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Reactions of Fullerenes with Reactive Methylene Organophosphorus Reagents: Efficient Synthesis of Organophosphorus Group Substituted C_{60} and C_{70} Derivatives

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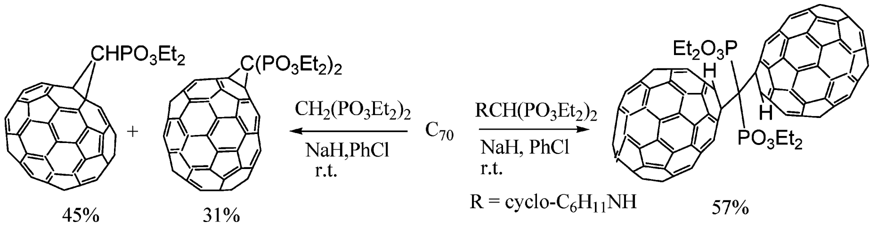

Treatment of C_{70} with cycloalkylaminomethylenebisphosphonates in the presence of NaH gave corresponding C_{70} dimers **1** in good yield, while the methanofullerenes, $C_{70}{>}CH(PO_3Et_2)$ (**3**) and $C_{70}{>}C(PO_3Et_2)_2$ (**4**) or $C_{60}{>}CH(PO_3Et_2)$ (**5**) and $C_{60}{>}C(PO_3Et_2)_2$ (**6**), were obtained, respectively, by the reaction of C_{70} or C_{60} with tetraethyl methylenediphosphonate in the presence of NaH. Diethyl cyanomethylphosphonate reacted with C_{60} or C_{70} under similar conditions to afford $C_{60}{>}C(PO_3Et_2)CN$ (**7**) and $C_{70}{>}C(PO_3Et_2)CN$ (**8**). Furthermore, the presence of weak electronic interactions between two fullerene cages of fullerene dimers was demonstrated by cyclic voltammetry. A radical mechanism was proposed for the formation of the fullerene derivatives on the basis of the ESR studies.

Introduction

Fullerenes and their derivatives have wide applications in the scientific research of nonlinear optics,[1] artificial photosynthesis,[2] organic materials,[3] biology and medicine,[4] and so on. An interesting and useful class of the new materials is organophosphorus fullerene derivatives, which bear bone-vectored bisphosphonate groups and may offer great promise as new therapeutic drugs for various bone diseases of metabolism.[5−7] However, efforts shall be made in developing more methods to synthesize organophosphorus fullerene derivatives or fullerene bisphosphonates that are prepared currently to a large extent through nucleophilic additions, namely, the Bingel−Hirsch reaction,[8] which is based on the theme of nucleophilic attacks on fullerenes by an ionic pathway in the presence of bromine or iodine.

Recently, we have reported that the cycloalkylaminomethylenebisphosphonates are one kind of particularly effective reagents for the C_{60} dimerization.[9] In this paper, the reaction of C_{70} and aminomethylene bisphosphonate and the electrochemical properties of the resulting dimeric products are presented.

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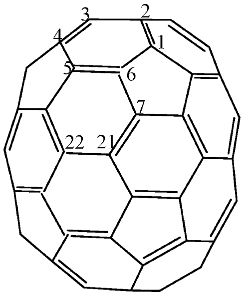

FIGURE 1. Partial numbering of some of the carbon atoms of C_{70}.

The reactions of C_{70}/C_{60} with some other reactive methylene organophosphorus reagents, such as $CH_2(PO_3Et_2)_2$ and $CH_2(CN)(PO_3Et_2)$, are reported, too.

Results and Discussion

C_{70} chemistry has always lagged behind as a result of its low symmetry (D_{5h}) as compared with that of C_{60} (I_h) and, thereby, differentiates in reactivity between various double bonds.[10−12] As shown in Figure 1, a C_{70} buckyball has four different [6,6] ring fusions (C(1)−C(2), C(5)−C(6), C(7)−C(21), and C(21)−C(22)).

Thus, the covalent fuctionalization of C_{70} gives rise to more regioisomers than does C_{60}. In this work, the reaction of C_{70} with *cyclo*-$C_6H_{11}NHCH(PO_3Et_2)_2$ was carried out in the presence of NaH in dry chlorobenzene at room temperature for several minutes to form more isomers (Scheme 1). The products **1** (57%) and **2** (1%) were obtained and fully characterized by ^1H, ^{13}C, and ^{31}P NMR, HMBC [(^1H-detected) heteronuclear multiple-bond correlation], HMQC [(^1H-detected) heteronuclear multiple-quantum coherence], IR, MS, and UV−vis spectra.

Spectroscopic data of compounds **1** and **2** are similar. The [5,6]-opened addition pattern for **1** and **2** could be eliminated by the number of sp^3 carbon signals in the ^{13}C NMR spectra. Further evidence was obtained from the two-dimensional (2D) NMR. The HMQC spectra of **1** and **2** showed that hydrogen atoms linked directly to the fullerene carbons. Both the ^{13}C NMR spectra of **1** and the ^{13}C NMR spectra of **2** gave 37 signals at $\delta = 130-160$ ppm for sp^2 hybridized carbon atoms of the C_{70} skeleton, being consistent with a plane of symmetry. All these demonstrate that the additions do not occur at C(7)−C(21) and C(21)−C(22) bonds (Figure 1). Additionally, the chemical shifts of the proton signals of **1** and **2**, connected directly to C_{70} cores, are both around 5.20 ppm. Therefore, we can infer that the protons are added to the polar carbons (carbon number 2 in Figure 1) according to the previously reported results of Meier et al.,[13−15] and the absorption spectra of **1** and **2** confirmed the position of the protons.[16] The HMBC spectrum of **1** showed that the quaternary carbon resonance (bridged carbon, $\delta = 5.14$ ppm) strongly correlates to the protons directly linked to C_{70}, while the correlation is weak for **2**. On the basis of these results, we proposed that the structure of the major isomer **1** is a 1,2 addition (C(1)−C(2) isomer), while the structure of the minor isomer **2** is a 1,4 addition (C(2)−C(5) isomer). Notably, the low yield of **2** (1%) was probably due to the high heat value of forming the [5,6] double bond (C(1)−C(6)) in the 1,4 addition product (8.5 kcal/mol for each such double bond).[17]

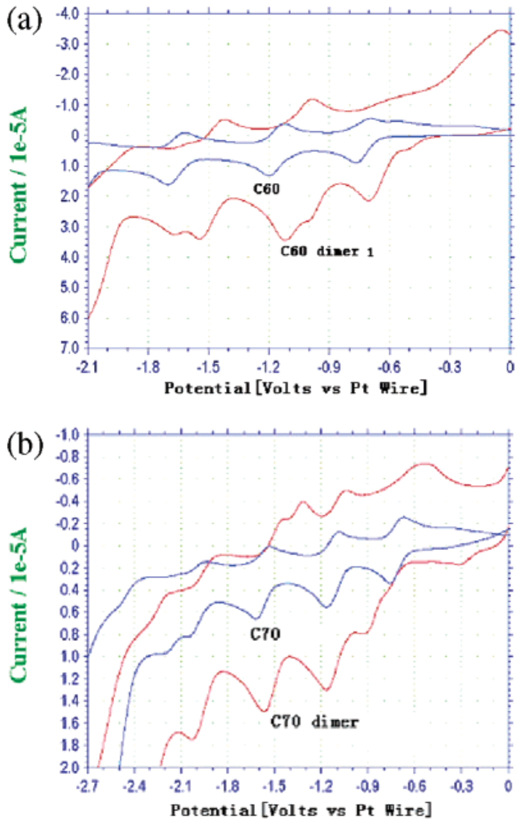

FIGURE 2. CV of (a) C_{60} and the C_{60} dimer ($HC_{61}-CR_2-C_{61}H$ (R = PO_3Et_2); (b) C_{70} and the C_{70} dimer (isomer **1**) in 0.1 M $TBAPF_6$/4:1 toluene/acetonitrile, using a scan rate of 100 mV/s at room temperature. Glass-carbon working electrode, Pt disk (2 mm diameter) reference electrode, and Pt wire counter electrode.

A cyclic voltammetry (CV) study was also used to confirm the structure. As shown clearly from Figure 2a, the CV of $HC_{60}-CR_2-C_{60}H$ (R = PO_3Et_2) gave superimposable redox processes in most of the spectrum parts, with three closely spaced split quasi-reversible one-electron redox processes within the solvent windows of $E_1 = -507$ mV, $E_2 = -697$ mV, $E_3 = -997$ mV, $E_4 = -1115$ mV, $E_5 = -1537$ mV, and $E_6 = -1667$ mV. For two fullerene cores, the peak currents were almost twice those of the parent fullerene under the same concentration. This suggests that the product does contain two molecular fullerenes. The closely spaced waves in the CV spectra indicate clearly that our systems do not behave totally independent of each other but consist of weakly interacting electrophores.[18] The observed general tendency of the reduction peaks to shifting in a cathodic

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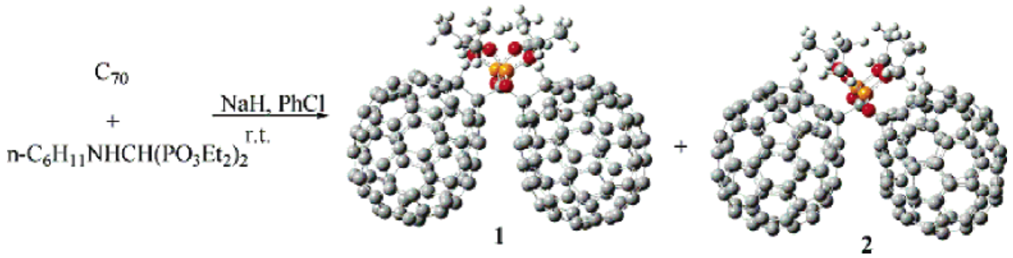
SCHEME 1. Reaction of C_{70} with *cyclo*-$C_6H_{11}NHCH(PO_3Et_2)_2$ (Red, Oxygen; Brown, Phosphor)



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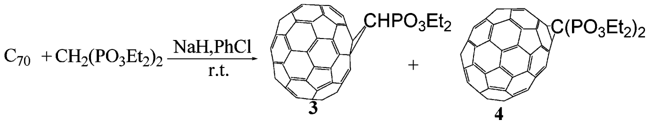

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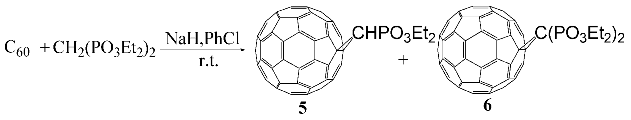

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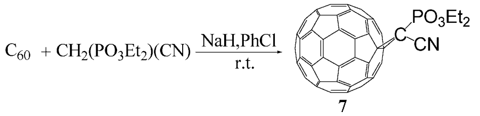
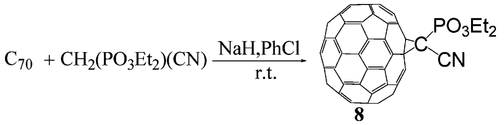


SCHEME 5



direction is attributed to the electronic effect of the PO_3Et_2 group, which overcompensates for the effect of saturating a fullerene double bond. For the parent C_{70} and isomer **1** (Figure 2b), the CV spectra are more complex than Figure 2a, with a subtle peak slit in the oxidation and reduction peaks. Similar to the C_{60} and its dimer, the double peaks of C_{70} under the same concentration show that **1** consists of two fullerene cages.

The reaction of other alkylaminomethylene bisphosphonates, that is, $(CH_3)_2NHCH(PO_3Et_2)_2$,[19] with fullerene in the presence of sodium hydride, yield the same dimer products.

These results initiated our interest in investigating the fullerene reaction with some other non-α-substituted bisphosphonates. Interestingly, treating $CH_2(PO_3Et_2)_2$ with C_{70} in the presence of NaH produced compounds **3** (45%) and **4**[20] (31%), rather than the dimer (Scheme 2). Structures of the products were fully assigned with ^1H, ^{13}C, and ^{31}P NMR, UV−vis, IR, and HRMS spectroscopy. The ^{13}C NMR spectrum of **3** displays 71 signals of sp^2 carbons and two nonequivalent sp^3 hybridized carbons of the fullerene core, indicating that **3** should be functionalized at the C(7)−C(21) bond.[10−12,21] It is important that these products have been formed for the first time in the absence of bromine or iodine under common Bingel reaction conditions.

Similarly, the reaction of C_{60} and $CH_2(PO_3Et_2)_2$ also yielded products **5** [22] and **6**[7,22] (Scheme 3). It was found that yields of the products depended heavily on the reaction time. For example, both the conversions and yields were best obtained by treating the reaction mixture for 6 min (Figure 3).

The reaction could be extended to other phosphonates. For example, $CH_2(PO_3Et_2)(CN)$ with C_{60} in the presence of NaH produced **7** (Scheme 4), while $CH_2(PO_3Et_2)(CN)$ with C_{70} produced **8** in the absence of I_2 in good yields (Scheme 5). The number of ^{13}C NMR signals (some sp^2 signals are overlapped by ODCB-d_4) indicated that compound **8** has C_1 symmetry and is functionalized at the C(7)−C(21) bond. Additionally, the UV−vis spectrum of **8** also confirmed the conclusion.

Unlike common Bingel reactions, which are an anionic addition process, the fullerene reactions may involve a radical mechanism with cycloalkylaminomethylenebisphosphonates, as they could be inhibited by the presence of hydroquinone. This was further confirmed by ESR measurements of the products (Figure 4a). The ESR signals are typical of a single ^{14}N hyperfine splitting ($a_N = 0.8$ G, $a_P = 2.0$ G, and $a_H = 0.8$ G), with a partly superimposable doublet of three sharp lines (due to the coupling with ^1H) and a triplet of three lines (due to the coupling with ^{31}P). The signal intensity decreased rapidly with the reaction time. *cyclo*-$C_6H_{11}-NH_2$, formed during the reaction of C_{70}, and *cyclo*-C_6H_{11}-aminomethylenebisphosphonate was also detected by GC-MS.

Similarly, the reaction of the C_{60} with $CH_2(PO_3Et_2)_2$ could be inhibited by the presence of hydroquinone, too. Additionally, the radical signals are also detected by ESR measurement (Figure 4b). As seen from Figure 4b, one set of the radical signals belongs to the presursor of $C_{60}>CH(PO_3Et_2)$ (two sets of 1:1 peaks), and the other is the radical intermediate of $C_{60}>C(PO_3Et_2)_2$ (two sets of 1:2:1 peaks). Most likely, the radical addition of $^{\bullet}CH(PO_3Et_2)_2$, generated by a single electron transfer from $^{-}CH(PO_3Et_2)_2$ onto C_{60}, gives the substituted C_{60} radical, which, on one hand, cyclizes to form **3** after hydrogen elimination and produces **4** after diethyl phosphonate radical elimination.

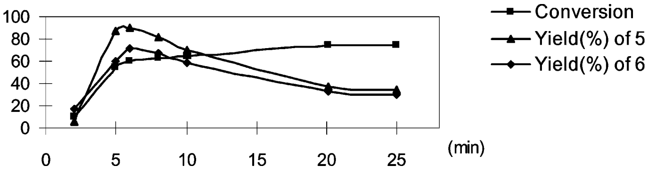


FIGURE 3. Reaction of C_{60} and $CH_2(PO_3Et_2)_2$ in the presence of NaH in PhCl. Yields were based on the consumed C_{60}.

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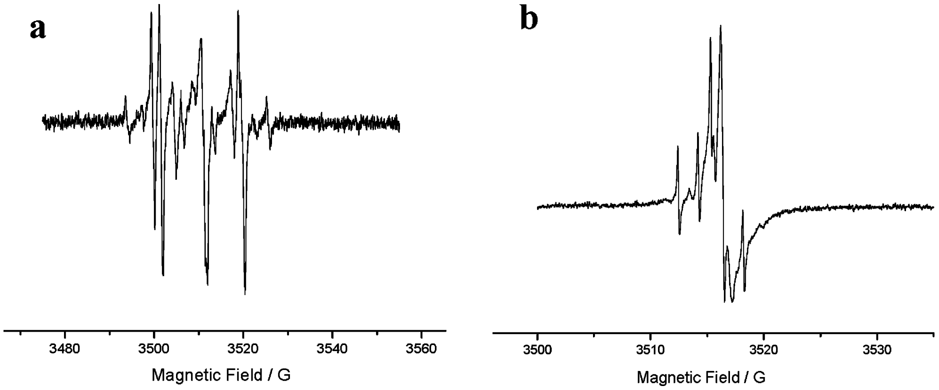

FIGURE 4. ESR spectrum of the (a) intermediate in the C_{70} dimeric reaction (5.9 mol/L C_{70} and 10 equiv *cyclo*-$C_6H_{11}NHCH(PO_3Et_2)_2$) and (b) radicals in the solution of 4.6 mol/L C_{60} and 10 equiv $CH_2(PO_3Et_2)_2$ in chlorobenzene at room temperature.

Conclusion

In summary, we have successfully developed the dimerization of C_{70}. The weak electronic interactions between the two fullerene cages were demonstrated by electrochemical studies. And for the first time, we demonstrated that the fullerenes react in some other reactions of methylene organophosphorus in the absence of bromine or iodine. ESR studies show that the reactions might involve a radical mechanism.

Experimental Section

Synthesis of 1 and 2. To a solution of C_{70} (20 mg, 0.024 mmol) and *cyclo*-$C_6H_{11}NHCH(PO_3Et_2)_2$ (183 mg, 0.476 mmol) in dry chlorobenzene (4 mL) at room temperature was added NaH (0.3 g). After several minutes (detected with TLC, usually 1 min), the reaction mixture was quenched with drops of brine, and the organic phase was poured onto a silica gel column and eluted with chlorobenzene/acetone (100:0.7; **1** as the first fraction and **2** as the third fraction). Compounds **1** and **2** were obtained as a brownish solid with a yield of 57 and 1%, respectively (based on consumed C_{70}). Other isomers were also detected, but they cannot be fully characterized due to low yield and low solubility. Spectral data of **1**:^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63 (t, 12H, J = 7.1 Hz, OCH_2CH_3), 4.64 (m, 8H, OCH_2CH_3), 5.14 (s, H, $C_{60}-H$), 5.22 (s, H, $C_{60}-H$). ^{31}P NMR (160 MHz, $CDCl_3$) δ 20.08 (m, 2P). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.92 (d, $^3J_{P-C} = 5.4$ Hz, OCH_2CH_3), 48.67 (sp^3 C of C_{60}, bonded to hydrogen), 55.45 (the bridge carbon bonded to the two phosphorus atoms), 57.05 (sp^3 C of C_{60}, bonded to the carbon bridge), 65.09 (d, $^2J_{P-C} = 7.4$ Hz, OCH_2CH_3), 131.25, 131.38, 131.44, 134.04, 134.58, 137.16, 139.35, 139.46, 140,33, 140.98, 141.03, 142.71, 142.88, 142.99, 143.24, 146.07, 146.46, 146.79, 147.02, 147.30, 147.41, 147.46, 148.89, 148.93, 148.95, 149,02, 149.74, 149.77, 149.91, 150.70, 150.91, 151.40, 151.52, 151.56, 151.62, 155.35, 155.42, 156.66. ESI *m/z*: 1966 $[M - 2]^+$. UV−vis (CH_2Cl_2) λ_{max}, nm: absorption peak, 237, 395, 451; absorption valley, 371, 423. Anal. Calcd for $C_{149}H_{22}P_2O_6{\cdot}4H_2O$: C, 87.65; H, 1.48; N, 0. Found: C, 87.65; H, 1.69; N, 0. Spectral data of **2**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.63 (t, 12H, J = 7.0 Hz, OCH_2CH_3), 4.64 (m, 8H, OCH_2CH_3), 5.19 (s, H, C60−H), 5.25 (s, H, C60−H). ^{31}P NMR (160 MHz, $CDCl_3$) δ 20.47 (m, 2P). ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.89 (d, $^3J_{P-C} = 5.5$ Hz, OCH_2CH_3), 48.29 (sp^3 C of C_{60}, bonded to hydrogen), 57.90 (the bridge carbon bonded to the two phosphorus atoms), 57.64 (sp^3 C of C_{60}, bonded to the carbon bridge), 65.03 (q, $^2J_{P-C} = 3.5$ Hz, OCH_2CH_3), 132.08, 132,79, 133.90, 134.21, 134.69, 137.39, 138.00,138.60, 139.36, 140.56, 141.00, 141.14, 141.23, 142.03, 143.74, 143.93, 144.09, 146.96, 147.15, 147.46, 148.48, 148,56, 149.65, 149.77, 150.15, 150.51, 151.17, 151.41, 152.33, 154.71, 154.77, 156.20, 156.73, 157.61, 158.98. ESI *m/z*: 1966 $[M - 2]^+$. UV−vis (CH_2Cl_2) λ_{max}, nm: absorption peak, 237, 395, 423, 461; absorption valley, 371, 425. Anal. Calcd for $C_{149}H_{22}P_2O_6{\cdot}5H_2O$: C, 86.88; H, 1.57; N, 0. Found: C, 86.33; H, 1.38; N, 0.

Synthesis of 3 and 4. To a solution of C_{70} (20 mg, 0.024 mmol) and tetraethylmethylenediphosphonate ($CH_2(PO_3Et_2)_2$; 6 μL, 0.024 mmol) in dry chlorobenzene (10 mL) at room temperature was added NaH (0.25 g). After several minutes (detected with TLC), the reaction mixture was quenched with drops of brine, and the organic phase was poured onto a silica gel column and eluted with chlorobenzene/acetone (20:1). The first and second vandyke brown fractions containing the products **3** and **4**, respectively, were collected. Spectral data of **3**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.44 (dm, 6H, J = 7.2 Hz, OCH_2CH_3), 2.85 (d, 1H, J = 4.9 Hz, $C_{70}{>}CHPO_3Et_2$), 4.49 (dm, 4H, J = 7.2 Hz, OCH_2CH_3). ^{31}P NMR (160 MHz, $CDCl_3$) δ 17.31 (m, 1P). ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.74 (m, $^3J_{P-C} = 5.8$ Hz, OCH_2CH_3), 29.68 (d, $^1J_{P-C} = 185.2$ Hz, $C_{70}{>}CHPO_3Et_2$), 62.06 (d, $^2J_{P-C} = 4.89$ Hz, sp^3 carbon atom of C_{70}), 63.06 (d, $^2J_{P-C} = 4.96$ Hz, sp^3 carbon atom of C_{70}), 63.56 (m, $^2J_{P-C} = 6.2$ Hz, OCH_2CH_3), 130.76, 130.79, 130.84, 130.85, 130.90, 131.77, 131.90, 132.73, 132.77, 133.73, 133.89, 137.26, 137.29, 138.81, 139.97, 140.23, 141.87, 141.96, 142.04, 142.64, 142.69, 143.11, 143.25, 143.31, 143.42, 143.63, 143.86, 143.87, 144.01, 144.24, 145.31, 145.92, 146.00, 146.40, 146.61, 146.67, 146.89, 146.96, 147.32, 147.40, 147.56, 147.65, 147.70, 148.34, 148.40, 148.41, 148.43, 148.47, 148.57, 148.61, 148.63, 148.70, 148.71, 149.04, 149.08, 149.26, 149.31, 149.33, 149.35, 149.42, 150.59, 150.62, 150.68, 151.02, 151.18, 151.20, 151.47, 151.61, 152.03, 155.27, 155.95. UV−vis (CH_2Cl_2) λ_{max}, nm: 232, 353, 371, 457. IR (KBr): ν 2963, 1429, 1261, 1120, 1039, 1021, 848, 801, 728, 699, 670, 642, 573, 532, 484, 452 cm^{-1}. HPLC: 94.4% pure; $t_R = 6.4$ min; eluted with hexane/dimethyl carbinol (7:3); column, 4.6 × 250 mm. FT-MALDI *m/z*: 991 $[MH^+]$. HRMS (FT-MALDI) *m/z* calcd for $C_{75}H_{12}PO_3$, 991.0519; found, 991.0526. Spectral data of **4**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.46 (t, 6H, J = 6.9 Hz, OCH_2CH_3), 1.59 (t, 6H, J = 6.9 Hz, OCH_2CH_3), 4.40 (m, 4H, J = 8.1 Hz, OCH_2CH_3), 4.52 (m, 4H, J = 8.1 Hz, OCH_2CH_3). ^{31}P NMR (160 MHz, $CDCl_3$) δ 15.09 (m, 2P). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.69 (dt, OCH_2CH_3), 63.99 (dt, OCH_2CH_3, sp^3 carbon atoms of C_{70} are overlapped), 130.85, 131.11, 131.16, 133.24, 133.53, 137.38, 141.03, 142.79, 142.87, 143.41, 143.71, 143.75, 143.79, 143.91, 143.95, 144.51, 145.55, 146.05, 146.17, 146.64, 146.85, 146.98, 147.19, 147.70, 148.48, 148.60, 148.78, 149.10, 149.15, 149.30, 149.43, 150.67, 150.71, 150.85, 151.24, 151.36, 155.49. UV−vis (CH_2Cl_2) λ_{max}, nm: 227, 350, 407, 460. IR (KBr): ν 2958, 2924, 2853, 1429, 1261, 1095, 1021, 971, 797, 729, 664, 579, 531 cm^{-1}. FT-MALDI *m/z*: 1127 $[MH^+]$, 1149 $[M + Na]^+$. HRMS (FT-MALDI) *m/z* calcd for $C_{79}H_{21}P_2O_6$, 1127.0784; found, 1127.0791.

Synthesis of 5 and 6. To a solution of C_{60} (20 mg, 0.028 mmol) and tetraethylmethylenediphosphonate ($CH_2(PO_3Et_2)_2$; 7 μL, 0.028 mmol) in dry chlorobenzene (10 mL) at room temperature was added NaH (0.25 g). After several minutes (detected with TLC, usually 7 min), the reaction mixture was quenched with drops of brine, and the organic phase was poured onto a silica gel column and eluted with chlorobenzene/acetone (20:1). The first and second vandyke brown fractions containing the products **5** and **6**, respectively, were collected. Spectral data of **5**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.53 (t, 6H, $J = 7.2$ Hz, OCH_2CH_3), 4.21 (d, 1H, $J =$ 4.8 Hz, $C_{60}{>}CHPO_3Et_2$), 4.49 (quint, 4H, $J = 7.2$ Hz, OCH_2CH_3). ^{31}P NMR (160 MHz, $CDCl_3$) δ 16.57 (m, 1P). ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.74 (t, $^3J_{P-C} = 5.8$ Hz, OCH_2CH_3), 32.23 (d, $^1J_{P-C} =$ 184.4 Hz, $C_{60}{>}CHPO_3Et_2$), 63.48 (d, $^2J_{P-C} = 6.2$ Hz, OCH_2CH_3), 69.01 (d, $^2J_{P-C} = 4.9$ Hz, two sp^3 carbon atoms of C_{60}), 136.15, 140.52, 140.89, 141.09, 142.11, 142.13, 142.18, 142.24, 142.47, 142.82, 142.99, 143.04, 143.13, 143.33, 143.77, 144.00, 144.44, 144.60, 144.65, 144.72, 144.80, 145.16, 145.22, 145.29, 145.31, 145.65, 146.46, 146.50, 146.54, 149.34, 149.40. UV−vis (CH_2Cl_2) λ_{max}, nm: 243, 325, 427. HPLC: 98.1% pure; $t_R = 6.3$ min; eluted with hexane/dimethyl carbinol (7:3); column, 4.6 × 250 mm. MALDI-TOF *m*/*z*: 871 [M$^+$], 893 [M + Na]$^+$. HRMS (MALDI-TOF) *m*/*z* calcd for $C_{65}H_{11}PO_3$ (MH$^+$), 871.0519; found, 871.0524. Spectral data of **6**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.53 (t, 12H, J = 7.2 Hz, OCH_2CH_3), 4.47 (m, 8H, OCH_2CH_3). ^{31}P NMR (160 MHz, $CDCl_3$) δ 14.89 (m, 2P). ^{13}C NMR (75 MHz, ODCB-d_4) δ 16.60 (t, $^3J_{P-C} = 2.98$ Hz, OCH_2CH_3), 63.90 (t, $^2J_{P-C} = 3.15$ Hz, OCH_2CH_3), 140.36, 140.99, 142.26, 142.37, 142.94, 143.03, 143.09, 144.08, 144.67, 144.72, 144.91, 144.97, 145.09, 145.19, 145.35, 146.03, 146.09, 146.16. UV−vis (CH_2Cl_2) λ_{max}, nm: 228, 255, 324, 434. MALDI-TOF *m*/*z*: 1029 [M + Na]$^+$.

Synthesis of 7. To a solution of C_{60} (20 mg, 0.028 mmol) and $CHCN(PO_3Et_2)$ (5 mg, 0.028 mmol) in dry chlorobenzene (10 mL) at room temperature was added NaH (0.25 g) to give out H_2 and yield a dark brown solution. The reaction mixture was stirred for 4 h, poured onto a silica gel column, and eluted with chlorobenzene/acetone (20:1). The first brown band containing **7** was collected (4 mg, 16.1%). Spectral data of **7**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.64 (t, 6H, $J = 7.2$ Hz, OCH_2CH_3), 4.61 (m, 4H, $J = 7.2$ Hz, OCH_2CH_3). ^{31}P NMR (160 MHz, $CDCl_3$) δ 8.74 (m, 1P). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.65 (d, OCH_2CH_3), 65.46 (d, OCH_2CH_3), 67.95 (two sp^3 carbon atoms of C_{60}), 67.97 (bridge carbon), 113 ($-CN$), 130.88, 138.76, 141.13, 141.25, 141.74, 142.14, 142.20, 142.26, 142.29, 142.96, 143.04, 143.07, 143.09, 143.13, 143.15, 143.20, 143.36, 143.99, 144.16, 144.42, 144.56, 144.58, 144.63, 144.72, 144.84, 144.93, 145.03, 145.05, 145.29, 145.34, 145.41, 145.51, 145.57, 145.63. UV−vis (CH_2Cl_2) λ_{max}, nm: 324, 425, 487. IR (KBr): ν 2921, 1428, 1275, 1185, 1160, 1043, 1017, 856, 832, 740, 703, 588, 571, 539, 526, 482 cm^{-1}. FT-MALDI *m*/*z*: 895 [M$^+$], 918 [M + Na]$^+$. HRMS (FT-MALDI) *m*/*z* calcd for $C_{66}H_{10}PO_3N$, 895.0393; found, 895.0364.

Synthesis of 8. To a solution of C_{70} (20 mg, 0.024 mmol) and $CHCN(PO_3Et_2)$ (4.3 mg, 0.024 mmol) in dry chlorobenzene (10 mL) at room temperature was added NaH (0.25 g) to yield a dark brown solution and to give out H_2 immediately. After stirring for 4 h, the reaction mixture was poured onto a silica gel column and eluted with chlorobenzene/acetone (20:1) for separation. The first vandyke brown band containing **8** was collected (3 mg, 10.6%). Spectral data of **8**: ^{1}H NMR (300 MHz, C_6D_6) δ 1.56 (t, 3H, $J =$ 6.9 Hz, OCH_2CH_3), 1.73 (t, 3H, $J = 6.9$ Hz, OCH_2CH_3), 4.51 (m, 2H, $J = 6.9$ Hz, OCH_2CH_3), 4.69 (m, 2H, $J = 6.9$ Hz, OCH_2CH_3). ^{31}P NMR (160 MHz, $CDCl_3$) δ 9.52 (m, 1P). ^{13}C NMR (100 MHz, ODCB-d_4) δ 17.17 (dd, OCH_2CH_3), 65.92, 65.83 (dd, OCH_2CH_3), 65.18, 114.13 ($-CN$), 140.45, 140.55, 141.55, 141.96, 141.99, 143.15, 143.31, 143.40, 143.98, 144.03, 144.06, 144.10, 144.22, 144.24, 144.32, 144.99, 145.51, 145.87, 146.16, 146.20, 146.51, 146.55, 146.84, 147.25, 147.28, 147.49, 147.54, 147.62, 147.80, 147.83, 148.48, 148.79, 149.08, 149.15, 149.31, 149.42, 149.48, 149.53, 149.66, 149.74, 150.84, 150.88, 151.22, 151.36, 151.44, 151.59, 154.95, 155.69. UV−vis (CH_2Cl_2) λ_{max}, nm: 237, 352, 460. IR (KBr) ν: 2920, 1427, 1272, 1160, 1132, 796, 742, 672, 643, 580, 533, 458 cm^{-1}. FT-MALDI *m*/*z*: 1015 [M]$^+$. HRMS (FT-MALDI) *m*/*z* calcd for $C_{76}H_{10}PO_3N$, 1015.0393; found, 1015.0380.

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Supporting Information Available: Characterization data (^{1}H, ^{31}P, ^{13}C, and 2D NMR spectra) for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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