

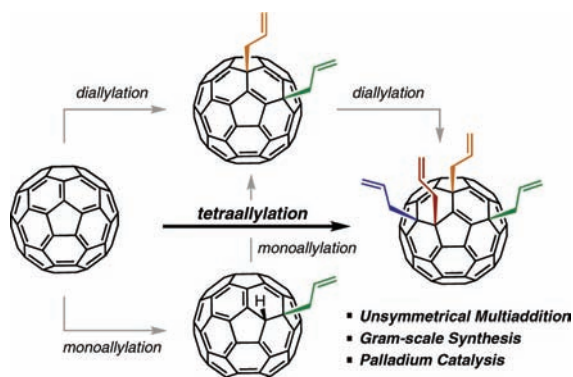
## Regioselective Unsymmetrical Tetraallylation of C<sub>60</sub> through Palladium Catalysis

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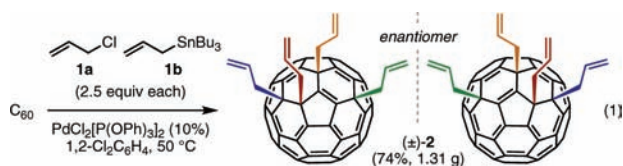
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Multiaddition reactions of fullerenes furnish aesthetically appealing molecular entities with many potential applications in chemical, biological, and materials science.<sup>1–3</sup> While various powerful multi-addition methods, as exemplified by organocopper additions and cycloadditions, have been developed,<sup>1</sup> high-yielding one-pot reactions that selectively occur with an unsymmetrical addition pattern are rare.<sup>2</sup> A direct reaction of this kind would open up new opportunities for the synthesis of chiral nanocarbons. We herein report our finding that a regioselective unsymmetrical tetraaddition<sup>4</sup> of the synthetically useful allyl group to C<sub>60</sub> can be achieved by palladium catalysis.<sup>5,6</sup> Further investigations not only implicated the involvement of an interesting allylpalladium mechanism but also led to the development of mono- and diallylation protocols.



Treatment of C<sub>60</sub> with CH<sub>2</sub>=CHCH<sub>2</sub>Cl (**1a**), CH<sub>2</sub>=CHCH<sub>2</sub>SnBu<sub>3</sub> (**1b**), and PdCl<sub>2</sub>[P(OPh)<sub>3</sub>]<sub>2</sub> in 1,2-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub> at 50 °C for 11 h (1: 2.5:2.5:0.1 C<sub>60</sub>/1a/1b/Pd molar ratio) afforded the tetraallylated fullerene **2** as a brown solid in 74% yield with virtually complete regioselectivity (eq 1).<sup>7</sup> As a minor product, the diallylated compound **4** (1,2-diallyl-C<sub>60</sub>) was obtained in 8% yield.<sup>8</sup> It is noteworthy that the reaction can be conducted on a gram scale.



The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **2** indicate four chemically nonequivalent allyl groups on the C<sub>60</sub> core. Further unambiguous proof of the unsymmetrical addition pattern was obtained by X-ray crystal structure analysis (Figure 1).<sup>9</sup> The crystals were composed of a 1:1 mixture of two mirror-image enantiomers.

The achievement of regioselective unsymmetrical tetraallylation is notable from both synthetic and mechanistic viewpoints. To gain mechanistic insight into this unprecedented multiaddition, we began by investigating stepwise reactions. When the reaction was conducted with reduced amounts of allylating agents (**1a** and **1b**),

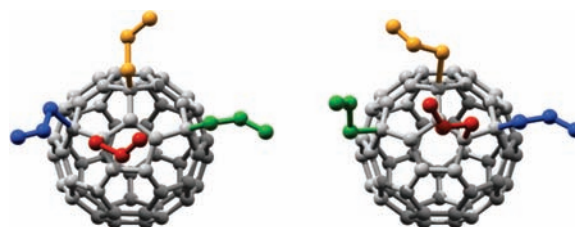
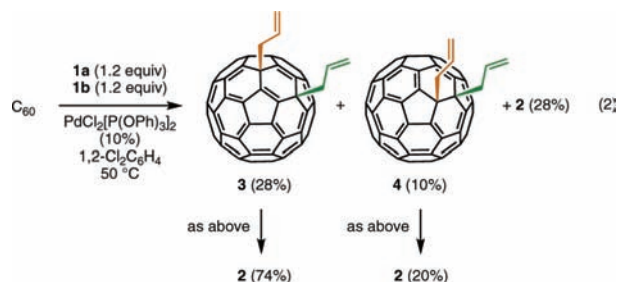


Figure 1. X-ray structures of the enantiomeric pair **2** observed in a crystal (H atoms have been omitted for clarity).

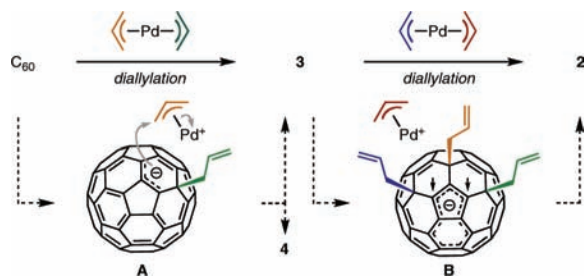
1,4-diallyl-C<sub>60</sub> (**3**; 28%)<sup>7b</sup> and 1,2-diallyl-C<sub>60</sub> (**4**; 10%)<sup>8</sup> were obtained along with **2** (28%) and C<sub>60</sub> (29%) (eq 2): It was subsequently found that the diallylation conditions could convert **3** to **2** smoothly (74%), while the diallylation of **4** was sluggish. These results indicate that the tetraallylation occurs by two sequential diallylations mainly via **3**. If this is the case, the regioselectivity in the initial diallylation of C<sub>60</sub> is estimated to be ~5:1 for 1,4-addition (vs 1,2-addition).



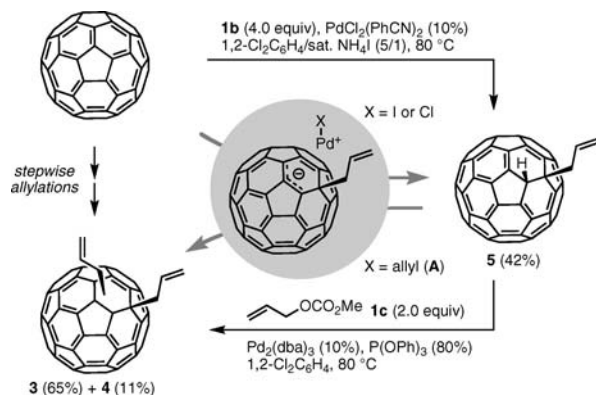
Our strategy for multiple allylation has been to utilize the unique amphiphilic nature of bis(π-allyl)palladium for fullerene functionalization. As elegantly demonstrated by Yamamoto, bis(π-allyl)palladium can react with both nucleophilic and electrophilic sites of some activated unsaturated compounds to produce 1,2-diallylation products.<sup>10</sup>

A mechanistic rationale for the regioselective tetraallylation of C<sub>60</sub> is shown in Scheme 1. Bis(π-allyl)palladium, generated from **1a**, **1b**, and Pd, first reacts as an allyl nucleophile with C<sub>60</sub> to give the delocalized fullereryl anion **A** having (π-allyl)Pd<sup>+</sup> as the counteranion. Formation of the second C<sub>60</sub>–allyl bond then occurs, likely through nucleophilic attack by the fullereryl anion on the electrophilic allyl on Pd, giving the diallylation products **3** and **4**. The preferential attack of fullereryl anion at the 4-position (leading to **3**) might be due to steric reasons.<sup>11,12</sup> The second nucleophilic attack of bis(π-allyl)palladium on **3** takes place in a manner that forms the stable 10π indenyl anion<sup>13</sup> **B** having (π-allyl)Pd<sup>+</sup> as the counteranion. The final C<sub>60</sub>–allyl bond-forming reactions at the indicated fullereryl carbons produce the enantiomeric pair **2**. The observed regiochemical outcome in the last step is consistent with the calculated HOMO of the anion **B**.<sup>9</sup>

With a mechanistic picture of the tetraallylation in hand, we next investigated the two possible elementary steps in the diallylation

**Scheme 1.** Possible Mechanism for Tetraallylation of C<sub>60</sub>

(nucleophilic allylation and electrophilic allylation) to assess the possible involvement of (fullerenyl)Pd<sup>II</sup> species such as **A** en route to the diallylation products **3** and **4**. First, we developed a new catalytic system for nucleophilic monoallylation of C<sub>60</sub>.<sup>7,14</sup> The treatment of C<sub>60</sub>, **1b**, and saturated aqueous NH<sub>4</sub>I solution with PdCl<sub>2</sub>(PhCN)<sub>2</sub> catalyst in 1,2-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub> at 80 °C afforded the hydroallylation product **5** in 42% isolated yield (Scheme 2). Controlling factors for this new catalytic process are discussed in the Supporting Information. Nevertheless, the reaction most likely proceeds through nucleophilic allylpalladation of C<sub>60</sub> followed by protonation of the (fullerenyl)Pd<sup>II</sup> species, as shown in Scheme 2.

**Scheme 2.** Stepwise Nucleophilic/Electrophilic Allylations of C<sub>60</sub>

The electrophilic allylation of **5** was also achieved through Pd catalysis. Thus, the reaction of **5** with allyl methyl carbonate (**1c**)<sup>5c</sup> in the presence of Pd<sub>2</sub>(dba)<sub>3</sub>/P(OPh)<sub>3</sub> catalyst afforded the diallylation products **3** (65%) and **4** (11%) (Scheme 2). A plausible mechanism would involve Pd<sup>0</sup>/Pd<sup>II</sup> redox catalysis via (i) oxidative addition of **1c** to Pd<sup>0</sup>, producing a (MeO)(π-allyl)Pd<sup>II</sup> species, (ii) deprotonation of **5**, generating (fullerenyl)(π-allyl)Pd<sup>II</sup> (**A**), and (iii) electrophilic C<sub>60</sub>-allyl bond formation (see above) with the regeneration of Pd<sup>0</sup>. Importantly, the same intermediate **A** intervenes in the diallylation of C<sub>60</sub> (Scheme 1). Consistently, the present reaction manifests a regioselectivity (**3/4** = 6:1) similar to that of the one-pot diallylation of C<sub>60</sub> [5:1 selectivity for 1,4-diallylation (eq 2)]. We believe that these results lend credence to our proposal that the tetraallylation of C<sub>60</sub> proceeds through consecutive nucleophilic/electrophilic allylations [likely via a bis(π-allyl)palladium intermediate].

In summary, a Pd-catalyzed tetraallylation of C<sub>60</sub> that selectively occurs with an unsymmetrical addition pattern has been established. Mechanistic analysis has revealed that both steric (for the first diallylation) and electronic (for the second diallylation) factors are responsible for the high regioselectivity. Moreover, interesting ramifications of the current mechanistic picture (Scheme 1) include significant opportunities for enantioselective synthesis of **2** by rendering the final C<sub>60</sub>-allyl bond-forming event enantioselective with

a chiral ligand on Pd. As the four chemically nonequivalent allyl groups should in principle be discriminated in further chemical transformations, a variety of chiral nanoarchitectures would be accessible.

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**Supporting Information Available:** Experimental procedures, characterization data for all new compounds, and crystallographic data for **2** and **4** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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