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Review

Complexes of tris(pentafluorophenyl)boron with nitrogen-containing compounds: Synthesis, reactivity and metallocene activation

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Contents

Abstract

The strong Lewis acid tris(pentafluorophenyl)boron, $B(C_6F_5)_3$, reacts with several nitrogen-containing Lewis bases (nitriles, amines, imines, pyridines, etc.) and also with non-basic substrates (such as pyrroles and indoles) producing in both cases the B—N coordination adduct. With particular substrates (some tertiary amines, the imine ^{t}Bu(Me)C=NBn, *N*-methyl-pyrrole and -indole,) the 1:1 borane/*N*-compound reaction produces zwitterions where a new B—C bond is generated. Some of the borane–*N*-compound adducts present Brønsted acidity and can be reacted with di-methyl group 4 complexes with generation of weakly associated ion pairs, which are active catalysts for the polymerization of olefins.

Keywords: Perfluoroarylboranes; Boron—nitrogen complexes; Lewis acid–Lewis base adducts; Metallocenes; Ion pairs

1. Introduction

The development of homogeneous transition metal complexes as catalysts for olefin polymerization, such as group 4 metallocenes and other group 4–10 organometallics, has triggered a parallel quest for more and more efficient activators, or cocatalysts [1]. The industrially most widely used cocatalyst is methylalumoxane (MAO). MAO, an ill-defined mixture of the partial hydrolysis of trimethylaluminum, is commercially available, generally as toluene solutions. This material requires special handling and storage conditions, being both pyrophoric and chemically unstable, and a large excess of it (100–10,000 eq per eq of transition metal) is often required in order to reach optimum catalyst activity. The search for alternative, more stable

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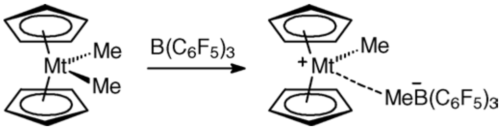


Scheme 1.

activators [2] generated a family of fluorinated aryl boron compounds, such as $B(C_6F_5)_3$, [3] or borate salts, e.g. $[Ph_3C][B(C_6F_5)_4]$ or $[PhNHMe_2][B(C_6F_5)_4]$. These Lewis or Brønsted acidic molecules are used as stoichiometric cocatalysts in olefin polymerization with a large number of alkylated organometallic complexes [4].

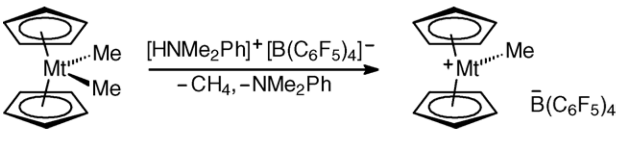
$B(C_6F_5)_3$ is among the strongest Lewis acids, [5] and in some instances it was found able to activate dialkylmetallocenes via a reversible dissociation of one alkyl ligand from the transition metal. The methylmetallocenium/methylborate ion pair formed in the case of the reaction with Cp_2MtMe_2 (Mt: Ti, Zr, Hf) is shown in Scheme 1 [6,7].

Due to the reversible nature of the above reaction, and the "tight ion-pair" obtained, $B(C_6F_5)_3$ is only seldom an efficient activator. $B(C_6F_5)_3$ is highly hygroscopic due to its high Lewis acidity and oxygen affinity, and, upon reaction with L_nMtMe_2, does not produce stable catalyst systems, possibly due to transfer of a C_6F_5 anion back to the transition metal center, with formation of neutral, inactive species $L_nMtCH_3(C_6F_5)$ and $CH_3B(C_6F_5)_2$ [8]. This decomposition pathway is obviously a problem when the catalyst/cocatalyst mixture cannot be prepared in situ in the presence of the monomer(s). A major improvement in activating performance is shown by the trihydrocarbylammonium perfluoroarylborates, which generates the alkylmetallocenium/borate catalyst systems by protonation of the $Mt{-}CH_3$ bond, with formation of the tertiary amine and methane. In this case, the perfluoroarylborates behave as weakly- or non-coordinating anions (Scheme 2) [9].

One potential drawback of ammonium perfluoroarylborates is the possible coordination of the tertiary amine to the metallocenium cation that could lead to catalyst deactivation.

In a similar way, but without the aforementioned downside, $[Ph_3C][B(C_6F_5)_4]$ generates the metal alkyl cation by abstracting a methyl group from the metal center, with formation of CH_3CPh_3 [10].

Despite the advantage of using a perfluoroborate salt as a stoichiometric activator, thus solving the major problem connected with the use of the MAO cocatalyst, there are some technical problems associated with the use of such borates, mainly the cost associated with the use of pentafluoroaryl groups: the tetrakis(perfluoroaryl)borates, being of high molar mass and requiring an additional synthetic step compared to $B(C_6F_5)_3$, are more expensive on a molar base. In addition, the borate salts have limited solubility in the solvents used for olefin polymerization.



Scheme 2.

$$B(C_6F_5)_3 \xrightarrow{XOH} (XHO)B(C_6F_5)_3 \xrightarrow{:L} [HL]^+[(XO)B(C_6F_5)_3]^-$$

Scheme 3.

Besides use in the field of homogeneous polymerization catalysis, $B(C_6F_5)_3$ has also found several applications in organic chemistry as strong but selective Lewis acid. $B(C_6F_5)_3$, compared to other Lewis acids such as BF_3, $AlCl_3$ or $SnCl_4$, has the important advantage of being quite stable and air- and water-tolerant, and can be used to efficiently catalyze many organic transformations [11,17].

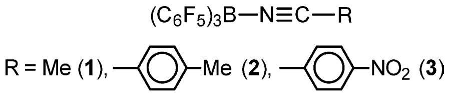
The Lewis acidity of $B(C_6F_5)_3$ has been used to convert it into a Brønsted acid, by complexation with water or alcohols (Scheme 3).

The water–$B(C_6F_5)_3$ system has been recently studied in detail by Norton and coworkers, [12] and Beringhelli and coworkers [13]. The acidity of boron-coordinated XOH has been demonstrated and applied to catalytic reactions in a number of instances, [11,14] but the borate $[(C_6F_5)_3BOR]^-$ (R=H, alkyl, aryl) is not expected to be a stable counterion for transition metal alkyl cations, due to the coordination ability of oxygen and irreversible transfer to the −OR group to the oxophylic Zr metal [15].

On the other side, the use of *N*-containing molecules to form complexes with $B(C_6F_5)_3$ has been the focus of some recent investigations, and provided a series of efficient and synthetically easily accessible activators for metallocene precatalysts. This review covers such recent developments.

2. Adducts with nitriles

The acetonitrile–tris(pentafluorophenyl)borane complex, $(C_6F_5)_3B{\cdot}NCCH_3$ (**1**), was first synthesized by Erker and coworkers [5] together with two aromatic nitrilic derivatives **2** and **3**.



These complexes were easily obtained by adding at room temperature the nitrile in slight excess to the borane, both dissolved in pentane, and isolating the final compound by precipitation. The nitrile–$B(C_6F_5)_3$ adducts were analyzed with IR and X-ray diffraction analyses, focusing on the C≡N bond length which changes significantly on going from the free nitrile to the boron-coordinated nitrile. The C−N inter-atomic distance in the adduct is shorter than in the free nitrile, being, for instance, 1.124(3) Å in compound **1** versus 1.141(2) in acetonitrile. IR spectra gave additional support to this bond length modification, the IR $\nu_{C\equiv N}$ for the adducts are actually shifted to higher wavenumbers of about 95–99 cm^{-1} with respect to the free nitrile.