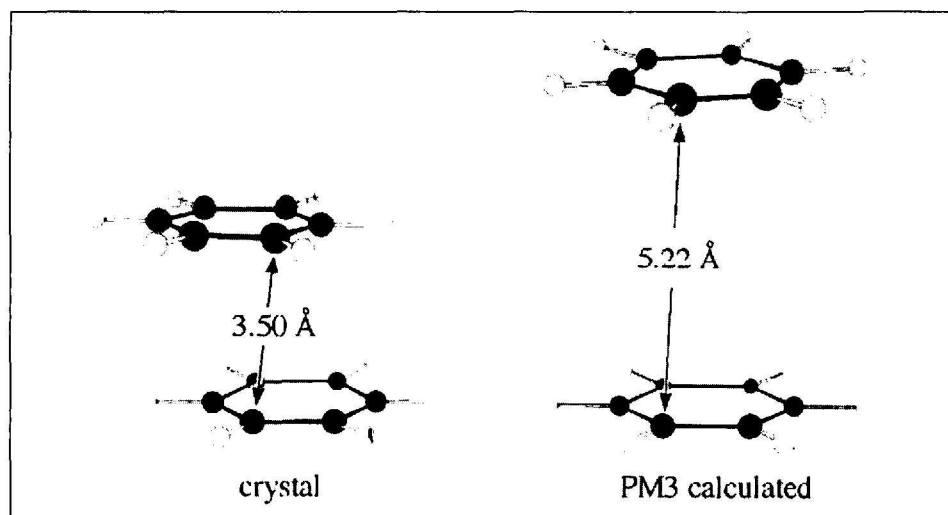
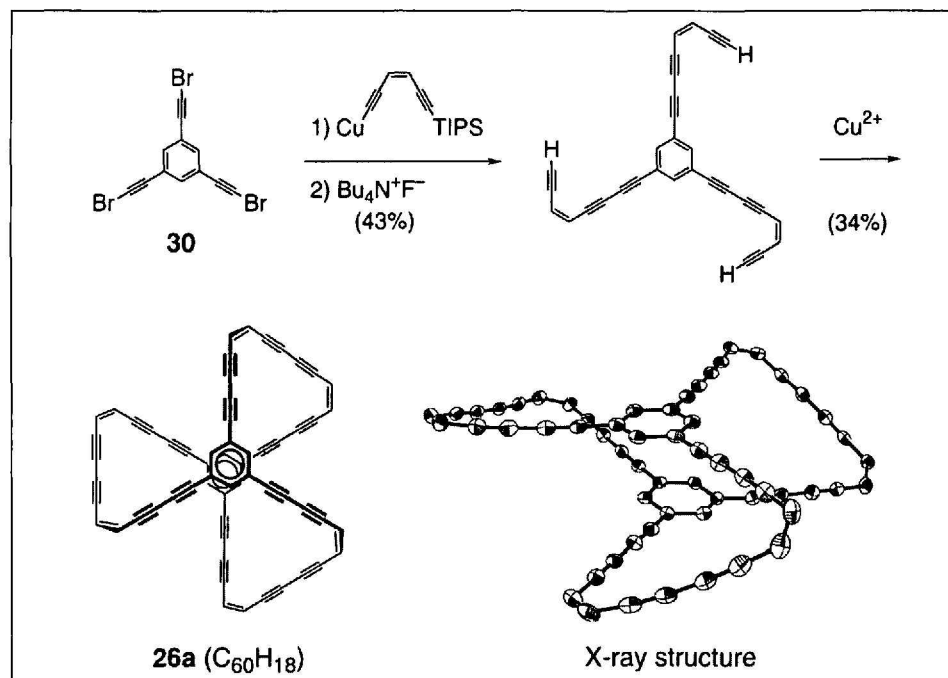
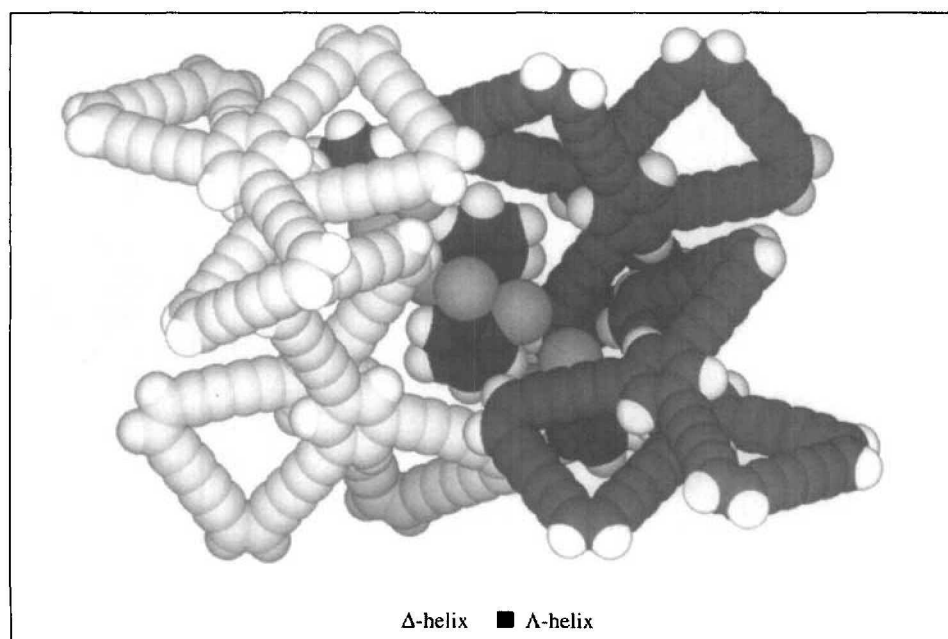


Fig. 6. Structures of the carbon-rich macrocyclic fullerene precursors **25–29**

Scheme 8. Synthesis of the Fullerene Precursor **26a** ($C_{60}H_{18}$)Fig. 7. Arene ring relationships of **26a** in the crystal (left) and in the PM3 minimized structure (right)Fig. 8. Partial view of the packing structure of **26a** with 1,2-dichlorobenzene inclusion

prepare several interesting hexaethynylbenzenes (HEBs) derived from the 1,3,5/2,4,6-differentially functionalized tribromo-trialdehyde **33** (Scheme 10) [19b]. The only other synthesis of hexaethynylbenzenes involves sixfold palladium-catalyzed ethynylation of hexabromobenzene, leading to D_{6h} derivatives [25]. Starting from mesitylene, the versatile trialdehyde **33** was prepared in five steps in 36% overall yield. Palladium-catalyzed coupling of aldehyde **33** with a silyl or an aryl alkyne provided the triethynyl-trialdehydes **34a** and **34b**, which were readily converted into the respective hexaethynyl compounds **35a–c** by application of the *Corey-Fuchs* dibromo-olefination followed by treatment with LDA.

The tribromo-trialkyne **36a**, necessary for the construction of the brominated C_{60} precursor **32**, can be prepared easily from the trialdehyde **33** in good yield using our methodology (Scheme 11). Tribromo-triynes **36a** can be considered as a precursor of graphyne [27], although its self-coupling will most likely afford highly cross-linked polymers with large amounts of defects.

While the synthesis of the three-dimensional carbon frameworks of fullerenes is the main focus of our research, two-dimensional networks such as the graphynes are also very interesting entities [27]. With currently available methodology, such regularly connected systems cannot be obtained by oligomerization reactions, because formation of the C–C bonds is not reversible. This drawback can be bypassed to a certain extent by synthesizing large pieces of these networks with properties approaching those of the polymeric material [28]. A sensible approach to the graphdiyne fragment **41b** was developed from the differentially protected hexaethynylbenzene **40** (Scheme 12) [29]. Oxidative cyclization afforded the dimer **41a** as the main product, and also the desired trimer **41b** and tetramer **41c**. Formation of the hexaethynylbenzene **40** was achieved starting from the *Diels-Alder* cycloaddition product **39** formed from cyclopentadienone **37** and alkyne **38**. Subsequent transformations to compound **40** are analogous to those of Scheme 10.

The X-ray structure of **41a** reveals the strained nature of this dehydro[12]annulene where steric shielding by *t*-Bu groups and $CHCl_3$ molecules stabilizes it against polymerization (Fig. 9). The fluorescence of **41a** as well as that of the trimer **41b** and tetramer **41c** is already a property characteristic of these hexaethynylbenzenes not seen in simpler analogs. The formation of these systems has geared us

up to the synthesis of the much larger graphdiyne piece **42**.

Conclusion

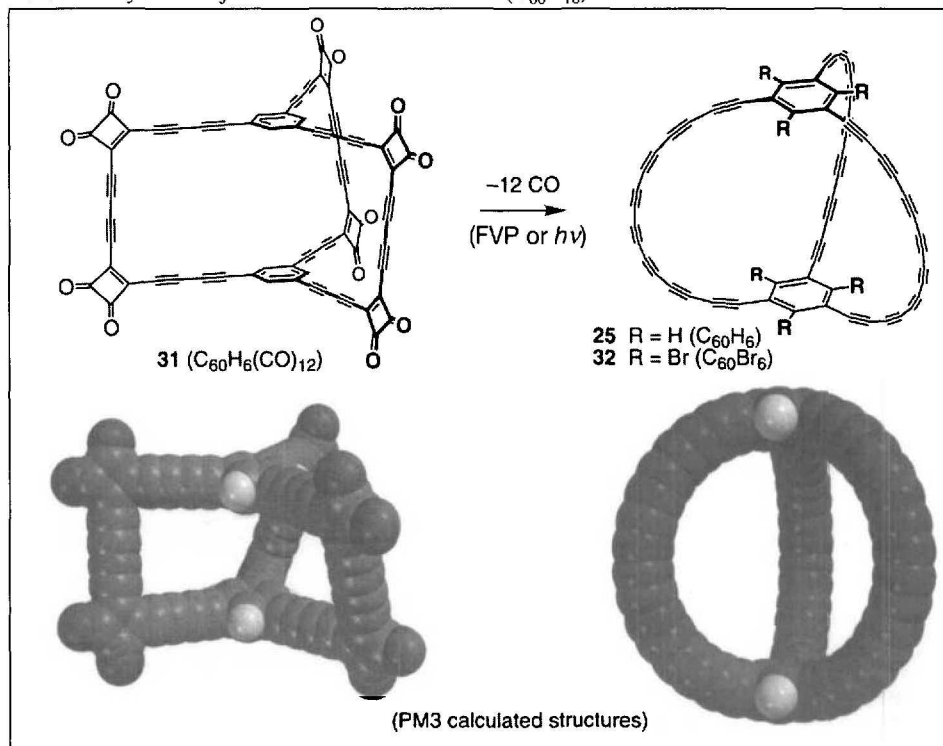
This work has provided us with an interesting and enriching view of fullerene and acetylene chemistry. Access to sizable openings on fullerenes is now possible and has to be pursued further for ultimate insertion of any of the metals of the periodic table inside these intriguing structures. Similarly, the formation of large acetylenic precursors of fullerenes has proven feasible and rewarding. Although the possibility of their conversion to a fullerene structure remains to be demonstrated, there is a considerable amount of fundamental knowledge to be gained from this chemistry.

Ultimately, the fact that such structural chemistry may result in materials properties that are useful constitutes a legitimate aspiration. From the little we know of endohedral complexes of C_{60} currently represented by ${}^3\text{He}@C_{60}$ or $\text{N}@C_{60}$ [6][7], it can be said without too much pretense that other endohedral elements will add considerable diversity to the chemistry and physics of fullerenes.

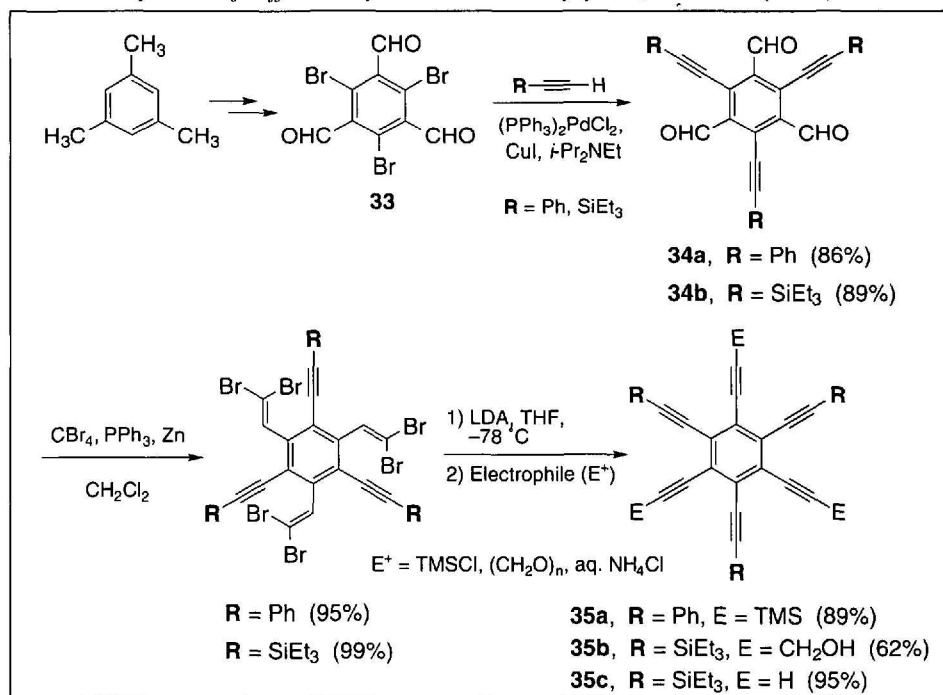
Received: February 2, 1998

- [1] a) H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, *Nature (London)* **1985**, 318, 162; b) W. Krätschmer, L.D. Lamb, K. Fostiropoulos, D.R. Huffman, *ibid.* **1990**, 347, 354.
- [2] H. Ajie, M.M. Alvarez, S.J. Anz, R.D. Beck, F. Diederich, K. Fostiropoulos, D.R. Huffman, W. Krätschmer, Y. Rubin, K.E. Schriver, D. Sensharma, R.L. Whetten, *J. Phys. Chem.* **1990**, 94, 8630.
- [3] A. Hirsch, Q. Li, F. Wudl, *Angew. Chem.* **1991**, 103, 1339; *ibid.*, *Int. Ed. Engl.* **1991**, 30, 1309.
- [4] a) Y. Rubin, *Chem. Eur. J.* **1997**, 3, 1009; b) M.J. Arce, A.L. Viado, Y.Z. An, S.I. Khan, Y. Rubin, *J. Am. Chem. Soc.* **1996**, 118, 3775.
- [5] a) K. Holczer, O. Klein, S.M. Huang, R.B. Kaner, K.J. Fu, R.L. Whetten, F. Diederich, *Science* **1991**, 252, 1154; b) P.M. Allemand, K.C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Grüner, J.D. Thompson, *ibid.* **1991**, 253, 301; c) H.S. Nalwa, *Adv. Mater.* **1993**, 5, 341.
- [6] For the insertion of nitrogen atoms, see: a) T.A. Murphy, T. Pawlik, A. Weidinger, M. Hohne, R. Alcalá, J.M. Spaeth, *Phys. Rev. Lett.* **1996**, 77, 1075; b) H. Mauser, N.J.R. van Eikema Hommes, T. Clark, A. Hirsch, B. Pietzak, A. Weidinger, L. Dunsch, *Angew. Chem.* **1997**, 109, 2858; *ibid.*, *Int. Ed. Engl.* **1997**, 36, 2835.
- [7] For the insertion of noble gases into C_{60} , see: M. Saunders, R.J. Cross, H.A. Jiménez

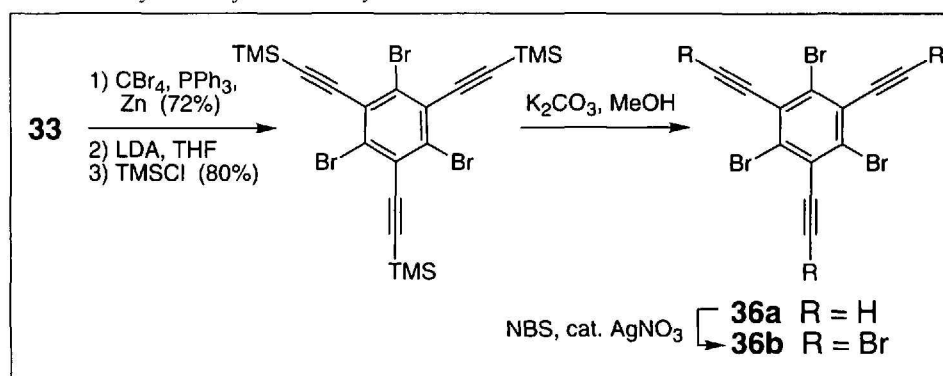
Scheme 9. Synthesis of the Fullerene Precursor **25** ($C_{60}H_{18}$)



Scheme 10. Synthesis of Differentially Protected Hexaethynylbenzenes **35a-c** (HEBs)



Scheme 11. Synthesis of Tribromotriynes **36a** and **36b**



ez-Vázquez, R. Shimshi, A. Khong, *Science* **1996**, 271, 1693.

- [8] a) F.T. Edlmann, *Angew. Chem.* **1995**, 107, 1071; *ibid.*, *Int. Ed. Engl.* **1995**, 34, 981; b) S. Nagase, K. Kobayashi, T. Akasaka, *Bull. Chem. Soc. Jpn.* **1996**, 69, 2131.
- [9] Y. Rubin, S. Khan, D.I. Freedberg, C. Yeretizian, *J. Am. Chem. Soc.* **1993**, 115, 344.
- [10] A. Hirsch, 'The Chemistry of the Fullerenes', Thieme Verlag, Stuttgart, 1994.
- [11] a) J.A. Schlueter, J.M. Seaman, S. Taha, H. Cohen, K.R. Lykke, H.H. Wang, J.M. Williams, *J. Chem. Soc., Chem. Commun.* **1993**, 972; b) M. Tsuda, T. Ishida, T. Nogami, S. Kurono, M. Ohashi, *ibid.* **1993**, 1296; c) K. Komatsu, Y. Murata, N. Sugita, K. Takeuchi, T.S.M. Wan, *Tetrahedron Lett.* **1993**, 34, 8473; d) V.M. Rotello, J.B. Howard, T. Yadav, M.M. Conn, E. Viani, L.M. Giovane, A.L. Lafleur, *ibid.* **1993**, 34, 1561.
- [12] Y.Z. An, A.L. Viado, M.J. Arce, Y. Rubin, *J. Org. Chem.* **1995**, 60, 8330.
- [13] Y.Z. An, G.A. Ellis, A.L. Viado, Y. Rubin, *J. Org. Chem.* **1995**, 60, 6353.
- [14] a) P.J. Fagan, J.C. Calabrese, B. Malone, *Acc. Chem. Res.* **1992**, 25, 134; b) A.L. Balch, J.W. Lee, B.C. Noll, M.M. Olmstead, *J. Am. Chem. Soc.* **1992**, 114, 10984.
- [15] a) J.C. Hummelen, M. Prato, F. Wudl, *J. Am. Chem. Soc.* **1995**, 117, 7003; b) P.R. Birkett, A.G. Avent, A.D. Darwish, H.W. Kroto, R. Taylor, D.R.M. Walton, *J. Chem. Soc., Chem. Commun.* **1995**, 1869; c) G. Schick, A. Hirsch, H. Mauser, T. Clark, *Chem. Eur. J.* **1996**, 2, 935; d) L.L. Shiu, K.M. Chien, T.Y. Liu, T.I. Lin, G.R. Her, T.Y. Luh, *J. Chem. Soc., Chem. Commun.* **1995**, 1159; e) G.X. Dong, J.S. Li, T.H. Chan, *ibid.* **1995**, 1725.
- [16] S. Zhang, A. Sastre, Y. Rubin, unpublished.
- [17] C.M. Edwards, I.S. Butler, W. Qian, Y. Rubin, *J. Mol. Struct.* **1997**, in press.
- [18] 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; b) L. Isaacs, R.F. Haldimann, F. Diederich, *Angew. Chem.* **1994**, 106, 2434; *ibid.*, *Int. Ed. Engl.* **1994**, 33, 2339.
- [19] a) Y. Rubin, T.C. Parker, S.I. Khan, C.L. Holliman, S.W. McElvany, *J. Am. Chem. Soc.* **1996**, 118, 5308; b) J.E. Anthony, S.I. Khan, Y. Rubin, *Tetrahedron Lett.* **1997**, 38, 3499.
- [20] For a similar approach with metallocenes, see: N. Jux, K. Holczer, Y. Rubin, *Angew. Chem.* **1996**, 108, 2116; *ibid.*, *Int. Ed. Engl.* **1996**, 35, 1986.
- [21] a) Y. Rubin, M. Kahr, C.B. Knobler, F. Diederich, C.L. Wilkins, *J. Am. Chem. Soc.* **1991**, 113, 495; b) S.W. McElvany, M.M. Ross, N.S. Goroff, F. Diederich, *Science* **1993**, 259, 1594.
- [22] a) N.S. Goroff, *Acc. Chem. Res.* **1996**, 29, 77; b) G.E. Scuseria, *Science* **1996**, 271, 942; c) D.L. Strout, G.E. Scuseria, *J. Phys. Chem.* **1996**, 100, 6492.
- [23] a) H.G. Von, M.T. Hsu, P.R. Kemper, M.T. Bowers, *J. Chem. Phys.* **1991**, 95, 3835; b) G. von Helden, N.G. Gotts, M.T. Bowers, *J. Am. Chem. Soc.* **1993**, 115, 4363.
- [24] a) J. Hunter, J. Fye, M.F. Jarrold, *Science*

Scheme 12. Synthesis of Differentially Protected Hexaethynylbenzene **40** and Macrocycles **41a-c**

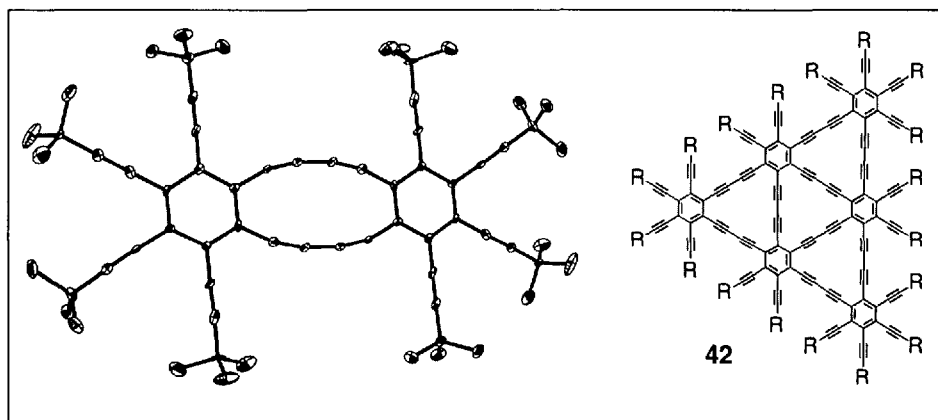
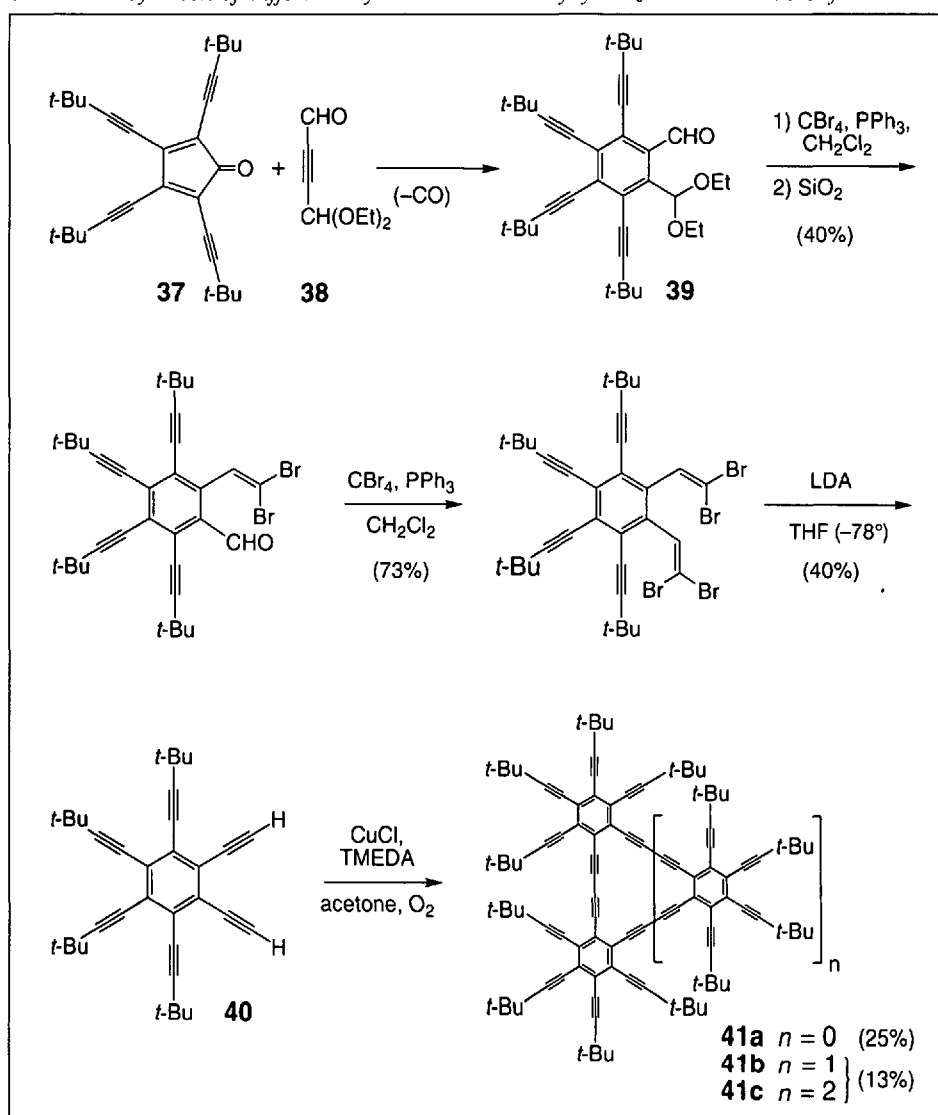


Fig. 9. X-ray structure of dimer **41a** and structure of graphdiyne fragment **42**

- 1993**, 260, 784; K. B. Shelimov, D.E. Clemmer, M.F. Jarrold, *J. Chem. Soc., Dalton Trans.* **1996**, 567.
- [25] For leading references on hexalkynylbenzenes, see: a) R. Diercks, J.C. Armstrong, R. Boese, K.P.C. Vollhardt, *Angew. Chem.* **1986**, 25, 270; *ibid.*, *Int. Ed. Engl.* **1986**, 25, 268; b) R. Boese, J.R. Green, J. Mittendorf, D.L. Mohler, K.P.C. Vollhardt, *Angew. Chem.* **1992**, 104, 1643; *ibid.*, *Int. Ed. Engl.* **1992**, 31, 1643.
- [26] T.C. Parker, 'A Synthetic Route to Alkyne

Rich Cyclophanes', Ph.D. Thesis, University of California, Los Angeles, 1997.

- [27] a) F. Diederich, Y. Rubin, *Angew. Chem.* **1992**, 104, 1123; *ibid.*, *Int. Ed. Engl.* **1992**, 31, 1101; b) F. Diederich, *Nature (London)* **1994**, 369, 199.
- [28] R.R. Tykwinski, F. Diederich, *Liebigs Ann. Chem.* **1997**, 649.
- [29] J.D. Tovar, N. Jux, T. Jarroson, S.I. Khan, Y. Rubin, *J. Org. Chem.* **1997**, 62, 3432.