# Organic Approaches to Endohedral Metallofullerenes: Cracking Open or Zipping Up Carbon Shells?

## Yves Rubin*

*Dedicated to Robert Curl, Harrold Kroto, and Richard Smalley,*
*who share the 1996 Nobel Prize for Chemistry for their discovery of buckminsterfullerene*

**Abstract:** We have been investigating the synthesis of endo-hedral metallofullerenes since we successfully opened an orifice on the framework of $C_{60}$ in the form of a cobalt complex having the metal sitting on top of the opening. A second approach aims at the synthesis of spherically-shaped acetylenic macrocycles, which are expected to rear-range to endohedral metal complexes of fullerenes in a controlled process analogous to the gas-phase coalescence of mono- and polycyclic polyynes during fullerene forma-tion by the graphite evaporation method. Since the poten-tial benefits from obtaining endohedral metal complexes of $C_{60}$ are enormous, both approaches are being actively pur-sued in our group.

**Keywords:** alkynes · cobalt · endohedral metallofullerenes · fullerenes · macrocycles

## Introduction

A particularly interesting and prolific topic of research has emerged from the discovery of the third form of carbon, the fullerene molecules.[1] Unexpected and spectacular physical properties found for $C_{60}$ have created a rush of research efforts in this area.[2] In particular, $C_{60}$ exhibits superconductivity in its alkali metal salts $K_3C_{60}$ ($T_c = 18$ K) and $Rb_3C_{60}$ ($T_c = 30$ K),[2, 3] soft ferromagnetism ($T_c = 16$ K) in the charge transfer salt with $(Me_2N)_2C=C(NMe_2)_2$,[4] and a large third-order optical nonlinearity ($\chi^{(3)} = 7 \times 10^{-12} - 6 \times 10^{-8}$ esu).[5]

A potentially much richer variety of physical and chemical properties can be awaited from the incorporation of transition and other metals inside the empty cavity of fullerenes (cavity size $\geq 3.5$ Å). The most desirable metallofullerenes are likely to be

those based on icosahedral $C_{60}$ (**1**) because this high symmetry confers its special properties to the empty fullerene. Metallofull-erenes are presently difficult to prepare in pure form in quanti-ties greater than the milligram.[6] A limitation of the graphite evaporation method used in these studies is that there is no control over molecular structure and size-selectivity. As a result, a lengthy separation of the various empty fullerenes ($C_{60}$, $C_{70}$, $C_{76}$, $C_{84}$) and the endohedral complexes is required, and metals other than the lanthanides, Ca, Sr, and Ba do not get incorpo-rated. Representative metallofullerenes that have been charac-terized include $La@C_{76}$, $La@C_{78}$, and $Ln@C_{82}$ (Ln = La, Y, Sc, Gd, Tm),[7] as well as fullerenes incorporating two or three metals ($La_2@C_{80}$,[8] $Sc_2@C_{74}$,[9] $Ce_2@C_{80}$,[10] $Sc_2@C_{82}$,[9] $Sc_2@C_{84}$,[9] and $Sc_3@C_{82}$[11]). Endohedral metal complexes of $C_{60}$ have recently been extracted by aniline although they have not yet been characterized in pure form.[12]

The development of a general synthetic-organic approach to fullerenes[13, 14] and their endohedral metal complexes should address the limitations of the graphite evaporation method. Greater versatility in metal incorporation is critical since transi-tion metals are especially attractive owing to their multivalences and varied spin configurations.

## Strategies

**Cracking open fullerenes:** An immediate choice in an organic approach to endohedral fullerenes is to use the existing frame-work of empty fullerenes, especially that of $C_{60}$, to create an opening wide enough to allow a metal to pass through before closing it back.[15] One of our strategies considers a retro [2 + 2 + 2] cycloaddition reaction of a hexahydrofullerene such as **2a** ($C_{60}H_6$) affording the opened form **2b** (Figure 1 A).[16] It appears from the energetics of this reaction, at least judged from MM 3, AM 1, and PM 3 calculations (Table 1), that substituents other than H will be required to obtain spontaneous ring open-ing.[17] However, representative strained systems like **3b–d** un-dergo this transformation with low activation energies to pro-duce trienes **4b–d**, respectively (Figure 1 B).[18]

The cavity created by the 15-atom opening in **2b**, although significant, is not wide enough to allow a metal atom to pass through easily (Figure 2). However, this cavity can be enlarged

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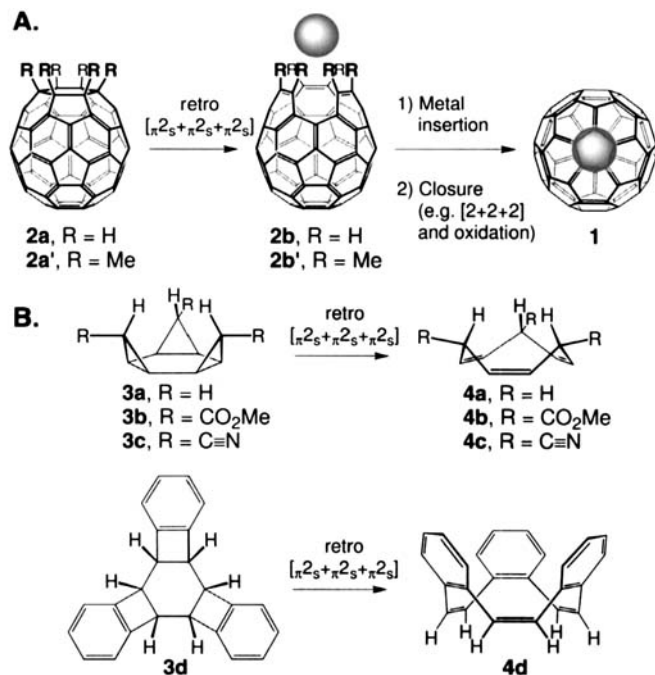Fax: Int. code +(310)206-7649
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**A.**



2a, R = H
2a', R = Me

retro
[$_\pi 2_s + _\pi 2_s + _\pi 2_s$]

2b, R = H
2b', R = Me

1) Metal insertion

2) Closure (e.g. [2+2+2] and oxidation)

1

**B.**

3a, R = H
3b, R = CO$_2$Me
3c, R = C≡N

retro
[$_\pi 2_s + _\pi 2_s + _\pi 2_s$]

4a, R = H
4b, R = CO$_2$Me
4c, R = C≡N

retro
[$_\pi 2_s + _\pi 2_s + _\pi 2_s$]

3d

4d

Figure 1. A) Conceptual representation of a possible way to open C$_{60}$ to form endohedral metallofullerenes. B) Known retro [2+2+2] ring opening reactions in the strained systems 3b–d.

Table 1. Relative steric energies (MM3) and semiempirical heats of enthalpy (PM3) for 2a–c and 2a'–c' given in kcal mol$^{-1}$ [a]. PM3-calculated structures for 2a–c.



Closed          Five-open          Six-open

| Structures ($C_{3v}$) | MM3 | AM1 | PM3 |
|---|---|---|---|
| **R = H** | | | |
| 2a (closed) | 0 | 0 | 0 |
| 2b (five-open) | +12.5 | +9.0 | +14.1 |
| 2c (six-open) | +44.0 | +64.2 | +56.3 |
| **R = CH$_3$** | | | |
| 2a' (closed) | 0 | 0 | 0 |
| 2b' (five-open) | +44.3 | −36.4 | −19.4 |
| 2c' (six-open) | +21.4 | +8.3 | +16.3 |

[a] AM1 and PM3 semiempirical methods in the Spartan 4.0 package for SGI computer. MM3 force field in the MacroModel V3.1 package (SGI), C. Still, Columbia University.
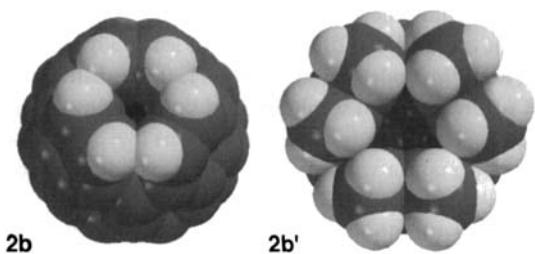


2b          2b'

Figure 2. Space-filling representations of the PM3 calculated structures of 2b and 2b'.

through vibrational activation assisted by the intermediate complexation of the three HC=CH π bonds to a metal. Vibrational analysis of 2b at the PM3 level gives a $C_3$-symmetric low-frequency $A_1$ mode at 361 cm$^{-1}$ which greatly expands its cavity. This calculation shows very nicely that a vibrational mode can expand the orifice to a point that will allow the metal to slip inside the fullerene under proper thermal activation or pressure. In addition, metals appear to be strongly bound to the inside fullerene surface;[19] this should provide a thermodynamic incentive for metal insertion.

A considerably larger cavity can be obtained by replacing the hydrogens of 2b with more sterically demanding groups such as methyls in 2b' (Figures 1 and 2).[20] Curiously, the calculations in Table 1 seem to give a wide margin for interpretation as to which trend the opening of this precursor will follow: will it be endothermic or exothermic? While ab initio methods correctly predict small differences in energies between the isomers of $C_{60}H_4$ or $C_{60}(CH_2)_2$, they are computationally very demanding.[17, 21] The PM3 semiempirical method appears to give reliable results within ±2 kcal mol$^{-1}$.[17, 21] On the other hand, molecular mechanics methods tend to overestimate van der Waals interactions.[21] It seems peculiar that in MM3 the opened forms 2b' and 2c' are considerably higher in energy than 2a' since severe interactions between the methyl groups are present in the closed form. Presumably, MM3 does not account properly for the distortions of the cage sp$^2$ carbons in C$_{60}$ derivatives.

It can be safely assumed that the opened form 2b' will be formed from precursor 2a' with a large thermodynamic advantage. However, it is a considerable challenge to synthesize such a strained system, and more accessible compounds were sought first. A practical realization of the retro [2+2+2] ring opening of a strained C$_{60}$ derivative leading to a 15-membered ring opening, albeit in a stepwise fashion, is related in the discussion section for compound 17. This is the first result in a project we anticipate will lead to the insertion of metals into fullerenes.

**Zipping up fullerene precursors:** With a very different approach in mind, we have tackled the total synthesis of endohedral metallofullerenes in a highly convergent manner, counting on a favorable multiple bond reorganization process in the critical step of synthesis to form as many C–C bonds of the fullerene framework as possible (thus, the term "zipper").[22, 23] Carbon-rich acetylenic spherical macrocycles idealized by structures 5 and 6, but also more stable precursors such as compounds 7, 8, or 9, are expected to rearrange under flash vacuum pyrolytic conditions, or even in solution under metal catalysis, to the C$_{60}$ framework by a thermodynamically favorable process in which highly energetic sp-hybridized carbons become sp$^2$-hybridized (Figure 3). The PM3-calculated conversion of the isomeric C$_{60}$ cyclophane 6 to its isomer buckminsterfullerene releases an enormous amount of energy ($\Delta(\Delta H_f^\circ) = -673$ kcal mol$^{-1}$, or −11.2 kcal mol$^{-1}$ per carbon atom).[23a, 24] A metal guest included in the cavity of these precursors should be trapped endohedrally when rearrangement occurs. This strategy was inspired from the development of a clearer mechanistic picture for fullerene formation[25] established from drift-tube ion-mobility measurements in the groups of Bowers[26] and Jarrold.[27] These
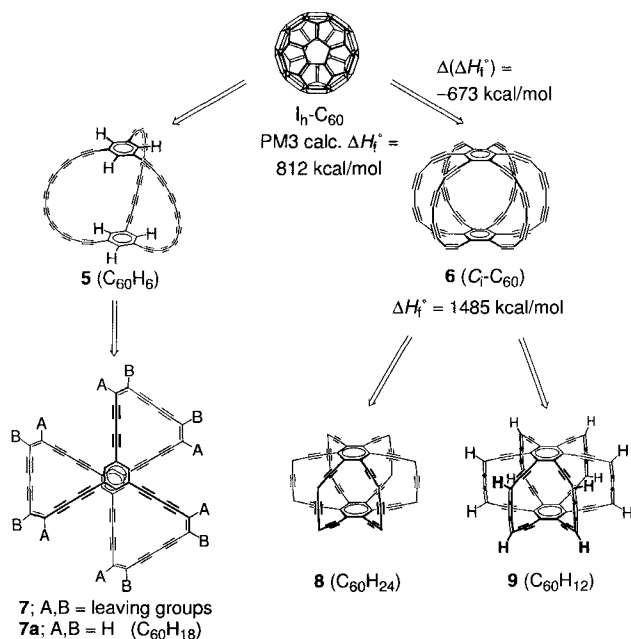
Figure 3. Structures of the carbon-rich spherically-shaped fullerene precursors 5–9.

7; A,B = leaving groups
7a; A,B = H   (C₆₀H₁₈)

studies, following our first observations,[28] have shown that mono- and polycyclic polyynes anneal to the spherical fullerene frameworks under the thermal collisions conditions of "ion chromatography" (Figure 4).
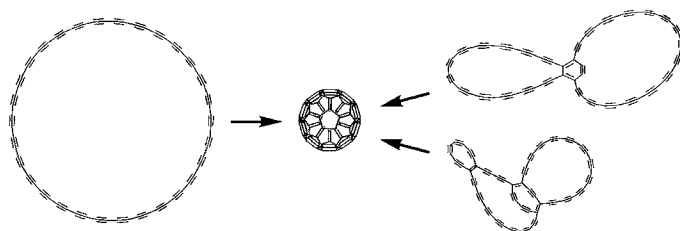


Figure 4. Coalescence of mono- and polycyclic polyynes to buckminsterfullerene in drift-tube experiments.

The excess of thermodynamic energy incorporated by design in precursors 5 and 6 contrasts with more "classical" routes currently being investigated in the groups of Rabideau, Scott, Siegel, and Zimmermann.[29–33] With the exception of Siegel's approach, these methods require high kinetic energies (temperatures up to 1100 °C) to form reactive carbene or radical centers as well as to bend planar polycyclic aromatic precursors in flash vacuum pyrolysis (FVP) reactions. Sizable bowl-shaped fragments of fullerene frameworks, for example, corannulene (10)[34] and the larger analogues shown in Figure 5, have been successfully prepared.[31, 32] However, serious synthetic obstacles may be faced in completing the synthesis of C₆₀ by this route in view of the scarcity of available material resulting from the low yields obtained in the FVP step (Figure 5).[31]
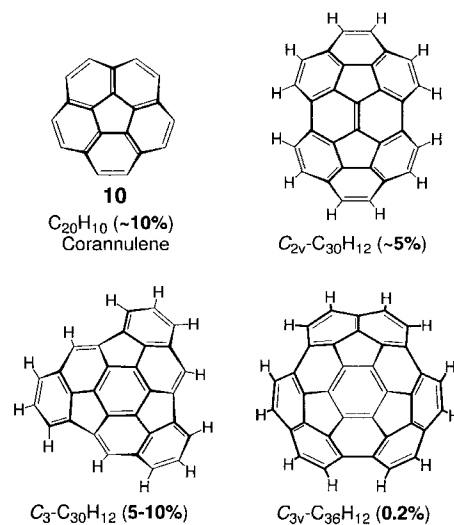


Figure 5. Representative bowl-shaped aromatic hydrocarbons prepared by FVP. Indicated yields are for the FVP step.

## Results and Discussion

**Cracking open fullerenes—"holey buckys":** The task of cracking open a fullerene carbon shell in a controlled fashion seemed hardly obvious until recently. A breakthrough was reached when the group of Wudl observed that the enamine-like MEM-azafulleroid 11 (MEM = methoxyethoxymethyl) reacts in a [2 + 2] fashion with singlet oxygen ($^1O_2$) to form, via a dioxetane intermediate, the keto–lactam 12 having an 11-membered ring opening (Scheme 1).[35, 36] Taylor discovered a similar ring-
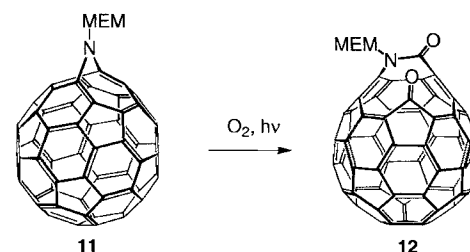


Scheme 1. Wudl's oxidation reaction of 11 leading to keto–lactam 12.

expansion reaction in $Ph_8C_{70}$ undergoing spontaneous air oxidation to the bislactone 13 (13-atom orifice, Figure 6).[37] Hirsch and others have subsequently carried out ring expansions from bisazide additions to $C_{60}$, affording 14-, 13-, and 13-membered ring openings, respectively (14, 15a, and 15b, Figure 6).[38]

Our group has recently discovered the formation of the cobalt(III) complex 17 resulting from oxidative insertion of a CpCo fragment into a single bond of the bisfulleroid 16 (Figure 7).[39, 40] It is the product of an overall sequential triple scission of a 6-membered ring on $C_{60}$ affording a 15-membered ring, whereby the retro [2 + 2 + 2] ring opening step in going from 16′ to 16 is analogous to that hypothesized for $C_{60}H_6$ (2a, Figure 1A). Two of the three 5-membered rings surrounding this 6-membered ring open up at this step, while the last bond scission occurs during the cobalt-complexation step.
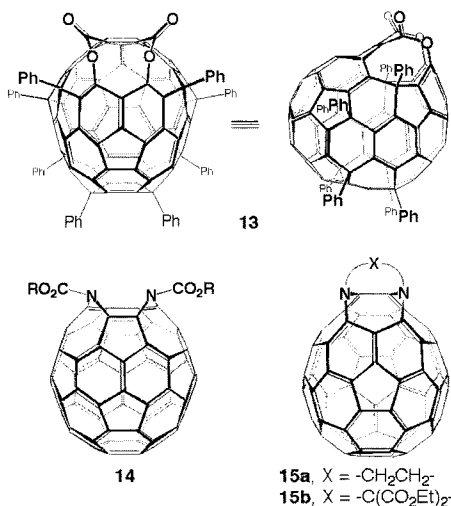
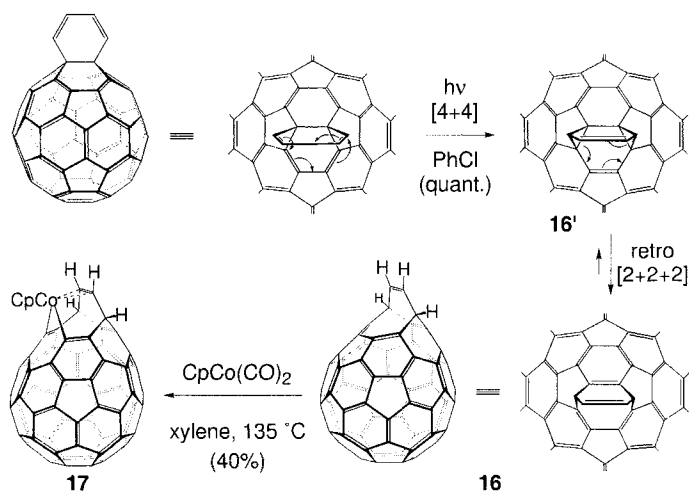Figure 6. Structures of the "holey" fullerenes prepared by Taylor,[38] Hirsch, Luh, and Chan.[39]

15a, X = -CH₂CH₂-
15b, X = -C(CO₂Et)₂-
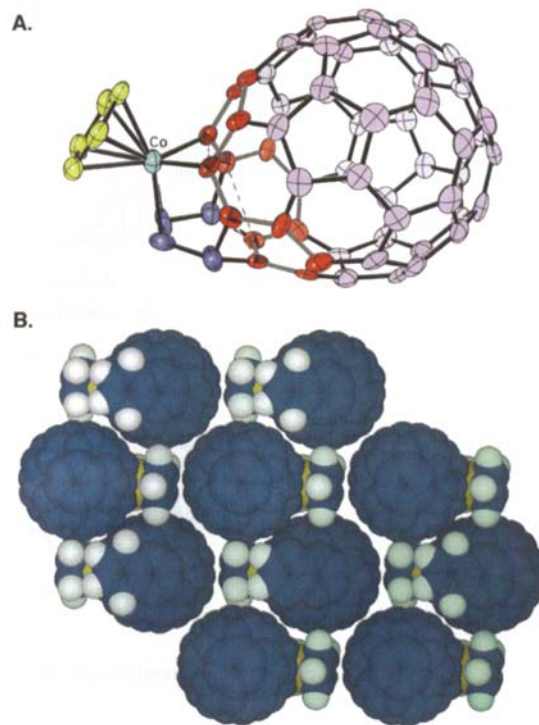


Figure 7. Synthesis of the cobalt(III) complex 17.



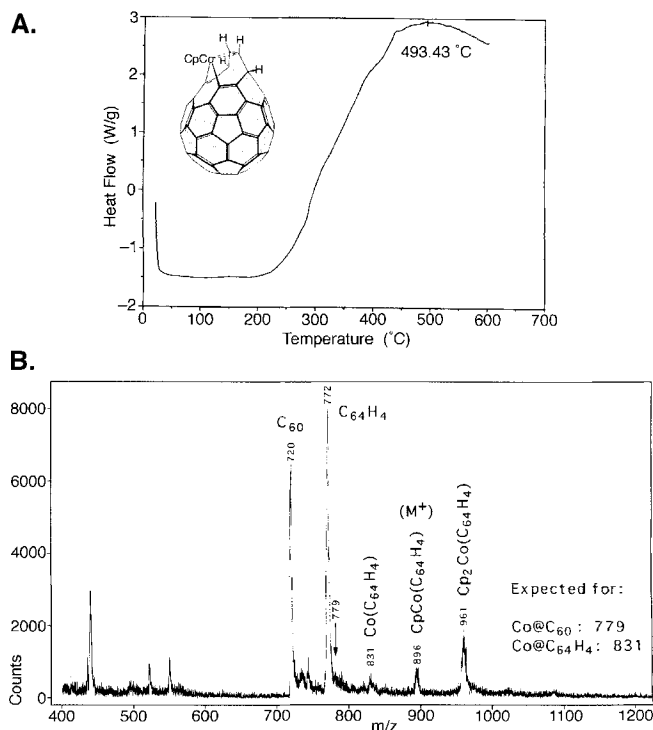Figure 8. A) X-ray crystal structure of complex 17 and B) its packing structure.



Figure 9. A) Differential scanning calorimetry (DSC) of cobalt complex 17. B) LD-MS of cobalt complex 17 obtained without matrix.

The structure of complex 17 was confirmed by X-ray crystallography (Figure 8A). It shows that the cobalt atom is poised to insert into the orifice of the fullerene, provided that the cyclopentadienyl, or a much less strongly bound ligand, can be removed in the process. In addition, the space separating the two carbon atoms bound to cobalt is quite small (2.41 Å). It will therefore be necessary to expand it by vibrational activation and/or the use of high pressure.[41]

An intriguing prospect arose upon consideration of the crystal packing structure of complex 17 (Figure 8 B) suggesting that crystal vibrations (along the horizontal axis) may add to internal molecular vibrations to force the metal inside the fullerene with concomitant loss of the Cp ligand. To check this possibility, we have investigated the thermal behavior of compound 17 in the crystal by differential scanning calorimetry (DSC). Remarkably, this experiment shows that the complex is stable up to 220 °C (Figure 9A). However, complex 17 starts polymerizing above 250 °C in the crystalline state. Milligram quantities of compound 17 were heated for prolonged periods below its decomposition temperature (220 °C up to 10 h per sample). Remarkably, practically no decomposition of 17 was observed, while no new compound could be detected.

On the other hand, laser desorption mass spectrometry (LD-MS) performed directly on compound 17 gives a peak corresponding to $Co@C_{64}H_4$ at $m/z = 831$ (Figure 9 B). Whether the metal is endohedral or not needs to be determined. Interestingly, a fairly intense peak at $m/z = 961$ is observed for the parent ion with an additional Cp unit ($Cp_2CoC_{64}H_4$). This could be signif-

icant, since the additional $C_5H_5$ unit may come from an adjacent molecule of **17** in the crystal through a collision-activated reaction.

Further efforts to induce the metal to insert inside the fullerene framework, such as changing the Cp ligand of **17** for a more labile system like the indenyl ligand, are currently under way. As things stand, the opening of fullerenes seems to be a very promising approach to endohedral metallofullerenes. An exciting prospect lies in the opening of an entire seam on the surface of $C_{60}$ by a twofold application of the sequence of reactions that lead to the cobalt complex **17**. We have already prepared the rearranged product **20a**, although as a presently inseparable mixture with its diastereomer **20b** (Scheme 2). Once



Scheme 2. On the way to opening a seam on $C_{60}$.
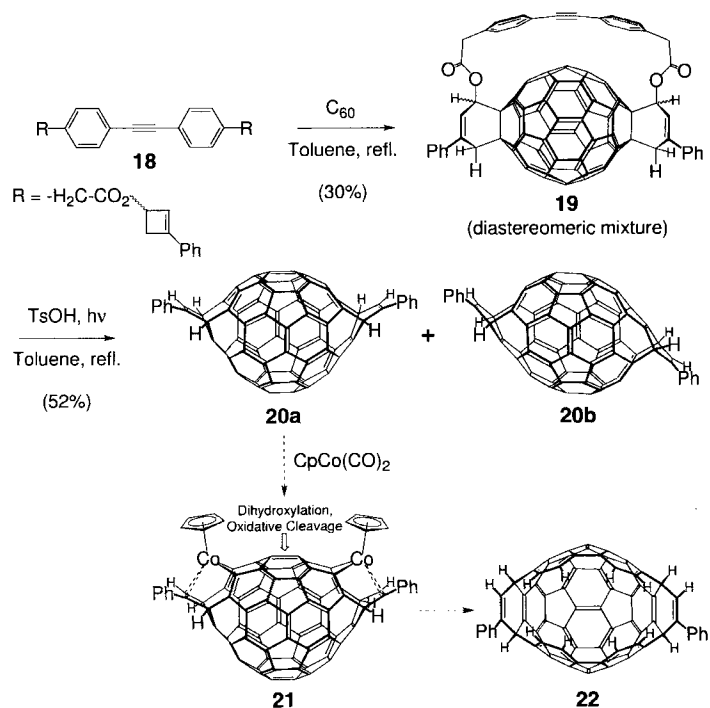
pure samples of **20a** can be obtained, the biscobalt complex **21** will be formed. We anticipate that the C=C bond separating the two 15-atom openings in **21** can be dihydroxylated and cleaved to a dicarbonyl product,[42] which may be further transformed to the open system **22** or a similar wide-open "clam-shell" compound.

**Zipping up fullerene precursors—advances and prospects:** The challenging synthesis of acetylenic precursors such as **8** or **9** (Figure 3) is currently being pursued.[43–45] We have recently prepared fullerene precursors less substituted at benzene—and therefore easier to access—namely, compound **7a** ($C_{60}H_{18}$) and **7b** ($C_{84}H_{30}$) (Scheme 3).[23a, 46] These compounds are synthe-
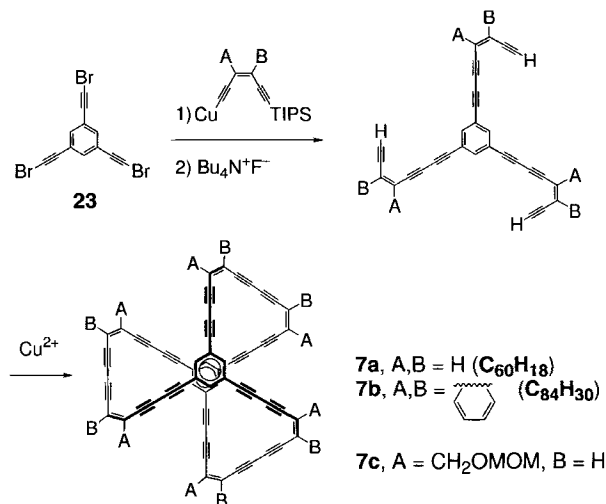


Scheme 3. Synthesis of the stable fullerene precursors **7a** ($C_{60}H_{18}$) and **7b** ($C_{84}H_{30}$).

sized in a few steps from trisbromoalkyne **23** in sizable quantities. The methoxymethyl-protected allylic alcohol (**7c**) was prepared to study the conformational exchange process in this interesting helical system.[46]

MALDI mass spectrometric studies on **7a** and **7b** give parent ions showing surprisingly little propensity to lose hydrogen.[23a] In this particular case, Bergman cyclization of the enediyne moieties must dominate the reaction pathway, which at first seems advantageous (Figure 10). Bergman cyclization of unstrained enediynes in solution occurs at relatively mild temperatures ($\geq 180\,°C$, $E_a = 20–30\ kcal\,mol^{-1}$).[47] We are currently attempting to trap the valence-saturated compound corresponding to intermediate **24**. In the gas phase under the MALDI conditions, it is conceivable that stepwise rearrangement of all the enediyne moieties to **25** with subsequent radical recombination can lead to **26** or a similar species with 1,2-shifted hydrogens. The rigid species **26** is not likely to rearrange to $C_{60}$ under the mild conditions of MALDI, because the required bond formations are severely hindered by its topology. It can be argued that the poor tendency of the $C_{60}H_{18}$ radical cation to lose hydrogen in the LD-MS experiments results from the formation of **26** or similar "locked" intermediates that are unable to "zip up" to the desired framework of $C_{60}$, itself known to give up hydrogen very easily.[23a]

Various as yet unsuccessful attempts to effect the conversion of **7a** to $C_{60}$ or **7b** to $C_{84}$ by flash vacuum pyrolysis or in
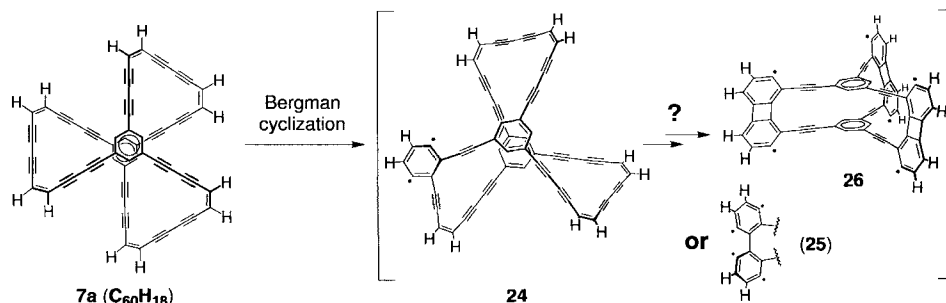


Figure 10. Conceivable intermediates in the LD-MS of precursor **7a** ($C_{60}H_{18}$).

solution—with or without the presence of transition metals—indicate that the precursors may need to be better preorganized to undergo efficient cascade bond rearrangements to the desired fullerenes.

A suitable bond reorganization scheme for an intermediate (28) resulting from multiple Bergman cyclizations is represented by the Schlegel diagram in Figure 11. It necessitates the modifi-
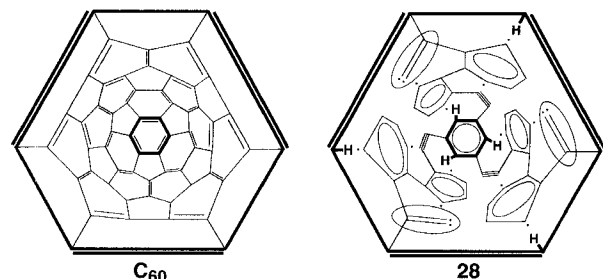


Figure 11. Schlegel diagrams of $C_{60}$ and species 28 viewed down $C_3$-axes.

cation of one half of 7a, whereby the alkyne units connected directly to the top benzene (outermost bold ring) are replaced by ethylidene units (circled). This can be realized with the dibromo-olefinated precursor 27 (Scheme 4, Figure 12), which will be able to generate the required vinylidene carbene units in the gas phase, in a stepwise fashion of course.
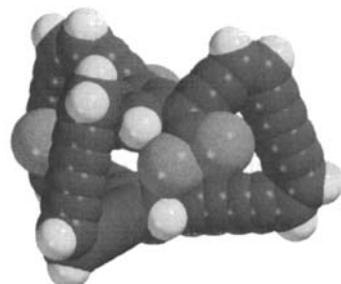


Figure 12. PM 3-minimized structure of precursor 27 ($C_{60}H_{18}Br_6$).

It seems appropriate for the purpose of this article to look closer at a possible bond-formation pathway that may convert precursor 27 to $C_{60}$ (Scheme 4). It is based on relatively common mechanistic pathways for radicals and carbenes and it is made to proceed symmetrically for easier visualization. Should the set of bond-formations occur as shown, it is readily apparent from the geometry of the intermediates that conversion to $C_{60}$ will be greatly facilitated over that of precursor 7a. The structures of Scheme 4 have close reactive centers at each step of bond formation. This set of rearrangements illustrates how the sequential formation of 27 carbon–carbon bonds in one transformation has the potential to induce the extended system of 27 to "zip up" to the framework of $C_{60}$.
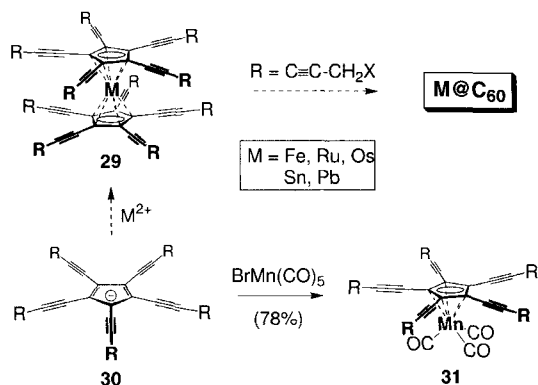
## Outlook

There are many ways that one can approach the problem of endohedral metallofullerene synthesis. It is possible that the graphite evaporation method will ultimately allow the isolation of pure samples of $C_{60}$ endohedral complexes. However, the novel approaches discussed in this article have the potential of providing easier and more practical access to a wide variety of endohedral metallofullerenes, especially those incorporating transition metals. The vision of reaping high benefits from this novel class of materials is a strong incentive to explore their preparation in any way possible.

The incorporation of a transition metal into a fullerene precursor in the form of a metallocene may help bypass the difficulties associated with the synthesis of large macrocycles. We have recently reported on this variation of the "zipper" strategy by targeting decaalkynylmetallocenes 29 (Scheme 5).[23b] These unknown derivatives of metallocenes are the required intermediates for the preparation of the fullerene precursors (29, R = C≡C–CH$_2$X, where X is a leaving group) with molecular formula $M \cdot C_{60}H_{20}X_{10}$.

Anion 30 can be generated in THF by halogen–lithium exchange of the corresponding chloride.[23b] Since our initial attempts to produce a decaalkynylmetallocene (29) were made
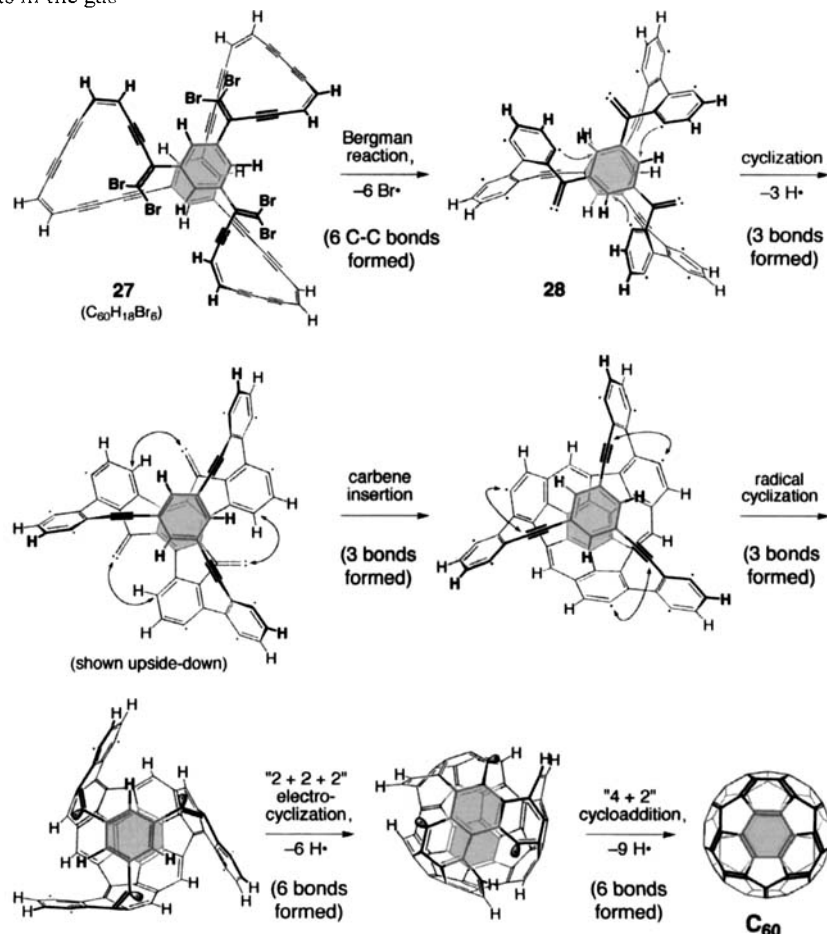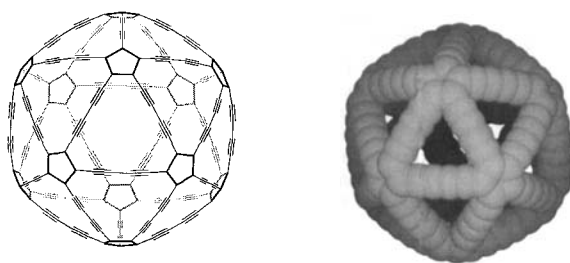


Scheme 4. A conceivable gas-phase rearrangement pathway converting compound 27 to $C_{60}$ under thermolytic conditions. Each step implies sequential rearrangements around the threefold axes of the intermediates, but only for easier visualization. Structures were created by projection of the corresponding valence-saturated systems minimized by MM 3.

Scheme 5. The metallocene approach to endohedral metallofullerenes.



Figure 14. Ball-and-stick and space-filling representations of a hypothetical fullereneynenickel(o) complex, $C_{120}Ni_{20}$.

with the TIPS-protected system (owing to the large stabilization provided by this bulky group), even large metals like Sn and Pb did not produce the metallocenes **29**. However, we have verified the validity of this approach by treating anion **30** (R = TIPS) with [BrMn(CO)$_5$] to afford the half-sandwich complex **31** in good yield.[48] We are currently pursuing the synthesis of the decalkynylmetallocenes **29** with smaller silyl protecting group, as well as with the butadiynyl system (R = C≡C–TIPS).

An exciting prospect which will be made possible by the methodology outlined in the preceding paragraph lies in the potential ability to form very large porous carbon spheres called fullereneynes (Figure 13).[49] These systems have fullerene

newed discoveries, and perhaps to important technological applications. There is a great opportunity for synthetic organic chemists to develop a practical synthesis of these compounds. By preparing either "holey" fullerenes with large cavities or by synthesizing well-characterized precursors containing complexed metals, synthesis could be the key to providing endohedral metallofullerenes in pure form with a large variety of metals inside.

**C$_{180}$(MCp)$_{12}$**
(pentagons represent CpFe-**Cp** units)

Figure 13. Structure of a dodecakis(cyclopentadienyl)iron complex of $C_{180}$ (left) and space-filling representation of fullereneyne $C_{180}$ (right).

frameworks expanded by acetylene or butadiyne units, which create sizable holes in their structures. They should be approachable by a stepwise coupling/cyclization strategy starting from differentially protected half-sandwich complexes analogous to **31** or the corresponding pentaethynylmetallocenes (CpM[C$_5$(C≡C–R)$_5$]), leading to the structure depicted in Figure 13 (left).

Even more intriguing is the possibility that the $C_{120}$-fullereneyne based on the acetylene-expanded framework (more exactly a [5]radialene–[4]cumulene motif) may become the basis of metal–carbon frameworks in which the metal fills up its pores (e.g. $C_{120}Ni_{20}$, Figure 14) in a manner analogous to the known tribenzo[12]cyclynenickel(o) complex.[50] Such structures may lead to a new family of conductors or superconductors since the tribenzocyclyne complex is itself conducting.[50]

In view of the short but astonishing history of $C_{60}$ and other fullerenes, endohedral metallofullerenes can only lead to re-
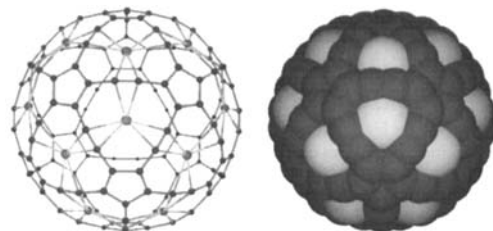
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