

UNH Materials Science Seminar

11:10-12:00, Thursday, November 30, 2006
DeMeritt Hall 209B, University of New Hampshire

Weakly Coordinating Anions: Application in Olefin Polymerization Reactions – A Review

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Weakly Coordinating Anions (WCA) are anions that coordinate weakly with metallocene cations. Salts of weakly coordinating anions are used as activators for polymerization catalysts as well as counter anions. In all these cases the WCA let the reactive cations be exploited (in other words makes it more 'available'-ref **Fig. 1**). As the desired cations become more and more reactive, the anions must be less and less reactive. An ideal WCA simply should balance the charge of the cationic species without coordinating strongly to or otherwise strongly reacting with the cation. Therefore WCA should have low overall charge which can be dispersed over a large number of atoms. The atoms on the surface should be basic like hydrogen or halogens. These atoms on the periphery of the anions should be strongly bound to the rest of the anions so that they are not abstracted by the reactive cations. Also, the WCA should be stable to oxidation since many reactive electrophilic cations are also very oxidizing.

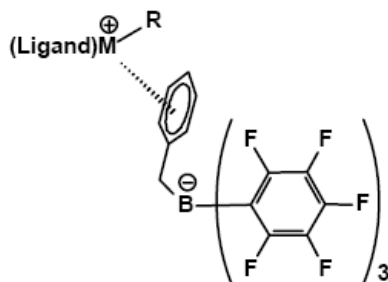
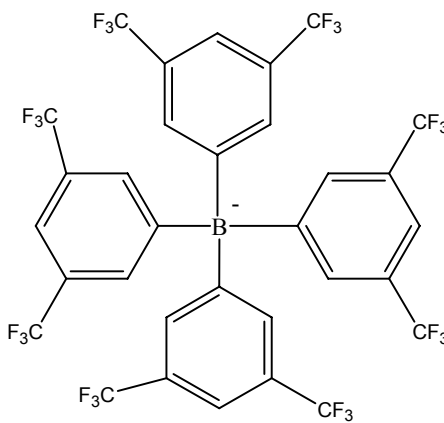
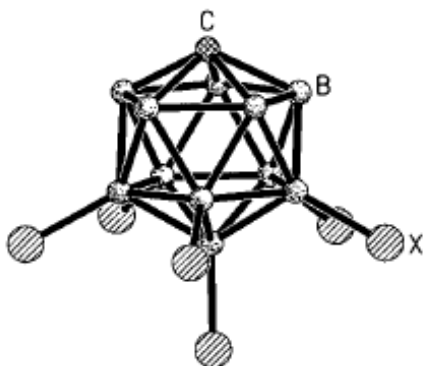


Fig. 1: Interaction of WCA with the Cation

The most common WCA had been ClO_4^- , CF_3SO_3^- , BF_4^- , PF_6^- , AsF_6^- , SbF_6^- until they were found to be in fact strongly coordinating by Beck et al ¹ in 1988. This conclusion was based on well-studied IR and NMR data. Interionic H...F interactions were detected. Thus the search for larger and more weakly coordinating anions began.

More commonly used examples of WCA are Carboranes (**Fig. 2a**), OTeF_5^- , $\text{B}(\text{Ar}_f)_4^-$ commonly called BARF (**Fig. 2b**).

With a brief introduction to the topic, various types of anions that are reported in the literature will be reviewed. Applications of these anions in olefin polymerization reactions will also be presented.



Examples of large WCA: (2a) Carborane $\text{CB}_{11}\text{H}_6\text{X}_6^-$

(2b) BARF: $[\text{B}[3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3]_4]^-$

¹ Beck, W.; Sunkel, K. *Chem Rev.* **1988**, 88,1405.