



# A rapid, two step construction of novel $C_{48}H_{24}$ and $C_{54}H_{24}$ polycyclic aromatic hydrocarbons represented on the $C_{60}$ -fullerene surface via a threefold intramolecular Heck coupling reaction

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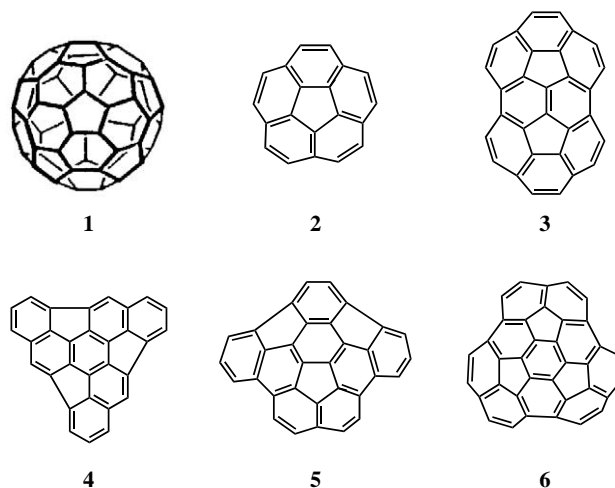
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**Abstract**—In a new approach towards deeper, higher order ‘bucky bowls’, two step syntheses of novel polycyclic aromatic hydrocarbons,  $C_{48}H_{24}$  and  $C_{54}H_{24}$ , having 13 and 16 rings, respectively, from readily available precursors and involving threefold palladium mediated intramolecular Heck coupling as the pivotal step is described. © 2002 Published by Elsevier Science Ltd.

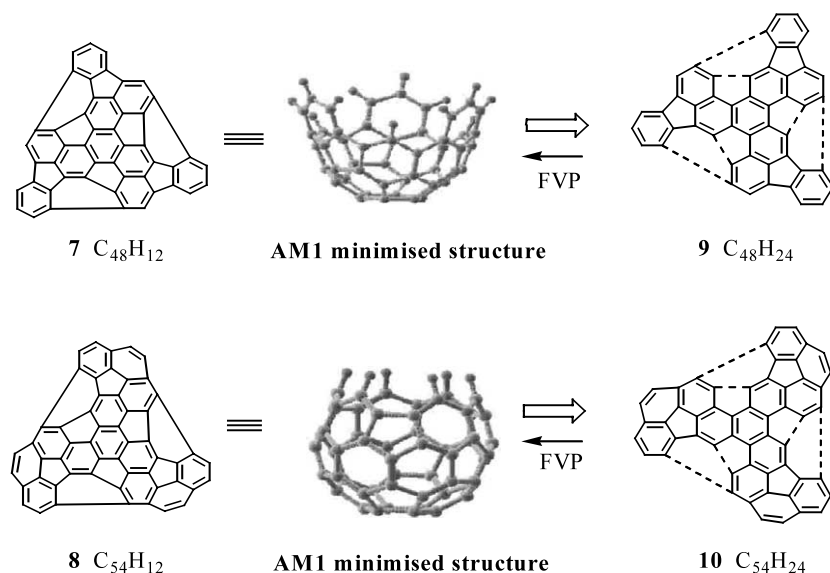
Ever since its discovery in the soot generated through arcing of graphite, the architecturally beautiful, high symmetry  $C_{60}$  **1** (‘bucky ball’) has caught the attention of synthetic chemists and its acquisition through rational or classical synthetic design has been a formidable challenge.<sup>1,2</sup> It is rather ironical that graphite vaporization leads only to cyclic cages and many spherical, high symmetry intermediates, ‘bucky bowls’, that must have been involved in the evolution of flat graphite to caged fullerenes have never been encountered. However, ‘bucky bowls’ which can be generated by ripping open the  $C_{60}$  cage along different symmetry pathways with appropriate attachment of hydrogen atoms constitutes an interesting family of hydrocarbons and can be expected to exhibit surface selective chemistry. These ‘bucky bowls’ can only be accessed through synthesis and their acquisition has been recognized as an important stepping stone in the direction of synthesis of  $C_{60}$  itself.<sup>2</sup> In the past decade, synthesis of several ‘bucky bowls’ such as  $C_{20}$ -corannulene **2**,<sup>3</sup>  $C_{30}$ -semifullerene **3** ( $C_{2v}$ -symmetry),<sup>4</sup>  $C_{30}$ -hemifullerene **4** ( $C_3$ -symmetry),<sup>5</sup>  $C_{32}$ -acenaphthoindacenopincene **5**<sup>6</sup> and  $C_{36}$ -circumtrindene **6**<sup>7</sup> has been accomplished through the efforts of research groups around the world. We too have been interested in the area<sup>3f,4c,5b,8</sup> and have conceptualized novel approaches to higher  $C_{60}$  fullerene fragments and deeper ‘bowls’,  $C_{48}H_{12}$ , **7** and  $C_{54}H_{12}$ , **8**. In this context, two  $C_3$ -symmetric aromatic hydrocarbons, the tridecacyclic,  $C_{48}H_{24}$ , **9** and hexadecacyclic,  $C_{54}H_{24}$ , **10** were

identified as the precursors of **7** and **8**, respectively (Scheme 1). The expectation was that under FVP conditions **9** and **10** could be ‘stitched up’ through sixfold cyclization (see dotted lines in **9** and **10**), a process that has proved singularly effective, though not always very efficient, in the synthesis of several ‘bucky bowls’ and very recently of  $C_{60}$ -fullerene.<sup>1–7</sup> Herein, we report an exceptionally short (two step) approach to the key precursors **9** and **10** from readily available starting materials.

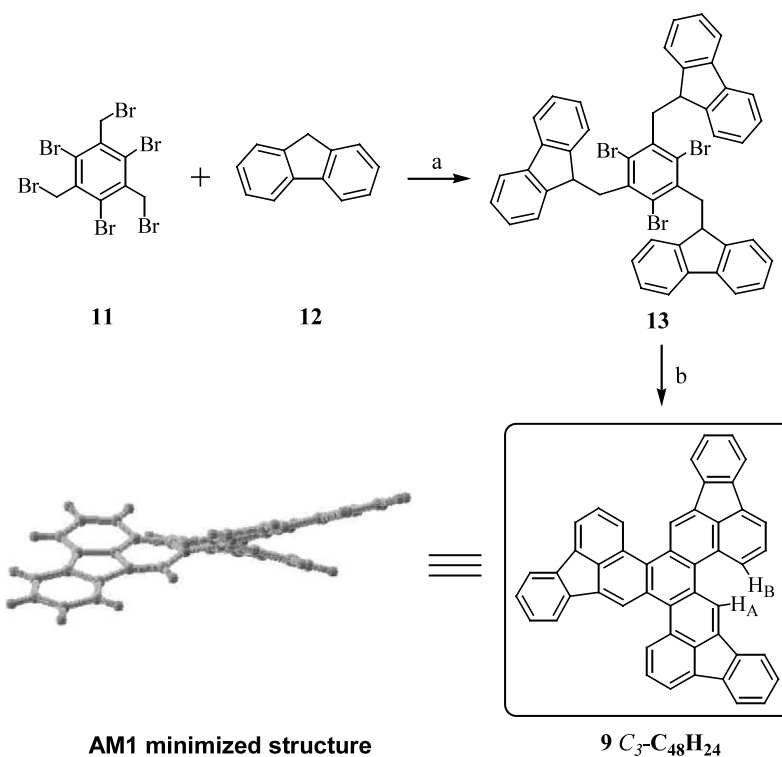


For the synthesis of the  $C_3$ -symmetric,  $C_{48}H_{24}$ , polycyclic aromatic hydrocarbon **9**, hexabromobenzene derivative **11** of the same symmetry was employed as

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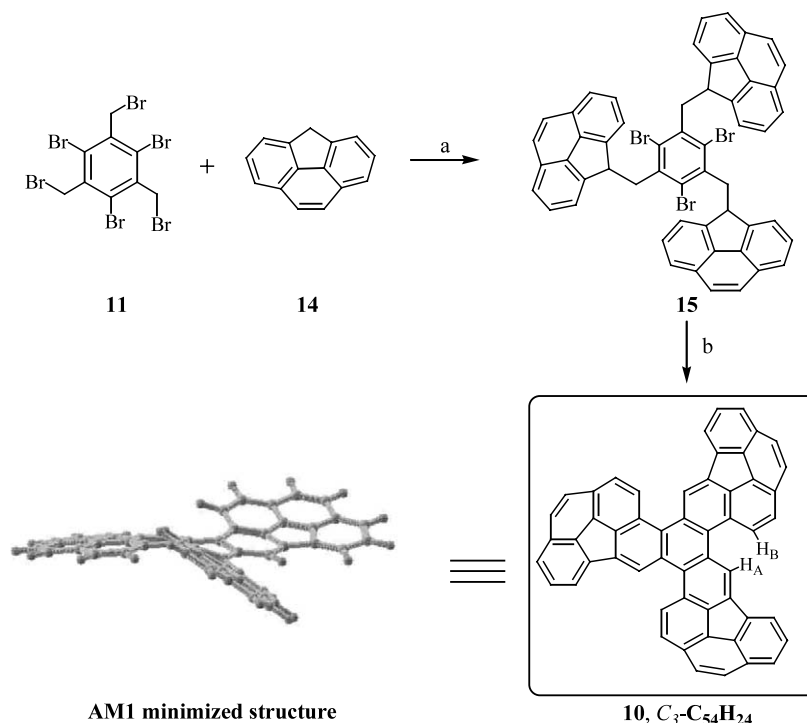
Scheme 1.

Scheme 2. Reagents and conditions: (a)  $n$ BuLi, THF, 70%; (b) Pd(OAc) $_2$ , BnMe $_3$ NBr, K $_2$ CO $_3$ , DMF, 140°C, 2 days, 22%.

the key starting material. Precursor **11** is readily obtainable from the commercially available mesitylene (1,3,5-trimethylbenzene) in two high yielding steps involving sequential nuclear bromination (Fe, Br $_2$ ) and benzylic bromination (Br $_2$ ,  $h\nu$ ) as reported recently.<sup>9</sup> Threefold displacement of the bromomethyl groups in **11** by the fluorenyl anion **12** was smooth and put in place all the 48-carbons to deliver **13** in good yield.<sup>10</sup> Reaction of **13** with palladium(II) acetate in the presence of BnMe $_3$ NBr in DMF solvent at elevated temperature resulted in threefold intramolecular Heck coupling to

deliver **9** which precipitated out of the reaction (Scheme 2).<sup>10</sup> The structure of this tridecacyclic product and its expected  $C_3$ -symmetry was revealed through detailed analysis of its  $^1$ H NMR data, particularly the  $^1$ H– $^1$ H COSY spectrum, with the presence of two highly deshielded protons  $H_A$  ( $\delta$  9.61, s, 3H) and  $H_B$  ( $\delta$  9.05, d,  $J=8.0$  Hz, 3H) in the fjord region.

The synthesis of the hexadecacyclic,  $C_3$ -symmetric,  $C_{54}H_{24}$ , **10** also emanated from the hexabromo precursor **11**. Triple displacement on **11** by the lithium anion,



**Scheme 3.** Reagents and conditions: (a) *n*BuLi, THF,  $-78^{\circ}\text{C}$ , 60%; (b) Pd(OAc)<sub>2</sub>, BnMe<sub>3</sub>NBr, K<sub>2</sub>CO<sub>3</sub>, DMF,  $140^{\circ}\text{C}$ , 2 days, 11%.

derived from the commercially available 4*H*-cyclopenta[*def*]phenanthrene **14**, furnished **15** (Scheme 3).<sup>10</sup> With the acquisition of all the requisite 54-carbon atoms in a single step, **15** was also subjected to three-fold Pd(II) mediated intramolecular Heck coupling as described above for **13** to yield **10** as a highly insoluble material that precipitated out from the reaction mixture (Scheme 3).<sup>10</sup> In view of its insolubility, the <sup>1</sup>H NMR and <sup>1</sup>H–<sup>1</sup>H COSY spectra of **10** could only be recorded in 1,1,1,2,2-tetrachloroethane-*d*<sub>2</sub> at  $127^{\circ}\text{C}$ . The exceptionally low field signals were ascribed to the fjord region protons H<sub>A</sub> ( $\delta$  10.04, s, 3H) and H<sub>B</sub> ( $\delta$  9.28, d, *J*=8.8 Hz, 3H).

We have outlined an exceptionally short (two-step) approach to polycyclic aromatic hydrocarbons C<sub>48</sub>H<sub>24</sub> and C<sub>54</sub>H<sub>24</sub> having 13 and 16 rings, respectively, from readily available precursors. The energy-minimized (AM1 level) structures of both **9** and **10** exhibit interesting propellor shaped topology. Efforts are underway to induce cyclization in **9** and **10** under FVP conditions. The general synthetic approach outlined here is being extended to assemble C<sub>60</sub>H<sub>30</sub>, the penultimate precursor of C<sub>60</sub>.

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10. Experimental procedure: synthesis of **9**: To a solution of fluorene **12** (369 mg, 2.22 mmol) in THF (20 ml) was added <sup>n</sup>BuLi (1.46 ml of 1.6 M in hexanes, 2.33 mmol) at  $-78^{\circ}\text{C}$  and the mixture was allowed to warm to  $-10^{\circ}\text{C}$  (3 h). The resulting red solution of the anion was treated with hexabromo compound **11** (400 mg, 0.673 mmol) in THF (8 ml) and after 30 min the reaction mixture was worked-up in the usual way. The crude product was charged on a silica gel column and elution with dichloromethane/hexane (1:9) furnished **13** (400 mg, 70% yield), mp  $240^{\circ}\text{C}$ , IR (KBr): 3061, 3016, 2939, 1475, 929, 756, 736  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.79 (d, 6H,  $J=7.5$  Hz), 7.35 (t, 6H,  $J=7.5$  Hz), 7.27–7.23 (m, 6H), 7.18 (t, 6H,  $J=7.2$  Hz), 4.58 (t, 3H,  $J=8.2$  Hz), 3.69 (d, 6H,  $J=8.4$  Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  146.3 (6C), 140.9 (6C), 139.5 (3C), 128.9 (3C), 127.3 (6C), 126.8 (6C), 124.7 (6C), 120.0 (6C), 45.1 (3C), 43.5 (3C); MS ( $m/z$ ): 849 ( $M^+$ ). Anal. calcd for C<sub>48</sub>H<sub>33</sub>Br<sub>3</sub>: C, 67.87; H, 3.91. Found: C, 67.62; H, 3.91. A mixture of **13** (50 mg, 0.059 mmol), Pd(OAc)<sub>2</sub> (13 mg, 0.059 mmol), BnMe<sub>3</sub>NBr (27 mg, 0.12 mmol), and K<sub>2</sub>CO<sub>3</sub> (80 mg, 0.59 mmol) in DMF (3 ml) was stirred at  $140^{\circ}\text{C}$  for 48 h. The mixture was cooled and the solid was filtered off and washed with ice-cold dichloromethane and acetone. The solid was suspended in aqueous sodium cyanide and stirred for 1 h and filtered and again washed with water and acetone to give **9** as a brown powder (8 mg, 22% yield), mp  $>300^{\circ}\text{C}$ , UV (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  = 240, 297, 379 nm; IR (KBr): 3054, 2921, 1603, 1445, 734  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  9.61 (s, 3H), 9.05 (d, 3H,  $J=8$  Hz), 8.23–8.21 (m, 3H), 8.16 (d, 3H,  $J=7$  Hz), 8.08–8.06 (m, 3H), 7.98–7.95 (m, 3H), 7.55–7.53 (m, 6H); MS ( $m/z$ ): 600 ( $M^+$ ) (100%), 299 ( $M^{2+}$ ) (40%); HRMS calcd for C<sub>48</sub>H<sub>24</sub>: 600.1878. Found: 600.1866. Synthesis of **10**: To a solution of 4*H*-cyclopenta[*def*]phenanthrene **14** (50 mg, 0.263 mmol) in THF (3 ml) was added <sup>n</sup>BuLi (0.18 ml, 1.6 M in hexanes, 0.289 mmol) at  $-78^{\circ}\text{C}$  and the mixture was stirred for 5 min. The resulting red solution was treated with the hexabromo compound **11** (49 mg, 0.083 mmol) in THF (2 ml). Usual work-up gave a residue which was charged on a silica gel column and eluted with dichloromethane/hexane (1:9) to furnish **15** (46 mg, 60% yield), mp  $312^{\circ}\text{C}$ , IR (KBr): 3039, 2922, 1441, 821, 728  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.86 (s, 6H), 7.82 (d, 6H,  $J=8.1$  Hz), 7.56–7.49 (m, 12H), 5.2 (t, 3H,  $J=8.1$  Hz), 4.00 (d, 6H,  $J=8.4$  Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  144.7 (6C), 139.6 (3C), 137.3 (6C), 128.9 (3C), 128.0 (6C), 127.3 (6C), 125.4 (6C), 123.3 (6C), 121.2 (6C), 47.4 (3C), 42.3 (3C); MS ( $m/z$ ): 921 ( $M^+$ ). Anal. calcd for C<sub>54</sub>H<sub>33</sub>Br<sub>3</sub>: C, 70.38; H, 3.61. Found: C, 69.88; H, 3.78. A mixture of **15** (40 mg, 0.043 mmol), Pd(OAc)<sub>2</sub> (10 mg, 0.045 mmol), BnMe<sub>3</sub>NBr (20 mg, 0.086 mmol), and K<sub>2</sub>CO<sub>3</sub> (59 mg, 0.43 mmol) in DMF (3 ml) was stirred at  $140^{\circ}\text{C}$  for 48 h. The mixture was cooled and the solid was filtered off and washed with ice-cold dichloromethane and acetone. The solid was suspended in aqueous NaCN solution and stirred for 2 h. It was again filtered and washed with water and acetone to give **10** as a dark brown powder 3 mg (11% yield), mp  $>300^{\circ}\text{C}$ , UV (1,1,2,2-tetrachloroethane):  $\lambda_{\text{max}}$  = 253, 333 (sh) nm; IR (KBr): 3040, 2924, 1403, 1247, 825, 729  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR (500 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>,  $127^{\circ}\text{C}$ ): 10.04 (s, 3H), 9.28 (d, 3H,  $J=8.8$  Hz), 8.42 (d, 3H,  $J=6.85$  Hz), 8.30 (d, 3H,  $J=8.7$  Hz), 8.10 (br s, 6H), 8.05 (d, 3H,  $J=7.85$  Hz), 7.85 (t, 3H,  $J=7.5$  Hz); MS (MALDI-TOF):  $m/z$  (%) = 673.2 (100), ( $M^+$ ) (calcd for C<sub>54</sub>H<sub>24</sub> = 672.78).