CATIONIC ALUMINUM ALKYL COMPLEXES INCORPORATING AMIDINATE LIGANDS AS POLYMERIZATION CATALYSTS

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ABSTRACT
Non-transition metal containing Ziegler-Natta like catalysts are prepared and used for polymerization reactions. The catalysts are cationic aluminum amidinate compounds. The compounds successfully catalyze polymerization of unsaturated hydrocarbons such as alpha olefins and avoid the expense of transition metals and, as well, the environmental objections to the use of the same.

6 Claims, No Drawings
1 CATIONIC ALUMINUM ALKYL COMPLEXES INCORPORATING AMIDATE LIGANDS AS POLYMERIZATION CATALYSTS

CROSS REFERENCE TO A RELATED APPLICATION

This application is a division of Ser. No. 08/818,297 filed Mar. 14, 1997 now U.S. Pat. No. 5,777,120.

GRANT REFERENCE

Work for this invention was funded in part by a grant from the National Science Foundation, Grant No. NSF CHE94-13022(003). The Government may have certain rights in this invention.

BACKGROUND OF THE INVENTION

Ziegler-Natta type catalysts for polymerization of unsaturated hydrocarbons, such as alpha olefins, have long been the state of the art catalysts for such reactions. Typically, Ziegler-Natta type catalysts are composed of transition metal salts and aluminum alkyl compounds. While these catalysts are very effective and have a long-established record of use, they are not without drawbacks. For example, transition metals are expensive, potentially present some toxicity hazards, and to some are environmentally objectionable. Therefore, continuing efforts toward development of other suitable olefin polymerization catalysts have occurred. For example, metallocene catalysts have been developed for use in alpha olefin polymerization.

This invention has as its primary objective the development of catalysts for polymerization of unsaturated hydrocarbons which successfully polymerize without a transition metal moiety as part of the catalyst.

Another objective of the present invention is to prepare such catalysts in high yields and by use of convenient and practical synthetic methods.

A yet further objective of the present invention is a method of polymerizing unsaturated hydrocarbons using Ziegler-Natta type catalysts in the sense that the catalyst behaves similarly to Ziegler-Natta catalysts, but yet avoids the use of transition metals.

The method and manner of accomplishing each of the above objectives, as well as others, will become apparent from the detailed description of the invention which follows hereinafter.

2 SUMMARY OF THE INVENTION

The invention relates to novel catalysts, processes of synthesizing the catalysts, and to olefin polymerization reactions using the catalysts. The catalysts are cationic aluminum amide compounds. These compounds behave similarly to Ziegler-Natta catalysts, but avoid the use of transition metals.

DETAILED DESCRIPTION OF THE INVENTION

The formation of polyethylene from the reaction of neutral aluminum compounds including Cl₂AlCH(Me)AlCl₃ or (AIR₃)₂ with ethylene in the temperature range 25 to 50°C has been reported in Martin, H., Breitinger, H. Makromol. Chem. 1992, 193, 1283. However, the reported catalytic activities are very low (1.6×10⁻¹ - 3.8×10⁻⁴ g PE/ (mol·h·atm)).

After extensive work with transition metal catalysts and investigation into the polymerization of unsaturated hydrocarbons such as olefins with a view to improving on the conventional processes by eliminating transition elements, a process has been discovered for polymerizing such unsaturated hydrocarbons with an entirely new class of catalyst compounds.

The catalysts are cationic aluminum amide compounds of the following formula:

\[
\text{R}^1 \quad \text{R}^2 \quad \text{X} \quad \text{R}^3
\]

wherein R¹, R² and R³ are selected from the group consisting of C₁ to C₅₂ alkyl, aryl, or silyl groups, X is an anionic ligand, m=0 or 1, L is a labile Lewis base or donor ligand or a neutral aluminum species capable of coordination, and A⁻ is a counterbalancing non-coordinating or weakly coordinating anion.

The amide ligands (in anionic form) may be represented by structure C, which is the resonance hybrid of localized resonance structures A and B. Similarly, the base-free cationic aluminum complexes (n=0) may be represented by structure F, which is the resonance hybrid of localized resonance structures D and E. The situation for the base-stabilized cationic aluminum complexes (n=1) is analogous.
In the above description of the resonance structures, R1, R2, and R3 are as earlier described. With regard to the invention, while they broadly can be C1 to C40, generally speaking, preferred R1, R2 and R3 groups are C1 to C12, alkyl, aryl or silyl.

The X moiety can represent a hydride radical, a dialkylamido radical, an alkoxide radical, an aryloxide radical, a hydrocarbyl radical, a substituted hydrocarbyl radical, a halocarbyl radical, or a thiolate radical. L is, of course, labile and can be displaced by other Lewis bases or donor ligands, including olefins, di-olefins, or any other unsaturated monomer.

The A+ moiety represents the non-coordinating or weakly coordinating counterbalancing anion. In particular, it represents a compatible, non-coordinating anion containing a single coordination complex comprising a charge-bearing metal or metalloid core which is relatively large (bulky), capable of stabilizing the active catalyst species and being sufficiently labile to be displaced by olefinic, di-olefinic or acetylenically unsaturated substrates, or other neutral Lewis bases or donor groups, such as ethers, nitriles and the like. Polychloroborane anions, carborane anions and metalcarbonyl derivatives are also useful as non-coordinating or weakly coordinating counterbalancing anions.

The key to proper anion design requires that the anionic complex is labile and stable toward reactions in the final catalyst species. Anions which are stable toward reactions with water or Bronsted acids and which do not have acidic protons located on the exterior of the anion (i.e. anionic complexes which do not react with strong acids or bases) possess the stability necessary to qualify as a stable anion for the catalyst system. The properties of the anion which are important for maximum stability include overall size, and shape (i.e. large radius of curvature), and nucleophilicity. Using these guidelines one can use the chemical literature to choose non-coordinating anions which can serve as components in the catalyst system. In general, suitable anions for the second component may be any stable and bulky anionic complex having the following molecular attributes: 1) the anion should have a molecular diameter about or greater than 4 angstroms; 2) the anion should form stable salts with reducible Lewis Acids and protonated Lewis bases; 3) the negative charge on the anion should be delocalized over the framework of the anion or be localized within the core of the anion; 4) the anion should be a relatively poor nucleophile; and 5) the anion should not be a powerful reducing or oxidizing agent. Anions meeting these criteria—such as polynuclear boranes, carboranes, metalcarboranes, polyanion complexes and anionic coordination complexes—are well described in the chemical literature.

Illustrative, but not limiting examples of non-coordinating or weakly coordinating counterbalancing anions are tetra (phenyl)borate, tetra (p-toly1)borate, tetra (pentfluorophenyl)borate, tetra (3,5-bis-trifluoromethylphenyl)borate, (methyltris(pentfluorophenyl)borate, C2B11H12-, C12H5B2 -, B3H3H22-, and (C6B3H11)2-.

As earlier stated, generally, these anions are (1) labile and can be displaced by an olefin, di-olefin or acetylenically unsaturated monomer, have a molecular diameter about or greater than 4 angstroms, form stable salts with reducible Lewis acids and protonated Lewis bases, have a negative charge delocalized over the framework on the anion of which the core thereof is not a reducing or oxidizing agent, and are relatively poor nucleophiles. For other examples of such counterbalancing, non-coordinating or weakly coordinating anions, see Strauss, S. H.; Chemical Reviews, 1993, 93, 927-942.

L, the optional labile Lewis base ligand, is also conventional and well known. It can, for example, be represented by tetrahydrofuran, ethers such as dimethyl ether, amines, alkyl amines, pyridine, substituted pyridines, and phosphines. L may also be represented by a neutral aluminum species which coordinates to the cation through a bridging group, such as [Me3(CN)Pr]+AlMe3; AlMe2; and AlCl3. The presence of such neutral coordinating ligands L is not critical, and they may or may not be present as deemed appropriate in any particular reaction.

The cationic aluminum amide complexes may be prepared by reacting a neutral precursor complex of the type [B2(CNR2)2(NR3)]AlX4, where R2, R3, and X are as defined above, with an activator compound which is capable of abstracting one X- group from the precursor complex or of cleaving one Al—X bond of the precursor complex. Suitable activator compounds include Bronsted acids, such as ammonium salts, Lewis acids, such as AlCl3 and B(C6F5)3, ionic reagents such as Ag+ and trityl salts, and oxidizing agents such as ferrocenium salts. Illustrative, but not limiting examples of suitable activator compounds are N,N-dimethylenalammonium tetra(pentfluorophenyl)borate, methylidiphenylammonium tetra(pentfluorophenyl)borate, aluminum trichloride, tris(pentfluorophenyl)boron, silver (1) tetra(phenyl)borate, triphenylcarbenium tetra (pentfluorophenyl)borate, and ferrocenium tetra(phenyl)borate.

The synthesis of the catalyst compounds as earlier described for the present invention is particularly straightforward. Ideally, they are prepared on a high vacuum line under an inert atmosphere in the presence of solvents in the manner illustrated in the examples below. These examples of synthesis are illustrative and not intended to be limiting of the invention.

All manipulations were performed on a high-vacuum line or in a glove box under a purified N2 atmosphere. Solvents were distilled from Na/benzophenone ketyl, except for chlorinated solvents, which were distilled from activated molecular sieves (3 Å) or P2O5.

NMR spectra were recorded on a Bruker AMX 360 spectrometer in sealed or Teflon-valved tubes at ambient probe temperature unless otherwise indicated. 1H and 13C chemical shifts are reported versus SiMe3 and were determined by reference to the residual 1H and 13C solvent peaks.

All coupling constants are reported in Hz. The NMR spectra of cationic complexes contained resonances for B(C6F5)4- or [B(C6F5)2]2-.

NMR data for B(C6F5)4-: 13C NMR (CD2Cl2): δ 148.6 (d, 1JCF = 240.0 Hz), 138.7 (d, 1JCF = 245.4 Hz), 136.8 (d, 1JCF = 245.4 Hz), 124.7 (br s, iso-PF3). NMR data for MeB(C6F5)2-: 1H NMR (CD2Cl2): δ 0.47 (br s, 3H, B—CH3). 13C NMR (CD2Cl2): δ 148.6 (d, 1JCF = 235.5 Hz), 137.9 (d, 1JCF = 242.7 Hz), 136.8 (d, 1JCF = 246.4 Hz), 129.7 (br s, iso-PF3), 10.34 (br s, B—CH3).

Mass spectra were obtained using the Direct Insertion Probe (DIP) method, on a VG Analyticals Trilogy I instrument operating at 70 eV. Elemental analyses were performed by Desert Analytics Laboratory.

**EXAMPLE 1**

{McN(CNP)2}AlMe3

A solution of 1,3-diisopropylcarbodiimide (2.00 g, 10.7 mmol) in hexane (25 mL) was added dropwise via pipette to a rapidly stirred solution of AlMe3 (1.06 mL, 11.0 mmol) in hexane (10 mL). An exothermic reaction was observed. The reaction mixture was stirred at room temperature for 18 h,
after which time the volatiles were removed under vacuum affording pure \([\text{MeCN(NC})_2]\)\text{AlMe}_3\), as a pale yellow liquid (2.30 g, 71%). \(^1\)H NMR (CDCl\textsubscript{3}): \(\delta 3.50\) (sept, \(J_{HF}=6.0\) Hz, 2H, CH\textsubscript{2}Me), 1.94 (s, 3H, CMe\textsubscript{3}), 1.05 (d, \(J_{HF}=6.1\) Hz, 12H, CH\textsubscript{2}Me), 0.82 (s, 6H, AlMe\textsubscript{3}). \(^{13}\)C NMR (CDCl\textsubscript{3}): \(\delta 172.5\) (s, CMe\textsubscript{3}), 45.3 (d, \(J_{CF}=132.2\) Hz, CH\textsubscript{2}Me), 25.3 (q, \(J_{CF}=125.6\) Hz, CH\textsubscript{2}Me), 11.1 (q, \(J_{CF}=128.3\) Hz, CMe\textsubscript{3}), -9.94 (br q), \(J_{CF}=114.1\) Hz, AlMe\textsubscript{3}). Anal. Calc. for C\textsubscript{9}H\textsubscript{15}N\textsubscript{3}Al: C, 60.57; H, 11.69; N, 14.13. Found: C, 60.41; H, 11.96; N, 14.50.

**EXAMPLE 2**

\([\text{MeCN(NC})_2]\)\text{AlMe}_3

A solution of 1,3-diisopropoxycarbylidimide (5.00 g, 24.2 mmol) in hexane (40 mL) was added slowly to a solution of AlMe\textsubscript{3} (2.40 mL, 25.0 mmol) in hexane (15 mL). The solution was stirred for 15 h and the volatiles were removed under vacuum yielding a pale yellow liquid that crystallized upon standing to afford pure \([\text{MeCN(NC})_2]\)\text{AlMe}_3, as off-white crystals. (6.49 g, 93%). \(^1\)H NMR (CDCl\textsubscript{3}): \(\delta 8.30\) (m, 2H, Cy), 1.92 (s, 3H, CMe\textsubscript{3}), 1.69 (m, 8H,Cy), 1.56 (m, 2H, Cy), 1.35–1.06 (m, 8H, AlMe\textsubscript{3}). \(^{13}\)C NMR (CDCl\textsubscript{3}): \(\delta 172.4\) (s, CMe\textsubscript{3}), 53.0 (d, \(J_{CF}=131.4\) Hz, Cy-C), 36.0 (t, \(J_{CF}=126.5\) Hz, Cy), 26.1 (t, \(J_{CF}=125.8\) Hz, Cy), 25.4 (t, \(J_{CF}=126.9\) Hz, CMe\textsubscript{3}), 11.2 (q, \(J_{CF}=128.0\) Hz, CMe\textsubscript{3}), -9.78 (br q), \(J_{CF}=112.6\) Hz, AlMe\textsubscript{3}). Anal. Calc. for C\textsubscript{9}H\textsubscript{15}N\textsubscript{3}Al: C, 69.02; H, 11.22; N, 10.06. Found: C, 68.88; H, 10.44; N, 10.15. Mass Spec. (EI, m/z): 263 [M]\textsuperscript{+}.

**EXAMPLE 3**

\([\text{Bu(NP})_2]\)\text{AlCl}_2

A solution of 1,3-diisopropoxycarbodiimide (5.00 g, 39.6 mmol) in Et\textsubscript{2}O (50 mL) was cooled to 0°C. BuLi (23.30 mL of a 1.7 M solution in pentane, 39.6 mmol) was added dropwise via syringe and the mixture was allowed to warm to room temperature. After 30 min the solvent was removed under vacuum affording a yellow oily solid which was dried under vacuum (18°C). To give a pale yellow solid. Trituration with hexane gave \([\text{Bu(NP})_2]\)\text{AlCl}_2 as an off-white powder (4.56 g, 61%). \(^1\)H NMR (THF-d\textsubscript{6}): \(\delta 3.84\) (sept, \(J_{HF}=5.7\) Hz, 2H, CH\textsubscript{2}Me), 1.31 (s, 9H, CMe\textsubscript{3}), 0.96 (d, \(J_{HF}=6.1\) Hz, 12H, CH\textsubscript{2}Me). \(^{13}\)C NMR (THF-d\textsubscript{6}): \(\delta 168.4\) (s, CMe\textsubscript{3}), 46.6 (d, \(J_{CF}=122.3\) Hz, CHMe\textsubscript{3}), 39.4 (s, CMe\textsubscript{3}), 31.0 (q, \(J_{CF}=116.1\) Hz, CHMe\textsubscript{3}), 26.3 (q, \(J_{CF}=116.1\) Hz, CMe\textsubscript{3}).

**EXAMPLE 4**

\([\text{Bu(NP})_2]\)\text{AlCl}_2

A solution of 1,3-diisopropoxy carbodiimide (5.00 g, 24.2 mmol) in Et\textsubscript{2}O (50 mL) was cooled to 0°C. BuLi (14.3 mL of a 1.7 M solution in pentane, 24.2 mmol) was added via syringe and the mixture was allowed to warm to room temperature. After 30 min the volatile components were removed under vacuum affording a yellow oily solid which was dried overnight under vacuum to yield a pale yellow powder. Trituration of this solid with pentane gave \([\text{Bu(NP})_2]\)\text{AlCl}_2 as a pale yellow powder (4.91 g, 75%). \(^1\)H NMR (THF-d\textsubscript{6}): \(\delta 3.50\) (m, 2H,Cy), 1.81–0.93 (m, 2H,Cy), 1.10 (s,9H, CMe\textsubscript{3}). \(^{13}\)C NMR (THF-d\textsubscript{6}): \(\delta 68.33\) (s, CMe\textsubscript{3}), 55.9 (d, \(J_{CF}=119.8\) Hz, Cy-C), 39.5 (s, CMe\textsubscript{3}), 37.7 (t, \(J_{CF}=118.9\) Hz,Cy), 31.1 (q, \(J_{CF}=117.7\) Hz, CMe\textsubscript{3}), 28.2 (t, partially obscured, Cy), 26.8 (t, \(J_{CF}=119.4\) Hz, Cy).
h. The volatiles were removed under vacuum (3×15 mL). The extract was concentrated to 30 mL and maintained at room temperature affording [BuC(NC)(tBu)]AlMe(2.00 g, 83%) as large colorless crystals which were collected by filtration. 3H NMR (CDCl₃): δ 3.56 (m, 2H, CH₂), 1.80–1.69 (m, 8H, CH₃), 1.61–1.57 (m, 2H, CH₂), 1.36 (s, 9H, CHMe₂). 13C NMR (CDCl₃): δ 178.5 (s, C(AlMe)), 54.2 (d, JCHC = 155.9 Hz, CH₂-C(AlMe)), 39.1 (d, JCHC = 157.3 Hz, CH₂-C(AlMe)), 37.3 (t, JCHC = 119.3 Hz, CH₃), 26.1 (t, JCHC = 119.3 Hz), 26.0 (t, JCHC = 119.3 Hz), –9.1 (br q, JCHC = 103.9 Hz, AlMe₃). Anal. Calcd. for C₃H₄AlN₂Al: C, 71.20; H, 11.64; N, 8.74. Found: C, 71.18; H, 11.88; N, 8.73. Mass Spec. (El,m/z): 320 [M⁺]+, 305 [M-CH₃]⁺.

**EXAMPLE 9**

\[
\text{[BuC(N(CF₃))₂]Al(CH₃)}_2
\]

A solution of \([\text{BuC(N(CF₃))₂]AlCl}_2 (0.50 g, 1.8 mmol)\) in Et₂O (25 mL) was cooled to –78°C and PhCH₂MgCl (3.56 mL of a 1.0 M solution in Et₂O, 3.6 mmol) was added dropwise via syringe. The reaction mixture was warmed to room temperature and was stirred for 15 h. The volatiles were removed under vacuum and the residue was extracted with pentane. The extract was evaporated to dryness under vacuum affording pure \([\text{BuC(N(CF₃))₂]Al(CH₃)}_2\) as a viscous white oil (0.55 g, 79%).

**EXAMPLE 10**

\[
\text{[BuC(N(CF₃))₂]AlCl}_2
\]

A solution of \([\text{BuC(N(CF₃))₂]AlCl}_2 (0.50 g, 1.4 mmol)\) in Et₂O (20 mL) was cooled to –78°C and PhCH₂MgCl (2.76 mL of a 1.0 M solution in Et₂O, 2.8 mmol) was added dropwise via syringe. The mixture was warmed to slow to room temperature and was stirred for 15 h. The volatiles were removed under vacuum and the residue was extracted with pentane. The extract was evaporated to dryness under vacuum affording pure \([\text{BuC(N(CF₃))₂]Al(CH₃)}_2\) as a white solid material (1.13 g, 94%).

**EXAMPLE 11**

\[
\text{[BuC(N(CF₃))₂]Al(Ph)}_2
\]

A solution of \([\text{BuC(N(CF₃))₂]AlCl}_2 (0.50 g, 1.8 mmol)\) and LiCH₂CMe₂ (0.28 g, 3.6 mmol) were mixed as solids in the glove box.

**EXAMPLE 12**

\[
\text{[BuC(N(CF₃))₂]Al(Ph)}_2
\]

A solution of LiCH₂CMe₂ (0.43 g, 5.5 mmol) in Et₂O (20 mL) was added dropwise at –78°C to a solution of [BuC(N(CF₃))₂]Al(C₂H₅) (1.00 g, 2.8 mmol). The reaction mixture was allowed to warm to room temperature and was stirred for 15 h. The volatiles were removed under vacuum and the residue was extracted with pentane. The extract was evaporated to dryness under vacuum affording pure \([\text{BuC(N(CF₃))₂]Al(C₂H₅)}_2\) as a white solid material (1.31 g, 55%).

**EXAMPLE 13**

\[
\text{[MeC(N(Pr)₃)]AlMe(μ-Me)MeB(C,F,Me)}_3
\]

A solution of B(C₃F₇)₃ (0.77 g, 1.5 mmol) in CH₂Cl₂ (20 mL) was added to [MeC(N(Pr)₃)]AlMe (0.60 g, 3.0 mmol) also in CH₂Cl₂ (15 mL). The reaction mixture was allowed to stir for 30 min at room temperature and the volatiles were removed under vacuum leaving an oily white solid.

**EXAMPLE 14**

\[
\text{[MeC(N(Pr)₃)]AlMe(NMe,Ph)IB(C,F,Me)}_3
\]

A CD₂Cl₂ solution (600 mL) of [HNMe₂Ph]B(C₃F₇)₃ (85.3 mg, 0.11 mmol) was added to a vial containing
The mixture was transferred to an NMR tube and NMR spectra were recorded showing complete conversion to \([\text{MeC(NPr)}_2\text{AlMe}_3] [\text{MeC(NMePh)}] [\text{C}_6\text{H}_4\text{F}_3]_2\). \(^1\text{H}\) NMR (CDCl\(_3\)): \(\delta 7.63\) (t, \(J_{H,F} = 7.9\) Hz, 2H, m-Ph), 7.51 (t, \(J_{H,F} = 7.3\) Hz, 1H, p-Ph), 7.47 (d, \(J_{H,F} = 7.9\) Hz, 2H, o-Ph), 3.58 (sept, \(J_{H,H} = 6.4\) Hz, 2H, CHMe), 3.50 (s, 6H, NeMe), 2.17 (s, 3H, CMe), 1.03 (d, \(J_{H,H} = 6.5\) Hz, 6H, CHMe), 0.92 (d, \(J_{H,H} = 6.4\) Hz, 6H, CHMe), -0.30 (s, 3H, AlMe). \(^{13}\text{C}\) NMR (CDCl\(_3\)): \(\delta 182.0\) (s,CMe), 143.7 (s, iso-Ph), 131.4 (d, \(J_{C,F} = 159.4\) Hz, o-Ph), 129.8 (d, \(J_{C,F} = 164.8\) Hz, p-Ph), 120.9 (d, \(J_{C,F} = 153.1\) Hz, m-Ph), 46.7 (q, \(J_{C,F} = 134.7\) Hz, NeMe), 46.0 (d, \(J_{C,F} = 125.2\) Hz, CHMe), 24.7 (q, \(J_{C,F} = 119.7\) Hz, CHMe), 24.6 (q, \(J_{C,F} = 119.7\) Hz, CHMe), 12.7 (q, \(J_{C,F} = 122.6\) Hz, CMe), -13.4 (br q, \(J_{C,F} = 116.8\) Hz, AlMe).

**EXAMPLE 15**

\([\text{MeC(NPr)}_2\text{AlMe(PMe)}_3] [\text{MeB(CF}_3\text{)}_2]\) A CD\(_2\)Cl\(_2\) solution of \([\text{MeC(NPr)}_2\text{AlMe(PMe)}_3][\text{MeB(CF}_3\text{)}_2]\) was cooled in liquid N\(_2\) and PMe\(_3\) (5 equiv) was condensed onto the frozen solution. The mixture was warmed to room temperature and the \(^1\text{H}\) NMR spectrum was recorded, showing that complete formation of the trimethylphosphine adduct \([\text{MeC(NPr)}_2\text{AlMe(PMe)}_3][\text{MeB(CF}_3\text{)}_2]\) and \([\text{MeC(NPr)}_2\text{AlMe}] [\text{MeB(CF}_3\text{)}_2]\) had occurred. To obtain a sample free from reaction byproducts, the NMR tube was evacuated and pumped on for 18 h. The resulting oily solid was redissolved in CD\(_2\)Cl\(_2\) and the NMR spectrum was recorded, and showed that only \([\text{MeC(NPr)}_2\text{AlMe(PMe)}_3][\text{MeB(CF}_3\text{)}_2]\) was present. \(^1\text{H}\) NMR (CDCl\(_3\)): \(\delta 3.62\) (sept, \(J_{H,H} = 6.3\) Hz, 2H, CHMe), 2.17 (s, 3H, CMe), 1.52 (d, \(J_{H,H} = 9.4\) Hz, 9H, PMe\(_3\)), 1.10 (d, \(J_{H,H} = 6.3\) Hz, 12H, CHMe), -0.27 (s, 3H, AlMe). \(^{13}\text{C}\) NMR (CDCl\(_3\)): \(\delta 180.6\) (s, CMe), 45.5 (d, \(J_{C,F} = 131.1\) Hz, CHMe), 25.3 (q, \(J_{C,F} = 121.0\) Hz, CHMe), 12.4 (q, \(J_{C,F} = 124.7\) Hz, CHMe), 9.1 (d, \(J_{C,F} = 29.6\) Hz, \(J_{C,F} = 127.6\) Hz, PMe\(_3\)), -12.8 (br q, \(J_{C,F} = 109.6\) Hz, AlMe).

**EXAMPLE 16**

\([\text{MeC(NPr)}_2\text{AlMe(PMe)}_3][\text{B(CF}_3\text{)}_2]\) A CD\(_2\)Cl\(_2\) solution of \([\text{MeC(NPr)}_2\text{AlMe(NMePh)}] [\text{B(CF}_3\text{)}_2]\) was cooled in liquid N\(_2\) and PMe\(_3\) (5 equiv) was condensed onto the frozen solution. The mixture was warmed to room temperature and the \(^1\text{H}\) NMR spectrum was recorded, showing that formation of the trimethylphosphine adduct \([\text{MeC(NPr)}_2\text{AlMe(PMe)}_3][\text{B(CF}_3\text{)}_2]\) and free NMe\(_2\)Ph had occurred. 1H NMR (CDCl\(_3\)): \(\delta 3.62\) (d, \(J_{H,H} = 6.3\) Hz, 2H, CHMe), 2.17 (s, 3H, CMe), 1.52 (d, \(J_{H,H} = 9.4\) Hz, 9H, PMe\(_3\)), 1.10 (d, \(J_{H,H} = 6.3\) Hz, 12H, CHMe), -0.27 (s, 3H, AlMe). \(^{13}\text{C}\) NMR (CDCl\(_3\)): \(\delta 180.6\) (s, CMe), 45.5 (d, \(J_{C,F} = 131.1\) Hz, CHMe), 25.3 (q, \(J_{C,F} = 121.0\) Hz, CHMe), 12.4 (q, \(J_{C,F} = 124.7\) Hz, CHMe), 9.1 (d, \(J_{C,F} = 29.6\) Hz, \(J_{C,F} = 127.6\) Hz, PMe\(_3\)), -12.8 (br q, \(J_{C,F} = 109.6\) Hz, AlMe).

**EXAMPLE 18**

\([\text{BuC(NCy)}_2\text{AlMe}[\text{MeB(CF}_3\text{)}_2]\) The product was prepared in an identical manner to that outlined above, using 0.033 g (4.80\%) \(\text{AlMe}_2\) (0.10 mmol) and 0.053 g \(\text{B(CF}_3\text{)}_2\) (1 equiv, 0.10 mmol). Again 100\% conversion to the base-free cation was observed. 1H NMR (CDCl\(_3\)): \(\delta 3.61\) (m, 2H, Cy), 1.83–1.74 (br m, 4H, Cy), 1.66 (br s, 3H, BCH), 1.55 (br t, 4H, Cy), 1.37 (s, 9H, CMMe), 1.25–0.98 (m, 8H, Cy), 0.89–0.79 (m, 4H, Cy), -0.46 (s, 3H, AlMe). \(^{13}\text{C}\) NMR (CDCl\(_3\)): \(\delta 181.1\) (s, CCMMe), 54.1 (d, \(J_{C,F} = 134.0\) Hz, Cy-C), 39.9 (s, CMe), 37.5 (t, \(J_{C,F} = 129.0\) Hz, Cy), 36.6 (t, \(J_{C,F} = 126.2\) Hz, Cy), 29.3 (q, \(J_{C,F} = 122.3\) Hz, CMMe), 25.8 (t, \(J_{C,F} = 122.5\) Hz, Cy), -8.5 (q, \(J_{C,F} = 114.7\) Hz, AlMe).

**EXAMPLE 19**

Polymerization Procedure for Ethylene

All polymerizations were carried out using transition-metal-free conditions, employing glass apparatus and Teflon-coated stirrer bars. In a typical experiment, 0.02 g of \([\text{BuC(NPr)}_2\text{AlMe}_2\) was weighed out into a glass vial in the dry box, and 3 mL of dry toluene was added. 1 equiv of activator, based on the aluminum compound was weighed into a Fisher-Porter bottle and ca. 50 cm\(^3\) of toluene was added. The aluminum complex solution was added dropwise over 2 minutes (using a pipette) to the rapidly stirring activator solution, ensuring efficient mixing of the 2 components, and a constant excess of activator (to limit formation of base adduct species). The apparatus was then removed from the dry box and connected to the polymerizer.
ization equipment, consisting of an ethylene cylinder, metal vacuum line and gas purification system. This had been previously evacuated to remove any residual gas from the system. The mixture was allowed to equilibrate at the temperature required for the experiment (10–20 minutes) before the introduction of ethylene (Note, the Fisher-Porter bottle was placed under slight vacuum prior to introduction of the ethylene, to reduce the nitrogen content within and maximize ethylene dissolution in the solvent). The polymerization was typically allowed to run for 60 minutes, after which time the ethylene flow to the system was halted. The apparatus was vented in a fume hood and disassembled.

50–80 mL of a mixture of methanol (ca. 150 mL) and conc. HCl (ca. 1.5 mL) was added to the solution to quench the reaction and the precipitate (if any) was collected by filtration. The polymer was then washed with acidified water (ca. 1.5 mL conc. HCl in 100 mL H₂O) to ensure removal of the Al-salts, and dried in a vacuum oven at 60°C for 2–8 hours. The weight was recorded and the activity calculated (see table).

The results of the ethylene polymerizations are summarized in the table below.

<table>
<thead>
<tr>
<th>Run</th>
<th>Activator Compound</th>
<th>Time (min)</th>
<th>Temp (°C)</th>
<th>Yield PE (g)</th>
<th>Activity (g PE/mol cat/hr/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>B(C₆F₅)₃</td>
<td>60</td>
<td>26</td>
<td>0.053</td>
<td>293</td>
</tr>
<tr>
<td>2</td>
<td>B(C₆F₅)₃</td>
<td>60</td>
<td>60</td>
<td>0.115</td>
<td>697</td>
</tr>
<tr>
<td>3</td>
<td>B(C₆F₅)₃</td>
<td>60</td>
<td>85</td>
<td>0.026</td>
<td>162</td>
</tr>
<tr>
<td>4</td>
<td>Ph₃C[Br(C₆F₅)₃]</td>
<td>60</td>
<td>26</td>
<td>0.084</td>
<td>590</td>
</tr>
<tr>
<td>5</td>
<td>Ph₃C[Br(C₆F₅)₃]</td>
<td>60</td>
<td>60</td>
<td>0.293</td>
<td>1177</td>
</tr>
<tr>
<td>6</td>
<td>Ph₃C[Br(C₆F₅)₃]</td>
<td>30*</td>
<td>85</td>
<td>0.351</td>
<td>4145</td>
</tr>
</tbody>
</table>

(* = solution stopped stirring due to precipitates forming, therefore stopped after 30 mins)

As can be seen from the above, effective catalysts for alpha-olefin polymerizations in particular were prepared that avoid any transition metals. It therefore can be seen that the invention accomplishes at least all of its stated objectives.

What is claimed is:

1. A method of polymerizing unsaturated hydrocarbons comprising:

   contacting unsaturated hydrocarbon monomer with a small but catalytically-effective promoting amount of a cationic aluminum aminate compound of the formula:

   

   wherein R¹, R², and R³ are selected from the group consisting of C₃ to C₃₀ alkyl, aryl or silyl groups, X is an anionic ligand, n=0 or 1, L may or may not be present, and if present, L is an labile Lewis-base ligand or a neutral aluminum species which coordinates to the cation through a bridging group, and A⁻ is a counterbalancing non-coordinating or weakly coordinating anion;

   said contact occurring under polymerizing conditions.

2. The process of claim 1 wherein R¹, R² and R³ of the catalyst species are selected from the group consisting of C₃ to C₃₀ alkyl, aryl or silyl groups.

3. The process of claim 1 wherein X of the catalyst species is a hydride, dialkyl amido, alkoxide, aryloxide, hydrocarbyl, substituted hydrocarbyl, halocarbyl or thiolate.

4. The process of claim 1 wherein n=1 and L is selected from the group consisting of tetrahydrofuran, ethers, amines, alkylamines, pyridine and phosphines.

5. The process of claim 1 wherein A⁻ is a boron-derived anion.

6. The process of claim 1 wherein the cationic aluminum aminate compound is generated in situ and not isolated prior to its use as a catalyst.

* * * * *