

## Copper-Mediated Cascade Synthesis of Open-Cage Fullerenes

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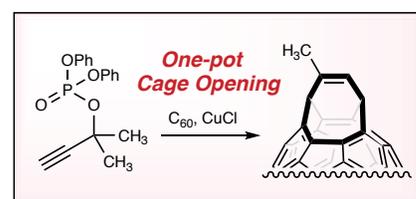
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Supporting Information Placeholder

**ABSTRACT:** An open-cage fullerene bearing an eight-membered ring orifice has been synthesized in one pot by the reaction of C<sub>60</sub> with propargylic phosphate in the presence of CuCl. The reaction cascade involves the transformation of the phosphate to the 1,3-dienyl phosphate, which enables the reaction with C<sub>60</sub> by [4 + 2] cycloaddition to form the cyclohexene-annulated intermediate, and subsequent intramolecular *syn*-elimination of the phosphodiester affords the cyclohexadiene-annulated fullerene derivative as the precursor for the open-cage fullerene.



Open-cage fullerenes have been attracted special interest for their ability to serve as scaffolds for building molecular containers for host-guest chemistry, and also as precursors for endohedral fullerenes that encage small atom(s) or molecule(s).<sup>1</sup> Recent studies have also shown that open-cage fullerenes are applicable for electron-accepting materials in organic photovoltaic devices.<sup>2</sup> The preparation of open-cage bisfulleroids bearing an eight-membered ring orifice via formation of cyclohexadiene-annulated fullerene derivatives (cyclohexadienofullerenes) followed by photochemical [4 + 4] and subsequent retro-[2 + 2 + 2] cycloaddition sequence is regarded as a highly reliable approach among the reported cage-opening reactions.<sup>3-7</sup> Furthermore, the enlargement of the eight-membered ring orifice of the bisfulleroid to a 12-membered one is feasible via photo-oxygenation with singlet oxygen.<sup>8</sup> Further orifice-enlargement is also possible through additional reactions, such as sulfur insertion and the reactions with hydrazones,<sup>9</sup> which furnish open-cage fullerenes possessing large orifices suitable for encapsulating small molecules.<sup>10</sup> In this scenario, the preparation of endohedral fullerenes can be achieved by subsequent orifice-closing reactions. To date, organic syntheses of H<sub>2</sub>@C<sub>60</sub>,<sup>11</sup> H<sub>2</sub>O@C<sub>60</sub>,<sup>12</sup> HF@C<sub>60</sub>,<sup>13</sup> and CH<sub>4</sub>@C<sub>60</sub><sup>14</sup> from C<sub>60</sub> have been accomplished through the formation of such bisfulleroids and their dioxxygenated intermediates.<sup>11</sup>

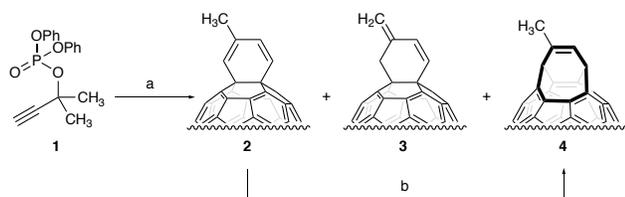
Nevertheless, the synthetic methodologies which allow access to cyclohexadienofullerenes and their analogues are limited, which is the key bottleneck in the development of applications in this area. In addition, most of them are rely

on the use of tethered diynes,<sup>4</sup> pyridazines,<sup>5</sup> or palladacyclopentadienes,<sup>6</sup> which shows the limited substrate scope of these approaches. In this context, the exploration of efficient approaches for the synthesis of cyclohexadienofullerenes and bisfulleroids is in great demand for developing a variety of open-cage and endohedral fullerenes. We recently demonstrated formal [2 + 2] and [4 + 2] cycloadditions between C<sub>60</sub> and propargylic esters under transition-metal catalysis.<sup>15</sup> During this study, we encountered an unprecedented formation of cyclohexadienofullerene and bisfulleroid via a one-pot CuCl-mediated reaction of C<sub>60</sub> with the easily accessible propargylic phosphate, which is depicted in Scheme 1.

The typical procedure for the reaction comprised mixing C<sub>60</sub> and propargylic phosphate **1** in 1,2-dichlorobenzene (1,2-DCB), and its treatment with CuCl at elevated temperatures under an argon atmosphere. The purification and isolation were accomplished by preparative HPLC to afford the brown-colored cyclohexadienofullerene **2**, the brown-colored alkylidenecyclohexene-annulated fullerene **3**, and the purple-colored open-cage bisfulleroid **4** (see Table 1). While the reactions did not proceed at 80 °C, they proceeded smoothly at above 110 °C and yielded the derivatives in reasonable yields. Under dark conditions, the thermal reaction of C<sub>60</sub> with **1** at 110 °C for 24 h afforded **2** as the major product, along with **3** and **4** as the minor products (entry 1). Increasing the reaction temperature to 180 °C shortened the reaction time from 24 to 3 h without significant changes in the yields (entry 2). In contrast, **4** was dominantly formed when the reaction was conducted under

ambient light illumination (entry 3). Notably, **2** is thermally stable but photosensitive, and isolated **2** transforms predominantly to **4** (56% yield) upon photo-irradiation using a LED lamp<sup>8c</sup> along with a retro-cycloaddition reaction to give C<sub>60</sub> (22% yield).

### Scheme 1



a) C<sub>60</sub>, CuCl, 1,2-DCB. Yields of **2**, **3**, and **4** are summarized in Table 1. b) CS<sub>2</sub>, *hν*, 56% (**4**).

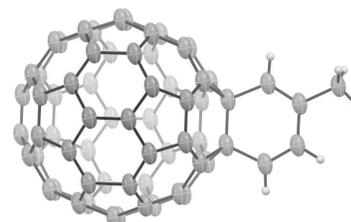
**Table 1.** CuCl-mediated reaction of C<sub>60</sub> with **1**<sup>a</sup>

entry	temp. / °C	condition	time / h	% yield of <b>2</b> <sup>b</sup>	% yield of <b>3</b> <sup>b</sup>	% yield of <b>4</b> <sup>b</sup>
1	110	Dark	24	24 (56)	9 (21)	5 (12)
2	180	Dark	3	24 (26)	2 (2)	Trace
3	180	Light <sup>c</sup>	4	– <sup>d</sup>	– <sup>d</sup>	35 (46)

<sup>a</sup>Reactions were performed in 1,2-DCB under argon. <sup>b</sup>The values in parentheses show conversion yields (conv. y.) based on the amount of C<sub>60</sub> consumed. <sup>c</sup>Reactions were performed under ambient light illumination. <sup>d</sup>Not isolated owing to contaminating complex byproducts.

The molecular structures of **2**, **3**, and **4** were characterized using MALDI-TOF MS spectrometry and NMR spectroscopy, as well as absorption spectroscopy. The <sup>1</sup>H NMR chemical shifts and the spin–spin couplings of **2**, **3**, and **4** are depicted in Figure S40 in the Supporting Information. The <sup>1</sup>H NMR spectrum of **2** exhibited a doublet at 1.58 ppm, which corresponds to a methyl proton, and also three methine signals as multiplet, double doublet, and doublet signals at ~5.54, 5.76, and 5.87 ppm, respectively, wherein, the observed small coupling constants are attributable to the allylic long-range spin–spin couplings.<sup>16</sup> The observed NMR spectra agree well with the cyclohexadiene-annulated structure of **2**. In contrast, the <sup>1</sup>H NMR spectrum of **4** exhibited similar chemical shifts but different coupling patterns as compared with that of **2**, and the appearance of signals indicating one methyl proton at 1.66 ppm as a doublet, and three methine signals at 5.65 ppm as a singlet, at 5.79 ppm as a doublet, and at 5.84 ppm as a double quartet signals, respectively, is in agreement with the bisfulleroid structure of **4**. In stark contrast, the signal corresponding to a methyl proton was not found in the <sup>1</sup>H NMR spectrum of **3**, and instead, a methylene proton signal at ca. 3.65 ppm as a multiplet, and two olefinic CH protons at ~4.78 and ~4.85 ppm as multiplets, and two additional olefinic CH

protons at 6.31 and 6.52 ppm as doublet signals, appeared respectively. The existence of a methyldiene structure in **3** was also supported by the HMQC NMR spectrum, where the two methylene-proton signals at 4.78 and 4.85 ppm correlate with the same carbon signal appearing at 115.26 ppm. The observed <sup>1</sup>H and <sup>13</sup>C chemical shifts of **2**, **3**, and **4** accord well with the ones calculated at the GIAO<sup>17</sup>-B3LYP<sup>18</sup>/6-31G(d)<sup>19</sup> level of theory. These sound agreements also support the structures of **2**, **3**, and **4**. The molecular structure of **2** was also confirmed by X-ray crystallography, as shown in Figure 1.<sup>20</sup>

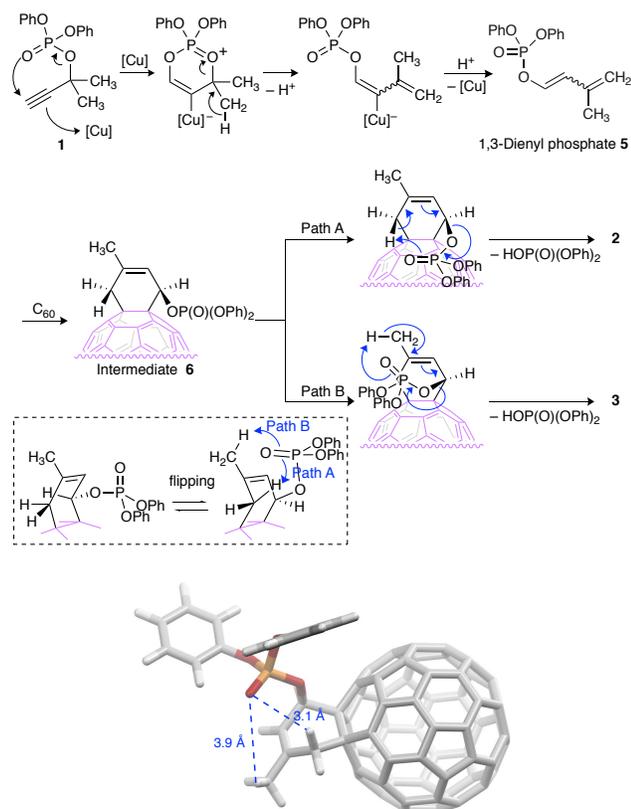


**Figure 1.** ORTEP drawing of **2** with thermal ellipsoids shown at the 30% probability level. Solvent molecules and disordered components are omitted for clarity.

A plausible reaction mechanism for the formation of **2** and **3** in the presented reaction is depicted in Scheme 2. It is likely that **1** is transformed first to the 1,3-dienyl phosphate **5** through 1,3-phosphoryloxy migration, followed by proton elimination and subsequent protodemetalation. In related work, Gevorgyan et al. reported the transformation of propargylic phosphates into 1,3-dienyl phosphates under gold catalysts,<sup>21</sup> and we propose that a similar transformation occurred in the presented reaction in the presence of CuCl. The subsequent [4 + 2] cycloaddition leads to the formation of the cyclohexene-annulated intermediate **6** in a pathway, which is similar to the reactions of C<sub>60</sub> with propargylic esters reported previously.<sup>15a</sup> In **6**, the ring flipping of the cyclohexene moiety causes a close contact between the oxygen of the phosphate group and the methylene proton of the opposite side as well as one of the methyl protons. Thus, we propose that subsequent intramolecular *syn*-elimination<sup>22</sup> of the phosphodiester through path A gives **2** or that through path B gives **3**, respectively. Such an elimination reaction does not occur during the thermal treatment of previously reported cyclohexene-annulated fullerene derivatives bearing carboxylate groups instead of phosphodiester groups.<sup>15a</sup> In fact, the close proximity (3.1 Å) between the oxygen atom of the phosphodiester group and the proton of the methyl group, which are at a distance that is close to the sum of their van der Waals radii (2.9 Å) was found in the DFT-optimized structure of a ring-flipped conformer of **6**, as shown in Figure 2. In addition, the proton of the methylene group is also located rather close to the oxygen atom with an interatomic distance of 3.9 Å. In this context, it is reasonable to conclude that the predominant formation of **2** over **4** is caused by the easier abstraction of the methylene proton, rather than the methyl proton. Subsequently, the transformation of **2** to **4** can be explained by invoking the well-established intramolecular [4 + 4] cycloaddition followed by retro-[2 + 2 + 2]

cycloaddition.<sup>3-7</sup> Furthermore, DFT calculations showed that **2** and **3** are 10.35 and 11.25 kcal mol<sup>-1</sup> higher in energy than **4**, respectively. However, the results presented do not exclude the possibility that the Cu-complex intermediate adds to C<sub>60</sub>, followed by the dissociation of Cu to yield **6**.<sup>23</sup> In addition, copper may be coordinated<sup>24</sup> to the phosphate group in intermediates such as **5** and **6**.

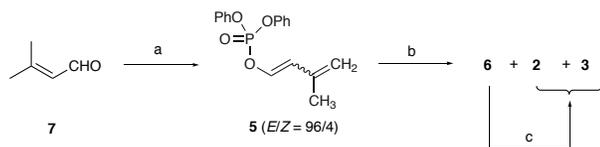
**Scheme 2. Plausible reaction pathways for the formation of **2** and **3**.**<sup>a</sup>



<sup>a</sup>Fullerenene cage carbons are highlighted in purple. Inset shows the flipping motion of the cyclohexene moiety in the cyclohexene-annulated intermediate **6**.

**Figure 2.** B<sub>3</sub>LYP/6-31G(d,p)-optimized structure of the ring-flipped conformer of **6**.

**Scheme 3**



a) 1. *t*-BuOK, THF, *N*-Methylpyrrolidinone, -78 °C; 2. ClP(O)(OPh)<sub>2</sub>, -78°C to r.t., 44% (**5**). b) C<sub>60</sub>, toluene, 80 °C, 12% (**6**), 12% (**2**), 3% (**3**). c) toluene, 80 °C, 69% (**2**), 9% (**3**).

To address the contribution of **5** and **6** for the formation of **2** and **3** in the CuCl-mediated reaction of C<sub>60</sub> with **1**, we investigated the formation of **5** from **1** and the reactivity of C<sub>60</sub> with **5**. Heating **1** at 110 °C in the presence of CuCl for 3

h resulted in the formation of **5** in 5% yield (*E/Z* = 78/22), and the reaction proceeded with the complete consumption of **1**. On the other hand, heating **1** at 80 °C in the presence of CuCl for 3 h resulted in the formation of **5** in a trace amount (NMR yield, <1%) and the reaction proceeded with the incomplete consumption of **1**, indicating that the rearrangement is incomplete at 80 °C. Alternatively, we synthesized **5** from 3-methyl-2-butenal (**7**) with diphenyl chlorophosphate in 44% yield as an *E*-enriched mixture (*E/Z* = 96/4) by employing methods for the synthesis of related compounds (see Scheme 3).<sup>25</sup> The reaction of C<sub>60</sub> with **5** did not proceed at ambient temperature but proceeded smoothly to afford **6** at 80 °C. The gradual formation of **2** and **3** was also observed in the HPLC traces of the reaction mixture with an increase in the reaction time. Accordingly, **6** was obtained in 12% (conv. y. 25% based on the amount of C<sub>60</sub> consumed) in addition to **2** (12%; conv. y., 29%) and **3** (3%; conv. y., 7 %) after heating for 5 h. Furthermore, the thermolysis of the isolated **6** at 80 °C for 24 h resulted in its excellent conversion to **2** (69%) and **3** (9%).

The molecular structure of **6** was characterized using MALDI-TOF mass spectrometry and NMR spectroscopy, as well as absorption spectroscopy. While the parent peak corresponding to **6** in the MALDI-TOF mass spectrum was very weak, strong fragment peaks due to the loss of [OP(O)(OPh)<sub>2</sub>] and [OP(O)(OPh)<sub>2</sub> + H] fragments in addition to those due to the loss of the whole addendum were observed, which suggest the facile elimination of the phosphodiester during mass spectrometry. The fragmentations were further confirmed with the MALDI-TOF/TOF mass spectra. Further, the <sup>1</sup>H NMR spectrum of **6** resembled that of a previously reported cyclohexene-annulated fullerene derivative bearing a carboxylate group instead of a phosphodiester group.<sup>15a</sup> The <sup>13</sup>C NMR spectrum of **6** showed 47 peaks in the ~120–160 ppm range, which are attributable to the sp<sup>2</sup> carbon atoms of the C<sub>60</sub> skeleton and the addendum, and are consistent with the C<sub>1</sub> symmetric structure. We revisited the HPLC traces of the reaction mixtures of the CuCl-mediated reactions of C<sub>60</sub> with **1** at 110 and at 180 °C (i.e., entries 1–3 in Table 1), and concluded that the formation of **6** was not detected possibly due to its thermal instability. On the other hand, when the reaction of C<sub>60</sub> with **1** was conducted at 80 °C in the presence of CuCl, **2** and **3** were formed scarcely. In the HPLC trace of the reaction mixture after heating for 22 h, a small peak was found at 4.8 min, the same retention time with that of **6**, in addition to the small peaks corresponding to **2** and **3**. In addition, the <sup>1</sup>H NMR spectrum of the reaction mixture suggested the formation of **5**. Overall, these results point to the validity of the proposed reaction mechanism depicted in Scheme 2.

In summary, we have developed a new strategy for the synthesis of open-cage fullerenes by utilizing the copper-mediated reaction cascades of C<sub>60</sub> with propargylic phosphate. A plausible reaction mechanism is proposed and the key intermediate species were also isolated and characterized. Additionally, we have found that 1,3-dienyl phosphate is useful for the preparation of open-cage fullerenes under mild conditions. We expect the presented reactions to

have a broad scope in terms of applicability for the preparation of new open-cage and endohedral fullerenes. Further investigation to evaluate the generality and substrate scope of the presented method for preparing new open-cage fullerenes remains ongoing, and relevant results will be reported as discoveries arise.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Synthetic procedures, HPLC chromatograms, mass spectra, absorption spectra, X-ray crystallographic data, NMR spectra, and computational results (PDF)

Crystallographic data of **2** (CIF)

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### Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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