A Parallel Library of all Seven $A_2 + B_2 + C_2$ T_h Regioisomeric Hexakisadducts of Fullerene C_{60}: Inspiration from Werner's Octahedral Stereoisomerism**

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Compact multivalent molecules can be viewed as ideal cores for the synthesis of libraries with very high diversity.[1–3] Cubane and trimesic acid-based scaffolds,[2] among others,[3] have been proposed for this purpose. Extending functional valency of these cores to octahedral or higher symmetry objects, while maintaining control of the spatial directivity of branches derived from their anchor points, would give access to "spherical" diversity suitable for probing cell surface receptors and signaling pathways. Based on these premises, octahedral stereochemistry,[4, 5] originally proposed by Werner to explain the configuration of transition metal complexes, inspired us to develop approaches to novel scaffolds with potential applications in combinatorial chemistry.

With its six coordination sites, the octahedron has a much more complex stereochemistry than its tetrahedron counterpart, the latter possessing only configurational isomerism.[6] In fact, if six *different* groups are placed at the O_h sites, up to fifteen diastereomers can be generated.[5b] In a simpler case, the spatial arrangement of three pairs ($A_2 + B_2 + C_2$) of monodentate ligands at the O_h sites in transition metal complexes leads to the five diastereomers **1a**–**e** (Figure 1). In practice, this analysis is complicated by the lability of the ligands, hence bridging bi- or multidentate coordinating groups are required to gain control over molecular configuration.[5, 7] This aspect restricts the number of isomers that can be prepared and does not lead to the easy elaboration of libraries with different groups at all six O_h positions.

The high symmetry of C_{60} provides an opportunity to expand the diversity of molecular libraries by using a relatively compact (10-Å van der Waals radius "nanobead") and easily functionalizable spherical framework of thirty C=C bonds (Figure 2).[8, 9] Although this question has been addressed in part,[8–12] regio- and stereocontrolled additions to fullerenes remain a real challenge, and the functionalization of any of their double bonds, at will, is unthinkable at the present time.[8a] To simplify the problem by keeping the local symmetry to a maximum, one can make a useful analogy between C_{60} and Werner's octahedral framework (Figure 2, left).[9, 11] There are six symmetrically disposed double bonds situated at the vertices of an octahedron, which if functionalized selectively, give access to a variety of well-defined

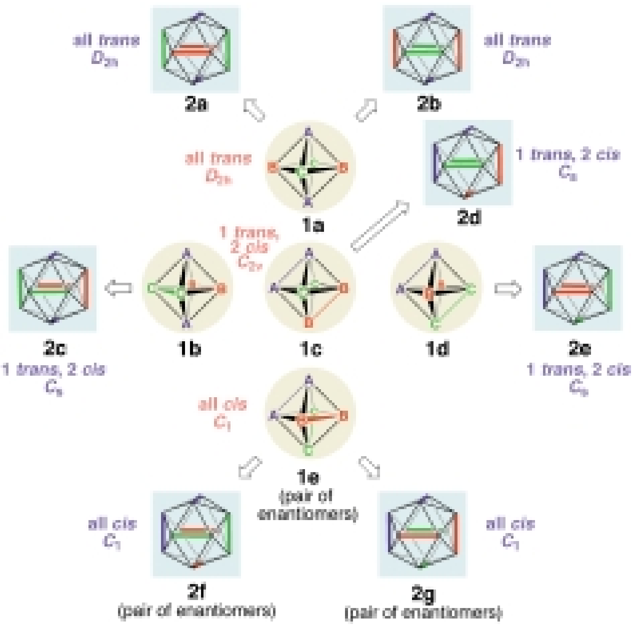

Figure 1. Stereoisomerism of $A_2 + B_2 + C_2$ addends within octahedral (**1a**–**e**) and pseudo-octahedral (T_h) topologies (**2a**–**g**).