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Total Synthesis of Buckminsterfullerene (C_{60}) and Endohedral Metal Complexes

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13. ABSTRACT *(Maximum 200 words)*

A summary of our work aimed at the synthesis of a variety of endohedral metal complexes of fullerenes is presented. The completion of the synthesis of suitable highly unsaturated macrocyclic precursors containing 60 carbon atoms is described. These compounds were required to study their rearrangement to a fullerene framework in a process analogous to the gas-phase rearrangement of mono- and polycyclic polyynes (acetylenic rings) in the formation of C_{60} and higher fullerenes. Three types of synthetic acetylenic precursors were targeted, namely triply-linked bis-benzene-cyclophanes with octayne linking units, sextuply-linked bis-benzene-cyclophanes with tetrayne linkers, and deca-alkynylated metallocenes which include a metal in their structure early in the synthesis. The rearrangement to C_{60} of the first examples of these compounds has been studied in the gas phase by LDMS and in solution by various chemical reactions.

Another aspect of our work was initiated by the successful opening of the largest orifice on the framework of C_{60} known to date in the form of a cobalt(III) complex of ethenobisfulleroid $C_{64}H_4$. This strategy is being applied in a double fashion on adjacent sites of the surface of C_{60} to form an even larger opening, aimed at eventual metal insertion inside the cage.

14. SUBJECT TERMS
Fullerene, endohedral metallofullerene, cyclophane, alkyne, C_{60}

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OFFICE OF NAVAL RESEARCH

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Summary of Goals: In view of the important properties displayed by empty C_{60} and its compounds (superconductivity, ferromagnetism, nonlinear optical activity), it is important to develop an approach to fullerene structures filled with any one of the numerous transition metals. The highly variable electronic properties of transition metal complexes undoubtedly will lead to a rich array of physical properties when they are associated with fullerenes. Because C_{60}'s high symmetry plays an important role in its unique physical properties compared to larger fullerenes (C_{70}, C_{76}, C_{84}, etc.), we are aiming at the synthesis of endohedral metal complexes of C_{60} ($M@C_{60}$). The endohedrals of C_{60} are presently not known in pure form, but some of the lanthanide complexes in the higher series (e.g. $La@C_{76}$, $La@C_{78}$, $Ln@C_{82}$ (Ln = La, Y, Sc, Gd, Tm), $Sc_2@C_{84}$, $Sc_3@C_{82}$) have been isolated in very limited quantities. There is every indication that endohedral metallofullerenes will provide as rich and diverse a chemistry as the empty fullerenes. Thus, an efficient approach to endohedral complexes on a significant scale is highly desirable, and synthesis seems to be one of the most promising ways to achieve this versatility.

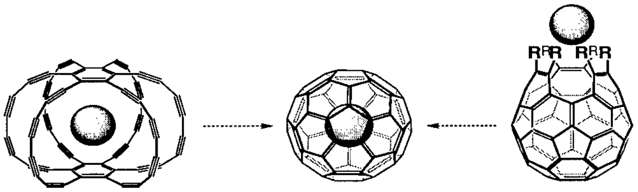


Figure 1. Synthetic approaches to endohedral metallofullerenes.

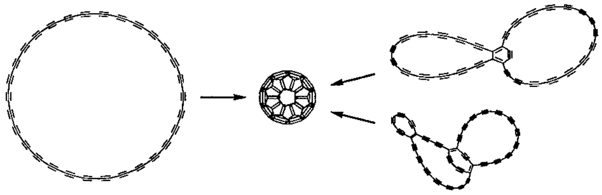
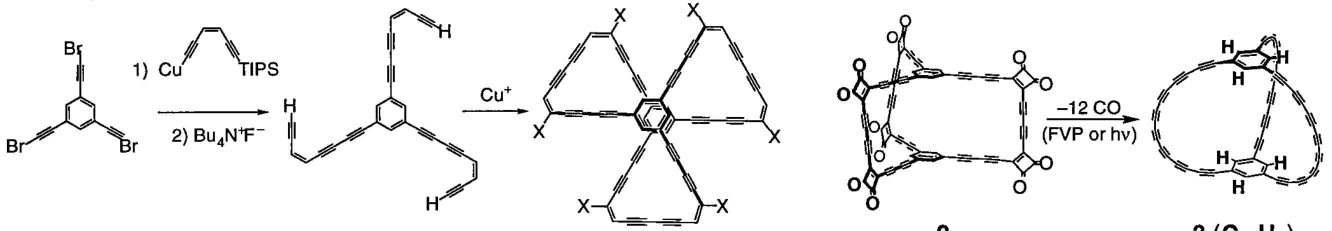


Figure 2. Gas-phase coalescence of polyynes to C_{60}.

We have been investigating two main approaches to the synthesis of endohedral metallofullerenes (Fig. 1): (a) One approach aims at the synthesis of spherically-shaped acetylenic macrocycles which are expected to rearrange to endohedral metal complexes of fullerenes in a controlled process analogous to the gas-phase coalescence of mono- and polycyclic polyynes during fullerene formation by the graphite evaporation method (Fig. 2). (b) The second approach considers chemical transformations to open an orifice on the framework of C_{60}. From our functionalization studies on C_{60}, a recent achievement was the formation of a cobalt complex having the metal attached right on top of the opening. More recently, we have been pursuing this approach by combining this methodology to form two adjacent modification sites on C_{60}, thus greatly enhancing the potential size of the cavity.

Research Progress During Funding Period

1. Total Synthesis of Endohedral Metallofullerenes: (a) Trialkynylbenzene Precursors: In the last 3 years, we have prepared the first members of a series of highly-unsaturated cyclophanes designed to rearrange to the C_{60} framework by a series of thermodynamically favorable reactions. Macrocycle **1a** ($C_{60}H_{18}$), the parent compound of this series, was studied by several mass spectroscopic techniques (MALDI TOF, APCI), showing little propensity to lose hydrogen. Since this is somewhat surprising in view of the expected chemistry of the enediyne moieties within these systems (which should undergo Bergman cyclization to benzene-1,4-diradicals), we have recently started a collaboration with the group of Martin Jarrold at Northwestern University, suspecting that the laser desorption conditions used in the initial study were too mild. The Jarrold group is currently studying the thermal behavior of **1a** using their very successful drift-tube technique allowing precise control of the kinetic energy injected into these systems.

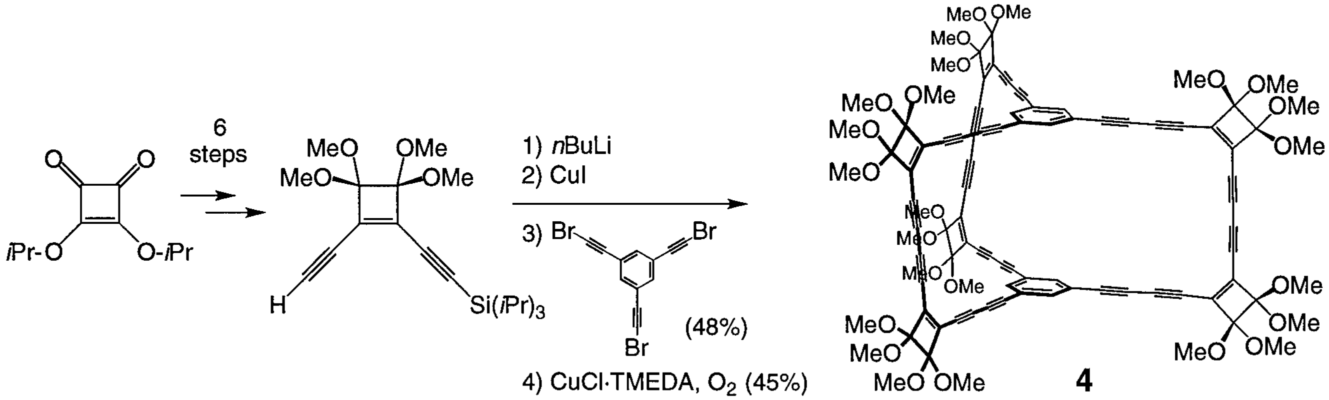


1a, X = H ($C_{60}H_{18}$)
1b, X = Cl
1c, X = OTf

2

3 ($C_{60}H_6$)

On our side, we have worked on the synthesis of precursors of cyclophane **3** ($C_{60}H_6$). This system lacks all but six hydrogens on the way to C_{60}, and should be much better suited for rearrangement to the fullerene than **1a**. Since **3** will be most likely rather unstable, we have investigated three routes to more stable precursors, i.e. compounds **1b**, **1c**, and **2**. Our synthetic efforts on the synthesis of suitable enediynes leading to both **1b** and **1c** have not yet come to fruition, we have concentrated our efforts on the preparation of **2** in the past 6 months. Thus, the synthesis of macrocycle **4** has recently been successfully completed. We envisage no problem in the final acid-catalyzed deprotection to form **2**.



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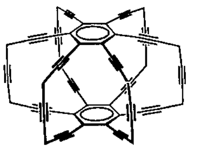
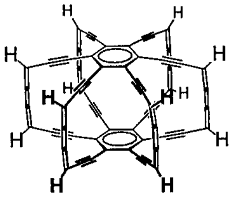
LD-MS experiments on **2** will be performed immediately in house and in collaboration with Stephen McElvany (NRL). We are quite confident that system **2** will finally provide an answer to our question regarding the rearrangement of macrocyclic precursors to buckminsterfullerene.

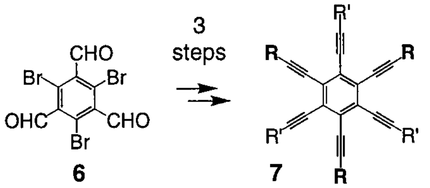


5a, ($C_{60}H_{24}$)

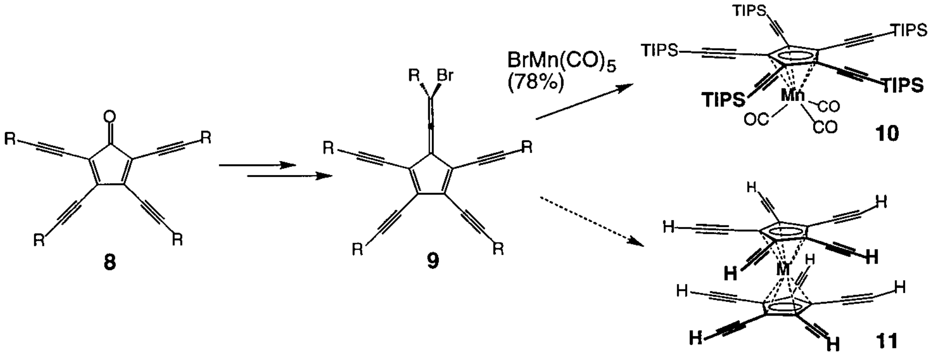


5b, ($C_{60}H_{12}$)

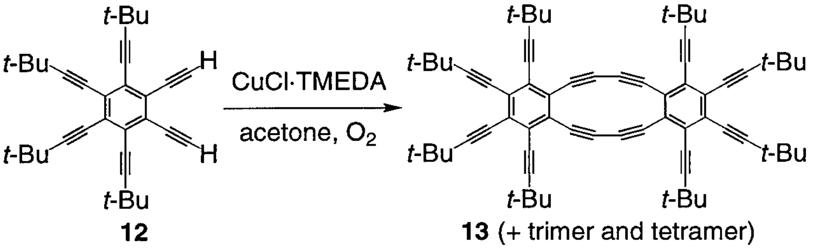
(b) Hexaalkynylbenzene Precursors: The synthesis of hexalinked cyclophanes such as **5a** and **5b** is one of the ultimate goals in this approach because such compact precursors would permit the complexation of an array of transition metals in their preorganized cavity. Toward this goal, we have developed a remarkably straightforward methodology to prepare 1,3,5/2,4,6-differentially functionalized hexaalkynylbenzenes (**7**) derived from tribromotrialdehyde **6** (5 steps from mesitylene). Current progress on this project is as far along as preparing the half molecule (R = $SiEt_3$, R' = $CH_2–C≡C–CH_2OTBS$ units at 1,3,5-positions) required for ultimate one-step cyclization to **5a**. We are very excited about this project because availability of **5a** would permit interesting metal complexation studies independently of the rearrangement studies to endohedral metallofullerenes, should the latter prove difficult.

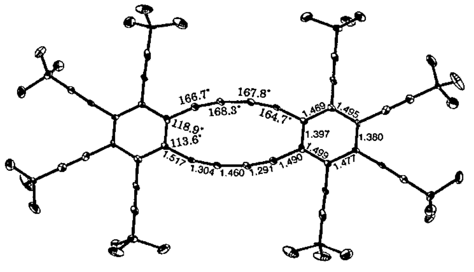


(c) Decaalkynylmetallocene Precursors: Last year, we reported the synthesis of the halogenated systems **9** as potential precursors of decaethynylmetallocenes (**11**). These compounds should lead to 60-carbon precursors with molecular formula $M·C_{60}H_{20}X_{10}$ by simple decakis-propargylation. The latter are likely to lead to endohedral metallofullerenes ($M@C_{60}$) in flash vacuum pyrolytic or even in solution-phase rearrangements induced by metal catalysis or radical or ionic processes. We have verified the validity of this approach by forming the half-sandwich complex **10** in good yield. Since the bulk of the TIPS-groups prevents the formation of the corresponding metallocenes, we have started repeating this work with smaller protecting groups.



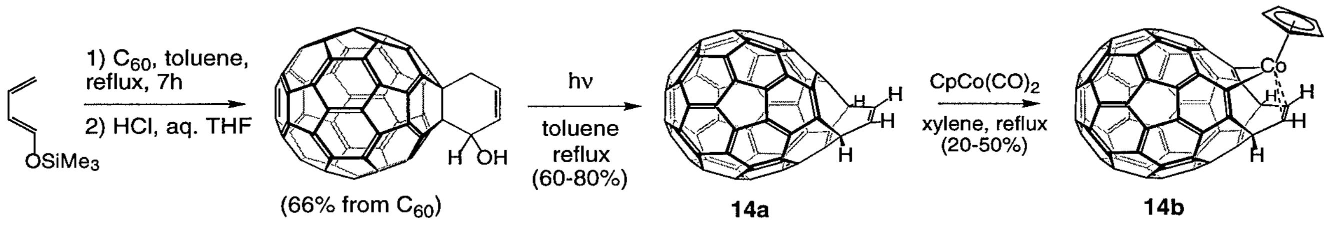
The preparation of *planar* fragments of 2-dimensional carbon allotropes in which the graphitic texture is extended by acetylene or butadiyne units (graphynes) has recently become possible by application of the methodology leading to cyclopentadienones **8**. The preparation of differentially protected hexaalkynylbenzenes (HEBs, e.g. **12**), which are otherwise not accessible by other methods, has allowed the synthesis of the interesting and stable graphyne fragment **13** showing unusual bond elongations in the crystal. We are now pursuing this work toward the synthesis of larger pieces of graphynes (*via* the trimers of differentially protected HEBs) to relate the properties of such soluble, extended molecules to those of the 2D-polymeric sheets, which are unattainable with present methodology.



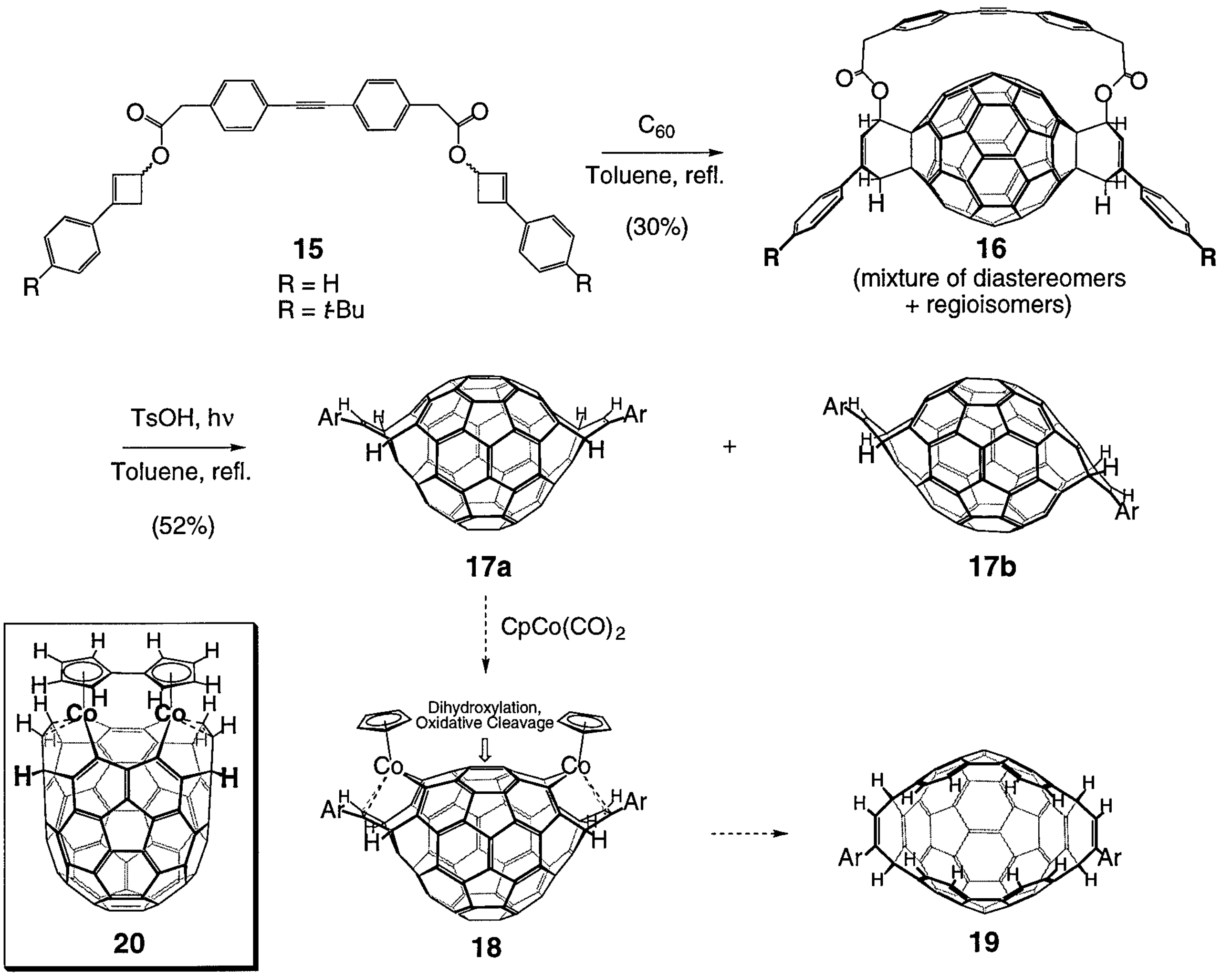


2. Functionalization of Fullerenes. Towards Metal Insertion into Fullerenes.

We have been exploring the possibility of opening a temporary orifice within a fullerene framework to form endohedral complexes by metal insertion. We have discovered the unprecedented formation of the cobalt(III) complex **14b** from bis-fulleroid **14a**. The opening within this molecule is still the largest created so far on a fullerene. However, simple attempts (heating, high pressure) to force the metal inside have not yet been successful. The main reason behind this lies in the fact that the cavity is restrained by the C_4H_4 bridge (2.4 Å between the carbons attached to Co), and the Cp ligand on cobalt is too strongly attached to the metal. For this reason, we have invested a major effort in the synthesis of systems with much larger cavities, as well as started exploring the chemistry of different ligands on cobalt and other transition metals.



An exciting prospect lies in the opening of an entire seam on the surface of C_{60} by a two-fold application of the sequence of reactions that lead to the cobalt complex **14b**. We have prepared the rearranged product **17a**, although as a presently inseparable mixture with its diastereomer **17b**. Once pure samples of **17a** can be obtained (by preparative HPLC), the bis-cobalt complex **18** will be formed. We anticipate that the C=C bond separating the two 15-atom openings in **18** can be dihydroxylated and cleaved to a dicarbonyl product, which may be further transformed to the open system **19** or a similar wide-open "clam-shell" compound. An alternative way to open a larger cavity is concomitantly being explored (complex **20**). Both routes utilize *challenging* regioselective bis-functionalizations of C_{60} and much effort has been invested in the computational design and synthetic work leading to these bis-adducts.



Our main goal is to obtain endohedral metallofullerenes, which we believe will lead to an extremely rich array of chemical and physical investigations. The results obtained under this grant have been extremely fruitful and have led to important results. We are pursuing this work with currentl funding from NSF and a renewal grant from ONR.