Synthesis and Chemistry of Fullerene Derivatives Bearing Phosphorus Substituents. Unusual Reaction of Phosphines with Electron-Deficient Acetylenes and C_{60}

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A unique method to introduce phosphorus substituents onto C_{60} is based on the reaction of phosphines with acetylenes and C_{60}. Treatment of C_{60} with phosphines (PR_3) and electron-deficient acetylenes (A) in toluene at ambient temperature gave fullerene derivatives (**1**, R = C_6H_5 and A = $MeO_2CC{\equiv}CCO_2Me$; **2**, R = C_6D_5 and A = $MeO_2CC{\equiv}CCO_2Me$; **3**, R = C_6H_5 and A = $EtO_2CC{\equiv}CCO_2Et$; **4**, R = *p*-$CH_3C_6H_5$ and A = $MeO_2CC{\equiv}CCO_2Me$; **6**, R = C_6H_5 and A = *trans*-$MeO_2CC{\equiv}CCH{=}CHCO_2Me$) consisting of a phosphorus ylide group and a cyclopropane ring on the fullerene moiety in good to excellent yields. The structures of these ylide derivatives are determined on the basis of their spectral data and single-crystal X-ray diffraction measurements. All these ylides show temperature-dependent NMR spectra that can be rationalized on the basis of interchange between two *Z*,*E* isomers and restricted rotation of the substituents on the fullerene moiety. Based on the known chemistry of phosphines and acetylenes, we propose a mechanism to account for the formation of these ylide derivatives. Phosphine ylides **1** and **4** readily undergo protonation and decarboxylation in the presence of acid to give phosphonium salts **7** and **8**, respectively.

Introduction

Functionalization of fullerenes continues to attract great attention.[1−3] A major effort in this area is the synthesis of fullerene derivatives consisting of polar functionalities for biological applications.[4−6] These fullerene derivatives show promising biological activities such as anti-HIV,[7] DNA cleavage,[8] and cytotoxicity.[9] Thus, the development of synthetic methods for the introduction of new polar functional groups onto a fullerene moiety is not only a great challenge to synthetic chemists but also practically important. In view of the fact that many organic phosphorus compounds are important and well-known biologically active species,[10] fullerene derivatives with phosphorus substituents are expected to provide

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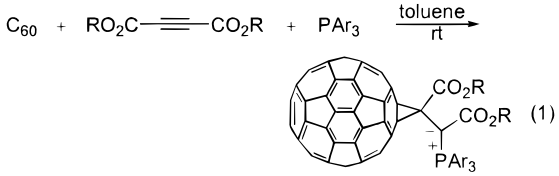
interesting activities in biological systems. Although many methods for the preparation of fullerene derivatives consisting of various functional groups have been developed,[2,3] only one report is known concerning introduction of phosphorus substituents to a fullerene moiety.[11] Nakamura et al. have shown that lithiated phosphine−borane or phosphinite−borane reacts with C_{60} to give a fullerene derivative having a phosphine or phosphonate group. Other than these products, there are no fullerene derivatives bearing phosphorus substituents appearing in the literature.

Recently, we[12] and others[13] have reported the reaction of electron-deficient acetylenes with C_{60} in the presence of phosphines leading to the synthesis of several types of acetylene adducts. In all these reactions, phosphines act only as catalysts and are not included in the acetylene adducts. Here, we report the first synthesis of a series of fullerene derivatives bearing a phosphorus ylide in high yields by the reaction of C_{60} with an electron-deficient acetylene and a phosphine.

Results and Discussion

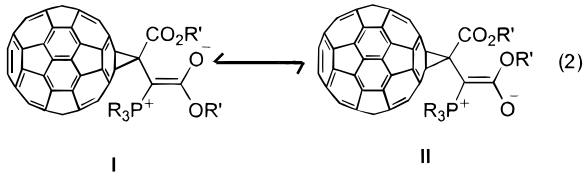
Treatment of C_{60} with dimethyl acetylenedicarboxylate (DMAD) and triphenylphosphine in toluene at ambient temperature gave fullerene derivative **1** in excellent yield (eq 1). Compound **1** consists of a phosphorus ylide group



R = Me	Ar = Ph	**1**
R = Me	Ar = C_6D_5	**2**
R = Et	Ar = Ph	**3**
R = Me	Ar = *p*-MeC_6H_5	**4**

and a cyclopropane ring on the fullerene moiety. The structure is determined on the basis of its MS, ^{1}H and ^{13}C NMR, IR, and UV spectral data and single-crystal X-ray diffraction measurements. MS data of **1** that display a molecular ion (M + 1) at 1125 firmly support an adduct of DMAD and PPh_3 units onto a C_{60} moiety. The ^{1}H NMR spectrum shows four signals in the region 3−4 ppm and broad signals in the region 7−8 ppm, assigned to methoxy and phenyl protons, respectively. To prove that the broad signals arise from the PPh_3 moiety, product **2** was synthesized by the reaction of C_{60} with DMAD and deuterated phosphine $P(C_6D_5)_3$; this product shows no ^{1}H NMR signal in the aromatic region but exhibits methoxy signals in the region 3−4 ppm similar to those of compound **1**. The signals in the 3−4 ppm region of **1** are shown to be from the DMAD moiety on comparison with the ^{1}H NMR spectrum of compound **3** isolated from reaction of C_{60} with diethyl acetylenedicarboxylate (DEAD) and PPh_3.

Product **1** shows fluxional behavior in the ^{1}H NMR spectrum. At ambient temperature, the ^{1}H NMR spectrum exhibits two sets of methoxy resonances at 3.87 and 3.21 ppm and at 3.80 and 3.76 ppm with relative intensity ca. 2:3. As the temperature was increased, broadening of the signals occurred, and only a set of resonances at 3.60 and 3.44 ppm was observed at 363 K. These results are rationalized on the basis of the presence of two *Z*,*E* isomers **I** and **II** (eq 2) that undergo rapid interchange on the NMR time scale. This *Z*,*E* isomerism of α-ylide esters was observed previously.[14] Further evidence for the presence of an ylide ester group in **1** is the observation of a characteristically strong low-frequency carbonyl absorption at 1605 cm^{-1} in the IR spectrum.[15] The other ester carbonyl absorption in **1** appears at 1725 cm^{-1}.



I II

^{13}C and ^{31}P NMR spectra of **1** also indicate the presence of two isomers and lack of a symmetry element of these isomers. The ^{13}C spectrum consists of two sets of signals that comprise more than 110 resonances in total. Characteristic carbonyl resonances appear clearly at 170.78 (d, $^2J_{PC}$ = 17.2 Hz), 168.35 (d, $^2J_{PC}$ = 15.1 Hz), 168.72, and 168.30 ppm, whereas the ylide carbon exhibits resonances at 37.48 (d, $^1J_{PC}$= 130.8 Hz) and 36.34 (d, $^1J_{PC}$ = 121.8 Hz) ppm. The observed $^2J_{PC}$ and $^1J_{PC}$ coupling constants are typical of an α-ylide ester. For comparison, the values of $^1J_{PC}$ and $^2J_{PC}$ are 126.7 and 12.7 Hz for ylide $MeOOCCHPPh_3$.[16] Evidence for the presence of a cyclopropane ring in **1** is shown by the observed ^{13}C signals at 74.75 (d), 74.46 (d), 73.74, and 73.38 ppm (two sets) for the two sp^3 carbons on the fullerene moiety and at 47.63 and 47.54 ppm for the quaternary sp^3 carbon resonances on the DMAD moiety. The observed chemical

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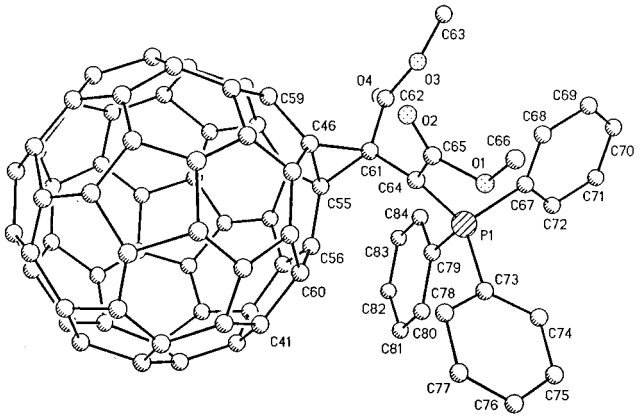


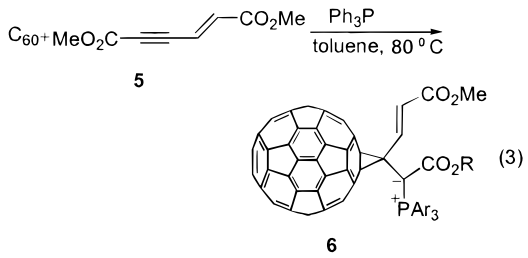
Figure 1. X-ray structure of compound **1**.

shifts are comparable to values for reported methanofullerenes.[17] Similar to the ^{1}H and ^{13}C NMR results, two ^{31}P NMR signals were found at 22.34 and 21.97 ppm for ylide **1**.

X-ray Structure of Compound 1. As a representative of these ylide derivatives, **1** was selected for structural determination by X-ray diffraction methods. Crystals were grown in a NMR tube from a *d*-chloroform solution. The X-ray structure of compound **1** is drawn in Figure 1. In agreement with the implications of spectral data, the results of X-ray analysis clearly show that **1** consists of a cyclopropane ring and an ylide group. The observed angles for P1−C64−C61, P1−C64−C65, and C61−C64−C65 are 120, 119, and 117°, respectively, indicative of a sp^2 hybridization for the ylide carbon (C64). The dihedral angle for planes P1−C64−C61 and C65−O1−O2 is only 18°, supporting substantial $\pi-\pi$ interaction between C64 and C65. The distance between atoms C64 and C65 is consistent with a partial double bond between these two atoms.

To understand the scope of the reaction, different acetylenes and phosphines were employed to react with C_{60}. Similar to PPh_3, P(*p*-MeC_6H_4)$_3$ reacts with DMAD and C_{60} at ambient temperature to give the corresponding ylide **4** in 43% yield. This fullerene derivative is also characterized by its spectral data. Methoxy signals appear in two sets in the region 3.20−3.90 ppm in the ^{1}H NMR spectrum, indicating the presence of two isomers (**I** and **II**) similar to the results observed for **1**.

In addition to DMAD and DEAD, enyne **5**[18] reacts with PPh_3 and C_{60} under similar conditions to give ylide **6** (eq 3) along with bisadducts. Spectral data observed for



(3)

compound **6** indicate that its structure consists of an ylide group and a cyclopropane ring and that it exists as a mixture of isomers **I** and **II**. As the carbon−carbon triple

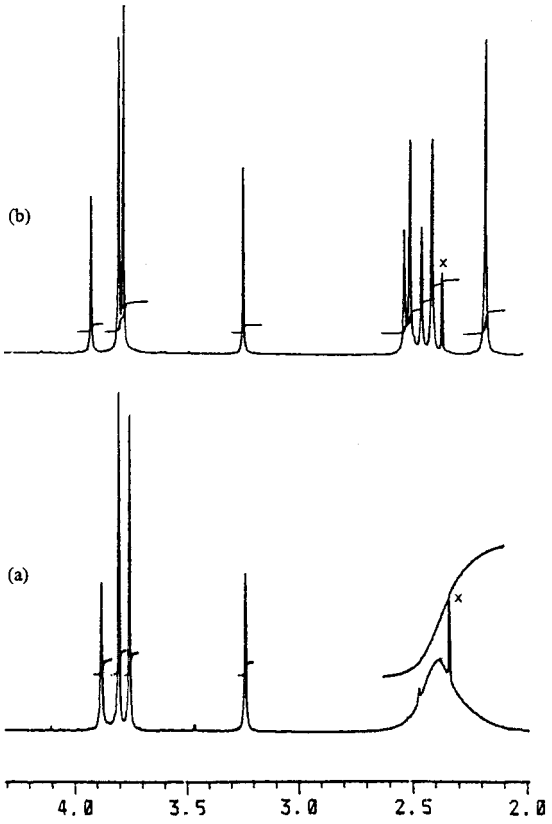
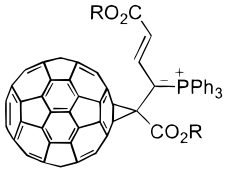


Figure 2. ^{1}H NMR spectra in the region of methyl resonances of compound **4** (a) at 293 K and (b) at 216 K. The signals in the range 3.1−4.0 ppm are assigned to methyl protons attached to ester groups, and those in the range 2.0−2.7 ppm are due to the methyl protons on the tolyl groups. The signals marked are from toluene.

bond of **5** is unsymmetrical, it is interesting to learn how the alkyne carbons are bonded to the fullerene and the phosphine moieties. NMR spectra of **6** provide detailed information about the bonding. In the ^{1}H NMR spectrum of **6**, the olefin protons appear as two pairs of doublets at 8.15 and 6.52 ppm and at 7.88 and 6.38 ppm. The observed coupling constants of ∼15.5 Hz for these olefin protons indicate a trans geometry for the carbon−carbon double bond on the enyne moiety. Furthermore, the coupling pattern indicates that no phosphorus is connected to the allylic carbon. The observed ^{13}C−^{31}P coupling constants of 17.4 and 14.4 Hz for the carbonyl carbon at 171.9 and 169.7 ppm, respectively, and of 15.9 and 15.0 Hz for the quaternary carbon of the cyclopropane ring at 46.7 and 45.6 ppm, respectively, are close to the corresponding values of compound **1**. These results clearly support a proposed structure in which the PPh_3 moiety is bonded to the α-carbon of an ester group as shown in structure **6**. Another possible structure **6′** in which the PPh_3 moiety is bonded to the *β*-carbon of an ester group is unlikely on the basis of observed NMR coupling patterns.



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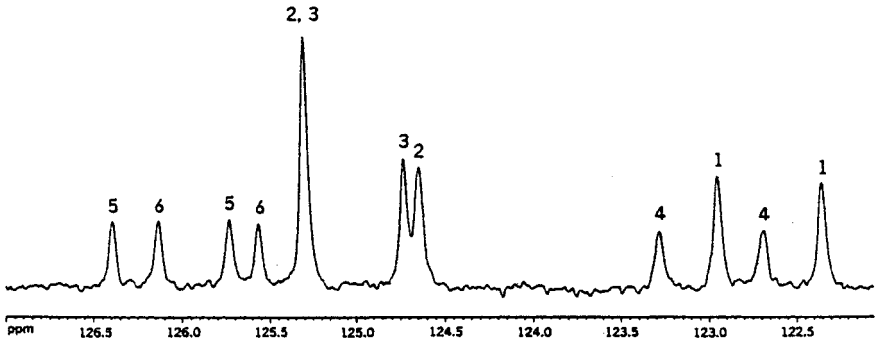


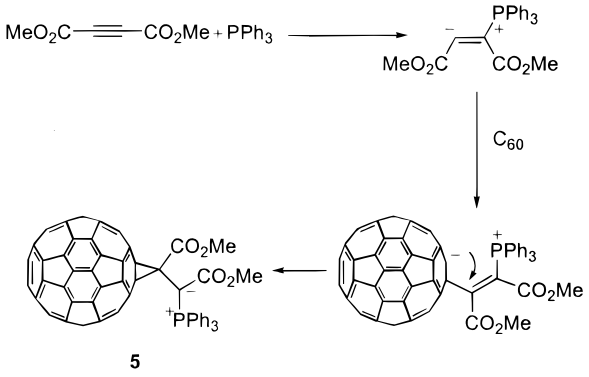
Figure 3. ^{13}C NMR spectrum for ipso carbons of the triphenylphosphine moiety of compound **1** at 300 K. The spectrum consists of two sets of signals with each set having three pairs of resonances. For clarity, each pair of signals is marked by a number.

Restricted Rotation of Ylide Substituents. Analysis of NMR data of ylides provides further detailed information about the structure of these compounds. For example, the methyl protons on the tri-*p*-tolylphosphine moiety of compound **4** appear as a broad signal at 2.38 ppm at room temperature in the ^1H NMR spectrum (Figure 2a). This broad signal clearly splits into two sets of resonances corresponding to two isomers at a temperature below 258 K. Signals in each set of consist of three resonances, one set at 2.50, 2.42, and 2.15 ppm and the other at 2.48, 2.38, and 2.15 ppm (Figure 2b). The observations strongly indicate that the three tolyl groups have different magnetic environments and the exchange with each other is slow on the ^1H NMR time scale at a temperature below 258 K. Similar results were found for the ^{13}C NMR signals for the triphenylphosphine moiety of compounds **1**, **3**, and **6**. As an example, ^{13}C NMR signals for ipso carbons on the triphenylphosphine moiety in compound **1** are shown in Figure 3. The spectrum reveals two sets of signals with each set consisting of three doublets. These observations may be explained on the basis of the crystal structure of compound **1** shown in Figure 1. To afford three magnetically different phenyl groups, it is necessary that rotation about the ylide (P1−C64) and C61−C64 bonds is slow on the NMR time scale. Restricted rotation about the P1−C64 bond is expected in view of its partial double bond character. Restricted rotation about the single bond C61−C64 is less obvious from the structure; it is likely resulted from the extremely bulky substituents on these carbons.

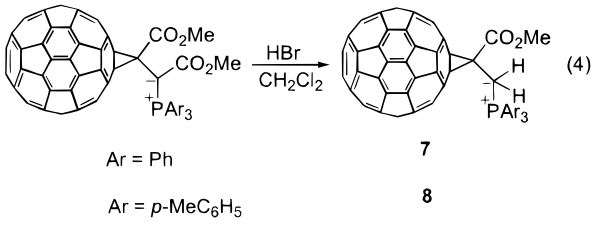
Mechanism for the Formation of Ylide Derivatives. On the basis of the known reaction chemistry of phosphine and electron-withdrawing acetylenes,[19] the pathways shown in Scheme 1 are proposed to account for the formation of ylides from the reaction of PPh_3, DMAD, and C_{60}. The first step involves attack of PPh_3 at an acetylene carbon to give a zwitterion. Further attack of the latter at a C_{60} molecule followed by back attack at the carbon β to the PPh_3 moiety yields the final ylide product. For the formation of compound **6**, attack of PPh_3 must occur at the α-carbon (see eq 3) in order to yield the observed product.

Protonation of Fullerene Ylides. Unlike typical ylides, the present fullerene derivatives do not undergo Wittig reaction with benzaldehyde. The lack of reactivity of these fullerene ylides is attributed to the presence of electron-withdrawing ester groups and the C_{60} moiety and the large steric effect of these groups. However,

Scheme 1



phosphine ylides **1** and **4** readily undergo protonation and decarboxylation in the presence of hydrobromic acid to give phosphonium salts **7** and **8**, respectively, in good yields (eq 4). These products are characterized by their



MS, NMR, and IR spectra. In the ^1H NMR spectrum of **7**, key signals for α-protons and methoxy protons appear at 5.55 (d) and at 3.66 (s) ppm, respectively. Strong evidence for the presence of only a methoxy group and an α-methylene group is the intensity ratio 3/2 of these two signals. The ^{13}C NMR spectrum of **7** also agrees with the proposed structure. On the basis of the symmetry (C_s) of the proposed structure, 35 different sp^2 carbons are expected for the fullerene and triphenylphosphine moieties, and in fact, 31 signals are resolved in the ^{13}C NMR spectrum. In addition, signals at 166.3 ppm for the carbonyl carbon, at 53.9 ppm for the methoxy carbon, at 25.0 (d) ppm for the methylene carbon and at 41.6 and 72.8 (d) ppm for the sp^3 quaternary carbons of the cyclopropane ring were observed. Due to the presence of plane symmetry and the absence of *E*,*Z* isomers of **7**, the observed number of ^{13}C NMR resonances decrease greatly to ca. 1/4 that of corresponding ylide **1**. Similar to the ^1H and ^{13}C NMR results, only a single isomer was detected from ^{31}P NMR measurement.

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Conclusion

We have demonstrated a novel method to introduce phosphorus substituents onto C_{60} based on reaction of phosphines with electron-deficient acetylenes and C_{60}. Crystal-structure analysis of a representative ylide unambiguously establishes the structure. Temperature-dependent NMR experiments clearly show that each phosphorus ylide exists as two *Z*,*E* isomers. Protonation of these ylides leads to decarboxylation and formation of phosphonium salts. Tests of biological activities of these phosphorus fullerene derivatives are in progress.

Experimental Section

Synthesis of Compound 1 from C_{60}, Dimethyl Acetylenedicarboxylate, and Triphenylphosphine. A mixture of C_{60} (0.0357 g, 0.050 mmol), PPh_3 (0.0259 g, 0.099 mmol), and toluene (25 mL) in a 50-mL sidearm flask was stirred at ambient temperature until all solid material dissolved. To the system was injected via a syringe pump a solution consisting of dimethyl acetylenedicarboxylate (0.0107 g, 0.075 mmol) and toluene (10 mL) with an injection rate of 3.4 mL/h. After addition, the system was further stirred for 3 h at room temperature. The solution was concentrated in a vacuum system to ca. 2 mL. The mixture was separated on a silica gel column and eluted first with toluene to recover C_{60} (0.0022 g) in 6% yield and then with a mixture of hexane, ethyl acetate, and dichloromethane (2:1:1). The fraction consisting of monoadduct **1** (R_f = 0.41) was collected. After solvent removal, the solid was washed with hexane to afford the desired pure product (0.0490 g) in 94% yield. Spectral data for compound **1** follow. ^{1}H NMR (400 MHz, $CDCl_3$) 293 K: δ 7.84 (br, Ph), 7.52 (br, Ph), 3.87 (s, OCH_3), 3.80 (s, OCH_3), 3.76 (s, OCH_3), 3.21 (s, OCH_3). ^{1}H NMR (400 MHz, C_6D_5Br) 363 K: δ 7.87−7.82 (m, 6 H, Ph), 7.20−7.17 (m, 9 H, Ph), 3.60 (s, 3 H, OCH_3), 3.44 (s, 3 H, OCH_3). ^{31}P NMR (162 MHz, $CDCl_3$) 273 K: δ 22.32, 20.95 ppm. ^{31}P NMR (162 MHz, C_6D_5Br) 363 K: δ 21.31 ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.78 (d, $^3J_{PC}$ = 17.2 Hz), 168.72, 168.35 (d, $^3J_{PC}$ = 15.1 Hz), 168.30, 149.95, 149.38, 148.22, 147.89, 146.52, 146.22, 146.20, 145.75, 145.74, 145.07, 144.79, 144.44, 144.42, 144.37, 144.22, 144.15, 143.92, 143.86, 143.73, 143.67, 143.64, 143.61, 143.54, 143.52, 143.40, 143.28, 143.22, 143.20, 143.13, 143.03, 142.97, 142.95, 142.94, 142.86, 142.78, 142.72, 142.70, 142.38, 142.36, 142.28, 142.21, 141.81, 141.53, 141.51, 141.45, 141.42, 141.34, 141.05, 140.95, 140.93, 140.85, 140.80, 140.71, 140.69, 140.67, 140.30, 140.12, 140.09, 139.47, 139.34, 139.15, 138.44, 138.39, 137.97, 137.84, 137.28, 136.77, 136.74, 136.64, 136.30, 136.02, 135.46, 134.66, 134.04 (d, $^2J_{PC}$ = 9.7 Hz, *C*H), 132.49 (d, $^2J_{PC}$ = 9.5 Hz, *C*H), 132.43 (d, $^2J_{PC}$ = 9.1 Hz, *C*H), 131.64 (*C*H), 131.54 (*C*H), 131.48 (*C*H), 131.27 (*C*H), 130.98 (*C*H), 128.08 (*C*H), 128.00 (*C*H), 127.92 (*C*H), 127.85 (*C*H), 127.77 (*C*H), 127.66 (*C*H), 127.63 (*C*H), 127.55 (*C*H), 126.06 (d, $^1J_{PC}$ = 99.5 Hz), 125.84 (d, $^1J_{PC}$ = 85.6 Hz), 125.01 (d, $^1J_{PC}$ = 85.7 Hz), 124.94 (d, $^1J_{PC}$ = 98.9 Hz), 122.98 (d, $^1J_{PC}$ = 89.5 Hz), 122.65 (d, $^1J_{PC}$ = 90.6 Hz), 74.75 (d, $^3J_{PC}$ = 12.6 Hz), 74.46 (d, $^3J_{PC}$ = 14.2 Hz), 73.74, 73.38, 52.18 (O*C*H$_3$), 51,85 (O*C*H$_3$), 50.01 (O*C*H$_3$), 48.57 (O*C*H$_3$), 47.63, 47.54, 37.48 (d, $^1J_{PC}$ = 130.8 Hz), 36.34 (d, $^1J_{PC}$ = 121.8 Hz). FTIR (KBr): 3058, 3024, 2945, 1729, 1621 cm^{-1}. UV−vis λ_{max} (ϵ) (CH_2Cl_2): 697 (221), 429 (2340), 325 (15700), 257 (46000), 226 (46900) nm. FAB-MS *m*/*z*: 1125 (M^+ + 1, 50), 720 (80). HRMS (FAB): calcd for $C_{84}H_{22}O_4P$ ($M + H^+$) 1125.1256, found 1125.1245.

Compounds **2**−**4** were prepared similarly to compound **1**. Key spectral data of these products follow.

Compound 2 from C_{60}, DMAD, and P(C_6D_5)$_3$. Yield: 91%. R_f = 0.4 (TLC, SiO_2, hexane/ethyl acetate/dichloromethane = 1.5:1:1). ^{1}H NMR (600 MHz, CD_2Cl_2): δ 3.83 (s, OCH_3), 3.79 (s, OCH_3), 3.65 (s, OCH_3), 3.13 (s, OCH_3). ^{31}P NMR (162 MHz, CD_2Cl_2) 305 K: δ 22.23, 20.61 ppm. FTIR (KBr): 2976, 2945, 2244, 1728, 1619 cm^{-1}. UV−vis λ_{max} (ϵ) (CH_2Cl_2): 698 (233), 429 (2484), 327 (35722), 2158 (104860), 228 (102590) nm. FAB-MS *m*/*z*: 1140 (M^+ + 1, 24), 720 (C_{60}, 100).

Compound 3 from C_{60}, DEAD, and P(C_6H_5)$_3$. Yield: 71%. R_f = 0.375 (TLC, SiO_2, hexane/ethyl acetate/dichloromethane = 1.5:1:1). ^{1}H NMR (400 MHz, $CDCl_3$) 298 K: δ 7.84 (br), 7.54 (br), 4.38−4.24 (m), 4.14 (m), 3.91 (br), 3.74 (br), 1.34 (m), 1.27 (m), 0.51 (br). ^{1}H NMR (400 MHz, $CDCl_3$) 248 K: δ 7.96 (m, Ph), 7.79 (m, Ph), 7.69 (m, Ph), 7.66 (m, Ph), 7.38 (m, Ph), 7.31 (m, Ph), 4.39−4.19 (m, OCH_2), 4.22−4.19 (m, OCH_2), 4.13−4.08 (m, OCH_2), 3.95−3.90 (q, J = 7.0 Hz, OCH_2), 3.69−3.68 (q, J = 7.0 Hz, OCH_2), 1.34 (t, J = 7.0 Hz, CH_3), 1.22−1.16 (t, J = 7.0 Hz, CH_3), 0.42 (t, J = 7.0 Hz, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) 233 K: δ 171.59 (d, $^3J_{PC}$ = 17.2 Hz), 168.89, 168.78 (d, $^3J_{PC}$ = 12.7 Hz), 168.68, 151.56, 150.87, 150.04, 149.85, 147.58, 147.47, 147.31, 146.23, 145.78, 145.72, 145.67, 145.62, 145.00, 144.94, 144.84, 144.82, 144.77, 144.74, 144.72, 144.66, 144.65, 144.50, 144.44, 144.38, 144.36, 144.34, 144.33, 144.29, 144.27, 144.25, 144.23, 144.19, 144.06, 144.04, 144.01, 143.91, 143.85, 143.82, 143.45, 143.39, 143.34, 143.30, 142.90, 142.81, 142.65, 142.63, 142.57, 142.56, 142.53, 142.50, 142.48, 142.44, 142.40, 142.37, 142.15, 142.06, 142.01, 141.98, 141.94, 141.91, 141.87, 141.78, 141.72, 141.41, 141.36, 141.01, 140.53, 140.42, 140.25, 139.49, 139.02, 138.91, 138.08, 137.96, 137.67, 137.36, 137.22, 137.04, 136.53, 135.69, 135.29 (d, $^2J_{PC}$ = 8.3 Hz, *C*H), 135.23 (d, $^2J_{PC}$ = 9.2 Hz, *C*H), 133.84 (d, $^2J_{PC}$ = 10.0 Hz, *C*H), 133.82 (d, $^2J_{PC}$ = 10.3 Hz, *C*H), 132.76 (d, $^2J_{PC}$ = 9.8 Hz, *C*H), 132.56 (d, $^2J_{PC}$ = 10.6 Hz, *C*H), 132.19 (*C*H), 131.91 (*C*H), 131.84 (*C*H), 131.82 (*C*H), 131.78 (*C*H), 128.97 (d, $^3J_{PC}$ = 12.1 Hz, *C*H), 128.94 (d, $^3J_{PC}$ = 11.2 Hz, *C*H), 128.67 (d, $^3J_{PC}$ = 12.1 Hz, *C*H), 128.60 (d, $^3J_{PC}$ = 9.4 Hz, *C*H), 128.48 (d, $^3J_{PC}$ = 11.9 Hz, *C*H), 128.43 (d, $^3J_{PC}$ = 12.6 Hz, *C*H), 127.57 (d, $^1J_{PC}$ = 85.1 Hz), 127.10 (d, $^1J_{PC}$ = 85.4 Hz), 127.03 (d, $^1J_{PC}$ = 90.1 Hz), 126.53 (d, $^1J_{PC}$ = 87.8 Hz), 124.21 (d, $^1J_{PC}$ = 89.5 Hz), 124.13 (d, $^1J_{PC}$ = 89.8 Hz), 76.23 (d, $^3J_{PC}$ = 12.8 Hz), 75.97 (d, $^3J_{PC}$ = 11.6 Hz), 74.98, 74.70, 62.13 (O*C*H$_2$), 61.93 (O*C*H$_2$), 59.00 (O*C*H$_2$), 58.00 (O*C*H$_2$), 50.20 (d, $^2J_{PC}$ = 15.6 Hz), 49.49 (d, $^2J_{PC}$ = 14.6 Hz), 38.73 (d, $^1J_{PC}$ = 130.1 Hz), 37.05 (d, $^2J_{PC}$ = 122.2 Hz), 15.24 (*C*H$_3$), 14.03 (*C*H$_3$), 13.87 (*C*H$_3$), 13.54 (*C*H$_3$). ^{31}P NMR (162 MHz) 305 K: δ 22.15, 20.86 ppm. FTIR (KBr): 3060, 2979, 1724, 1617 cm^{-1}. UV−vis λ_{max} (ϵ) (CH_2Cl_2): 699 (237), 429 (2559), 326 (15662) nm. FABMS *m*/*z*: 1153 (M^+ + 1, 34), 720 (C_{60}, 100).

Compound 4 from C_{60}, DMAD, and P(*p*-$CH_3C_6H_5$)$_3$. Yield 43%. R_f = 0.31 (TLC, SiO_2, hexane/ethyl acetate/dichloromethane = 3.5:1:1). ^{1}H NMR (600 MHz, $CDCl_3$) 216 K: δ 7.83 (m, Ph), 7.65 (m, Ph), 7.38 (m, Ph), 7.07 (m, Ph), 3.89 (s, OCH_3), 3.78 (s, OCH_3), 3.75 (s, OCH_3), 3.22 (s, OCH_3), 2.50 (s, CH_3), 2.48 (s, CH_3), 2.42 (s, CH_3), 2.38 (s, CH_3), 2.15 (s, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.66 (d, $^3J_{PC}$ = 17.4 Hz), 169.90(d, $^2J_{PC}$ = 17 Hz), 168.85, 168.27, 167.72, 148.29, 148.11, 146.82, 146.71, 146.45, 146.41, 144.77, 144.54, 144.20, 143.99, 143.94, 143.89, 143.85, 143.81, 143.71, 143.52, 143.40, 143.36, 143.28, 143.22, 142.99, 142.84, 142.80, 142.56, 142.49, 141.69, 141.66, 141.60, 141.51, 141.46, 141.10, 141.07, 141.05, 141.02, 140.90, 140.84, 140.62, 139.67, 139.55, 139.42, 138.51, 138.40, 137.60, 137.49, 136.43, 136.17, 136.08, 135.99, 135.67, 135.25, 134.76, 134.38(br), 132.62(br), 131.48(br), 128.68(br), 122.03, 121.66, 121.09, 119.73, 119.12. 74.40(d, $^3J_{PC}$ = 13.1 Hz), 74.21(d, $^3J_{PC}$ = 12 Hz), 73.49, 73.27, 69.27, 53.62 (O*C*H$_3$), 53.26(O*C*H$_3$), 52.99(O*C*H$_3$) 52.32(O*C*H$_3$), 52.12(O*C*H$_3$), 48.32, 48.22, 37.07 (d, $^1J_{PC}$ = 129.3 Hz), 35.54 (d, $^1J_{PC}$ = 128.2 Hz), 21.02, 20.69. ^{31}P NMR (162 MHz, $CDCl_3$) 305 K: δ 21.26, 20.12 ppm. FTIR (KBr): 2945, 1728, 1615 cm^{-1}. UV−vis λ_{max} (ϵ) (CH_2Cl_2): 699, 489, 429, 326, 258, 235 nm. FAB-MS *m*/*z*: 1168 (M + 2, 33), 720 (C_{60}, 100). HRMS (FAB): calcd for $C_{87}H_{28}O_4P$ ($M + H^+$) 1167.1725, found 1167.1741.

Synthesis of Compound 6 from C_{60}, Dimethyl *trans*-But-1-en-3-yne-1,4-dicarboxylate (5) and Triphenylphosphine. A mixture of C_{60} (0.0372 g, 0.0517 mmol), PPh_3 (0.262 g, 0.100 mmol), and toluene (25 mL) in a 50-mL sidearm flask was stirred at 50 °C under nitrogen until all solid material dissolved. To the system was injected via a syringe pump a toluene solution consisting of **5**[18] (0.0165 g, 0.098 mmol) and toluene (10 mL) with an injection rate of 4.7 mL/h. After injection, the system was further stirred for 3 h at the same temperature. The solution was concentrated in a vacuum system to ca. 2 mL. The mixture was separated on a silica gel

column. The column was eluted first with toluene to give C_{60} (0.0122 g) in 30% yield and then with a mixture of hexane, ethyl acetate, and dichloromethane (1:1:1). Two fractions consisting of monoadduct **6** (R_f = 0.07) and bisadducts were collected. After solvent removal, the solids were washed with hexane to afford the desired pure monoadduct **6** (0.0060 g) in 15% yield and bisadducts (0.0292 g) in 54% yield. Spectral data for the monoadduct **6** follow. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, ^3J = 15.4 Hz, C*H*), 8.00 (br), 7.88 (d, ^3J = 15.6 Hz, C*H*), 7.54 (br), 6.52 (d, ^3J = 15.4 Hz, C*H*), 6.38 (d, ^3J = 15.6 Hz, C*H*), 3.80 (s, OCH_3), 3.79 (s, OCH_3), 3.75 (s, OCH_3), 3.24 (s, OCH_3). ^{31}P NMR (162 MHz, $CDCl_3$) 305 K: δ 21.32, 20.00 ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.86 (d, $^2J_{PC}$ = 17.4 Hz), 169.69 (d, $^2J_{PC}$ = 14.4 Hz), 167.38, 167.34, 152.24, 151.74, 149.38, 149.31, 148.71 (CH), 148.20, 147.36, 147.22, 146.62, 146.50, 146.23, 145.69, 145.55, 145.36, 145.33, 145.22, 145.16, 145.10, 145.05, 144.98, 144.96, 144.92, 144.88, 144.85, 144.77, 144.68, 144.66, 144.64, 144.50, 144.47, 144.43, 144.37, 144.35, 144.31, 144.29, 144.23, 144.17, 144.11, 144.10, 144.07, 144.03, 144.01, 143.98, 143.91, 143.87, 143.82, 143.49 (*CH*), 143.36, 143.33, 142.81, 142.80, 142.76, 142.74, 142.72, 142.68, 142.65, 142.60, 142.58, 142.57, 142.54, 142.49, 142.42, 142.24, 142.22, 142.06, 142.01, 141.96, 141.93, 141.84, 141.82, 141.74, 141.47, 141.45, 141.18, 140.78, 140.58, 139.83, 139.63, 139.25, 139.17, 138.86, 138.42, 138.12, 137.93, 137.46, 137.29, 137.01, 136.25, 134.69 (d, $^2J_{PC}$ = 9.7 Hz, *CH*), 134.46 (d, $^2J_{PC}$ = 9.1 Hz, *C*H), 134.23 (d, $^2J_{PC}$ = 10.0 Hz, *C*H), 133.80 (d, $^2J_{PC}$ = 10.4 Hz, *C*H), 133.11 (d, $^2J_{PC}$ = 10.0 Hz, C*H*), 132.93 (*C*H), 132.77 (*C*H), 132.53 (d, $^2J_{PC}$ = 10.0 Hz, *C*H), 132.38 (*C*H), 132.27 (*C*H), 132.15 (*C*H), 131.98 (*C*H), 129.25 (d, $^3J_{PC}$ = 11.3 Hz, *C*H), 129.01 (d, $^3J_{PC}$ = 11.6 Hz, *C*H), 128.89 (d, $^3J_{PC}$ = 12.2 Hz, *C*H), 128.64 (d, $^3J_{PC}$ = 13.0 Hz, *C*H), 128.30 (d, $^3J_{PC}$ = 12.7 Hz, *C*H), 125.41 (d, $^1J_{PC}$ = 98.3 Hz, *C*H), 123.76 (*C*H), 123.13 (d, $^3J_{PC}$ = 23.2 Hz, CH), 79.26 (d, $^3J_{PC}$ = 11.8 Hz), 79.20 (d, $^3J_{PC}$ = 12.7 Hz), 78.54 (d, $^3J_{PC}$ = 12.2 Hz), 78.25 (d, $^3J_{PC}$ = 2.9 Hz), 52.10 (O*C*H$_3$), 51.99 (O*C*H$_3$), 50.91 (O*C*H$_3$), 49.62 (O*C*H$_3$), 46.73 (d, $^2J_{PC}$ = 15.9 Hz), 45.61 (d, $^2J_{PC}$ = 15.0 Hz), 38.98 (d, $^1J_{PC}$ = 123.3 Hz), 38.66 (d, $^1J_{PC}$ = 130.8 Hz). FTIR KBr (Disk): 3060, 2939, 1718, 1620 cm^{-1}. UV−vis λ_{max} (ϵ) (CH_2Cl_2): 698 (290), 493 (2194), 431 (2691), 327 (4.46×10^4), 259 (1.25×10^5), 227 (1.26×10^5) nm. FAB-MS *m*/*z*: 1151 ($M^+ + 1$, 50), 720 (C_{60}, 100). HRMS (FAB): calcd for $C_{86}H_{24}O_4P$ ($M + H^+$) 1151.1412, found 1151.1423.

Reaction of Compound 1 with Hydrobromic Acid. Synthesis of Compound 7. To a 50-mL flask were added compound **1** (0.0081 g, 7.2 mmol), dichloromethane (10 mL), and concentrated hydrobromic acid (0.5 mL). The mixture was refluxed with stirring until compound **1** disappeared as indicated by TLC monitoring results. The solution was concentrated on a rotary evaporator and then separated on a silica gel column with a mixture of hexane, ethyl acetate, and dichloromethane (1:1:1) as eluent to give the desired product (0.0080 g) in 97% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (m, Ph), 7.79 (m, Ph), 5.55 (d, $^2J_{HP}$ = 11.9 Hz), 3.66 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.30, 145.91, 145.43, 145.36, 145.35, 145.32, 144.96, 144.94, 144.82, 144.72, 144.58, 144.53, 144.44, 144.36, 143.93, 143.60, 143.13, 143.09, 143.02, 142.71, 142.10, 142.09, 141.90, 141.85, 140.76, 140.71, 138.38, 137.18, 135.51 (*C*H), 134.60 (d, $^3J_{PC}$ = 10.3 Hz, *C*H), 130.83 (d, $^2J_{PC}$ = 12.8 Hz, *C*H), 117.31 (d, $^1J_{PC}$ = 86.3 Hz), 72.84 (d, $^3J_{PC}$ = 9.5 Hz), 53.92 (O*C*H$_3$), 41.57, 25.00 (d, $^1J_{PC}$ = 52.4 Hz, *C*H$_2$). ^{31}P NMR (162 MHz, $CDCl_3$): δ 18.31 ppm. FTIR (KBr): 3053, 2948, 1739 cm^{-1}. UV−vis λ_{max} (ϵ) (CH_2Cl_2): 227 (105610), 256 (104750), 425 (36453), 426 (2446), 470 (1603), 681 (279) nm. FAB-MS *m*/*z*: 1067 (M^+ − Br, 35), 720 (C_{60}, 100).

Compound **8** was prepared in essentially quantitative yield according to a procedure similar to that for compound **7** using compound **4** as starting material. Key spectral data follow. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (m, 6 H), 7.55 (m, 6 H), 4.89 (d, ^2J = 11.5 Hz, 2 H), 3.66 (s, 3 H), 2.64 (s, 9 H). ^{31}P NMR (162 MHz): δ 20.86 ppm. FABMS *m*/*z*: 1111 ($M^+ + 2$, 44), 1110 ($M^+ + 1$, 77), 1109 (M^+, 68), 720 (C_{60}, 100).

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Supporting Information Available: Copies of ^{1}H, ^{13}C, and ^{31}P NMR and mass spectra for all compounds and X-ray structure determination summary and lists of coordinates, anisotropic displacement factors, bond lengths, and bond angles for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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