



Improved synthesis, characterization and catalytic application of $[\text{H}(\text{OEt}_2)_2][\text{B}\{\text{C}_6\text{H}_3(m\text{-CF}_3)_2\}_4]$

Ahmed K. Hijazi^{a,*}, Ziyad A. Taha^a, Abdulaziz Ajlouni^a, Narayanan Radhakrishnan^b, Brigitte Voit^b, Fritz E. Kühn^{c,**}

^a Dept. of Chemical Sciences, Faculty of Science and Arts, Jordan University of Science and Technology, P.O. Box 3030, Irbid 22110, Jordan

^b Leibniz-Institut für Polymerforschung Dresden e.V., Department of Polymer Structures, Hohe Strasse 6, 01069 Dresden, Germany

^c Molecular Catalysis, Catalysis Research Center, Ernst Otto Fischer Str. 1 and Department of Chemistry, Technische Universität München, Lichtenbergstr. 4, D-85747 Garching bei München, Germany

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ABSTRACT

$[\text{H}(\text{OEt}_2)_2][\text{B}\{\text{C}_6\text{H}_3(m\text{-CF}_3)_2\}_4]$ has been straightforwardly prepared through a one pot reaction. The product has been characterized by elemental and thermogravimetric analysis, ¹H, ¹³C NMR and IR spectroscopy. The catalytic activity of the acid in the polymerization of isobutene has been studied. Polymerizations were performed at a temperature interval from 0 to 30 °C. The catalytic results show conversions between 34 and 88% and between 84 and 92% in about 30 min for complexes $[\text{H}(\text{OEt}_2)_2][\text{B}\{\text{C}_6\text{H}_3(m\text{-CF}_3)_2\}_4]$ and $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{F}_5)_4]$, respectively.

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Introduction

The use of weakly or non-coordinating anions (WCA) as counterions both in synthesis and catalysis is of significant current interest, due to their ability in enhancing the reactivity of metal complexes in isobutene polymerization [1–3]. It has been 30 years since the term “non-coordinating anion” [4] was coined to describe anions such as ClO_4^- , NO_3^- , and BF_4^- , which are found to be non-coordinating in aqueous solution. However, with the advent of routine X-ray crystallography it has become evident that in many cases a “non-coordinating” complex anion is actually (weakly) coordinating [5]. Accordingly, the term weakly coordinating anion (WCA) was created for the coordination of these complex anions. Owing to the importance of such WCAs in fundamental and applied chemistry, a considerable amount of work has been undertaken in order to obtain more examples of these interesting anions. Complexes bearing WCAs are synthesized using different preparation methods [6,7]. Their applications have attracted a remarkable interest in very wide areas in chemistry, due to the high degree of

charge delocalization, which improves the reactivity of their cationic counterparts [8]. These complexes can be applied, for example, as catalysts or initiators in polymerization reactions of different alkenes [9,10,1,2]. It is well established that isobutene can be polymerized by means of cationic initiators such as protons or Lewis acids. Typical catalysts are AlCl_3 , BCl_3 , BF_3 and water as co-initiator. Typical solvents are methylchloride, dichloromethane and ethene at temperatures of –80 °C or below (–100 °C in case of ethene as solvent). Polymerization under these conditions, however, is extremely fast and exothermic. BF_3 combined with aliphatic alcohols as deactivators is applied for the production of highly reactive polyisobutene. Reaction temperatures of –30 °C up to 0 °C are usually applied for this process.

The oxonium acid $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ was previously prepared in a time consuming process spanning several days [11,12]. Recently, its preparation was optimized through a one pot synthesis [13]. The acid $[\text{H}(\text{OEt}_2)_2][\text{B}\{\text{C}_6\text{H}_3(m\text{-CF}_3)_2\}_4]$, has also been synthesized before and applied in different reactions of chemistry [14].

In this paper, a straight-forward synthesis for the preparation of the oxonium acid $[\text{H}(\text{OEt}_2)_2][\text{B}\{\text{C}_6\text{H}_3(m\text{-CF}_3)_2\}_4]$ is described. Furthermore, the catalytic behavior of the acid is briefly reported in the polymerization of isobutene to produce the so-called highly reactive polyisobutenes at room temperature and above.

* Corresponding author. Tel.: +962 2 7201000.

** Corresponding author. Tel.: +49 89 289 13477.

E-mail addresses: akhijazi@just.edu.jo (A.K. Hijazi), fritz.kuehn@ch.tum.de (F.E. Kühn).

Experimental part

General methods

All preparations were done under Argon atmosphere using standard Schlenk techniques. Diethyl ether was distilled from Na and benzophenone and was used directly. All reagents and solvents used were purchased from Sigma–Aldrich chemicals and used without any further purification unless reported. Elemental analyses were recorded by a vario EL metal analyzer at the micro analytical laboratory of the TU München. NMR spectra were recorded on a Bruker AVANCE-DPX-400 MHz spectrometer. IR spectra were recorded on a JASCO FT/IR-4100 Fourier transform infrared spectrometer by using KBr pellets as matrix. Thermogravimetric analyses (TGA) were done with a Netzsch TG 209 system under argon at a heating rate of 10 °C/min.

Preparation of $[H(OEt_2)_2][B\{C_6H_3(m-CF_3)_2\}_4]$

A 2.0 M solution of *n*-BuLi in *n*-hexane (2.45 ml, 4.9 mmol) was added dropwise to a solution of $[Br\{C_6H_3(m-CF_3)_2\}]$ (1.44 g, 4.9 mmol) in 15 ml diethyl ether at -78 °C. After 30 min, 1 M solution of BCl_3 in *n*-hexane (1.23 ml, 1.23 mmol) was added. The reaction was warmed up to room temperature, where LiCl precipitated. A 1 M solution of HCl in diethyl ether (1.23 ml, 1.23 mmol) was added and the reaction kept stirring overnight. The resulting solution was concentrated under oil pump vacuum, and the addition of 50 ml *n*-hexane gave the white solid product. The desired product was collected by filtration and dried under vacuum. Yield: 39.5%. 1H NMR (400 MHz, $CDCl_3$, $T = 298$ K, δ (ppm)): 3.74 (q, 8H, CH_2), 1.37 (t, 12H, CH_3), 7.56 (s, 4H, aromatic), 7.69 (s, 8H, aromatic). ^{13}C NMR ($CDCl_3$, $T = 298$ K, δ (ppm)): 60.56 (CH_2), 18.62 (CH_3), 134.10 (C–CB), 128.63 (C– CF_3), 125.35 (CB), 122.64 (CF_3), 119.93 (C– CF_3). Anal. Calcd. (%) for $C_{40}H_{33}O_2BF_{24}$ (1012.22): C 47.45, H 3.29, F 45.03; Found: C 47.23, H 3.48, F 45.36.

Isobutene polymerization

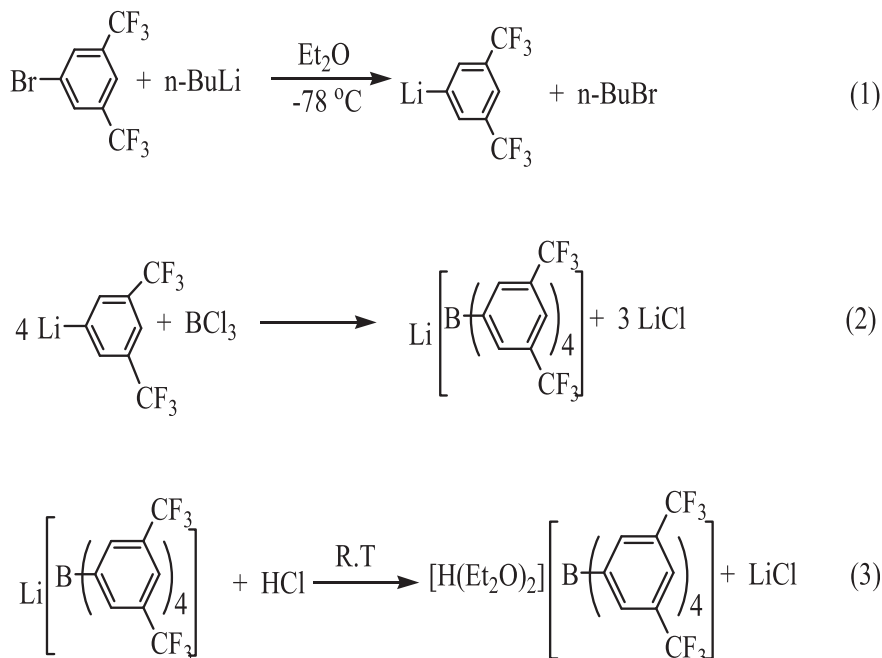
Isobutene polymerization experiments were carried out in a dry box using special tubes. 20 ml of dry CH_2Cl_2 and the catalyst

(oxonium acid) (5.0×10^{-3} mol/L) were added to each tube at -25 °C. Different amounts of isobutene were also added. The tubes were sealed and the process of polymerization was performed in a controlled temperature water bath at the desired temperature. The polymerization was quenched with CH_3OH and oxidation prevention was controlled by adding 1 g of 2, 2'-methylene-bis(4-methyl-6-di-*tert*-butyl)phenol. Solvents were removed under oil pump vacuum. The remaining polymer was dried at 40 °C until constant weight was reached. Gel Permeation Chromatography (GPC) measurements were done with a Lichrogel PS40 column and UV detector. End group characterization was performed by 1H and ^{13}C NMR spectroscopy [2]. A Bruker Avance 500 spectrometer was used to record the spectra. Deuterated chloroform was used as a solvent.

Results and discussion

The oxonium acid, $[H(OEt_2)_2][B\{C_6H_3(m-CF_3)_2\}_4]$ (complex **1**), was synthesized according to Scheme 1. The acid $[H(OEt_2)_2][B(C_6F_5)_4]$ (complex **2**) was synthesized following a literature established process [13]. After removal of diethyl ether and the addition of *n*-hexane, **1** was obtained in a good yield as a white solid after appropriate workup. It is slightly moisture and air sensitive, and can be handled under laboratory atmosphere for a few minutes. The acid is found to be stable and soluble in many organic solvents. The values of 1H and ^{13}C NMR spectroscopy in addition to the elemental analyses data, confirmed the purity of the desired product. According to the TGA-MS data, **1** is more stable than **2**. When heating, complex **1** starts to decompose at 100.3 °C. Complex **2** starts to decompose at 90.8 °C. At the end of the decomposition, a total weight loss of ~83.5% and ~73.6% can be recorded for complexes **1** and **2**, respectively (Table 1 & Fig. 1). Selected IR spectra for the product are (cm^{-1}): ν (CH) stretching 2963, 2926; ν (C=C) 1625; ν (CH_3) bending 1359; ν (C–O–C) & (C–F) 1285, 1135, 1092; ν (CH_2) bending 712.

Complexes **1** and **2** were applied as a catalyst for isobutene polymerization (Scheme 2). The polymerization reaction was performed at different temperatures in the interval between 0 and 30 °C and different mixtures of solvents in different proportions



Scheme 1. Synthesis of complex **1**.

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