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Novel Acid-Catalyzed Rearrangement of Methanofullerenes Bearing an α-Ylidic Ester to Cyclopentanofullerenes: A Vinyl Cyclopropane-Type Ring Expansion

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A novel acid-catalyzed ring expansion of methanofullerenes bearing an α-ylidic ester has been investigated. Treatment of dialkyl acetylenedicarboxylate and tricycloalkylphosphine with C_{60} led to the isolation of a methanofullerene ylide after passing the reaction mixtures through a basic alumina column. If the reaction mixture was passed through a silica gel column, a cyclopentanofullerene was isolated instead. These new cyclopentanofullerenes consisted of a fused cyclopentanone ring bearing an α-hydroxy ester and a phosphonium ylide and were confirmed by their NMR, mass, and X-ray diffraction data. The cyclopentanofullerenes were formed by the ring expansion of the corresponding methanofullerenes in the presence of silica gel. The ring expansion also proceeded by treating methanofullerene with acetic acid in chloroform. On the other hand, the methanofullerenes from RO_2CCCCO_2R, PAr_3, and C_{60} were stable in silica gel. However, upon heating with acetic acid at 50 °C, they underwent ring expansion and dephosphination to give cyclopentenofullerenes. An implicit vinyl cyclopropane ring expansion mechanism was proposed to account for this novel acid-catalyzed rearrangement.

Introduction

Fullerene derivatives consisting of polar functionalities have been shown to possess important biological activities.[1] As a result, the design and synthesis of fullerene derivatives with new functionalities have continued to be a fascinating area in fullerene research. The synthesis of fullerene derivatives bearing phosphorus substituents is attractive since organophosphorus compounds are known to play important roles in biological systems.[2] Until now, only a couple of methods for the preparation of fullerene−phosphorus derivatives were reported.[3−5]

Recently, we[6,7] and others[8] reported an unusual reaction of electron-deficient acetylenes and triarylphosphines (or phosphites) with C_{60} to give methanofullerenes **1** bearing an α-ylidic ester. Subsequent conversion of the ylide group in the presence of acids offered a unique approach to fullerene derivatives with phosphonium salt, phosphine oxide, phosphonate ester, and phosphinic acid moieties.[9,10] The unusual structure of methanofullerene ylides **1** prompts us to explore further the chemical properties of this class of compounds. Herein, we report a novel acid-catalyzed ring expansion of methanofullerene ylides **1** and **2** to cyclopentanofullerene and to cyclopentenofullerene derivatives. This unprecedented ring expansion provides an efficient new route for the synthesis of a series of [60]fullerene derivatives bearing a fused cyclopentanone or cyclopentenone ring.

The currently observed ring expansion can be considered as a vinylcyclopropane-type ring expansion in view of the double-bond character between the ester carbon and α-ylide carbon of methanofullerene **1** and **2** (vide

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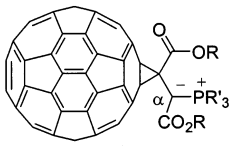
infra). While vinylcyclopropane ring expansion has been very useful for the preparation of a variety of five-membered ring compounds and applied to the synthesis of natural occurring products, these reactions generally require very high temperature and drastic conditions.[11] In contrast, the present acid-catalyzed methanofullerene ylide rearrangement proceeds under extremely mild conditions.

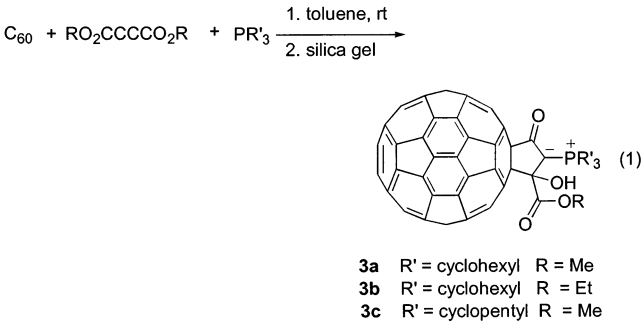


1

R = Me, Et
R' = Ph, *p*-MeC$_6$H$_4$, OMe

Results and Discussion

Synthesis and Characterization of Cyclopentanofullerenes 3. On the basis of our previous synthetic methods,[7,9] slow addition of dimethyl acetylenedicarboxylate (DMAD) to a mixture of C_{60} and tricyclohexylphosphine ($(C_6H_{11})_3P$) in toluene at ambient temperature should lead to the formation of a methanofullerene structurally similar to **1** after silica gel chromatography. Surprisingly, separation of the mixture on a silica gel column results in a different fullerene derivative. A color change from red-purple to brown is observed when the reaction mixture is passed through the column. The brown color fraction is collected and characterized to be ylide **3a** (eq 1). This product consists of an α-hydroxy



3a R' = cyclohexyl R = Me
3b R' = cyclohexyl R = Et
3c R' = cyclopentyl R = Me

ester, a fused cyclopentanone, and a phosphorus ylide group on the basis of its MS, NMR, IR, and UV−vis spectral data. In agreement with the structural formula, the MS data of compound **3a** displays a molecular ion (M + 1) at 1129 (which is 14 less that the summation of the molecular weights of the three starting materials). In the ^{1}H NMR spectrum, a broad signal in the region of 1.35−2.18 ppm and a multiplet at 3.15 ppm are assigned to the methylene and methine protons of the cyclohexyl group, respectively. The signals at 5.05 and 3.96 ppm are due to the hydroxy and methoxy protons resonance, respectively. (The ^{1}H NMR spectrum also shows evidence of two individual singlets at 5.05 and 3.96 ppm that are due to the hydroxy and methoxy proton resonances, respectively. These give us a sense that a methyl group is lost.) In the IR spectrum, a characteristic broad absorption for the hydroxy group appears at 3455 cm^{-1}. Additionally, the spectrum shows a strong low-frequency carbonyl absorption at 1597 cm^{-1} for the ylidic enone moiety and an absorption at 1726 cm^{-1} for the ester group.

^{31}P and ^{13}C NMR spectral data of ylide **3a** are also consistent with the proposed structure. A single resonance at 28.1 ppm in the ^{31}P NMR supports the presence of a phosphorus ylide group. The observation is in contrast to the results of ylide **1** that exists as two isomers and shows two resonances in the ^{31}P NMR spectrum.[7] The presence of a cyclopentanone ring in **3a** is clearly shown in the ^{13}C NMR spectrum. The absorptions at 81.6 and 77.7 (d, $^3J_{PC}$ = 8.9 Hz) ppm are due to the two sp^3 carbons on the fullerene moiety and the signals at 185.2 (d, $^2J_{PC}$ = 10.6 Hz), 91.5 (d, $^2J_{PC}$ = 8.8 Hz), and 56.9 (d, $^1J_{PC}$ = 91.4 Hz) ppm are assigned to the carbonyl, α-hydroxy, and ylidic carbons, respectively. Other characteristic ^{13}C signals at 178.9, 53.55, and 32.09 (d, $^1J_{PC}$ = 46.2 Hz) ppm are assigned to the carbonyl and methoxy carbons of the ester group and the methine carbon of cyclohexyl group, respectively. Compared to known phosphorus ylides, the observed $^2J_{PC}$ and $^1J_{PC}$ constants are typical of an α-ylidic ketone.[12,13] Consistent with the proposed structure possessing a C_1 symmetry, a total of 56 sp^2 signals in the region of 132−159 ppm for the fullerene moiety are observed.

Similarly, ylides **3b** and **3c** are isolated with silica gel chromatography from the reaction of C_{60} with diethyl acetylenedicarboxylate (DEAD) and tricyclohexylphosphine and with DMAD and tricyclopentylphosphine, respectively, in good yields (20−30%). A large portion of the C_{60} is recovered. On the basis of the spectral data, the structures of these two products are proposed to be similar to **3a**.

Crystal Structure of Cyclopentanofullerene 3b. To confirm the structure proposed for compounds **3a**−**c**, a representative of these ylide derivatives **3b** is selected for the structural determination by the X-ray diffraction methods. Single crystals suitable for X-ray analysis are grown in an NMR tube from a chloroform-*d* solution. A crystal structure of compound **3b** is shown in Figure 1. In agreement with the proposed structure based on the spectral data of this species, the X-ray results firmly establish that **3b** consists of a cyclopentanone ring, an α-hydroxy ester, and an ylide group.

Synthesis of Methanofullerenes Containing an α-Ylidic Ester. The reaction of C_{60} with dialkyl acetylenedicarboxylate and tricycloalkylphosphine giving cyclopentanofullerenes **3a**−**c** is surprising. The observed color change from red-purple to brown as the reaction mixture is passed through the silica gel column indicates that the isolation of ylide **3** may be caused by the acidic nature of silica gel. Thus, it is likely that product **3** is not the initial product of the reaction. In an attempt to

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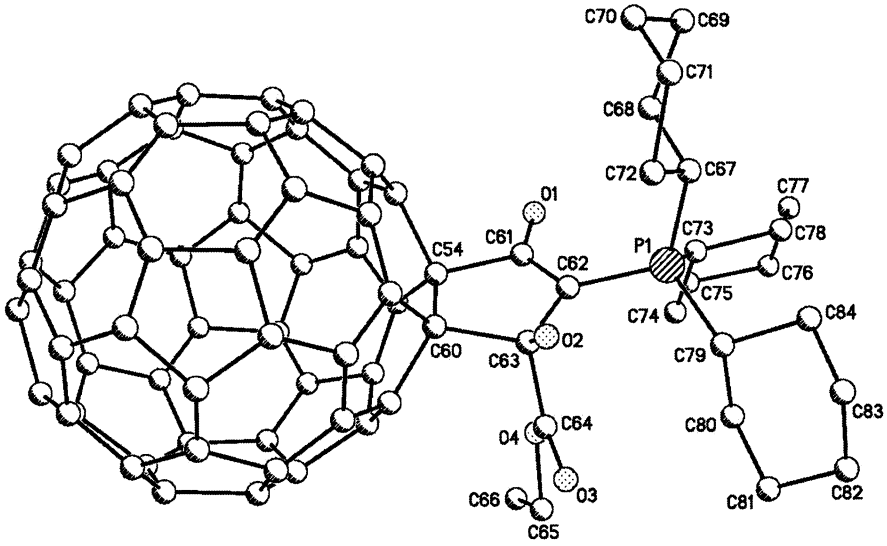
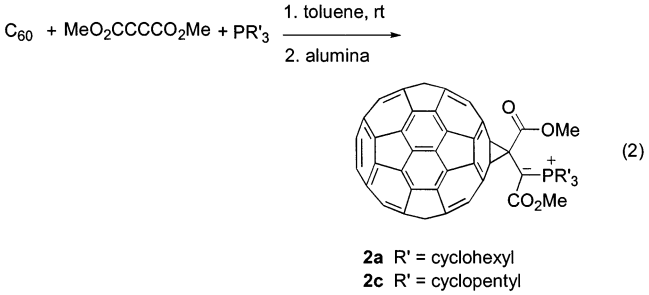


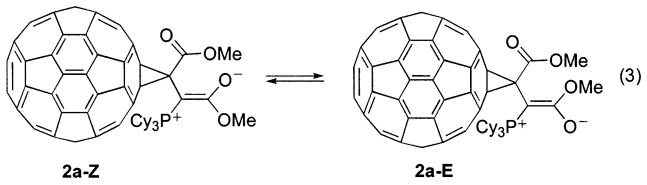
FIGURE 1. X-ray structure of cyclopentanofullerene **3b**.

isolate the initial reaction product, the reaction mixture is separated on a basic alumina column instead of a silica gel column. No color change is observed as the reaction mixture is passed through the alumina column. The red-purple band is collected and the solution is concentrated to give compound **2a** in 28% yield (eq 2). The structure



of compound **2a**, similar to that of **1**, is determined on the basis of its MS, ^{1}H, ^{31}P, and ^{13}C NMR, and IR spectral data. HRMS data of compound **2a** displaying a molecular ion (M + 1) at 1143 firmly support an adduct of DMAD and tricyclohexylphosphine units onto a C_{60} moiety. The ^{1}H NMR spectrum of **2a** shows two sets of methoxy resonances at 3.89 and 3.63 ppm and 3.89 and 3.61 ppm with relative intensity of 4:1 indicating the existence of two isomers **2a**-**E** and **2a**-**Z** (eq 3). Additionally, there are also two ^{31}P NMR signals at 32.94 and 31.42 ppm for this species. These observed NMR spectral data are characteristic for a fullerene ylide containing a cyclopropane ring similar in structure to methanofullerene **1**.[7] The IR data showing $\nu_{C=O}$ at 1726 and 1610 cm^{-1} also suggest the presence of a normal ester and a conjugated α-ylidic ester. The strong low-frequency absorption at 1610 cm^{-1} is a characteristic peak for an ylidic ester.[14]

Similarly, the reaction of C_{60} with dimethyl acetylenedicarboxylate (DMAD) and tricyclopentylphosphine ($(C_5H_9)_3P$) in toluene gave fullerene ylide **2c** possessing a cyclopropane ring when the mixture is separated on an alumina column. Compound **2c** is also characterized by its MS, ^{1}H and ^{13}C NMR, and IR spectral data and by comparison of these data with those of **2a**.



Ring Expansion of Methanofullerenes 2. The successful isolation of compound **2a** from a flash alumina gel column strongly supports the mechanism that the reaction of C_{60}, DMAD, and tricyclohexylphosphine ($P(C_6H_{11})_3$) initially gives methanofullerene **2a**, which then rearranges to compound **3a** in a silica gel column (eq 4). This is further proved when pure methanofullerene **2a** is passed through a silica gel column. The red-purple solution changes to the expected brown color and the isolated fullerene species is identified as ylide **3a**. In view of the acidic nature of silica gel, the rearrangement of compound **2a** to **3a** is likely catalyzed by acid. This notion is supported by the observation that methanofullerene **2a** undergoes a rapid rearrangement to ylide **3a** in the presence of acetic acid and water. Similarly, methanofullerene **2c** undergoes ring expansion reaction to give the corresponding cyclopentanone derivative **3c** in the presence of silica gel or acetic acid and water.

A new brown fullerene species is observed in addition to compound **3c** if methanofullerene **2c** is passed through a short silica gel column. The mass spectral data of this new brown fullerene derivative shows a molecular ion (M + 1) at 1101, the same as that of compound **2c**. In the ^{1}H NMR spectrum of the mixture, two new methoxy signals at 3.84 and 4.13 ppm appear other than the methoxy signal at 3.96 ppm for **3c**. Based on the observed spectral data, we assign structure **3c′**, similar in structure to **2c** but consisting of an α-methoxy group instead of an α-hydroxy substituent, to this new species. In view of the fact that the transformation of **2c** to **3c** releases a methanol and requires a water molecule, the formation of compound **3c′** as a ring expansion product is reason-

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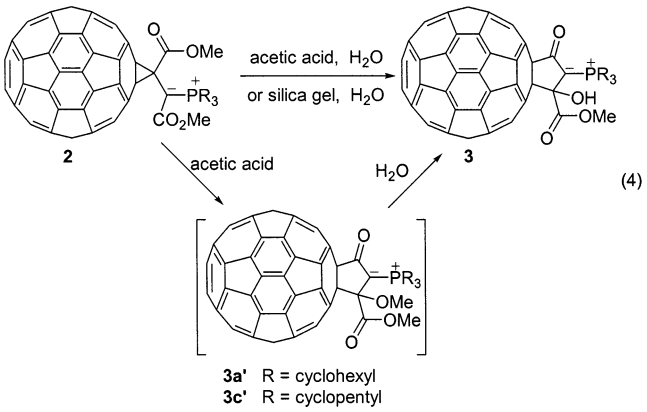
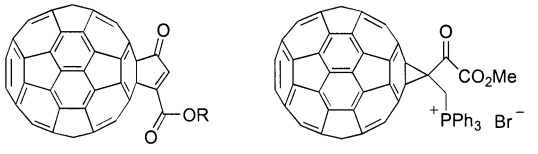


(4)

able particularly when water is insufficient in the system. Compound **3c′** is rapidly converted to **3c** and methanol in *d*-chloroform in the presence of 5 mol % acetic acid as indicated by the ^{1}H NMR spectrum of the reaction mixture. Similarly, methanofullerene **2a** is converted to **3a** and **3a′** when it is passed through a short silica gel column. In the presence of acetic acid (5% relative to **2a**) in chloroform **2a** is also transformed to a mixture of **3a** and **3a′** and then finally to **3a**.

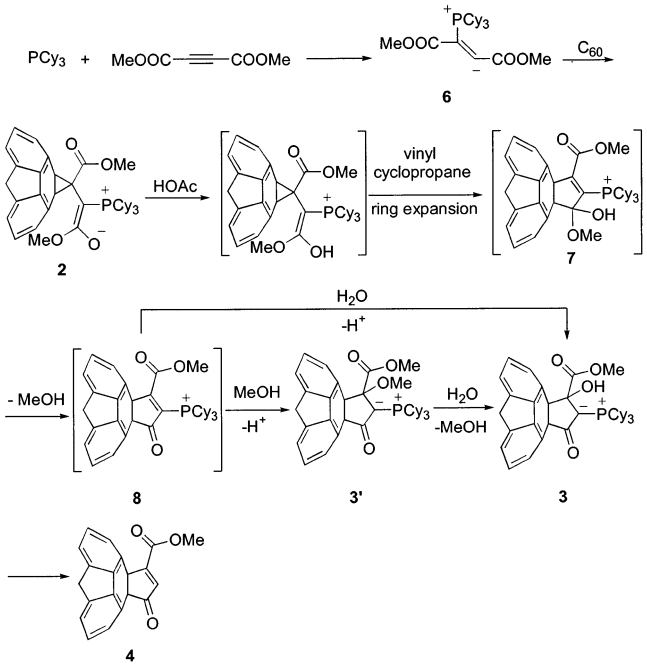
Ring Expansion of Methanofullerenes 1. Unlike methanofullerenes **2**, methanofullerenes **1** from the reaction of C_{60}, RO_2CCCCO_2R, and PPh_3 (**1a**: R = Me; **1b**: R = Et) do not undergo ring expansion in the silica gel column. However, treatment of methanofullerenes **1a** and **1b** with acetic acid at 50 °C in toluene for 2 days leads to the isolation of products **4a** and **4b**, respectively. The ^{1}H NMR spectra of these products are surprisingly simple. For example, only two signals at 7.87 and 4.08 ppm appear in the spectrum for compound **4a**. Based on these data and those of its MS, IR, and ^{13}C NMR spectra, we assign structure **4** bearing a cyclopentenone ring and an ester group for these species. The formation of **4** may be explained on the basis of a three- to five-membered ring expansion followed by phosphine oxide elimination. Consistent with our observation, prolonged treatment of methanofullerenes **2a** and **2c** or ylides **3a** and **3c** with acetic acid also results in the formation of product **4a**. It is noteworthy that in contrast to the ring expansion and dephosphination results, the reaction of methanofullerene **1a** with strong acid $HBr_{(aq)}$ gave phosphonium salt **5**.[9]



Mechanistic Consideration. On the basis of the foregoing results, the reaction of C_{60}, tricycloalkylphosphine, and DMAD appears to first give methanofullerene ylide **2**. Compound **2** then undergoes acid-catalyzed rearrangement to afford ylides **3′** or **3**. In the presence of water, the α-methoxy group in ylide **3′** readily exchanges with water to give ylide **3**.

The formation of ylide **2** is initiated by a nucleophilic attack of a tricycloalkylphosphine at an acetylene carbon

SCHEME 1. Proposed Mechanism for the Formation of 3 and 4



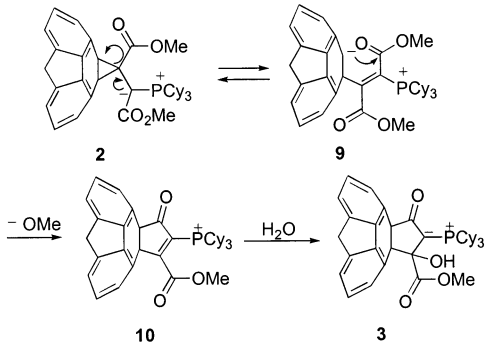
of DMAD to give a zwitterion **6**. Subsequent attack of this zwitterion at a carbon−carbon double bond of a C_{60} molecule followed by back attack at the acetylene carbon of DMAD distal to the phosphine moiety affords product **2**.

An acid-assisted pathway for the transformation of a methanofullerene ylide **2** to the corresponding five-membered cyclopetanone ylide **3** is proposed as depicted in Scheme 1. This proposed mechanism is based on the known ring expansion of vinyl cyclopropane derivatives.[11] Protonation at the carbonyl oxygen of the α-ylide ester group in methanofullerene **2** increases the carbon−carbon double-bond order between the α-ylidic and carbonyl carbons and facilitates the three- to five-membered ring expansion to afford a five-membered ring intermediate **7**. Elimination of a methanol molecule from the intermediate gives a cyclopentenone phosphonium salt **8**. Nucleophilic addition of a methoxy group to the olefinic carbon α to the ester group leads to product **3′**. On the other hand, addition of a hydroxy group gives product **3**. Hydroxy/methoxy exchange of product **3′** also leads to ylide **3**. Phosphine oxide elimination of ylide **3** results in the formation of cyclopentenofullerene **4**.

While tricycloalkylphosphine ylide **2** readily rearranges to the corresponding five-membered ylide **3** in silica gel, triphenylphosphine ylides **1a**,**b** are stable in the same media. The facile ring expansion of methanofullerene **2** compared to **1a**,**b** is likely due to the greater electron-donating ability of tricycloalkylphosphine relative to triphenylphosphine. As a result of the difference of electron donating ability of phosphine, methanofullerene **1** is expected to show a less carbon−carbon double bond character between the α-ylidic and carbonyl carbons than **2** and to be more difficult for the ring expansion reaction.

An alternative for the transformation of derivative **2** to **3** involves a reversible ring opening of **2** to yield a zwitterion **9** followed by back attack of the zwitterion at

SCHEME 2. Alternative Mechanism for the Formation of Ylide 3



the carbonyl carbon of the ester group β to the tricyclohexylphosphine to yield an intermediate **10**. Addition of a hydroxy group to the ene carbon β to the tricycloalkylphosphine group of the intermediate gives ylide **3** (Scheme 2). However, the mechanism cannot explain the observation that acid greatly enhances the rate of the present ring expansion reaction.

Conclusions

We have demonstrated a novel acid-catalyzed ring expansion of methanofullerenes with an α-ylidic ester to give cyclopentanofullerenes. The reaction rate of this acid-catalyzed ring expansion reaction depends mainly upon the nature of the phosphine. The ring expansion reaction is faster with an electron-donating phosphine than with an electron-withdrawing one. While the present transformation may be considered as a vinylcyclopropane/cyclopentene-type ring expansion reaction, it proceeds under much milder conditions than those for the known vinylcyclopropane/cyclopentene rearrangements. This unprecedented ring expansion reaction opens a new area in ylide and fullerene chemistry. Efforts are in progress toward the details of the mechanism and the application of this facile ring expansion reaction in organic synthesis.

Experimental Section

Synthesis of Methanofullerene 2a from C_{60}, Dimethyl Acetylenedicarboxylate, and Tricyclohexylphosphine. To a 100-mL sidearm flask consisting of C_{60} (0.0724 g, 0.100 mmol) and tricyclohexylphosphine (0.2820 g, 1.007 mmol) in toluene (50 mL) under nitrogen was injected a solution of dimethyl acetylenedicarboxylate (0.0386 g, 0.272 mmol) in toluene (20 mL) via a syringe pump at a rate of 6.8 mL/h at ambient temperature. After injection, the solution was concentrated in vacuo to ca. 2 mL, and the mixture was chromatographed on a basic alumina column. Elution of the column with toluene led to isolation of unreacted C_{60} (0.0468 g) in 65% yield. Further elution with a mixture of hexanes, ethyl acetate, and dichloromethane (2:1:1) afforded a red-purple solution. After concentration, the solution was precipitated with diethyl ether to give ylide **2a** (0.0323 g) in 28% yield, $R_f = 0.52$ (TLC, basic Al_2O_3, hexanes/ethyl acetate/dichloromethane = 4:1:1). Important spectral data of **2a** follow. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.89 (s), 3.64 (s), 3.61 (s), 3.07 (br), 2.13−1.28 (br). ^{31}P NMR ($CDCl_3$, 243 MHz) 300 K: δ 32.94, 31.42. FTIR (KBr Disk): 2930, 2853, 1726, 1610, 1440, 1300, 1169, 1085, 1010, 892, 850, 734, 525 cm^{-1}. HRMS (FAB): calcd for $C_{84}H_{40}O_4P$ ($M + H^+$) 1143.2664, found 1143.2613. ^{13}C NMR (150 MHz, $CDCl_3$) 273 K: δ 171.96 (d, $^3J_{PC}$ = 18.0 Hz), 170.52, 150.86, 149.85, 149.43, 147.07, 146.08, 145.25, 145.23, 145.07, 145.05, 145.00, 144.99, 144.98, 144.86, 144.84, 144.78, 144.67, 144.64, 144.55, 144.52, 144.51, 144.48, 144.35, 144.31, 144.28, 144.06, 144.04, 143.89, 143.86, 143.84, 143.70, 143.54, 143.50, 143.45, 143.13, 143.11, 142.91, 142.82, 142.81, 142.77, 142.73, 142.71, 142.69, 142.66, 142.61, 142.50, 142.45, 142.29, 142.21, 142.11, 142.10, 142.00, 141.95, 141.92, 141.79, 141.69, 140.79, 140.54, 140.31, 139.76, 139.59, 139.14, 138.95, 137.47, 136.79, 135.84, 134.75, 95.93, 75.33, 52.91, 52.36 (d, $^2J_{PC}$ = 13.4 Hz), 50.49, 37.41 (d, $^1J_{PC}$ = 108.7 Hz), 33.85, 27.94−27.51, 26.00. UV−vis λ_{max} (CH_2Cl_2): 705, 430, 325, 258, 222 nm.

Synthesis of Methanofullerene 2c from C_{60}, Dimethyl Acetylenedicarboxylate, and Tricyclopentylphosphine. The procedure was similar to that of the synthesis of ylide **2a**. C_{60} was recovered in 72% yield, yield 23%, $R_f = 0.4$ (TLC, basic alumina, hexane/ethyl acetate/dichloromethane = 4:1:1). Important spectral data of **2c** follow. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.91 (s), 3.66 (s), 3.63 (s), 3.21 (m), 2.30−1.65 (br). ^{31}P NMR (243 MHz, $CDCl_3$): δ 35.8, 35.5. ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.22 (d, $^3J_{PC}$ = 17.8 Hz), 170.19, 151.12, 149.61, 149.46, 147.31, 146.27, 145.44, 145.33, 145.27, 145.24, 145.22, 145.17, 145.05, 144.97, 144.95, 144.86, 144.83, 144.76, 144.74, 144.70, 144.58, 144.46, 144.27, 144.15, 144.12, 143.88, 143.66, 143.09, 142.95, 142.83, 142.81, 142.77, 142.50, 142.43, 142.34, 142.14, 142.11, 141.85, 141.80, 141.05, 140.73, 140.65, 140.30, 139.78, 138.31, 137.76, 136.28, 75.42, 52.72, 51.89 (d, $^2J_{PC}$ = 12.9 Hz), 50.31, 41.41 (d, $^1J_{PC}$ = 112.8 Hz), 34.74 (d, $^1J_{PC}$ = 52.9 Hz), 29.28, 29.09, 26.42 (d, $^3J_{PC}$ = 10.9 Hz), 25.86 (d, $^3J_{PC}$ = 11.1 Hz). HRMS (FAB): calcd for $C_{81}H_{34}O_4P$ ($M + H^+$) 1101.2195, found 1101.2161. FTIR (KBr disk): 2927, 1724, 1606, 1434, 1298, 1185, 1084, 1016, 909, 761, 730, 526 cm^{-1}. UV−vis λ_{max} (CH_2Cl_2): 692, 430, 327, 258 nm.

Synthesis of Cyclopentanofullerene Ylide 3a from C_{60}, Dimethyl Acetylenedicarboxylate, and Tricyclohexylphosphine. To a 100-mL sidearm flask consisting of C_{60} (0.0363 g, 0.050 mmol) and tricyclohexylphosphine (0.0189 g, 0.068 mmol) in toluene (30 mL) under nitrogen was added a solution of dimethyl acetylenedicarboxylate (0.0108 g, 0.076 mmol) in toluene (10 mL) via a syringe pump at a rate of 2.5 mL/h at ambient temperature. Upon injection, the mixture was further stirred for 3 h at the same temperature. The solution was concentrated in vacuo to ca. 2 mL and chromatographed on a silica gel column. Elution with toluene led to the isolation of unreacted C_{60} (0.0224 g) in 62% yield. Further elution with a mixture of hexanes, ethyl acetate, and dichloromethane (2:1:1) afforded a brown solution. The solution was concentrated and precipitated with diethyl ether to give brown solids (0.0185 g) in 33% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.05 (s, 1H), 3.96 (s, 3H), 3.15 (m, 3H), 2.18 (br), 1.99−1.77 (m), 1.45−1.35 (m). ^{31}P NMR (162 MHz): δ 28.08. ^{13}C NMR (150 MHz, $CDCl_3$): δ 185.15 (d, $^2J_{PC}$ = 10.6 Hz) 178.94, 158.38, 153.97, 153.48, 152.66, 150.08, 147.40, 147.33, 147.17, 146.86, 146.47, 146.15 (2C), 146.09, 146.05, 145.95, 145.89, 145.86, 145.83, 145.75, 145.47, 145.43, 145.34, 145.29, 145.18, 145.12, 145.09, 144.97, 144.91, 144.90, 144.46, 144.19, 143.01, 142.79, 142.64, 142.54 (2C), 142.49, 142.46, 142.27, 142.21, 142.08 (2C), 142.06, 141.70, 141.68, 141.56, 141.51 (2C), 141.07, 140.59, 139.60, 139.17, 136.75, 135.84, 135.10, 132.73, 91.48 (d, $^2J_{PC}$ = 8.8 Hz), 81.61, 77.71 (d, $^3J_{PC}$ = 8.9 Hz), 56.87 (d, $^1J_{PC}$ = 91.4 Hz), 53.55, 32.09 (d, $^1J_{PC}$ = 46.2 Hz), 27.89 ($^2J_{PC}$ = 2.2 Hz), 27.75 (d, $^2J_{PC}$ = 3.0 Hz), 27.46 (d, $^3J_{PC}$ = 12.4 Hz), 27.36 (d, $^3J_{PC}$ = 12.4 Hz), 26.28. FTIR (KBr disk): 3455, 2932, 2853, 1726, 1597, 1442, 1296, 1272, 1184, 909, 730, 575, 527 cm^{-1}. HRMS (FAB): calcd for $C_{83}H_{38}O_4P$ ($M + H^+$) 1129.2508, found 1129.2526. UV−vis λ_{max} (CH_2Cl_2): 711, 432, 309, 255, 227 nm.

Synthesis of Cyclopentanofullerene Ylide 3b. Compound **3b** was obtained with a procedure similar to that of ylide **3a**, yield 54%, R_f = 0.57 (TLC, SiO_2, hexanes/ethyl acetate/dichloromethane = 2:1:1). Recovered C_{60} = 42%. Important spectral data follow. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.08 (s, 1H), 4.35 (m, 2H), 3.14 (m, 3H), 2.20−1.84 (br), 1.47 (t, 3H). ^{31}P NMR (202 MHz): δ 28.56. ^{13}C NMR (125 MHz,

$CDCl_3$): δ 185.19 (d, $^2J_{PC}$ = 11.3 Hz), 178.54, 158.52. 154.18, 153.76, 152.63, 150.12, 147.43, 147.40, 147.21, 146.88, 146.58, 146.18, 146.14, 146.08, 145.98, 145.89, 145.77, 145.54, 145.43, 144.37, 145.34, 145.22, 145.16, 145.10, 145.00, 144.95, 144.50, 144.21, 143.08, 143.04, 142.84, 142.58, 142.52, 142.30, 142.26, 142.10, 141.74, 141.71, 141.58, 141.55, 141.40, 141.10, 140.62, 139.63, 139.17, 136.99, 135.83, 135.09, 132.76, 91.12 (d, $^2J_{PC}$ = 7.7 Hz), 81.54 (d, $^3J_{PC}$ = 13.4 Hz), 77.85 (d, $^3J_{PC}$ = 9.6 Hz), 63.45, 57.11 (d, $^1J_{PC}$ = 90.3 Hz), 32.09 (d, $^1J_{PC}$ = 46.1 Hz), 27.89 (d, $^3J_{PC}$ = 13.4 Hz), 27.46 (d, $^3J_{PC}$ = 11.6 Hz), 27.36 (d, $^3J_{PC}$ = 13.4 Hz), 26.28, 14.37. HRMS (FAB): calcd for $C_{84}H_{40}O_4P$ ($M + H^+$) 1143.2664, found 1143.2613. FTIR (KBr disk): 3400, 2928, 2852, 1722, 1605, 1448, 1271, 1154, 892, 852, 806, 730, 526 cm^{-1}. UV−vis λ_{max} (CH_2Cl_2): 708, 430, 304, 253, 222 nm.

Synthesis of Cyclopentanofullerene Ylide 3c from C_{60}, Tricyclopentylphosphine, and Dimethyl Acetylenedicarboxylate. To a solution of C_{60} (0.0367 g, 0.050 mmol) and tricyclopentylphosphine (0.0248 g, 0.104 mmol) in toluene (25 mL) under nitrogen was added a solution of dimethyl acetylenedicarboxylate (0.0142 g, 0.100 mmol) in toluene (10 mL) via a syringe pump at a rate of 5 mL/h at ambient temperature. Upon injection, the resultant mixture was further stirred for 3 h at the same temperature. The solution was concentrated in vacuo to ca. 2 mL and separated on a silica gel column. Elution of the column with toluene led to isolation of unreacted C_{60} (0.0136 g) in 37% yield. Further elution with a mixture of hexanes, ethyl acetate, and dichloromethane (2:1:1) afforded a brown solution containing ylide **3c** and **3c′**. After concentration, the solution was treated with silica gel (10 g), water (1 mL), acetone (2 mL), and dichloromethane (50 mL) and was then stirred at room temperature for 24 h. The mixture was filtered and washed with dichloromethane. The filtrate was concentrated and then precipitated with diethyl ether to afford compound **3c** in 41% yield. Important spectral data for the derivative **3c** follow. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.95 (s, 1H), 3.96 (s, 3H), 3.13 (m, 3H), 2.23−1.72 (br, 24H). ^{31}P NMR (202 MHz): δ 31.36. ^{13}C NMR (125 MHz, $CDCl_3$): δ 185.80 (d, $^2J_{PC}$ = 12.1 Hz) 178.78, 157.76, 153.81, 153.66, 152.56, 149.77, 147.49, 147.46, 146.92, 146.89, 146.43, 146.16, 146.12, 146.07, 145.97, 145.91, 145.87, 145.80, 145.77, 145.51, 145.41, 145.32, 145.23, 145.16, 145.10, 144.97, 144.94, 144.89, 144.53, 144.21, 144.18, 143.01, 142.85, 142.58, 142.54, 142.51, 142.50, 142.41, 142.25, 142.15, 142.09, 141.77, 141.66, 141.59, 141.55, 141.12, 140.61, 139.62, 139.12, 136.55, 135.47, 135.43, 133.17, 96.10, 91.50 (d, $^2J_{PC}$ = 9.9 Hz), 80.94, 77.98 (d, $^3J_{PC}$ = 10.2 Hz), 62.12 (d, $^1J_{PC}$ = 92.8 Hz), 53.42, 33.16 (d, $^1J_{PC}$ = 51.9. Hz), 28.45, 28.15, 26.77 (d, $^3J_{PC}$ = 9.9 Hz), 26.33 (d, $^3J_{PC}$ = 10.1 Hz). HRMS (FAB): calcd for $C_{80}H_{32}O_4P$ 1087.2038, found 1087.2047. FTIR (KBr disk): 2890 (br), 1722, 1594, 1260, 912, 740, 526 cm^{-1}. UV−vis λ_{max} (CH_2Cl_2): 692, 428, 306, 252, 222 nm.

Synthesis of Cyclopentenofullerene 4b from Methanofullerene Ylide 1b (1, R = Et, R′ = Ph). To a solution consisting of compound **1b** (0.0300 g, 0.0260 mmol) and toluene (20 mL) in a 100-mL round-bottom flask was added glacial acetic acid (8.00 mg, 0.133 mmol). The resultant mixture was stirred at 50 °C for 2 days. The solvent was then removed from the reaction mixture under reduced pressure, and the residue was precipitated with diethyl ether. The solid was collected, washed thoroughly with diethyl ether and dried in a vacuum to give derivative **4b** (0.0200 g) in 91% yield. ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ = 9:1): δ 7.88 (s, 1H), 4.56 (q, 2H), 1.47(t, 3H). ^{13}C NMR (150 MHz, $CDCl_3/CS_2$ = 9:1): δ 201.00, 166.32, 162.49, 152.45, 149.82, 147.68, 147.20, 147.04, 146.90, 146.38, 146.36, 146.03, 145.93, 145.61, 145.52, 145.38, 145.24, 145.23, 144.38, 144.11, 142.93, 142.89, 142.69, 142.65, 142.31, 142.29, 141.95, 141.51, 141.36, 140.66, 139.18, 137.64, 136.34, 135.11, 78.23, 72.69, 62.69, 14.15. HRMS (FAB): calcd for $C_{66}H_7O_4$ ($M + H^+$) 847.0393 found 847.0389. FTIR (KBr): 2970, 1722, 1610, 1430, 1211, 1179, 1151, 1097, 729, 573, 526 cm^{-1}. UV−vis λ_{max} (CH_2Cl_2): 693, 427, 309, 255 nm.

Synthesis of Cyclopentenofullerene 4a from Methanofullerene Ylide 1a (R = Me, R′ = Ph). Compound **4a** was prepared in 88% yield according to a procedure similar to that for the synthesis of **4b**. Due to very low solubility of this species in solvents, no ^{13}C NMR spectrum was recorded. Important spectral data other than those from ^{13}C NMR follow. ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ = 9:1): δ 7.87 (s, 1H), 4.08 (s, 3H). HMRS (FAB): calcd for $C_{65}H_5O_3$ ($M + H^+$) 833.0238, found 833.0233. FTIR (KBr): 2973, 1723, 1603, 1428, 1210, 1098, 527 cm^{-1}. UV−vis λ_{max} (CH_2Cl_2): 686, 429, 308, 254 nm.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for all compounds and X-ray data of **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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