

**Synthesis of New Fullerene Dimers and Open-Cage Fullerenes by Solid-State and Liquid-Phase Reactions of C<sub>60</sub> with N-Containing Aromatics and with Organosilicon Compounds**

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We recently developed a new method to functionalize C<sub>60</sub> in the solid state, by the use of a mechanochemical technique of high-speed vibration milling. This method has been successfully applied to the first [2+2] dimerization of C<sub>60</sub>,<sup>1</sup> cross-dimerization of C<sub>60</sub> and C<sub>70</sub>,<sup>2</sup> trimerization<sup>3</sup> and [4+2] cycloadditions of C<sub>60</sub>,<sup>4</sup> in addition to the complexation with water-soluble host molecules<sup>5</sup> and a nucleophilic addition to C<sub>60</sub>.<sup>6</sup>

Particularly when the reaction was conducted with a nitrogen-containing (diaz) aromatic compound such as phthalazine, the [4+2] reaction took place, which was followed by extrusion of nitrogen and further addition or rearrangements to give novel C<sub>60</sub> derivatives, a dimer connected by a bicyclic framework **1** (by a solid-state reaction) and a bonzo-derivative of an open-cage fullerene **2** with an eight-membered ring orifice (by a thermal liquid-phase reaction).<sup>7</sup>

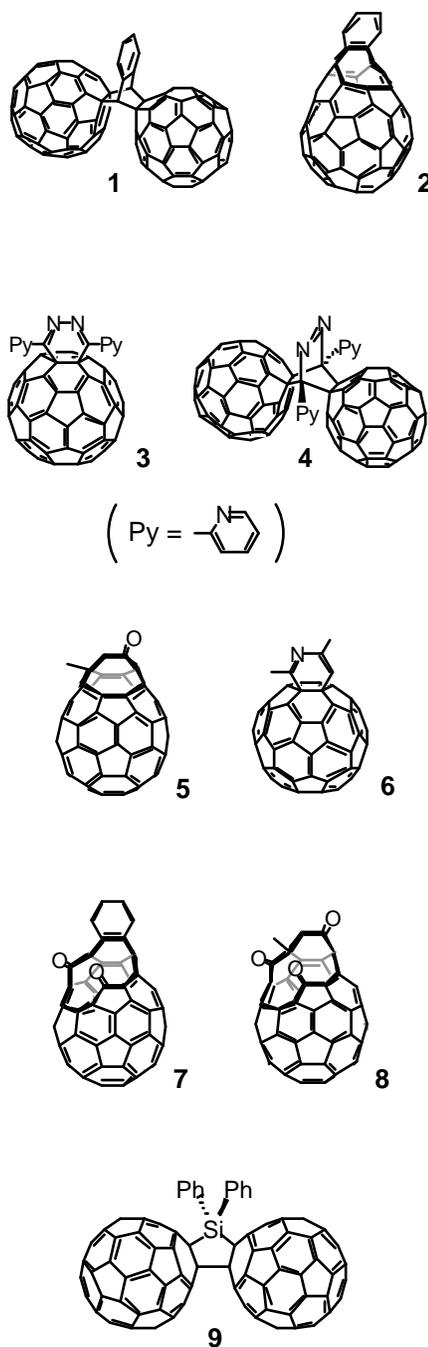
Similarly, when a solid-state reaction of C<sub>60</sub> was conducted with 3,6-di-2-pyridyl-1,2,4,5-tetrazine under high-speed vibration milling, the [4+2] addition/nitrogen-extrusion product **3** was formed quantitatively. This can further react with C<sub>60</sub> in solid state to give the dimer **4**. Both dimers **1** and **4** undergo the photochemical intramolecular [2+2] reaction between the two C<sub>60</sub> cages.

On the other hand, a thermal liquid-phase reaction of C<sub>60</sub> with 4,6-dimethyl-1,2,3-triazine at 180 °C afforded, after silica-gel chromatography, an open-cage fullerene derivative **5** with an eight-membered ring orifice in addition to an azacyclohexadiene fused C<sub>60</sub> **6**. A photochemical reaction of the open-cage fullerenes **2** and **5** with singlet oxygen was found to give the fullerene derivatives with 12-membered ring orifice **7** and **8** respectively.

Furthermore, the solid-state reaction of C<sub>60</sub> with dichlorodiphenylsilane and lithium metal afforded a new C<sub>60</sub> dimer with the two C<sub>60</sub> cages connected by a silicon atom and a single bond, **9**.

For the new fullerene dimers **1**, **4**, and **9**, the two C<sub>60</sub> cages were found to be able to communicate with each other upon electrochemical reduction, and were reduced stepwise but not at the same time for each of the three-wave redox steps as observed by cyclic voltammetry.

7. Murata, Y.; Komatsu, K. et al., *J. Org. Chem.*, **2001**, *66*, 7235.



References:

1. Wang, G-W.; Komatsu, K. et al. *Nature* **1997**, *387*, 583.
2. Komatsu, K. et al. *Chem. Commun.*, **2000**, 1583.
3. Komatsu, K. et al. *Chem. Lett.*, **2000**, 1016; Kunitake, M.; Komatsu, K. et al., *Angew. Chem. Int Ed.*, in press.
4. Murata, Y.; Komatsu, K. et al. *J. Org. Chem.*, **1999**, *64*, 3483.
5. Komatsu, K. et al. *J. Chem. Soc., Perkin 1*, **1999**, 2963.
6. Wang, G.-W.; Komatsu, K. et al. *Chem. Commun.* **1996**, 2059.