

## New Method of Selective Electrophilic Addition to Trifluoromethyl Fullerenes

by James Whitaker

Perfluoroalkylfullerenes (PFAFs) constitute an intriguing class of compounds due to their high thermal stability, stability of the corresponding anions, and unique electrochemical behavior. PFAFs have shown promise for the development of advanced photovoltaic cells and other applications. Recently, rapid developments in the preparatory methodologies of trifluoromethylated fullerenes (TMF) have resulted in the isolation and structural characterization of more than 60  $\text{CF}_3$  derivatives. These TMFs display a wide range of first reduction potentials (0.8 V); furthermore, it is known that the reduction potentials of fullerene derivatives depend on the nature of the substituents and, especially, on their addition patterns.<sup>1</sup>

However, bare-cage fullerene addition reactions are notoriously difficult to control, and they often result in a large number of compositionally and isomerically different compounds exhibiting vastly different electron accepting properties. It was the goal of this work to develop a method, in which a wide range of addend types could be introduced to TMFs more regioselectively in the hopes of expanding the knowledge of basic fullerene science as well as to identify fullerene derivatives for use as suitable electron accepting materials in organic electronics and, more specifically, photovoltaics (OPVs).

In this work, a previously unreported TMF,  $p^3\text{-C}_{60}(\text{CF}_3)_4$ , was prepared. The corresponding dianion  $p^3\text{-C}_{60}(\text{CF}_3)_4^{2-}$  was generated by chemical reduction via potassium metal in THF. One of three electrophiles, either  $\text{BnBr}$ ,  $\text{EtBr}$ , or  $\text{ICl}_2\text{COOEt}$ , was added to the dianion solution in 10-fold excess (i.e., three separate reactions were investigated). The resulting reaction was quenched with trifluoroacetic acid (TFA). Using  $^{19}\text{F}$  NMR spectroscopy, APCI-MS, and HPLC the resulting crude material was characterized. In every case, APCI-MS indicated that one electrophile and one proton were successfully added to the cage.

This observation that only one electrophile adds to any one cage is presumably due to steric crowding around the active double bond on  $p^3\text{-C}_{60}(\text{CF}_3)_4$ . Additionally, each reaction resulted in a manageable number of isomers (< 5). The total number of isomers formed after the addition of TFA is misleading as the electrophile may have selectively added to a single carbon atom on the cage while the proton did not (Fig. 1).

This phenomenon was demonstrated by the simplification of the  $^{19}\text{F}$  NMR spectrum after the addition of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) to remove the cage proton. The cage can be protonated again with the addition of TFA resulting in the original  $^{19}\text{F}$  NMR spectrum. A consequence of the lability of the proton is that these compounds exhibit an irreversible first reduction.

These protonated TMFs offer an excellent opportunity to study a new class of fullerene acids.<sup>2</sup> The overall selectivity of these reactions can be attributed to the addition pattern of the  $\text{CF}_3$  groups on this newly characterized TMF,  $p^3\text{-C}_{60}(\text{CF}_3)_4$ . These  $\text{CF}_3$  groups constrain the LUMO resulting in one highly activated cage double bond. The hypothesis that the localized LUMO would increase selectivity was confirmed when these reactions were repeated with  $\text{C}_{60}(\text{CF}_3)_2^{2-}$  that does not have a localized LUMO. The selectivity of these reactions greatly decreased. ■

### About the Author

JAMES WHITAKER is in the fourth year of his PhD work in inorganic chemistry at Colorado State University working under the supervision of Steven Strauss and Olga Boltalina.

### References

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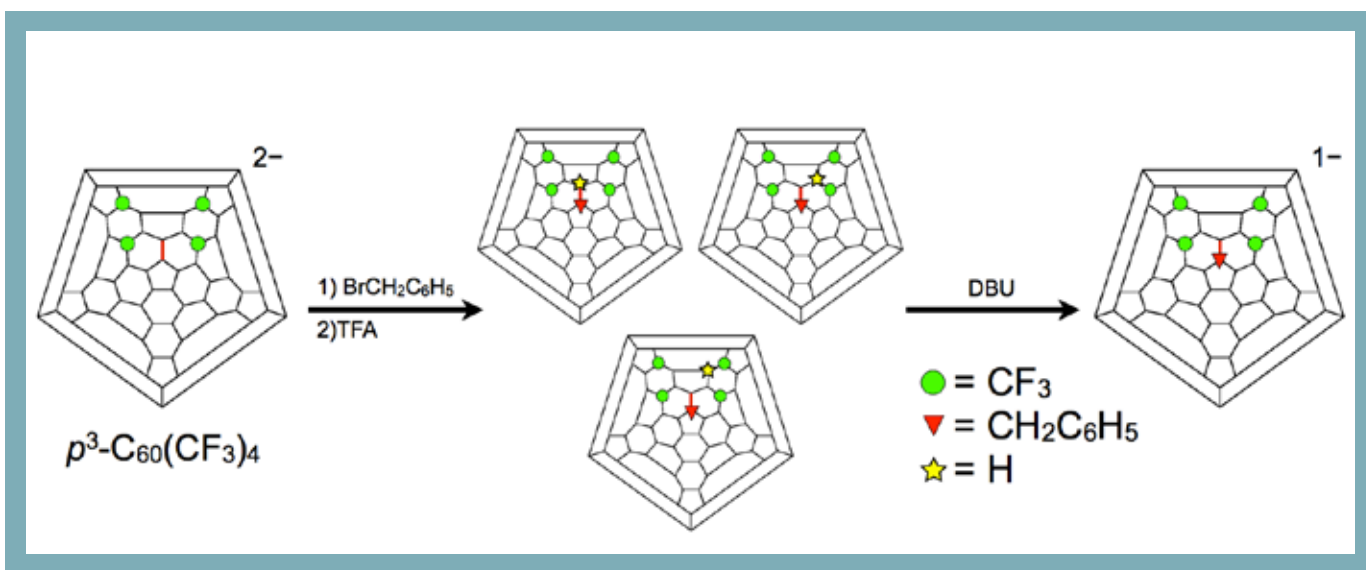


FIG. 1. Schlegel diagrams of  $p^3\text{-C}_{60}(\text{CF}_3)_4$  showing the activated double bond (red), the addition site of benzyl bromide, and the 3 protonation sites after acidification with trifluoroacetic acid.