JOC Notes

Fullerene Derivatives Incorporating Phosphoramidous Ylide and Phosphoramidate: Synthesis and Property

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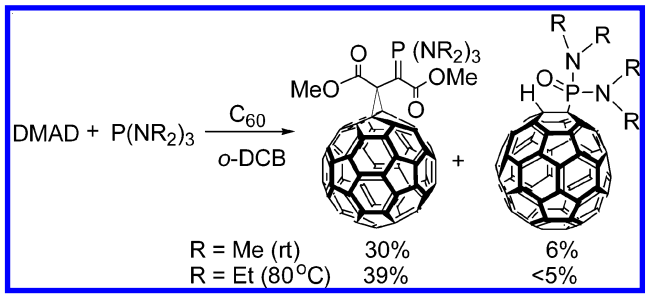
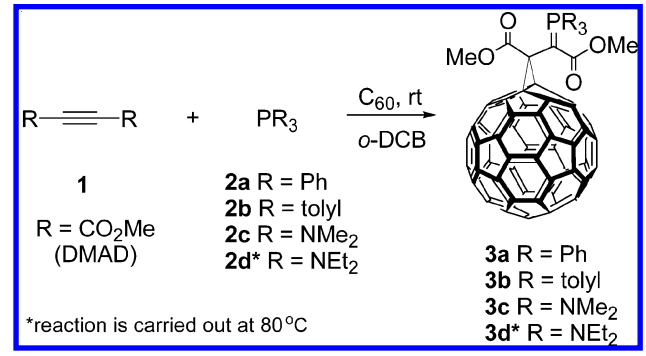


The reaction of dimethyl acetylenedicarboxylate (DMAD) with C_{60} in the presence of hexamethylphosphorous triamide (HMPT) or hexaethylphosphorus triamide (HEPT) results in fullerene derivatives incorporating HMPT or HEPT ylides. The ylide derivatives exhibit unusual electronic absorptions in the visible region (435−660 nm), likely due to the presence of the ylide moiety. Electrochemical studies revealed that the first reductive potential of these compounds was more negative relative to those of both C_{60} (ΔE = 130 mV) and a simple Bingel adduct (ΔE = 90 mV). A phosphoramidate side product, which resulted from the addition of HMPT or HEPT to C_{60} followed by hydrolysis, exhibited a featureless absorption spectrum in the visible region and a more negative first reductive potential (ΔE = 70 mV) relative to that of C_{60}.

Fullerene derivatives display extensive applications.[1] Although fullerene derivatives featuring phosphorus moieties have potentially interesting biological applications,[2] research in this field has been restricted by the limited availability of these compounds[3] and the absence of any such derivatives that are soluble in water.[4] We and others have reported the functionalization of C_{60} with phosphorus moieties via cycloadditions of the electron-deficient acetylene dimethyl acetylenedicarboxylate (DMAD, **1**) with triarylphosphines (**2a**,**b**) and C_{60} stoichiometrically (Scheme 1).[5] Because water-soluble fullerene derivatives possessing several positively charged amino groups might act as nonviral gene delivery vectors,[6] we wished to explore whether the addition of hexamethylphosphorous triamide (HMPT, **2c**) moieties to fullerenes would be possible by displacing the triarylphosphines in Scheme 1 with HMPT. We suspected that the three closely assembled amino groups on the phosphorus atom would impart different activities relative to those of

SCHEME 1. Synthesis of Fullerene Derivatives Incorporating Phosphorus Ylides



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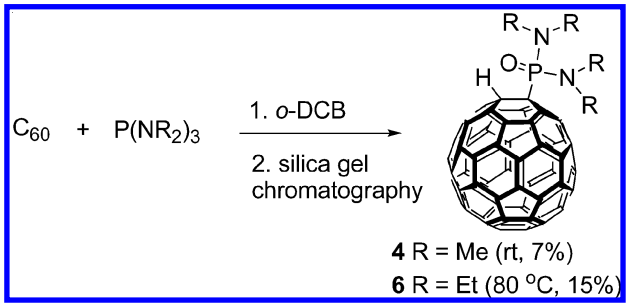
SCHEME 2. Formation of Phosphoramidates 4 and 6



previously reported gene delivery vectors featuring amino groups dispersed around the fullerene cores. In this paper, we demonstrate the incorporation of an HMPT or HEPT moiety into a [60]fullerene derivative, which we characterized using spectroscopic methods and electrochemistry.

HMPT is a nucleophilic and basic phosphine derivative[7] that is employed commonly in organic synthesis. Recently, it has also found a role in phosphine-catalyzed cycloadditions.[8] To incorporate an HMPT unit within the structure of a fullerene derivative, we employed our previously developed synthetic methods to investigate the reactivity of HMPT with DMAD and C_{60}. Our initial attempts—performing the reaction of DMAD (1.2 equiv) and C_{60} (1 equiv) in the presence of HMPT (1 equiv) in toluene or *o*-dichlorobenzene—did not give the desired product **3c**.[5] When we increased the content of HMPT to a large excess (10 equiv) with respect to C_{60}, however, we obtained derivative **3c** in modest yield. We attribute this excess demand of HMPT to possible electron transfer from HMPT to C_{60} or direct nucleophilic attack at C_{60}, thereby limiting the amount of HMPT available to undergo addition to DMAD to generate the 1,3-dipolar intermediate for subsequent addition to C_{60}. Under our optimal conditions, we obtained **3c** in isolated yields of 30−35% (84% based on recovered C_{60}). In addition to compound **3c**, we also obtained an unusual more polar byproduct **4**, which became more pronounced when greater amounts of HMPT were added and the mixture was left to react for longer periods of time. We isolated **4** in 6% yield from a large-scale reaction of C_{60} (300 mg) with **1** and **2c**. In a control experiment—treating C_{60} with 10 equiv of HMPT in the absence of **1** (Scheme 2)—we obtained **4** in 7% yield (67% based on recovered C_{60}). Thus, the formation of **4** most likely resulted from direct addition of HMPT to C_{60}, followed by hydrolysis during flash chromatography; its isolation provides evidence for the requirement of excess HMPT for the synthesis of **3c**. Extension of the studied reaction with HEPT **2d** required reaction condition carried out at higher temperature (80 °C) because HEPT exerts more steric hindrance. Products **3d** and **6** were not observed when reactions were carried out at room temperature.

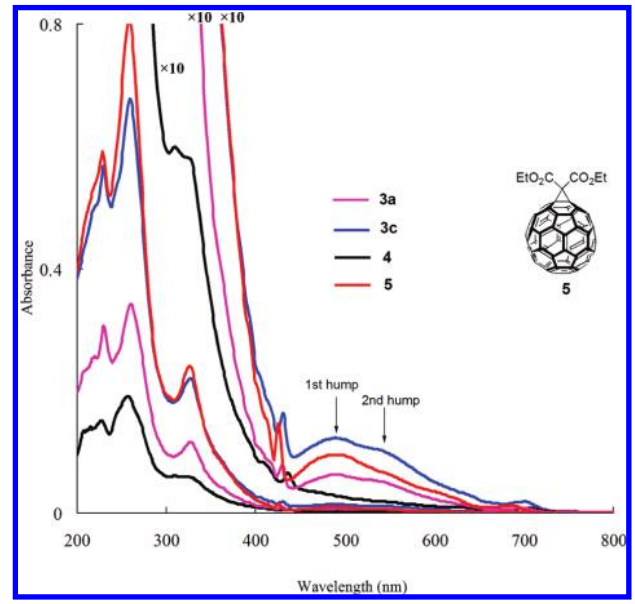


FIGURE 1. UV−vis spectra of **3a** (2.5×10^{-5} M), **3c** (5.0×10^{-5} M), **4** (4.3×10^{-5} M), and **5** (6.4×10^{-5} M) in $CHCl_3$.

We characterized the hexaalkylphosphorus-containing ylides and the phosphoramidates using ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, IR spectroscopy, and mass spectrometry (MS). For examples, the molecular ion of **3c** (*m*/*z* 1026, [M + H$^+$]) provided unequivocal evidence for its assembly from DMAD, HMPT, and C_{60} in a 1:1:1 ratio. The fullerene derivative **3c** displayed *E*/*Z* isomerism similar to that of **3a** and **3b**—namely, four signals (3.67, 3.72, 3.94, 3.95 ppm) for methoxyl protons in the ^{1}H NMR spectrum and two signals (61.68, 61.77 ppm) in the ^{31}P NMR spectrum recorded at 223 K. The presence of the *E* and *Z* isomers resulted in rather complicated ^{13}C NMR spectra, which presented averaged signals for the two isomers. The absorption peak at 1620 cm^{-1} in the IR spectrum of **3c** corresponds to an ester group connected to an α-ylidic carbon atom. Furthermore, the molecular ion in the mass spectrum of compound **4** (*m*/*z* 857, [M + H$^+$]) corresponds to the compound formed through the addition of HMPT to C_{60}, followed by the addition of a water molecule and the elimination of dimethylamine. The ^{1}H NMR spectrum of **4** reveals the presence of a doublet (J = 27 Hz) at 7.35 ppm that corresponds to an sp^3-hybridized CH unit directly attached to the fullerene cage; the ^{31}P NMR spectrum reveals only one signal at 33.86 ppm, which is close to those of common organic alkyl phosphordiamidates (ca. 31−34 ppm)[9] and phosphortriamidates (ca. 24 ppm).[10] The ^{13}C NMR spectrum reveals the signals of the two sp^3-hybridized carbon atoms of the fullerene unit at 57.53 and 70.04 ppm, the latter as a doublet ($^1J_{PC}$ = 100.9 Hz). Compounds **3d** and **6** were similarly characterized as **3c** and **4**.

Figure 1 displays the interesting features observed for the electronic absorptions of **3a**, **3c**, and **4** in the UV−vis region. The fullerene derivatives **3a** and **3c**, which contain phosphorus ylide groups, reveal a typical absorption at 430 nm, two humps

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TABLE 1. Half-Wave Reduction Potentials (V)[a] of C_{60}, 3a, 3c, 3d, 4, 5, and 6

compound	E^1	E^2	E^3	E^4
C_{60}	−1.13	−1.52	−1.98	−2.47
3a	−1.25	−1.65	−2.18	−
3c	−1.26	−1.66	−2.22	−
3d	−1.27	−1.66	−2.20	−
4[b]	−1.20	−1.57	−1.96	−2.11
5	−1.17	−1.53	−2.01	−2.46
6[b]	−1.19	−1.61	−2.00	−

[a] Versus ferrocene/ferrocenium. Conditions: ca. 0.50 mM C_{60}, **3a**, **3c**, **3d**, **4**, **5**, **6** and 0.050 mM Bu_4NPF_6 in anhydrous *o*-DCB; reference electrode: Ag/0.01 M $AgNO_3$ and 0.050 mM $(n\text{-Bu})_4NClO_4$ in anhydrous acetonitrile; working electrode: glassy carbon; auxiliary electrode: Pt; scanning rate: 50 mV s^{-1}. [b] Potential obtained from DPV traces; see Supporting Information for details.

centered at 485 and 545 nm, and a small absorption at ca. 700 nm; in contrast, **4** displays an absorption at 436 nm and an absorption decay starting at 445 nm. The two-hump absorptions are not observed for **4** because of the absence of a cyclopropyl moiety. The UV−vis spectrum of **5**, a typical methanofullerene incorporating a cyclopropyl group,[11] does not, however, feature the clearer "second hump" displayed in the spectra of **3a** and **3c**.[12] This difference is likely due to the presence of the ylide moieties in **3a** and **3c**.

We used cyclic voltammetry (CV), differential pulse voltammetry (DPV), and Osteryoung square wave voltammetry (OSWV) to examine the redox properties of **3a**, **3c**, **3d**, **4**, and **6**; Table 1 lists their half-wave reduction potentials relative to ferrocene/ferrocenium.[13] Each of these derivatives exhibited a first reductive potential that was more negative than that of C_{60} under the same conditions (Figure 2). We observed three similar reversible waves for compounds **3a**, **3c**, and **3d**, even though they featured different moieties on their phosphorus atoms. The presence of the ylide units in **3a**, **3c**, and **3d** made it slightly more difficult (by, 80, 90 and 100 mV, respectively) to reduce them relative to the methanofullerene **5**. The redox properties of **4** and **6** are interesting because their first reductions appear to be irreversible. Their first cathodic peaks (−1.25 and −1.29 V, respectively) correspond to the formation of fullerene radicals $RC_{60}^{\bullet}$; the second peaks (−1.65 and −1.72 V, respectively) correspond to the formation of fullerene anions RC_{60}^{-} [where R is $PO(NR_2)_2$]; their anodic peaks at −0.57 and −0.54 V, respectively, suggest the oxidation of fullerene monoanions to monoradicals, similar to the anodic peaks observed in fullerene dimers.[14] A continuous CV scan of **4** ranging from 0 to −2.00 V at a rate of 20 mV s^{-1} for 50 cycles revealed that the redox waves in the first cycle were similar to those of the fiftieth cycle.

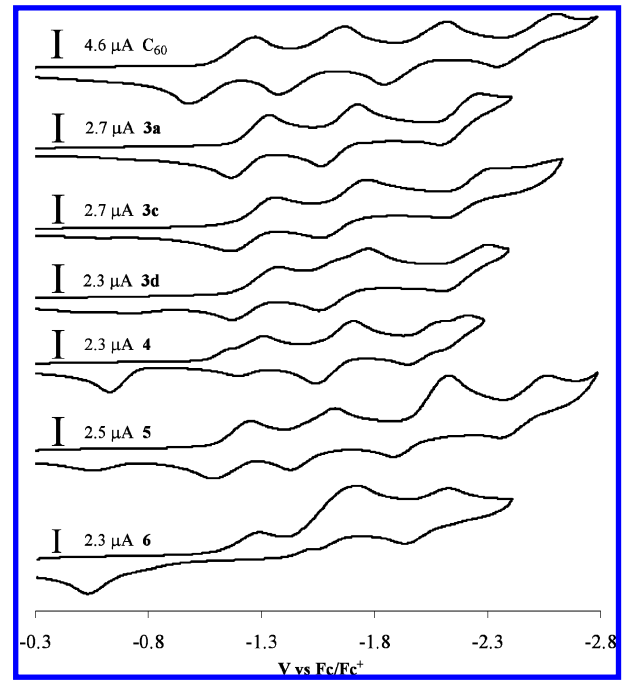

FIGURE 2. CV traces of C_{60} (0.51 mM), **3a** (0.50 mM), **3c** (0.45 mM), **3d** (0.50 mM), **4** (0.50 mM), **5** (0.49 mM), and **6** (0.50 mM) in anhydrous *o*-DCB. Scanning rate: 50 mV s^{-1}.

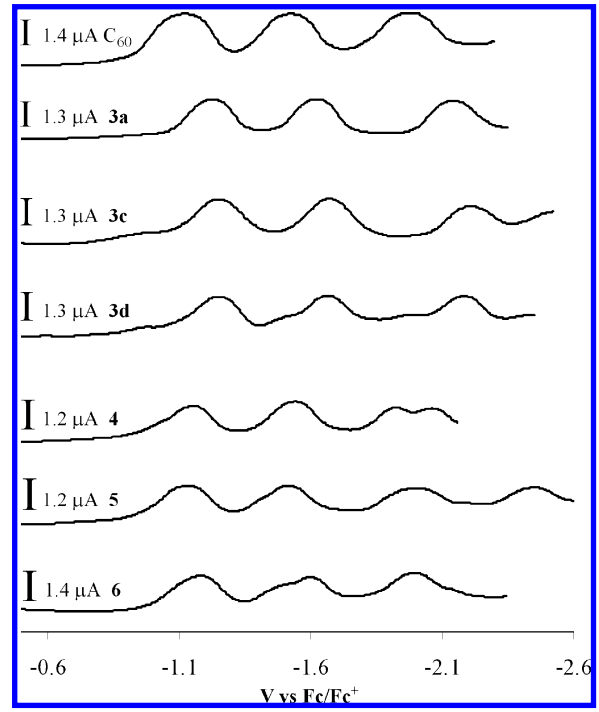

FIGURE 3. OSWV traces of C_{60}, **3a**, **3c**, **3d**, **4**, **5**, and **6**. Square amplitude: 25 mV; frequency: 15 Hz; step *E*: 4 mV.

The OSWV traces in Figure 3 provide unequivocal values for these reductive potentials.

In summary, the incorporation of HMPT or HEPT moiety within fullerene derivatives is possible through the reaction of DMAD with C_{60} in the presence of HMPT (or HEPT); the main derivative features a phosphorus ylide, and the side product contains a phosphoramidate group. These compounds display interesting electronic and redox properties. Progress is ongoing toward the development of nonviral gene delivery vectors using these molecules.

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Experimental Section

Phosphoramidous Ylide 3c. A solution of DMAD (9.6 mg, 0.067 mmol) in toluene (10 mL) was injected via syringe pump (addition rate: 5.0 mL h^{-1}) to a round-bottom flask containing C_{60} (0.036 g, 0.050 mmol) and HMPT (0.083 g, 0.50 mmol) in toluene (25 mL) under Ar at ambient temperature. After completing the addition, the mixture was stirred for 3 h, and then the solution was subject to flash chromatography (SiO_2). Elution with toluene led to the isolation of unreacted C_{60} (0.021 g, 58% recovery). Further elution with a mixture of hexanes, EtOAc, and CH_2Cl_2 (1:1:1) afforded a red-purple solution. After concentration, the residue was precipitated with pentane to give the ylide **3c** [0.018 g, 35% (84% based on recovered C_{60})]. Product **4** was isolated in only trace amounts from this small-scale reaction. A larger-scale reaction of C_{60} (0.300 g), HMPT (0.684 g), and DMAD (71 mg) gave **3c** (130 mg, 30%), **4** (22 mg, 6%), and unreacted C_{60} (154 mg, 51%). **3c**: R_f = 0.27 (SiO_2; hexanes/EtOAc/CH_2Cl_2, 1:1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.87 (br, 36H), 3.70 (s, 3H), 3.74 (s, 3H), 3.96 (s, 6H); ^{31}P NMR ($CDCl_3$, 202 MHz) δ (ppm) 61.68, 61.77; ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 36.88 (d, $^2J_{PC}$ = 5.3 Hz), 36.94 (d, $^2J_{PC}$ = 4.9 Hz), 37.22 (d, $^2J_{PC}$ = 5.5 Hz), 37.40 (d, $^2J_{PC}$ = 5.0 Hz), 37.50 (d, $^2J_{PC}$ = 5.4 Hz), 37.96 (d, $^2J_{PC}$ = 4.5 Hz), 44.96 (d, $^1J_{PC}$ = 197 Hz), 47.19 (d, $^1J_{PC}$ = 204 Hz), 50.18 (2 O*C*H$_3$), 50.40 (d, $^2J_{PC}$ = 15.7 Hz), 51.05 (O*C*H$_3$), 51.21 (d, $^2J_{PC}$ = 16.1 Hz), 53.03 (O*C*H$_3$), 74.48, 74.99, 135.69, 136.25, 136.91, 137.46, 137.54, 137.69, 137.74, 137.95, 139.99, 140.10, 140.14, 140.20, 140.38, 140.50, 140.71, 141.24, 141.55, 141.61, 141.81, 141.87, 141.90, 142.03, 142.08, 142.18, 142.20, 142.28, 142.35, 142.38, 142.39, 142.45, 142.49, 142.51, 142.54, 142.55, 142.57, 142.61, 142.64, 142.66, 142.69, 142.72, 142.74, 142.79, 142.82, 142.97, 143.41, 143.43, 143.52, 143.56, 143.81, 143.82, 143.88, 143.92, 143.96, 144.01, 144.22, 144.24, 144.30, 144.35, 144.36, 144.42, 144.43, 144.47, 144.49, 144.53, 144.57, 144.69, 144.71, 144.73, 144.77, 144.83, 144.87, 144.90, 144.93, 144.95, 145.05, 145.08, 145.40, 145.55, 145.62, 145.90, 146.12, 146.44, 148.69, 148.73, 148.81, 148.92, 149.05, 149.29, 150.60, 151.28, 169.59 (d, $^2J_{PC}$ = 18.1 Hz), 169.71, 169.90, 170.97 (d, $^2J_{PC}$ = 22.9 Hz); FT-IR (KBr) 526, 662, 749, 1066, 1095, 1178, 1224, 1288, 1429, 1461, 1620, 1738, 2800, 2846, 2923 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (nm) [log ε (mol^{-1} cm^{-1} L)] 230 (5.06), 259 (5.13), 327 (4.65), 430 (3.58), 489 (3.45), 684 (2.60), 695 (2.60); HRMS (FAB$^+$) calcd for $C_{72}H_{25}N_3O_4P$ [M + H$^+$] 1026.1583, found 1026.1599.

Phosphoramidate 4. HMPT (0.082 g, 0.50 mmol) was added to a solution of C_{60} (0.036 g, 0.050 mmol) in *o*-DCB (4 mL) under Ar, and then the mixture was stirred for 3 h at room temperature. Column chromatography (SiO_2), eluting first with toluene to recover C_{60} (0.032 g, 88%) and then with a mixture of hexanes, EtOAc, and CH_2Cl_2 (1:1:1), provided a fraction containing the monoadduct **4** [R_f = 0.16 (SiO_2; hexanes/EtOAc/CH_2Cl_2, 1:1:1]. After evaporation of the solvent, the residue was washed with pentane to afford **4** as a solid [0.0032 g, 7% (67% based on recovered C_{60})]: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 3.27 (d, $^3J_{PH}$ = 9.3 Hz, 12H), 7.34 (d, $^3J_{PH}$ = 26.7 Hz, 1H); ^{31}P NMR (202 MHz, $CDCl_3$) δ (ppm) 33.86; ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 37.83, 57.53, 70.04 (d, $^1J_{PC}$ = 100.9 Hz), 135.19, 135.40, 139.93, 140.28, 141.31, 141.50, 141.76, 141.81, 142.38, 142.46, 143.07, 144.20, 144.43, 145.04, 145.21, 145.55, 145.99, 146.05, 146.13, 146.76, 146.91, 146.98, 147.36, 151.46, 152.43; FT-IR (KBr) 527, 678, 962, 991, 1159, 1210, 1299, 1427, 1498, 1509, 2922 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (nm) [log ε (mol^{-1} cm^{-1} L)] 208 (4.49), 211 (4.50), 215 (4.51), 218 (4.51), 228 (4.54), 257 (4.65), 310 (4.15), 436 (3.14), 459 (2.97), 461 (2.97), 463 (2.97), 465 (2.97), 703 (4.15); HRMS (FAB$^+$) calcd for $C_{64}H_{14}N_2OP$ [M + H$^+$] 857.0844, found 857.0845.

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Supporting Information Available: Synthesis of compounds **3d** and **6**; spectral data; CV and DPV data. This material is available free of charge via the Internet at http://pubs.acs.org.

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