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Dissolving Metal Reductions of Fullerenes

Robert G. Bergosh, Mark S. Meier,* Janeen A. Laske Cooke, H. Peter Spielmann,[†] and Brad R. Weedon

Department of Chemistry and Department of Biochemistry, University of Kentucky, Lexington, Kentucky 40506-0055

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Treatment of fullerenes with reducing metals and a proton source leads to the formation of hydrogenated fullerenes ($C_{60}H_n$ and $C_{70}H_n$). The reaction of C_{60} with a variety of metals was investigated, using metals that span a broad range of reducing power, from tin ($E° = -0.14$ V) to magnesium ($E° = -2.36$ V). We report useful synthetic routes to a number of reduced fullerenes, including $C_{60}H_2$, $C_{60}H_4$, and $C_{60}H_6$, and we have determined that, despite the huge number of isomers that are possible, a small number are actually formed in these cases. For example, only two isomers of $C_{60}H_6$ are obtained in the Zn(Cu) reduction of C_{60}, in a 6:1 ratio. Three isomers of $C_{70}H_{10}$ are produced, in ratios that are dependent on reaction time.

Introduction

Reduced fullerenes, alternatively called fullerene hydrides or fulleranes, are the simplest derivatives of the fullerene class of molecules.[1] While there are potentially 30 different neutral $C_{60}H_{2n}$ species (*not* including the numerous possible isomers for most),[2−11] detailed structural characterization of individual isomers has been reported only for $C_{60}H_2$,[2−4] $C_{60}H_4$,[5,6] $C_{60}H_6$,[7] and $C_{60}H_{18}$.[12]

The preparation of one specific $C_{60}H_{2n}$ species is difficult, due to numerous adjacent oxidation states between C_{60} and a hypothetical $C_{60}H_{60}$ species. Established routes to hydrogenated fullerenes include Birch reduction,[10] hydroboration,[2,6,11,13] hydrozirconation,[14] solution phase[3] and solid phase hydrogenation,[15,16] hydrogenation by addition of hydrogen atoms,[17] transfer hydrogenation,[9] electrochemical reduction[18] as well as chemical reduction with diimide,[6] chromous acetate,[6] photoinduced electron transfer,[19] and with hydride reducing agents.[20] Some species ($C_{60}H_2$) have been formed as byproducts in the photochemical addition of amines to C_{60}.[21] We have been interested in the use of dissolving metal reductions to produce novel reduced fullerenes.[7,22] Dissolving metal reductions have some potentially advantageous characteristics. Specifically, some metals are quite weak reducing agents and should not convert C_{60} to highly reduced species, while others are powerful reducing agents and can reduce C_{60} to highly reduced materials. For example, the Birch reduction of C_{60} stops at (or near[23]) the $C_{60}H_{36}$ stage,[10] presumably because lithium metal ($E° = -3.0$ V) is not powerful enough to reduce the remaining double bonds. In principle, the degree of reduction will be determined by the reduction potential of the metal used.

There are numerous metals that may be useful for the preparation of $C_{60}H_{2n}$. We have selected metals that are capable of reducing C_{60} as well as reducing the initial products, such as $C_{60}H_2$, which is 0.12 V more difficult to reduce than C_{60}. The metals used in this study include Zn ($E° = -0.76$ V), Ti ($E° = -1.63$ V), Al ($E° = -1.66$ V), and Mg ($E° = -2.37$ V).

Results and Discussion

We have previously reported that reduction of C_{60} with zinc dust ($E° = -0.76$ V), in a two-phase, toluene/aqueous

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[†] Department of Biochemistry.

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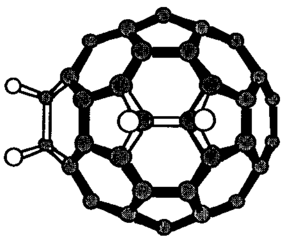
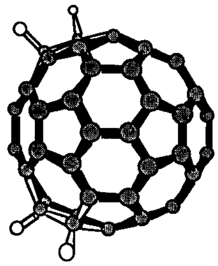
acid mixture produced a series of reduced fullerenes, including $C_{60}H_2$, $C_{60}H_4$, and $C_{60}H_6$,[22] although with low conversion. However, treating C_{60} in toluene with wet Zn(Cu) couple results in a more efficient reduction that produces, in turn, $C_{60}H_2$, $C_{60}H_4$, and finally $C_{60}H_6$. Monitoring the progress of the reaction by HPLC (see Experimental Section) permits good yields of each of these species to be obtained from Zn(Cu) reactions that are stopped at appropriate times. Reaction times are largely determined by the efficiency of stirring and by the ratio of metal to C_{60}. For example, in a reaction using 250 mg of C_{60} and Zn(Cu) prepared from 5 g of Zn dust, $C_{60}H_2$ (**1**) accounted for 78% (by HPLC) of the reaction mixture after 1 h. This product was separated from other components in the mixture by GPC,[22] resulting in a 66% isolated yield.

Similar reactions that proceeded for 90 min produced $C_{60}H_4$ (**2**), which was isolated by HPLC (see Experimental Section) in 45% yield from C_{60}. A small amount (18%) of $C_{60}H_6$ is also present at this point. Analysis of the $C_{60}H_4$ sample revealed that three isomers (**2a**, **2b**, and **2c**) are present in a 1:1:0.3 ratio, respectively. As we observed previously,[22] the composition of this mixture is different from the mixture which results from hydroboration of $C_{60}H_2$.[5,22] We suspect that this distribution of isomers is a kinetic mixture, but the difficulty of separating macroscopic amounts of these species has prevented definitive proof of this. Comparison of chromatograms and ^1H NMR spectra confirmed that **2a** is 1,2,18,36-$C_{60}H_4$, reported previously by Cahill.[5] In the bond labeling scheme of Hirsch, the second pair of hydrogens add to an equatorial (e′) bond, also denoted as I, eI.[25] The ^1H NMR (CS_2/acetone-d_6) spectrum of this isomer exhibited a singlet at 6.42 ppm and an AB pattern centered at 6.11 ppm. The ^1H NMR spectrum of **2b** exhibited a single AB pattern centered at 6.66 ppm in CS_2 solution with J_{AB} = 15.5 Hz. These data alone are insufficient for a definitive structural assignment, but are consistent with the 1,2,33,50 isomer of $C_{60}H_4$ (trans-3 isomer[25]), important in the formation of the dominant isomer of $C_{60}H_6$ (see below). The identity of the minor isomer of $C_{60}H_4$ (**2c**) has not been firmly established, due to the limited amounts formed and its tendency to decompose to unidentified material.

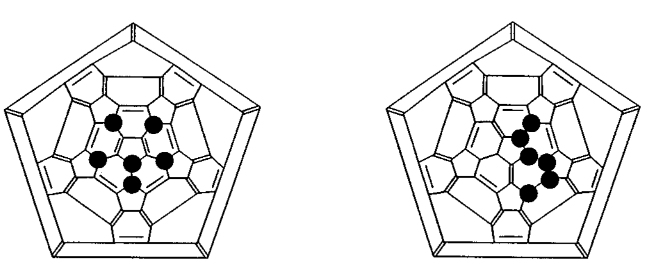


1,2,18,36 (**2a**)



1,2,33,50 (**2b**)

When a mixture of C_{60} in toluene was heated with wet Zn(Cu) for 3 h, the resulting mixture contained two isomers of $C_{60}H_6$ (**3a** and **3b**) in a 6:1 ratio and two (or more) $C_{60}H_6O$ species.[7] The major isomer, obtained in 30%−40% yield by preparative HPLC (see Experimental Section), showed a very simple ^1H NMR spectrum (a singlet at 6.0 ppm in CS_2). This spectrum was not changed by cooling the sample to −80 °C, suggesting that the singlet is not the result of a dynamic process, nor was it affected by the addition of TFA, suggesting that the singlet is not the result of a highly symmetrical $C_{60}H_5$ anion, unless $C_{60}H_6$ is extraordinarily acidic.



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5

Figure 1. Schlegel diagrams of $C_{60}R_6$ structures **4** and **5**.

Only ten lines were observed in the ^1H-decoupled ^{13}C NMR spectrum, including one sp^3 carbon at 52.28 ppm and nine sp^2 carbon resonances of equal intensity. The presence of ten distinct types of carbon atoms suggested that the hydrogens were arranged symmetrically around *both* 2-fold and 3-fold symmetry axes. The ^1H and ^{13}C NMR spectra cannot be rationalized in terms of $C_{60}X_6$ structures formed by reaction of C_{60} with Cl_2 or Br_2. For example, the structure of $C_{60}Cl_6$[26] and of $C_{60}Br_6$,[27] have C_s-symmetry (**4**, Figure 1). Such structures ideally exhibit 32 lines in the ^{13}C NMR spectrum, far more than we observe.

An alternative structure, **5**, proposed by Cahill based on 6-31G** *ab initio* calculations[28] and nearly isoenergetic with a substitution pattern like that in $C_{60}Cl_6$[26] essentially involves extension of the established[5] thermodynamic isomer of $C_{60}H_4$ by two additional hydrogens. This structure should also show many more lines than we observe in the ^{13}C spectrum of the major isomer of $C_{60}H_6$, and neither **4** nor **5** would be expected to produce a singlet in the ^1H spectrum.

Comparison of the ^1H-coupled ^{13}C NMR spectrum of the major isomer of $C_{60}H_6$ (**3a**) with the ^1H-coupled ^{13}C NMR spectrum of $C_{60}H_2$ (**1**) was very illuminating. $C_{60}H_2$ is known to have a 1,2-arrangement of hydrogens.[2] The sp^3 carbon resonances of $C_{60}H_2$ and **3** are split by nearly identical 141 and 142 Hz couplings,[24] respectively, and by identical −6.7 Hz two-bond C−H coupling (Figure 2). Simulation[29] of this section of the spectrum as an AA′X system revealed a 14.7 Hz $^1H-^1H$ coupling constant and the (−) sign of the two-bond J-coupling.[30] The near identical coupling patterns establishes that the hydrogens in **3a** are arranged in pairs on adjacent carbons as they are in $C_{60}H_2$.

The requirement that the hydrogens be arranged in pairs on adjacent carbons, in addition to the constraints imposed by the singlet in the ^1H spectrum and the presence of 10 lines in the ^{13}C spectrum (2-fold and 3-fold

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[24] One-bond C−H coupling constants of 141.2 Hz and 142 Hz in $C_{60}H_2$ have been reported: see references 11 and 14.

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[30] Cahill has reported (reference 13) a 15.7 Hz H−H coupling constant in $C_{60}H_2$. Our best fit, using both the sp^3 resonance and the downfield multiplet, is for a 14.7 Hz coupling constant. However, while the best fit is for 14.7 Hz, due to the low signal-to-noise ratio, the multiplet can be adequately fit with a H−H coupling constant of 13−17 Hz.

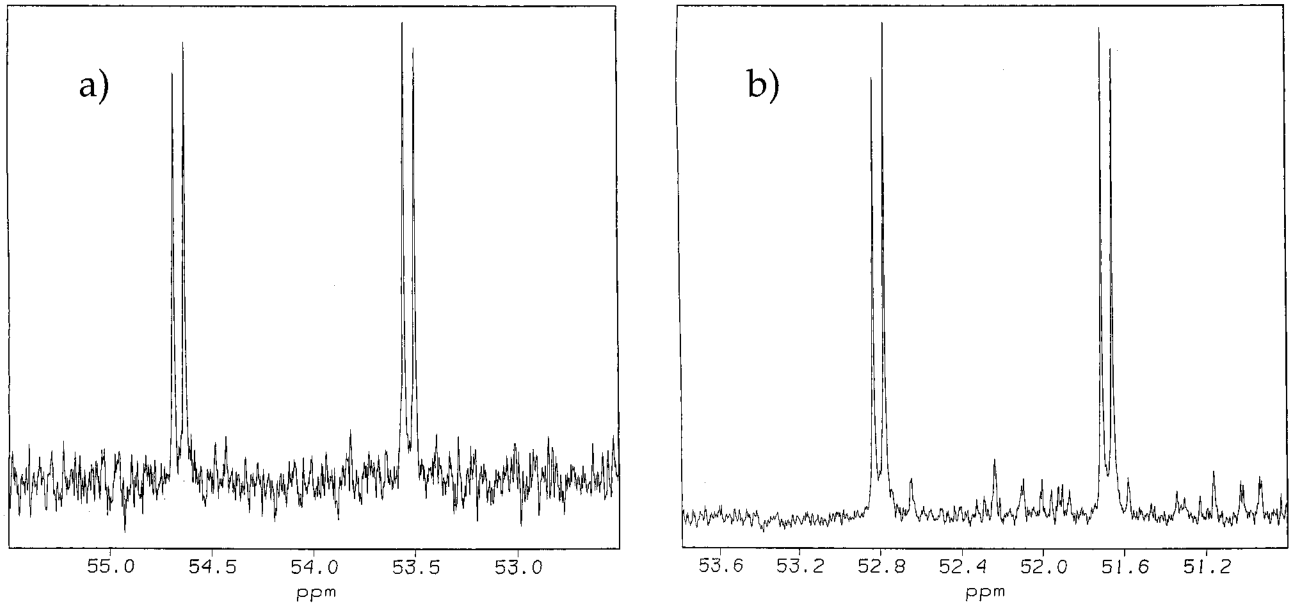


Figure 2. $^1H-^{13}C$ NMR spectra of the sp^3 resonance of (a) $C_{60}H_2$ and (b) $C_{60}H_6$ (**3a**), showing the H–C coupling in each.

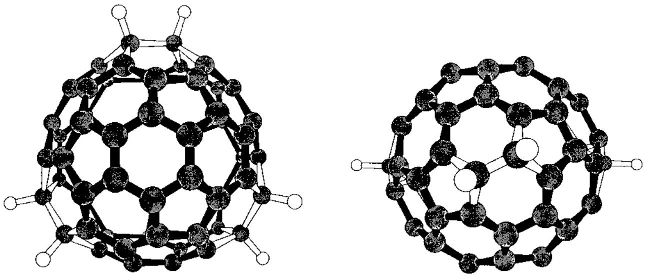
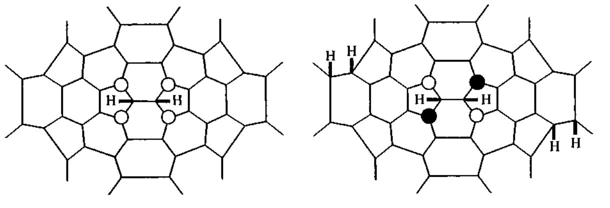


Figure 3. Two views of the structure of the major isomer of $C_{60}H_6$ formed by Zn(Cu) reduction of C_{60} using water as the proton source.

symmetry axes), permits assignment of **3a** as the 1,2,33,41,42,50 isomer of $C_{60}H_6$ (Figure 3).[31]

Additional support for this structural assignment is provided by the presence of long-range $^1H-^{13}C$ couplings in the ^{13}C NMR spectra of these two compounds. In the spectrum of $C_{60}H_2$, the most downfield of the sp^2 resonances (153.28 ppm) in the spectrum appears as a five-line multiplet, and in the spectrum of $C_{60}H_6$, the *two* most downfield (158.05 and 153.97 ppm) lines appear as identical five-line multiplets. This is consistent with the presence of a plane of symmetry in 1,2-$C_{60}H_2$ and a C_2 axis in **3a**, as shown in Figure 4.

The downfield multiplets are the X portion of an AA′X spin system. We assign these resonances to the carbons adjacent to the protonated sp^3 carbons. In 1,2-$C_{60}H_2$, the central three lines of the 153.28 ppm resonance (assigned to the four equivalent carbons adjacent to the sp^3 carbons) are separated by 3.6 Hz, and the outer two lines of the multiplet are separated by 33.8 Hz due to two-bond and three-bond H–C couplings. Simulation[29] of this section of the spectrum as an AA′X system with a 14.7 Hz $^1H-^1H$ coupling constant revealed −12 Hz two-bond CH and 4.7 Hz three-bond CH coupling constants. In 1,2,33,41,42,50-$C_{60}H_6$, there are two symmetrically distinct carbons adjacent to the sp^3 carbons, again split into five-line multiplets by two-bond and three-bond couplings. The pattern of the multiplets are identical, the only difference being the chemical shift. Longer-range couplings can be observed in both $C_{60}H_2$ and in $C_{60}H_6$, but not enough of these long-range couplings are resolved to allow definitive assignments of other carbon resonances. The two- and three-bond coupling constants calculated from the simulation of the AA′X spin system for $C_{60}H_2$ is shown in Figure 5.



a) 1,2-$C_{60}H_2$ (1)

b) 1,2,33,41,42,50-$C_{60}H_6$ (3a)

Figure 4. Projections of partial structures of (a) $C_{60}H_2$ (**1**) and (b) **3a**, showing four equivalent sp^2 carbons (open circles) exhibiting (two and three bond) C–H coupling in $C_{60}H_2$, and two pairs of equivalent sp^2 carbons (filled circles and open circles) showing C–H coupling in **3a**.

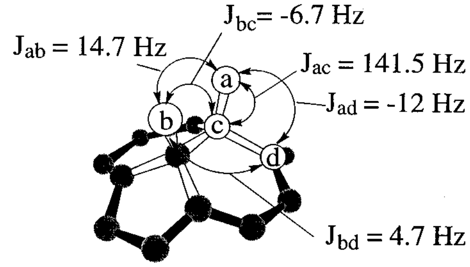


Figure 5. Spin system of $C_{60}H_2$.

Due to the low yield and difficult chromatography, only small amounts of the minor isomer **3b** could be isolated. After repeated chromatography and peak shaving, sufficient material was obtained for a ^1H NMR spectrum, which showed an AB pattern centered at 5.25 ppm, indicating another highly symmetrical structure. We

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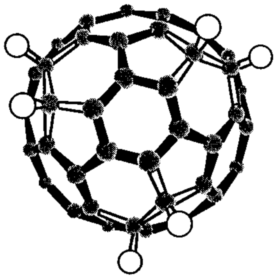
[31] A compound with this substitution pattern has been isolated from a mixture of tris(dimethyl bromomalonate) adducts: Hirsch, A.; Lamparth, I.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 437–438.



3b

Figure 6. Tentative structure for **3b**, the minor isomer of $C_{60}H_6$. Atoms behind the plane of the page (the back half of the sphere) have been deleted, and the size of the hydrogens have been exaggerated for clarity.

consider the structure shown in Figure 6 to be a likely structure for **3b**. This compound would be produced from **2a** by reduction of the 22,23 bond.

We have seen no evidence for interconversion between the isomers of $C_{60}H_4$ or between the isomers of $C_{60}H_6$ under these reaction conditions (see below). In the absence of isomerization, the 1,2,33,41,42,50 (major) isomer of $C_{60}H_6$ would be expected to form from the 1,2,41,42 isomer of $C_{60}H_4$. The reported[5] ^1H NMR spectrum is consistent with the 1,2,33,50 isomer of $C_{60}H_4$.

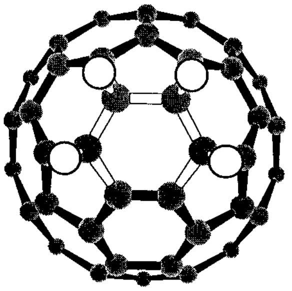
The hydrogen atoms in **3a** do not exchange rapidly with D_2O. No deuterium incorporation could be detected after a sample of $C_{60}H_6$ in toluene had been agitated with D_2O for several hours. Barring extreme kinetic problems, this implies that the pK_a of $C_{60}H_6$ is significantly higher than the pK_a of tBuC_{60}H.[32]

We believe that the dominance of the 1,2,33,41,42,50 isomer in the reaction mixture is due to several factors, including kinetic effects. The fact that **3b** is a minor component when its $C_{60}H_4$ precursor (**2a**) is a major component suggests either **2a** or **3b** is relatively unstable to the reaction conditions and is selectively removed.

The relatively low mass balance precludes us from making firm conclusions about the mechanism for the formation of these compounds. It is clear that the distribution of $C_{60}H_6$ isomers is simpler than the distribution of $C_{60}H_4$ isomers, and this could result from any of several processes, including (a) isomerization of $C_{60}H_4$ species, followed by rapid reduction of one isomer to $C_{60}H_6$; (b) by selective *destruction* of one or more $C_{60}H_4$ *or* $C_{60}H_6$ species; or (c) isomerization of $C_{60}H_6$ species to **3a** in a process where the thermodynamic isomers are mechanistically inaccessible. We consider (c) to be unlikely.

Attempts to isomerize **3a** with Pd/C and with Pt/C[5] have resulted in rapid dehydrogenation rather than isomerization. In an effort to find evidence for isomerization during the reduction, we prepared $C_{60}D_4$ by Zn(Cu) reduction of C_{60} in the presence of D_2O. The bands corresponding to $C_{60}D_4$ were isolated together and subjected to further reduction with Zn(Cu) using H_2O as the proton source. This produced a mixture of $C_{60}D_4H_2$ ($m/z = 730$) species that displayed a sharp singlet at 6.14 ppm and an AB pattern centered at 5.28 ppm in the ^1H NMR spectrum. These signals are consistent with the reduction of D_4-**2a** and D_4-**2b** to form D_4H_2-**3a** (^1H singlet) and D_4H_2-**3b** (^1H AB pattern) with no loss of deuterium and with no isomerization of the deuterium atoms from their original positions. If isomerization had occurred in the course of the last reduction step by way of exchange with metal-bound hydrogens, some of the ^2H would have likely been replaced by ^1H, resulting in a more complicated spectrum. If discrete $C_{60}D_4$ anions were formed in solution, these could isomerize without exchange, although given the behavior of $C_{60}H_2$ anions in solution,[33] we feel that dehydrogenation would be the dominant process. On the basis of this experiment, we believe that $C_{60}H_4$ and $C_{60}H_6$ do not isomerize during the course of the reduction.

Since **2a** and **2b** are formed in a 1:1 ratio and since it appears that **2a** leads to **3b** and **2b** leads to **3a**, it seems likely that either **2a** or **3b** is less stable under the reaction conditions than is **2b** or **3a**. The **2a**/**2b** ratio does not appear to change over the course of the reaction, suggesting that the dominance of **3a** in the reaction mixture is due (at least in part) to higher stability than **3b**. The $C_{60}H_6O$ species do not appear in the reaction mixture until $C_{60}H_6$ species are being formed, so it is possible that these uncharacterized compounds are the result of the decomposition of much of the **3b** produced in the reaction. In addition, neither of the major isomers of $C_{60}H_4$ produced by Zn/HCl[22] or by Zn(Cu) reduction of C_{60} is the thermodynamically most stable[5] 1,2,3,4-$C_{60}H_4$ isomer (**2c**), so clearly, nonthermodynamic isomers of $C_{60}H_6$ should be expected.



1,2,3,4 (**2c**)

It is known from crystallographic studies of $(PPN^+)_2C_{60}{}^{2-}$ that the $C_{60}{}^{2-}$ ion is somewhat elongated and flattened and has a buildup of negative charge on the equatorial region.[34] The conditions we use here are sufficient to generate $C_{60}{}^{2-}$, and a buildup of negative charge on the equator may provide a basis for the kinetic preference for protonation in this region. Certainly, the most important protonation step is the protonation of $C_{60}H_2{}^{n-}$, since at this step the distribution of isomers of $C_{60}H_4$, and therefore of $C_{60}H_6$, is determined. We suspect that if $C_{60}H_2{}^{2-}$ forms and has a similar buildup of negative charge in an equatorial region, the most favorable sites for protonation would produce the observed isomer of $C_{60}H_6$.

Reduction of C_{70} Using Zn(Cu). The reduction of C_{70} with Zn(Cu) proceeded to a greater extent than did the reaction of C_{60} with Zn(Cu), despite the fact that C_{70} has reduction potentials very similar to those of C_{60}.[35] Under the same conditions that produce $C_{60}H_6$, C_{70} reduced to the $C_{70}H_{10}$ level, with a small amount of

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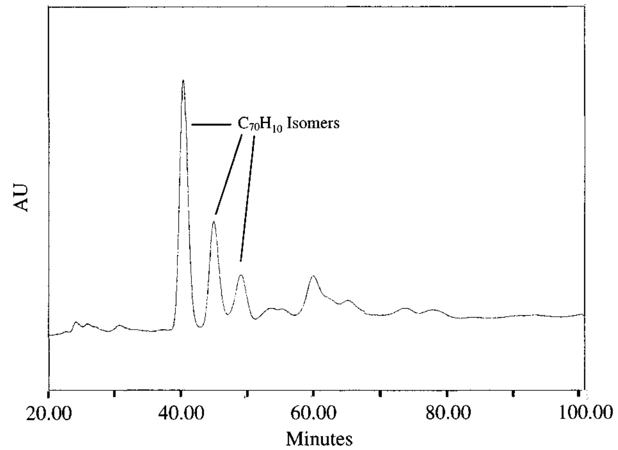

Figure 7. Chromatogram of the C_{70}/Zn(Cu) reaction mixture, showing the different isomers of $C_{70}H_{10}$. Conditions: Semipreparative Buckyclutcher column, CH_2Cl_2/hexane (40/60), 4.5 mL/min).

residual $C_{70}H_8$, and a series of smaller, unresolved bands containing $C_{70}H_{12}$ and $C_{70}H_{10}O$ species. The $C_{70}H_{10}$ produced under these conditions was formed as three different isomers (Figure 7) in a 4 to 2 to 1 ratio.

The ^1H NMR spectra of the different isomers of $C_{70}H_{10}$ showed multiplets in the 5.2−5.8 ppm region. This is consistent with any of a number of different isomers, and we are not able to assign specific structures at this time. However, the first eluting compound exhibits only five, closely spaced resonances, spanning a narrow (0.2 ppm) chemical shift range. This is consistent with the 7,8,19,26,33,37,45,49,53,63 structure determined for $C_{70}Ph_{10}$ produced from $C_{70}Cl_{10}$.[36] Further characterization of these $C_{70}H_{10}$ isomers is in progress.

The use of zinc metal alone, rather than Zn(Cu), led to a slower reaction of C_{60} but also to more complete reduction. In 2 h, a mixture of C_{60} and zinc dust (H_2O as the proton source) had produced only small quantities of $C_{60}H_6$, but after 48 h, the reaction mixture was composed of $C_{60}H_6$, $C_{60}H_{10}$, and $C_{60}H_{12}$. In the C_{70} series, a similar pattern was observed: the reduction proceeded more slowly than the analogous Zn(Cu) couple reaction, only having formed $C_{70}H_4$ after 48 h. However, after 5 days the reduction had produced a distribution of $C_{70}H_{10}$ and $C_{70}H_{12}$ similar to that produced by Zn(Cu).

The product distribution in Zn(Cu) reductions of C_{60} and C_{70} are highly dependent upon the specific proton source. Reactions using "dry" methanol proceed to a small degree and then stop, presumably when the residual water in the alcohol and on the metal is consumed. Good yields of $C_{60}H_2$ have been obtained by using limited amounts of water in otherwise dry solvents. Alcohols that are more acidic than water (e.g. CF_3CH_2OH) fail as proton sources in reactions, as do alcohols that are largely immiscible with toluene, such as glycerol. It is possible that the formation of ZnO supplies much of the driving force for the reaction. Acids, including glacial acetic acid and phosphoric acid, lead to rapid reactions and mixtures of more highly reduced species.[11]

Reduction of C_{60} with Titanium, Aluminum, and Magnesium. The reduction of C_{60} using commercial titanium powder and acid was unsuccessful, presumably due to a layer of TiO_2 on the metal surface. However, reaction of C_{60} in toluene with activated titanium (produced by *in situ* reduction of $TiCl_3$ with sodium) and 50:50 methanol/glacial acetic acid as proton source afforded a mixture of $C_{60}H_4$ isomers (45%), $C_{60}H_6$ (2 isomers in a 2:1 ratio), and $C_{60}H_6$ oxides. The reaction did not proceed past this point after water or additional acid were added.

Activated aluminum (produced by reduction of $AlCl_3$ with sodium) did not produce significant amounts of reduced fullerenes when methanol, water, or dilute acid was used as the proton source. Reduction products were observed when glacial acetic acid was used, resulting in a yellow solution containing several different species, with $C_{60}H_{12}$ being the most highly reduced. However, a large amount of uncharacterized insoluble material precipitates from solution in these experiments. We have not been able to identify this material, although the orange color and the low mass balance obtained for soluble fullerenes suggest that this is an insoluble fullerene derivative or fullerene-containing metal complex.

Heating a solution of C_{60} in toluene containing magnesium turnings with water as the proton source led to a rapid reaction, producing a mixture composed primarily of C_{60}, $C_{60}H_2$, and three isomers of $C_{60}H_4$ observed before. The reaction ceased (as determined by HPLC) soon after it started, despite the presence of excess metal and excess water. Addition of another portion of fresh metal led to renewed reaction, suggesting that the original metal had become inactive, presumably galvanized with MgO, as the reduction proceeded. When glacial acetic acid was used as the proton source, the metal did not become inactivated, and the reaction proceeded rapidly, producing a mixture of species from $C_{60}H_2$ to $C_{60}H_6$. The same two isomers of $C_{60}H_6$ produced by Zn(Cu) reduction were produced here, although in a 1:1 ratio instead of the 6:1 ratio observed earlier. Large excesses of metal and acid led to further reduction, producing species from $C_{60}H_6$, $C_{60}H_{12}$, and intractable mixtures of more highly reduced materials. Stronger acid (aqueous HCl) led to the evolution of hydrogen and little reduction of the fullerene.

Conclusions

Reductions of C_{60} using Ti, Al, and Mg did not "converge" on a single $C_{60}H_n$ species. We are currently working on the development of preparatively useful procedures for the preparation of more highly reduced species using these metals. However, dissolving metal reductions of C_{60} and C_{70} using Zn(Cu) can be used to produce a number of different reduced fullerenes. We have developed efficient syntheses for $C_{60}H_2$, $C_{60}H_4$, $C_{60}H_6$, and $C_{70}H_{10}$ that produce a limited number of isomers, and in the $C_{60}H_6$ series, two highly symmetrical isomers are produced. Zinc−copper couple, with a reduction potential near the $C_{60}{}^{-1/-2}$ potential, produces predominantly $C_{60}H_6$ and $C_{70}H_{10}$. It is clear that changes in the reaction conditions can result in significant changes in the distribution of products obtained. The specific proton source is as important in determining the species produced as is the reducing metal. Water seems to be the most reliable proton source for producing good yields of $C_{60}H_2$, $C_{60}H_4$, $C_{60}H_6$, and $C_{70}H_{10}$. Alcohols are not effective proton sources, and acids result in production of highly reduced species. The isomer distributions produced by these methods appear to be kinetically controlled, and this feature offers access to structures not easily prepared by other methods. The $C_{60}H_6$ species

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produced by the Zn(Cu) method are highly symmetrical species that have a great deal of potential as building blocks for large, highly organized assemblies. We are currently investigating the chemistry required for further elaboration of these structures.

Experimental Section

General. Fullerenes were obtained from MER corp. as a C_{60}/C_{70} mixture and purified by preparative GPC.[37] All reactions were performed in acid-washed glassware under N_2 or Ar atmospheres, and solvents were sparged with the inert atmosphere for 45 min before use. Activated Al and Ti were freshly prepared by *in situ* reduction of the chlorides with Na metal. HPLC analyses and GPC preparations were performed as reported earlier.[37] All ^{13}C spectra were measured at 125.7 MHz on samples in freeze-pump-thaw deoxygenated solutions in flame-sealed tubes. $^{1}H-^{13}C$ coupling constants of less than 1 Hz are not reported.

$C_{60}H_2$. A solution of C_{60} (255 mg, 0.354 mmol) in 250 mL of toluene was sparged with Ar for 45 min, and then Zn(Cu) (freshly prepared from 5.1 g of Zn dust[38]) and 2.5 mL of water was added. The mixture was stirred vigorously and heated at 50 °C for 1 h. Analysis by HPLC (semipreparative Buckyclutcher column, 1:1 toluene/hexane mobile phase, 4.5 mL/min flow rate, and monitored at 335 nm) at this point indicated that the mixture was 8% C_{60}, 78% $C_{60}H_2$, 12% $C_{60}H_4$ (mixture of isomers), and 2% $C_{60}H_6$. The brown suspension was cooled, filtered, and purified by preparative GPC using four columns in series: a Jordi-Gel (500 Å pore size) followed by three Waters Ultrastyragel (two 500 Å and one 100 Å), with toluene as eluent and monitored at 400 nm, producing $C_{60}H_2$ (168 mg, 0.233 mmol, 66% yield). ^{1}H NMR (CS_2/acetone-d_6) δ 7.17 ppm. ^{13}C NMR (^{1}H-coupled, CS_2/acetone-d_6) δ 54.10 (center of AB pattern, $J_1 = 141.5$ Hz, $J_2 = 6.7$ Hz) 136.92, 141.05, 142.20, 142.52, 142.57, 143.14, 143.66, 143.91, 145.28, 145.99, 146.10, 146.61, 146.87, 146.93, 147.90, 148.38, 153.28 (AB part of ABX system). Negative ion FABS mass spectrum (3-nitrobenzyl alcohol matrix) $m/z = 722$. FT-IR (KBr, cm^{-1}): 2919 (w), 2848 (w), 1424 (w), 1177 (w), 860 (w), 728 (w), 576 (w), 566 (w), 523 (s).

$C_{60}H_4$. C_{60} (60.6 mg, 0.0842 mmol) and 60 mL of toluene were combined in a 100 mL three-neck flask and deoxygenated with argon. Zn(Cu) couple (1.20 g, 18.4 mmoles Zn) and water (0.75 mL) were added. The resulting mixture was heated in a 50 °C oil bath and stirred vigorously with a 1 in. egg-shaped stir bar. After 1.5 h, the mixture was cooled to room temperature, the supernatant was decanted, and the residual solid was washed twice with 1.5 mL portions of toluene. The combined supernatant and washings were concentrated in vacuo, filtered through a 0.2 μm nylon filter, and purified by HPLC (preparative Buckyclutcher column with a 1:1 toluene/hexane mobile phase, 15 mL/min flow rate, and monitored at 335 nm). The $C_{60}H_4$ band (27.7 mg) was isolated as a 5.5:1 mixture of two peaks (three isomers) in 45% yield. The major band was separated into two bands by HPLC on a semipreparative Buckyclutcher column using heptane/CH_2Cl_2 (87:13) as the mobile phase. **2a:** ^{1}H NMR (CS_2/acetone-d_6) δ 6.42 (s, 2H), 6.11 (AB pattern, $\Delta\delta = 0.30$ ppm, $J_{AB} = 15.6$ Hz, 2 H (lit.[5] $\Delta\delta$ (δ_8-toluene) = 0.25 ppm, $J_{AB} = 15.5$ Hz)). **2b:** ^{1}H NMR (CS_2/acetone-d_6) δ 6.66 (AB pattern, $\Delta\delta = 0.20$ ppm, $J_{AB} = 15.5$ Hz, (lit.[5] $\Delta\delta$ (δ_8-toluene) = 0.15 ppm, $J_{AB} = 15.5$ Hz)). A mixture of **2a** and **2b**: negative ion FAB mass spectrum (*m*-nitrobenzyl alcohol) m/z 724 (M^-).

$C_{60}H_6$. C_{60} (60.1 mg, 0.0835 mmol) and 60 mL of toluene were combined in a 100 mL three-neck flask and deoxygenated with argon. Zn(Cu) couple (1.20 g, 18.4 mmoles Zn) and water (0.75 mL) were added. The resulting mixture was heated in a 50 °C oil bath and stirred vigorously with a 1 in. egg-shaped stir bar. After 3 h the mixture was cooled to room temperature, the supernatant was decanted, and the residual solid was washed twice with 1.5 mL portions of toluene. The combined supernatant and washings were concentrated in vacuo, filtered through a 0.2 μm nylon filter, and purified by HPLC (preparative Buckyclutcher column with a 1:1 toluene/hexane mobile phase, 15 mL/min flow rate, and monitored at 335 nm). The $C_{60}H_6$ band (21.2 mg) was isolated as a 5:1 mixture of two peaks in 35% yield. The two bands were separated by further HPLC using a preparative Buckyclutcher column and 1:1 toluene/hexane as the mobile phase (15 mL/min) and monitored at 330 nm. **3a:** ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 6.00. ^{13}C NMR (9:1 CS_2/acetone-d_6, 125 MHz) δ 158.05, 153.97, 153.66, 151.65, 151.45, 145.71, 144.18, 142.60, 141.55, 52.28 (AB pattern, $J_1 = 142$ Hz, $J_2 = 6.7$ Hz). Negative ion FABS (*m*-nitrobenzyl alcohol) m/z 726 (M^-). FT-IR (KBr, cm^{-1}): 2907 (w), 2845 (w), 1449 (w), 1423 (w), 1178 (w), 852 (w), 761 (w), 728 (w), 668 (s), 545 (w), 517 (s). **3b:** ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 5.25 (AB pattern, $\Delta\delta = 0.33$ ppm, $J_{AB} = 16.0$ Hz.)

Zn(Cu) Reduction of C_{70}. C_{70} (150.4 mg, 0.179 mmol) and toluene (200 mL) were combined in a 500 mL three-neck Schlenk flask and deoxygenated with argon. Zn−Cu couple (3.264 g, 49.86 mmol of Zn) and water (2.0 mL) were added. The resulting mixture was heated in a 80 °C oil bath and stirred vigorously. After 4 d the mixture was cooled to room temperature, the supernatant was decanted, and the residual solid was washed twice with 25 mL portions of toluene. The combined supernatant and washings were filtered through a 0.2 μm nylon filter and purified by HPLC as described in the text. The $C_{70}H_8$ band (12 mg) was isolated in 8% yield, while the $C_{70}H_{10}$ bands were isolated as one major isomer and two minor isomers (62% yield combined). All of these species were air-sensitive and difficult to store.

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