

Regioselective *Bis*-Additions to Empty and Endohedral Clusterfullerenes: Tether or Cluster Control?

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Several strategies have been utilized to control the regiochemistry of multiple additions on fullerene cages, most notable being the tether-directed-remote functionalization method, originally introduced by Diederich et al. In this method, two reactive centers, separated by a rationally designed tether (preferably rigid and with the appropriate length to guide the *bis*-addition regioselectively) are attached to the fullerene cages, see structures at the left. This strategy works well with C₆₀ and to some degree with C₇₀, but surprisingly it fails completely when applied to endohedral clusterfullerenes, such as Sc₃N@C₈₀. In these cases only one reactive center leads to a fullerene adduct while the other remains unattached. These observations are interesting because independent *bis*-adducts (non-tethered) are easily formed without difficulty, see structure at the right. More interestingly, the number of *bis*-adduct regioisomers that form is very limited, indicating that the cluster inside must play an important role in directing the exohedral additions. These results will be presented and discussed in detail.

