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(54) HALOGEN EXCHANGE REACTIONS AND USES THEREOF

HALOGENAUSTAUSCH-REAKTIONEN UND IHRE ANWENDUNGEN

REACTIONS DE SUBSTITUTION D'HALOGENES ET LEURS UTILISATIONS

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- **PATENT ABSTRACTS OF JAPAN vol. 015, no. 038 (C-0800), 30 January 1991 & JP 02 273626 A (NIPPON NOHYAKU CO LTD), 8 November 1990,**
- **PATENT ABSTRACTS OF JAPAN vol. 013, no. 187 (C-592), 2 May 1989 & JP 01 013037 A (IHARA CHEM IND CO LTD), 17 January 1989,**

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Description

[0001] This invention relates to halogen exchange reactions involving haloaromatic compounds and alkali metal fluorides, and more particularly to improved processes for producing polyfluorinated aromatics by catalyzed halogen exchange reactions, and to industrially important applications of such process technology.

BACKGROUND

[0002] Halogen exchange reactions for fluorinating haloaromatic compounds using alkali metal fluorides have been extensively studied heretofore. Typically they involve the reaction of a chloroaromatic compound with potassium fluoride, rubidium fluoride or cesium fluoride by heating the reactants to extremely high temperatures (above about 400°C) in the absence of an ancillary diluent or solvent, or by conducting the reaction at temperatures of around 200-230°C in an aprotic solvent such as sulfolane. It has also been reported that organic fluorine compounds such as pentafluorobenzonitrile, tetrafluorophthalonitriles and pentafluoropyridine can be formed by reacting a corresponding chloro- or bromo-substituted compound with alkali metal halide such as potassium fluoride in benzonitrile as solvent at 190°C to 400°C in a sealed autoclave under autogenous pressure.

[0003] Use of catalysts in some exchange reactions has also been studied. Such catalysts have included quaternary ammonium salts, metal carbonyls, crown ethers and cryptates.

[0004] In most cases, the halogen exchange reaction is sluggish and tends to form product mixtures in which yields of polyfluorinated aromatics are relatively low, especially if the haloaromatic compound used is a polyhaloaromatic compound free from activating functionality such as nitro or carbonyl. For example, with hexachlorobenzene and potassium fluoride, typical product mixtures contain a mixture of co-products including hexafluorobenzene together with various chlorofluorobenzenes.

[0005] A few examples of the extensive literature in this field of halogen exchange reactions include US Pat. No. 3,064, 058 to Duesel et al.; Finger et al., *J Am. Chem. Soc.,* **1956**, 78, 6034; Finger et al., *J. Org. Chem.,* **1963**, 28,1666; Maynard, *J. Org. Chem.,* **1963**, 28,112; Holbrook et al., *J. Org. Chem.,* 1966, 31, 1259; and Hitzke, *J. Fluor. Chem.,* **1980**, 16, 103.

[0006] A need presently exists for a commercially feasible process whereby the halogen exchange reaction as applied to a wide variety of haloaromatic compounds may be conducted in large scale reaction equipment under relatively mild reaction conditions while providing commercially acceptable yields of the desired products. In addition, a particularly welcome contribution to the art would be the provision of a process whereby fluorinated perhaloaromatic compounds such as chloropentafluorobenzene, bromopentafluorobenzene, and hexafluorobenzene can be produced on a large scale in good yield under relatively mild reaction conditions.

[0007] This invention is deemed to fulfill these needs most expeditiously. In addition, this invention makes possible the more efficient, lower cost production of a variety of industrially important end products.

SUMMARY OF THE INVENTION

[0008] This invention provides a new catalytic halogen exchange reaction using an alkali metal fluoride as the fluorine source. The process enables production of a wide variety of fluorinated aromatic compounds under relatively mild reaction conditions. Moreover, the process is applicable to use as starting materials of haloaromatic compounds containing one or more halogen atoms other than fluorine, including compounds which are devoid of activating groups, as well as compounds which possess one or more activating groups in the molecule. In fact, the process is especially well adapted for polyfluorination of perhaloaromatic compounds such as hexachlorobenzene, hexabromobenzene, pentachlorofluorobenzene, tetrachlorodifluorobenzene, trichlorotrifluorobenzene, dichlorotetrafluorobenzene, etc., which have no activating group in the molecule. In addition, the catalyzed process can be conducted with smaller excesses of the alkali metal fluoride than generally required in prior processes.

[0009] The substantial improvements made possible by this invention are brought about at least in part by use of an aminophosphonium catalyst such as tetrakis(diethylamino)-phosphonium chloride or tetrakis(diethylamino)phosphonium bromide in the process. As an example of such improvements, comparative studies on a 50-liter scale have shown that in reactions using hexachlorobenzene and potassium fluoride to form chloropentafluorobenzene and hexafluorobenzene, the inclusion of the aminophosphonium catalyst, tetrakis-(diethylamino)phosphonium bromide, pursuant to this invention resulted in the following yield improvements:

a) Yields of desired products based on raw material inputs were increased from 12% to 25%.
b) Yields of desired products based on hexachlorobenzene input were increased from 35% to 95%.
c) Molar yields of desired products were increased from 49% to 86%.

[0010] Thus, in accordance with this invention there is provided in one of its embodiments a halogen exchange process which comprises heating an agitated mixture formed from ingredients comprising (i) at least one finely-divided alkali metal fluoride, (ii) at least one haloaromatic compound having on an aromatic ring at least one halogen atom of atomic number greater than 9, and (iii) an aminophosphonium catalyst, at one or more reaction temperatures at which at least one said halogen atom of said haloaromatic compound is replaced by a fluorine atom.

[0011] In a preferred embodiment of this invention, the process is conducted using as the initial haloaromatic compound(s) for the halogen exchange, at least one haloaromatic compound that is devoid of any activating functional group on the aromatic ring to which the halogen atom of atomic number greater than 9 is bonded.

[0012] A particularly preferred embodiment involves using as the initial haloaromatic ingredient to be subjected to the halogen exchange processing, one or more haloaromatic compounds that are not only devoid of any activating functional group on the aromatic ring to which the halogen atom of atomic number greater than 9 is bonded, but in addition have no hydrogen atom on that aromatic ring. Especially preferred haloaromatic compounds of this type are perhaloaromatic compounds of the formula $C_6Cl_nBr_mF_p$ where n is from 0 to 6, m is from 0 to 6 and p is from 0 to 5, and where the sum of n, m and p is 6. Compounds in which m is zero have been used with outstanding success.

[0013] Another preferred embodiment includes conducting the process of this invention such that the essentially anhydrous agitated mixture when heated to one or more reaction temperatures is predominately a mixture of solids dispersed in a continuous liquid phase. Operations wherein the continuous liquid phase comprises at least one halogen-free, polar, anhydrous aprotic solvent constitute additional preferred embodiments of this invention.

[0014] Preferred catalyst ingredients for use in the various process embodiments of this invention are tetra(dihydrocarbylamino)phosphonium halides.

[0015] These and other embodiments, features and advantages of this invention will be further apparent from the ensuing description, accompanying drawing, and appended claims.

BRIEF DESCRIPTION OF THE DRAWING

[0016] Figure 1 illustrates schematically a batch type plant facility for conducting the process without use of an ancillary solvent/diluent.

FURTHER DESCRIPTION OF THE INVENTION

[0017] The basic feed materials to the process of this invention are one or more haloaromatic compounds containing one or more ar-halogen atoms other than fluorine, alkali metal fluoride(s) of one or more alkali metals other than lithium (preferably alkali metal of atomic number 19 or above), and one or more aminophosphonium catalysts. Use of one or more ancillary solvents or diluents is optional, but preferable.

Haloaromatic Ingredient

[0018] Any aromatic compound that has at least one replaceable halogen atom other than fluorine on the aromatic ring is a candidate ingredient for use in the process. The compound may have a homocyclic aromatic nucleus (i.e., at least one benzene ring system) or a heteroaromatic ring system. Also, the compound may contain one or more activating groups such as nitro, nitroso, carbonyl, cyano, and sulfonic acid, or it may be devoid of any such group. The compound contains one or more chlorine, bromine or iodine atoms, or any combination of Cl, Br, and/or I atoms on the aromatic ring and may also have one or more such halogen atoms on one or more side chains and/or on one or more non-aromatic homocyclic or heterocyclic rings bonded or fused to the aromatic ring system. In addition the compound may contain one or more fluorine atoms anywhere in the molecule including one or more ar-fluorine atoms provided the compound has at least one aromatic ring that contains at least one replaceable ar-halogen atom other than fluorine. The hetero atom in the halo-substituted aromatic ring where the fluorine substitution is desired is from 1 to 3 nitrogen atoms (e.g., the compound is, or has at least the ring system of, an ar-halopyridine, an ar-halopyridazine, an ar-halopyrimidine, an ar-halopyrazine, an ar-halotriazine where at least one ar-halogen atom is other than a fluorine atom). Other hetero atoms which can be present in side chains or additional ring systems of the compound include one or more nitrogen, oxygen, sulfur, phosphorus, boron or silicon atoms, or combinations of two or more of these. Generally speaking, the haloaromatic ingredient may contain in the range of up to 50 carbon atoms in the molecule, and preferably contains in the range of up to 20 carbon atoms in the molecule.

[0019] Preferred are haloaromatic compounds that are devoid of any activating group(s) in the molecule, as these usually undergo a halogen exchange reaction much less readily than their counterparts which have activating functionality in the molecule.

[0020] As between the homocyclic and heterocyclic haloaromatics, the homocyclic haloaromatics are preferred ingredients. As noted above, haloaromatics that are devoid of any activating functional group on the aromatic ring to

which the halogen atom of atomic number greater than 9 is bonded and in addition, are devoid of any hydrogen atom on that aromatic ring constitute another preferred category of haloaromatic ingredient or feed material for the process. Especially preferred haloaromatic compounds of this type are perhaloaromatic compounds of the formula $C_6Cl_nBr_mF_p$ where n is from 0 to 6, m is from 0 to 6 and p is from 0 to 5, and where the sum of n, m and p is 6. Compounds in which m is zero are especially desirable ingredients because of good reactivity in the process and generally lower cost. Moreover, there is a particularly pressing present need for methods for effectively producing polyfluorobenzenes, especially chloropentafluorobenzene and hexafluorobenzene, from their polychloro analogs such as hexachlorobenzene, pentachlorofluorobenzene, tetrachlorodifluorobenzene, trichlorotrifluorobenzene, or dichlorotetrafluorobenzene, or mixtures of any two or more of these, a need fulfilled by this invention.

[0021] Also fulfilled by this invention is the need for a method for effectively producing bromopentafluorobenzene from its polybromo analogs such as hexabromobenzene, pentabromofluorobenzene, tetrabromodifluorobenzene, tribromotrifluorobenzene, or dibromotetrafluorobenzene, or mixtures of any two or more of these.

[0022] Other haloaromatic compounds which can be converted into ar-fluorinated compounds by use of this invention include, for example, mono-, di-, tri-, tetra- and pentachlorobenzenes, and bromo and iodo analogs thereof; mono and polychloro, bromo and iodo naphthalenes, tetrahydronaphthalenes, acenaphthalenes, biphenyls and terphenyls; alkyl- and haloalkyl-substituted analogs of the foregoing; chloro, bromo and iodo diarylethers and monoalkylmonoaryl ethers; 2-chloronitrobenzene; 4-chloronitrobenzene; 2,4-dinitrochlorobenzene; 3,4-dichloronitrobenzene; 3-chloro-4-fluoronitrobenzene; 2,4,6-trichloropyrimidine; tetrachloropyrimidine; 2-chlorobenzonitrile; 4-chlorobenzonitrile; pentachlorobenzonitrile; tetrachloroisophthalonitrile; 2-chloropyridine; 2,5-dichloropyridine; pentachloropyridine; 4-chlorophthalic anhydride; and still other similar compounds, such as are referred to in U.S. Pat. No. 4,684,734 to Kaieda, et al.

Alkali Metal Fluoride Ingredient

[0023] Potassium fluoride, rubidium fluoride, and cesium fluoride are the preferred alkali metal halides used in the practice of this invention because of their higher reactivity in the exchange reaction. However, sodium fluoride can be used, especially where the haloaromatic ingredient has activating functionality on the haloaromatic ring, and in cases where only partial replacement of ar-chloride, ar-bromide or ar-iodide is desired.

[0024] Combinations of any two or more of the alkali metal fluorides can be used, including combinations in which lithium fluoride is present. Thus, mixtures of potassium fluoride, rubidium fluoride and/or cesium fluoride together with sodium fluoride or lithium fluoride, or both, can also be used if desired, although this is not recommended. To enhance its reactivity, the alkali metal fluoride should be in finely-divided or powdery anhydrous form. Potassium fluoride is the preferred fluorinating agent as it is the most cost effective reagent. At least one embodiment of the present invention uses KF principally or exclusively as the alkali metal fluoride ingredient. One convenient way of ensuring that the fluorinating agent is suitably anhydrous is to form a slurry of the fluoride salt in a suitable volatile hydrocarbon such as benzene that forms an azeotrope with water, and heat the mixture to dryness, while of course suitably handling and disposing of the vapors. A particularly useful form of potassium fluoride for use in the process is the active form of KF produced using the procedure described by T. P. Smyth, A. Carey and B. K. Hodnett in *Tetrahedron,* Volume 51, No. 22, pp. 6363-6376 (1995). In brief, the procedure involves recrystallizing KF from a methanol solution by slow evaporation of the solvent, followed by drying at 100°C. Another useful form of potassium fluoride is KF dispersed on CaF_2. This material is described by J. H. Clark, A. J. Hyde and D. K. Smith in *J. Chem. Soc. Chem. Commun,* **1986**, 791. Other activated forms of KF such as spray dried KF (N. Ishikawa, et al. *Chem. Letts,* **1981**, 761), and freeze dried KF (Y. Kimura, et al. *Tetrahedron Letters,* **1989**, 1271) can be used. It is also deemed possible to apply one or more of the foregoing activating procedures to other alkali metal fluorides such as cesium fluoride and/or sodium fluoride.

[0025] To enhance its reactivity, the alkali metal fluoride as charged to the reaction mixture is preferably in finely-divided or powdery anhydrous or substantially anhydrous form, i.e., it should not contain, if any, more than 3000 parts per million (ppm) of water on a weight basis. Potassium fluoride is the preferred fluorinating agent as it is the most cost-effective reagent, and most preferably it will have a water content, if any, below 1000 ppm. Ordinarily the alkali metal fluoride particles should have an average surface area of at least 0.20 m^2/g. In this connection, the larger the average surface area of the alkali metal fluoride particles, the better. Thus it is preferred that the alkali metal fluoride initially have an average surface area of at least 0.40 m^2/g, and more preferably at least 0.80 m^2/g. For example, as charged to the reactor in the practice of this invention, spray dried potassium fluoride with a typical water content of 1000 ppm and an average surface area of 0.85 m^2/g has been found to give a reaction rate that is approximately four times the rate given under the same conditions by spray dried potassium fluoride with an average surface area of 0.25 m^2/g.

[0026] The proportions of alkali metal fluoride to the haloaromatic ingredient(s) being used can be varied. In theory there is no upper limit on the amount of alkali metal fluoride used relative to the amount of haloaromatic compound(s) used. If a very large excess of alkali metal fluoride is used relative to the amount of replaceable halogen present in the haloaromatic ingredient(s) present, the latter becomes the limiting reactant and the excess alkali metal halide remains

as such. When the reaction is performed in the absence of an ancillary diluent, an excess amount of the alkali metal fluoride can serve to facilitate stirring or other agitation of the reaction mixture, and thus to this extent use of a suitable excess of alkali metal fluoride can be beneficial. Nevertheless, beyond a certain level of excess alkali metal fluoride, common sense and practicality come into play. Thus ordinarily the amount of alkali metal fluoride will not exceed 10 or 15 mols per mol of replaceable halogen in the initial haloaromatic ingredient(s) used, and in most cases will be less than this. If on the other hand the amount of replaceable halogen in the haloaromatic ingredient(s) used exceeds the molar quantity of alkali metal fluoride used, the latter becomes the limiting reactant. Thus in most cases this factor will also be taken into consideration when selecting the proportions for use in any given reaction. Generally speaking, the reactants will often be employed in proportions falling in the range of from about 0.8 to about 5 mols of alkali metal fluoride per mol of replaceable halogen in the haloaromatic ingredient(s) used therewith, and in some preferred cases such as where an ancillary diluent is employed, the reactants will be charged in proportions in the range of from about 1 to about 3 mols of alkali metal fluoride per mol of replaceable halogen in the haloaromatic ingredient(s) used therewith.

Aminophosphonium Catalyst Ingredient

[0027] An essential catalyst ingredient of this invention is at least one aminophosphonium catalyst ingredient. One or more other co-catalysts may also be included, if desired, as long as at least one aminophosphonium catalyst ingredient is charged, concurrently or in any sequence, into the reaction zone or reaction mixture. Use of the aminophosphonium catalyst without use of a co-catalyst is currently deemed preferable.

[0028] The aminophosphonium catalysts are preferably charged in the form of tetra(di-hydrocarbylamino)phosphonium halides. Such compounds can be represented by the formula:

$$(R_2N)_4P^{\oplus}\ X^{\ominus}$$

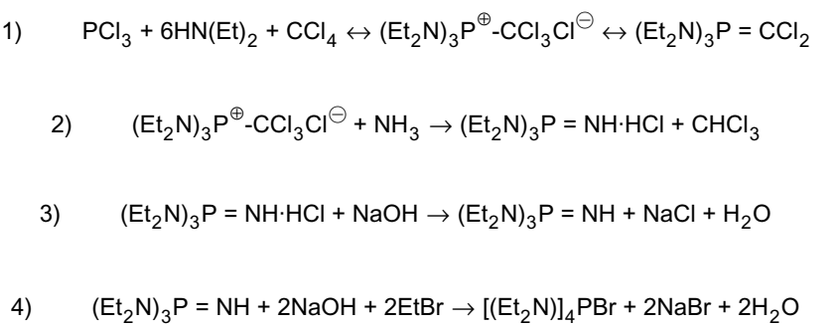
where each R is, independently, a hydrocarbyl group, preferably an alkyl group, and X is a halogen atom, preferably a chlorine or bromine atom, and most preferably a bromine atom. Examples of such aminophosphonium compounds are:

tetrakis(diethylamino)phosphonium fluoride
tetrakis(dibutylamino)phosphonium bromide
tris(diethylamino)(dipropylamino)phosphonium iodide
tetrakis(dibutylamino)phosphonium iodide
tris(dibutylamino)(diethylamino)phosphonium iodide
tris(dipropylamino)(diheptylamino)phosphonium iodide
tetrakis(dipropylamino)phosphonium bromide
tris(diethylamino)(dihexylamino)phosphonium iodide
tris(diethylamino)(dibutylamino)phosphonium iodide
tris(dipropylamino)(heptylpropylamino)phosphonium iodide
tetrakis(dipropylamino)phosphonium iodide
tris(dipropylamino)(ethylpropylamino)phosphonium iodide
tetrakis(diethylamino)phosphonium iodide
tetrakis(diethylamino)phosphonium bromide
tetrakis(diphenylamino)phosphonium bromide
tetrakis(di-m-tolylamino)phosphonium bromide
tetrakis(dibenzylamino)phosphonium bromide
tetrakis(dicyclohexylamino)phosphonium bromide
tetrakis(dioctylamino)phosphonium bromide
tetrakis(didecylamino)phosphonium bromide
tetrakis(diethylamino)phosphonium chloride
tetrakis(dipropylamino)phosphonium chloride
tetrakis(dibutylamino)phosphonium chloride
tetrakis(dihexylamino)phosphonium chloride.

One preferred group of aminophosphonium catalyst in the form as charged to the reactor is comprised of the tetra (dialkylamino)phosphonium chlorides and/or bromides. Of these, the aminophosphonium catalyst ingredient is more preferably one or more tetra(dialkylamino)phosphonium bromides in which the alkyl groups can be the same or different and each has up to 12 carbon atoms. At present, the most preferred compound is tetrakis(diethylaminophosphonium

bromide. For a method for the preparation of such compounds, see Koidan, Marchenko, Kudryavtsev, and Pinchuk, *Zh. Obshch. Khim.,* 1982, 52, 2001, an English language translation of which is available from Plenum Publishing Corporation.

[0029] A procedure which has been used for preparing tetra(diethylamino)phosphonium bromide involves the following four steps (where Et represents an ethyl group):



In this procedure, carbon tetrachloride and phosphorus trichloride are charged to the reactor followed by the slow addition of diethyl amine at low temperature (30°C maximum). This results in the formation of dichloromethylene phosphoroamidite intermediate. Ammonia (gas) is then charged to the reactor resulting in the formation of an imino hydrochloride phosphoroamidite intermediate. Following a period of stirring, the reactor contents are filtered, and the filtrate is concentrated by evaporation under vacuum. The concentrated filtrate is then treated with sodium hydroxide solution causing the formation of the free base imino phosphoroamidite. This is extracted with dichloromethane. The extracted solution is dried with calcium chloride and the dichloromethane is removed by evaporation. The solid product is mixed with sodium hydroxide and bromoethane is charged. This results in the formation of the product tetra(diethylamino) phosphonium bromide. The product is then extracted with dichloromethane. The extract is dried and the dichloromethane is removed by evaporation. The crude product is then recrystallized from a mixture of dichloromethane and diethyl ether. The recrystallized, wet, product is then dried.

[0030] Typical raw materials input for such sequential operations is as follows: carbon tetrachloride, 3985 grams (25.7 moles); phosphorous trichloride, 270 grams (1.96 moles); diethyl amine, 880 grams (12.39 moles); ammonia, 40 grams (2.35 moles); 50% sodium hydroxide, 315 grams; dichloromethane, 472 grams; calcium chloride (anhydrous), 23.6 grams; 20% sodium hydroxide, 534 grams; bromoethane, 230 grams (2.12 moles); dichloromethane, 1643 grams; calcium chloride (anhydrous) 82.1 grams; dichloromethane 450 grams; diethyl ether, and 450 grams. Typically this provides a yield of 300 grams (0.754 moles) per batch.

[0031] The aminophosphonium catalyst is used in catalytically effective amounts, and such amounts typically fall in the range of 3 to 6 mol%, and preferably in the range of 4 to 5 mol%, based on the total amount (in mols) of the haloaromatic compound(s) with which the aminophosphonium catalyst is being associated in the reaction zone.

Co-catalyst Ingredient

[0032] The tetra(dihydrocarbylamino)phosphonium halide catalysts are effective when utilized as the only catalyst component charged directly or indirectly (i.e., after admixture with one or more other components being charged to the reaction system). Such catalytic mode of operation is preferred. However, as noted above, one or more co-catalyst ingredients may be used, if desired.

[0033] One type of such co-catalyst materials is comprised of one or more crown ethers or crypt compounds. These compounds, sometimes referred to as "cage compounds" can prove helpful in further enhancing the reactivity of the alkali metal fluoride. See in this connection, U.S. Pat. No. 4,174,349 to Evans, et al. A full description of the crown ethers and the crypt compounds is provided in the Evans, et al. patent and references cited therein relating to these materials, namely U.S. Pat. No. 3,687,978; J. J. Christensen, et al., *Chem. Rev.,* 1974, 74, 351; J. S. Bradshaw, et al., *Heterocycl. Chem.,* 1974, 11, 649; C. J. Pedersen, et al., *Angew. Chem. Int. Ed. Engl.,* 1972, 11, 16; the Technical Bulletin of PCR Incorporated entitled KRYPTOFIX; and *J. Org. Chem.,* 1977, Vol 42, No. 10, 2A. The crown ether or crypt compound is used in a catalytically effective amount, which typically is in the range of 0.01 to 1 mol per mol of haloaromatic compound(s) in the reaction mixture.

[0034] Another type of co-catalyst that can be used is composed of (i) at least one polyvalent inorganic fluoride of boron, aluminum, tin, phosphorus, titanium, zirconium, hafnium, or silicon, or (ii) at least one double salt of the polyvalent inorganic fluoride and alkali metal fluoride, or (iii) a combination of (i) and (ii), with the proviso that the inorganic fluoride of (i), (ii) and (iii) is in a stable valency state so that (i), (ii) and (iii), as the case may be, has no oxidizing properties.

U.S. Pat. No. 3,453,337 to Bennett, et al., reports that in the uncatalyzed reaction between hexachlorobenzene and KF or NaF, the inclusion of compounds of the types (i), (ii) and (iii) above provides enhanced product yields using milder reaction conditions and shorter reaction times. Examples of suitable polyvalent compounds include $LiBF_4$, $NaBF_4$, KBF_4, K_2SnF_6, KPF_6, K_2SiF_6, Na_2TiF_6, K_2TiF_6, Na_2ZrF_6, K_2ZrF_6, Na_2HfF_6, K_2HfF_6, among others. Such compounds can be used in catalytically effective amounts of up to 50% or more of the weight of the alkali metal fluoride charged to the reaction mixture. Typically the amount will fall in the range of 2 to 25 % of the weight of alkali metal fluoride used.

[0035] Other co-catalysts which may be considered for use include quaternary ammonium salts such as described for example by J. Dockx, *Synthesis,* **1973**, 441; C.M. Starks and C. Liotta, *Phase Transfer Catalysts,* **1978**, Academic Press, New York; and W.P. Weber and G.W. Gokel, *Phase Transfer Catalysis in Organic Synthesis,* **1977**, Springer-Verlag, Berlin-Heidelberg-New York); and metal carbonyls such as described by M.F. Semmelhack and H.T. Hall, *J. Am. Chem. Soc.,* **1974**, 96, 7091.

[0036] The aminophosphonium catalyst and the above co-catalyst(s), if used, can vary both in function and in composition. As to function, they can serve to promote or enhance the fluorination exchange reaction, e.g., (a) by increasing reaction rate without affecting yield or selectivity, (b) by increasing yield or selectivity, or both, without affecting reaction rate, or (c) by increasing reaction rate and improving yield or selectivity, or both. Thus the term "catalyst" or "co-catalyst" is used herein to denote that the material in the manner used improves or enhances the reaction process in some way or other so that the inclusion or presence of that material or its progeny in the reaction mixture provides at least one beneficial consequence of its use. The mechanism by which it exerts its effect(s) is of no consequence, provided of course that the advantage(s) of its use outweigh(s) the disadvantage(s), if any, of its use.

[0037] As regards catalyst and co-catalyst composition, the material is identified herein as to its composition prior to being combined with any other substance being used in the process. After addition to, and/or mixing with, one or more other ingredients used in the process and/or during the course of the process itself, the catalyst may change in its composition, and if so, the resultant changed material, whatever its makeup and however many changes it may undergo, may be responsible in whole or in part for the functioning of the catalyst.

Process Conditions

[0038] The process can be conducted by dry mixing the finely-divided essentially anhydrous alkali metal fluoride, the haloaromatic compound having at least one halogen atom of atomic number greater than 9 on an aromatic ring, and an aminophosphonium catalyst, and heating the mixture at one or more reaction temperatures at which at least one such halogen atom of the haloaromatic compound is replaced by a fluorine atom. Alternatively, the foregoing ingredients may be heated to one or more such reaction temperatures while in admixture with an ancillary solvent/diluent. The solvent or diluent used is preferably a polar aprotic solvent such as, for example, sulfolane (tetramethylene sulfone), N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfone, dimethylsulfoxide, triglyme (triethylene glycol dimethyl ether), N-methyl pyrrolidinone, or benzonitrile, or mixtures of two or more of such materials, and like polar aprotic solvents that are in the liquid state at the reaction temperature selected for use, and more preferably that are also in the liquid state at 10°C or below. Benzonitrile, liquid alkyl bensonitrile, and ring-substituted liquid alkylbenzonitriles (e.g., o-methylbenzonitrile, m-methylbenzonitrile, etc.), and especially benzonitrile itself, are the preferred solvents. Another preferred aprotic solvent is nitrobenzene because of its excellent solvency characteristics and relatively low cost. Other solvent/diluents for use in the process are haloaromatics that are in the liquid state at least at, and preferably below, the reaction temperature(s) being employed. Examples include hexafluorobenzene, octafluorotoluene, perfluorodecalin, dichlorotetrafluorobenzene, trichlorotrifluorobenzene and tetrachlorodifluorobenzene. The last three such compounds are especially desirable as solvent/diluents when producing pentachlorofluorobenzene as they not only serve as solvent/diluents, but as reactants as well. Thus, the aprotic solvent can be predominantly or entirely (a) benzonitrile, (b) at least one liquid alkylbenzonitrile, (c) nitrobenzene, (d) at least one liquid alkylmononitrobenzene, or (e) a mixture of at least two of (a), (b), (c), and (d).

[0039] Whether the reaction mixture is formed with or without a solvent/diluent, the reaction mixture should be thoroughly agitated during the course of the reaction to ensure intimate contact among the different materials in the mixture. Thus use of mechanical agitation equipment such as mechanical stirrers, rocking autoclaves, or similar apparatus is highly recommended.

[0040] The reaction mixture prior to heating may be predominantly a solid phase mixture. When the reaction mixture is heated to one or more reaction temperatures in a solvent, it is predominantly a mixture of solids dispersed in a continuous liquid phase comprising at least one halogen-free, polar, anhydrous or substantially anhydrous aprotic solvent.

[0041] Reaction temperatures will typically be in the range of about 150°C to about 350°C and preferably in the range of about 170°C to about 250°C. When the process is conducted as a slurry process using a liquid aprotic solvent or diluent, it is preferred to conduct the process at one or more temperatures in the range of about 200°C to about 240°C. The reaction may be conducted at atmospheric, sub-atmospheric or super-atmospheric pressures. In many cases it

is desirable as well as convenient to carry out the reaction in a closed system at autogenous pressures. Reaction periods will typically fall in the range of about 2 to about 48 hours, and preferably in the range of about 5 to about 20 hours. It will be appreciated that on the basis of this disclosure, departures from any of the ranges of proportions and/or reaction conditions given above may be made whenever such departures are deemed necessary or desirable.

[0042] There may be one embodiment where a vapor phase mixture of perhalobenzenes is formed and, from this, at least one of the more volatile perhalobenzene components is separated and recovered from one or more less volatile perhalobenzene components of the vapor phase mixture. At least a portion of the one or more less volatile perhalobenzene components is recycled to the present or a subsequent halogen exchange reaction.

[0043] The following Examples 1-12 illustrate the halogen exchange process of this invention when performed without use of an ancillary solvent or diluent. These and all ensuing examples herein are for the purpose of illustration and not limitation.

EXAMPLES 1-12

[0044] A facility of the type schematically depicted in Figure 1 is used. It comprises a 50-liter capacity stainless steel reactor (316S) **10** fitted with an electrical heating system (not depicted), bottom discharge valve **12**, vapor condenser **14**, receiver **16**, vacuum system **18**, a pressure release system (not depicted) that operates via the overheads, nitrogen line **20** for vacuum breaking, pressure gauge/monitor **22**, temperature gauge/monitor **24**, and manway **26** for solids charging. Reactor **10** is capable of operating at working pressures up to 125 psi, and vacuum system **18** has the capability of operating to 10 mmHg pressure. Agitator **28** is preferably a modified gate-type agitator having scraping knife-edges on the gate agitator to minimize sticking of the semi-molten paste-like reaction mass especially at the reactor wall. The facility should also include a spray drier (not depicted).

[0045] In the operation of the facility freshly prepared anhydrous potassium fluoride is used for each batch. This is conveniently prepared by forming a 40% weight/volume solution of potassium fluoride, heating the solution to the boiling point and pumping the solution via a dried atomizer into a drier operated at 350-400°C, e.g., 370°C. The dry powder is placed into suitable containers and used immediately. Alternatively, an activated form of KF such as referred to above, or a commercially available spray dried KF (whether milled or not milled), can be used. Before initiating a reaction, steps should be taken to ensure that the reactor **10** and the overheads are clean and dry, that all systems are operational, and that all raw materials are available for use. In addition the system should be checked to ensure that the bottom valve **12** is closed. If there is any doubt as regards vessel dryness, the reactor should be heated to 105°C with full vacuum applied for two hours. After two hours the vessel should be allowed to cool while under vacuum. At ambient temperature the vacuum is then broken with nitrogen, and at this point the reaction procedure may be commenced.

[0046] At the start of the batch operation, reactor agitator **28** should be activated to be sure that the agitator is running smoothly. To the reactor with the agitator in operation, 21 kg of dry potassium fluoride powder is charged via manway **26**. Then through the manway are charged 15 kg of hexachlorobenzene followed by 0.96 kg of tetrakis(diethylamino) phosphonium bromide. Manway **26** and valve **30** are closed. The reactor contents are then heated over a period of one hour to 180°C. It is important to use this rapid heating to ensure sufficient agitation of this particular reaction mixture. During the heating the pressure in the reactor rises gradually. When the reactor contents reach 180°C, the reactor heating controls are adjusted to provide a heating rate increase of 4°C per six hours. The reactor contents are allowed to heat up over this rate over 42 hours (7 increments of temperature increase for a total temperature increase of 28°C). Slow heating at this stage of the process is important to ensure adequate mixing of this particular reaction mixture. At this point the reaction mixture should have reached a temperature of approximately 208°C and the internal pressure of the reactor is monitored hourly. When the pressure does not vary between two successive hourly readings, the reaction can be deemed to have proceeded to completion. When the pressure becomes constant in the range of 75-100 psi the heating system is turned off and the reactor is allowed to cool. At this point valve **30** is cautiously opened to allow the pressure to vent from the reactor to condenser **14** and thence to receiver **16**. When ambient pressure is reached in the reactor nitrogen is slowly introduced via nitrogen line **20**. Vacuum system **18** is put into operation to provide a vacuum of 725 mmHg to reactor **10**. The nitrogen bleed to the reactor is slowly reduced while observing the rate of distillate recovery to receiver **16** to ensure that distillate recovery is not excessive. The vacuum is then gradually increased while continuing to monitor distillate recovery rate until maximum (flat) vacuum is achieved. When the system reaches ambient temperature the vacuum is broken with nitrogen, the vacuum system is shut off, and then the nitrogen bleed is discontinued. The reaction product mixture is then recovered from the reactor through valve **12**. The reactor is cleaned with boiling aqueous caustic solution, washed with water and dried. A series of 12 batch operations was conducted generally in accordance with this procedure. The facility was as described except that in Examples 1 and 2, a low speed gate agitator was used. Because of tackiness of the reaction mixture, portions of the mixture tended to stick to the reactor wall. This problem was reduced by changing the agitator used in the remainder of the operations so that it included the above-referred-to knife-blades on the gate agitator. The conditions and results of these 12 runs

are summarized in Table 1 along with the conditions and results of a control run where no catalyst was used. The acronyms in the Table are: HCB is hexachlorobenzene, CPFB is chloropentafluorobenzene, and DCTFB is dichlorotetrafluorobenzene.

TABLE 1

Ex. No.	KF Charged, kg	HCB Charged, kg	Catalyst Charged, kg	Molar Ratio, KF:HCB	Reaction Time, hr	HFB Yield, kg	CPFB Yield, kg	DCTFB Yield, kg	Conversion of HCB, %	% Molar Yield HFB + CPFB
--*	34.0	15.0	None	11.1:1	24	2.5	2.5	--	--	49
1	15.4	11.0	0.97	6.866:1	60	2.555	2.608	0.7353	77.64	69
2	15.4	11.0	0.98	6.866:1	82	2.4336	2.8137	0.6253	77.67	70
3	15.4	11.0	0.98	6.866:1	32	3.0964	2.9500	0.7906	90.21	81
4	21.0	15.0	1.30	6.867:1	22.5	3.7200	4.0000	1.2090	85.98	76
5	21.0	15.0	1.03	6.867:1	20	3.7011	4.2515	0.1900	78.95	78
6	21.0	15.0	1.03	6.867:1	46	4.5472	2.8490	1.8282	88.96	73
7	21.0	15.0	0.942	6.867:1	38	3.9763	4.1376	0.1900	81.09	79
8	21.0	15.0	0.96	6.867:1	44	3.9861	3.8378	0.7416	83.16	77
9	21.0	15.0	0.96	6.867:1	29.5	2.7824	4.1454	1.9082	83.86	67
10	21.0	15.0	0.96	6.867:1	34.5	3.1420	4.1447	1.7954	86.54	71
11	21.0	15.0	0.96	6.867:1	46	4.3521	4.1302	1.2931	94.41	83
12	21.0	15.0	0.96	6.867:1	46	4.4160	4.3008	1.1232	95.19	86

* Control run.

[0047] In the Table, reaction time is the time from reaching reaction temperature of 190°C and yields of products are

expressed as kilograms derived from analysis of the fraction of hexafluorobenzene, chloropentafluorobenzene and dichlorotetrafluorobenzene flash distilled from the respective reaction mixtures. Fractional distillation of the combined products from Examples 1-12 matched these analytical results almost exactly. Examples 1-12 yielded 104.765 kilograms of mixed chlorofluorobenzenes. The bulk fractional distillation resulted in the isolation and recovery of:

41.085 kg of Hexafluorobenzene
43.020 kg of Chloropentafluorobenzene
11.440 kg of Dichlorotetrafluorobenzene

Each such product assayed 99% minimum purity.

[0048] It is to be noted that in the above examples, the catalyzed process of this invention was conducted at a maximum temperature of 208°C without use of any added ancillary solvent or diluent. A conventional non-catalyzed non-solvent reaction of hexachlorobenzene with potassium fluoride typically involves use of 20-liter autoclaves operating at a temperature of 450°C and a pressure of up to 1,500 psi and employs an 85% excess of potassium fluoride. Based on total raw material input, batch yield of desired products is around 12%.

[0049] A number of modifications in the process are possible without departing from the scope of this invention. By way of illustration and not limitation, the following modifications are presented:

a) The catalyst or catalyst residues may be recycled.
b) When the desired product is a polyfluoroaromatic compound, intermediates formed that contain a lesser than desired number of fluorine atoms per molecule may be recycled.
c) If the desired product has suitably high volatility, it may be removed from the reaction zone during the course of the reaction, e.g., essentially as soon as it is formed, so as to prevent or at least minimize overfluorination.
d) Special procedures, e.g., drying by azeotropic distillation or by high temperature spray drying, may be employed for drying the alkali metal fluoride before use.
e) Multistage drying procedures may be used for drying the alkali metal fluoride before use.
f) The alkali metal fluoride may be micronized or reduced to a colloidal state in one or more stages prior to use.
g) Combinations of one or more drying stages with one or more micronizing stages, or vice versa, may be applied to the alkali metal fluoride before use.
h) Whether operating with or without an ancillary solvent, the alkali metal fluoride may be an optimized mixture composed of a major amount of dry, finely-divided potassium fluoride with a minor reaction-enhancing amount of dry, finely-divided cesium fluoride.
i) When producing a desired product having one or more intermediates that are in the liquid state at or below the selected reaction temperature(s), such intermediates may be employed as solvent/diluents in the process.
j) The proportions of the selected ingredients for use in any given situation may, and should be, optimized by performing carefully designed pilot experiments and scale-up trials before settling upon the mode of operation in a large scale commercial facility.
k) In lieu of or in addition to one or more simple alkali metal fluorides, e.g. KF, the alkali metal reactant may be or include a more complex alkali metal salt such as a double salt, examples of which include KBF_4, $CsBF_4$, $NaBF_4$, K_3AlF_6, K_2SnF_6, Cs_2SnF_6, KPF_6, $CsPF_6$, K_2SiF_6, Cs_2SiF_6, Na_2TiF_6, K_2TiF_6, Na_2ZrF_6, K_2ZrF_6, Na_2HfF_6, K_2HfF_6, among others.
l) Simple quaternary phosphonium salts such as tetraethylphosphonium bromide, tetraphenylphosphonium bromide, tetraethylphosphonium chloride, tetraphenylphosphonium chloride, tetraethylphosphonium iodide, tetraphenylphosphonium iodide, etc., may be used as co-catalyst ingredients.

[0050] An example of one such modification which constitutes an embodiment of this invention relates to the synthesis of chloropentafluorobenzene and/or hexafluorobenzene from hexachlorobenzene. In this process the alkali metal fluoride ingredient used preferably comprises potassium fluoride, and the aminophosphonium catalyst ingredient used is preferably at least one tetra(dialkylamino)phosphonium halide (especially tetra(diethylamino)phosphonium bromide), and the agitated mixture formed from hexachlorobenzene, potassium fluoride, and the aminophosphonium catalyst ingredient is heated at one or more reaction temperatures in the range of 170 to 240°C (preferably in the range of 200 to 230°C) for at least a substantial portion of the reaction. In this particular embodiment the agitated mixture comprises solids suspended or dispersed in continuous liquid phase, which preferably comprises a major amount (preferably 60 volume % or more at the outset of the reaction) of at least one chlorofluoroperhalobenzene that is in the liquid state at least while the agitated mixture is at one or more reaction temperatures in the range of 170 to 240°C. Examples of such chlorofluoroperhalobenzenes include dichlorotetrafluorobenzene (b.p. at atmospheric pressure, approximately 151°C), trichlorotrifluorobenzene (m.p., approximately 62°C), and tetrachlordifluorobenzene (m.p., approximately 138°C). Of these, dichlorotetrafluorobenzene is particularly desirable as it is a liquid at room temperature and can

readily be kept in the liquid state at temperatures in the range of 170 to 220°C by conducting the reaction at suitable superatmospheric pressures.

[0051] A preferred embodiment is to conduct the halogen exchange reaction of this invention as a slurry process using at least one aprotic solvent or diluent. When conducting the halogen exchange process as a slurry process, the reaction mixture should be anhydrous or substantially anhydrous before reaching the temperature at which the halogen exchange reaction is initiated, and preferably the reaction mixture should be anhydrous or substantially anhydrous *ab initio.* The term "substantially anhydrous" as used in this document with reference to the reaction mixture, i.e., the mixture of the reactants, catalyst(s), and solvent(s), means that the total water content of the mixture at the commencement of the exchange reaction at 160°C or above is below 2000 ppm (wt/wt) and preferably below 1500 ppm. In general, the lower the water content, the better. Excessive water can kill the reaction. Therefore it is desirable not only to use anhydrous or substantially anhydrous alkali metal fluoride (not more than 3000 ppm, as noted above), but to ensure that the other components being used are sufficiently dry (i.e., have water contents, if any, that are sufficiently low as to keep the total water content of the overall mixture below 2000 ppm (wt/wt) and preferably below 1500 ppm. For example, if industrial grades of polar aprotic solvents contain excessive amounts of water, it is desirable to dry the solvent to a level of, say, 100 ppm, preferably down to a level of 50 ppm (wt/wt) by means of azeotropic distillation or use of molecular sieves. It is usually very difficult to produce, maintain and use chemicals, especially in a large scale chemical facility, in an absolutely anhydrous condition. Thus the term "anhydrous" is used herein in the same sense as those skilled in the art understand the term. Thus, if by chance the substance used has absolutely zero water content, it is, of course "anhydrous". But even if it does not have zero water content, as long as the water content is in the trace range so that the effect of the water present is of no material consequence and the water content complies with manufacturer's specifications and/or designations of "anhydrous", the substance is deemed herein to be "anhydrous". Without limiting the generality of the foregoing, one commercial supplier, Aldrich Chemical Company, in its 1996-1997 Catalog Handbook of Fine Chemicals refers to a group of listed "anhydrous solvents" on page 1773 thereof as having a water content of < 0.005%. Other suppliers may specify other maximum water contents for their "anhydrous" grades, so there is no exact fine line of distinction between "anhydrous" and "substantially anhydrous".

[0052] The following Examples 13-21 illustrate procedures for conducting the halogen exchange process of this invention as a slurry process in an aprotic solvent. All parts given in these examples are by weight.

EXAMPLE 13

[0053] The reaction equipment used is a reactor equipped with heating means, mechanical stirrer, charge and discharge ports, and an overhead take-off line for feeding vaporous product from the reactor to an intermediate portion of a fractionation column. The column in turn is equipped with an overhead line for collecting the chloropentafluorobenzene and a line for returning the condensed bottoms from the condenser to a discharge point in the reactor below the liquid level therein. A mixture of 285 parts of hexachlorobenzene, 406 parts of anhydrous ball-milled potassium fluoride powder, 600 parts of sulfolane, and 80 parts of tetrakis(diethylamino)phosphonium bromide is heated with stirring at 200°C for 40 hours while continuously removing and fractionating the volatiles. The overhead from the column is chloropentafluorobenzene. The bottoms from the column are continuously returned to below the surface of the slurry within the reactor.

EXAMPLE 14

[0054] A mixture of 285 parts of hexachlorobenzene, 406 parts of anhydrous potassium fluoride powder activated by the procedure of T. P. Smyth, A. Carey and B. K. Hodnett (*loc. cit.*), 80 parts of tetrakis(diethylamino)phosphonium bromide, 600 parts of triglyme, and 80 parts of potassium fluoborate is heated in the above reactor with stirring at 195-210°C for 40 hours. Vaporous perchlorofluorobenzenes are continuously taken off overhead and fractionated as in Example 1.

EXAMPLE 15

[0055] The procedure of Example 13 is repeated in the same manner except that 80 parts of 18-crown-6 ether is also included in the initial reaction mixture.

EXAMPLE 16

[0056] The procedure of Example 13 is repeated in the same manner except that 80 parts of crypt 222 is also included in the initial reaction mixture.

EXAMPLE 17

[0057] The procedure of Example 14 is repeated in the same manner except that 80 parts of 18-crown-6 ether is also included in the initial reaction mixture.

EXAMPLE 18

[0058] The procedure of Example 13 is repeated in the same manner except that 150 parts of a mixture of pentachlorofluorobenzene, tetrachlorodifluorobenzene, and trichlorotrifluorobenzene (such as recovered from the reaction mixture of a prior reaction) is also included in the initial reaction mixture, and a total of 450 parts of spray dried potassium fluoride is charged to the reactor.

EXAMPLE 19

[0059] The procedure of Example 13 is repeated in the same manner except that 80 parts of 18-crown-6 ether and 150 parts of dichlorotetrafluorobenzene, are also included in the initial reaction mixture, and a total of 450 parts of spray dried potassium fluoride is charged to the reactor.

[0060] Example 20 which follows, illustrates a preferred process for pretreating the quaternary phosphonium catalyst to remove therefrom at least a portion, *inter alia,* quaternary ammonium halide impurity. Further details concerning such process are set forth in commonly-owned WO-A-99/26950 filed contemporaneously herewith, and incorporated herein. In Examples 21 and 22 the pretreated, purified catalyst was used, and in Example 23 the original non-pretreated catalyst was used. A comparison between Examples 22 and 23 performed in the same way illustrates the advantages of using a pretreated, purified catalyst when practicing any of the embodiments of this invention.

EXAMPLE 20

[0061] To a 1-liter flask containing 156 grams of tetrahydrofuran was added with stirring 38.90 grams of tetrakis (diethylamino)phosphonium bromide catalyst (Chordip Limited, England, 75% purity). The residual insoluble material (2.8 grams) was filtered from the solution, and was determined by ^{1}H-NMR to be primarily tetraethylammonium bromide. To the tetrahydrofuran solution of the catalyst was then added 245 grams of anhydrous diethyl ether resulting in the precipitation of the tetrakis(diethylamino)phosphonium bromide catalyst. The solid catalyst was then filtered and dried under full vacuum at about 50°C for one hour. The purified catalyst (29.8 grams) was analyzed by ^{31}P-NMR and was found to be at least 95% pure.

EXAMPLE 21

[0062] To a 1-liter stainless steel stirred pressure reactor was added a solution of 12 grams of purified catalyst from Example 20 in 421 grams of benzonitrile (Aldrich, <50 ppm water), 164 grams of spray-dried potassium fluoride (Hashimoto Chemical Corporation, Japan, 0.87 m^2/g), and 115 grams of hexachlorobenzene. The overhead of the reactor comprised of a 1/2 inch (1.27 cm)-OD column packed with 15-inch (38.1cm) long Pro-Pak® packing, an air-cooled partial condenser (also known as a knockback condenser), an air-cooled total condenser, and a product receiver with a back-pressure control valve. The reaction mixture, a slurry, was heated and maintained at 218-220°C for 5 hours while maintaining the system pressure at 14 psig (197.9 kPa) and the column distillate temperature at 140°C. The vaporized perhalobenzenes, predominately chloropentafluorobenzene and some hexafluorobenzene, were carried to the overhead about as soon as they were formed, and thereupon were condensed and recovered. Concurrently, other condensed perhalobenzenes were being returned from the knockback condenser to the reaction mixture. At the end of the 5-hour reaction period, the heating was discontinued and all the volatile products remaining in the reactor were removed by distillation by application of progressively increased vacuum to the system in order to recover all volatile products formed in the reaction. The entire distillate product mixture was analyzed by gas chromatography. The yields, based on hexachlorobenzene, and were 2.5% hexafluorobenzene, 58.6% chloropentafluorobenzene, 23.8% dichlorotetrafluorobenzene, and 7.5% trichlorotrifluorobenzene.

EXAMPLE 22

[0063] A solution of 12.0 grams of purified tetrakis(diethylamino)phosphonium chloride catalyst from Example 20 in 420 grams of benzonitrile (Aldrich, <50 ppm water) was charged to a 1-liter stainless steel stirred pressure reactor. Spray-dried potassium fluoride (164 grams, Hashimoto Chemical Corporation, Japan, 0.87 m^2/g) and hexachlorobenzene (115 grams) were then added to the reactor. The reaction mixture was reacted for 5.5 hours at 220°C. The heating

was then discontinued and all the volatile products were removed by simple distillation at progressively increased vacuum. The distillate mixture was analyzed by gas chromatography. The yields, based on hexachlorobenzene, were 24.4% hexafluorobenzene, 39.9% chloropentafluorobenzene, 21.9% dichlorotetrafluorobenzene, and 8.1% trichlorotrifluorobenzene.

EXAMPLE 23

[0064] A solution of 15.1 grams of tetrakis(diethylamino)phosphonium chloride (Chordip Limited; 75% purity) in 420 grams of benzonitrile (Aldrich, <50 ppm water) was charged to a 1-liter stainless steel stirred pressure reactor. Spray-dried potassium fluoride (164 grams, Hashimoto Chemical Corporation, Japan, 0.87 m^2/g) and hexachlorobenzene (115 grams) were then added to the reactor. The reaction mixture was reacted for 6.5 hours at 220°C. The heating was then discontinued and all the volatile products were removed by simple distillation at progressively increased vacuum. The distillate mixture was analyzed by gas chromatography. The yields, based on hexachlorobenzene, were 34.7% hexafluorobenzene, 37.7% chloropentafluorobenzene, 12.3% dichlorotetrafluorobenzene, and 3.9% trichlorotrifluorobenzene.

[0065] A most efficacious way presently known for carrying out the halogen exchange process in order to produce perhalobenzenes having at least 3, preferably at least 4, and more preferably either 5 or 6 fluorine atoms on the ring is a process which comprises heating a slurry formed from ingredients comprising (i) at least one finely-divided alkali metal fluoride having an atomic number of 19 or more, (ii) a perhalobenzene of the formula $C_6F_nX_{6-n}$ where n is 0 to 4, and each X is, independently, a chlorine or bromine atom, (iii) a tetra(dihydrocarbylamino)phosphonium halide catalyst, most preferably tetrakis(diethylamino)phosphonium bromide or chloride, and (iv) at least one halogen-free, polar, aprotic solvent, preferably benzonitrile and/or an alkyl-substituted benzonitrile that is in the liquid state at a temperature at least as low as 20°C., and/or nitrobenzene under conditions to form perhalobenzene having at least 3, preferably at least 4, and most preferably 5 or 6 fluorine atoms per molecule. The most efficacious way of producing perhalobenzenes having either 5 and/or 6 fluorine atoms on the ring is the process which comprises:

a) heating the above slurry formed from the foregoing ingredients comprising (i)-(iv) at one or more reaction temperatures at which a vapor phase comprising at least one perhalobenzene having at least 5 fluorine atoms per molecule is formed; and
b) continuously removing vapor phase from the slurry;
c) separating perhalobenzene having at least 5 fluorine atoms on the ring from the vapor phase; and
d) returning all or at least a portion of the remainder of the component(s) of the vapor phase, if any, into the slurry.

In a preferred embodiment, steps c) and d) are conducted continuously so that steady state conditions exist in the reaction zone. It is also preferred that the initial water content of the slurry is below 1500 ppm on a weight basis before heating to the selected reaction temperature(s). Also the slurry preferably is formed from 5 to 8 moles of said alkali metal fluoride and from 0.05 to 0.3 mole of said catalyst per mole of perhalobenzene used in forming the slurry. When this process is used for producing chloropenta-fluorobenzene as the main product, a preferred starting material is hexachlorobenzene, and the reaction conditions in the reaction zone are maintained such that when the reaction slurry is at the selected reaction temperature(s) (most preferably no higher than 250°C), the amount, if any, of chloropentafluorobenzene in the liquid phase of the slurry averages no more than 5 percent by weight based on the total weight of the liquids in the slurry. In such cases the vapor phase is typically composed of vaporized polar, aprotic solvent, hexafluoro-benzene, chloropentafluorobenzene, dichlorotetrafluorobenzene, and trichlorotrifluoro-benzene, and most preferably, of the perhalobenzenes in the vapor phase, chloropenta-fluorobenzene is present in the largest amount.

[0066] The discovery pursuant to this invention of the unprecedented effectiveness aminophosphonium catalysts in a halogen exchange reaction makes it possible pursuant to this invention to produce industrially important end products with greater efficiency and reduced costs as compared to most, if not all, prior halogen exchange technology. Some of the improvements in, and applications of, this discovery are described below.

Production of Pentafluorophenylorganometallic Compounds

[0067] Production of pentafluorophenylorganometallic compounds is effected by a process which comprises (A) producing a perhalobenzene having 5 fluorine atoms on the ring, preferably chloropentafluorobenzene, by a halogen exchange process of this invention, and (B) reacting perhalobenzene produced and recovered in the process of (A) with a Grignard reagent under conditions forming a pentafluorophenyl Grignard reagent, preferably by a Grignard exchange reaction. These steps (A) and (B) can be performed in one continuous sequential operation in a given plant facility, or these steps can be conducted separately at different times, and also at different plant locations.

[0068] Alternatively, in step (B), perhalobenzene produced and recovered in the process of (A) can be reacted under

carefully controlled conditions (e.g., very low temperatures such as -78°C with an alkali metal alkyl of the formula MR, where M is an alkali metal such as lithium, sodium or potassium, and R is an alkyl group having 4 to about 12 carbon atoms under conditions forming pentafluorophenyl alkali metal compound such as C_6F_5Li, C_6F_5Na, or C_6F_5K. Because these alkali metal compounds can be explosive, this alternative process, while feasible, is not recommended.

[0069] In conducting the Grignard exchange reaction it is preferred to react chloropenta-fluorobenzene with a C_3 to C_{20} hydrocarbyl magnesium halide Grignard reagent in an ether solvent and under anhydrous reaction conditions. Preferred C_3 to C_{20} hydrocarbyl magnesium halide Grignard reagents are those in which the halide is bromide or iodide and in which the hydrocarbyl group is an alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl or aralkyl group, and Grignard reagents having 2 to 10 carbon atoms are the more preferred reactants. Most preferred are the isopropyl magnesium halides, especially the bromide. While proportions can be varied, it is best to employ about 1-2 moles of chloropentafluorobenzene per mole of the hydrocarbyl Grignard reagent used as the reactant. For further details concerning this preferred Grignard exchange procedure, see Krzystowczyk et al., EP 728,760 A2, published August 28, 1996.

[0070] Example 24, which is based in part on the Grignard exchange process of the foregoing published EP application of Krzystowczyk et al., illustrates a preferred procedure for conducting this process.

EXAMPLE 24

[0071] In a drybox, 31.45 g of chloropentafluorobenzene prepared as in Example 21 above (0.155 mole) and 64.42 g of a 2 molar ether solution of isopropylmagnesium bromide (iPrMgBr) (0.141 mole) are charged to a Fisher Porter reactor and heated to 60°C for 4.5 hours. Pentafluorophenylmagnesium bromide is formed. So far as is presently known, this overall operation represents the most cost-effective commercially feasible process for producing pentafluorophenyl Grignard reagent that has ever been discovered.

[0072] When using bromopentafluorobenzene in the Grignard exchange reaction, ethyl magnesium bromide can be used as the initial Grignard reagent. However as shown by Tamborski, et al., *J. Organometal. Chem.,* **1971**, 26, 153-156, it is desirable to use short reaction periods when employing that procedure.

[0073] Pentafluorophenyl alkali metal compounds pursuant to this invention is best accomplished by reacting perhalobenzene produced and recovered in the halogen exchange process such as in Example 21 above with an alkali metal alkyl such as butyllithium or ethylsodium at -78°C in an anhydrous paraffinic or cycloparaffinic hydrocarbon medium (e.g., hexane or heptane) under an inert atmosphere. Alternatively, controlled reaction of metallic sodium with chloropentafluorobenzene or bromopentafluorobenzene in an inert hydrocarbon or ether reaction medium at -78 °C can be used to produce the alkali metal pentafluorophenyl alkali metal compound. In this case any solids formed are removed by filtration or other similar procedure. Normally small portions of the alkali metal are introduced slowly into a hydrocarbon or ether solution of the chloropentafluorbenzene or bromopentafluorbenzene while stirring the resulting reaction mixture and maintaining the mixture at a temperature at -78°C.

Production of Pentafluorophenyl Boron Compounds

[0074] To produce pentafluorophenyl boron compounds, the process comprises the following steps conducted sequentially, either in one continuous operation or in a series of two or three separate operations which can be conducted at different time periods at a given plant site, or at different plant locations:

A) producing a perhalobenzene having 5 fluorine atoms on the ring, preferably chloropentafluorobenzene, by a halogen exchange process of this invention,
B) converting perhalobenzene from A) into a pentafluorophenyl organometallic compound, preferably a pentafluorophenyl Grignard reagent, using a process such as described above, and
C) converting pentafluorophenyl organometallic compound from B) into a pentafluorophenyl boron compound by reacting the pentafluorophenyl organometallic compound with a boron trihalide or an etherate complex thereof, preferably boron trifluoride or a boron trifluoride etherate complex.

In performing this process, it is preferred to form chloropentafluorobenzene in A), form pentafluoromagnesium bromide Grignard reagent in ethyl ether in B), and form tris(pentafluorophenyl)boron (also known as tris(pentafluorophenyl) borane) in C) by reacting the Grignard reagent with boron trifluoride etherate in ethyl ether.

[0075] Example 25, based in part on the above Krzystowczyk et al. published EP application, illustrates the synthesis of tris(pentafluorophenyl)borane from pentafluorophenylmagnesium bromide.

EXAMPLE 25

[0076] To a four-neck round bottom flask is added 131 mmoles of the pentafluorophenylmagnesium bromide solution

in diethyl ether formed as in Example 24 above. To this solution is charged 5.84 g (41.4 mmoles) of boron trifluoride diethyletherate while maintaining the temperature at 0°C. The resulting solution is allowed to warm to room temperature and is stirred for 16 hours whereby tris(pentafluorophenyl)borane is formed. So far as is presently known, this overall operation represents the most cost-effective commercially feasible process for producing tris(pentafluorophenyl)borane that has ever been discovered.

Production of Tetra(pentafluorophenyl)boron Anion

[0077] In order to produce tetra(pentafluorophenyl)boron anion, the process comprises the following steps conducted sequentially, either in one continuous or intermittent operation at a given plant site, or in a series of two or more separate operations which can be conducted at different time periods and at different plant sites:

A) producing a perhalobenzene having 5 fluorine atoms on the ring, preferably chloropentafluorobenzene, by a halogen exchange process of this invention,
B) converting perhalobenzene from A) into a pentafluorophenyl organometallic compound using a process such as described above,
C) converting pentafluorophenyl organometallic compound from B) into a pentafluorophenyl boron compound by reacting the organometallic compound with a boron trihalide or an etherate complex thereof, preferably boron trifluoride or a boron trifluoride etherate complex such as described above, and
D) converting pentafluorophenyl boron compound from C) in a suitable solvent or diluent into a single coordination complex that comprises a labile tetra(pentafluorophenyl)boron anion.

In conducting this operation it is preferred in C) to mix together in an ether medium, a pentafluorophenyl Grignard reagent and boron trifluoride or a boron trifluoride etherate in proportions of 4.1 to 4.5 moles of the Grignard reagent per mole of the BF_3, and maintain the temperature in the range of 25 to 45°C. The product of this reaction is an ether-soluble complex, $(C_6F_5)_4BMgX$. Likewise, it is preferred in D) to mix together an aqueous solution of a hydrocarbyl ammonium chloride or bromide such as N,N-dimethylanilinium chloride or tributylammonium chloride, and the ethereal solution of the complex formed in C) by slowly adding the aqueous hydrocarbyl ammonium halide solution to the ether solution of the complex formed in C) while keeping the temperature at 5°C or below and stirring the mixture. In this reaction use of an excess of the hydrocarbyl ammonium chloride or bromide is desirable.

[0078] Examples 26 and 27 illustrate production of N,N-dimethylanilinium tetrakis-(pentafluorophenyl)borane and tributylammonium tetrakis(pentafluorophenyl)borane, respectively, which are typical coordination complexes that comprise a labile tetra(pentafluorophenyl)boron anion and a cation capable of irreversibly reacting with a ligand (e.g., a methyl group) bonded to the transition metal atom of a Group 4 metallocene to thereby form an ionic catalyst composition.

EXAMPLE 26

[0079] Boron trifluoride diethyl etherate (138.7 g, 0.98 mole) is added to a diethyl ether solution of pentafluorophenylmagnesium bromide (3326 g, 4.17 moles) formed as in Example 24. The addition is at a rate allowing the mixture to reach reflux temperature. The mixture is heated at reflux for 18 hours. This mixture is then cooled to -10°C and N, N-dimethylanilinium chloride (1142 grams, 2.06 moles) previously formed from concentrated HCl, water, and N,N-dimethylaniline is slowly added while keeping the temperature at 0°C. After the addition, the mixture is stirred for one hour at -5°C to 0°C. Then the two phases are separated, and the organic phase is washed with water and dried over $MgSO_4$. The N,N-dimethylanilinium tetrakis(pentafluorophenyl)borane is precipitated by addition of hexane with stirring, and recovered by filtration.

EXAMPLE 27

[0080] Tributylammonium tetrakis(pentafluorophenyl)borane is produced by substituting 2.06 moles of tributylammonium chloride for the N,N-dimethylanilinium chloride.

Production of Active Polymerization Catalysts

[0081] To produce one type of active polymerization catalysts suitable for use in forming homopolymers and copolymers of polymerizable monoolefin, diolefin, and acetylenic monomers, the process comprises the following steps conducted sequentially, either in one continuous operation or in a series of two or more separate operations which can be conducted at different time periods either at one plant site or at two or more different plant sites:

A) producing a perhalobenzene having 5 fluorine atoms on the ring, preferably chloropentafluorobenzene, by a halogen exchange process of this invention,
B) converting perhalobenzene from A) into a pentafluorophenyl organometallic compound using a process such as described above,
C) converting pentafluorophenyl organometallic compound from B) into a pentafluorophenyl boron compound by reacting the organometallic compound with a boron trihalide or an etherate complex thereof, preferably boron trifluoride or a boron trifluoride etherate complex such as described above,
D) converting pentafluorophenyl boron compound from C) in a suitable solvent or diluent into a single coordination complex that comprises a labile tetra(pentafluorophenyl)boron anion such as described above, and
E) forming an active catalyst by a process comprising mixing together in a suitable solvent or diluent, (i) a cyclopentadienyl metal compound containing a Group 4 transition metal, and (ii) at least a second component comprising said complex, under conditions and for a period of time such that the cation of said complex reacts irreversibly with at least one ligand of the cyclopentadienyl compound, and such that the pentafluorophenyl anion forms a non-coordinating ion pair with a resulting cation produced from the cyclopentadienyl metal compound.

The following examples further illustrate the preparation of active catalysts and use of such catalysts in the polymerization of unsaturated monomers to form useful polymeric materials. Examples 28-50 are based in part on Examples appearing in U.S. Pat. No. 5,198,401, and Examples 51-56 are based in part on U.S. Pat. No. 5,153,157.

EXAMPLE 28

[0082] To a one-liter stainless-steel autoclave containing a dry nitrogen atmosphere are charged 400 mL of dry, oxygen-free hexane, a solution of 15 mg of bis(cyclopentadienyl)hafnium dimethyl in 30 mL of toluene, and then a toluene solution (50 mL) containing 12 mg of bis(cyclopentadienyl)hafnium dimethyl and 30 mg of tri(n-butyl)ammonium tetrakis(pentafluorophenyl)boron formed as in Example 27 above. The autoclave is pressured with 90 psig of ethylene and stirred at 60°C for one hour. The autoclave is vented and opened and the polyethylene formed is recovered.

EXAMPLE 29

[0083] To the autoclave of Example 15 previously purged with dry nitrogen are charged 400 mL of dry, oxygen-free hexane, and a solution of 9 mg of bis(tertbutylcyclopentadienyl)zirconium dimethyl and 2.9 mg of N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron formed as in Example 26 above, in 25 mL of toluene. The autoclave is then charged with 100 mL of 1-butene and further pressured with 65 psig of ethylene and stirred at 50°C for one hour. The autoclave is vented, cooled and the contents dried. The ethylene-1-butene copolymer formed in the process is recovered.

EXAMPLE 30

[0084] To a one-liter stainless-steel autoclave containing a dry nitrogen atmosphere are charged 400 mL of dry, oxygen-free hexane, a solution of 15 mg of bis(cyclopentadienyl)hafnium dimethyl in 25 mL of toluene, and then a toluene solution (50 mL) containing 17 mg of bis(cyclopentadienyl)hafnium dimethyl and 42 mg of tri(n-butyl)ammonium tetrakis(pentafluorophenyl)boron formed as in Example 27 above. Propylene (200mL) was added and the autoclave is pressured with 50 psig of ethylene and stirred at 60°C for fifteen minutes. The autoclave is vented and opened and the residual hexane in the contents evaporated under a stream of air. The ethylene and propylene formed are recovered.

EXAMPLES 31-38

[0085] Using procedures as in Examples 28-30 a series of catalyst compositions, all pursuant to this invention are prepared and polymerization runs are performed. Table 1 summarizes the materials used in the respective polymerization runs. In each run summarized in Table 2, the anion source is either tributylammonium tetrakis(pentafluorophenyl) boron (BAPFB) produced as in Example 27 above or N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron (MAPFB) produced as in Example 26 above. The Group 4 metallocene and the anion source are added in each case as a solution in an appropriate amount of toluene.

TABLE 2

Ex.	Group 4 compound (mg)	Anion Source (mg)	Ancillary Diluent	Temp.	Time	Monomer(s)
31	$(Cp)_2Hf(Me)_2$ (36)	MAPFB (11)	None*	50°C	15 min.	Propylene (400 mL), ethylene (120 psig)
32	$(Cp)_2Hf(Me)_2$ (12)	BAPFB (30)	Hexane	50°C	60 min.	1-Butene (50 mL), ethylene (65 psig)
33	$(Cp)_2Hf(Me)_2$ (19)	BAPFB (15)	Hexane	50°C	45 min.	1-Butene (50 mL), propylene (25 mL), ethylene (60 psig)
34	$(Cp)_2Hf(Me)_2$ (72)	MAPFB (16)	Hexane	50°C	10 min.	1,4-Hexadiene (100 mL), propylene (50 mL), ethylene (90 psig)
35	$(Cp)_2Hf(Me)_2$ (27)	BAPFB (30)	Hexane	50°C	60 min.	1-Hexene (100 mL), ethylene (65 psig)
36	$(Cp)_2Hf(Me)_2$ (72)	MAPFB (22)	Hexane	40°C	65 min.	Propylene (200 mL)
37	$(Cp)_2Hf(Me)_2$ (77)	MAPFB (22)	None*	40°C	90 min.	Propylene (400 mL)
38	rac-dimethylsilyl(In)$_2$Hf(Me)$_2$ (10)	MAPFB (5)	None*	40°C	270 min.	Propylene (500 mL)

* Polymerization conducted in bulk propylene.

EXAMPLE 39

[0086] To a polymerization vessel are added 0.22 g of tributylammonium tetrakis(pentafluorophenyl)boron (produced as in Example 27 above) in 50 mL of toluene, followed by 0.1 g of bis(pentamethylcyclopentadienyl)zirconium dimethyl. The vessel is capped with a rubber septum and stirred at room temperature for 10 minutes. Then the vessel is pressured with 1.5 atmospheres of ethylene and stirred vigorously. After 15 minutes the reaction vessel is vented and methanol is added to destroy the catalyst. Linear polyethylene is recovered from the resulting mixture.

EXAMPLE 40

[0087] The procedure of Example 39 is repeated with the following changes: 0.34 g of the anion source produced as in Example 27 above is used, the Group 4 metallocene used is 0.13 g of (cyclopentadienyl)(pentamethylcyclopentadienyl)zirconium dimethyl, and the reaction is terminated with methanol after 10 minutes. Polyethylene is produced.

EXAMPLE 41

[0088] Polyethylene is produced by conducting the procedure of Example 39 with the following changes: 0.18 g of the same anion source produced as in Example 27 above is used, the Group 4 metallocene is 0.12 g of bis[1,3-bis (trimethylsilyl)cyclopentadienyl]zirconium dimethyl, and the reaction is terminated with methanol after 10 minutes.

EXAMPLE 42

[0089] The procedure of Example 39 is repeated except that 0.34 g of the anion source formed as in Example 27 above is used together with 0.1 g of bis(cyclopentadienyl)zirconium dimethyl, and the polymerization reaction is terminated after 10 minutes. Polyethylene produced in the polymerization is recovered.

EXAMPLE 43

[0090] To a polymerization vessel are added 0.12 g of tributylammonium tetrakis(pentafluorophenyl)boron (produced as in Example 27 above) and 0.04 g of bis(cyclopentadienyl)zirconium dimethyl in 100 mL of toluene. The vessel is capped with a rubber septum and stirred at 60°C for 3 minutes. Then 3 mL of 1-hexene and ethylene at 1.5 atmospheres are added to the vessel. After 20 minutes the reaction vessel is vented and methanol is added to deactivate the catalyst. An ethylene-hexene copolymer is recovered from the resulting mixture.

EXAMPLE 44

[0091] An active catalyst is formed pursuant to this invention by reacting 550 mg of bis(trimethylsilylcyclopentadienyl) hafnium dimethyl with 800 mg of N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron (formed as in Example 26 above) in 50 mL of toluene in a polymerization vessel. On passing ethylene into the solution, an exothermic reaction occurs with the formation of polyethylene.

EXAMPLES 45-50

[0092] Six active catalysts are produced in accordance with this invention by mixing together in toluene the following components:

Ex. 45: 40 mg of N.N-dimethylanilinium tetrakis(pentafluorophenyl)boron (formed as in Example 26 above) and 17 mg of 1-bis(cyclopentadienyl)zircona-3-dimethylsilacyclobutane.

Ex. 46: 80 mg of N.N-dimethylanilinium tetrakis(pentafluorophenyl)boron (formed as in Example 26 above) and 36 mg of 1-bis(cyclopentadienyl)titana-3-dimethylsilacyclobutadiene.

Ex. 47: 85 mg of tributylammonium tetrakis(pentafluorophenyl)boron (formed as in Example 27 above) and 34 mg of bis(cyclopentadienyl)zirconium (2,3-dimethyl-1,3-butadiene.

Ex. 48 39 mg of N.N-dimethylanilinium tetrakis(pentafluorophenyl)boron (formed as in Example 26 above) and 20 mg of 1-bis(cyclopentadienyl)hafna-3-dimethylsilacyclobutane.

Ex. 49 41 mg of tributylammonium tetrakis(pentafluorophenyl)boron (formed as in Example 27 above) and 21 mg of bis(cyclopentadienyl)hafnium (2,3-dimethyl-1,3-butadiene.

Ex. 50 75 mg of N.N-dimethylanilinium tetrakis(pentafluorophenyl)boron (formed as in Example 26 above) and 53 mg of (pentamethylcyclopentadienyl)(tetramethylcyclopentadienylmethylene)hafnium benzyl.

Polyethylene is produced by passing ethylene through each of these 6 respective catalyst solutions.

EXAMPLE 51

[0093] To an autoclave containing a dry nitrogen atmosphere are added a toluene solution (20 mL) containing 0.2 mmoles of triethylborane, and then a solution formed from 5 mL of toluene, 3 mg of bis(cyclopentadienyl)zirconium dimethyl, and 1.5 mg of N,N-dimethylanilinium tetrakis-(pentafluorophenyl)boron produced as in Example 26 above. The vessel is pressured with 90 psig of ethylene and stirred at 40°C for one hour. The vessel is vented and opened, and linear polyethylene is recovered from the autoclave.

EXAMPLE 52

[0094] Example 51 is repeated except that a toluene solution formed from 5 mL of toluene, 4 mg of bis(cyclopentadienyl)hafnium dimethyl and 1.5 mg of N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron produced as in Example 26 above is used. Linear polyethylene is produced.

EXAMPLE 53

[0095] Example 51 is repeated except that a solution formed from 20 mL of toluene and 0.2 mmole of triethylaluminum is charged to the autoclave followed by a solution formed from 10 mL of toluene, 3 mg of bis(cyclopentadienyl)zirconium dimethyl and 3 mg of N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron produced as in Example 26 above. Linear polyethylene is produced.

EXAMPLE 54

[0096] Example 51 is repeated except that after charging the toluene solution of triethylaluminum, a solution formed from 20 mL of toluene, 3 mg of bis(cyclopentadienyl)hafnium dimethyl and 6 mg of N,N-dimethylanilinium tetrakis (pentafluorophenyl)boron produced as in Example 26 above is used. Linear polyethylene is produced.

EXAMPLE 55

[0097] To a one-liter stainless steel autoclave containing a dry nitrogen atmosphere are added 0.2 ml of a 35 wt% solution of triethylaluminum in hexane followed by 10 mL of a solution formed from 10 mL of toluene, 36 mg of bis (cyclopentadienyl)hafnium dimethyl, and 11 mg of N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron produced as in Example 26 above. Propylene (400 mL) is added to the autoclave and the contents are heated to 40°C. The vessel is then pressured with 200 psig of ethylene and stirred at 40°C for 0.5 hour. The vessel is vented and opened, and a copolymer of ethylene and propylene is recovered from the autoclave.

EXAMPLE 56

[0098] Example 43 is repeated except that the triethylaluminum is replaced by 0.2 mmole of triethylborane, and the ensuing solution used is formed from 10 mL of toluene, 24 mg of bis(cyclopentadienyl)hafnium dimethyl, and 8 mg of N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron produced as in Example 26 above. Produced is an ethylene-propylene copolymer.

EXAMPLES 57-71

[0099] Supported catalyst compositions are produced and used as polymerization catalysts by carrying out the procedures described in detail in the 15 examples of PCT published application WO 91/09882 A1 (as published 11 July 1991), but in each case using N,N-dimethylanilinium tetrakis(pentafluorophenyl)boron formed as in Example 26 above. In each instance the unit cost of the catalyst is significantly reduced without sacrifice of operating efficiency.

[0100] Another process for producing supported catalysts comprises reacting a pentafluorophenyl boron compound produced pursuant to this invention such as described above, preferably so-produced tris(pentafluorophenyl)borane, with hydroxy groups of a metal/metalloid oxide support under conditions to form a support-bound anionic activator, and then contacting said support-bound anionic activator with a suitable metallocene of a Group 4 transition metal such that the activator protonates the metallocene whereby a supported ionic catalyst system is produced comprising a transition metal cation and a support bound anion. The supports should have surface hydroxyl groups exhibiting a pK_a equal to or less than that of amorphous silica, i.e., a pK_a less than or equal to 11. Silica and silica-alumina meeting

these criteria are preferred support materials. For complete details concerning procedures and materials suitable for use in preparing supported catalysts of this type one should refer to PCT Published Patent Application WO 96/04319 A1 as published on 15 February 1996. Examples 72-92 illustrate this process.

EXAMPLES 72-92

[0101] Supported catalyst compositions are produced and used as polymerization catalysts by carrying out the procedures described in detail in Examples 1-21 of PCT published application WO 96/04319 A1 (as published 15 February 1996), but in each case where tris(pentafluorophenyl)boron is used in forming the catalyst, the tris(pentafluorophenyl) boron used is produced as in Example 25 above. In each instance the unit cost of the catalyst is significantly reduced without sacrifice of operating efficiency.

[0102] Another group of active catalysts which can be produced with high efficiency and lower cost by use of this invention are catalysts formed by a process which comprises the following steps conducted sequentially, either in one continuous or discontinuous operation at a given plant site, or in a series of two or more separate operations which can be conducted at different time periods and at different plant sites:

A) producing a perhalobenzene having 5 fluorine atoms on the ring, preferably chloropentafluorobenzene, by a halogen exchange process of this invention,
B) converting perhalobenzene from A) into a pentafluorophenyl organometallic compound using a process such as described above,
C) converting pentafluorophenyl organometallic compound from B) into a pentafluorophenyl boron compound by reacting the organometallic compound with a boron trihalide or an etherate complex thereof, preferably boron trifluoride or a boron trifluoride etherate complex such as described above,
D) contacting pentafluorophenyl boron compound from C) with a metallocene of the formula LMX_2 wherein L is a derivative of a delocalized pi-bonded group imparting a constrained geometry to the metal active site and contains up to 50 non-hydrogen atoms, M is a Group 4 metal, and each X is, independently, hydride, or a hydrocarbyl, silyl, or germyl group having up to 20 carbon, silicon, or germanium atoms under conditions to form a catalyst having a limiting charge separated structure of the formula

$$LMX^{\oplus}\ XA^{\ominus}$$

wherein A is an anion formed from said pentafluorophenyl boron compound. Of the pentafluorophenyl boron compounds suitable for use in this process, tris(pentafluorophenyl)borane is the most preferred reactant. Examples of suitable metallocenes of the formula LMX_2, as well as complete details for producing and using such catalysts, are set forth in EP 520,732 A1 as published 30 December, 1992, and in U.S. Pat. No. 5,132,380, issued to J. C. Stevens, et al. on July 21, 1992.

[0103] Examples 93-207 further illustrate the production of active catalysts of the formula $LMX^{\oplus}\ XA^{\ominus}$ and the utilization of such catalysts in the polymerization of unsaturated monomers to form useful polymeric materials.

EXAMPLES 93-207

[0104] Catalyst compositions are produced and used as polymerization catalysts by carrying out the procedures described in detail in the first 115 examples of EP 520,732 A1 (as published 30 December 1992), but in each case where tris(pentafluorophenyl)boron is used, it is tris(pentafluorophenyl)boron produced as in Example 25 above. In each instance the unit cost of the catalyst is significantly reduced without sacrifice of operating efficiency.

[0105] It is to be understood that the ingredients referred to by chemical name or formula anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (e.g., another reactant, a solvent, or a diluent). It matters not what preliminary chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution or reaction medium as such changes, transformations and/or reactions are the natural result of bringing the specified reactants and/or components together under the conditions called for pursuant to this disclosure. Thus the reactants and other materials are identified as ingredients to be brought together in connection with performing a desired chemical reaction or in forming a mixture to be used in conducting a desired reaction. Accordingly, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", etc.), the reference is to the substance or ingredient as it existed at the time just before it was first contacted, blended or mixed with one or more other substances or ingredients in accordance with the present disclosure. The fact that the substance or ingredient may have lost its original identity through a chemical reaction or transformation

or complex formation or assumption of some other chemical form during the course of such contacting, blending or mixing operations, is thus wholly immaterial for an accurate understanding and appreciation of this disclosure and the claims thereof. Nor does reference to an ingredient by chemical name or formula exclude the possibility that during the desired reaction itself an ingredient becomes transformed to one or more transitory intermediates that actually enter into or otherwise participate in the reaction. In short, no representation is made or is to be inferred that the named ingredients must participate in the reaction while in their original chemical composition, structure or form.

[0106] This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented hereinabove. Rather, what is intended to be covered is as set forth in the ensuing claims.

Claims

1. A process which comprises heating a mixture formed from ingredients comprising (i) at least one finely-divided alkali metal fluoride, (ii) at least one haloaromatic compound having at least one halogen atom of atomic number greater than 9 on an aromatic ring, and (iii) a tetra(dihydrocarbylamino)phosphonium halide catalyst, at one or more reaction temperatures at which at least one said halogen atom of said haloaromatic compound is replaced by a fluorine atom.

2. A process according to claim 1 wherein the aminophosphonium catalyst ingredient is at least one tetra(dialkylamino)phosphonium chloride and/or bromide.

3. A process according to claim 1 wherein the aminophosphonium catalyst ingredient is one or more tetra(dialkylamino)phosphonium chlorides or bromides in which the alkyl groups can be the same or different and each has up to about 12 carbon atoms.

4. A process according to claim 1 wherein the aminophosphonium catalyst ingredient is tetrakis(diethylamino)phosphonium bromide.

5. A process according to claim 1 wherein the aminophosphonium catalyst ingredient is tetrakis(diethylamino)phosphonium chloride.

6. A process according to any of claims 1-5 wherein ingredient (i) is an alkali metal fluoride in which the alkali metal has an atomic number of 19 or more.

7. A process according to any of claims 1-5 wherein ingredient (i) is principally or exclusively potassium fluoride.

8. A process according to any of claims 1-5 wherein said mixture, at least prior to heating, is predominately a solid phase mixture.

9. A process according to any of claims 1-5 or 7 wherein said mixture, at least when heated to at least one of said one or more reaction temperatures, is predominately a mixture of solids dispersed in a continuous liquid phase comprising at least one halogen-free, polar, anhydrous or substantially anhydrous aprotic solvent.

10. A process according to any of claims 1-5, 7, or 9 wherein ingredient (ii) is at least one haloaromatic compound ingredient devoid of any activating functional group on the aromatic ring to which said halogen atom of atomic number greater than 9 is bonded.

11. A process according to any of claims 1-5 wherein ingredient (i) is principally or exclusively potassium fluoride, wherein ingredient (ii) is at least one haloaromatic compound devoid of any activating functional group on the aromatic ring to which said halogen atom of atomic number greater than 9 is bonded, and wherein said mixture, at least when heated to at least one of said one or more reaction temperatures, is predominately a mixture of solids dispersed in a continuous liquid phase comprising at least one halogen-free, polar, anhydrous or substantially anhydrous aprotic solvent.

12. A process according to any of claims 1-5 wherein ingredient (ii) is at least one perhaloaromatic compound of the formula $C_6Cl_nBr_mF_p$ where n is from 0 to 6, m is from 0 to 6 and p is from 0 to 5, and where the sum of n, m and p is 6.

13. A process according to any of claims 1-5 wherein ingredient (ii) is at least one perhaloaromatic compound of the formula $C_6Cl_nF_p$ where n is from 1 to 6, and p is from 0 to 5, and where the sum of n and p is 6.

14. A process according to any of claims 1-5 wherein ingredient (ii) includes at least hexachlorobenzene, dichlorotetrafluorobenzene or trichlorotrifluorobenzene, or any combination of any two or all three of the foregoing.

15. A process according to any of claims 1-5 wherein ingredient (ii) is hexachlorobenzene.

16. A process according to claim 11 wherein said haloaromatic compound is at least one perhaloaromatic compound of the formula $C_6Cl_nBr_mF_p$ where n is from 0 to 6, m is from 0 to 6 and p is from 0 to 5, and where the sum of n, m and p is 6.

17. A process according to claim 11 wherein said haloaromatic compound is at least one perhaloaromatic compound of the formula $C_6Cl_nF_p$ where n is from 1 to 6, and p is from 0 to 5, and where the sum of n and p is 6.

18. A process according to any of claims 16-17 wherein a vapor phase mixture of perhalobenzenes is formed from which at least one of the more volatile perhalobenzene components is separated and recovered from one or more less volatile perhalobenzene components of said vapor phase mixture; and wherein at least a portion of said one or more less volatile perhalobenzene components is recycled to the present or a subsequent halogen exchange reaction.

19. A process according to any of claims 16-18 wherein said aprotic solvent is predominately or entirely (a) benzonitrile, (b) at least one liquid alkylbenzonitrile, (c) nitrobenzene, (d) at least one liquid alkylmononitrobenzene, or (e) a mixture of at least two of (a), (b), (c), and (d).0

20. A process according to any of claims 1-5 wherein:

A) ingredient (i) is principally or exclusively potassium fluoride;
B) ingredient (ii) is at least one perhaloaromatic compound of the formula $C_6Cl_nBr_mF_p$ where n is from 0 to 6, m is from 0 to 6 and p is from 0 to 5, and where the sum of n, m and p is 6;
C) said mixture is predominately a mixture of solids dispersed or slurried in a continuous liquid phase comprising at least one halogen-free, polar, anhydrous or substantially anhydrous aprotic solvent;
D) said mixture is heated at one or more reaction temperatures at which a vapor phase comprising perhalobenzene having at least 5 fluorine atoms on the ring, is formed;
E) vapor phase is continuously removed from the reaction mixture;
F) perhalobenzene having at least 5 fluorine atoms on the ring is recovered from the vapor phase; and
G) all or at least a portion of the remainder of the component(s) of the vapor phase, if any, is returned into the dispersion or slurry.

21. A process according to Claim 20 wherein F) and G) are conducted continuously so that steady state conditions exist in the reaction zone.

22. A process according to Claim 20 wherein ingredient (ii) is devoid of chlorine.

23. A process according to Claim 22 wherein ingredient (ii) comprises hexabromobenzene.

24. A process according to Claim 20 wherein ingredient (ii) is devoid ofbromine.

25. A process according to Claim 24 wherein ingredient (ii) comprises hexachlorobenzene.

26. A process according to Claim 20 wherein the water content, if any, of the dispersion or slurry before reaching reaction temperature is below about 1500 ppm on a weight basis.

27. A process according to Claim 20 wherein said aprotic solvent is predominately or entirely (a) benzonitrile, (b) at least one liquid alkylbenzonitrile, (c) nitrobenzene, (d) at least one liquid alkylmononitrobenzene, or (e) a mixture of at least two of (a), (b), (c), and (d).

28. A process according to Claim 20 wherein the dispersion or slurry is formed from about 5 to about 8 mole of said

alkali metal fluoride and from about 0.05 to about 0.3 mole of said catalyst per mole of perhalobenzene used in forming the dispersion or slurry.

29. A process according to Claim 20 wherein the reaction conditions are such that when the reaction slurry is at said one or more reaction temperatures, the amount, if any, of chloropentafluorobenzene in the liquid phase of the slurry averages no more than about 5 percent by weight based on the total weight of the liquids in the dispersion or slurry.

30. A process according to Claim 20 wherein the reaction temperature is, or the reaction temperatures are, no higher than about 250°C, wherein ingredient (ii) is devoid of bromine, and wherein the vapor phase consists essentially of vaporized polar, aprotic solvent, hexafluorobenzene, chloropentafluorobenzene, dichlorotetrafluorobenzene, and trichlorotrifluorobenzene.

31. A process according to Claim 30 wherein the reaction conditions used are such that of the perhalobenzenes in the vapor phase, chloropentafluorobenzene is present in the largest amount.

32. A process according to Claim 30 wherein the reaction conditions used are such that at least 50% by weight of all of the perhalobenzenes in the vapor phase is chloropentafluorobenzene.

33. A process according to Claim 20 wherein said aprotic solvent is predominately or entirely (a) benzonitrile, (b) at least one liquid alkylbenzonitrile, (c) nitrobenzene, (d) at least one liquid alkylmononitrobenzene, or (e) a mixture of at least two of (a), (b), (c), and (d), and wherein the water content, if any, of the dispersion or slurry before reaching reaction temperature is below about 1500 ppm on a weight basis.

34. A process according to Claim 33 wherein ingredient (ii) is devoid of bromine.

35. Aprocess according to Claim 34 wherein ingredient (ii) is hexachlorobenzene.

36. A process according to Claim 35 wherein F) and G) are conducted continuously so that steady state conditions exist in the reaction zone.

37. A process according to Claim 36 wherein the dispersion or slurry is formed from about 5 to about 8 moles of said alkali metal fluoride and from about 0.05 to about 0.3 mole of said catalyst per mole of hexachlorobenzene used in forming the dispersion or slurry, and wherein the reaction conditions are such that when the reaction slurry is at said one or more reaction temperatures, the amount, if any, of chloropentafluorobenzene in the liquid phase of the dispersion or slurry averages no more than about 5 percent by weight based on the total weight of the liquids in the dispersion or slurry.

38. A process according to Claim 37 wherein at least 80 per cent by weight of the condensed vapor phase, all or a portion of which is returned to the reaction mixture, is composed of liquefied polar, aprotic solvent, solvent, liquefied dichlorotetrafluorobenzene, and liquefied trichlorotrifluorobenzene.

39. A process according to Claim 6 wherein said haloaromatic compound is at least one perhalobenzene of the formula $C_6F_nX_{6-n}$ where n is 0 to 4, and each X is, independently, a chlorine or bromine atom; wherein the mixture is heated at one or more reaction temperatures at which chloropentafluorobenzene or bromopentafluorobenzene is formed; and wherein said chloropentafluorobenzene or bromopentafluorobenzene is recovered and converted into a pentafluorophenyl Grignard reagent or a pentafluoro alkali metal compound.

40. A process according to Claim 39 further comprising converting said pentafluorophenyl Grignard reagent or pentafluorophenyl alkali metal compound into a pentafluorophenyl boron compound by reacting the pentafluorophenyl Grignard reagent or pentafluorophenyl alkali metal compound with a boron trihalide or an etherate complex thereof.

41. A process according to Claim 40 further comprising converting said pentafluorophenyl boron compound in a suitable solvent or diluent into a single coordination complex comprising a labile tetra(pentafluorophenyl)boron anion.

42. A process according to Claim 40 further comprising contacting said pentafluorophenyl boron compound with a metallocene of the formula LMX_2 wherein L is a derivative of a delocalized pi-bonded group imparting a constrained geometry to the metal active site and contains up to 50 non-hydrogen atoms, M is a Group 4 metal, and each X

is, independently, hydride, or a hydrocarbyl, silyl, or germyl group having up to 20 carbon, silicon, or germanium atoms under conditions to form a catalyst having a limiting charge separated structure of the formula $LMX^{\oplus}\ XA^{\ominus}$ wherein A is an anion formed from said pentafluorophenyl boron compound.

43. A process according to Claim 39 wherein said chloropentafluorobenzene or bromopentafluorobenzene is converted into a pentafluorophenyl Grignard reagent.

44. A process according to Claim 43 further comprising converting said pentafluorophenyl Grignard reagent into a tris (pentafluorophenyl)borane by reacting the pentafluorophenyl Grignard reagent with a boron trihalide or an etherate complex thereof.

45. A process according to Claim 44 further comprising converting said tris(pentafluorophenyl)borane in a suitable solvent or diluent into a single coordination complex comprising a labile tetra(pentafluorophenyl)boron anion.

46. A process according to Claim 44 further comprising contacting said tris(pentafluorophenyl)borane with a metallocene of the formula LMX_2 wherein L is a derivative of a delocalized pi-bonded group imparting a constrained geometry to the metal active site and contains up to 50 non-hydrogen atoms, M is a Group 4 metal, and each X is, independently, hydride, or a hydrocarbyl, silyl, or germyl group having up to 20 carbon, silicon, or germanium atoms under conditions to form a catalyst having a limiting charge separated structure of the formula $LMX^{\oplus}\ XA^{\ominus}$ wherein A is an anion formed from said pentafluorophenyl boron compound.

47. A process according to claim 39 wherein said mixture is a slurry in at least one halogen-free, polar, aprotic solvent; wherein the heating at said temperature forms a vaporphase comprising the chloropentafluorobenzene or bromopentafluorobenzene; wherein said vapor phase is continuously removed from the slurry;
wherein said chloropentafluorobenzene or bromopentafluorobenzene is recovered by separation from the vapor phase; and wherein all or at least a portion of the remainder of the component(s) of the vapor phase, if any, is returned into the slurry.

48. A process according to Claim 47 wherein said recovered chloropentafluorobenzene or bromopentafluorobenzene is converted into a pentafluorophenyl Grignard reagent by a Grignard exchange reaction performed in an ether reaction medium.

49. A process according to Claim 47 further comprising converting said pentafluorophenyl Grignard reagent or pentafluorophenyl alkali metal compound into a pentafluorophenyl boron compound by reacting the pentafluorophenyl Grignard reagent or pentafluorophenyl alkali metal compound with a boron trihalide or an etherate complex thereof.

50. A process according to Claim 48 further comprising converting said pentafluorophenyl Grignard reagent into tris (pentafluorophenyl)borane by reacting in an ether reaction medium, the pentafluorophenyl Grignard reagent with boron trifluoride or an etherate complex thereof.

51. A process according to Claim 49 further comprising converting at least a portion of said pentafluorophenyl boron compound in a suitable solvent or diluent into a single coordination complex that comprises a labile tetra(pentafluorophenyl)boron anion.

52. A process according to Claim 50 further comprising converting at least a portion of said tris(pentafluorophenyl) borane in a suitable solvent or diluent into a single coordination complex comprising a labile tetra(pentafluorophenyl)boron anion.

53. A process according to Claim 52 wherein said complex is a hydrocarbylammonium tetra(pentafluorophenyl)boron complex that is soluble in said solvent or diluent.

54. A process according to Claim 52 wherein said complex is a trialkylammonium tetra(pentafluorophenyl)boron complex or an N,N-dimethylanilinium tetra(pentafluorophenyl)boron complex.

55. A process according to any of Claims 51-54 further comprising forming an active catalyst by a process comprising mixing together in a suitable solvent or diluent, (A) a cyclopentadienyl metal compound containing a Group 4 transition metal, and (B) at least a second component comprising said complex, under conditions and for a period of time such that the cation of said complex reacts irreversibly with at least one ligand of the cyclopentadienyl

compound, and such that the pentafluorophenyl anion forms a non-coordinating ion pair with a resulting cation produced from the cyclopentadienyl metal compound.

56. A process according to Claim 55 wherein the mixture formed from (A) and (B) further comprises at least one additional component which is (C) at least one organometallic additive compound of the formula R_3M wherein each R is, independently, a hydrocarbyl group or an alkoxide group with the proviso that at least one R is a hydrocarbyl group, and wherein M is an aluminum or boron atom; or (D) a catalyst support; or (E) a combination of (C) and (D).

57. A process according to Claim 56 wherein said additional component is at least one trihydrocarbylaluminum compound or at least one trihydrocarbylboron compound.

58. A process according to Claim 56 wherein said additional component is an inorganic oxide in particulate form.

59. A process according to Claim 58 wherein said inorganic oxide is silica, alumina or silica-alumina.

60. A process according to Claim 49 further comprising reacting at least a portion of said pentafluorophenyl boron compound with hydroxy groups of a metal oxide support under conditions to form a support-bound anionic activator, and then contacting said support-bound anionic activator with a suitable metallocene of a Group 4 transition metal such that the activator protonates the metallocene whereby a supported ionic catalyst system is produced comprising a transition metal cation and a support bound anion.

61. A process according to Claim 50 further comprising reacting at least a portion of said tris(pentafluorophenyl)borane with hydroxy groups of a silica or silica-alumina support under conditions to form a support-bound anionic activator, and then contacting said support-bound anionic activator with a suitable metallocene of a Group 4 transition metal such that the activator protonates the metallocene whereby a supported ionic catalyst system is produced comprising a transition metal cation and a support bound anion.

62. A process according to Claim 49 further comprising contacting said pentafluorophenyl boron compound with a metallocene of the formula LMX_2 wherein L is a derivative of a delocalized pi-bonded group imparting a constrained geometry to the metal active site and contains up to 50 non-hydrogen atoms, M is a Group 4 metal, and each X is, independently, hydride, or a hydrocarbyl, silyl, or germyl group having up to 20 carbon, silicon, or germanium atoms under conditions to form a catalyst having a limiting charge separated structure of the formula $LMX^{\oplus}\ XA^{\ominus}$ wherein A is an anion formed from said pentafluorophenyl boron compound.

63. A process according to Claim 50 further comprising contacting said tris(pentafluorophenyl)borane with a metallocene of the formula LMX_2 wherein L is a derivative of a delocalized pi-bonded group imparting a constrained geometry to the metal active site and where L contains up to 50 non-hydrogen atoms, M is a Group 4 metal, and each X is, independently, hydride, or a hydrocarbyl, silyl, or germyl group having up to 20 carbon, silicon, or germanium atoms under conditions to form a catalyst having a limiting charge separated structure of the formula $LMX^{\oplus}\ XA^{\ominus}$ wherein A is an anion formed from the tris(pentafluorophenyl)borane.

Patentansprüche

1. Verfahren, bei dem eine Mischung, die aus Bestandteilen gebildet ist, die (i) mindestens ein feinteiliges Alkalimetallfluorid, (ii) mindestens eine halogenaromatische Verbindung mit mindestens einem Halogenatom mit einer Ordnungszahl größer als 9 an einem aromatischen Ring und (iii) Tetra(dikohlenwasserstoffamino)phosphoniumhalogenid-Katälysator umfassen, auf eine oder mehrere Reaktionstemperaturen erwärmt wird, bei der bzw. denen mindestens eines der Halogenatome der halogenaromatischen Verbindung durch ein Fluoratom ersetzt wird.

2. Verfahren nach Anspruch 1, bei dem der Aminophosphoniumkatalysatorbestandteil mindestens ein Tetra(dialkylamino)-phosphoniumchlorid und/oder -bromid ist.

3. Verfahren nach Anspruch 1, bei dem der Aminophosphoniumkatalysatorbestandteil ein oder mehrere Tetra(dialkylamino)phosphoniumchloride oder -bromide ist, bei denen die Alkylgruppen gleich oder unterschiedlich sein können und jede bis zu etwa 12 Kohlenstoffatome aufweist.

4. Verfahren nach Anspruch 1, bei dem der Aminophosphoniumkatalysatorbestandteil Tetrakis(diethylamino)phosphoniumbromid ist.

5. Verfahren nach Anspruch 1, bei dem der Aminophosphoniumkatalysatorbestandteil Tetrakis(diethylamino)phosphoniumchlorid ist.

6. Verfahren nach einem der Ansprüche 1 bis 5, bei dem Bestandteil (i) Alkalimetallfluorid ist, bei dem das Alkalimetall eine Ordnungszahl von 19 oder mehr hat.

7. Verfahren nach einem der Ansprüche 1 bis 5, bei dem Bestandteil (i) vorwiegend oder ausschließlich Kaliumfluorid ist.

8. Verfahren nach einem der Ansprüche 1 bis 5, bei dem die Mischung zumindest vor dem Erwärmen vorwiegend eine Feststoffphasenmischung ist.

9. Verfahren nach einem der Ansprüche 1 bis 5 oder 7, bei dem die Mischung zumindest beim Erwärmen auf mindestens eine der einen oder mehreren Reaktionstemperaturen vorwiegend eine Mischung von Feststoffen ist, die in einer kontinuierlichen flüssigen Phase dispergiert ist, die mindestens ein halogenfreies, polares, wasserfreies oder im Wesentlichen wasserfreies aprotisches Lösungsmittel umfasst.

10. Verfahren nach einem der Ansprüche 1 bis 5, 7 oder 9, bei dem Bestandteil (ii) mindestens ein halogenaromatische Verbindung-Bestandteil ist, der frei von irgendwelchen aktivierenden funktionellen Gruppen an dem aromatischen Ring ist, an den das Halogenatom mit der Ordnungszahl größer als 9 gebunden ist.

11. Verfahren nach einem der Ansprüche 1 bis 5, bei dem Bestandteil (i) vorwiegend oder ausschließlich Kaliumfluorid ist, wobei Bestandteil (ii) mindestens eine halogenaromatische Verbindung ist, die frei von irgendwelchen aktivierenden funktionellen Gruppen an dem aromatischen Ring ist, an den das Halogenatom mit der Ordnungszahl größer als 9 gebunden ist, und bei dem die Mischung zumindest beim Erwärmen auf mindestens eine der einen oder mehreren Reaktionstemperaturen vorwiegend eine Mischung von Feststoffen ist, die in einer kontinuierlichen flüssigen Phase dispergiert ist, die mindestens ein halogenfreies, polares, wasserfreies oder im Wesentlichen wasserfreies aprotisches Lösungsmittel umfasst.

12. Verfahren nach einem der Ansprüche 1 bis 5, bei dem Bestandteil (ii) mindestens eine perhalogenaromatische Verbindung mit der Formel $C_6Cl_nBr_mF_p$ ist, wobei n 0 bis 6 ist, m 0 bis 6 ist und p 0 bis 5 ist, und wobei die Summe aus n, m und p 6 beträgt.

13. Verfahren nach einem der Ansprüche 1 bis 5, bei dem Bestandteil (ii) mindestens eine perhalogenaromatische Verbindung mit der Formel $C_6Cl_nF_p$ ist, wobei n 1 bis 6 ist und p 0 bis 5 ist, und wobei die Summe aus n und p 6 beträgt.

14. Verfahren nach einem der Ansprüche 1 bis 5, bei dem Bestandteil (ii) mindestens Hexachlorbenzol, Dichlortetrafluorbenzol oder Trichlortrifluorbenzol oder irgendwelche Kombination aus irgenwelchen zwei oder allen drei der vorhergehenden einschließt.

15. Verfahren nach einem der Ansprüche 1 bis 5, bei dem Bestandteil (ii) Hexachlorbenzol ist.

16. Verfahren nach Anspruch 11, bei dem die halogenaromatische Verbindung mindestens eine perhalogenaromatische Verbindung mit der Formel $C_6Cl_nBr_mF_P$ ist, wobei n 0 bis 6 ist, m 0 bis 6 ist und p 0 bis 5 ist, und wobei die Summe aus n, m und p 6 beträgt.

17. Verfahren nach Anspruch 11, bei dem die halogenaromatische Verbindung mindestens eine perhalogenaromatische Verbindung mit der Formel $C_6Cl_nF_P$ ist, wobei n 1 bis 6 ist und p 0 bis 5 ist, und wobei die Summe aus n und p 6 beträgt.

18. Verfahren nach einem der Ansprüche 16 bis 17, bei dem eine Dampfphasenmischung aus Perhalogenbenzolen gebildet wird, von der mindestens eine der flüchtigeren Perhalogenbenzolkomponenten von einer oder mehreren weniger flüchtigen Perhalogenbenzolkomponenten der Dampfphasenmischung abgetrennt und gewonnen wird, und bei dem mindestens ein Teil der einen oder mehreren weniger flüchtigen Perhalogenbenzolkomponenten in

die vorliegende oder eine folgende Halogenaustauschreaktion zurückgeführt wird.

19. Verfahren nach einem der Ansprüche 16 bis 18, bei dem.das aprotische Lösungsmittel überwiegend oder vollständig (a) Benzonitril, (b) mindestens ein flüssiges Alkylbenzonitril, (c) Nitrobenzol, (d) mindestens ein flüssiges Alkylmononitrobenzol oder (e) eine Mischung aus mindestens zwei von (a), (b), (c) und (d) ist.

20. Verfahren nach einem der Ansprüche 1 bis 5, bei dem

A) Bestandteil (i) überwiegend oder ausschließlich Kaliumfluorid ist,
B) Bestandteil (ii) mindestens eine perhalogenaromatische Verbindung mit der Formel $C_6Cl_nBr_mF_p$ ist, wobei n 0 bis 6 ist, m 0 bis 6 ist und p 0 bis 5 ist, und wobei die Summe aus n, m und p 6 beträgt,
C) die Mischung überwiegend eine Mischung von Feststoffen ist, die in einer kontinuierlichen flüssigen Phase dispergiert oder aufgeschlämmt ist, die mindestens ein halogenfreies, polares, wasserfreies oder im Wesentlichen wasserfreies aprotisches Lösungsmittel umfasst,
D) die Mischung auf eine oder mehrere Reaktionstemperaturen erwärmt wird, bei denen eine Dampfphase gebildet wird, die Perhalogenbenzol mit mindestens 5 Fluoratomen am Ring umfasst,
E) Dampfphase kontinuierlich aus der Reaktionsmischung abgezogen wird,
F) Perhalogenbanzol mit mindestens 5 Fluoratomen am Ring aus der Dampfphase gewonnen wird, und
G) die gesamten oder mindestens ein Teil des Rests der Komponente(n) der Dampfphase, falls vorhanden, in die Dispersion oder Aufschlämmung zurückgegeben wird/werden.

21. Verfahren nach Anspruch 20, bei dem F) und G) kontinuierlich durchgeführt werden, so dass in der Reaktionszone stationäre Zustandsbedingungen herrschen.

22. Verfahren nach Anspruch 20, bei dem Bestandteil (ii) chlorfrei ist.

23. Verfahren nach Anspruch 22, bei dem Bestandteil (ii) Hexabrombenzol umfasst.

24. Verfahren nach Anspruch 20, bei dem Bestandteil (ii) bromfrei ist.

25. Verfahren nach Anspruch 24, bei dem Bestandteil (ii) Hexachlorbenzol umfasst.

26. Verfahren nach Anspruch 20, bei dem der Wassergehalt, falls vorhanden, der Dispersion oder Aufschlämmung vor Erreichen der Reaktionstemperatur unter etwa 1500 ppm auf Gewichtsbasis beträgt.

27. Verfahren nach Anspruch 20, bei dem das aprotische Lösungsmittel überwiegend oder vollständig (a) Benzonitril, (b) mindestens ein flüssiges Alkylbenzonitril, (c) Nitrobenzol, (d) mindestens ein flüssiges Alkylmononitrobenzol oder (e) eine Mischung aus mindestens zwei von (a), (b), (c) und (d) ist.

28. Verfahren nach Anspruch 20, bei dem die Dispersion oder Aufschlämmung aus etwa 5 bis etwa 8 Mol des Alkalimetallfluorids und etwa 0,05 bis etwa 0,3 Mol des Katalysators pro Mol Perhalogenbenzol gebildet ist, das zur Bildung der Dispersion oder Aufschlämmung verwendet worden ist.

29. Verfahren nach Anspruch 20, bei dem die Reaktionsbedingungen so sind, dass, wenn die Reaktionsaufschlämmung sich auf der einen oder den mehreren Reaktionstemperaturen befindet, die Menge an Chlorpentafluorbenzol, falls vorhanden, in der flüssigen Phase der Aufschlämmung durchschnittlich nicht mehr als etwa 5 Gew.% beträgt, bezogen auf das Gesamtgewicht der Flüssigkeiten in der Dispersion oder Aufschlämmung.

30. Verfahren nach Anspruch 20, bei dem die Reaktionstemperatur oder die Reaktionstemperaturen nicht höher als etwa 250°C ist bzw. sind, wobei Bestandteil (ii) bromfrei ist und die Dampfphase im Wesentlichen aus verdampftem, polarem aprotischem Lösungsmittel, Hexafluorbenzol, Chlorpentafluorbenzol, Dichlortetrafluorbenzol und Trichlortrifluorbenzol besteht.

31. Verfahren nach Anspruch 30, bei dem die verwendeten Reaktionsbedingungen so sind, dass von den Perhalogenbenzolen in der Dampfphase Chlorpentafluorbenzol in der größten Menge vorhanden ist.

32. Verfahren nach Anspruch 30, bei dem die verwendeten Reaktionsbedingungen so sind, dass mindestens 50 Gew. % aller Perhalogenbenzole in der Dampfphase Chlorpentafluorbenzol sind.

33. Verfahren nach Anspruch 20, bei dem das aprotische Lösungsmittel überwiegend oder vollständig (a) Benzonitril, (b) mindestens ein flüssiges Alkylbenzonitril, (c) Nitrobenzol, (d) mindestens ein flüssiges Alkylmononitrobenzol oder (e) eine Mischung aus mindestens zwei von (a), (b), (c) und (d) ist, und wobei der Wassergehalt, falls vorhanden, der Dispersion oder Aufschlämmung vor Erreichen der Reaktionstemperatur unter etwa 1500 ppm auf Gewichtsbasis liegt.

34. Verfahren nach Anspruch 33, bei dem Bestandteil (ii) bromfrei ist.

35. Verfahren nach Anspruch 34, bei dem Bestandteil (ii) Hexachlorbenzol ist.

36. Verfahren nach Anspruch 35, bei dem F) und G) kontinuierlich durchgeführt werden, so dass in der Reaktionszone stationäre Zustandsbedingungen herrschen.

37. Verfahren nach Anspruch 36, bei dem die Dispersion oder Aufschlämmung aus etwa 5 bis etwa 8 Mol des Alkalimetallfluorids und etwa 0,05 bis etwa 0,3 Mol des Katalysators pro Mol Hexachlorbenzol gebildet ist, das zur Bildung der Dispersion oder Aufschlämmung verwendet worden ist, und die Reaktionsbedingungen so sind, dass, wenn die Reaktionsaufschlämmung sich auf der einen oder den mehreren Reaktionstemperaturen befindet, die Menge an Chlorpentafluorbenzol, falls vorhanden, in der flüssigen Phase der Dispersion oder Aufschlämmung durchschnittlich nicht mehr als etwa 5 Gew.% beträgt, bezogen auf das Gesamtgewicht der Flüssigkeiten in der Dispersion oder Aufschlämmung.

38. Verfahren nach Anspruch 37, bei dem mindestens 80 Gew.% der kondensierten Dampfphase, die ganz oder teilweise in die Reaktionsmischung zurückgegeben wird, aus verflüssigtem polarem aprotischem Lösungsmittel, Lösungsmittel, verflüssigtem Dichlortetrafluorbenzol und verflüssigtem Trichlortrifluorbenzol zusammengesetzt ist.

39. Verfahren nach Anspruch 6, bei dem die halogenaromatische Verbindung mindestens ein Halogenbenzol der Formel $C_6F_nX_{6-n}$ ist, in dem n 0 bis 4 ist und jedes X unabhängig ein Chlor- oder Bromatom ist, wobei die Mischung auf eine oder mehrere Reaktionstemperaturen erwärmt wird, bei denen Chlorpentafluorbenzol oder Brompentafluorbenzol gebildet wird, und wobei das Chlorpentafluorbenzol oder Brompentafluorbenzol gewonnen und in ein Pentafluorphenyl-Grignard-Reagenz oder eine Pentafluor-Alkalimetallverbindung umgewandelt wird.

40. Verfahren nach Anspruch 39, bei dem ferner das Pentafluorphenyl-Grignard-Reagenz oder die Pentafluorphenyl-Alkalimetallverbindung in eine Pentafluorphenyl-Borverbindung umgewandelt wird, indem das Pentafluorphenyl-Grignard-Reagenz oder die Pentafluorphenyl-Alkalimetallverbindung mit Bortrihalogenid oder einem Etheratkomplex desselben umgesetzt wird.

41. Verfahren nach Anspruch 40, bei dem ferner die Pentafluorphenyl-Borverbindung in geeignetem Lösungsmittel oder Verdünnungsmittel in einen Einzelkoordinationskomplex umgewandelt wird, der ein labiles Tetra(pentafluorphenyl)boranion umfasst.

42. Verfahren nach Anspruch 40, bei dem ferner die Pentafluorphenyl-Borverbindung mit einem Metallocen mit der Formel LMX_2, wobei L ein Derivat einer delokalisierten n-gebundenen Gruppe ist, die der aktiven Metallstelle eine gespannte Geometrie verleiht und bis zu 50 Nicht-Wasserstoffatome enthält, M ein Gruppe 4 Metall ist und jedes X unabhängig Hydrid oder eine Kohlenwasserstoff-, Silyl- oder Germylgruppe mit bis zu 20 Kohlenstoff-, Silicium- oder Germaniumatomen ist, unter Bedingungen kontaktiert wird, um einen Katalysator mit begrenzender ladungsgetrennter Struktur der Formel LMX^+XA^- zu bilden, wobei A ein aus der Pentafluorphenyl-Borverbindung gebildetes Anion ist.

43. Verfahren nach Anspruch 39, bei dem das Chlorpentafluorbenzol oder Brompentafluorbenzol in ein Pentafluorphenyl-Grignard-Reagenz umgewandelt wird.

44. Verfahren nach Anspruch 43, bei dem ferner das Pentafluorphenyl-Grignard-Reagenz in Tris(pentafluorphenyl) boran umgewandelt wird, indem das Pentafluorphenyl-Grignard-Reagenz mit Bortrihalogenid oder einem Etheratkomplex desselben umgesetzt wird.

45. Verfahren nach Anspruch 44, bei dem ferner das Tris(pentafluorphenyl)boran in geeignetem Lösungsmittel oder Verdünnungsmittel in einen Einzelkoordinationskomplex umgewandelt wird, der ein labiles Tetra(pentafluorphenyl) boranion umfasst.

46. Verfahren nach Anspruch 44, bei dem ferner das Tris(pentafluorphenyl)boran mit einem Metallocen mit der Formel LMX_2, wobei L ein Derivat einer delokalisierten π-gebundenen Gruppe ist, die der aktiven Metallstelle eine gespannte Geometrie verleiht und bis zu 50 Nicht-Wasserstoffatome enthält, M ein Gruppe 4 Metall ist und jedes X unabhängig Hydrid oder eine Kohlenwasserstoff-, Silyl- oder Germylgruppe mit bis zu 20 Kohlenstoff-, Silicium- oder Germaniumatomen ist, unter Bedingungen kontaktiert wird, um einen Katalysator mit begrenzender ladungsgetrennter Struktur der Formel LMX^+XA^- zu bilden, wobei A ein aus der Pentafluorphenyl-Borverbindung gebildetes Anion ist.

47. Verfahren nach Anspruch 39, bei dem die Mischung eine Aufschlämmung in mindestens einem halogenfreien, polaren, aprotischen Lösungsmittel ist, das Erwärmen auf die Temperatur eine Dampfphase bildet, die das Chlorpentafluorbenzol oder Brompentafluorbenzol umfasst, die Dampfphase kontinuierlich aus der Aufschlämmung entfernt wird, das Chlorpentafluorbenzol oder Brompentafluorbenzol durch Abtrennung aus der Dampfphase gewonnen wird, und der gesamte oder mindestens ein Teil des Rests der Komponente(n) der Dampfphase, falls vorhanden, in die Aufschlämmung zurückgegeben wird.

48. Verfahren nach Anspruch 47, bei dem das gewonnene Chlorpentafluorbenzol oder Brompentafluorbenzol durch eine in einem Ether-Reaktionsmedium durchgeführte Grignard-Austauschreaktion in ein Pentafluorphenyl-Grignard-Reagenz umgewandelt wird.

49. Verfahren nach Anspruch 47, bei dem ferner das Pentafluorphenyl-Grignard-Reagenz oder die Pentafluorphenyl-Alkalimetallverbindung in eine Pentafluorphenyl-Borverbindung umgewandelt wird, indem das Pentafluorphenyl-Grignard-Reagenz oder die Pentafluorphenyl-Alkalimetallverbindung mit Bortrihalogenid oder einem Etheratkomplex desselben umgesetzt wird.

50. Verfahren nach Anspruch 48, bei dem ferner das Pentafluorphenyl-Grignard-Reagenz durch Umsetzung des Pentafluorphenyl-Grignard-Reagenzes mit Bortrifluorid oder einem Etheratkomplex desselben in einem Ether-Reaktionsmedium in Tris(pentafluorphenyl)boran umgewandelt wird.

51. Verfahren nach Anspruch 49, bei dem ferner mindestens ein Teil der Pentafluorphenyl-Borverbindung in geeignetem Lösungsmittel oder Verdünnungsmittel in einen Einzelkoordinationskomplex umgewandelt wird, der ein labiles Tetra(pentafluorphenyl)boranion umfasst.

52. Verfahren nach Anspruch 50, bei dem ferner mindestens ein Teil des Tris(pentafluorphenyl)borans in geeignetem Lösungsmittel oder Verdünnungsmittel in einen Einzelkoordinationskomplex umgewandelt wird, der ein labiles Tetra(pentafluorphenyl)boranion umfasst.

53. Verfahren nach Anspruch 52, bei dem der Komplex ein Kohlenwasserstoffammoniumtetra(pentafluorphenyl)borkomplex ist, der in dem Lösungsmittel oder Verdünnungsmittel löslich ist.

54. Verfahren nach Anspruch 52, bei dem der Komplex Trialkylammoniumtetra(pentafluorphenyl)borkomplex oder ein N,N-Di-methylaniliniumtetra(pentafluorphenyl)borkomplex ist.

55. Verfahren nach einem der Ansprüche 51 bis 54, bei dem ferner ein aktiver Katalysator nach einem Verfahren gebildet wird, bei dem in geeignetem Lösungsmittel oder Verdünnungsmittel (A) eine ein Gruppe 4 Übergangsmetall enthaltende Cyclopentadienylmetallverbindung, und (B) mindestens eine zweite Komponente, die den Komplex umfasst, unter Bedingungen und für einen Zeitraum gemischt werden, so dass das Kation des Komplexes irreversibel mit mindestens einem Liganden der Cyclopentadienylverbindung reagiert und das Pentafluorphenylanion mit einem aus der Cyclopentadienylmetallverbindung erzeugten resultierenden Kation ein nichtkoordinierendes Ionenpaar bildet.

56. Verfahren nach Anspruch 55, bei dem die aus (A) und (B) gebildete Mischung ferner mindestens eine zusätzliche Komponente umfasst, die (C) mindestens eine organometallische Additivverbindung mit der Formel R_3M, wobei jedes R unabhängig eine Kohlenwasserstoffgruppe oder Alkoxidgruppe ist, mit der Maßgabe, dass mindestens ein R eine Kohlenwasserstoffgruppe ist, und wobei M ein Aluminium- oder Boratom ist, oder (D) ein Katalysatorträger oder (E) eine Kombination aus (C) und (D) ist.

57. Verfahren nach Anspruch 56, bei dem die zusätzliche Komponente mindestens eine Trikohlenwasserstoffaluminiumverbindung oder mindestens eine Trikohlenwasserstoffborverbindung ist.

58. Verfahren nach Anspruch 56, bei dem die zusätzliche Komponente anorganisches Oxid in Teilchenform ist.

59. Verfahren nach Anspruch 58, bei dem das anorganische Oxid Siliciumdioxid, Aluminiumoxid oder Siliciumdioxid-Aluminiumoxid ist.

60. Verfahren nach Anspruch 49, bei dem ferner mindestens ein Teil der Pentafluorphenylborverbindung mit Hydroxygruppen eines Metalloxidträgers unter Bedingungen umgesetzt wird, um einen trägergebundenen anionischen Aktivator zu bilden, und nachfolgend der trägergebundene anionische Aktivator mit einem geeigneten Metallocen von Gruppe 4 Übergangsmetall kontaktiert wird, so dass der Aktivator das Metallocen protoniert, wodurch ein trägergestütztes ionisches Katalysatorsystem erzeugt wird, das ein Übergangsmetallkation und ein trägergebundenes Anion umfasst.

61. Verfahren nach Anspruch 50, bei dem mindestens ein Teil des Tris(pentafluorphenyl)borans mit Hydroxygruppen eines Siliciumdioxid- oder Siliciumdioxid-Aluminiumoxid-Trägers unter Bedingungen umgesetzt wird, um einen trägergebundenen anionischen Aktivator zu bilden, und nachfolgend der trägergebundene anionische Aktivator mit einem geeigneten Metallocen von Gruppe 4 Übergangsmetall kontaktiert wird, so dass der Aktivator das Metallocen protoniert, wodurch ein trägergestütztes ionisches Katalysatorsystem erzeugt wird, das ein Übergangsmetallkation und ein trägergebundenes Anion umfasst.

62. Verfahren nach Anspruch 49, bei dem die Pentafluorphenyl-borverbindung ferner mit einem Metallocen der Formel LMX_2, wobei L ein Derivat einer delokalisierten π-gebundenen Gruppe ist, die der aktiven Metallstelle eine gespannte Geometrie verleiht und bis zu 50 Nicht-Wasserstoffatome enthält, M ein Gruppe 4 Metall ist und jedes X unabhängig Hydrid oder eine Kohlenwasserstoff-, Silyl- oder Germylgruppe mit bis zu 20 Kohlenstoff-, Silicium- oder Germaniumatomen ist, unter Bedingungen kontaktiert wird, um einen Katalysator mit begrenzender ladungsgetrennter Struktur der Formel LMX^+XA^- zu bilden, wobei A ein aus der Pentafluorphenylborverbindung gebildetes Anion ist.

63. Verfahren nach Anspruch 50, bei dem ferner das Tris(pentafluorphenyl)boran mit einem Metallocen mit der Formel LMX_2, wobei L ein Derivat einer delokalisierten π-gebundenen Gruppe ist, die der aktiven Metallstelle eine gespannte Geometrie verleiht und wobei L bis zu 50 Nicht-Wasserstoffatome enthält, M ein Gruppe 4 Metall ist und jedes X unabhängig Hydrid oder eine Kohlenwasserstoff-, Silyl- oder Germylgruppe mit bis zu 20 Kohlenstoff-, Silicium- oder Germaniumatomen ist, unter Bedingungen kontaktiert wird, um einen Katalysator mit begrenzender ladungsgetrennter Struktur der Formel LMX^+XA^- zu bilden, wobei A ein aus der Pentafluorphenylborverbindung gebildetes Anion ist.

Revendications

1. Procédé qui comprend le chauffage d'un mélange formé à partir d'ingrédients comprenant (i) au moins un fluorure de métal alcalin finement divisé, (ii) au moins un composé aromatique halogéné présentant au moins un atome d'halogène de numéro atomique supérieur à 9 sur un noyau aromatique, et (iii) un catalyseur de type halogénure de tétra(dihydrocarbylamino)phosphonium, à une ou plusieurs températures de réaction auxquelles ledit atome d'halogène présent en au moins un exemplaire sur ledit composé aromatique halogéné est remplacé par un atome de fluor.

2. Procédé selon la revendication 1, dans lequel l'ingrédient catalyseur de type aminophosphonium est au moins un chlorure et/ou bromure de tétra(dialkylamino)phosphonium.

3. Procédé selon la revendication 1, dans lequel l'ingrédient catalyseur de type aminophosphonium est constitué d'un ou plusieurs chlorures ou bromures de tétra(dialkylamino)phosphonium dans lesquels les groupes alkyle peuvent être identiques ou différents et comptent chacun jusqu'à environ 12 atomes de carbone.

4. Procédé selon la revendication 1, dans lequel l'ingrédient catalyseur de type aminophosphonium est le bromure de tétrakis(diéthylamino)phosphonium.

5. Procédé selon la revendication 1, dans lequel l'ingrédient catalyseur de type aminophosphonium est le chlorure de tétrakis(diéthylamino)phosphonium.

6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel l'ingrédient (i) est un fluorure de métal alcalin dans lequel le métal alcalin a un numéro atomique de 19 ou plus.

7. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel l'ingrédient (i) est principalement ou exclusivement du fluorure de potassium.

8. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel ledit mélange, au moins avant le chauffage, est en majeure partie un mélange en phase solide.

9. Procédé selon l'une quelconque des revendications 1 à 5 ou 7, dans lequel ledit mélange, au moins lorsqu'il est chauffé à au moins l'une desdites une ou plusieurs températures de réaction, est en majeure partie un mélange de solides dispersés dans une phase liquide continue comprenant au moins un solvant aprotique polaire non halogéné, anhydre ou sensiblement anhydre.

10. Procédé selon l'une quelconque des revendications 1 à 5, 7 ou 9, dans lequel l'ingrédient (ii) est au moins un composé aromatique halogéné dépourvu de tout groupe fonctionnel activateur sur le noyau aromatique auquel est lié ledit atome d'halogène de numéro atomique supérieur à 9.

11. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel l'ingrédient (i) est principalement ou exclusivement du fluorure de potassium, dans lequel l'ingrédient (ii) est au moins un composé aromatique halogéné dépourvu de tout groupe fonctionnel activateur sur le noyau aromatique auquel est lié ledit atome d'halogène de numéro atomique supérieur à 9, et dans lequel ledit mélange, au moins lorsqu'il est chauffé à au moins l'une desdites une ou plusieurs températures de réaction, est en majeure partie un mélange de solides dispersés dans une phase liquide continue comprenant au moins un solvant aprotique polaire non halogéné, anhydre ou sensiblement anhydre.

12. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel l'ingrédient (ii) est au moins un composé aromatique perhalogéné de formule $C_6Cl_nBr_mF_p$ où n est de 0 à 6, m est de 0 à 6 et p est de 0 à 5, et où la somme de n, m et p est égale à 6.

13. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel l'ingrédient (ii) est au moins un composé aromatique perhalogéné de formule $C_6Cl_nF_p$ où n est de 1 à 6 et p est de 0 à 5, et où la somme de n et p est égale à 6.

14. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel l'ingrédient (ii) comprend au moins de l'hexachlorobenzène, du dichlorotétrafluorobenzène ou du trichlorotrifluorobenzène, ou une association de deux quelconques de ces composés, ou des trois.

15. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel l'ingrédient (ii) est l'hexachlorobenzène.

16. Procédé selon la revendication 11, dans lequel ledit composé aromatique halogéné est au moins un composé aromatique perhalogéné de formule $C_6Cl_nBr_mF_p$ où n est de 0 à 6, m est de 0 à 6 et p est de 0 à 5, et où la somme de n, m et p est égale à 6.

17. Procédé selon la revendication 11, dans lequel ledit composé aromatique halogéné est au moins un composé aromatique perhalogéné de formule $C_6Cl_nF_p$ où n est de 1 à 6 et p est de 0 à 5, et où la somme de n et p est égale à 6.

18. Procédé selon l'une quelconque des revendications 16 et 17, dans lequel on forme un mélange en phase vapeur de perhalogénobenzènes, à partir duquel au moins l'un des composants perhalogénobenzéniques plus volatils est séparé et isolé d'un ou plusieurs composants perhalogénobenzéniques moins volatils dudit mélange en phase vapeur ; et dans lequel au moins une partie desdits un ou plusieurs composants perhalogénobenzéniques moins volatils est recyclée dans la présente réaction d'échange d'halogène ou une réaction d'échange d'halogène subséquente.

19. Procédé selon l'une quelconque des revendications 16 à 18, dans lequel ledit solvant aprotique est en majeure partie ou entièrement (a) du benzonitrile, (b) au moins un alkylbenzonitrile liquide, (c) du nitrobenzène, (d) au moins un alkylmononitrobenzène liquide ou (e) un mélange d'au moins deux de (a), (b), (c) et (d).

20. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel :

A) l'ingrédient (i) est principalement ou exclusivement du fluorure de potassium ;

B) l'ingrédient (ii) est au moins un composé aromatique perhalogéné de formule $C_6Cl_nBr_mF_p$ où n est de 0 à 6, m est de 0 à 6 et p est de 0 à 5, et où la somme de n, m et p est égale à 6 ;

C) ledit mélange est en majeure partie un mélange de solides dispersés ou en suspension dans une phase liquide continue comprenant au moins un solvant aprotique polaire non halogéné, anhydre ou sensiblement anhydre ;

D) ledit mélange est chauffé à une ou plusieurs températures de réaction auxquelles est formée une phase vapeur comprenant un perhalogénobenzène ayant au moins 5 atomes de fluor sur le noyau ;

E) la phase vapeur est enlevée en continu du mélange réactionnel ;

F) le perhalogénobenzène ayant au moins 5 atomes de fluor sur le noyau est retiré de la phase vapeur ; et

G) la totalité ou une partie du reste du ou des composants de la phase vapeur, s'il y en a, est ramenée dans la dispersion ou suspension.

21. Procédé selon la revendication 20, dans lequel F) et g) sont conduits en continu de telle sorte que des conditions de régime constant existent dans la zone de réaction.

22. Procédé selon la revendication 20, dans lequel l'ingrédient (ii) est dépourvu de chlore.

23. Procédé selon la revendication 22, dans lequel l'ingrédient (ii) comprend de l'hexabromobenzène.

24. Procédé selon la revendication 20, dans lequel l'ingrédient (ii) est dépourvu de brome.

25. Procédé selon la revendication 24, dans lequel l'ingrédient (ii) comprend de l'hexachlorobenzène.

26. Procédé selon la revendication 20, dans lequel la teneur en eau, s'il y en a, de la dispersion ou suspension avant qu'elle atteigne la température de réaction est inférieure à environ 1500 ppm sur base pondérale.

27. Procédé selon la revendication 20, dans lequel ledit solvant aprotique est en majeure partie ou entièrement (a) du benzonitrile, (b) au moins un alkylbenzonitrile liquide, (c) du nitrobenzène, (d) au moins un alkylmononitrobenzène liquide, ou (e) un mélange d'au moins deux de (a), (b), (c) et (d) .

28. Procédé selon la revendication 20, dans lequel la dispersion ou suspension est formée à partir d'environ 5 à environ 8 moles dudit fluorure de métal alcalin et d'environ 0,05 à environ 0,4 mole dudit catalyseur par mole de perhalogénobenzène utilisé pour former la dispersion ou suspension.

29. Procédé selon la revendication 20, dans lequel les conditions de réaction sont telles que lorsque la suspension réactionnelle se trouve à ladite ou auxdites une ou plusieurs températures de réaction, la quantité de chloropentafluorobenzène, s'il y en a, dans la phase liquide de la suspension n'est en moyenne pas supérieure à environ 5 pour cent en poids par rapport au poids total des liquides présents dans la dispersion ou suspension.

30. Procédé selon la revendication 20, dans lequel la température de réaction n'est, ou les températures de réaction ne sont, pas supérieures à environ 250°C, dans lequel l'ingrédient (ii) est dépourvu de brome et dans lequel la phase vapeur consiste essentiellement en solvant aprotique polaire vaporisé, hexafluorobenzène, chloropentafluorobenzène, dichlorotétrafluorobenzène et trichlorotrifluorobenzène.

31. Procédé selon la revendication 30, dans lequel les conditions de réaction employées sont telles que, parmi les perhalogénobenzènes existant dans la phase vapeur, le chloropentafluorobenzène est présent en la plus grande quantité.

32. Procédé selon la revendication 30, dans lequel les conditions de réaction employées sont telles qu'au moins 50 % en poids de la totalité des perhalogénobenzènes existant dans la phase vapeur sont constitués de chloropentafluorobenzène.

33. Procédé selon la revendication 20, dans lequel ledit solvant aprotique est en majeure partie ou entièrement (a) du benzonitrile, (b) au moins un alkylbenzonitrile liquide, (c) du nitrobenzène, (d) au moins un alkylmononitrobenzène liquide, ou (e) un mélange d'au moins deux de (a), (b), (c) et (d), et dans lequel la teneur en eau, s'il y en a, de la dispersion ou suspension avant qu'elle atteigne la température de réaction est inférieure à environ 1500 ppm sur base pondérale.

34. Procédé selon la revendication 33, dans lequel l'ingrédient (ii) est dépourvu de brome.

35. Procédé selon la revendication 34, dans lequel l'ingrédient (ii) est l'hexachlorobenzène.

36. Procédé selon la revendication 35, dans lequel F) et g) sont conduits en continu de telle sorte que des conditions de régime constant existent dans la zone de réaction.

37. Procédé selon la revendication 36, dans lequel la dispersion ou suspension est formée à partir d'environ 5 à environ 8 moles dudit fluorure de métal alcalin et d'environ 0,05 à environ 0,3 mole dudit catalyseur par mole d'hexachlorobenzène utilisé pour former la dispersion ou suspension, et dans lequel les conditions de réaction sont telles que, lorsque la suspension réactionnelle se trouve à ladite ou auxdites une ou plusieurs températures de réaction, la quantité de chloropentafluorobenzène, s'il y en a, dans la phase liquide de la dispersion ou suspension n'est en moyenne pas supérieure à environ 5 pour cent en poids par rapport au poids total des liquides présents dans la dispersion ou suspension.

38. Procédé selon la revendication 37, dans lequel au moins 80 pour cent en poids de la phase vapeur condensée, dont la totalité ou une partie est ramenée au mélange réactionnel, consistent en solvant aprotique polaire liquéfié, solvant, dichlorotétrafluorobenzène liquéfié et trichlorotrifluorobenzène liquéfié.

39. Procédé selon la revendication 6, dans lequel ledit composé aromatique halogéné est au moins un perhalogénobenzène de formule $C_6F_nX_{6-n}$ où n est de 0 à 4, et chaque X est, indépendamment, un atome de chlore ou de brome ; dans lequel le mélange est chauffé à une ou plusieurs températures de réaction auxquelles se forme du chloropentafluorobenzène ou du bromopentafluorobenzène ; et dans lequel ledit chloropentafluorobenzène ou bromopentafluorobenzène est récupéré et converti en un réactif de Grignard pentafluorophénylique ou un pentafluorophényl-métal alcalin.

40. Procédé selon la revendication 39, comprenant de plus la conversion du réactif de Grignard pentafluorophénylique ou du pentafluorophényl-métal alcalin en un composé de pentafluorophényl-bore, par réaction du réactif de Grignard pentafluorophénylique ou du pentafluorophényl-métal alcalin avec un trihalogénure de bore ou un complexe éthéré de celui-ci.

41. Procédé selon la revendication 40, comprenant de plus la conversion du composé de pentafluorophényl-bore dans un solvant ou diluant approprié en un complexe de monocoordination comprenant un anion de tétra(pentafluorophényl)bore labile.

42. Procédé selon la revendication 40, comprenant de plus la mise en contact dudit composé de pentafluorophényl-bore avec un métallocène de formule LMX_2 où L est un dérivé d'un groupe à liaison pi délocalisée conférant une géométrie contrainte au site actif métallique et contient jusqu'à 50 atomes autres que des atomes d'hydrogène, M est un métal du Groupe 4 et chaque X est indépendamment un hydrure ou un groupe hydrocarbyle, silyle ou germyle ayant jusqu'à 20 atomes de carbone, de silicium ou de germanium, dans des conditions convenant pour former un catalyseur ayant une structure limite à charges séparées de formule $LMX^{\oplus}XA^-$ où A est un anion formé à partir dudit composé de pentafluorophényl-bore.

43. Procédé selon la revendication 39, dans lequel ledit chloropentafluorobenzène ou bromopentafluorobenzène est converti en un réactif de Grignard pentafluorophénylique.

44. Procédé selon la revendication 43, comprenant de plus la conversion dudit réactif de Grignard pentafluorophénylique en tris(pentafluorophényl)borane en faisant réagir le réactif de Grignard pentafluorophénylique avec un trihalogénure de bore ou un complexe éthéré de celui-ci.

45. Procédé selon la revendication 44, comprenant de plus la conversion dudit tris(pentafluorophényl)borane dans un solvant ou diluant approprié en un complexe de monocoordination comprenant un anion de tétra(pentafluorophé-

nyl)bore labile.

46. Procédé selon la revendication 44, comprenant de plus la mise en contact dudit tris(pentafluorophényl)borane avec un métallocène de formule LMX_2 où L est un dérivé d'un groupe à liaison pi délocalisée conférant une géométrie contrainte au site actif métallique et contient jusqu'à 50 atomes autres que des atomes d'hydrogène, M est un métal du Groupe 4 et chaque X est indépendamment un hydrure ou un groupe hydrocarbyle, silyle ou germyle ayant jusqu'à 20 atomes de carbone, de silicium ou de germanium, dans des conditions convenant pour former un catalyseur ayant une structure limite à charges séparées de formule $LMX^{\oplus}XA^-$ où A est un anion formé à partir dudit composé de pentafluorophényl-bore.

47. Procédé selon la revendication 39, dans lequel ledit mélange est une suspension dans au moins un solvant aprotique polaire non halogène ; dans lequel le chauffage à ladite température forme une phase vapeur comprenant le chloropentafluorobenzène ou le bromopentafluorobenzène ; dans lequel ladite phase vapeur est enlevée en continu de la suspension ; dans lequel ledit chloropentafluorobenzène ou bromopentafluorobenzène est retiré de la phase vapeur par séparation ; et dans lequel la totalité ou au moins une partie du reste du ou des composants de la phase vapeur, s'il y en a, est ramenée dans la suspension.

48. Procédé selon la revendication 47, dans lequel ledit chloropentafluorobenzène ou bromopentafluorobenzène retiré est converti en un réactif de Grignard pentafluorophénylique par une réaction d'échange de Grignard effectuée dans un milieu réactionnel éthéré.

49. Procédé selon la revendication 47, comprenant de plus la conversion du le réactif de Grignard pentafluorophénylique ou du pentafluorophényl-métal alcalin en un composé de pentafluorophényl-bore en faisant réagir le réactif de Grignard pentafluorophénylique ou le pentafluorophényl-métal alcalin avec un trihalogénure de bore ou un complexe éthéré de celui-ci.

50. Procédé selon la revendication 48, comprenant de plus la conversion dudit réactif de Grignard pentafluorophénylique en un tris(pentafluorophényl)borane en faisant réagir dans un milieu réactionnel éthéré le réactif de Grignard pentafluorophénylique avec du trifluorure de bore ou un complexe éthéré de celui-ci.

51. Procédé selon la revendication 49, comprenant de plus la conversion d'au moins une partie dudit composé de pentafluorophényl-bore dans un solvant ou diluant approprié en un complexe de monocoordination qui comprend un anion de tétra(pentafluorophényl)bore labile.

52. Procédé selon la revendication 50, comprenant de plus la conversion d'au moins une partie dudit tris-(pentafluorophényl)borane dans un solvant ou diluant approprié en un complexe de monocoordination comprenant un anion de tétra(pentafluorophényl)bore labile.

53. Procédé selon la revendication 52, dans lequel ledit complexe est un complexe d'hydrocarbylammonium-tétra (pentafluorophényl)bore qui est soluble dans ledit solvant ou diluant.

54. Procédé selon la revendication 52, dans lequel ledit complexe est un complexe de trialkylammonium-tétra-(pentafluorophényl)bore ou un complexe de N,N-diméthylanilinium-tétra(pentafluorophényl)bore.

55. Procédé selon l'une quelconque des revendications 51 à 54, comprenant de plus la formation d'un catalyseur actif par un procédé consistant à mélanger ensemble, dans un solvant ou diluant approprié, (A) un composé de cyclopentadiényl-métal contenant un métal de transition du Groupe 4, et (B) au moins un second composant comprenant ledit complexe, dans des conditions et pendant une période de temps telles que le cation dudit complexe réagisse irréversiblement avec au moins un ligand du composé de cyclopentadiényle, et que l'anion pentafluorophénylique forme une paire ionique non coordinatrice avec un cation résultant produit à partir du composé de cyclopentadiényl-métal.

56. Procédé selon la revendication 55, dans lequel le mélange formé à partir de (A) et (B) comprend de plus au moins un composant supplémentaire qui est (C) au moins un composé additif organométallique de formule R_3M où chaque R est indépendamment un groupe hydrocarbyle ou un groupe alcoolate, à condition qu'au moins un R soit un groupe hydrocarbyle, et où M est un atome d'aluminium ou de bore ; ou (D) un support de catalyseur ; ou (E) une association de (C) et (D).

57. Procédé selon la revendication 56, dans lequel ledit composant supplémentaire est au moins un trihydrocarbylaluminium ou au moins un trihydrocarbylbore.

58. Procédé selon la revendication 56, dans lequel ledit composant supplémentaire est un oxyde minéral sous forme particulaire.

59. Procédé selon la revendication 58, dans lequel ledit oxyde minéral est la silice, l'alumine ou la silice-alumine.

60. Procédé selon la revendication 49, comprenant de plus la réaction d'au moins une partie dudit composé de pentafluorophényl-bore avec des groupes hydroxyle d'un support en oxyde métallique dans des conditions convenant pour former un activateur anionique lié au support, puis la mise en contact dudit activateur anionique lié au support avec un métallocène approprié d'un métal de transition du Groupe 4 de telle manière que l'activateur protone le métallocène ce par quoi on réalise un système de catalyseur ionique supporté comprenant un cation de métal de transition et un anion lié au support.

61. Procédé selon la revendication 50, comprenant de plus la réaction d'au moins une partie dudit tris(pentafluorophényl)borane avec les groupes hydroxyle d'un support de silice ou silice-alumine dans des conditions convenant pour former un activateur anionique lié au support, puis la mise en contact dudit activateur anionique lié au support avec un métallocène approprié d'un métal de transition du Groupe 4 de telle manière que l'activateur protone le métallocène ce par quoi on réalise un système de catalyseur ionique supporté comprenant un cation de métal de transition et un anion lié au support.

62. Procédé selon la revendication 49, comprenant de plus la mise en contact dudit composé de pentafluorophényl-bore avec un métallocène de formule LMX_2, où L est un dérivé d'un groupe à liaison pi délocalisée conférant une géométrie contrainte au site métallique actif et contient jusqu'à 50 atomes autres que des atomes d'hydrogène, M est un métal du Groupe 4 et chaque X est indépendamment un hydrure ou un groupe hydrocarbyle, silyle ou germyle ayant jusqu'à 20 atomes de carbone, de silicium ou de germanium, dans des conditions convenant pour former un catalyseur ayant une structure limite à charges séparées de formule $LMX^{\oplus}XA^-$ où A est un anion formé à partir dudit composé de pentafluorophényl-bore.

63. Procédé selon la revendication 50, comprenant de plus la mise en contact dudit tris(pentafluorophényl)borane avec un métallocène de formule LMX_2, où L est un dérivé d'un groupe à liaison pi délocalisée conférant une géométrie contrainte au site métallique actif et où L contient jusqu'à 50 atomes autres que des atomes d'hydrogène, M est un métal du Groupe 4 et chaque X est indépendamment un hydrure ou un groupe hydrocarbyle, silyle ou germyle ayant jusqu'à 20 atomes de carbone, de silicium ou de germanium, dans des conditions convenant pour former un catalyseur ayant une structure limite à charges séparées de formule $LMX^{\oplus}XA^-$ où A est un anion formé à partir du tris(pentafluorophényl)borane.

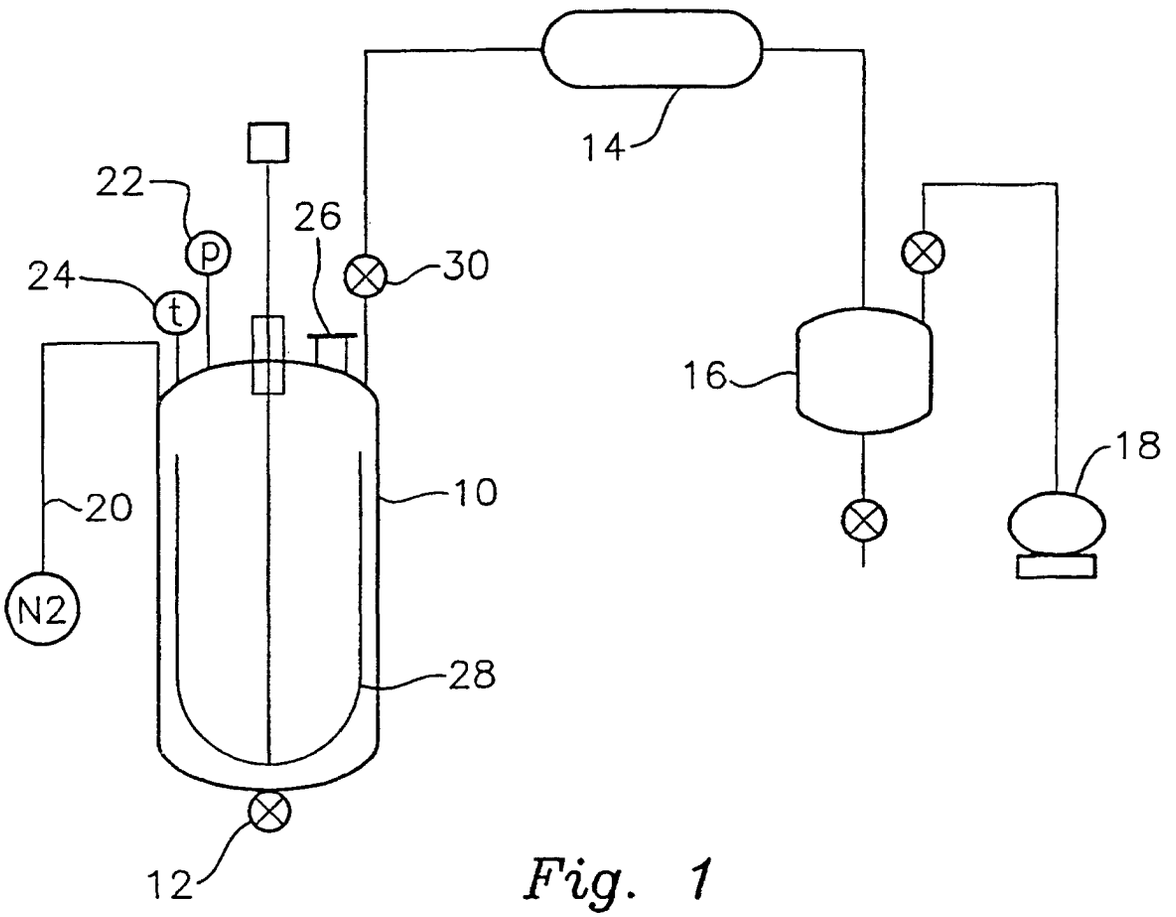


Fig. 1