BEYOND THE ICOSAHEDRON: THE POLYHEDRAL EXPANSION OF CARBORANES.

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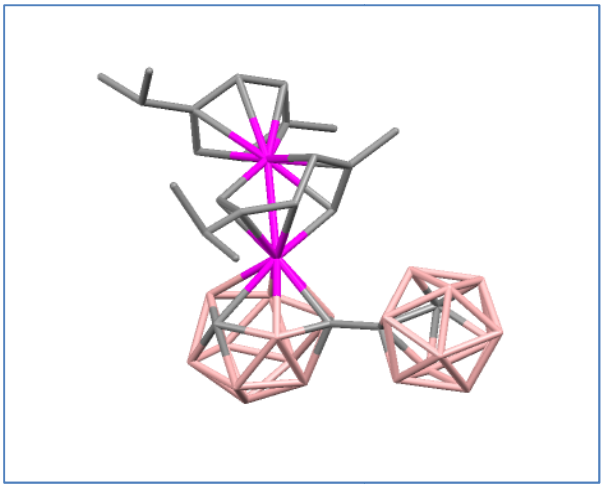
For much of its history carborane chemistry has centred on the icosahedral clusters, $C_2B_{10}H_{12}$, with significant interest in the field of subicosahedral species. Pioneering work by Hawthorne led to the preparation of the first 13-vertex metallacarborane in 1971[1] and some thirty years later the heteroborane group at Heriot-Watt University invoked the same polyhedral expansion protocol to synthesise the first supraicosahedral carborane[2]. For well-understood reasons the stability of the expanded cluster is increased by the incorporation of transition metal atom(s), indeed the largest known heteroborane to date possesses a cluster core with the formulation MC_2B_{12}[3]. Over recent years, much has been learned about the nature of these species with new isomers and novel cage architectures being identified.

Very recently, our group has begun to develop the expansion chemistry of so-called biscarboranes where the icosahedral parents form dimers *via* a C_{cage}-C_{cage} bond. This is proving an extremely fertile area and is already generating some fascinating results. Below is shown the structure of the product formed on attempting to expand biscarborane by incorporation of a Ru(arene) fragment. Remarkably the reaction leads to the cleavage of an aromatic C-C bond and the formation of a Ru-bound μ-allylidene ligand[4]. Room-temperature bond activation of this type is unprecedented in organometallic chemistry.

This presentation will review the current state of supraicosahedral heteroborane chemistry and will introduce the latest results in the field of biscarborane expansion.



1. G.B. Dunks, M.M. McKown and M.F. Hawthorne, *J. Am. Chem. Soc*., 1971, **93**, 2541.
2. A. Burke, D. Ellis, B.T. Giles, B.E. Hodson, S.A. Macgregor, G.M. Rosair and A.J. Welch, *Angew. Chem. Int. Ed*., 2003, **42**, 225.
3. R.D. McIntosh, D. Ellis, G.M. Rosair and A. J. Welch, *Angew. Chem. Int. Ed*., 2006, **45**, 4313.
L. Deng, J. Zhang, H.-S Chan and Z. Xie, *Angew. Chem. Int. Ed.,* 2006, **45,** 4309.
4. D. Ellis, D. McKay, S.A. Macgregor, G.M. Rosair and A.J. Welch, *Angew. Chem. Int. Ed.,* 2010, **49,** 4943.