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[3+2] Cycloaddition of Dialkyl (*E*)-Hex-2-en-4-ynedioates to [60]Fullerene by Phosphane-Promoted Tandem α(δ′)-Michael Additions

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Organophosphanes promote the [3+2] cycloaddition reactions of dialkyl (*E*)-hex-2-en-4-ynedioates and [60]fullerene, giving a series of cyclopenteno-fullerenes **3a**–**k** bearing phosphorus ylides. This cycloaddition reaction is initiated by the attack of nucleophilic phosphanes at the α(δ′)-C atom of the dialkyl (*E*)-hex-2-en-4-ynedioate, which generates a 1,3-dipolar species. These 1,3-dipoles then react with C_{60} followed by intramolecular cyclization to give cyclopenteno-fullerenes in moderate-to-good yields. In a cyclic voltmmetry study, these novel fullerenes show a larger cathodic shift in their first reduction potential relative to [6,6]phenyl-C_{61} methyl butyrate, which indicates that these new derivatives possess higher LUMO energy levels.

Introduction

Ever since the discovery that organophosphorus reagents could be used for functional group transformations, for example, Wittig and Mitsunobu reactions, reagents incorporating phosphanes have played an important role in synthetic chemistry.[1] Their application in organic chemistry has not only been limited to the simple transformation of molecular functionalities, in the past few decades their use has been extended to catalytic carbon–carbon bond-forming reactions.[2] The pioneering work of Zhang and Lu revealed that phosphanes could play a catalytic role in the construction of cyclic structures in cycloaddition chemistry.[3] To date, numerous reports have been published on the synthetic applications of organophosphanes,[4] for example, phosphanes are key reagents in the cyclization step of the total synthesis of spinosyn A.[4b] In this context, the many precursors used to generate reactive dipoles with phosphanes have been generally electron-deficient enones, allenoates, alkynoates, or conjugated dienes.[5]

We and others have previously been interested in the cycloaddition of electron-deficient acetylenes to C_{60} mediated by phosphanes.[6] The phosphane moiety can be incorporated into the molecules through a three-component assembly of DMAD, phosphane, and C_{60}. Such a methodology has also been used successfully for the functionalization of carbon nanotubes[7] and endohedral metallofullerenes.[8] Recently, we unambiguously demonstrated that phosphanes can nucleophilically attack the α(δ′)-C atom of enyne **1**,[9] as evidenced by X-ray crystal structure analysis of the lactone products.[10] This α(δ′)-attack of alkynyl carbon atoms by phosphanes suggests another possible route for the phosphane-mediated reaction of certain alkynoates. In this paper we show that five-membered-ring phosphane-containing fullerene derivatives can be isolated as stable species through the tandem α(δ′)-attack of phosphanes at ester-substituted enynes in moderate-to-good yields. The stabilities of the isolated intermediate structures are highly dependent on the electronic properties of the phosphanes and these unusual structures present interesting electrochemical properties.

Results and Discussion

We first present the optimized results of the reaction of enyne **1** with various trisubstituted phosphanes and C_{60}. The reactions of C_{60} and the carbenoid species generated from phosphanes **2a**–**i** and enynes **1a**,**b** in 1,2-dichlorobenzene gave **3a**–**k** as the major products in moderate-to-good yields (Table 1, 16–57%, 34–78% based on converted C_{60}). We observed that the electronic properties of the phosphanes significantly influence the conditions required for the reaction to proceed. For example, the reactions with phosphanes with more electron-donating groups, such as tricyclohexylphosphane (**2a**), tri-*p*-tolylphosphane (**2c**), tris(dimethylamino)phosphane (**2d**), and tris(4-methoxyphenyl)-phosphane (**2f**; entries 1, 3, 4, and 6, respectively), take place at room temperature and give good yields of **3** based on converted C_{60} (41–78%). Those with sterically more bulky substituents, such as tris(diethylamino)phosphane (**2e**; entry 5), or with electron-withdrawing groups, such as

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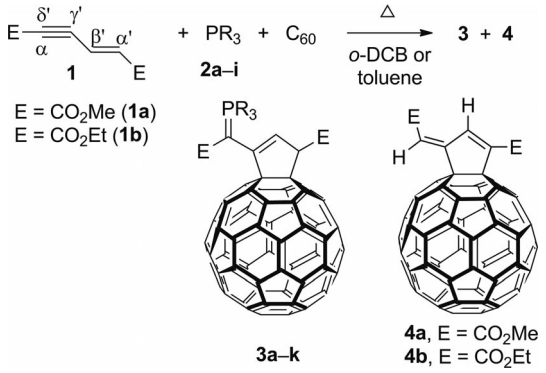
Table 1. Synthesis of **3a**–**k** through double α-Michael reactions under optimized conditions.

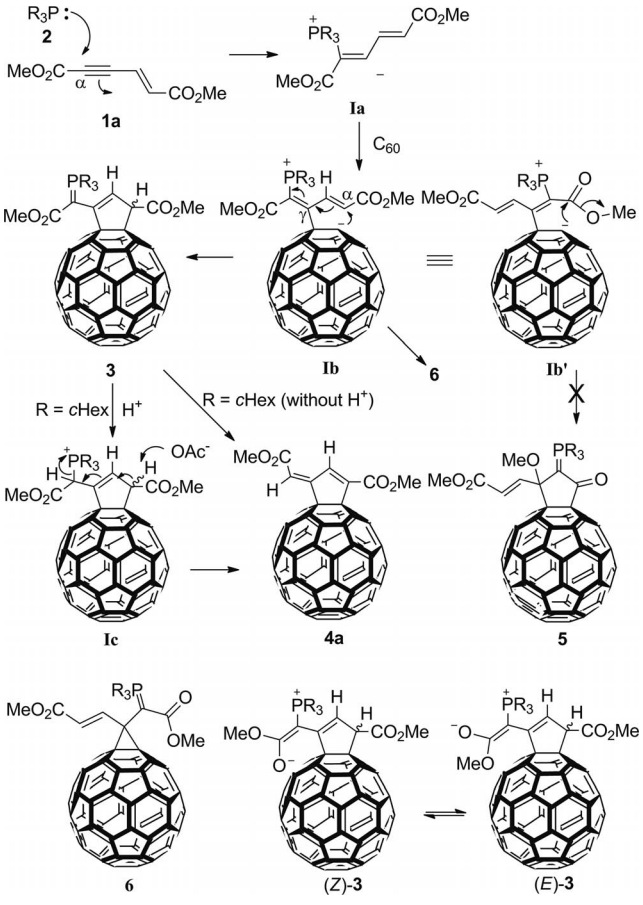


Entry	1	PR_3 (2)	T [°C]	Time [h]	Yield of 3 [%][a]	Yield of 4 [%][a]
1	1a	P(*c*Hex)$_3$ (2a)	25	4	3a; 27 (41)[b]	4a; 31 (46)
2[c]	1a	PPh_3 (2b)	50	24	3b; 52 (65)	4a; 0
3	1a	P(*p*-tolyl)$_3$ (2c)	25	6	3c; 52 (69)	4a; 0
4	1a	$P(NMe_2)_3$ (2d)	25	4	3d; 49	4a; 0
5	1a	$P(NEt_2)_3$ (2e)	110	4	3e; 33	4a; 0
6	1a	P(4-MeOPh)$_3$ (2f)	25	4	3f; 57 (78)	4a; 0
7	1a	P(4-ClPh)$_3$ (2g)	110	4	3g; 16 (64)	4a; 0
8	1a	P(4-FPh)$_3$ (2h)	140	16	3h; 19 (34)	4a; 0
9	1a	P(2-thienyl)$_3$ (2i)	80	18	3i; 24 (66)	4a; 0
10	1b	P(*p*-tolyl)$_3$ (2c)	25	6	3j; 39 (77)	4b; 0
11	1b	PPh_3 (2b)	50	12	3k;32 (68)	4b; 0

[a] Yields in parentheses are based on converted C_{60}. [b] Compound **3a** is labile and constantly mixed with **4a** upon isolation. Their yields were determined by HPLC analysis (Buckyprep column; see Supporting Information, Figure S1a). [c] A trace amount of a cyclopropano-fullerene was isolated, see the structure of the product in ref.[6b].

tris(4-chlorophenyl)phosphane (**2g**) and tris(4-fluorophenyl)phosphane (**2h**; entries 7 and 8), require higher temperatures and they produce lower isolated yields of **3** (16–33%). In particular, the poor nucleophilicity of tris(4-fluorophenyl)phosphane (**2h**) makes the reaction sluggish, as noted from its long reaction time (16 h) at 140 °C (entry 8). Heteroarylphosphane **2i** also promotes this three-component reaction, giving 24% (66% based on converted C_{60}) at 80 °C after 18 h (entry 9). Due to its bulkier and more nucleophilic nature, reactions with tricyclohexylphosphane produce not only five-membered-ring compound **3a** (27%; 41% based on converted C_{60}), but also a dephosphanated product **4a** (31%; 46% based on converted C_{60}). We did not observe the phosphane moiety in **4a**, as evidenced by its ^{1}H NMR and MS data. Note that compounds **4a**,**b** were previously isolated in the cycloaddition reaction between methyl propiolate and C_{60} catalyzed by P(*c*Hex)$_3$ in only 23% yield.[11] The stability of these derivatives with a phosphane moiety is interesting and depends on the electronic properties of the phosphanes. We note that compound **3a** is labile and decomposes easily to **4a**, likely due to the presence of the bulkier and more electron-donating nature of P(*c*Hex)$_3$. The other isolated products are quite stable because of the stabilization of the α-anion by an adjacent carbonyl group. The isolated reaction mixture of C_{60}/**3a**/**4a** can be converted into C_{60}/**4a** under reflux in toluene for 24 h (see Supporting Information, Figure S1) or with 1 equiv. of acetic acid for 6 h.

We propose that this three-component reaction occurs through tandem α(δ′)-Michael reactions. The reaction is initiated by nucleophilic attack of phosphane **2** on the α(δ′)-carbon of enyne **1a** to form a 1,3-dipolar species **Ia** (Scheme 1). Addition of **Ia** to C_{60} followed by intramolecular 5-*endo*-trig cyclization at the α-carbon of **Ib** affords product **3**. Subsequent dephosphination of **3**, possibly mediated by P(*c*Hex)$_3$, gives product **4a** (Table 1, entry 1). It is also possible that dephosphination takes place through **Ic** in the presence of proton sources. Compound **3a** could not be isolated for complete structural characterization because **3a** tends to decompose to **4a** easily under ambient conditions and thus it is constantly contaminated with **4a**. Note that the hypothetical product **5** is not formed by attack of the fullerenyl anion at the ester carbonyl carbon of **Ib**′, likely due to the higher reactivity of the α-carbon of **Ib**. A previously studied reaction, carried out at 80 °C over a short period of time (3 h), gave cyclopropano-fullerene adduct **6** in a low chemical yield by attack of the fullerenyl anion at the γ carbon.[6b] The present optimized conditions provided cyclopenteno-fullerenes **3** as the major products with only traces or undetectable amounts of **6**. We found that **6** cannot be converted into **3** under thermal reaction



Scheme 1. Proposed mechanism for the formation of **3** and **4a**.

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conditions and that they are not interconvertible. This suggests that **3** and **6** are formed through independent pathways and that **3** is preferentially formed under the conditions of the study.

The three-component compounds **3a**–**k** were structurally characterized by MS, IR and ^{1}H, ^{13}C, ^{31}P, 2D HMQC, and 2D HMBC NMR spectroscopic methods. The mass spectral data of these isolated compounds clearly demonstrate a combination of the three starting reactants. For example, the HRMS (FAB$^+$) spectrum of **3d** exhibits *m*/*z* = 1052.1741 [M + H]$^+$, which corresponds to the sum of the molecular mass of hexamethylphosphorus triamide (HMPT), enyne **1a**, and C_{60}. With the exception of **3d**, all the isolated compounds exhibit relatively slow *E*/*Z* isomerism at room temperature. Two sets of signals corresponding to (*Z*)- and (*E*)-**3** in a 1:2 ratio are observed in the ^{1}H, ^{13}C, and ^{31}P NMR spectra; (*E*)-**3** is the dominant isomer because of the proximity of the charged O and P atoms. Two carbonyl stretching bands at 1615 and 1738 cm^{-1}, which correspond to the α-ylidic ester and normal ester groups, respectively, are observed in the IR spectra. The two signals in the ^{31}P NMR spectrum at δ = 57.8 and 58.8 ppm are indicative of *E*/*Z* isomerism.[6] Due to the presence of the *E* and *Z* isomers, signals between 135 and 155 ppm, which correspond to the sp^2 carbon atoms in the fullerene, overlap and exhibit complicated peak patterns in the ^{13}C NMR spectra. Despite the complexity observed in the ^{13}C NMR spectra, correlations between protons and some carbons can be observed. We selected compound **3d** to present the ^{1}H–^{13}C NMR correlation data because it exhibits faster *E*/*Z* isomerism at room temperature. Clear signals corresponding to the averaged spectra of the *E* and *Z* isomers were obtained. As shown in Figure 1, the HMBC spectrum of **3d** shows clear correlations of H_a (δ = 6.25 ppm) with carbons that are two (C2 and C5) or three (C3 and C4) bonds away. However, another proton, H_b, shows no correlations with C1, C3, C4, and C5, also at a distance of two or three bonds, due to weak coupling. Note that the signal of H_b is broad and its integration is nearly the same as that of H_a. We also find that the broadened H_b signal corresponds to the sp^3 C–H at δ = 62.24 ppm (C2) by 2D gradient HMQC analysis (Figure S12), rather than a proton on a heteroatom. This is evidence that H_b is a methine proton in **3d**. In fact, we observed the [M – H]$^+$ peak in the negative mode MALDI-TOF MS analysis (see examples of the mass spectra of compounds **3b**, **3c**, **3d**, **3f**, and **3i** in the Supporting Information). One may argue that the resonance at δ = 82.9 ppm, assigned to C4 (sp^3 carbon of C_{60}), would be likely to originate from an sp^3 carbon of C_{60} that is bonded to a heteroatom. However, we find that a phosphorus ylide moiety shifts the resonance downfield by approximately 2.38 ppm[6b] in comparison with the ^{13}C NMR spectroscopic data of a Bingel adduct.[12] In parallel with this phenomenon, a cyclopenteno-fullerene with a phosphorus ylide moiety could have an sp^3 C chemical shift of up to 80.61 ppm, by reference to a simple cyclopenteno-fullerene.[13] This study has shown that chemical shifts of around 82.0 to 82.9 ppm are reasonable for the compounds reported herein as they deviate by only about 2 ppm from expected values. A heteroatom such as oxygen bonded to the C_{60} cage would show chemical shifts of around 100 pm.[14]

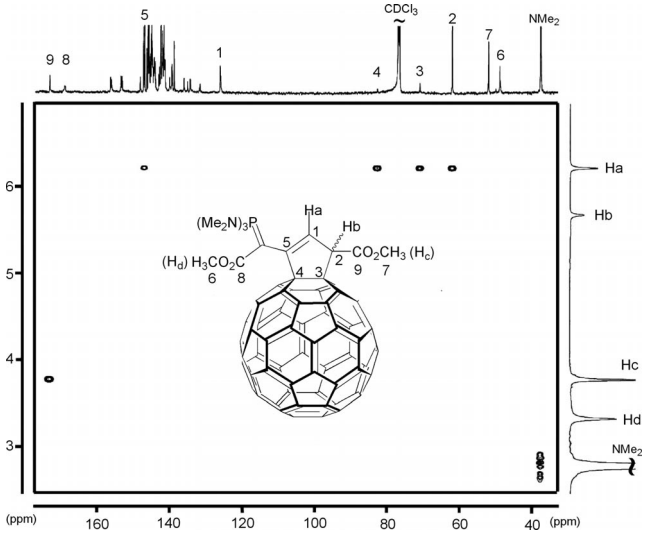

Figure 1. HMBC spectrum of compound **3d**.

The drastic difference in the stabilities of compounds **3**, affected by P(*c*Hex)$_3$ and other triarylphosphanes or hexaalkylphosphorus triamide, can be accounted for by the leaving-group ability of PR_3 from **3**. The removal of P(*c*Hex)$_3$ from **3a** is easier than the removal of HMPT from **3d** as compound **4a** is always observed on attempting to isolate **3a** under ambient conditions. In addition, we have also found that the HMPT moiety can be removed in the presence of 1 equiv. of $Mn(OAc)_3 \cdot 2H_2O$ in 1,2-dichlorobenzene at 150 °C to afford **4a** in 60% yield. To further understand their relative stabilities, we performed calculations on the structures of **3a** and **3d** by using the semi-empirical AM1 method.[15] We found that the charge densities at the α-ylidic carbon differ and are consistent with their observed reactivities. The Mulliken charge densities for compounds **3a** and **3d** are –1.384 and –1.315, respectively, which indicates that the α-ylidic carbon of **3a** is more prone to react with any proton source than **3d**. Hence, compound **3a** is more reactive and elimination of a P(*c*Hex)$_3$ tends to be easier.

In addition to the above interesting reactivities, the electronic absorptions of compounds **3b**–**k** and **4a** in the UV/Vis region display some unusual features. Because the absorptions are independent of the nature of the incorporated phosphane, we show in Figure 2 the UV/Vis spectra of **3d** and **4a** for comparison. Both **3d** and **4a** show typical absorptions arising from the monofunctionalized C_{60} derivative at 424 nm. The HMPT derivative **3d** shows a broad absorption spanning from 435 to 650 nm and a small absorption at around 700 nm. In particular, compound **3d** exhibits stronger absorptivity in the range 440–650 nm. Their dephosphinated product **4a** does not exhibit these absorptions in the visible region, but shows a similar absorption pattern in the ultraviolet portion.

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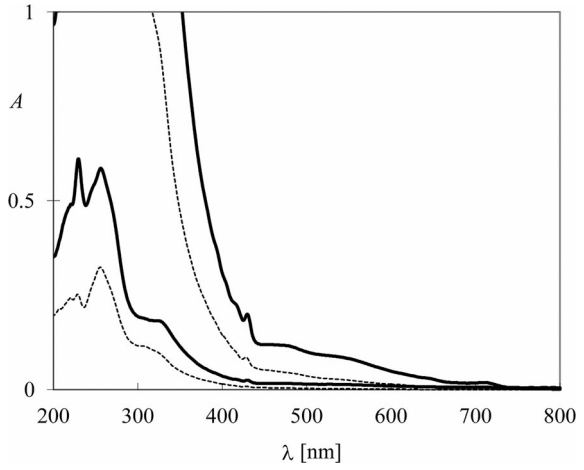

Figure 2. UV/Vis spectra of **3d** (solid line, 5.1×10^{-5} M) and **4a** (dashed line, 5.0×10^{-5} M) in $CHCl_3$. The spectra of **3d** and **4a** in the ultraviolet region were measured by 10-fold dilution of their solutions.

The electrochemical studies of isolated **3b**–**k** and **4a** show unusual redox features. Their half-wave reduction potentials ($E_{1/2}$), with values determined relative to ferrocene/ferrocenium, are summarized in Table 2. It is notable that **3b**–**k** exhibit strong cathodic shifts in their first reduction potentials, ranging form –1.23 to –1.27 V. These derivatives have higher LUMO energy levels than that of PCBM ([6,6]phenyl-C_{61} methyl butyrate) an n-type material typically used in organic photovoltaics. In particular, the derivative **3b**, which incorporates a triphenylphosphorus ylide, shows an exceptionally high LUMO energy level with an $E_{1/2}$ of –1.27 V. Interestingly, the first reduction potential of **4a**, without the phosphorus ylide, is less negative at –1.19 V. It is anodically shifted by around 40 mV compared with that of the more easily reduced compound **3h**. In addition, the relatively high LUMO energy levels of these derivatives incorporating phosphorus yildes account for the lower reactivity of the monoadducts and therefore of the slightly higher yields in these reactions. We observe that fewer bis-adducts are formed in these reactions unless large excesses of **1** and phosphanes are added to generate excess reactive dipolar species.

Table 2. Half-wave reduction potentials[a] of compound **3b**–**k** and **4a**.

Compound	$^1E_{1/2}$ [V]	$^2E_{1/2}$ [V]	$^3E_{1/2}$ [V]
C_{60}	–1.05	–1.47	–1.96
PCBM	–1.21	–1.58	–2.08
3b	–1.27	–1.65	–1.92
3c	–1.26	–1.65	–2.19
3d	–1.24	–1.62	–2.17
3e[b]	–1.26	–1.66	–2.20
3f	–1.26	–1.65	–2.19
3g	–1.26	–1.66	–2.21
3h	–1.23	–1.63	–2.16
3i	–1.24	–1.62	–2.16
3j	–1.26	–1.66	–2.21
3k	–1.25	–1.62	–2.20
4a	–1.19	–1.58	–

[a] Determined vs. ferrocene/ferrocenium; conditions: 6.0×10^{-4} M **3b**–**k** and 5.0×10^{-5} M **4a** in anhydrous 1,2-dichlorobenzene, 0.050 mM of Bu_4NPF_6. Reference electrode: Ag/0.01 M $AgNO_3$ and 0.050 mM $(nBu)_4NClO_4$ in anhydrous MeCN; working electrode: glassy carbon; auxiliary electrode: Pt; scanning rate: 50 mV s^{-1}. [b] Compound **3e** decomposes upon reduction. The value of $E_{1/2}$ was obtained by Osteryoung square-wave voltammetry (OSWV).

Conclusions

We have demonstrated a cycloaddition reaction of electron-deficient enynes with C_{60} by phosphane-promoted tandem α(δ′)-Michael addition reactions leading to a new class of cyclopenteno-fullerenes bearing phosphorus ylides with unusually high LUMO energy levels.

Experimental Section

General Methods: All reactions were performed under argon. Anhydrous *o*-DCB (1,2-dichlorobenzene) was distilled from CaH_2 under argon. The ^1H and ^{13}C NMR chemical shifts are given relative to tetramethylsilane (TMS) or $CHCl_3$. All chemicals were purchased and used as received unless otherwise noted.

Synthesis of 3a and 4a: A mixture of C_{60} (0.108 g, 0.150 mmol), tricyclohexylphosphane (0.210 g, 0.750 mmol), and *o*-DCB (10 mL) in a 150 mL flask with a side-arm was stirred at ambient temperature under argon until all the solid materials had dissolved. A solution consisting of **1a** (0.0300 g, 0.180 mmol) in dichloromethane (10 mL) was added to this mixture through a syringe pump with an injection rate of 5 mL h^{-1}. After the addition, the system was stirred for a further 2 h at room temperature. The solution was concentrated under vacuum to around 5 mL. The mixture was separated on a column of silica gel and eluted first with toluene to recover C_{60} (0.0360 g) in 33% yield and then the fraction containing **4a** (t_R = 7.7 min) and **3a** (t_R = 10.1 min; Buckyprep column, flow rate: 1 mL min^{-1}) was collected. After removal of the solvent, the solid was washed with hexanes to afford a mixture of **4a** (0.0410 g) in 31% yield (46% based on converted C_{60}) and **3a** (0.0480 g) in 27% yield (41% based on converted C_{60}) according to the HPLC integration data. Compound **3a** was labile and always contaminated with compound **4a** upon isolation. The mixture of **3a** and **4a** decomposed to **4a** quantitatively in toluene under reflux for 16 h (the spectroscopic data of **4a** are identical to those in ref.[11]).

Spectral Data of 4a: ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.91 (s, 3 H, OC*H*$_3$), 4.00 (s, 3 H, OC*H*$_3$), 7.11 (s, 1 H, C*H*), 9.15 (s, 1 H, C*H*) ppm. LRMS (FAB$^+$): *m*/*z* (%) = 888 (33) [M]$^+$, 720 (100) [C_{60}]$^+$.

Synthesis of 3b: A mixture of C_{60} (0.0360 g, 0.0500 mmol) and PPh_3 (0.130 g, 0.500 mmol) in toluene (25 mL) was stirred in a 100 mL flask with a side-arm under argon until all the solid materials had dissolved. A solution of dimethyl *trans*-but-1-en-3-yne-1,4-dicarboxylate (**1a**; 0.0100 g, 0.0600 mmol) in toluene (10 mL) was injected into the mixture through a syringe pump at an injection rate of 5 mL h^{-1}. After the addition, the mixture was stirred for a further 24 h at 50 °C. The mixture was then cooled and poured into a silica gel column and eluted first with toluene to recover unreacted C_{60} (0.0070 mg) in 19% yield. Further elution gave **3b** (R_f = 0.1, toluene/ethyl acetate = 10:1). After removal of the solvent, the solid was washed with hexanes to afford pure product **3b** (0.0300 g) in 52% yield (65% based on converted C_{60}). In the spectral data, the

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signals of the minor isomer are marked with an asterisk (*) unless unable to be specified. ^{1}H NMR (700 MHz, $CDCl_3$, 25 °C): δ = 3.34* (s, OCH_3), 3.41 (s, OCH_3), 3.72 (s, 2 OCH_3), 4.80* (s, 1 H, C*H*), 5.55 (s, 1 H, C*H*), 5.75* (s, 1 H, C*H*), 6.38 (s, 1 H, C*H*), 7.46 (br., Ar-H), 7.55 (m, Ar-H), 7.71 (m, Ar-H) ppm. ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = 17.8, 20.4* ppm. ^{13}C NMR (175 MHz, $CDCl_3$, 25 °C): δ = 39.24 [d, ^1J(C,P) = 127.9 Hz], 42.55 [d, ^1J(C,P) = 140.5 Hz], 49.70 (O*C*H$_3$), 49.77 (O*C*H$_3$), 52.21 (O*C*H$_3$), 52.47 (O*C*H$_3$), 62.06 (*C*H), 62.17 (*C*H), 70.58*, 70.86, 82.43*, 82.86, 126.15 [d, ^1J(C,P) = 44.3 Hz], 126.71 [d, ^1J(C,P) = 45.0 Hz], 128.79 [d, ^3J(C,P) = 13.2 Hz, *C*H], 132.13 (*C*H), 134.02 [d, ^2J(C,P) = 7.6 Hz, *C*H], 134.74, 135.27, 136.43, 137.31, 138.75, 139.11, 139.22, 139.46, 139.73, 139.84, 140.24, 141.55, 141.71, 142.08, 142.15, 142.19, 142.23, 142.58, 142.89, 143.24, 144.28, 144.42, 144.59, 145.08, 145.19, 145.87, 146.09, 146.38, 146.49, 146.10, 147.11, 147.43, 147.94, 148.78, 150.94, 151.69, 152.21, 153.26, 155.61, 155.95, 156.66, 158.54, 170.33 (br., C=O), 172.38 (C=O) ppm. FTIR (KBr): $\tilde{\nu}$ = 527, 575, 620, 691, 746, 806, 853, 927, 999, 1028, 1085, 1103, 1187, 1218, 1462, 1482, 1613, 1620, 1739, 2944, 3056 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} [log(ε/L mol^{-1} cm^{-1})] = 220 [5.01], 230 [5.08], 259 [5.13], 327 [4.66], 429 [3.55], 491 [3.50], 496 [3.50] nm. LRMS (MALDI-TOF$^-$): calcd. for $C_{86}H_{22}O_4P$ [M – H]$^-$ 1149.1; found 1149.9.

Synthesis of 3c: A solution of **1a** (0.0260 g, 0.155 mmol) in toluene (30 mL) was injected through a syringe pump at a rate of 5 mL h^{-1} at room temp. to a round-bottomed flask containing C_{60} (0.109 g, 0.151 mmol) and tri-*p*-tolylphosphane (0.0460 g, 0.151 mmol) in *o*-DCB (15 mL) under argon. Then the solution was purified by chromatography on a column of silica gel. Elution of the column with toluene led to isolation of unreacted C_{60} (0.0270 g) in 25% yield. Further elution with toluene/ethyl acetate (9:1) gave ylide **3c** (0.0940 g) in 52% yield (69% based on recovered C_{60}). R_f = 0.18 (toluene/ethyl acetate = 9:1). In the spectral data, the signals of the minor isomer are marked with an asterisk (*) unless unable to be specified. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.42 (s, 18 H, 6 CH_3), 3.42–3.45 (m, 6 H, 2 OCH_3), 3.79–3.83 (m, 6 H, 2 OCH_3), 5.03* (br., 1 H, C*H*), 5.62 (br., 1 H, C*H*), 6.08* (br., 1 H, C*H*), 6.48 (br., 1 H, C*H*), 7.56–7.63 (m, 24 H, Ar-H) ppm. ^{13}C NMR (175 MHz, $CDCl_3$, 25 °C): δ = 21.68, 22.00*, 39.20 [d, ^1J(C,P) = 132.9 Hz], 41.74* [d, ^1J(C,P) = 132.0 Hz], 49.63 (O*C*H$_3$), 52.19 (O*C*H$_3$), 52.47 (O*C*H$_3$), 52.54 (O*C*H$_3$), 62.14 (*C*H), 63.10* (*C*H), 70.65*, 70.81, 82.42*, 82.65, 115.27 [d, ^1J(C,P) = 89.4 Hz], 122.94 [d, ^2J(C,P) = 36.1 Hz], 123.46 [d, ^2J(C,P) = 36.8 Hz], 123.35, 129.11, 129.18, 129.48, 129.56, 129.63, 129.71, 130.00, 131.24 [d, ^3J(C,P) = 13.0 Hz], 131.70, 131.75, 132.07 [d, ^2J(C,P) = 10.6 Hz], 132.25, 132.36, 132.53, 132.87, 133.94 [d, ^2J(C,P) = 9.2 Hz], 134.34, [d, ^3J(C,P) = 10.6 Hz], 134.81, 134.90, 134.95, 135.09, 135.17, 135.23, 135.56, 135.99, 136.09, 136.35, 136.74, 137.34, 138.68, 138.88, 138.96, 139.15, 139.41, 139.64, 139.72, 139.80, 139.99, 140.08, 140.21, 140.45, 140.65, 141.30, 141.45, 141.58, 141.69, 141.75, 141.81, 141.94, 141.97, 142.05, 142.08, 142.13, 142.19, 142.26, 142.35, 142.41, 142.52, 142.56, 142.69, 142.73, 142.78, 142.81, 142.93, 143.08, 143.19, 143.37, 144.07, 144.12, 144.28, 144.40, 144.46, 144.55, 144.58, 144.75, 145.05, 145.07, 145.10, 145.13, 145.27, 145.41, 145.52, 145.57, 145.58, 145.65, 145.77, 145.83, 145.89, 145.94, 146.03, 146.06, 146.08, 146.13, 146.18, 146.23, 146.44, 146.46, 146.59, 147.05, 147.31, 147.42, 147.47, 147.96, 148.03, 148.61, 148.78, 150.35, 151.64, 151.87, 153.27, 154.76, 155.48, 155.73, 156.22, 156.86, 158.45, 170.05, 170.17, 172.05, 172.46 ppm. ^{31}P NMR (202 MHz, $CDCl_3$, 25 °C): δ = 18.0, 20.1* ppm. FTIR (KBr): $\tilde{\nu}$ = 527, 546, 576, 624, 652, 731, 760, 805, 907, 1088, 1104, 1189, 1218, 1245, 1294, 1431, 1462, 1499, 1616, 1739, 2856, 2945 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} [log(ε/L mol^{-1} cm^{-1})] = 231 [5.13], 257 [5.09], 326 [4.60], 430 [3.61] nm. LRMS (MALDI-TOF$^-$): calcd. for $C_{89}H_{28}O_4P$ [M – H]$^-$ 1191.2; found 1191.1. HRMS (FAB$^+$): calcd. for $C_{89}H_{30}O_4P$ [M + H]$^+$ 1193.1882; found 1193.1869.

Synthesis of 3d: A mixture of C_{60} (0.108 g, 0.150 mmol), HMPT (0.100 g, 0.600 mmol), and *o*-DCB (10 mL) in a 150 mL flask with a side-arm was stirred at ambient temperature under argon until all the solid materials had dissolved. A solution of **1a** (0.0390 g, 0.230 mmol) in toluene (30 mL) was injected into the mixture through a syringe pump at a rate of 15 mL h^{-1}. After the addition, the mixture was stirred for a further 2 h at room temperature. The solution was concentrated under vacuum to around 10 mL. The mixture was then separated on a column of silica gel and eluted first with toluene to recover trace C_{60}. Next, the fraction containing monoadduct **3d** with R_f = 0.08 (TLC, dichloromethane/ethyl acetate/hexanes = 1:1:1) was collected. After removal of the solvent, the solid was washed with pentane to afford the desired pure product **3d** (0.0780 g) in 49% yield. In the spectral data, the signals of the minor isomer are marked with an asterisk (*) unless unable to be specified. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 2.79 [d, ^3J(P,H) = 7.1 Hz, NCH_3], 3.32 (s, OCH_3), 3.77 (s, OCH_3), 5.68 (s, C*H*), 6.22 (s, C*H*) ppm. ^{31}P NMR (202 MHz, $CDCl_3$, –25 °C): δ = 57.8*, 58.8 ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 37.79 [N(*C*H$_3$)$_2$], 49.08 (O*C*H$_3$), 52.26 (O*C*H$_3$), 62.25 (*C*H), 71.22, 82.90, 126.26 (*C*H), 131.85, 134.54, 135.32, 136.24, 138.96, 139.46, 139.57, 139.72, 140.24, 141.43, 141.54, 141.63, 141.78, 141.84, 142.05, 142.07, 142.17, 142.24, 142.37, 142.52, 142.55, 142.60, 142.69, 142.95, 143.27, 144.11, 144.30, 144.39, 144.48, 144.63, 144.88, 145.01, 145.13, 145.33, 145.49, 145.83, 145.88, 145.91, 146.07, 146.12, 146.20, 146.50, 147.11, 147.41, 148.31, 153.32, 153.62, 156.22, 156.50, 169.13 [d, ^2J(C,P) = 17.2 Hz], 173.32 ppm. FTIR (KBr): $\tilde{\nu}$ = 527, 575, 663, 681, 750, 854, 982, 1066, 1097, 1189, 1224, 1289, 1430, 1456, 1463, 1615, 1738, 2808, 2846, 2895, 2926, 2990 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} [log(ε/L mol^{-1} cm^{-1})] = 221 [4.91], 230 [5.01], 256 [4.99], 430 [3.60], 518 [3.37], 527 [3.37], 766 [2.92], 781 [2.92], 792 [2.92] nm. LRMS (MALDI-TOF$^-$): calcd. for $C_{86}H_{23}O_4P$ [M – H]$^-$ 1150.1; found 1150.6. HRMS (FAB$^+$): calcd. for $C_{74}H_{27}N_3O_4P$ [M + H]$^+$ 1052.1739; found 1052.1741.

Synthesis of 4a: A solution of **3d** (0.0300 g, 0.0290 mmol) and $Mn(OAc)_3{\cdot}H_2O$ (0.0084 g, 0.031 mmol) in *o*-DCB (10 mL) was heated at 150 °C until all of compound **3d** had reacted. The mixture was passed through a short column of silica gel. The solvent of the solution obtained was removed under reduced pressure and precipitated with hexanes to give **4a** in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.91 (s, 3 H, OCH_3), 4.00 (s, 3 H, OCH_3), 7.11 (s, 1 H, C*H*), 9.15 (s, 1 H, C*H*) ppm.

Synthesis of 3e: A solution of **1a** (0.0199 g, 0.118 mmol) in toluene (20 mL) was injected through a syringe pump at a rate of 6.7 mL h^{-1} to a round-bottomed flask containing C_{60} (0.0720 g, 0.100 mmol) and hexaethylphosphorus triamide (0.247 g, 1.00 mmol) in *o*-DCB (20 mL) at 100 °C under argon. The progress of the reaction was monitored by TLC using toluene/ethyl acetate (4:1) as eluent. The reaction mixture was cooled to room temperature and then purified by flash chromatography on a column of silica gel using toluene as eluent to recover unreacted C_{60} (trace). Further elution by increasing the polarity of the eluent to toluene/EtOAc = 8:2 gave **3e** (0.0370 g, 33%) as a black solid. R_f = 0.32. In the spectral data, the signals of the minor isomer are marked with an asterisk (*) unless unable to be specified. ^{1}H NMR (300 MHz, $CDCl_3$, 0 °C): δ = 0.94* (br., 18 H, NCH$_2$CH_3), 1.22 (br., 18 H, NCH$_2$CH_3), 3.10–3.40 (br., 12 H, NCH_2CH$_3$), 3.26 (s, 3 H, OCH_3), 3.40–3.60 (br., 12 H, NCH_2CH$_3$), 3.46* (s, 3 H,

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OCH_3), 3.76 (s, 3 H, OCH_3), 3.82* (s, 3 H, OCH_3), 5.46* (br., 1 H), 5.70 (br., 1 H), 6.16* (br., 1 H), 6.21 (br., 1 H) ppm. ^{31}P NMR (202 MHz, $CDCl_3$, 20 °C): δ = 63.00, 63.86* ppm. ^{13}C NMR (176 MHz, $CDCl_3$, 25 °C): δ = 12.36 (NCH$_2$*C*H$_3$), 13.48 (NCH$_2$*C*H$_3$), 15.28 (NCH$_2$*C*H$_3$), 38.83 (br., N*C*H$_2$CH$_3$), 40.96 (br., N*C*H$_2$CH$_3$), 49.10 (O*C*H$_3$), 50.49 (O*C*H$_3$), 51.61 (O*C*H$_3$), 52.22 (O*C*H$_3$), 62.45 (*C*H), 71.27, 83.14, 125.14, 125.30, 128.23, 129.04, 131.54, 134.78, 135.26, 136.17, 139.01, 139.60, 140.21, 141.36, 141.67, 141.80, 142.06, 142.13, 142.23, 142.26, 142.44, 142.55, 142.64, 142.74, 142.96, 143.10, 143.33, 144.11, 144.25, 144.45, 144.57, 144.68, 144.90, 145.05, 145.13, 145.18, 145.34, 145.55, 145.83, 145.90, 146.10, 146.15, 146.25, 146.65, 147.15, 147.43, 148.34, 153.48, 153.92, 156.67, 156.73, 169.13 [d, ^2J(C,P) = 17.5 Hz], 169.59* [d, ^2J(C,P) = 17.5 Hz], 172.79*, 173.07 ppm. FTIR (KBr): $\tilde{\nu}$ = 527, 757, 831, 1018, 1171, 1381, 1434, 1583, 1739, 2871, 2961, 2926 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} [log(ε/L mol^{-1} cm^{-1})] = 227 [4.03], 252 [4.08], 325 [3.58], 423 [2.63] nm. LRMS (MALDI-TOF$^+$): calcd. for $C_{80}H_{39}N_3O_4P$ [M + H]$^+$ 1136.3; found 1136.1.

Synthesis of 3f: A solution of **1a** (0.0170 g, 0.100 mmol) in toluene (10 mL) was injected through a syringe pump (addition rate 3.4 mL h^{-1}) into a two-necked flask containing C_{60} (0.0750 g, 0.104 mmol) and tris(4-methoxyphenyl)phosphane (0.0370 g, 0.105 mmol) in *o*-DCB (20 mL) under argon at ambient temperature. After completing the addition, the mixture was subjected to flash chromatography (SiO_2). Elution with toluene led to isolation of unreacted C_{60} (0.0210 g, 28% recovery). Further elution with hexanes/ethyl acetate/dichloromethane (1:1:1) allowed **3f** to be collected. After removal of the solvent, the residue was precipitated with methanol to give compound **3f** (0.0730 g) in 57% yield (78% based on recovered C_{60}). R_f = 0.27 (hexanes/ethyl acetate/dichloromethane = 1:1:1). In the spectral data, the signals of the minor isomer are marked with an asterisk (*) unless unable to be specified. ^{1}H NMR (700 MHz, $CDCl_3$, 25 °C): δ = 3.42* (br., 3 H, OCH_3), 3.45 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 3.80* (s, 3 H, OCH_3), 3.84 (s, 9 H, OCH_3), 3.85 (s, 9 H, OCH_3), 5.03* (s, 1 H, C*H*), 5.59 (s, 1 H, C*H*), 6.03* (s, 1 H, C*H*), 6.40 (s, 1 H, C*H*), 6.98 (m, 6 H, Ar-H), 7.64 (m, 6 H, Ar-H) ppm. ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ = 19.5, 21.6* ppm. ^{13}C NMR (175 MHz, $CDCl_3$, 25 °C): δ = 40.12 [d, ^1J(C,P) = 132.9 Hz], 42.60* [d, ^1J(C,P) = 125.6 Hz], 49.59 (O*C*H$_3$), 52.17 (O*C*H$_3$), 52.47 (O*C*H$_3$), 55.34 (PhO*C*H$_3$), 55.48 (PhO*C*H$_3$), 55.89 (*C*H), 56.52 (O*C*H$_3$), 62.16 (*C*H), 70.61*, 70.84, 82.50*, 82.70, 113.96 [d, ^3J(C,P) = 12.7 Hz], 114.39 [d, ^3J(C,P) = 12.9 Hz], 114.55 [d, ^3J(C,P) = 12.7 Hz], 116.21 [d, ^1J(C,P) = 14.3 Hz], 116.78 [d, ^1J(C,P) = 14.3 Hz], 117.10, 117.18, 117.34, 117.52, 117.90, 118.07, 120.30, 129.51, 132.11, 132.66, 132.85, 133.84, 133.90, 134.30, 134.45, 135.28, 135.67 [d, ^2J(C,P) = 10.7 Hz], 136.42, 136.48, 136.69, 136.96, 137.03, 137.13, 138.70, 138.90, 139.05, 139.23, 139.44, 139.68, 140.11, 140.24, 141.33, 141.60, 141.64, 141.73, 141.75, 141.92, 142.04, 142.07, 142.16, 142.30, 142.35, 142.55, 144.16, 144.30, 144.42, 144.61, 144.77, 145.04, 145.16, 145.30, 145.33, 145.53, 145.80, 145.85, 145.93, 146.06, 146.16, 146.47, 146.58, 147.08, 147.43, 147.95, 148.04, 148.62, 148.80, 150.65, 151.91, 15343, 155.78, 156.09, 156.86, 158.55, 162.54, 170.00 [d, ^2J(C,P) = 21.1 Hz], 172.17 ppm. FTIR (KBr): $\tilde{\nu}$ = 527, 544, 625, 663, 753, 803, 829, 926, 1028, 1119, 1179, 1214, 1255, 1292, 1374, 1406, 1438, 1461, 1502, 1596, 1718, 2837, 2951, 3003 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} [log(ε/L mol^{-1} cm^{-1})] = 229 [4.99], 251 [5.03], 477 [3.08] nm. LRMS (MALDI-TOF$^-$): calcd. for $C_{89}H_{28}O_7P$ [M – H]$^-$ 1239.2; found 1239.1. HRMS (FAB$^+$): calcd. for $C_{89}H_{30}O_7P$ [M + H]$^+$ 1241.1729; found 1241.1732.

Synthesis of 3g: A solution containing C_{60} (0.0720 g, 0.100 mmol) and tris(4-chlorophenyl)phosphane (0.0730 g, 0.200 mmol) was stirred in *o*-DCB (10 mL) at 110 °C until all the solid materials had dissolved. Then a solution of **1a** (0.0250 mg, 0.150 mmol) in toluene (10 mL) was injected slowly into the solution over 3 h using a syringe pump. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature. Flash chromatography on a column of silica gel was performed first using toluene as eluent to recover unreacted C_{60} (0.0540 g, 75%). Further elution with toluene/ethyl acetate (15:1) afforded **3g** (0.0200 g) in 16% yield (64% based on converted C_{60}). R_f = 0.43 (toluene/ethyl acetate = 15:1). The minor isomer is indicated by the * sign unless unable to be specified. ^{1}H NMR (700 MHz, $CDCl_3$, 25 °C): δ = 3.44* (s, 3 H, OCH_3), 3.48 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 3.81* (s, 3 H, OCH_3), 5.07* (br., 1 H, C*H*), 5.60 (br., 1 H, C*H*), 6.10* (br., 1 H, C*H*), 6.48 (br., 1 H, C*H*), 7.46 (br., 6 H, C*H*), 7.62 (br., 6 H, C*H*) ppm. ^{13}C NMR (175 MHz, $CDCl_3$, 25 °C): δ = 38.66 [d, ^1J(C,P) = 136.9 Hz], 49.48, 49.99, 52.36, 52.53, 62.03 (*C*H), 70.60*, 70.84, 82.15*, 82.29, 124.04 [d, ^1J(C,P) = 43.4 Hz], 124.57 [d, ^1J(C,P) = 42.1 Hz], 129.11, 129.18, 129.40, 129.58 [d, ^3J(C,P) = 12.5 Hz], 133.17, 133.27, 133.33, 133.90, 135.06 [d, ^2J(C,P) = 8.6 Hz], 136.31, 138.88, 139.00, 139.51, 140.25, 141.52, 141.72, 141.77, 141.79, 141.97, 142.03, 142.21, 142.24, 142.31, 142.51, 142.60, 142.62, 142.67, 142.98, 143.27, 144.20, 144.26, 144.35, 144.47, 144.52, 144.73, 144.88, 145.07, 145.15, 145.21, 145.32, 145.54, 145.64, 145.85, 145.90, 146.08, 146.12, 146.18, 147.42, 148.17, 149.79, 151.06, 151.50, 152.88, 154.90, 155.18, 156.38, 158.08, 170.51 [d, ^2J(C,P) = 17.5 Hz], 170.54 [d, ^2J(C,P) = 16.7 Hz], 172.07, 172.50 ppm. ^{31}P NMR (202 MHz, $CDCl_3$, 25 °C): δ = 17.4, 19.4* ppm. FTIR (KBr): $\tilde{\nu}$ = 527, 575, 705, 1013, 1046, 1089, 1609, 1738, 1909, 2329, 2945, 3005 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} [log(ε/L mol^{-1} cm^{-1})] = 231 [5.17], 243 [5.13], 255 [5.11], 324 [4.64] nm. LRMS (MALDI-TOF$^+$): calcd. for $C_{86}H_{20}Cl_3O_4P$ 1252.0 [M]$^+$; found 1252.9. HRMS (FAB$^+$): calcd. for $C_{86}H_{20}Cl_3O_4P$ [M]$^+$ 1252.0165; found 1252.0130.

Synthesis of 3h: A mixture of C_{60} (0.0720 g, 0.100 mmol), tris(4-fluorophenyl)phosphane (0.0630 g, 0.200 mmol), and *o*-DCB (10 mL) in a 100 mL flask with a side-arm was stirred at 140 °C under argon until all the solid materials had dissolved. A solution of **1a** (0.0250 g, 0.150 mmol) in *o*-DCB (10 mL) was injected into the mixture at a rate of 0.77 mL h^{-1}. After the addition, the mixture was stirred for a further 2 h at 140 °C. The mixture was separated on a column of silica gel and eluted first with toluene to recover C_{60} (0.0310 g) in 43% yield; the fraction containing the adduct **3h** was then collected. After removal of the solvent, the solid was washed with pentane to afford **3h** (0.0230 g) in 19% yield (34% based on converted C_{60}). R_f = 0.23 (toluene/ethyl acetate = 20:1). In the spectral data, the signals of the minor isomer are marked with an asterisk (*) unless unable to be specified. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 3.40* (s, 3 H, OCH_3), 3.45 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 3.77* (s, 3 H, OCH_3), 4.97* (s, 1 H, C*H*), 5.58 (s, 1 H, C*H*), 5.93* (s, 1 H, C*H*), 6.41 (s, 1 H, C*H*), 7.20 (br., 6 H, Ar-H), 7.70 (br., 6 H, Ar-H) ppm. ^{31}P NMR (202 MHz, $CDCl_3$, 25 °C): δ = 17.0, 19.3* ppm. ^{13}C NMR (176 MHz, $CDCl_3$, 25 °C): δ = 39.64 [d, ^1J(C,P) = 132.7 Hz], 42.45* [d, ^1J(C,P) = 120.9 Hz], 49.88 (O*C*H$_3$, 2 C), 52.28, 52.52, 62.07 (*C*H, 2 C), 70.60*, 70.88, 82.29*, 82.43, 116.58 [dd, ^2J(C,P) = 1.3, ^2J(C,F) = 21.0 Hz], 121.79 [d, ^1J(C,P) = 45.7 Hz], 122.33 [d, ^1J(C,P) = 50.6 Hz], 130.11, 132.84, 133.15, 133.69, 134.00, 134.46, 135.18, 136.15, 136.28 [dd, ^3J(C,P) = 13.3, ^3J(C,P) = 18.2 Hz], 137.23, 138.87, 139.09, 139.52, 140.12, 140.26, 141.46, 141.66, 141.78, 141.98, 142.05, 142.21, 142.26, 142.31, 142.51, 142.63, 142.68, 143.01, 143.29, 144.21, 144.29, 144.48, 144.54, 144.61, 144.68, 144.88, 145.07, 145.15, 145.22, 145.28, 145.47, 145.54, 145.87,

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145.91, 146.08, 146.13, 146.19, 146.23, 147.15, 147.43, 147.58, 150.44, 151.48, 151.69, 152.02, 153.03, 155.11, 155.39, 156.40, 158.29, 165.35 [^1J(C,F) = 253.6 Hz], 170.45 [^2J(C,P) = 17.5 Hz], 170.47 [^2J(C,P) = 17.3 Hz], 172.18*, 172.46 ppm. FTIR (KBr): $\tilde{\nu}$ = 527, 545, 563, 623, 638, 667, 709, 756, 830, 930, 1014, 1047, 1104, 1161, 1240, 1303, 1396, 1432, 1463, 1498, 1591, 1612, 1739, 2948, 3005, 3069 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} [log(ε/L mol^{-1} cm^{-1})] = 230 [5.13], 257 [5.14], 325 [5.67], 429 [3.65] nm. LRMS (MALDI-TOF$^+$): calcd. for $C_{86}H_{21}F_3O_4P$ [M + H]$^+$ 1205.1; found 1205.1.

Synthesis of 3i: A mixture of C_{60} (0.108 g, 0.150 mmol), tris(2-thienyl)phosphane (0.211 g, 0.754 mmol), and *o*-DCB (15 mL) in a 100 mL flask with a side-arm was stirred at 80 °C under argon until all the solid materials had dissolved. A solution of **1a** (0.0300 g, 0.18 mmol) and toluene (20 mL) was injected into the mixture through a syringe pump at a rate of 1.5 mL h^{-1}. After the addition, the system was stirred for a further 2 h at 80 °C. The mixture was separated on a column of silica gel and eluted first with toluene to recover C_{60} (0.0690 g) in 64% yield; the fraction containing adduct **3i** was then collected. After removal of the solvent, the solid was washed with pentane to afford **3i** (0.0420 g) in 24% yield (66% based on recovered C_{60}). R_f = 0.22 (toluene/ethyl acetate = 10:1). In the spectral data, the signals of the minor isomer are marked with an asterisk (*) unless unable to be specified. ^{1}H NMR (700 MHz, $CDCl_3$, 25 °C): δ = 3.38* (s, 3 H, OCH_3), 3.44 (s, 3 H, OCH_3), 3.80 (s, 6 H, OCH_3), 5.16* (s, 1 H, C*H*), 5.57 (s, 1 H, C*H*), 6.21* (s, 1 H, C*H*), 6.49 (s, 1 H, C*H*), 7.22 (s, 3 H, Ar-H), 7.58–7.79 (m, 6 H, Ar-H) ppm. ^{31}P NMR (202 MHz, $CDCl_3$, 25 °C): δ = –6.44, –3.91* ppm. Due to the poor solubility of **3i**, its ^{13}C NMR spectroscopic data were not obtained. FTIR (KBr): $\tilde{\nu}$ = 527, 575, 663, 681, 750, 854, 982, 1066, 1097, 1189, 1224, 1289, 1430, 1456, 1463, 1615, 1738, 2808, 2846, 2895, 2926, 2990 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} [log(ε/L mol^{-1} cm^{-1})] = 230 [6.15], 256 [6.19], 325 [5.67] nm. LRMS (MALDI-TOF$^-$): calcd. for $C_{80}H_{17}O_4PS_3$ [M]$^-$ 1168.0; found 1168.7. HRMS (FAB$^+$): calcd. for $C_{80}H_{18}O_4PS_3$ [M + H]$^+$ 1168.0105; found 1169.0107.

Synthesis of 3j: A mixture of C_{60} (0.108 g, 0.150 mmol), tri-*p*-tolylphosphane (0.0460 g, 0.150 mmol), and *o*-DCB (15 mL) in a flask with a side-arm was stirred at room temperature until all the solid materials had dissolved. A solution of diethyl *trans*-but-1-en-3-yne-1,4-dicarboxylate (**1b**; 0.0290 g, 0.150 mmol) in toluene (15 mL) was injected into the mixture through a syringe pump at a rate of 5 mL h^{-1}. After the addition, the mixture was stirred for a further 6 h at room temperature. The solution was concentrated under reduced pressure to around 15 mL. Column chromatography (SiO_2) first with toluene gave recovered C_{60} (0.0540 g, 50%) and then with toluene/ethyl acetate (10:1) gave **3j**. After removal of the solvent, the solid was washed with methanol thoroughly to afford the desired pure compound **3j** (0.0720 g, 39%; 77% based on converted C_{60}). In the spectral data, the signals of the minor isomer are marked with an asterisk (*) unless unable to be specified. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.88–1.34 (m, 6 H, OCH$_2$CH_3), 2.42 (s, 9 H, CH_3), 3.50–4.27 (m, 4 H, OCH_2CH$_3$), 5.05 (s, 1 H, C*H*), 5.59 (s, 1 H, C*H*), 6.55 (s, 1 H, C*H*), 6.61 (s, 1 H, C*H*), 7.25–7.63 (m, 12 H, Ar-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 13.96 (OCH$_2$*C*H$_3$), 14.25 (OCH$_2$*C*H$_3$), 14.65 (OCH$_2$*C*H$_3$), 14.86 (OCH$_2$*C*H$_3$), 21.64 (*C*H$_3$), 39.14 [d, ^1J(C,P) = 130.9 Hz], 41.23 [d, ^1J(C,P) = 128.9 Hz], 57.68, 58.07, 58.35, 61.05 (O*C*H$_2$CH$_3$), 61.22 (O*C*H$_2$CH$_3$), 61.47 (*C*H, 2 C), 61.89 (O*C*H$_2$CH$_3$, 2 C), 70.69, 70.87, 82.59, 82.79, 123.53 [d, ^1J(C,P) = 94.1 Hz, Ar C], 124.20 [d, ^1J(C,P) = 94.5 Hz, Ar C], 129.12 [d, ^2J(C,P) = 14.6 Hz, Ar C], 129.63 [d, ^3J(C,P) = 14.6 Hz, Ar C], 130.91, 132.04 [d, ^2J(C,P) = 11.8 Hz, Ar C], 133.39, 133.59, 133.73, 133.92 [d, ^3J(C,P) = 11.1 Hz, Ar C], 134.27, 134.52, 135.12, 136.87, 137.33, 138.34, 138.66, 138.88, 139.22, 139.34, 139.47, 139.53, 139.63, 140.06, 140.16, 141.23, 141.52, 141.63, 141.70, 141.79, 141.85, 142.04, 142.30, 142.39, 142.48, 142.74, 142.78, 142.91, 143.05, 143.13, 144.10, 144.25, 144.38, 144.55, 144.71, 144.82, 144.98, 145.11, 145.15, 145.24, 145.36, 145.50, 145.73, 145.80, 145.99, 146.12, 146.22, 146.32, 146.35, 146.71, 146.79, 146.99, 147.04, 147.09, 147.38, 148.01, 148.67, 150.23, 151.45, 151.99, 153.19, 155.60, 155.82, 157.19, 158.38, 170.00, 170.10, 171.97, 172.05 ppm. ^{31}P NMR (242 MHz, $CDCl_3$, 25 °C): δ = 17.0, 19.0 ppm. FTIR (KBr): $\tilde{\nu}$ = 1599, 1733 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} [log(ε/L mol^{-1} cm^{-1})] = 231 [6.06], 257 [5.05], 326 [4.57], 430 [358], 474 [3.33] nm. LRMS (MALDI-TOF$^+$): calcd. for $C_{91}H_{33}O_4P$ [M]$^+$ 1220.2; found 1220.8.

Synthesis of 3k: A mixture of C_{60} (0.0360 g, 0.0500 mmol), triphenylphosphane (0.0310 g, 0.120 mmol), and *o*-DCB (15 mL) in a flask with a side-arm was stirred at 50 °C until all the solid materials had dissolved. A solution of **1b** (0.0240 g, 0.120 mmol) in toluene (15 mL) was injected into the mixture through a syringe pump at a rate of 5 mL h^{-1}. After the addition, the mixture was stirred for a further 6 h at room temp. The solution was concentrated in vacuo to around 15 mL. Column chromatography (SiO_2) first with toluene gave unreacted C_{60} (0.0190 g, 53%) and then with toluene/ethyl acetate (10:1) gave compound **3k**. After removal of the solvent, the solid was thoroughly washed with methanol to afford the desired pure compound **3k** (0.0190 g, 32%; 68% based on converted C_{60}). In the spectral data, the signals of the minor isomer are marked with an asterisk (*) unless unable to be specified. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.71–1.16 (m, 6 H, OCH$_2$CH_3), 3.55 (br., 2 H, OCH_2CH$_3$), 4.06 [q, ^3J(H,H) = 7.1 Hz, 2 H, OCH_2CH$_3$], 5.33 (s, 1 H, C*H*), 6.26 (s, 1 H, C*H*), 7.32–7.58 (m, 15 H, Ar-H) ppm. Due to the poor solubility of **3k**, its ^{13}C NMR spectroscopic data were not acquired. FTIR (KBr): $\tilde{\nu}$ = 1608, 1734 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} [log(ε/L mol^{-1} cm^{-1})] = 231 [5.00], 257 [5.05], 325 [3.57], 430 [3.66], 469 [3.50] nm. LRMS (MALDI-TOF$^+$): calcd. for $C_{88}H_{27}O_4P$ [M]$^+$ 1178.2; found 1178.0.

Supporting Information (see footnote on the first page of this article): Spectra for all new compounds.

Acknowledgments

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[11] In a previous paper (K.-F. Liou, C.-H. Cheng, *J. Chem. Soc., Chem. Commun.* **1995**, 1603–1604), the reaction product was proposed to be a cyclohexadieno-fullerene compound. Such a product should undergo a photochemical [4+4] cycloaddition to give a bis-fulleroid. We find that our reaction product **4a** appears to have the same spectroscopic data in the same deuteriated solvent as those reported in the above-mentioned paper. This product did not undergo photochemical [4+4] cycloaddition. Thus, we think that the cyclohexadieno-fullerene product previously proposed could be structurally mistaken. Compound **4a**, which results from the reaction of methyl propiolate and C_{60} in the presence of tricyclohexylphosphane, should be obtained by the dimerization of methyl propiolate mediated by P(*c*Hex)$_3$ followed by the P(*c*Hex)$_3$-promoted cycloaddition with C_{60} described herein. See Figures S33 and S34 for the gHMQC and gHMBC spectra, respectively, of the proposed **4a**.

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