Triple Scission of a Six-Membered Ring on the Surface of C_{60} *via* Consecutive Pericyclic Reactions and Oxidative Cobalt Insertion

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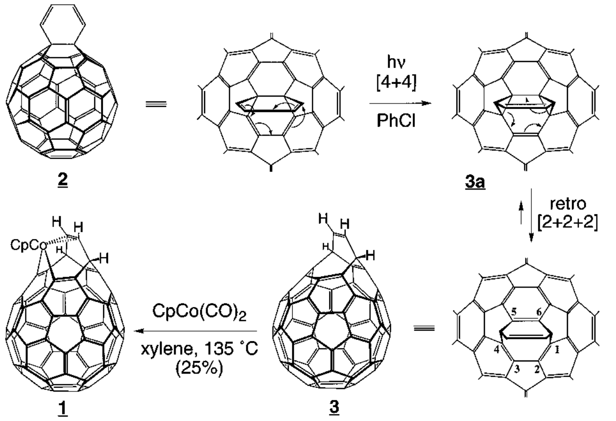
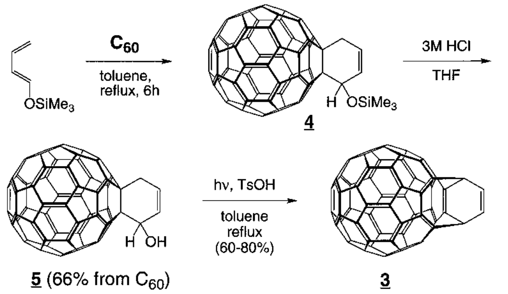
One of the main challenges in fullerene chemistry is the preparation of endohedral metal−C_{60} complexes in isolable and stable form, which would provide answers to a number of questions regarding their potential as novel superconductors, ferromagnets, or other interesting materials.[1] While lanthanide endohedral complexes of higher fullerenes (e.g. La@C_{82}) have been available for some time, analogous lanthanide−C_{60} complexes do not seem to be stable or readily isolable.[2,3] Thus, the graphite evaporation method[4] is limited in the choice of metal or fullerene size, and new approaches to endohedral fullerene complexes have become necessary. Apart from total synthetic approaches,[5] the alternative method consisting of opening a temporary hole within a fullerene framework has already shown its wonders in the preparation of noble-gas-labeled fullerenes under high temperature and pressure (e.g. ^{3}He@C_{60}).[6] Recent work has shown that permanent openings consisting of 11- and 14-membered rings can be created on C_{60},[7,8] but the hole is too small or hindered to allow the introduction of an atom into the fullerene framework. In this context, we are reporting the unprecedented formation of the cobalt(III) complex **1** resulting from a sequential triple scission of a six-membered ring on C_{60} affording a 15-membered ring. This type of complex could be one of the most promising candidates for the introduction of a metal into the C_{60} framework.

This work originated from the discovery that diene **2**[9] undergoes a very facile photochemically promoted rearrangement to the stable bridged bis-fulleroid **3**. This process occurs *via* the initial [4 + 4] photoadduct **3a** (not observed), which undergoes a thermally allowed [2 + 2 + 2] cycloreversion to afford a bis-methano[12]annulene structure (**3**). The [4 + 4] photocyclization reaction has precedent in the classic work of Masamune and Ginsburg on derivatives of 9,10-dihydronaphthalene, but these photoadducts are unstable.[10] Calculations at the AM1 and PM3 levels show that the [4 + 4] photocyclization reaction of **2** to **3a** goes uphill by ∼27 kcal/mol, and the [2 + 2 + 2] ring opening to **3** provides an overall 14−24 kcal/mol energy gain (Table 1).



To obtain significant amounts of compound **3**, we developed a straightforward synthesis bypassing the need to isolate the oxygen-sensitive diene **2**.[9] Addition of a 2-fold excess of 1-((trimethylsilyl)oxy)-1,3-butadiene to C_{60} ($PhCH_3$, reflux) afforded the silyl ether **4**, which was usually not isolated. Acidic aqueous workup furnished the allylic alcohol **5** in up to gram quantities, which was simply purified by filtration through a pad of silica gel with toluene. Photolysis (sunlamp) under reflux and acidic conditions (TsOH) afforded good yields of the bis-fulleroid **3**.



Bis-fulleroid **3** is purple in solution like all known fulleroids. The structure of **3** was deduced from the high symmetry displayed by the ^{1}H and ^{13}C NMR spectra and the characteristic UV−vis spectrum (supporting information). A gated decoupled ^{13}C NMR spectrum ($CDCl_3/CS_2$, 1:1) further confirmed the presence of a fulleroid bridgehead C−H resonance at 43.3 ppm (dt) with $^1J_{CH} = 140.4$ and $^{2(3)}J_{CH} = 7.1$ Hz (a cyclopropane C−H should have $^1J_{CH} \approx 160−175$ Hz).[12] The olefinic C−H at 127.9 ppm is a ddd with $^1J_{CH} = 167.8$, $^2J_{CH} = 7.0$, and $^3J_{CH} = 5.0$ Hz. In addition, five C_{60} carbons at 126.4 (d), 138.7 (m), 139.9 (d), 140.6 (d), and 149.9 ppm (d) also show long-range couplings (two two-bond and three three-bond J_{CH}). However, these data did not allow us to dispel another, but much less likely, positional isomer of **3** having the same C_s-symmetry (bridgeheads at the 1,2,3,4-positions),[13] and we set out to obtain an X-ray structure of this interesting compound.

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[1] (a) Funasaka, H.; Sakurai, K.; Oda, Y.; Yamamoto, K.; Takahashi, T. *Chem. Phys. Lett.* **1995**, *232*, 273−277. (b) Suzuki, T.; Maruyama, Y.; Kato, T.; Kikuchi, K.; Achiba, Y. *J. Am. Chem. Soc.* **1993**, *115*, 11006−11007.

[2] (a) Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 981−985. (b) Takata, M.; Umeda, B.; Nishibori, E.; Sakata, M.; Saito, Y.; Ohno, M.; Shinohara, H. *Nature* **1995**, *377*, 46−49. (c) Beyers, R.; Kiang, C. H.; Johnson, R. D.; Salem, J. R.; Devries, M. S.; Yannoni, C. S.; Bethune, D. S.; Dorn, H. C.; Burbank, P.; Harich, K.; Stevenson, S. *Nature* **1994**, *370*, 196−199. (d) Kikuchi, K.; Suzuki, S.; Nakao, Y.; Nakahara, N.; Wakabayashi, T.; Shiromaru, H.; Saito, K.; Ikemoto, I.; Achiba, Y. *Chem. Phys. Lett.* **1993**, *216*, 67−71.

[3] Ca@C_{60} is highly O_2 and water sensitive: Kubozono, Y.; Ohta, T.; Hayashibara, T.; Maeda, H.; Ishida, H.; Kashino, S.; Oshima, K.; Yamazaki, H.; Ukita, S.; Sogabe, T. *Chem. Lett.* **1995**, 457−458.

[4] Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354−358.

[5] Rubin, Y.; Parker, T. C.; Khan, S. I.; Holliman, C. L.; McElvany, S. W. Submitted for publication in *J. Am. Chem. Soc.*

[6] Saunders, M.; Jimenez-Vazquez, H. A.; Cross, R. J.; Mroczkowski, S.; Gross, M. L.; Giblin, D. E.; Poreda, R. J. *J. Am. Chem. Soc.* **1994**, *116*, 2193−2194.

[7] (a) Hummelen, J. C.; Prato, M.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 7003−7004. (b) Birkett, P. R.; Avent, A. G.; Darwish, A. D.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1995**, 1869−1870.

[8] Lamparth, I.; Nuber, B.; Schick, G.; Skiebe, A.; Grösser, T.; Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2257−2259.

[9] An, Y.-Z.; Ellis, G. A.; Viado, A. L.; Rubin, Y. *J. Org. Chem.* **1995**, *60*, 6353−6361.

[10] (a) Babad, E.; Ginsburg, D.; Rubin, M. B. *Tetrahedron Lett.* **1968**, 2361−2363. (b) Masamune, S.; Seidner, R. T.; Zenda, H.; Wiesel, M.; Nakatsuka, N.; Bigam, G. *J. Am. Chem. Soc.* **1968**, *90*, 5286−5288.

[11] *SPARTAN version 4.0.1*; Wavefunction Inc.: 18401 Von Karman Avenue, Suite 370, Irvine, CA 92715.

[12] Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J. *J. Am. Chem. Soc.* **1993**, *115*, 5829−5830.

[13] This surprising structure with open 6,6-ring junctions has been proposed for a bis-azafulleroid: see ref 8.

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Table 1. Calculated Heats of Formation and Relative Energies (kcal/mol) for Compounds **2**, **3a**, **3**, and C_{60}[11]

compd	AM1 (rel energy)	PM3 (rel energy)	compd	AM1 (rel energy)	PM3 (rel energy)
2	979.95 (24.09)	819.48 (13.47)	**3**	955.86 (0)	806.01 (0)
3a	1007.48 (51.62)	846.48 (40.47)	C_{60}	973.34 (17.48)	811.75 (5.74)

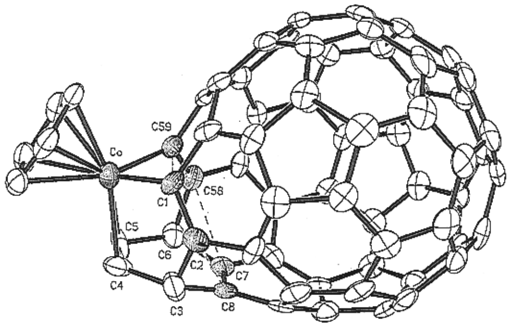
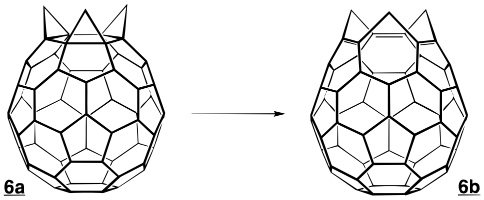


Figure 1. X-ray structure of cobalt complex **1**.

After several unsuccessful attempts on **3** and some alkyl derivatives,[14] we decided that a metal derivative would be the most likely candidate for X-ray diffraction. An attractive idea was that the eight-membered ring formed by the ethylene bridge, the two methano bridgeheads, and the 1,2,3,4-diene moiety on **3** strongly resembles the COD ligand (COD = 1,5-cyclooctadiene) in its geometry. Thus, we made the choice of using cyclopentadienylcobalt(I) as the metal fragment, and reaction of **3** with $CpCo(CO)_2$ successfully afforded a new stable complex (**1**). Slow evaporation of complex **1** from CS_2/toluene afforded small prisms suitable for X-ray structural determination.

The crystal structure of complex **1** shows that the ethylene bridge has indeed acted as an effective η^2-handle to the metal (Figure 1).[15] To our surprise and delight, the C1−C59 bond within the five-membered ring adjacent to the bis-methano[12]-annulene ring of **3** has been broken by oxidative insertion of the cobalt. The distance between the C1 and C59 carbons is 2.41(1) Å, and the C1−Co and C59−Co bond lengths are 1.923(8) and 1.902(8) Å, respectively, within known single $C(sp^2)-Co$ bond lengths,[16] while the C1−Co−C59 angle is 78.1(3)°. The facility by which the C1−C59 bond in **3** is broken is analogous to that seen in the reaction of $CpCo(CO)_2$ with cyclobutenediones.[17]

The bond lengths between the ethylene bridge carbons C4 and C5 and the cobalt are 2.119(9) and 2.112(10) Å, respectively, which are somewhat longer than those observed in CpCo(COD).[18] The alkene bridge C4−C5 bond length, at 1.329(14) Å, is barely different from that calculated for **3** (1.336 Å by AM1).[11] As shown by the shaded carbon atoms C1, C2, C8, C7, C58, and C59, the six-membered ring originally flanking the cyclohexadiene moiety in **2** has effectively been cleaved into three alkene moieties resembling compound **6b** through a formal $[\pi 2^s + \pi 2^s + \pi 2^s]$ cycloreversion of a *cis*-trishomobenzene (**6a**).[19] The distances in **1** between the sp^2 carbons C2−C8 and C7−C58 holding the methano bridges are 2.32(1) and 2.34(1) Å, respectively. The "trimethano[15]annulene" opening within the C_{60} framework is the largest annulene ring created thus far on a fullerene. Molecular dynamics calculations performed on the hypothetical C1−C59-bonded thioether to simulate the behavior of **1** show that vibrational modes favor the expansion of the cavity to a point that would allow a C1−C59-attached metal to slip inside the fullerene under proper thermal activation. We are currently pursuing this goal.



6a **6b**

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Supporting Information Available: ^1H and ^{13}C NMR spectra of **1**, **3**, and **5**; UV−vis absorption spectrum of **3**; X-ray structure of complex **1**: fully labeled view of the structure, tables of atomic coordinates, displacement parameters, bond lengths, bond angles, and torsion angles (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(14) **Note Added in Proof:** A recent X-ray diffraction of **3** as a 1:1 compound with C_{60} confirms its structure.

(15) Compound **1** ($C_{69}H_9Co{\cdot}C_6H_5CH_3$; $M_r = 988.92$) crystallized in the monoclinic space group $P2_1/c$ with cell dimensions of $a = 15.00$ (1) Å, $b = 13.53$ (1) Å, and $c = 19.95$ (1) Å, $\beta = 111.53$ (2)°, $V = 3767$ (4) Å^3, and an occupation of $Z = 4$ in the unit cell. Data were collected at 156 K on a Picker diffractometer using graphite-monochromated Mo Kα radiation, to a maximum $2\theta = 60°$, giving 11302 unique reflections; the structure was solved by direct methods (SHELX86) and refined within full matrix least squares, yielding $R = 0.076$, $R_w = 0.081$ for 3681 independent reflections with $I > 3\sigma(I)$.

(16) Zhou, Z.; Battaglia, L. P.; Chiusoli, G. P.; Costa, M.; Nardelli, M.; Pelizzi, C.; Predieri, G. *J. Organomet. Chem.* **1991**, *417*, 51−63.

(17) (a) Liebeskind, L. S.; Baysdon, S. L.; South, M. S.; Blount, J. F. *J. Organomet. Chem.* **1980**, *202*, C73-C76. (b) Cho, S. H.; Wirtz, K. R.; Liebeskind, L. S. *Organometallics* **1990**, *9*, 3067−3072.

(18) Ondracek, J.; Schehlmann, V.; Maixner, J.; Kratochvil, B. *Collect. Czech. Chem. Commun.* **1990**, *55*, 2447−2452.

(19) (a) de Meijere, A.; Kaufmann, D.; Schallner, O. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 417−418. (b) Kaufmann, D.; Fick, H.-H.; Schallner, O.; Spielman, W.; Meyer, L.-U.; Gölitz, P.; de Meijere, A. *Chem. Ber.* **1983**, *116*, 587−609. (c) Prinzbach, H.; Stusche, D. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 799−800.