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Radical Reaction of [60]Fullerene with Phosphorus Compounds Mediated by Manganese(III) Acetate

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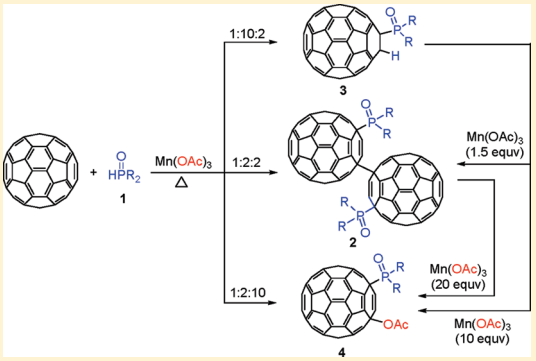
Supporting Information

ABSTRACT: Radical reaction of [60]fullerene with phosphonates or phosphine oxide mediated by manganese(III) acetate dihydrate in chlorobenzene under three different conditions afforded three different types of phosphorylated fullerenes: singly bonded fullerene dimers **2**, hydrophosphorylated fullerenes **3**, and acetoxylated fullerene derivatives **4**. In addition, interconversions among the three types of phosphorylated fullerene derivatives have also been investigated. A possible reaction mechanism was proposed to explain experimental results.



INTRODUCTION

Among the myriad of fullerene derivatives reported today, only a limited number of fullerene compounds containing a phosphorus atom are known.[1] Scarce examples of phosphorylated fullerene derivatives with the phosphorus atom attached directly to the fullerene skeleton have been reported and are limited to hydrofullerenes only.[2,3] Wu et al. explored the reaction of C_{60} with trialkylphosphine oxides and obtained hydrofullerenes $R_2(O)PC_{60}H$.[2] Nakamura and co-workers[3a] described the reaction of C_{60} with a lithiated phosphine−borane or a lithiated phosphinite borane followed by acid quenching and removal of the BH_3 group to afford a phosphine or a phosphinite bearing a fullerene substituent. They also found that the addition of $(MeO)_2(O)PLi$ to C_{60} followed by acid quenching gave $(MeO)_2(O)PC_{60}H$. A few years later, they improved the synthesis of $RR'(O)PC_{60}H$ by performing the reaction under neutral conditions.[3b] When Chuang and co-workers studied the reaction of C_{60} with dimethyl acetylenedicarboxylate and $P(NMe_2)_3$ or $P(NEt_2)_3$, they obtained hydrofullerene $(R_2N)_2(O)PC_{60}H$ (R = Me, Et) as a byproduct, which could be formed directly from the reaction of C_{60} with $P(NMe_2)_3$ or $P(NEt_2)_3$, albeit still in low yields (7% and 15%, respectively).[3c] Some of the phosphorus-containing fullerene derivatives were shown to have active biological activities[2,4] and optical properties.[5] Therefore, it is demanding to achieve the synthesis of other types of phosphorylated fullerene derivatives for the purpose of diversity and potential application.

Studies on the reaction of phosphorus radicals with fullerenes are rare. In continuation of our interest in manganese(III) acetate $Mn(OAc)_3$-mediated radical reactions of C_{60},[6,7] we recently reported the reaction of C_{60} with phosphorus radicals formed from phosphonate esters in the presence of $Mn(OAc)_3$ and obtained singly bonded fullerene dimers.[8] Later on, we found that the reaction could be extended to phosphine oxide. More interestingly, we uncovered that another two different types of products could be generated by simply adjusting the reaction conditions. Herein we disclose these intriguing results: the $Mn(OAc)_3$-mediated reaction of C_{60} with phosphonate esters or phosphine oxide affords selectively one of the three types of phosphorylated fullerene derivatives, that is, singly bonded fullerene dimers, hydrofullerenes, and acetoxylated fullerenes, simply under three different reaction conditions. In addition, interconversions among the three types of phosphorylated fullerene derivatives have also been explored.

RESULTS AND DISCUSSION

We previously reported that the $Mn(OAc)_3$-mediated reaction of C_{60} with phosphorus radicals generated from dimethyl phosphonate (**1a**), diethyl phosphonate (**1b**), and 5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (**1c**) afforded meso and racemic

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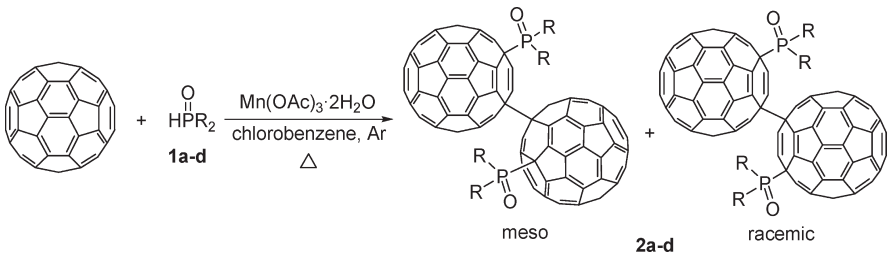
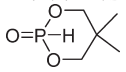
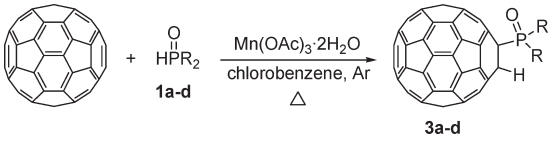
Table 1. Reaction Conditions, Product Yields, and Isomeric Ratios of Dimers 2a−d along with Recovered C_{60}

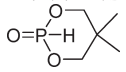


substrate 1	molar ratio of C_{60}/1/Mn(III)	product	temp (°C)[a]	reation time (min)	yield of **2** (%)	isometric ratio[b]	recovered C_{60} (%)
$HP(O)(OMe)_2$	1:2:2	**2a**	135	50	29	1.4:1	67
$HP(O)(OEt)_2$	1:2:2	**2b**	135	50	28	1.4:1	68
	1:2:4	**2c**	100	90	34	1.5:1	65
$HP(O)Ph_2$	1:2:6[c]	**2d**	60	20	29	1.2:1	68

[a] Oil bath temperature. [b] Major/minor ratio determined by ^{31}P MR spectrum. [c] 1 equiv of DMAP was added.

Table 2. Reaction Conditions and Product Yields of Hydrofullerenes 3 along with Recovered C_{60}



substrate 1	molar ratio of C_{60}/1/Mn(III)	product	temp (°C)[a]	reaction time (h)	yield of **3** (%)	recovered C_{60} (%)
$HP(O)(OMe)_2$	1:10:2	**3a**	135	12	32	62
$HP(O)(OEt)_2$	1:10:2	**3b**	135	26	41	37
	1:5:1	**3c**	100	11	31	42
$HP(O)Ph_2$	1:5:1	**3d**	60	0.7	32	40

[a] Oil bath temperature.

isomers of singly bonded fullerene dimers **2a**−**c**.[8] When the reaction was extended to diphenylphosphine oxide (**1d**), dimer **2d** could be isolated in 29% yield when the molar ratio of C_{60}:**1d**:$Mn(OAc)_3\cdot 2H_2O$ = 1:2:6 was employed in the presence of 1 equiv of 4-(dimethylamino)pyridine (DMAP). Table 1 lists the reaction conditions, product yield, and isomeric ratio for the $Mn(OAc)_3$-mediated reaction of C_{60} with **1d** together with those with **1a**−**c**.

The isolated yield of dimer **2d** was comparable to those (28−34%) of **2a**−**c**. Diphenylphosphine oxide **1d** was more reactive toward C_{60} than phosphonate esters **1a**−**c**, and its reaction with C_{60} could proceed at 60 °C, much lower than the reaction temperatures for **1a**,**b**. Nevertheless, a larger amount of $Mn(OAc)_3$ (6 equiv) and 1 equiv of additional DMAP were required to suppress the formation of another product **3d** (vide infra).

Singly bonded dimer **2d** was characterized by its HRMS, ^1H NMR, UV−vis, and FT-IR spectra. The HRMS (−ESI) of **2d** displayed a peak at 921.0478, corresponding to its half molecular ion. Similar phenomenon was described for **2a**−**c**[8] as well as other singly bonded dimers.[7a] The ^1H NMR spectrum of **2d** showed two sets of signals for the aromatic protons, agreeing with the existence of two isomers of **2d**. The ^{13}C NMR spectrum of **2d** exhibited 71 peaks in the 137−157 ppm range for the sp^2-carbons of the C_{60} skeleton, indicating that it had two C_{60} moieties, consistent with its dimeric structure. One doublet at 67.45 ppm with $^1J_{C-P}$ = 61.9 Hz and another doublet at 67.51 ppm with $^1J_{C-P}$ = 61.8 Hz for the fullerenyl sp^3-carbon connecting with the phosphorus atom were seen. It is noteworthy that the $^1J_{C-P}$ values (61.8−61.9 Hz) for the fullerenyl sp^3-C of **2d** is much smaller than those (144.6−146.9 Hz)[8] of **2a**−**c**. Nakamura and coworkers also recorded the dramatic effect of the substituents attached to the phosphorus atom on the $^1J_{C-P}$ values.[3a,b] The multiple peaks at 68.09−68.24 ppm were assigned to the pivot carbons joining the two fullerene skeletons. The pivot carbons were shown as multiple peaks because of the coupling with the phosphorus atoms from two dimeric isomers. The ^{31}P NMR spectrum of **2d** with 85% H_3PO_4 as the reference displayed two signals at 29.07 and 29.70 ppm in a ratio of 1.2:1. The observed broad absorption at 444 nm in the UV−vis spectrum of **2d** suggested that it adopted the 1,4-addition pattern.[7a,8−10]

It was interesting to find that when excess phosphorus compound was used, another type of products, i.e., hydrophosphorylated fullerenes **3a**−**d**, were selectively obtained from the Mn(OAc)$_3$-mediated reaction of C_{60} with **1a**−**d**. The reaction conditions and isolated yields of hydrofullerenes **3a**−**d** along with recovered C_{60} from the $Mn(OAc)_3$-mediated reaction of C_{60} with **1a**−**d** are summarized in Table 2.

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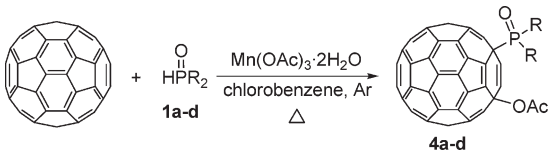
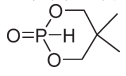
Table 3. Reaction Conditions and Product Yields of Acetoxylated Fullerenes 4 along with Recovered C_{60}



substrate 1	molar ratio of C_{60}/1/Mn(III)	product	temp (°C)[a]	reaction time (min)	yield of **4** (%)	recovered C_{60} (%)
$HP(O)(OMe)_2$	1:2:10	**4a**	135	50	32	53
$HP(O)(OEt)_2$	1:2:10	**4b**	135	50	27	58
	1:2:10	**4c**	135	50	24	71
$HP(O)Ph_2$	1:2:10[b]	**4d**	70	60	31	66

[a] Oil bath temperature. [b] 20 equiv of AcOH was added.

Hydrofullerenes **3a**−**d** were formed exclusively from the reaction of C_{60} with **1a**−**d** and $Mn(OAc)_3 \cdot 2H_2O$ in a molar ratio of 1:10:2 or 1:5:1. Compounds **1c** and **1d** showed higher reactivity toward C_{60}, and the reaction could take place at lower reaction temperature and less amount of phosphorus compound and $Mn(OAc)_3$, yet gave comparable product yields at less reaction time. No formation of hydrofullerenes **3a**−**c** and only ~2% yield of **3d** was observed for the reaction of C_{60} with **1a**−**d** in the absence of $Mn(OAc)_3$ under otherwise the same conditions. Therefore, $Mn(OAc)_3$ was essential for the successful formation of hydrofullerenes **3a**−**d** from the reaction of C_{60} with **1a**−**d** in the absence of DMSO, DMF, or HMPA, which may promote a charge transfer or an electron transfer between C_{60} and the phosphorus reagent.[3b] Although Nakamura and co-workers developed an elegant procedure for the synthesis of hydrophosphorylated fullerenes,[3b] our protocol using less amount of phosphonate esters offers an alternative access to these hydrofullerenes, which are expected to excellent precursors for further modifications (vide infra).[7d]

Products **3a**,[3a,b] **3c**,[3b] and **3d**[3a,b] are known compounds, and their identities were confirmed by comparison of their spectral data with the reported ones. Product **3b** is fully characterized by the HRMS, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, UV−vis, and FT-IR spectra. In the ^{1}H NMR spectrum of **3b**, the proton attached to the fullerene skeleton appeared at 7.22 ppm as a doublet with a large P−H coupling ($^3J_{P-H}$ = 29.6 Hz); the ethoxy group showed a multiplet for the CH_2 moiety due to the coupling with both the methyl group and the phosphorus atom in the region of 4.66−4.76 ppm and a triplet for the CH_3 group at 1.66 ppm. In its ^{31}P NMR spectrum, only one peak at 21.55 ppm was observed. In the ^{13}C NMR spectrum, there were 27 peaks, of which 3 peaks were overlapped and 5 peaks showed P−C couplings, in the 135−152 ppm range for the 58 sp^2-carbons of the C_{60} cage, and one doublet at 65.48 ppm ($^1J_{P-C}$ = 149.9 Hz) and a singlet at 56.30 ppm for the two sp^3-carbons of the fullerene moiety, fully consistent with its C_s molecular symmetry.

Gratifyingly, when excess $Mn(OAc)_3$ was employed, acetoxylated fullerenes **4a**−**d** were selectively obtained from the $Mn(OAc)_3$-mediated reaction of C_{60} with **1a**−**d**. The reaction conditions and isolated yields of acetoxylated fullerenes **4a**−**d** along with recovered C_{60} from the $Mn(OAc)_3$-mediated reaction of C_{60} with **1a**−**d** are listed in Table 3.

The synthesis of acetoxylated fullerenes **4a**−**d** was achieved in 24−32% isolated yields by performing the reaction of C_{60} with **1a**−**d** and $Mn(OAc)_3 \cdot 2H_2O$ in a molar ratio of 1:2:10. For the reaction with **1d**, the reaction temperature could be lowered to 70 °C, yet 20 equiv of acetic acid was added to facilitate the acetoxylation process and suppress the formation of dimer **1d**.

The structures of acetoxylated fullerenes **4a**−**d** were identified by the HRMS, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, UV−vis, and FT-IR spectra. The ^{1}H NMR spectra of products **4a**−**d** exhibited a singlet at 2.22−2.52 ppm for the acetoxy group besides the peaks due to the phosphonate or phosphine oxide moieties. The ^{13}C NMR spectra of **4a**−**d** displayed at least 52 peaks in the 137−151 ppm range owing to the 58 sp^2-carbons of the C_{60} skeleton and two peaks at 60.10−66.64 ppm ($^1J_{C-P}$ = 142.3−145.0 Hz for **4a**−**c** and 58.3 Hz for **4d**) and 78.20−78.58 ppm ($^4J_{C-P}$ = 4.6−5.0 Hz for **4a**−**c** and 3.7 Hz for **4d**) for the two sp^3-carbons of the C_{60} cage, consistent with its C_1 molecular symmetry. The observed smaller coupling constants (J_{C-P}) for both sp^2- and sp^3-carbons of **4d** bearing $P(O)Ph_2$ had precedent in the literature.[3a,b] The chemical shift (ca. 78.5 ppm) of the fullerenyl sp^3-carbon connected to the acetoxy group in **4a**−**d** was very close to that of similar 1,4-adducts reported previously by us.[7d,10] In addition, the ^{13}C NMR and FT-IR spectra of **4a**−**d** showed peaks at 169.55−170.06 ppm and 1745−1752 cm^{-1}, further confirming the presence of an ester group.

Further investigations revealed that both singly bonded dimers **2a**−**d** and hydrofullerenes **3a**−**d** could be converted efficiently to acetoxylated fullerenes **4a**−**d**, and hydrofullerenes **3a**−**d** could be transformed to singly bonded dimers **2a**−**d**. The reaction conditions and product yields are summarized in Tables 4−6.

It should be noted that the addition of acetic acid was required to increase the yield of acetoxylated product **4d** starting from both dimer **2d** and hydrofullerene **3d**, yet some amount of C_{60} was formed in these cases (Tables 4 and 5). In contrast, DMAP was added in the conversion of hydrofullerene **3d** to dimer **2d** to achieve higher product yield, while C_{60} (13%) was also isolated (Table 6).

Inert atmosphere was necessary to get the clean products for the reaction of C_{60} with **1**, especially **1d**. We propose a possible mechanism for the reaction of C_{60} with **1a**−**d** giving three different types of products (Scheme 1) based on the previous literature.[7,8,11]

Phosphorus radical **5**, generated from a phosphonate ester or phosphine oxide by $Mn(OAc)_3$, adds to C_{60} to give fullerenyl radical **6**, which is in equilibrium with fullerenyl radical **7**. Homocoupling of radical **7** affords singly bonded dimer **2**, while hydrogen abstraction of radical **6** produces hydrophosphorylated fullerene **3**. Reaction of radical **7** with excess $Mn(OAc)_3$ furnishes acetoxylated fullerene **4**.

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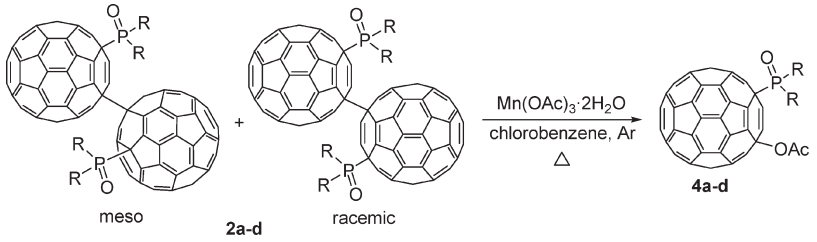
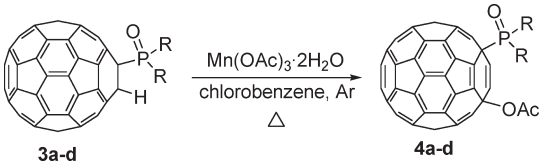
Table 4. Reaction Conditions and Product Yields for the Conversion of Dimers 2 to Acetoxylated Fullerenes 4



substrate **2**	molar ratio of **2**/Mn(III)	product	temp (°C)[a]	reaction time (min)	yield of **4** (%)
2a	1:20	**4a**	135	20	67
2b	1:20	**4b**	135	30	68
2c	1:20	**4c**	135	20	73
2d	1:20[b]	**4d**	70	30	56[c]

[a] Oil bath temperature. [b] 40 equiv of AcOH was added. [c] 22% of C_{60} was also obtained.

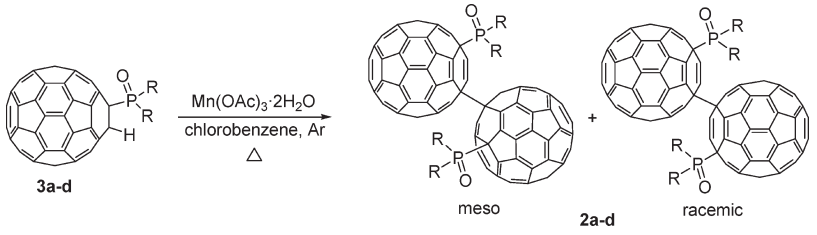
Table 5. Reaction Conditions and Product Yields for the Conversion of Hydrofullerenes 3 to Acetoxylated Fullerenes 4



substrate **3**	molar ratio of **3**/Mn(III)	product	temp (°C)[a]	reaction time (min)	yield of **4** (%)
3a	1:10	**4a**	135	20	70
3b	1:10	**4b**	135	25	76
3c	1:10	**4c**	135	20	78
3d	1:10[b]	**4d**	70	60	32[c]

[a] Oil bath temperature. [b] 20 equiv of AcOH was added. [c] 39% of C_{60} was also obtained, and 22% of **3d** was recovered.

Table 6. Reaction Conditions and Product Yields for the Conversion of Hydrofullerenes 3 to Dimers 2



substrate **3**	molar ratio **3**/Mn(III)	product	temp (°C)[a]	reaction time (min)	yield of **2** (%)
3a	1:1.5	**2a**	135	20	88
3b	1:1.5	**2b**	135	30	89
3c	1:1.5	**2c**	100	20	90
3d	1:1.5[b]	**2d**	60	5	84[c]

[a] Oil bath temperature. [b] 1 equiv of DMAP was added. [c] 13% of C_{60} was also obtained.

The postulated mechanisms shown in Scheme 1 can also explain all phenomena observed in the aforementioned experiments. Thin-layer chromatography (TLC) monitoring indicated that dimer **2** was formed and eventually disappeared in the reaction of C_{60} with **1a**−**d**, affording both hydrofullerenes **3a**,**b** and acetoxylated fullerenes **4a**−**d**. As shown in Scheme 1, both hydrofullerene **3** and acetoxylated fullerene **4** are formed via fullerenyl radicals **6** and **7**, which are in equilibrium with dimer **2**. The existence of the equilibrium was evident from the detection of the ESR signal of the dissociated monomer radical $\cdot C_{60}P(O)R_2$ by heating dimer **2**.[8] As the reaction proceeds to completion, consumption of fullerenyl radicals **6** and **7** will result in the disappearance of dimer **2**. The failure to observe dimer **2c** and **2d** in the formation of hydrofullerenes **3c** and **3d** probably arose

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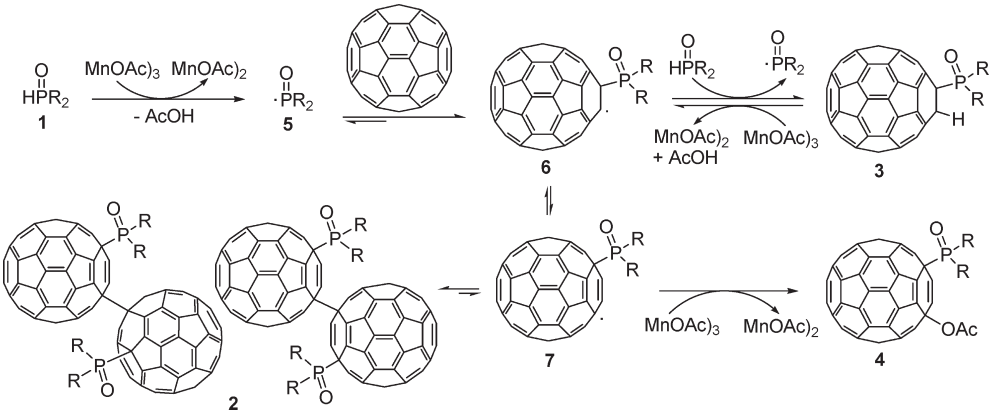
Scheme 1. Proposed Possible Reaction Mechanism



from the faster hydrogen abstraction of **1c** and **1d** by fullerenyl radical **6** due to the weaker P−H bond in the substrates. The transformations from **3** to **2**, **3** to **4**, and **2** to **4** can also be elucidated by the proposed mechanism. Hydrofullerene **3** contains a weak acidic C_{60}−H bond; thus, fullerenyl radical **6** could be formed from hydrofullerene **3** in the presence of $Mn(OAc)_3$. The subsequent processes are the same as the pathways leading to **2** and **4** from radical **7**. Another evidence for the proposed mechanism came from the fact that dimer **2** was also formed and then consumed during the conversion of **3a**−**d** to **4a**−**d**.

The addition of DMAP increased the product yield of **2d** (Table 1) and also helped consume the most facilely generated byproduct **3d** from the $Mn(OAc)_3$-mediated reaction of C_{60} with **1d** because DMAP could deprotonate **3d** to give anion **3d**$^-$, which was oxidized to radical **6d**, and then coupled to afford dimer **2d** via radical **7d**. The required addition of DMAP for the $Mn(OAc)_3$-mediated conversion of **3d** to **2d** (Table 6) can be explained in the same way. Acetic acid was demanded for the formation of acetoxylated fullerene **4d** in the $Mn(OAc)_3$-promoted reaction of C_{60} with **1d** (Table 3) probably due to the reason that acetic acid could facilitate the acetoxylation of radical **7d** and thus diminished the formation of dimer **2d**. The necessary addition of AcOH in the conversion from **2d** to **4d** (Table 4) and from **3d** to **4d** (Table 5) could be interpreted similarly. In addition, some amount of C_{60} was generated in these conversions probably because radical **7d** tended to decompose more rapidly to give C_{60} than **7a**−**c**.

CONCLUSION

We have successfully realized the reaction of C_{60} with phosphorus-centered radicals, generated from phosphonate esters or phosphine oxide by $Mn(OAc)_3$. Depending on the reaction conditions, three different types of phosphorylated fullerene derivatives, that is, singly bonded fullerene dimers **2**, hydrofullerenes **3**, and acetoxylated fullerenes **4**, could be selectively obtained. Interconversions among the three types of phosphorylated fullerene derivatives were also achieved. It was found that both singly bonded dimers **2** and hydrofullerenes **3** could be converted efficiently to acetoxylated fullerenes **4**, and hydrofullerenes **3** could be transformed to singly bonded dimers **2**. A possible reaction mechanism was proposed to explain the formation and interconversion of the fullerene products.

EXPERIMENTAL SECTION

$Mn(OAc)_3$-Mediated Reaction of C_{60} with 1d Affording Dimer 2d. A mixture of C_{60} (36.0 mg, 0.05 mmol), **1d** (20.2 mg, 0.10 mmol), $Mn(OAc)_3\cdot 2H_2O$ (80.4 mg, 0.30 mmol), and 4-(dimethylamino)pyridine (6.1 mg, 0.05 mmol) was dissolved in chlorobenzene (10 mL) and stirred at 60 °C (oil bath temperature) under argon atmosphere for 20 min. The reaction mixture was poured onto a silica gel column and eluted with CS_2 to afford recovered C_{60} (24.4 mg, 68%) and then with CS_2/CH_2Cl_2 (10:1) to give dimer **2d** (13.2 mg, 29%).

Spectral Data of 2d. ^{1}H NMR (300 MHz, CS_2−$CDCl_3$) δ 7.16−7.62 (m, 12H, meso and racemic), 8.27−8.37 (m, 8H × 0.49, minor), 8.50−8.61 (m, 8H × 0.51, major); ^{13}C NMR (100.6 MHz, CS_2−$CDCl_3$ with $Cr(acac)_3$ as relaxation reagent) δ 67.45 (d, J_{P-C} = 61.9 Hz, sp^3-C of C_{60}, meso or racemic), 67.51 (d, J_{P-C} = 61.8 Hz, sp^3-C of C_{60}, meso or racemic), 68.09−68.24 (sp^3-C of C_{60}, meso and racemic), 128.03 (d, J_{P-C} = 11.5 Hz, *o*-CH, meso or racemic), 128.04 (d, J_{P-C} = 11.4 Hz, *o*-CH, meso or racemic), 128.09 (d, J_{P-C} = 11.6 Hz, *o*-CH, meso and racemic), 129.29 (d, J_{P-C} = 99.3 Hz, PC, meso and racemic), 132.17 (d, J_{P-C} = 2.1 Hz, *p*-CH, meso or racemic), 132.25 (d, J_{P-C} = 2.2 Hz, *p*-CH, meso or racemic), 132.51 (*p*-CH, meso and racemic), 133.62 (d, J_{P-C} = 7.5 Hz, *m*-CH, meso or racemic), 133.82 (d, J_{P-C} = 8.8 Hz, *m*-CH, meso and racemic), 134.00 (d, J_{P-C} = 8.4 Hz, *m*-CH, meso or racemic), 137.76 (d, J_{P-C} = 4.3 Hz), 137.79 (d, J_{P-C} = 4.6 Hz), 138.09, 138.18 (d, J_{P-C} = 3.1 Hz), 138.27, 138.52, 138.88, 139.14 (d, J_{P-C} = 4.3 Hz), 139.29 (d, J_{P-C} = 4.1 Hz), 140.62, 140.69, 141.41, 141.58, 141.67, 141.69, 142.33, 142.37, 142.41, 142.51, 142.56, 142.66, 142.82, 142.90, 142.99, 143.01, 143.08, 143.12, 143.33, 143.36, 143.71, 143.87, 143.92, 143.94, 144.16, 144.21, 144.31, 144.35, 144.41, 144.58, 144.61, 145.06, 145.08, 145.11, 145.19, 145.42, 145.46, 145.52, 146.65, 146.69, 146.72, 146.93, 147.24, 147.36, 147.40, 147.44, 147.80 (d, J_{P-C} = 4.9 Hz), 148.43, 148.50, 148.60, 148.64, 149.11 (d, J_{P-C} = 5.6 Hz), 149.30, 149.51 (d, J_{P-C} = 6.8 Hz), 150.09, 150.21, 150.40, 150.93, 152.42, 152.52, 156.51, 156.89; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.07 (major), 29.70 (minor); FT-IR ν/cm^{-1} (KBr) 2920, 1461, 1435, 1210, 1190, 1115, 1098, 876, 843, 818, 747, 723, 697, 613, 558, 526; UV−vis λ_{max}/nm (log ε) (CHCl3) 258 (5.28), 324 (4.83), 444 (4.08); HRMS (−ESI): calcd for $C_{72}H_{10}PO$ [M/2]$^-$ 921.0469, found 921.0478.

General Procedure for the $Mn(OAc)_3$-Mediated Reaction of C_{60} with 1a−d Affording Hydrofullerenes 3a−d. A mixture of C_{60} (36.0 mg, 0.05 mmol), **1** (0.50 mmol for **1a** and **1b**; 0.25 mmol for **1c** and **1d**), and $Mn(OAc)_3\cdot 2H_2O$ (0.10 mmol for **1a** and **1b**; 0.05 mmol for **1c** and **1d**) was dissolved in chlorobenzene (10 mL) and stirred at a given temperature for the desired time under argon atmosphere (monitored by TLC). The reaction mixture was poured onto a

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silica gel column and eluted with CS_2 to afford recovered C_{60} and then with CS_2/AcOEt (10:1) to give hydrofullerenes **3a**−**d**.

Spectral Data of 3b. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.66 (t, J = 7.0 Hz, 6H), 4.66−4.76 (m, 4H), 7.22 (d, $^3J_{P-C}$ = 29.6 Hz, 1H); ^{13}C NMR (75.5 MHz, CS_2−$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 16.69 (d, $^3J_{P-C}$ = 5.5 Hz, CH_3), 56.30 (1C, sp^3-C of C_{60}), 64.72 (d, $^2J_{P-C}$ = 7.3 Hz, OCH_2), 65.48 (1C, d, $^1J_{P-C}$ = 149.9 Hz, sp^3-C of C_{60}), 135.20 (d, J_{P-C} = 1.8 Hz), 135.96 (d, J_{P-C} = 5.8 Hz), 140.00, 140.23, 141.24 (4C), 141.42, 141.67, 141.72 (4C), 142.28, 142.36, 142.95, 144.11, 144.37, 145.10, 145.18, 145.25 (4C), 145.56, 145.96, 146.03, 146.10, 146.17, 146.68, 146.94 (d, J_{P-C} = 5.8 Hz), 147.27 (d, J_{P-C} = 1.5 Hz), 148.81 (1C), 148.96 (1C), 151.58 (d, J_{P-C} = 6.2 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 21.44; FT-IR ν/cm^{-1} (KBr) 2975, 2901, 1512, 1462, 1428, 1389, 1365, 1254, 1183, 1160, 1095, 1046, 1019, 974, 960, 802, 763, 744, 702, 669, 632, 582, 572, 563, 548, 526; UV−vis λ_{max}/nm (log ε) ($CHCl_3$) 256 (5.11), 308 (4.63), 324 (4.63), 434 (3.66), 637 (2.72), 705 (2.72); HRMS (−ESI): calcd for $C_{64}H_{10}PO_3$ [M-H]$^-$ 857.0368, found 857.0382.

General Procedure for the Mn(OAc)$_3$-Mediated Reaction of C_{60} with 1a−d Affording Acetoxylated Fullerenes 4a−d. A mixture of C_{60} (36.0 mg, 0.05 mmol), **1** (0.10 mmol), Mn(OAc)$_3$·2H$_2$O (134.5 mg, 0.50 mmol), and AcOH (57 μL, 1.0 mmol in the case of **1d**) was dissolved in chlorobenzene (10 mL) and stirred at a given temperature for the desired time under argon atmosphere (monitored by TLC). The reaction mixture was poured onto a silica gel column and eluted with CS_2 to afford recovered C_{60} and then with CS_2/AcOEt (10:1) to give acetoxylated fullerenes **4**.

Spectral Data of 4a. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.52 (s, 3H, CH_3), 4.22 (d, 3H, J_{P-H} = 11.1 Hz, OCH_3), 4.24 (d, 3H, J_{P-H} = 11.1 Hz, OCH_3); ^{13}C NMR (75.5 MHz, CS_2−$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent) (all 1C unless indicated) δ 21.19 (CH_3), 54.86 (d, J_{P-C} = 7.4 Hz, OCH_3), 55.11 (d, J_{P-C} = 7.4 Hz, OCH_3), 60.10 (d, J_{P-C} = 145.0 Hz, sp^3-C of C_{60}), 78.27 (d, J_{P-C} = 4.6 Hz, sp^3-C of C_{60}), 137.35 (d, J_{P-C} = 3.2 Hz), 138.38 (d, J_{P-C} = 11.5 Hz), 138.73 (d, J_{P-C} = 5.4 Hz), 139.69 (d, J_{P-C} = 3.0 Hz), 140.08, 140.93, 141.08, 141.49, 141.74, 141.79, 141.86, 142.40 (2C), 142.42, 142.45, 142.53 (d, J_{P-C} = 1.4 Hz), 142.57, 142.83, 142.91 (d, J_{P-C} = 1.4 Hz), 142.97, 142.99, 143.03 (d, J_{P-C} = 2.9 Hz), 143.12, 143.30, 143.47, 143.49, 143.51, 143.55 (d, J_{P-C} = 2.2 Hz), 143.64, 143.71, 143.72 (d, J_{P-C} = 1.6 Hz), 143.92, 144.31 (d, J_{P-C} = 5.0 Hz), 144.32, 144.34, 144.49, 144.69 (d, J_{P-C} = 1.8 Hz), 144.82, 145.14 (d, J_{P-C} = 4.7 Hz), 145.17, 145.28, 145.39, 145.69, 146.31, 146.37, 146.52, 146.61 (d, J_{P-C} = 12.8 Hz), 146.69, 146.73, 146.78, 146.91 (d, J_{P-C} = 2.4 Hz), 147.16 (d, J_{P-C} = 7.8 Hz), 147.24, 147.89 (d, J_{P-C} = 1.4 Hz), 147.96, 147.98 (d, J_{P-C} = 3.1 Hz), 148.57, 148.82 (d, J_{P-C} = 11.7 Hz), 169.55 (C=O); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 16.23; FT-IR ν/cm^{-1} (KBr) 2947, 2847, 1749, 1429, 1363, 1263, 1221, 1187, 1046, 1027, 991, 841, 765, 670, 638, 624, 561, 525; UV−vis λ_{max}/ nm (log ε) ($CHCl_3$) 256 (4.94), 320 (4.46), 445 (3.73); HRMS (−ESI): calcd for $C_{64}H_9PO_5$ [M]$^-$ 888.0188, found 888.0203.

Spectral Data of 4b. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.56 (t, J = 6.6 Hz, 3H, OCH_2CH_3), 1.59 (t, J = 6.9 Hz, 3H, CH_2CH_3), 2.51 (s, 3H, CH_3), 4.51−4.68 (m, 4H, OCH_2CH_3); ^{13}C NMR (75.5 MHz, CS_2−$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent) (all 1C unless indicated) δ 16.63 (d, J_{P-C} = 5.8 Hz, OCH_2CH_3), 16.71 (d, J_{P-C} = 5.4 Hz, OCH_2CH_3), 21.42 (CH_3), 60.85 (d, J_{P-C} = 143.9 Hz, sp^3-C of C_{60}), 64.71 (d, J_{P-C} = 7.0 Hz, OCH_2CH3), 64.80 (d, J_{P-C} = 6.9 Hz, OCH_2CH_3), 78.58 (d, J_{P-C} = 4.7 Hz, sp^3-C of C_{60}), 137.47 (d, J_{P-C} = 3.2 Hz), 138.50 (d, J_{P-C} = 11.6 Hz), 138.73 (d, J_{P-C} = 5.3 Hz), 139.92 (d, J_{P-C} = 3.0 Hz), 140.26, 141.03, 141.22, 141.71, 141.95, 141.98, 142.07, 142.59 (3C), 142.61 (d, J_{P-C} = 1.6 Hz), 142.70 (d, J_{P-C} = 1.4 Hz), 142.75, 143.04 (d, J_{P-C} = 1.6 Hz), 143.06, 143.16 (2C), 143.31, 143.35 (d, J_{P-C} = 3.1 Hz), 143.48, 143.66, 143.70 (2C), 143.81 (d, J_{P-C} = 1.8 Hz), 143.87 (2C), 143.95 (d, J_{P-C} = 1.5 Hz), 144.11, 144.50, 144.54, 144.58 (d, J_{P-C} = 5.7 Hz), 144.65, 144.81 (d, J_{P-C} = 1.9 Hz), 145.03, 145.34, 145.37 (d, J_{P-C} = 4.6 Hz), 145.46, 145.56, 145.87, 146.49, 146.56, 146.71, 146.88, 146.92, 146.95, 147.18, 147.28 (d, J_{P-C} = 10.0 Hz), 147.53 (d, J_{P-C} = 1.7 Hz), 147.82 (d, J_{P-C} = 9.5 Hz), 148.12 (2C), 148.18 (d, J_{P-C} = 2.4 Hz), 148.76, 149.57 (d, J_{P-C} = 11.7 Hz), 170.06 (C=O); ^{31}P NMR (162 MHz, $CDCl_3$) δ 13.80; FT-IR ν/cm^{-1} (KBr) 2976, 1748, 1429, 1389, 1364, 1258, 1223, 1160, 1126, 1042, 1015, 990, 763, 670, 639, 624, 561, 524; UV−vis λ_{max}/nm (log ε) ($CHCl_3$) 259 (5.01), 320 (4.51), 445 (3.78); HRMS (−ESI): calcd for $C_{66}H_{13}PO_5$ [M]$^-$ 916.0501, found 916.0485.

Spectral Data of 4c. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (s, 3H, CCH_3), 1.35 (s, 3H, CCH_3), 2.50 (s, 3H, CH_3), 4.39−4.56 (m, 4H, CH_2); ^{13}C NMR (75.5 MHz, CS_2−$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent) (all 1C unless indicated) δ 21.42 ($OOCCH_3$), 21.47 (CCH_3), 21.59 (CCH_3), 32.96 (d, J_{P-C} = 7.8 Hz, CCH_3), 60.37 (d, J_{P-C} = 142.3 Hz, sp^3-C of C_{60}), 78.20 (d, J_{P-C} = 7.6 Hz, CH_2), 78.41 (d, J_{P-C} = 7.6 Hz, CH_2), 78.49 (d, J_{P-C} = 5.0 Hz, sp^3-C of C_{60}), 137.63 (d, J_{P-C} = 3.4 Hz), 138.86 (d, J_{P-C} = 11.8 Hz), 139.21 (d, J_{P-C} = 5.5 Hz), 140.20 (d, J_{P-C} = 3.2 Hz), 140.40, 141.27, 141.35 (d, J_{P-C} = 1.4 Hz), 141.75, 142.01, 142.08, 142.13, 142.68, 142.72, 142.75, 142.76 (d, J_{P-C} = 1.5 Hz), 142.81 (d, J_{P-C} = 1.6 Hz), 142.86, 143.13, 143.20 (d, J_{P-C} = 4.8 Hz), 143.21, 143.28, 143.30, 143.43, 143.62, 143.78 (2C), 143.80, 143.83 (d, J_{P-C} = 2.2 Hz), 143.94, 144.00 (d, J_{P-C} = 1.5 Hz), 144.03, 144.20, 144.58 (d, J_{P-C} = 5.7 Hz), 144.63 (2C), 144.80, 145.02 (d, J_{P-C} = 2.1 Hz), 145.11, 145.43 (d, J_{P-C} = 5.6 Hz), 145.47, 145.58, 145.70, 146.00, 146.36 (d, J_{P-C} = 12.7 Hz), 146.62, 146.66, 146.82, 147.00, 147.03 (d, J_{P-C} = 9.2 Hz), 147.04, 147.09, 147.20 (d, J_{P-C} = 2.5 Hz), 147.47 (d, J_{P-C} = 1.9 Hz), 148.10 (d, J_{P-C} = 1.6 Hz), 148.23 (d, J_{P-C} = 2.6 Hz), 148.27, 148.76 (d, J_{P-C} = 11.9 Hz), 148.88, 170.03 (C=O); ^{31}P NMR (162 MHz, $CDCl_3$) δ 5.47; FT-IR ν/cm^{-1} (KBr) 2920, 1752, 1512, 1463, 1429, 1366, 1273, 1221, 1061, 1003, 834, 767, 644, 622, 559, 524; UV−vis λ_{max} (log ε) ($CHCl_3$) 257 (4.97), 321 (4.48), 446 (3.75); HRMS (−ESI): calcd for $C_{67}H_{13}PO_5$ [M]$^-$ 928.0501, found 928.0522.

Spectral Data of 4d. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (s, 3H, CH_3) 7.62−7.74 (m, 6H), 8.37−8.43 (m, 4H); ^{13}C NMR (75.5 MHz, CS_2−$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent) (all 1C unless indicated) δ 21.52 (CH_3), 66.64 (d, J_{P-C} = 58.3 Hz, sp^3-C of C_{60}), 78.55 (d, J_{P-C} = 3.7 Hz, sp^3-C of C_{60}), 128.51 (2C, d, J_{P-C} = 12.1 Hz, o-CH), 128.56 (2C, d, J_{P-C} = 12.1 Hz, *o*-CH), 128.62 (d, J_{P-C} = 99.4 Hz, PC), 128.99 (d, J_{P-C} = 99.0 Hz, PC), 132.89 (2C, d, J_{P-C} = 8.9 Hz, *m*-CH), 132.93 (d, J_{P-C} = 2.2 Hz, *p*-CH), 132.96 (2C, d, J_{P-C} = 8.7 Hz, *m*-CH), 132.97 (d, J_{P-C} = 3.6 Hz, *p*-CH), 137.53 (d, J_{P-C} = 2.5 Hz), 139.13 (d, J_{P-C} = 4.4 Hz), 139.54 (d, J_{P-C} = 9.5 Hz), 140.20 (d, J_{P-C} = 2.8 Hz), 140.39, 140.90, 140.94, 141.81, 142.05, 142.08, 142.11, 142.54 (d, J_{P-C} = 1.4 Hz), 142.68, 142.69, 142.72, 142.73, 142.85, 143.05, 143.14, 143.27, 143.33, 143.38, 143.48, 143.61, 143.72, 143.76, 143.77 (d, J_{P-C} = 1.9 Hz), 143.85, 143.89, 143.95 (d, J_{P-C} = 2.4 Hz), 144.09 (d, J_{P-C} = 1.2 Hz), 144.21, 144.39, 144.64, 144.71, 144.75 (d, J_{P-C} = 1.8 Hz), 145.07 (d, J_{P-C} = 4.4 Hz), 145.19, 145.36 (d, J_{P-C} = 4.1 Hz), 145.45, 145.57, 145.64, 145.84, 146.61, 146.63, 146.82, 146.94, 146.98, 147.03, 147.37 (d, J_{P-C} = 5.8 Hz), 147.43, 148.04 (d, J_{P-C} = 1.5 Hz), 148.21 (d, J_{P-C} = 5.7 Hz), 148.22, 148.44 (d, J_{P-C} = 1.9 Hz), 148.47, 148.82, 150.05 (d, J_{P-C} = 7.2 Hz), 170.40 (C=O); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.08; FT-IR ν/cm^{-1} (KBr) 1745, 1435, 1362, 1222, 1205, 1184, 1114, 1097, 1012, 989, 725, 696, 614, 577, 560, 549, 526; UV−vis λ_{max}/nm (log ε) ($CHCl_3$) 259 (5.10), 326 (4.60), 447 (3.82); HRMS (−ESI): calcd for $C_{74}H_{13}PO_3$ [M]$^-$ 980.0602, found 980.0591.

General Procedure for the Converson of Dimer 2a−d to Acetoxylated Fullerenes 4a−d. A mixture of **2** (6.5−7.5 μmol), Mn(OAc)$_3$·2H$_2$O (20 equiv), and AcOH (40 equiv in the case of **1d**) was dissolved in chlorobenzene (3 mL) and stirred at a given temperature for the desired time under argon atmosphere (monitored by TLC). The reaction mixture was poured onto a silica gel column and eluted with CS_2/AcOEt (10:1) to give acetoxylated fullerenes **4**.

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General Procedure for the Converson of Hydrofullerenes 3a−d to Acetoxylated Fullerenes 4a−d. A mixture of **3** (12−16 μmol), $Mn(OAc)_3 \cdot 2H_2O$ (10 equiv), and AcOH (20 equiv in the case of **1d**) was dissolved in chlorobenzene (3 mL) and stirred at a given temperature for the desired time under argon atmosphere (monitored by TLC). The reaction mixture was poured onto a silica gel column and eluted with CS_2/AcOEt (10:1) to give acetoxylated fullerenes **4**.

General Procedure for the Converson of Hydrofullerenes 3a−d to Dimers 2a−d. A mixture of **3** (12−15 μmol), $Mn(OAc)_3 \cdot 2H_2O$ (1.5 equiv), and 4-(dimethylamino)pyridine (1 equiv in the case of **1d**) was dissolved in chlorobenzene (3 mL) and stirred at a given temperature for the desired time under argon atmosphere (monitored by TLC). The reaction mixture was poured onto a silica gel column and eluted with CS_2/AcOEt (10:1) (CS_2/CH_2Cl_2 = 10:1 in the case of **1d**) to get dimer **2**.

■ ASSOCIATED CONTENT

Supporting Information. ^1H NMR, ^{13}C NMR, and ^{31}P NMR spectra of **2d**, **3b**, and **4a−d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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