

## Double, Double Salt Catalysts for Electrophilic Reactions

### FIELD OF THE INVENTION

This invention relates to a method for inducing electrophilic reactions using double, double salt catalysts comprising a salt of a weakly coordinating anion with a salt capable of providing a proton. This invention further relates to the use of such catalysts to effect electrophilic reactions in the presence of large quantities of water.

### BACKGROUND OF THE INVENTION

Electrophilic reactions are pervasive in many industrially relevant processes including but not limited to alkylation, isomerization, disproportionation, cyclization, and cationic polymerization. The majority of these processes are catalyzed either by strong Brønsted (e.g., HF or F<sub>3</sub>CSO<sub>3</sub>H) or strong Lewis acid (e.g., AlCl<sub>3</sub>) catalysts in the substantial absence of moisture (i.e., anhydrous conditions). An illustrative application of the former catalysts are processes used for the alkylation of isoparaffins by alkenes in the presence of H<sub>2</sub>SO<sub>4</sub> or HF. Brønsted acids (BAs) typically must be highly concentrated (i.e., anhydrous) in order to exhibit sufficient activity as catalysts and obtaining these materials in an undiluted state on recycle can be difficult and costly. Moreover, highly concentrated BAs impose specialized handling and storage techniques in addition to equipment of specialized construction. An example of an industrial process that uses the latter class of catalysts (i.e., Lewis acids {LAs}) is the cationic polymerization of olefin monomers (e.g., isobutene {IB}) which in the case of the aforementioned olefin is typically conducted in halogenated solvents (e.g., MeCl) at low temperatures (ca. -100 °C) under anhydrous conditions. Technically, in the case of cationic polymerization, the LAs used are non-catalytic in their behavior and are more appropriately referred to as coinitiators that act as a consumable component of the initiating system. In the aforementioned case (i.e., IB), polymerization never goes to completion unless additional quantities of AlCl<sub>3</sub> are added. Also, due to the hydrolytic instability of most useful LAs these materials also require special handling considerations (e.g., inert atmosphere), their performance is severely lowered or completely negated by moisture exceeding trace levels, and they cannot be readily recycled.

In the instance of this invention, the term “double, double salt” refers to a mixture formed by the reaction of a salt bearing a weakly coordinating anion (WCA) with a salt (i.e., acid) capable of providing a proton (i.e., H<sup>+</sup>). In general terms, the double, double salt catalysts of the present invention consist of a salt of a weakly coordinating anion in conjunction with a Brønsted acid and exclude combinations solely consisting of a salt bearing a weakly coordinating anion in conjunction with species that can only furnish an electrophile other than a proton (e.g., Group 14 cation synthons {e.g., cumyl chloride} or transition metal ion complexes {e.g., dimethyl biscyclopentadienyl zirconocene}). Combinations of the latter type (e.g., WCA salt + Group 14 cation synthon) are not desirable as they do not perform in a catalytic manner, are highly sensitive to moisture, require chlorinated solvents and low reaction temperatures. As such, combinations of the latter type are not illustrative of the present invention. Representative examples of different categories of double, double salt catalysts that adhere to the criteria set forth in the current application include:

Metal ion salts of a weakly coordinating anion (e.g.,  $\text{Li}^+\text{B}[\text{C}_6\text{F}_5]_4^-$ ) in conjunction with a strong Brønsted acid, the latter which can be simple (e.g.,  $\text{H}_2\text{SO}_4$ ), or complex (e.g.,  $\text{H}^+[\text{SnCl}_4\text{OH}]^-$ ).

Carbocation salts of a weakly coordinating anion (e.g.,  $\text{Ph}_3\text{C}^+\text{B}[\text{C}_6\text{F}_5]_4^-$ ) in conjunction with a strong Brønsted acid, the latter which can be simple (e.g.,  $\text{HCl}$ ), or complex (e.g.,  $\text{H}^+[\text{BF}_3\text{OH}]^-$ ).

Silicenium salts of a weakly coordinating anion ( $\text{Et}_3\text{Si}^+\text{B}[\text{C}_6\text{F}_5]_4^-$ ) in conjunction with a strong Brønsted acid, the latter which can be simple (e.g.,  $\text{HNO}_3$ ), or complex (e.g.,  $\text{H}^+[\text{BF}_3\text{OAc}]^-$ ).

Hydrogen ion salts of a weakly coordinating anion (e.g.,  $\text{H}^+[\text{CHB}_{11}\text{F}_{11}]^-$ ) in conjunction with a strong Brønsted acid, the latter which can be simple (e.g.,  $\text{CF}_3\text{SO}_3\text{H}$ ), or complex (e.g.,  $\text{H}^+[\text{AlCl}_3\text{OH}]^-$ ).

Ammonium and organo ammonium salts of a weakly coordinating anion (e.g.,  $n\text{Oct}_3\text{NH}^+[\text{CHB}_{11}\text{Cl}_{11}]^-$ ) in conjunction with a strong Brønsted acid, the latter which can be simple (e.g.,  $\text{H}_3\text{PO}_4$ ), or complex (e.g.,  $\text{H}^+[\text{Ti}_2\text{Cl}_8\text{OH}]^-$ ).

Phosphonium and organo phosphonium salts of a weakly coordinating anion (e.g.,  $n\text{Oct}_4\text{P}^+\text{B}[\text{C}_6\text{F}_5]_4^-$ ) in conjunction with a strong Brønsted acid, the latter which can be simple (e.g.,  $\text{HF}$ ), or complex (e.g.,  $\text{H}^+[\text{GaCl}_3\text{OH}]^-$ ).

Zwitterionic “frustrated” Lewis pairs based on a weakly coordinating anion (e.g.  $\text{Cy}_3\text{P}-\text{C}_6\text{F}_4-\text{BF}[\text{C}_6\text{F}_5]_2$ ) in conjunction with a strong Brønsted acid, the latter which can be simple (e.g.,  $\text{FSO}_3\text{H}$ ), or complex (e.g.,  $\text{H}^+[\text{SbF}_5\text{OH}]^-$ ).

However, it is understood that any salt bearing a weakly coordinating anion can be used in conjunction with a Brønsted acid and still meet the requirements set forth in the current invention. It is further understood that the salt bearing a weakly coordinating anion can be prepared in situ (e.g.,  $\text{H}^+\text{ClB}(\text{C}_6\text{F}_5)_3^-$  derived from  $\text{B}(\text{C}_6\text{F}_5)_3 + \text{HCl}$ ).

Likewise any Brønsted acid with acidity higher than water may serve as the Brønsted acid component of the double, double salt catalyst. This is especially true when the reaction substrate is highly reactive (e.g., vinyl ethers, N-vinyl carbazole) and in such instances the double, double salt catalyst may consist of a salt containing a weakly coordinating anion in conjunction with a relatively weak Brønsted acid (e.g., acetic acid). Although, in certain instances, the Brønsted acid component of these double, double salt mixtures can be capable of catalyzing certain electrophilic reactions (by themselves) their catalytic activity is greatly enhanced by the addition of a salt of a weakly coordinating anion such that reaction can be effected in a much shorter period of time compared to more traditional methods based on Brønsted acid alone. Furthermore, in many instances, such combinations possess catalytic activity in the presence of large quantities of water that would normally preclude catalytic activity on part of the Brønsted acid itself. The acidity of the Brønsted acid must be above of a minimum threshold value and is

dependent on the reactivity of the substrate to be reacted. In the instance of polymerization, olefins of moderate reactivity (e.g., styrene, isobutene) require the use of Brønsted acids with acidity that exceeds that of standard carboxylic acids (e.g., acetic acid) when polymerization is conducted in the presence of a large quantity of water. On the other hand, for polymerization of olefins of higher reactivity (e.g., vinyl ethers, N-vinyl carbazole) Brønsted acids of moderate strength (e.g. carboxylic acids and their halogenated congeners) are sufficient in terms of performance to be used as the H<sup>+</sup> donor component of the double, double salt described in the present invention. The Brønsted acid component of the double, double salt catalyst must possess an acidity greater than water (i.e., water itself does not function as the Brønsted acid component of the catalyst).

Although a large number of patents have been issued pertaining to initiator systems for cationic polymerization that make use of weakly coordinating anions as an integral component, none have been demonstrated to function in a catalytic nature and most specifically, none recite that electrophilic reactions are advantageously conducted in the presence of a catalyst comprising a double, double salt containing a weakly coordinating component. Of the patents for cationic polymerization that do happen to list salts that contain a weakly coordinating anion as a component of an initiator system useful for cationic polymerization the list of possible initiator combinations (in some patents) has been constructed of such a great number of potential permutations that it is impossible to determine which ones actually are functional. For example, U.S. Pat. No. 6,008,307A states that Li<sup>+</sup>B[C<sub>6</sub>F<sub>5</sub>]<sub>4</sub><sup>-</sup> and Ph<sub>3</sub>C<sup>+</sup>B[C<sub>6</sub>F<sub>5</sub>]<sub>4</sub><sup>-</sup> (i.e., salts that contain a weakly coordinating anion) are useful for effecting cationic polymerization when used in conjunction with water in the form of a wet solvent. A number of studies [e.g., (Lewis, S. P. Project 1. Synthesis of PIB-Silsesquioxane Stars via The Sol-Gel Process Project 2. Solution and Aqueous Suspension/Emulsion Polymerization of Isobutylene Cointiated by 1,2-C<sub>6</sub>F<sub>4</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sub>2</sub>, Ph.D. Thesis, The Univ. of Akron, Diss. Abstr. Int. 2004, vol. 65, p. 770. Cf: Chem. Abs. 2004, vol. 143, p. 173195, 2004.) and (Lewis, S. P.; Henderson, L.; Parvez, M. R.; Piers, W. E.; Collins, S. Aqueous Suspension Polymerization of Isobutene Initiated by 1,2-C<sub>6</sub>F<sub>4</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sub>2</sub>. *J. Am. Chem. Soc.* **2005**, *127*, 46-47.)] have indeed shown that neither of these salts is useful for effecting cationic polymerization of monomers (e.g., IB) in the presence of large amounts of water (e.g., suspension polymerization). Likewise, from reported data [e.g. (U.S. 6,008,307), (Shaffer, T. D.; Ashbaugh, J. R. Carbocationic Polymerization with Noncoordinating Boron Gegenions. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1996**, *37*, 339-340.) and (Shaffer, T. D.; Ashbaugh, J. R. Noncoordinating anions in carbocationic polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 329.)] it would appear that neither of these salts is effective for such polymerization (i.e., IB) under anhydrous conditions in the absence of chlorinated solvent despite it being stated that polymerization can be effected in nonpolar media. Even in the case of single salts containing a weakly coordinating anion that can also furnish a proton (e.g., HOEt<sub>2</sub><sup>+</sup>B[C<sub>6</sub>F<sub>5</sub>]<sub>4</sub><sup>-</sup>) these materials have been shown [(Lewis, S. P. Project 1. Synthesis of PIB-Silsesquioxane Stars via The Sol-Gel Process Project 2. Solution and Aqueous Suspension/Emulsion Polymerization of Isobutylene Cointiated by 1,2-C<sub>6</sub>F<sub>4</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sub>2</sub>, Ph.D. Thesis, The Univ. of Akron, Diss. Abstr. Int. 2004, vol. 65, p. 770. Cf: Chem. Abs. 2004, vol. 143, p. 173195, 2004.) and (Lewis, S. P.; Henderson, L.; Parvez, M. R.; Piers, W. E.; Collins, S. Aqueous Suspension Polymerization of Isobutene Initiated by 1,2-C<sub>6</sub>F<sub>4</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sub>2</sub>. *J. Am. Chem. Soc.* **2005**, *127*, 46-47.)] to be ineffective for inducing polymerization of olefins (i.e., IB) in the presence of water.

Moreover, no unambiguous evidence has ever been provided to date that demonstrate for anhydrous polymerizations conducted in chlorinated media with  $\text{Li}^+\text{B}[\text{C}_6\text{F}_5]_4^-$  and  $\text{Ph}_3\text{C}^+\text{B}[\text{C}_6\text{F}_5]_4^-$  that initiation indeed involves water, as the sterically hindered pyridines used to probe the issue have been demonstrated [e.g., (Barsan, F.; Karan, A. R.; Parent, M. A.; Baird, M. C. Polymerization of Isobutylene and the Copolymerization of Isobutylene and Isoprene Initiated by the Metallocene Derivative  $\text{Cp}^*\text{TiMe}_2(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ . *Macromolecules* **1998**, *31*, 8439-8447.), (Lewis, S. P. Project 1. Synthesis of PIB-Silsesquioxane Stars via The Sol-Gel Process Project 2. Solution and Aqueous Suspension/Emulsion Polymerization of Isobutylene Coinitiated by  $1,2\text{-C}_6\text{F}_4[\text{B}(\text{C}_6\text{F}_5)_2]_2$ ., Ph.D. Thesis, The Univ. of Akron, Diss. Abstr. Int. 2004, vol. 65, p. 770. Cf: Chem. Abs. 2004, vol. 143, p. 173195, 2004.), and (Jianfang, C.; Lewis, S. P.; Kennedy, J. P.; Collins, S. Isobutene Polymerization Using Chelating Diboranes: Reactions of a Hindered Pyridine with Carbocations Bearing  $\alpha$ -Protons. *Macromolecules* **2007**, *40*, 7421-7424.)] to be nonselective in their reactivity towards electrophiles (i.e., they not are exclusively reactive with  $\text{H}^+$  when the anion is a weakly coordinating anion).

Most specifically, of all the patents and papers detailing the use of salts bearing a weakly coordinating anion none provide a specific example whereby a double, double salt as described herein (i.e., the current application) is useful as a catalyst for electrophilic reactions. Therefore, given the large number of inactive systems described in many of previous patents, no previous disclosure can be used in a predictive manner in regards to the current invention described herein. A few examples of inactive systems based on salts of weakly coordinating anions (i.e., those that possess no activity under conditions of the current invention {e.g., presence of large quantities of water}) contained in some of these patents have already been described but other limited examples include:  $\text{Li}^+\text{B}[\text{C}_6\text{F}_5]_4^-$  and  $\text{Ph}_3\text{C}^+\text{B}[\text{C}_6\text{F}_5]_4^-$  in conjunction with: carbocation synthons (e.g., cumyl chloride), silicon cation synthons (e.g., chlorotrimethylsilane), and transition metal ion synthons (e.g., metallocenes). It is important to point out that PFLA based systems as described in the bulk of prior art disclosures have a number of limitations including: their high sensitivity to moisture (requiring very high purity monomers and solvents), inability to operate at temperatures above  $-20^\circ\text{C}$ , and requisite use of expensive and highly sensitive (to moisture and oxygen) initiators (e.g., metallocenes, silyl halides). Many of these previously disclosed systems also require the use of chlorinated solvents in order to effect polymerization in an efficient manner. The current invention is unique in that it is not constrained in a similar manner. Moreover, the current invention is novel in that the catalyst systems described herein have uses for electrophilic reactions other than polymerization (e.g., Friedel-Crafts alkylation).

It is of interest to point out that all of the systems known to be capable of producing high yields of high molecular weight polymers by cationic polymerization of olefin monomers in aqueous media rely on the use of neutral (i.e., uncoordinated) perfluoroarylated Lewis acids (PFLAs). In fact, the original criteria set forth for the first such polymerization of this type [(Lewis, S. P. Project 1. Synthesis of PIB-Silsesquioxane Stars via The Sol-Gel Process Project 2. Solution and Aqueous Suspension/Emulsion Polymerization of Isobutylene Coinitiated by  $1,2\text{-C}_6\text{F}_4[\text{B}(\text{C}_6\text{F}_5)_2]_2$ ., Ph.D. Thesis, The Univ. of Akron, Diss. Abstr. Int. 2004, vol. 65, p. 770. Cf: Chem. Abs. 2004, vol. 143, p. 173195, 2004.), (Lewis, S. P.; Henderson, L.; Parvez, M. R.; Piers, W. E.; Collins, S. Aqueous Suspension Polymerization of Isobutene Initiated by  $1,2\text{-C}_6\text{F}_4[\text{B}(\text{C}_6\text{F}_5)_2]_2$ . *J. Am. Chem. Soc.* **2005**, *127*, 46-47.), and (Mathers, R. T.; Lewis, S. P.

Aqueous Cationic Olefin Polymerization Using Tris(pentafluorophenyl)gallium and Aluminum. *J. Polym. Sci., Part A. Polym. Chem.* **2012**, *50*, 1325-1332.)] specifically stipulated that a strong, water resistant (but uncoordinated) PFLAs (e.g., 1,2-C<sub>6</sub>F<sub>4</sub>[B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sub>2</sub>) be used under conditions that minimize coordination of water to the PFLA. A number of such polymerizations have been shown to be capable of polymerizing IB to high MWs; however, none are catalytic in nature and quantitative yields are never obtained unless PFLA is continually added. Since, in these instances, the PFLA is consumed (by water) the PFLA does not satisfy the traditional definition of a catalyst (which is a material used to engender a chemical reaction but is not consumed during the course of said reaction). It was discovered that the double, double salt catalysts as described herein are unusual compared to all initiator systems mentioned in previous patents and papers detailing use of PFLAs for aqueous cationic polymerization in that the former operate in a truly catalytic manner whereas none of the prior art examples work as a catalyst but instead only function as consumable initiator components. Moreover, these systems are further unique in that they are long lived and can be used to effect perpetual polymerization in aqueous media (i.e., following consumption of monomer polymerization ensues on the addition of a fresh aliquot of monomer without needed addition of more catalyst). Similar benefits are to be had for catalyst systems described in the current invention when used under more traditional reaction conditions (i.e., substantially anhydrous conditions).

#### SUMMARY OF THE INVENTION

This invention relates to the discovery that double, double salts consisting of a salt bearing a weakly coordinating anion in conjunction with a Brønsted acid form a catalyst system for electrophilic reactions. Furthermore, this invention also relates to the discovery that such catalyst systems are capable of catalyzing electrophilic reactions in the presence of large quantities of water. In addition, another discovery related to the invention is that these catalyst systems are long lived, even in the presence of large quantities of water.

Therefore, in accordance with this invention, there is provided an electrophilic reaction catalyst system, a method for conducting electrophilic reactions using a catalyst system that is a double, double salt which comprises a salt bearing a weakly coordinating anion in conjunction with a salt capable of furnishing a proton (Brønsted acid). Another aspect of the invention is directed toward certain novel catalyst systems for cationic polymerization and a method for using this catalyst system to effect polymerization of cationically polymerizable olefins. An additional aspect of the invention is directed toward certain novel catalyst systems for electrophilic alkylation reactions and a method for using this catalyst system to effect alkylation reactions. A final aspect of this invention is directed toward certain novel catalyst systems for electrophilic isomerization reactions and a method for using this catalyst system to effect isomerization reactions.

#### DESCRIPTION OF PREFERRED EMBODIMENTS

This invention relates to a method for conducting electrophilic reactions that utilize a double, double salt catalyst with a composition comprising a salt bearing a weakly coordinating anion in conjunction with a salt bearing a proton. The invention further relates to novel catalyst systems capable of operating in the presence of large quantities of water.

A “weakly coordinating anion” (hereinafter “WCA”) is defined to be an anion which does not strongly coordinate to a cation, or electrophilic center, and thereby remains sufficiently labile to be displaced by weak nucleophiles (e.g., olefins). Moreover, WCAs as described herein do not irreversibly interact with a cation or electrophile when functioning as the stabilizing anion of the catalyst systems described herein. Illustrative, but not limiting, examples of salts bearing WCAs which may be used are:

1. Perfluoroarylated salts based on perfluoroarylated Lewis acids: lithium tetrakis(pentafluorophenyl)borate ( $\text{Li}^+\text{B}[\text{C}_6\text{F}_5]_4^-$ ), trityl tetrakis(pentafluorophenyl)borate ( $\text{Ph}_3\text{C}^+\text{B}[\text{C}_6\text{F}_5]_4^-$ ), triethylsilicenium tetrakis(pentafluorophenyl)borate ( $\text{Et}_3\text{Si}^+\text{B}[\text{C}_6\text{F}_5]_4^-$ ), dimethylanilinium tetrakis(pentafluorophenyl)borate ( $\text{HMe}_2\text{NPh}^+\text{B}[\text{C}_6\text{F}_5]_4^-$ ), proto tris(pentafluorophenyl)hydroxyborate ( $\text{H}^+\text{HOB}[\text{C}_6\text{F}_5]_3^-$ ), proto tris(pentafluorophenyl)chloroborate ( $\text{H}^+\text{ClB}[\text{C}_6\text{F}_5]_3^-$ ), proto tris(pentafluorophenyl)fluoroborate ( $\text{H}^+\text{FB}[\text{C}_6\text{F}_5]_3^-$ ), lithium tetrakis(pentafluorophenyl)aluminate ( $\text{Li}^+\text{Al}[\text{C}_6\text{F}_5]_4^-$ ), trityl tetrakis(pentafluorophenyl)aluminate ( $\text{Ph}_3\text{C}^+\text{Al}[\text{C}_6\text{F}_5]_4^-$ ), triethylsilicenium tetrakis(pentafluorophenyl)aluminate ( $\text{Et}_3\text{Si}^+\text{Al}[\text{C}_6\text{F}_5]_4^-$ ), dimethylanilinium tetrakis(pentafluorophenyl)aluminate ( $\text{HMe}_2\text{NPh}^+\text{Al}[\text{C}_6\text{F}_5]_4^-$ ), proto tris(pentafluorophenyl)hydroxyaluminate ( $\text{H}^+\text{HOAl}[\text{C}_6\text{F}_5]_3^-$ ), proto tris(pentafluorophenyl)chloroaluminate ( $\text{H}^+\text{ClAl}[\text{C}_6\text{F}_5]_3^-$ ), proto tris(pentafluorophenyl)fluoroaluminate ( $\text{H}^+\text{FAl}[\text{C}_6\text{F}_5]_3^-$ ), lithium tetrakis(pentafluorophenyl)gallate ( $\text{Li}^+\text{Ga}[\text{C}_6\text{F}_5]_4^-$ ), trityl tetrakis(pentafluorophenyl)gallate ( $\text{Ph}_3\text{C}^+\text{Ga}[\text{C}_6\text{F}_5]_4^-$ ), triethylsilicenium tetrakis(pentafluorophenyl)gallate ( $\text{Et}_3\text{Si}^+\text{Ga}[\text{C}_6\text{F}_5]_4^-$ ), dimethylanilinium tetrakis(pentafluorophenyl)gallate ( $\text{HMe}_2\text{NPh}^+\text{Ga}[\text{C}_6\text{F}_5]_4^-$ ), proto tris(pentafluorophenyl)hydroxygallate ( $\text{H}^+\text{HOGa}[\text{C}_6\text{F}_5]_3^-$ ), proto tris(pentafluorophenyl)chlorogallate ( $\text{H}^+\text{ClGa}[\text{C}_6\text{F}_5]_3^-$ ), proto tris(pentafluorophenyl)fluorogallate ( $\text{H}^+\text{FGa}[\text{C}_6\text{F}_5]_3^-$ ), zwitterionic phosphonium-borates ( $[(i\text{Pr})_3\text{P}-\text{C}_6\text{F}_4-\text{BF}[\text{C}_6\text{F}_5]_2$ ,  $[t\text{Bu}]_2\text{HP}-\text{C}_6\text{F}_4-\text{BF}[\text{C}_6\text{F}_5]_2$ ,  $[t\text{Bu}]_2\text{HP}-\text{C}_6\text{F}_4-\text{BCl}[\text{C}_6\text{F}_5]_2$ ,  $[\text{C}_6\text{H}_2\text{Me}_3]_2\text{HP}-\text{C}_6\text{F}_4-\text{BF}[\text{C}_6\text{F}_5]_2$ ,  $[\text{C}_6\text{H}_2\text{Me}_3]_2\text{HP}-\text{C}_6\text{F}_4-\text{BCl}[\text{C}_6\text{F}_5]_2$ ,  $\text{Cy}_3\text{P}-\text{C}_6\text{F}_4-\text{BF}[\text{C}_6\text{F}_5]_2$ ,  $\text{Cy}_3\text{P}-\text{C}_6\text{F}_4-\text{BCl}[\text{C}_6\text{F}_5]_2$ ,  $[\text{C}_6\text{H}_2\text{Me}_3]_3\text{P}-\text{C}_6\text{F}_4-\text{B}[\text{C}_6\text{F}_5]_3$ , and  $[t\text{Bu}]_3\text{P}-\text{C}_2\text{H}_2-\text{B}[\text{C}_6\text{F}_5]_3$ ), and cationic phosphonium-borane tetrakis(pentafluorophenyl)borates ( $[(i\text{Pr})_3\text{P}-\text{C}_6\text{F}_4-\text{B}(\text{C}_6\text{F}_5)_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ,  $[(\text{Cy})_3\text{P}-\text{C}_6\text{F}_4-\text{B}(\text{C}_6\text{F}_5)_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ,  $[(t\text{Bu})_2\text{HP}-\text{C}_6\text{F}_4-\text{B}(\text{C}_6\text{F}_5)_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ,  $[(\text{C}_6\text{H}_2\text{Me}_3)_2\text{HP}-\text{C}_6\text{F}_4-\text{B}(\text{C}_6\text{F}_5)_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ , and  $[\text{C}_6\text{H}_2\text{Me}_3]_3\text{P}-\text{C}_2\text{H}_2-\text{B}[\text{C}_6\text{F}_5]_3$ ).
2. Perfluoroalkylated salts based on perfluoroalkylated Lewis acids: lithium tetrakis(trifluoromethyl)borate ( $\text{Li}^+\text{B}[\text{CF}_3]_4^-$ ), trityl tetrakis(trifluoromethyl)borate ( $\text{Ph}_3\text{C}^+\text{B}[\text{CF}_3]_4^-$ ), triethylsilicenium tetrakis(trifluoromethyl)borate ( $\text{Et}_3\text{Si}^+\text{B}[\text{CF}_3]_4^-$ ), dimethylanilinium tetrakis(trifluoromethyl)borate ( $\text{HMe}_2\text{NPh}^+\text{B}[\text{CF}_3]_4^-$ ), proto tris(trifluoromethyl)hydroxyborate ( $\text{H}^+\text{HOB}[\text{CF}_3]_3^-$ ), proto tris(trifluoromethyl)chloroborate ( $\text{H}^+\text{ClB}[\text{C}_6\text{F}_5]_3^-$ ), proto tris(trifluoromethyl)fluoroborate ( $\text{H}^+\text{FB}[\text{CF}_3]_3^-$ ).
3. Perfluoroaryloxy and perfluoroalkoxy borates, aluminates, gallates: lithium tetrakis(pentafluorophenoxy)borate ( $\text{Li}^+\text{B}[\text{OC}_6\text{F}_5]_4^-$ ), lithium

- tetrakis(pentafluorophenoxy)aluminate ( $\text{Li}^+\text{Al}[\text{OC}_6\text{F}_5]_4^-$ ), lithium tetrakis(pentafluorophenoxy)gallate ( $\text{Li}^+\text{Ga}[\text{OC}_6\text{F}_5]_4^-$ ), trityl tetrakis(pentafluorophenoxy)borate ( $\text{Ph}_3\text{C}^+\text{B}[\text{OC}_6\text{F}_5]_4^-$ ), trityl tetrakis(pentafluorophenoxy)aluminate ( $\text{Ph}_3\text{C}^+\text{Al}[\text{OC}_6\text{F}_5]_4^-$ ), trityl tetrakis(pentafluorophenoxy)gallate ( $\text{Ph}_3\text{C}^+\text{Ga}[\text{OC}_6\text{F}_5]_4^-$ ),  $\text{Cs}^+[\text{Al}\{\text{OC}(\text{H})(\text{CF}_3)_2\}_4]^-$ ,  $\text{Cs}^+[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ ,  $\text{Ph}_3\text{C}^+[\text{Al}\{\text{OC}(\text{H})(\text{CF}_3)_2\}_4]^-$ , and  $\text{Ph}_3\text{C}^+[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ .
- Carborane salts: including those with the generalized formula  $\text{M}^+[\text{CB}_{11}\text{X}_n\text{H}_{12-n}]^-$  ( $\text{M}^+$  = alkali metal cations, carbocations (e.g., trityl cation), ammonium ions {including alkyl and aryl substituted versions}, silicenium ions, phosphonium ions, or  $\text{H}^+$ ;  $n = 1-12$ ;  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{CH}_3, \text{CF}_3$ ) for example  $\text{Li}^+[\text{CB}_{11}(\text{CH}_3)_{12}]^-$ ,  $\text{Cs}^+[\text{CHB}_{11}\text{Cl}_{11}]^-$ ,  $\text{Et}_3\text{Si}^+[\text{CHB}_{11}\text{F}_{11}]^-$ ,  $\text{CH}_3^+[\text{CHB}_{11}\text{H}_5\text{Cl}_6]^-$ ,  $\text{Me}_3\text{NH}^+[\text{CHB}_{11}\text{Br}_{11}]^-$ ,  $\text{H}^+[\text{CHB}_{11}\text{F}_{11}]^-$ .
  - Metallocarborane salts: tri(*n*-octyl)ammonium bis(nonahydride-1,3-dicarba-naborato) cobaltate (III), tri(*n*-octyl)ammonium bis(undecahydride-7,8-dicarbaundecaborato) ferrate (III), tri(*n*-octyl)ammonium bis(undecahydride-7,8-dicarbaundecaborato) cobaltate (III), tri(*n*-octyl)ammonium bis(undecahydride-7,8-dicarbaundecaborato)nickelate (III), tri(*n*-octyl)ammonium bis(nonahydride-7,8-dimethyl-7,8-dicarbaundecaborato)ferrate (III), tri(*n*-octyl)ammonium bis(tribromooctahydride-7,8-dicarbaundecaborato)cobaltate (III), tri(*n*-octyl)ammonium bis(undecahydriddicarbadodecaborato) cobaltate (III) and bis[tri(*n*-octyl)ammonium] bis(undecahydride-7-carbaundecaborato)cobaltate (III).
  - Perfluoroalkylsulfonate and perfluoroarylsulfonate salts: lithium bis(trifluoromethane sulfonimide) ( $\text{Li}^+\text{N}[\text{SO}_2\text{CF}_3]_2^-$ ), potassium perfluorooctanesulfonate ( $\text{K}^+\text{SO}_3[\text{CF}_2]_7\text{CF}_3^-$ ), sodium pentafluorophenylsulfonate.

Salts bearing reactive protons ( $\text{H}^+$ ) are defined as Brønsted acids which can exist in either simple or complex forms. Simple Brønsted acids consist of a single component bearing a reactive proton. Illustrative, but not limiting, examples of simple Brønsted acids which may be used include: hydrohalogens (e.g., HF, HCl, HBr, HI), sulfuric acid, phosphoric acid, nitric acid, trifluoromethanesulfonic acid, methanesulfonic acid, fluorosulfonic acid, chlorosulfonic acid, trifluoroacetic acid, and acetic acid. Complex Brønsted acids are formed by the reaction of a Lewis acid with a Brønsted acid, the latter being the actual source of the reactive proton; however, the complex functions together as the Brønsted acid in the current invention. Illustrative, but not limiting, examples of complex Brønsted acids that may be used include:  $\text{H}^+[\text{AlCl}_3\text{OH}]^-$ ,  $\text{H}^+[\text{BF}_3\text{OH}]^-$ ,  $\text{H}^+[\text{SnCl}_4\text{OH}]^-$ ,  $\text{HOEt}_2^+[\text{BF}_3\text{OH}]^-$ ,  $\text{H}^+[\text{AlCl}_4]^-$ ,  $\text{H}^+[\text{BF}_3\text{OAc}]^-$ ,  $\text{H}^+[\text{BF}_3\text{OCH}_3]^-$ ,  $\text{H}^+[\text{BEt}_3\text{OH}]^-$ ,  $\text{H}^+[\text{ZnCl}_2\text{OH}]^-$ ,  $\text{H}^+[\text{Sc}(\text{O}_3\text{SCF}_3)_3\text{OH}]^-$ ,  $\text{H}^+[\text{Sc}(\text{O}_3\text{SCF}_3)_3\text{OCH}_3]^-$ ,  $\text{H}^+[\text{Yb}(\text{O}_3\text{SCF}_3)_3\text{OH}]^-$ , or  $\text{H}^+[\text{Yb}(\text{O}_3\text{SCF}_3)_3\text{OCH}_3]^-$ . Complex Brønsted acids can be readily formed in situ by the reaction of a Lewis acid in conjunction with adventitious moisture present in the reaction mixture that is substantially anhydrous. In general, the acidity of the Brønsted acid (whether simple or complex) is greater than or equal to that of acetic acid. Although some of the aforementioned Brønsted acids possess some catalytic activity by themselves (under anhydrous conditions) their activity is greatly enhanced when combined with the salt bearing the WCA and moreover in many instances their activity is retained in the presence of large quantities of water, most especially for the simple Brønsted acids.

In regards to the current invention, (in the case of cationic polymerization by the aforementioned double, double salt catalyst) olefin monomers which can be polymerized include but are not limited to: isobutene, 2-methyl-1-butene, 2-methyl-pentene, isoprene, butadiene, styrene,  $\alpha$ -methyl styrene, para-methylstyrene, vinyl carbazole,  $\beta$ -pinene,  $\alpha$ -pinene, methyl vinyl ether, and isobutyl vinyl ether. Furthermore, in the context of the current invention it is understood that the process described herein can be used to effect not only homopolymerization of such monomers but also their copolymerization.

In practice, electrophilic reactions described herein can be conducted over a large range of reaction temperatures ranging from cryogenic (ca. -100 °C) to those in excess of ambient (ca. 100 °C). Ideally, such reactions are conducted within  $\pm 40$  °C of ambient (ca. 25 °C) temperature.

The electrophilic reaction processes described herein may be conducted by any phasic method such as but not limited to: solution phase, slurry phase, suspension phase, or in neat. Moreover, the invention described in the present application can be conducted in a variety of operational production modes such as but not limited to: batch mode, semi-continuous mode, and continuous mode.

When desired, suitable solvents and diluents include polar and non-polar hydrocarbons such as alkane and aromatic compounds and their halogenated derivatives. Specific examples include, but are not limited to: *n*-hexane, *n*-heptane, cyclohexane, methyl cyclohexane, ethyl cyclohexane, toluene, chloro-benzene, methyl chloride, methyl fluoride, methylene dichloride. In certain instances water can also be used as the solvent or diluent. In some instances, a simple Brønsted acid (e.g., HCl, H<sub>2</sub>SO<sub>4</sub>) which also functions as a component of the double, double salt catalyst can also constitute the solvent or diluent.

## EXAMPLES

General experimental: All polymerizations were conducted under air in test tubes capped with rubber septa. Both monomer and diluent were precooled to the desired temperature using water, ice water, or solvent-dry ice baths for 10 minutes prior to being combined at which polymerization ensued immediately. Polymerization was allowed to proceed for a desired period of time and then the aqueous phase was rapidly diluted with deionized water and the organic layer removed and precipitated into ethanol.

### Example 1

Studies showed that concentrated hydrochloric acid was incapable of inducing the polymerization of ST, even at long reaction times (Table 1, entry 18) whereas when CsCHB<sub>11</sub>Cl<sub>11</sub> was added in order to form a double, double salt catalyst (Table 1, entries 1-17) polymerization ensued immediately to give high yields of polymer.

Table 1. Polymerization of toluene solutions of ST (30 wt % monomer) using HCl/CsCHB<sub>11</sub>Cl<sub>11</sub>.<sup>a</sup>

Entry	CsCHB <sub>11</sub> Cl <sub>11</sub> (mg)	Monomer (g)	Acid (mL)	Time (hr)	Temp. (°C)	Conv. (%)	$\overline{M}_w$ (g·mol <sup>-1</sup> )	PDI
1 <sup>b</sup>	2.5	ST 5.00	HCl/37% 5.50	0.008	0	98.95	14,300	3.24
2	0.68	ST 1.36	HCl/37% 5.00	1	23.5-24	78.39	9,340	1.24
3	0.50	ST 1.00	HCl/37% 3.67	1	25	74.01	9,620	1.28
4	0.68	ST 1.36	HCl/37% 5.00	2	24	82.93	8,940	1.32
5	0.82	ST 1.64	HCl/37% 6.00	0.5	0	14.22	14,600	1.18
6	0.82	ST 1.64	HCl/37% 6.00	1	0	34.78	12,800	1.39
7	0.68	ST 1.36	HCl/37% 5.00	2	0	56.83	12,100	1.26
8	0.50	ST 1.00	HCl/37% 3.67	2	0	62.10	12,200	1.40
9	0.50	ST 1.00	HCl/37% 3.67	3	0	64.98	11,600	1.22
10	0.68	ST 1.36	HCl/37% 5.00	4	0	74.74	11,400	1.20
11	0.50	ST 1.00	HCl/37% 3.67	4	0	72.49	11,200	1.32
12	0.50	ST 1.00	HCl/37% 3.67	1	-20	12.19	14,600	1.24
13	0.50	ST 1.00	HCl/37% 3.67	2	-20	23.69	13,700	1.26
14	0.50	ST 1.00	HCl/37% 3.67	3	-20	27.65	13,700	1.21
15	0.50	ST 1.00	HCl/37% 3.67	4	-20	31.17	14,200	1.23
16	0.50	ST 1.00	HCl/37% 3.67	5	-20	37.45	12,300	1.26
17	0.50	ST 1.00	HCl/37% 3.67	6	-20	41.50	13,000	1.25
18	—	ST 1.00	HCl/37% 3.67	> 6	0	—	—	—

a. Organic/aqueous 50 vol/50 vol.

b. No solvent present.

#### Example 2

Similar behavior was witnessed when polymerization was conducted using neat monomer (Table 2).

Table 2. Polymerization of small aliquots of neat ST.<sup>a</sup>

Entry	CsCHB <sub>11</sub> Cl <sub>11</sub> (mg)	Monomer (g)	Acid (mL)	Temp. (°C)	Conv. (%)	$\overline{M}_w$ (g·mol <sup>-1</sup> )	PDI
1	0.50	ST 1.00	HCl/37% 1.10	26	75.35	13,400	2.53
2	0.50	ST 1.00	HCl/37% 1.10	0	77.34	23,800	3.28

- a. 100 % ST introduced by 11, 0.100 m L injections spaced every 5 min apart. Pzn time = 1 hour. Organic/aqueous 50vol/50vol.

### Example 3

Very small amounts of salt bearing a weakly coordinating anion are required to form the double, double salt catalyst (Table 3).

Table 3. Polymerization of toluene solutions of ST (30 wt % monomer) using reduced CsCHB<sub>11</sub>Cl<sub>11</sub>.<sup>a</sup>

Entry	CsCHB <sub>11</sub> Cl <sub>11</sub> (mg)	Monomer (g)	Acid (mL)	Time (hr)	Temp. (°C)	Conv. (%)	$\overline{M}_w$ (g·mol <sup>-1</sup> )	PDI
1 <sup>b</sup>	0.50	ST 2.00	HCl/37% 3.67	2	25	81.25	9,260	1.30
2 <sup>b</sup>	0.50	ST 2.00	HCl/37% 3.67	2	-20	11.63	13,500	1.31
3 <sup>c</sup>	0.50	ST 2.00	HCl/37% 7.34	2	25	56.25	9,330	1.25
4 <sup>c</sup>	0.50	ST 2.00	HCl/37% 7.34	4	0	39.99	16,500	1.13

- a. Organic/aqueous 50vol/50vol.  
 b. All monomer in at beginning of reaction.  
 c. Second monomer aliquot added at midway point of reaction.

### Examples 4-7

The double, double salt catalyst can be formed using a number of simple Brønsted acids (Tables 4 and 6-7). Polymerizations can also be conducted in polar solvents and dilute Brønsted acids are also efficient at producing the double, double salt catalyst (Tables 5-7).

Table 4. Polymerization of toluene solutions of ST (30 wt % monomer) using  $\text{H}_3\text{PO}_4/\text{CsCHB}_{11}\text{Cl}_{11}$ .<sup>a</sup>

Entry	$\text{CsCHB}_{11}\text{Cl}_{11}$ (mg)	Monomer (g)	Acid (mL)	Time (hr)	Temp. (°C)	Conv. (%)	$\overline{M}_w$ ( $\text{g}\cdot\text{mol}^{-1}$ )	PDI
1	0.50	ST 1.00	$\text{H}_3\text{PO}_4/85\%$ 3.67	1	23	100	8,590	1.95
2	0.50	ST 1.00	$\text{H}_3\text{PO}_4/85\%$ 3.67	1	26	100	8,740	1.47

a. Organic/aqueous 50vol/50vol.

Table 5. Polymerization of dichloromethane solutions of ST (30 wt % monomer) using  $\text{HCl}/\text{CsCHB}_{11}\text{Cl}_{11}$ .<sup>a</sup>

Entry	$\text{CsCHB}_{11}\text{Cl}_{11}$ (mg)	Monomer (g)	Acid (mL)	Time (hr)	Temp. (°C)	Conv. (%)	$\overline{M}_w$ ( $\text{g}\cdot\text{mol}^{-1}$ )	PDI
1	1.00	ST 2.00	$\text{HCl}/37\%$ 7.33	1	20	100	38,700	1.47
2	1.00	ST 2.00	$\text{HCl}/37\%$ 7.33	1	20	97.25	42,200	1.51
3	1.00	ST 2.00	$\text{HCl}/37\%$ 7.33	1/2	0	100	75,700	1.52
4	1.00	ST 2.00	$\text{HCl}/37\%$ 7.33	2	0	100	77,200	1.62
5	1.00	ST 2.00	$\text{HCl}/37\%$ 7.33	1	-23	100	135,000	1.45
6	1.00	ST 2.00	$\text{HCl}/37\%$ 7.33	2	-23	100	137,000	1.47
7	1.00	ST 2.00	$\text{HCl}/37\%$ 7.33	3	-23	100	137,000	1.56

a. Organic/aqueous 50vol/50vol.

Table 6. Polymerization of dichloromethane solutions of ST (30 wt % monomer) using diluted acids.<sup>a</sup>

Entry	CsCHB <sub>11</sub> Cl <sub>11</sub> (mg)	Monomer (g)	Acid (mL)	Time (hr)	Temp. (°C)	Conv. (%)	$\overline{M}_w$ (g·mol <sup>-1</sup> )	PDI
1	0.50	ST 1.00	HCl/18.5% 3.67	1	20	5.15	11,000	1.18
2	0.50	ST 1.00	HCl/18.5% 3.67	2	22	9.74	14,000	1.20
3	0.50	ST 1.00	HCl/18.5% 3.67	3	22	16.37	16,000	1.19
4	0.50	ST 1.00	H <sub>2</sub> SO <sub>4</sub> /49% 3.67	1/2	21	61.27	34,200	1.31
5	0.50	ST 1.00	H <sub>2</sub> SO <sub>4</sub> /49% 3.67	1/2	21	56.13	34,700	1.31
6	0.50	ST 1.00	H <sub>2</sub> SO <sub>4</sub> /49% 3.67	1	21	89.29	38,900	1.35
7	0.50	ST 1.00	H <sub>2</sub> SO <sub>4</sub> /49% 3.67	1	21	94.31	39,800	1.31
8	0.50	ST 1.00	H <sub>3</sub> PO <sub>4</sub> /42.5% 3.67	2	22	1.98	9,610	1.14
9	0.50	ST 1.00	HCl/18.5% 3.67	1	0	0.73	17,400	1.26
10	0.50	ST 1.00	HCl/18.5% 3.67	1	0	3.44	16,700	1.27
11	0.50	ST 1.00	HCl/18.5% 3.67	3	0	3.21	20,300	1.26
12	0.50	ST 1.00	HCl/18.5% 3.67	4	0	4.61	20,800	1.25
13	0.50	ST 1.00	H <sub>2</sub> SO <sub>4</sub> /49% 3.67	1/2	0	26.58	31,900	1.27
14	0.50	ST 1.00	H <sub>2</sub> SO <sub>4</sub> /49% 3.67	1/2	0	35.71	46,400	1.26
15	0.50	ST 1.00	H <sub>2</sub> SO <sub>4</sub> /49.25% 3.67	1	0	47.76	39,600	1.29
16	0.50	ST 1.00	H <sub>2</sub> SO <sub>4</sub> /49.25% 3.67	1	0	40.28	49,000	1.29

a. Organic/aqueous 50vol/50vol.

Table 7. Polymerization of neat ST using diluted HCl and H<sub>2</sub>SO<sub>4</sub>.<sup>a</sup>

Entry	CsCHB <sub>11</sub> Cl <sub>11</sub> (mg)	Monomer (g)	Acid (mL)	Time (hr)	Temp. (°C)	Conv. (%)	$\overline{M}_w$ (g·mol <sup>-1</sup> )	PDI
1	0.50	ST 1.00	H <sub>2</sub> SO <sub>4</sub> /49% 1.10	1/2	21	61.16	20,800	1.58
2	0.50	ST 1.00	HCl/18.5% 1.10	1	21	9.62	15,900	1.14
3	0.50	ST 1.00	HCl/18.5% 1.10	1	20	8.82	15,700	1.19
4	0.50	ST 1.00	H <sub>2</sub> SO <sub>4</sub> /49.25% 1.10	1	20	89.91	21,800	1.98
5	0.50	ST 1.00	H <sub>2</sub> SO <sub>4</sub> /49.25% 1.10	1	21	77.78	21,300	1.66
6	0.50	ST 1.00	H <sub>2</sub> SO <sub>4</sub> /49.25% 1.10	1	21	69.39	20,800	1.82
7	0.50	ST 1.00	HCl/18.5% 1.10	2	21	19.45	17,200	1.21
8	0.50	ST 1.00	HCl/18.5% 1.10	2	20	19.76	18,000	1.23
9	0.50	ST 1.00	HCl/18.5% 1.10	3	22	34.50	17,800	1.22
10	0.50	ST 1.00	HCl/18.5% 1.10	3	22	32.83	16,600	1.27
11	0.50	ST 1.00	HCl/18.5% 1.10	4	22	44.31	16,700	1.27
12	0.50	ST 1.00	HCl/18.5% 1.10	4	22	41.46	17,400	1.31
13	0.50	ST 1.00	H <sub>2</sub> SO <sub>4</sub> /49.25% 1.10	1/2	0	38.71	30,800	1.44
14	0.50	ST 1.00	H <sub>2</sub> SO <sub>4</sub> /49.25% 1.10	1/2	0	38.79	31,700	1.38
15	0.50	ST 1.00	H <sub>2</sub> SO <sub>4</sub> /49.25% 1.10	1	0	52.91	27,700	1.56
16	0.50	ST 1.00	H <sub>2</sub> SO <sub>4</sub> /49.25% 1.10	1	0	50.83	29,400	1.49
17	0.50	ST 1.00	HCl/18.5% 1.10	2	0	5.97	19,100	1.22
11	0.50	ST 1.00	HCl/18.5% 1.10	3	0	7.49	21,000	1.18
12	0.50	ST 1.00	HCl/18.5% 1.10	4	0	9.31	22,000	1.20

13	0.50	ST 1.00	HCl/18.5% 1.10	5	0	11.81	21,600	1.23
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a. Organic/aqueous 50vol/50vol.

### Examples 8-9

Other salts bearing a weakly coordinating anion can be used to form the double, double salt catalyst (Tables 8 and 9).

Table 8. Polymerization of dichloromethane solutions of ST (30 wt % monomer) using  $\text{Ph}_3\text{C}^+$  and  $\text{Li}^+ \text{B}(\text{C}_6\text{F}_5)_4^-$  in concentrated acid.<sup>a</sup>

Entry	$\text{M}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (mg)	Monomer (g)	Acid (mL)	Time (hr)	Temp. (°C)	Conv. (%)	$\overline{M}_w$ ( $\text{g}\cdot\text{mol}^{-1}$ )	PDI
1	$\text{Ph}_3\text{C}^+$ 5.0	ST 2.00	HCl/37% 7.33	1	0	96.74	58,000	1.75
2	$\text{Ph}_3\text{C}^+$ 5.0	ST 2.00	HCl/37% 7.33	1	0	98.10	36,900	1.58
3 <sup>b</sup>	$\text{Li}^+$ 10.0	ST 2.00	HCl/37% 7.33	1	0	61.22	26,100	2.23
4	$\text{Li}^+$ 10.0	ST 2.00	HCl/37% 7.33	1	0	56.66	27,200	1.33

a. Organic/aqueous 50vol/50vol.

b. Explosion.

Table 9. Polymerization of dichloromethane solutions of ST (30 wt % monomer) using  $\text{Ph}_3\text{C}^+$  and  $\text{Li}^+ \text{B}(\text{C}_6\text{F}_5)_4^-$  in dilute acid.<sup>a</sup>

Entry	$\text{M}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (mg)	Monomer (g)	Acid (mL)	Time (hr)	Temp. (°C)	Conv. (%)	$\overline{M}_w$ ( $\text{g}\cdot\text{mol}^{-1}$ )	PDI
1	$\text{Ph}_3\text{C}^+$ 5.0	ST 2.00	HCl/18.5% 7.33	1	21	52.60	19,400	1.26
2	$\text{Ph}_3\text{C}^+$ 5.0	ST 2.00	HCl/18.5% 7.33	1	21	57.57	18,200	1.30
3	$\text{Li}^+$ 5.0	ST 2.00	HCl/18.5% 7.33	1	21	86.84	22,100	1.27
4	$\text{Li}^+$ 5.0	ST 2.00	HCl/18.5% 7.33	1	21	69.21	25,800	1.29
5	$\text{Ph}_3\text{C}^+$ 5.0	ST 2.00	HCl/18.5% 7.33	1	0	9.66	21,000	1.30
6	$\text{Ph}_3\text{C}^+$ 5.0	ST 2.00	HCl/18.5% 7.33	1	0	8.43	21,100	1.19
7	$\text{Li}^+$ 5.0	ST 2.00	HCl/18.5% 7.33	1	0	28.08	25,200	1.27

8	Li <sup>+</sup> 5.0	ST 2.00	HCl/18.5% 7.33	1	0	56.66	27,200	1.33
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a. Organic/aqueous 50vol/50vol.

## CLAIMS

I claim:

1. A process for effecting electrophilic reactions comprising contacting suitable reactants with a double, double salt catalyst comprising: a salt bearing a weakly coordinating anion, and a Brønsted acid.
2. The process according to claim 1 wherein the weakly coordinating anion is based on a perfluoroarylated Lewis acid, a perfluoroalkylated Lewis acid, a perfluoroaryloxy borate, a perfluoroaryloxy aluminate, a perfluoroaryloxy gallate, a perfluoroalkoxy borate, a perfluoroalkoxy aluminate, a carborane, a metallocarborane, a perfluoroalkylsulfonate, or a perfluoroarylsulfonate.
3. The process according to claim 1 wherein the Brønsted acid is simple in nature.
4. The process according to claim 3 wherein the Brønsted acid is hydrofluoric acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, sulfuric acid, phosphoric acid, nitric acid, perchloric acid, trifluoromethanesulfonic acid, methanesulfonic acid, fluorosulfonic acid, chlorosulfonic acid, trifluoroacetic acid, trichloroacetic acid, chloroacetic acid, formic acid, or acetic acid.
5. The process according to claim 1 wherein the Brønsted acid is complex in nature.
6. The process according to claim 5 wherein the Brønsted acid is  $H^+[AlCl_3OH]^-$ ,  $H^+[AlBr_3OH]^-$ ,  $H^+[BF_3OH]^-$ ,  $H^+[BCl_3OH]^-$ ,  $H^+[BBr_3OH]^-$ ,  $H^+[SnCl_4OH]^-$ ,  $HOEt_2^+[BF_3OH]^-$ ,  $H^+[AlCl_4]^-$ ,  $H^+[AlBr_4]^-$ ,  $H^+[BF_4]^-$ ,  $H^+[BCl_4]^-$ ,  $H^+[BBr_4]^-$ ,  $H^+[BF_3OAc]^-$ ,  $H^+[BF_3OCH_3]^-$ ,  $H^+[BEt_3OH]^-$ ,  $H^+[ZnCl_2OH]^-$ ,  $H^+[ZnCl_3]^-$ ,  $H^+[Sc(O_3SCF_3)_3OH]^-$ ,  $H^+[Sc(O_3SCF_3)_3OCH_3]^-$ ,  $H^+[Sc(O_3SCF_3)_3OAc]^-$ ,  $H^+[Sc(O_3SCF_3)_3Cl]^-$ ,  $H^+[Yb(O_3SCF_3)_3OH]^-$ ,  $H^+[Yb(O_3SCF_3)_3OCH_3]^-$ ,  $H^+[Yb(O_3SCF_3)_3OAc]^-$ , or  $H^+[Yb(O_3SCF_3)_3Cl]^-$ .
7. A process according to claim 1 wherein the electrophilic reaction is optionally conducted in the presence of large quantities of water.