

Bifunctional Perfluoroaryl Boranes as Cationic Initiators for Isobutylene Polymerization

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Introduction

Perfluorinated boranes are an important class of Lewis acids that act as catalysts and co-catalysts for a number of organic transformations and polymerization reactions.^[1] Their efficacy stems from not only their high Lewis acidity, but also the fact that anions derived from them are extraordinarily weakly coordinating and poorly reducing.

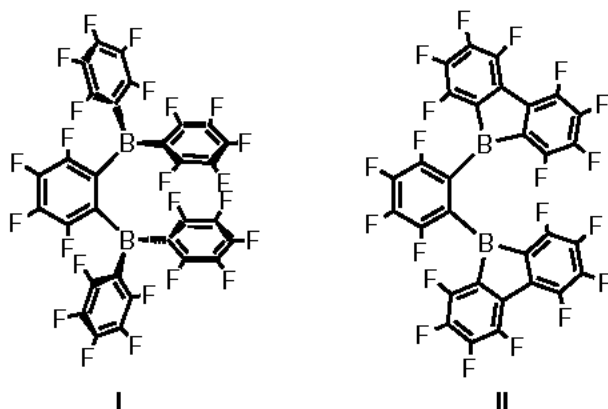


Figure 1. Bifunctional perfluoroaryl boranes

Perfluoroaryl diboranes,^[2] possessing borane centers in geographic proximity, are a subclass of this family of compounds that are in theory capable of chelating neutral and anionic bases, although only the latter are commonly observed to be chelated by both centers. We have prepared examples of this class of chelating diboranes, exemplified by diborane I^[3] and diborane II.^[4] The synthetic routes developed to these perfluoroaryl diboranes and others will be reviewed briefly. While we were initially interested in preparing conventional fluoroaryl borane and borate initiators from these species,^[5] recently, it was discovered that these compounds are effective initiators of isobutylene polymerization in the presence of cumyl-X initiators^[6] and even in aqueous suspension media.^[7] These striking observations have led us to examine the chemistry of I and II in detail with respect to their reactivity with both standard and protic Lewis bases.

Results and discussion

The combination of I or II with cumyl chloride or cumyl methoxide is an effective catalyst/initiator system for the polymerization of isobutene in apolar media such as hexanes, producing high MW polymer with high conversion. The chelating nature of the diboranes is critical, as monoborane analogs such as $B(C_6F_5)_3$ do not initiate polymerization. The mechanism of initiation appears to involve abstraction of Cl or OMe⁻ to form a chelated X⁻ anionic borate as a weakly coordinating anion capable of maintaining polymerization propagation.

Aspects of the talk will focus on the mechanism of the initiation process via model studies on the Lewis base coordination chemistry of these bifunctional Lewis acids. While there is likely a thermodynamic impetus to coordinate in the "inner pocket" (Figure 2), these studies reveal that "outer" coordination modes are preferred kinetically. The use of Lewis bases with various steric properties serve to highlight the factors that influence the mode of coordination to these bifunctional Lewis acids and illuminate the nature of the initiation process. For

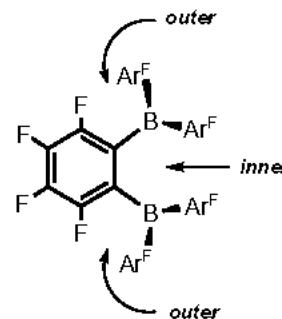


Figure 2. Coordination faces in bifunctional perfluoroaryl boranes.

example, in I, coordination to both inner and outer borane faces is observed, depending on the properties of the Lewis base, while initial coordination in II invariably occurs on the outer faces of the diborane framework. Nonetheless, anionic bases are readily chelated by both I and II, and the mechanism of incorporation of the X⁻ base from the outer face to the inner pocket is discussed, as well as the relevance of this process to effective polymerization initiation.

While diborane/cumyl-X initiation is quite effective, adventitious proton sources need to be removed in order to probe this initiator system without interference. Surprisingly, it was found that when isobutylene is suspended in aqueous media comprised of concentrated salt solutions, addition of I or II results in efficient production of polymer with reasonable conversions. Again, use of monofunctional boranes such as $B(C_6F_5)_3$ or other initiators such as $[Ph_3C]^+[B(C_6F_5)_4]^-$ under these conditions did not lead to polymer formation, suggesting that the presence of two cooperating borane centers is critical. The nature of the initiating species here is as yet unknown, but we speculate that a $\mu-OH_2$ species such as that shown in Figure 3 may be implicated. Such a species would be expected to be a strong Bronsted acid, capable of initiating isobutene polymerization.

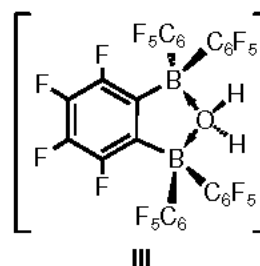


Figure 3. Bridging water adduct of I.

Efforts to detect such a species via stoichiometric reactions of both I and II suggest that these species are indeed powerful Bronsted acids. For example, while treatment of I with an excess of H_2O leads to stable solutions of the hydroxide chelated anion of the hydronium ion, $\{[C_6F_4-1,2-B(C_6F_5)_2](\mu-OH)\}[(H_2O)_nH]^+$, use of one equivalent of H_2O leads to rapid B-C bond cleavage to give the products $(C_6F_5)_2BOH$ and $(C_6F_5)_2BC_6F_4H$. These observations suggest that III is acidic enough to protonate not only excess water, but also the relatively non-nucleophilic B-C bonds of the diborane.

While III and species like it have not been directly detected, efforts to do so include careful stoichiometric reactions of I and II with H_2O and MeOH; this chemistry will be discussed. Alternate routes include the protonation of the anions $\{[C_6F_4-1,2-B(C_6F_5)_2](\mu-OR)\}^-$ (R = H, Me) with strong acids such as $[B(C_6F_5)_4][Et_2O_2H]^{[8]}$ or $[B(C_6F_5)_4][H_2CC_2Me_2]^{[9]}$. These studies have led to structural characterization of excellent models for III, albeit those that do not initiate isobutylene polymerization.

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