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(54) **Title:** OLIGOMERISATION PROCESS

(57) **Abstract:** Disclosed is an oligomerisation process for forming base oils for lubrication compositions, and in particular, a process for the selective oligomerisation of C₅ to C₂₀ alpha-olefins to produce polyalphaolefin oligomers, preferably with a molecular weight distribution that is suitable for use in lubricant base oils, in which the olefinic feedstock is contacted with an ionic liquid comprising (i) at least one borenium cation of the formula [BX₂L]⁺, wherein L is a Lewis basic donor ligand and each X is independently selected from fluorine, chlorine and bromine; and (ii) at least one non-coordinating anion.

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Oligomerisation Process

This invention relates to an oligomerisation process for forming base oils for lubricating compositions. In particular, the present invention provides a process for the selective
5 oligomerisation of C₅ to C₂₀ alpha-olefins to produce polyalphaolefin oligomers, preferably with a molecular weight distribution that is suitable for use in lubricant base oils.

Lubricant compositions generally comprise a base oil of lubricating viscosity together
10 with one or more additives to deliver properties such as reduced friction and wear, improved viscosity index, detergency, and resistance to oxidation and corrosion. A lubricant base oil may comprise one or more sources of lubricating oil, referred to as base stocks.

Lubricant base stocks useful in automotive engine lubricants may be obtained as higher
15 boiling fractions from the refining of crude oil or via synthetic routes, and are classified as Group I, II, III, IV and V base stocks according to API standard 1509, "ENGINE OIL LICENSING AND CERTIFICATION SYSTEM", April 2007 version 16th edition Appendix E. Group IV refers to polyalphaolefin (PAO) base stocks, which are typically synthesised
20 by oligomerisation of 1-decene. The principal component of these base stocks is decene trimer, although the dimer, tetramer and pentamer are typically also present in the various base stock blends.

A number of catalytic processes are currently in use for the oligomerisation of alpha
25 olefins to produce materials for use as lubricant base stocks.

Ziegler-Natta catalysts are a class of catalysts that comprise titanium compounds in combination with an organoaluminium compound. Typically, Ziegler-Natta catalysts used commercially for the polymerisation of alpha-olefins comprise a titanium complex (such
30 as TiCl₄) together with an organoaluminium compound (such as triethylaluminium) on a magnesium chloride support.

Metallocene complexes (such as dicyclopentadienylzirconium dichloride, Cp₂ZrCl₂) have also been used as catalysts for the oligomerisation of alpha-olefins in combination with a
35 methylaluminoxane activator.

It is also known that Lewis acids such as BF_3 , AlCl_3 and EtAlCl_2 can be used as catalysts for cationic polymerisation of alpha-olefins in conjunction with an alkyl halide (for instance *tert*-butyl chloride), alcohol or Brønsted acid.

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US 7,572,944 discloses the use of ionic liquids as catalysts for the cationic polymerisation of alpha-olefins. Ionic liquids are a class of compounds that have been developed over the last few decades. The term "ionic liquid" as used herein refers to a liquid that can be obtained by melting a salt, and which is composed entirely of ions. The term "ionic liquid" by standard definition includes salts melting below 100 °C. Ionic liquids having melting points below around 30 °C are commonly referred to as "room temperature ionic liquids" and are often derived from organic salts having nitrogen-containing heterocyclic cations, such as imidazolium and pyridinium-based cations.

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The ionic liquid catalysts disclosed in US 7,572,944 comprise pyridinium or imidazolium cations together with acidic chloroaluminate anions, such as $[\text{Al}_2\text{Cl}_7]^-$. The use of ionic liquids as polymerisation catalysts is known to provide certain advantages over conventional catalysts. In particular, ionic liquids are generally immiscible with hydrocarbons and thus can be separated from polyalphaolefin products by phase separation and recycled. In contrast, conventional Lewis acid catalysts are generally quenched during the isolation of products.

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However, a disadvantage of known ionic liquid systems is that the organic cations are spectator ions which play no part in the catalytic reaction, other than to moderate the melting point of the ionic liquid reaction medium. In the case of, for instance, chloroaluminate ionic liquids, the cation also represents an expensive component of the ionic liquid. A further disadvantage of known ionic liquid systems, in common with other Lewis acid catalysts, is that the catalysts can be extremely active, particularly those ionic liquids comprising acidic chloroaluminate anions, such as $[\text{Al}_2\text{Cl}_7]^-$. High catalytic activity tends to result in the formation of undesired highly oligomerised products, thereby wasting resources. While the use of dopants to moderate the Lewis acidity of chloroaluminate ionic liquid systems has been investigated, these provide in general only modest improvements.

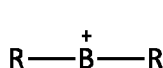
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Accordingly, there is a need in the art for new processes for the production of polyalphaolefin oligomers which overcome one or more of the disadvantages of the processes that are known in the art.

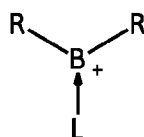
- 5 The present invention is based on the discovery that a certain class of Lewis acidic ionic liquids has been found to give unexpected selectivity when used as a catalyst for the production of polyalphaolefin oligomers. More specifically, the class of ionic liquids comprises a tricoordinate borenium(III) cation. This cation is a Lewis acidic species, and therefore not merely a spectator cation, as in known Lewis acid ionic liquid systems.

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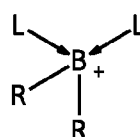
In general, boron(III) cations may be classified into three distinct structural classes based on the coordination number at boron. The three different classes, borinium (a), borenium (b) and boronium (c), are illustrated below:



(a) borinium(III)



(b) borenium(III)



(c) boronium(III)

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Neutral tricoordinate boron group species, such as BF_3 , have found use as Lewis acid catalysts in the past. Meanwhile, the corresponding tricoordinate borenium (b) cationic species illustrated above has been postulated to be an even stronger Lewis acid as a result of its increased electron deficiency (Angew. Chem. Int. Ed. 2005, 44, 5016 to 5036). Dicoordinate borinium (a) cations are speculated to be extremely strong Lewis acids, but are so reactive that they only exist transiently. Of the three classes of boron cationic species, tetracoordinate boronium (c) cations have received most attention historically, as they are inherently more stable as a result of a filled octet and a complete coordination sphere, but for the same reasons their Lewis acidity is compromised.

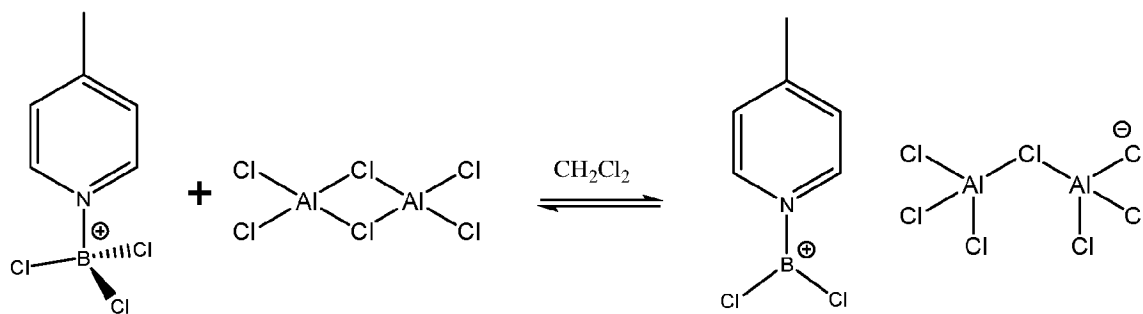
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De Vries *et al.*, Chem Rev. 2012 July 11; 112(7): 4246 to 4282, "Cationic Tricoordinate Boron Intermediates: Borenium Chemistry from the Organic Perspective" (hereinafter "De Vries *et al.*"), provides an overview of the reactivity of cationic, tricoordinated borenium ions, which are strongly Lewis acidic. As mentioned therein, the first observable borenium salt was reported by Ryschkewitsch *et al.*, J. Am. Chem. Soc., **92:6**, 1790-1791 (1970) and was formed when 2 equivalents of AlCl_3 were added to an

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adduct of BCl_3 and picoline in a solution of dichloromethane. In that case, the borenium cation is formed by chloride abstraction, as illustrated below.



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Notably, absent solvent, a 1:2 mixture of BCl_3 –picoline adduct and AlCl_3 was found to be a mobile liquid at room temperature, now understood to be an ionic liquid.

The observation by Ryschkewitsch *et al* set a precedent for the generation of other borenium species by B-X heterolysis in the presence of halophilic Lewis acids. Other examples of borenium cation containing salts have emerged as result. For instance, De Vries *et al* reports the formation of a borenium cation formed following chloride abstraction from an adduct of BCl_3 and 2,6-lutidine base, which was subsequently isolated in the form of the tetrachloroaluminate salt (Del Grosso A *et al.*, Chem Commun, 2011, **47**, 12459).

The present inventors have prepared ionic liquids comprising a borenium cation together with conventional anions, such as $[\text{AlCl}_4]^-$ or $[\text{NTf}_2]^-$, including Lewis acidic chloroaluminates, such as $[\text{Al}_2\text{Cl}_7]^-$, thereby forming a class of ionic liquids comprising two Lewis acidic centres, having overall Lewis acidities far exceeding those of conventional Lewis acidic ionic liquid systems. For instance, the Gutmann Acceptor Number (AN) value for Lewis acidity of the borenium cation alone is over 160, whilst the AN value for the chloroaluminate(III) anion is approximately 100.

In view of the level of Lewis acidity associated with the borenium ionic liquid systems described herein, it follows that catalytic activity is higher than with conventional Lewis acid ionic liquid catalyst systems, especially when there are two Lewis acidic centres present. However, in spite of such high catalytic activity, normally associated with the formation of undesired highly oligomerised products in oligomerisation reactions, it has been surprisingly found that the specific class of Lewis acidic ionic liquids described

herein leads to the formation of dimers, trimers, tetramers and pentamers in high proportion, and with little or no formation of undesired highly oligomerised products.

Thus, in a first aspect, the present invention provides a process for the preparation of
5 alpha-olefin oligomers, comprising contacting an olefinic feedstock comprising C₅ to C₂₀ alpha-olefins with an ionic liquid comprising:

- 10 (i) at least one borenium cation of the formula [BX₂L]⁺, wherein L is a Lewis basic donor ligand containing a donor atom selected from oxygen, sulphur, selenium, nitrogen, phosphorus, arsenic, and each X is independently selected from fluorine, chlorine and bromine; and
- (ii) at least one non-coordinating anion.

In preferred embodiments, each X is independently selected from fluorine and chlorine.
15 In more preferred embodiments, X is either fluorine or chlorine. In even more preferred embodiments, X is chlorine.

The Lewis basic donor ligand is preferably selected from small molecule donor ligands having a molecular weight of 500 or less, preferably a molecular weight of 400 or less,
20 more preferably a molecular weight of 300 or less, still more preferably a molecular weight of 200 or less, and most preferably a molecular weight of 100 or less.

In preferred embodiments, the Lewis basic donor ligand is selected from ligands containing a donor atom selected from oxygen, sulphur, selenium, nitrogen and phosphorus, more preferably from oxygen, nitrogen and phosphorus, still more
25 preferably from nitrogen and phosphorus. Most preferably, the Lewis basic donor ligand is selected from ligands containing a nitrogen donor atom.

In further preferred embodiments, the Lewis basic donor ligand is selected from the group of compounds consisting of ketones, sulfoxides, phosphine-oxides, ureas, esters, amides, ethers, thioketones, thioureas, thioamides, thioethers, amines, nitriles and
30 phosphines. More preferably, the Lewis basic donor ligand is selected from the group of compounds consisting of amines, amides and phosphines. Still more preferably, the Lewis basic donor ligand is selected from the group of compounds consisting of amines and amides. Most preferably, the Lewis basic donor ligand is an amine.

In other preferred embodiments, the Lewis basic donor ligand is selected from a heterocyclic group, which is an aromatic or non-aromatic cyclic, fused bi- or tri-cyclic, substituted or unsubstituted hydrocarbon group comprising one or more of O, N, NH and S in the ring. Examples of suitable Lewis basic donor ligands comprising a heterocyclic group include ethylene oxide, azetidiny, pyrrolidinyl, pyrrolyl, pyrazolyl, oxetanyl, pyrazolinyl, imidazolyl, imidazolinyl, imidazolidinyl, oxazolyl, oxazolidinyl, isoxazolinyl, isoxazolyl, thiazolyl, thiadiazolyl, thiazolidinyl, isothiazolyl, isothiazolidinyl, furyl, tetrahydrofuryl, thienyl, oxadiazolyl, piperidinyl, piperazinyl, azepinyl, pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl, triazinyl, triazolyl, tetrazolyl, tetrahydropyranyl, morpholinyl, thiamorpholinyl.

Preferred heterocyclic groups for use as the Lewis basic donor ligand in accordance with the present invention are selected from imidazolyl, pyridyl and pyrrolyl, more preferably selected from imidazolyl and pyridyl.

Heterocyclic group Lewis basic donor ligands for use in the present invention may be unsubstituted or substituted. Examples of suitable substituents include C_1 to C_{10} , preferably C_1 to C_6 , straight chain or branched alkyl, C_1 to C_6 alkoxy, C_2 to C_{12} alkoxyalkoxy, C_3 to C_8 cycloalkyl, C_3 to C_8 heterocyclic, C_6 to C_{10} aryl, C_7 to C_{10} alkaryl, C_7 to C_{10} aralkyl, -CN, -OH, -SH, -NO₂, -CO₂R^x, -OC(O)R^x, -C(O)R^x, -C(S)R^x, -CS₂R^x, -SC(S)R^x, -S(O)(C₁ to C₆)alkyl, -S(O)O(C₁ to C₆)alkyl, -OS(O)(C₁ to C₆)alkyl, -S(C₁ to C₆)alkyl, -S-S(C₁ to C₆)alkyl, -NR^xC(O)NR^yR^z, -NR^xC(O)OR^y, -OC(O)NR^yR^z, -NR^xC-(S)-OR^y, -OC(S)NR^yR^z, -NR^xC(S)SR^y, -SC(S)NR^yR^z, -NR^xC(S)NR^yR^z, -C(O)NR^yR^z, -C(S)NR^yR^z, or -NR^yR^z, wherein R^x, R^y and R^z are independently selected from hydrogen or C_1 to C_6 alkyl. Preferred substituents include C_1 to C_{10} , preferably C_1 to C_6 , straight chain or branched alkyl, C_1 to C_6 alkoxy, C_2 to C_8 alkoxyalkoxy, C_3 to C_8 cycloalkyl, -OH or -NR^yR^z, wherein R^y and R^z are independently selected from hydrogen or C_1 to C_6 straight chain or branched alkyl group.

Examples of suitable C_1 to C_{10} alkyl groups include methyl, ethyl, propyl, isopropyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, trifluoromethyl and pentafluoroethyl. Preferred alkyl groups include methyl, ethyl, propyl, isopropyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, and n-hexyl. More preferred alkyl groups include methyl, ethyl, propyl, and isopropyl. Most preferably, the alkyl group is methyl.

Examples of particularly preferred heterocyclic compounds for use as Lewis basic donor ligands in accordance with the present invention are selected from picoline, lutidine, pyridine, collidine, dimethylaminopyridine (DMAP), 1-alkylimidazole, for example 1-methylimidazole (mim).

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In other preferred embodiments, the Lewis basic donor ligand is selected from compounds having a formula selected from $R^1-C(O)-R^1$, $R^1-S(O)-R^1$, $R^2NH-C(O)-NHR^2$, $R^2NH-C(S)-NHR^2$, $R^1-C(O)-N(R^2)_2$, $R^1-C(O)-OR^1$, $(R^3)_3P$, $(R^3)_3P(O)$ and R^1-CN wherein:

each R^1 independently represents a C_1 to C_{10} straight chain or branched alkyl group, preferably a C_1 to C_6 alkyl group, more preferably a C_1 to C_3 alkyl group and most preferably a methyl group;

R^2 is selected from hydrogen or a C_1 to C_{10} straight chain or branched alkyl group, more preferably from hydrogen or a C_1 to C_6 alkyl group, still more preferably from hydrogen or a C_1 to C_3 alkyl group, and most preferably from hydrogen or a methyl group; and

R^3 represents a C_4 to C_{10} straight chain or branched alkyl group,

wherein any of R^1 , R^2 and R^3 may optionally be substituted by one or more fluorine atoms.

Examples of suitable C_1 to C_{10} alkyl groups include methyl, ethyl, propyl, isopropyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, trifluoromethyl and pentafluoroethyl. Preferred alkyl groups include methyl, ethyl, propyl, isopropyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, and n-hexyl. More preferred alkyl groups include methyl, ethyl, propyl, and isopropyl. Most preferably, the alkyl group is methyl.

In other preferred embodiments, the Lewis basic donor ligand is selected from compounds having a formula selected from $R^1-S(O)-R^1$, $R^2NH-C(O)-NHR^2$, $R^2NH-C(S)-NHR^2$, $R^1-C(O)-NR^2_2$, $(R^3)_3P$ and $(R^3)_3P(O)$; more preferably, the Lewis basic donor ligand is selected from compounds having a formula selected from $R^2NH-C(O)-NHR^2$ and $R^1-C(O)-N(R^2)_2$; and most preferably the Lewis basic donor ligand is a compound having the formula $R^2NH-C(O)-NHR^2$, wherein R^1 and R^2 are as defined above.

Examples of suitable Lewis basic donor ligands in accordance with the present invention include urea, *N,N'*-dimethylurea, *N,N'*-dimethylthiourea, acetamide, dimethylacetamide, acetone, ethyl acetate dimethylsulfoxide, trioctylphosphine oxide, and trioctylphosphine.

In some embodiments of the invention, the Lewis basic donor ligand may comprise a mixture of two or more Lewis basic donor ligands as described herein.

The term "non-coordinating anion" used herein, which is common in the field of olefin oligomerisation, is intended to mean an anion that does not coordinate with the metal cation, or does so only weakly. Typically, non-coordinating anions have their charge dispersed over several atoms in the molecule which significantly limits their coordinating capacity. Preferred non-coordinating anions are selected from a) halometallate anions of the formula $[MX_4]^-$ or $[M_2X_7]^-$, where M is Al or Ga, preferably Al, and X is independently Cl or Br, preferably Cl; b) bis(triflamide) $[(NTf_2)]^-$ or triflate $[(OTf)]^-$; c) bis(perfluoroalkylsulphonyl)imides (preferably methyl, ethyl, butyl and nonyl) d) tetrafluoroborate $[BF_4]^-$ or tetrachloroborate $[BCl_4]^-$; e) hexafluorophosphate $[PF_6]^-$; f) $[SnX_3]^-$ or $[Sn_2X_5]^-$, where X is independently Cl or Br g) dichlorocuprate $[CuCl_2]^-$; h) hexafluoroantimonate $[SbF_6]^-$; i) hexafluoroarsenate $[AsF_6]^-$; j) fluorosulphonate $[F-SO_2-O]^-$ and perfluoroalkyl sulphonates (preferably methyl); and k) chlorozincate(II) anions, such as $[ZnCl_4]^{2-}$ or $[Zn_2Cl_6]^{2-}$.

More preferred non-coordinating anions are selected from a) halometallate anions of the formula $[MX_4]^-$ or $[M_2X_7]^-$, where M is Al or Ga, preferably Al, and X is independently Cl or Br, preferably Cl; b) bis(triflamide) $[(NTf_2)]^-$; c) bis(perfluoroalkylsulphonyl)imides (preferably methyl, ethyl, butyl or nonyl); d) tetrafluoroborate $[BF_4]^-$; e) hexafluorophosphate $[PF_6]^-$; and f) $[SnX_3]^-$ or $[Sn_2X_5]^-$ where and X is independently Cl or Br.

Yet more preferred non-coordinating anions are selected from a) halometallate anions of the formula $[MX_4]^-$ or $[M_2X_7]^-$, where M is Al or Ga and X is independently Cl or Br.

Still more preferred non-coordinating anions are those selected from the preferred non-coordinating anions mentioned above which are also Lewis acidic, for example, $[M_2X_7]^-$, where M is Al or Ga, preferably Al, and X is independently Cl or Br, preferably Cl. Non-coordinating anions which are also Lewis acidic (as opposed to Lewis neutral) are particularly advantageous for use in the present invention, for example $[Al_2Cl_7]^-$,

$[\text{Ga}_2\text{Cl}_7]^-$, $[\text{Sn}_2\text{Cl}_5]^-$ or $[\text{Zn}_2\text{Cl}_6]^{2-}$. Most preferably, the non-coordinating anion is Lewis acidic anion $[\text{Al}_2\text{Cl}_7]^-$.

Particularly preferred ionic liquids for use in the present invention include

5 $[\text{BCl}_2(4\text{pic})][\text{Al}_2\text{Cl}_7]$, $[\text{BCl}_2(4\text{pic})][\text{AlCl}_4]$, $[\text{BCl}_2(4\text{pic})][\text{Ga}_2\text{Cl}_7]$, $[\text{BCl}_2(4\text{pic})][\text{GaCl}_4]$,
 $[\text{BCl}_2(\text{mim})][\text{Al}_2\text{Cl}_7]$, $[\text{BCl}_2(\text{mim})][\text{AlCl}_4]$, $[\text{BCl}_2(\text{mim})][\text{Ga}_2\text{Cl}_7]$, $[\text{BCl}_2(\text{mim})][\text{GaCl}_4]$,
 $[\text{BCl}_2(\text{P}_{888}\text{O})][\text{AlCl}_4]$, $[\text{BCl}_2(\text{P}_{888}\text{O})][\text{Al}_2\text{Cl}_7]$, $[\text{BCl}_2(\text{P}_{888}\text{O})][\text{GaCl}_4]$, $[\text{BCl}_2(\text{P}_{888}\text{O})][\text{Ga}_2\text{Cl}_7]$,
 $[\text{BCl}_2(\text{SUr})][\text{AlCl}_4]$, $[\text{BCl}_2(\text{SUr})][\text{Al}_2\text{Cl}_7]$, $[\text{BCl}_2(\text{SUr})][\text{GaCl}_4]$, $[\text{BCl}_2(\text{SUr})][\text{Ga}_2\text{Cl}_7]$,
10 $[\text{BCl}_2(\text{DMA})][\text{Al}_2\text{Cl}_7]$, $[\text{BCl}_2(\text{DMA})][\text{AlCl}_4]$, $[\text{BCl}_2(\text{DMA})][\text{Ga}_2\text{Cl}_7]$, and $[\text{BCl}_2(\text{DMA})][\text{GaCl}_4]$.

Most preferred ionic liquids for use in the present invention are those having a Lewis acidic, non-coordinating anion, for example: $[\text{BCl}_2(4\text{pic})][\text{Al}_2\text{Cl}_7]$, $[\text{BCl}_2(4\text{pic})][\text{Ga}_2\text{Cl}_7]$,
 $[\text{BCl}_2(\text{mim})][\text{Al}_2\text{Cl}_7]$, $[\text{BCl}_2(\text{mim})][\text{Ga}_2\text{Cl}_7]$, $[\text{BCl}_2(\text{P}_{888}\text{O})][\text{Al}_2\text{Cl}_7]$, $[\text{BCl}_2(\text{P}_{888}\text{O})][\text{Ga}_2\text{Cl}_7]$,
15 $[\text{BCl}_2(\text{SUr})][\text{Al}_2\text{Cl}_7]$, $[\text{BCl}_2(\text{SUr})][\text{Ga}_2\text{Cl}_7]$, $[\text{BCl}_2(\text{DMA})][\text{Al}_2\text{Cl}_7]$, and $[\text{BCl}_2(\text{DMA})][\text{Ga}_2\text{Cl}_7]$.

As will be appreciated by the person of skill in the art, where reference is made herein to the borenium ionic liquid comprising (i) at least one borenium cation of the formula $[\text{BX}_2\text{L}]^+$ and ii) at least one non-coordinating anion, this also covers the option of the ionic liquid consisting of only components (i) and (ii). Thus, in accordance with the

20 present invention, the borenium ionic liquid may consist solely of components (i) and (ii) defined hereinbefore. It will also be appreciated by the skilled person that the step of contacting the olefinic feedstock with the ionic liquid includes embodiments where the olefinic feedstock is contacted with the borenium ionic liquid described hereinbefore in the absence of a solvent and/or a carrier material.

The present inventors have surprisingly found that the use of borenium ionic liquids as defined above as catalysts for the oligomerisation of C_5 to C_{20} alpha-olefins provides an oligomerised product with a molecular weight distribution that is particularly suitable for use as a lubricant base stock, i.e. consisting predominantly of dimers, trimers, tetramers

30 and pentamers, and with only low levels of undesired highly oligomerised products, such nonamers and decamers. The ionic liquids are also immiscible with the oligomeric product and thus can readily be separated from the product by phase separation. Furthermore, the separated ionic liquids can be readily recycled to the oligomerisation reaction. A further advantage of the ionic liquid systems of the present invention is that

35 cheap, widely available Lewis donor ligands such as urea, thiourea, acetamide and

dimethylsulfoxide may be used to prepare the borenium ionic liquids. This is in contrast to conventional ionic liquids systems used in oligomerisation, such as chloroaluminates(III), where the halide salt of the spectator cation has to be typically prepared in an expensive quaternisation step.

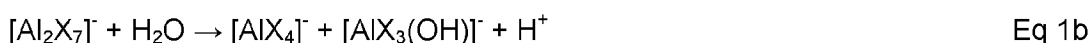
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Many mechanisms have been suggested for the catalysis of oligomerisation reactions. One suggested mechanism for oligomerisation of olefins is a carbocationic mechanism. According to that route, catalysis proceeds following the formation of acidic protons, formed by the presence of protic promoter (*e.g.* alcohol) or water (residual traces of moisture in the reaction system being sufficient). Thus, in some embodiments of the present invention, the oligomerisation reaction is performed in the presence of trace amounts of moisture (for example, between 50 and 500 ppm, preferably 50 to 150 ppm of water).

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15 In the borenium ionic liquids described herein, protons may be generated as illustrated in Equation 1 below. The acidity of these protons depends on the strongest base in the system, which in this case will be the anions of the ionic liquids. Consequently, the weaker the basicity of the anion, the weaker will be its association with the proton, hence the stronger will be the acidity of the protons.

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Generation of the carbocation according to the carbocation mechanism for oligomerisation involves attack of the acidic proton on the olefin. The reaction rate of this step depends on the acidity of the proton. The more acidic the system, the more exothermic the reaction and the more rapid is the generation of the carbocation. The ionic liquids described herein are strongly Lewis acidic and are thus able to generate very potent superacids, even protonating substrates that would normally be difficult to protonate.

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In some embodiments of the invention, the ionic liquid catalyst is used in the presence of a Brønsted acid. A Brønsted acid may act as a source of an acidic proton in addition to or in place of residual traces of moisture. The superior Lewis acid strength of the ionic liquids described herein is believed to lead to the formation of superacidic protons upon

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reaction with a Brønsted acid, which may further enhance the catalytic activity of the ionic liquids described herein. Suitable Brønsted acids include, for example, H_2SO_4 , HF, HCl, HBr, HI and H_3PO_4 . Other protic promoters, such as alcohols, may also be used in place of, or in combination with, Brønsted acids.

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After generation of the carbocation, which is rapid in the case of the ionic liquids described herein, charge migration along the chain and/or skeletal isomerisation may occur, eventually leading to attack of another olefin unit to form a dimer. Subsequent reactions involve further chain propagations and isomerisations, which compete with termination processes.

10

Surprisingly, despite the increased catalytic activity of the ionic liquids described herein in comparison to conventional chloroaluminate Lewis acidic ionic liquids, there is an increased selectivity for the formation of dimers, trimers, tetramers and pentamers, rather than undesired highly oligomerised products associated with the ionic liquids described herein. Without being bound by any particular theory, it is thought that the Lewis acidic borenium cation of the ionic liquids described herein affects ionic interactions with the propagating carbocation formed during the oligomerisation reaction, in a manner different to that of the cation of known chloroaluminate Lewis acid ionic liquid systems. Thus, the ionic liquid described herein, unexpectedly benefits from both high catalytic activity, and high selectivity for lower oligomers, which are particularly suitable for use in the manufacture of lubricating base oils.

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Moreover, it has also been found that the presence of the borenium cation as described herein mitigates against the lack of selectivity in oligomerisation reactions which is exhibited in the case of conventional Lewis acidic anions, such as $[\text{Al}_2\text{Cl}_7]^-$. Absent the borenium cation, use of an ionic liquid comprising Lewis acidic $[\text{Al}_2\text{Cl}_7]^-$ in combination with a spectator cation results in the formation of a significant proportion of undesirable highly oligomerised products. However, when a borenium cation as described herein is substituted for the spectator cation, catalytic activity is not only increased but also selectivity. Thus, the presence of the borenium cation also blocks any lack of selectivity which results from the presence of the Lewis acidic $[\text{Al}_2\text{Cl}_7]^-$ anion, whilst the benefit of increased catalytic activity resulting from the presence of two Lewis acidic centres is realised.

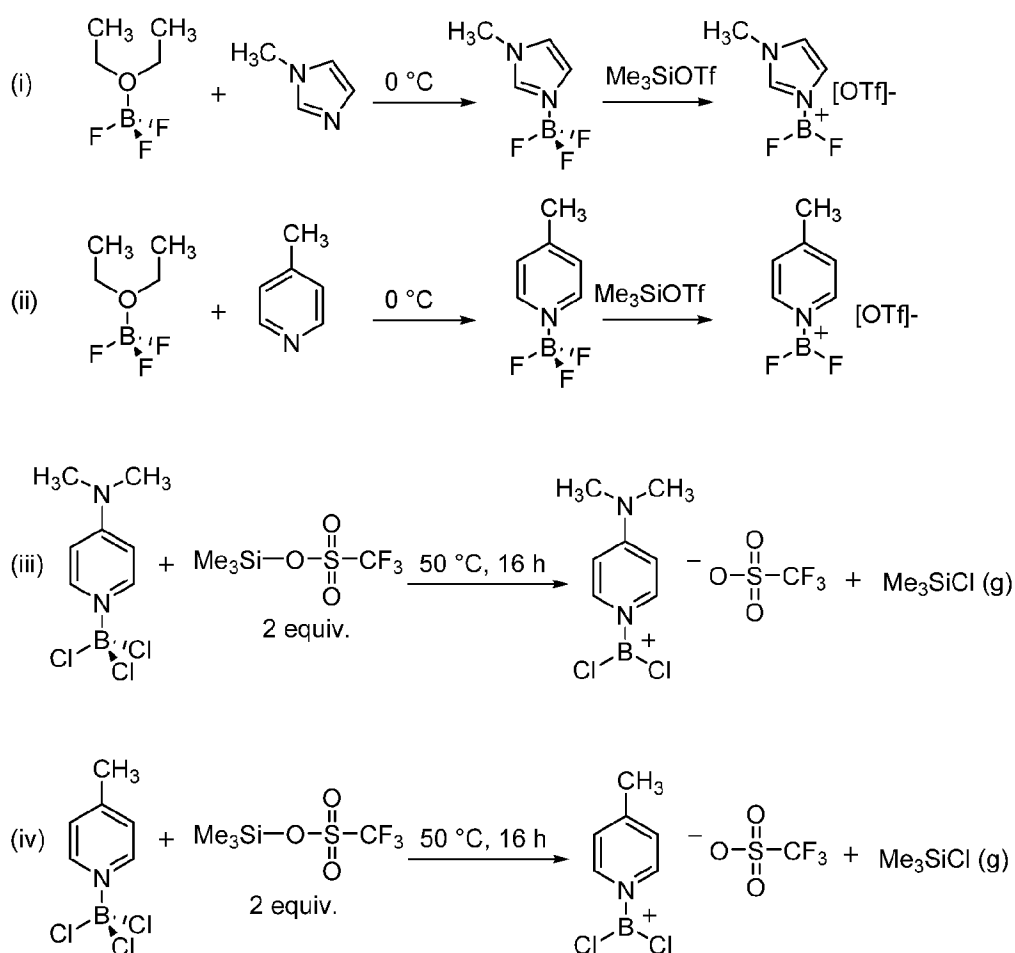
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The borenium ionic liquids used in the present invention may be prepared by methods known to the skilled person, and which are described in Ryschkewitsch *et al.*, J. Am. Chem. Soc., **92:6**, 1790-1791 (1970). Thus, a suitable method for preparing borenium ionic liquids comprises B-X bond heterolysis, as illustrated below in example reactions (i)

5 to (iv):



A notable advantage in the preparation of the borenium ionic liquid catalysts used in the process of the present invention is that they may be made by recycling a boron based compound which may have previously been used as a catalyst, such as a Lewis acid catalyst. For example, a boron trihalide, which has wide catalytic applications, may be converted into a borenium ionic liquid as illustrated above and in the Examples hereinbelow. This may make preparation of a borenium ionic liquid even more economical. For instance, existing systems utilising boron trihalides for catalysing oligomerisation reactions can be readily adapted so that the boron trihalide catalyst may be converted into a borenium ionic liquid oligomerisation catalyst as described herein.

Thus, in a preferred embodiment, the borenium ionic liquid used in the process of the invention is prepared from the recycle of a boron trihalide which has previously been used as a catalyst. Furthermore, by selecting a Lewis donor ligand from cheap, widely available donor ligands such as urea, thiourea, acetamide and dimethylsulfoxide,
5 preparation of the borenium ionic liquid catalyst may be prepared at even lower cost.

As used herein, the term "olefinic feedstock comprising C₅ to C₂₀ alpha-olefins" preferably refers to a hydrocarbonaceous feedstock that comprises at least one C₅ to C₂₀ alpha-olefin hydrocarbon. Preferably, the olefinic feedstock comprises at least 50
10 wt% of one or more C₅ to C₂₀ alpha-olefins, more preferably at least 60 wt% of one or more C₅ to C₂₀ alpha-olefins, more preferably at least 70 wt% of one or more C₅ to C₂₀ alpha-olefins, more preferably at least 80 wt% of one or more C₅ to C₂₀ alpha-olefins, more preferably at least 90 wt% of one or more C₅ to C₂₀ alpha-olefins, and most preferably at least 95 wt% of one or more C₅ to C₂₀ alpha-olefins. In some embodiments,
15 the olefinic feedstock may comprise at least 98 wt% of one or more C₅ to C₂₀ alpha-olefins, or at least 99 wt% of one or more C₅ to C₂₀ alpha-olefins. The remainder of the olefinic feedstock may suitably be composed of other olefins, paraffins, or a mixture thereof.

20 In preferred embodiments, the olefinic feedstock comprises at least 50 wt% C₆ to C₁₈ alpha-olefins, more preferably at least 60 wt% C₆ to C₁₈ alpha-olefins, more preferably at least 70 wt% C₆ to C₁₈ alpha-olefins, still more preferably at least 80 wt% C₆ to C₁₈ alphaolefins, and most preferably at least 90 wt% C₆ to C₁₈ alpha-olefins. For example, the olefinic feedstock 5 may comprise at least 95 wt% C₆ to C₁₈ alpha-olefins, at least 98
25 wt% C₆ to C₁₈ alpha-olefins or at least 99 wt% C₆ to C₁₈ alpha-olefins.

In some embodiments, the olefinic feedstock comprises at least 30 wt% C₈ to C₁₄ alphaolefins, more preferably at least 50 wt% C₈ to C₁₄ alpha-olefins, more preferably at least 70 wt% C₈ to C₁₄ alpha-olefins, still more preferably at least 80 wt% C₈ to C₁₄ alpha
30 olefins, and most preferably at least 90 wt% C₈ to C₁₄ alpha-olefins. For example, the olefinic feedstock may comprise at least 95 wt% C₈ to C₁₄ alpha-olefins, at least 98 wt% C₈ to C₁₄ alpha-olefins or at least 99 wt% C₈ to C₁₄ alpha-olefins.

In some embodiments, the olefinic feedstock comprises at least 30 wt% C₁₀ to C₁₄
35 alphaolefins, more preferably at least 50 wt% C₁₀ to C₁₄ alpha-olefins, more preferably at

least 70 wt% C₁₀ to C₁₄ alpha-olefins, still more preferably at least 80 wt% C₈ to C₁₄ alpha olefins, and most preferably at least 90 wt% C₁₀ to C₁₄ alpha-olefins. For example, the olefinic feedstock may comprise at least 95 wt% C₁₀ to C₁₄ alpha-olefins, at least 98 wt% C₁₀ to C₁₄ alpha-olefins or at least 99 wt% C₁₀ to C₁₄ alpha-olefins.

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In more preferred embodiments, the olefinic feedstock comprises at least 30 wt% C₁₀ to C₁₂ alpha-olefins, more preferably at least 50 wt% C₁₀ to C₁₂ alpha-olefins, more preferably at least 70 wt% C₁₀ to C₁₂ alpha-olefins, still more preferably at least 80 wt% C₁₀ to C₁₂ alpha-olefins, and most preferably at least 90 wt% C₁₀ to C₁₂ alpha-olefins.

10 For example, the olefinic feedstock may comprise at least 95 wt% C₁₀ to C₁₂ alphaolefins, at least 98 wt% C₁₀ to C₁₂ alpha-olefins or at least 99 wt% C₁₀ to C₁₂ alphaolefins.

In some embodiments, the olefinic feedstock preferably comprises at least 30 wt% 1-decene, more preferably at least 50 wt% 1-decene, more preferably at least 70 wt% 1-decene, still more preferably at least 80 wt% 1-decene, and most preferably at least 90 wt% 1-decene. For example, the olefinic feedstock may comprise at least 95 wt% 1-decene, at least 98 wt% 1-decene or at least 99 wt% 1-decene.

20 In other embodiments, the olefinic feedstock preferably comprises at least 30 wt% 1-dodecene, more preferably at least 50 wt% 1-dodecene, more preferably at least 70 wt% 1-dodecene, still more preferably at least 80 wt% 1-dodecene and most preferably at least 90 wt% 1-dodecene. For example, the olefinic feedstock may comprise at least 95 wt% 1-dodecene, at least 98 wt% 1-dodecene or at least 99 wt% 1-dodecene.

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In further embodiments, the olefinic feedstock may comprise at least 30 wt% C₁₆ to C₁₈ alpha-olefins, more preferably at least 50 wt% C₁₆ to C₁₈ alpha-olefins, more preferably at least 70 wt% C₁₆ to C₁₈ alpha-olefins, still more preferably at least 80 wt% C₁₆ to C₁₈ alpha-olefins, and most preferably at least 90 wt% C₁₆ to C₁₈ alpha-olefins. For example,

30 the olefinic feedstock may comprise at least 95 wt% C₁₆ to C₁₈ alpha-olefins, at least 98 wt% C₁₆ to C₁₈ alpha-olefins or at least 99 wt% C₁₆ to C₁₈ alpha-olefins.

In some embodiments, the olefinic feedstock preferably comprises at least 30 wt% 1-hexadecene, more preferably at least 50 wt% 1-hexadecene, more preferably at least 70 wt% 1-hexadecene, still more preferably at least 80 wt% 1-hexadecene, and most

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preferably at least 90 wt% 1-hexadecene. For example, the olefinic feedstock may comprise at least 95 wt% 1-hexadecene, at least 98 wt% 1-hexadecene or at least 99 wt% 1-hexadecene.

- 5 In other embodiments, the olefinic feedstock preferably comprises at least 30 wt% 1-octadecene, more preferably at least 50 wt% 1-octadecene, more preferably at least 70 wt% 1-octadecene, still more preferably at least 80 wt% 1-octadecene and most preferably at least 90 wt% 1-octadecene. For example, the olefinic feedstock may comprise at least 95 wt% 1-octadecene, at least 98 wt% 1-octadecene or at least 99 wt% 1-octadecene.

In some embodiments of the invention, the olefinic feedstock may also comprise paraffins. In general, the olefinic feedstock comprises a minor amount of paraffins. For instance, the olefinic feedstock may optionally comprise up to 20 wt% paraffins, for instance up to 10 wt% paraffins, or up to 5 wt% paraffins. However, it will be appreciated that olefinic feedstocks comprising larger amounts of paraffins are also suitable as feedstocks for the present invention. For instance, olefinic feedstocks comprising up to 60 wt%, 70 wt%, 80 wt% or 90 wt% paraffins are found to be suitable feedstocks for the process of the present invention. The presence of a minor amount of paraffins in the olefinic feedstock is observed to suppress the formation of undesired heavy oligomers. Suitable paraffins include C₅ to C₂₀ paraffins, such as C₁₀ to C₁₂ paraffins.

The olefinic feedstock may suitably be contacted with the borenium ionic liquid catalyst at a temperature of from 0 °C up to the boiling point of the alpha-olefins at the reaction pressure. Preferably, the olefinic feedstock is contacted with the ionic liquid at a temperature of from 0 to 160 °C, more preferably 40 to 140 °C, more preferably 80 to 140 °C, still more preferably 100 to 140 °C, and most preferably about 120 °C. The formation of oligomers in accordance with the present invention is exothermic, and thus cooling system may be used so as to maintain the desired reaction temperature.

The olefinic feedstock may suitably be contacted with the borenium ionic liquid catalyst at a pressure of from 10 to 1000 kPa, preferably from 20 to 500 kPa, more preferably from 50 to 200 kPa, for instance from 80 to 120 kPa. Preferably, the olefinic feedstock is contacted with the ionic liquid at ambient pressure, i.e. around 100 kPa.

The olefinic feedstock may suitably be contacted with the borenium ionic liquid catalyst for a 10 period of from 1 minute to 10 hours, for example from 10 minutes to 1 hour.

5 The reaction is preferably carried out under an inert atmosphere and substantially in the absence of moisture, defined as less than 500 ppm by weight water based on the total weight of ionic liquid and olefinic feedstock.

The process of the present invention may suitably be carried out by contacting the olefinic feedstock with at least 0.01 wt% of the ionic liquid catalyst, more preferably at
10 least 0.05 wt% of the borenium ionic liquid catalyst, still more preferably at least 0.1 wt% of the borenium ionic liquid catalyst, and most preferably at least 0.2 wt% of the borenium ionic liquid catalyst, based on the total weight of the borenium ionic liquid catalyst and olefinic feedstock. For example, the olefinic feedstock may suitably be contacted with from 0.01 to 5 wt% of 20 the borenium ionic liquid catalyst, preferably from 0.05 to 2 wt% of the borenium ionic liquid catalyst, still more preferably from 0.1 to 1 wt% of the borenium ionic liquid catalyst, and still more preferably from 0.2 to 0.8 wt% of the borenium ionic liquid catalyst, based on the total weight of the borenium ionic liquid catalyst and olefinic feedstock. Most preferably, the olefinic feedstock is contacted with about 0.5 wt% of the borenium ionic liquid catalyst, based on the total weight of the
20 borenium ionic liquid catalyst and olefinic feedstock.

It has been found that the oligomerised product distribution is not dependent on the catalyst loading to any significant degree. However, higher catalyst loadings generally reduce the reaction time and improve conversion of starting materials. Due to the
25 exothermic nature of the reaction, the use of higher catalyst loadings may in some cases necessitate additional measures to maintain the desired reaction temperature.

The oligomer product obtained by the present invention may be separated from the ionic liquid catalyst by any suitable means, for instance by gravity separation and decantation
30 or by centrifugation. In this way, the ionic liquid catalyst may also be recycled. Alternatively, the reaction may be quenched by the addition of water, optionally containing a mild base, and the organic and aqueous phases may be separated, for instance by gravity separation and decantation or by centrifugation. Quenching the reaction in this way may be preferred where recycling of the ionic liquid catalyst is not
35 practical or economical.

The oligomerised product obtained by the process of the present invention typically contains minor amounts of highly oligomerised products (defined herein as hexamers and higher oligomers) as well as unreacted starting material. In some embodiments, the process of the invention may further comprise distillation of the oligomerised product to separate starting material and/or highly oligomerised products from the desired lower oligomers (defined herein as dimers, trimers, tetramers and pentamers).

The catalytic oligomerisation of alpha-olefins generally provides oligomerised products that contain one remaining double bond. The presence of double bonds generally reduces the oxidative stability of a lubricating oil base stock. Thus, in some embodiments, the process of the present invention further comprises a step in which the remaining olefinic double bonds in the oligomerised product are reduced to carbon-carbon single bonds so as to improve the oxidation stability of the product. Suitably, the reduction of olefinic double bonds may be carried out by hydrogenation in the presence of a suitable hydrogenation catalyst, for instance a Group VIII metal such as platinum, palladium, nickel, rhodium or iridium on a solid support. In other embodiments, the process may further comprise a step in which the remaining olefinic double bonds in the oligomerised product are alkylated.

In preferred embodiments, the process of the present invention is selective for the preparation of dimers, trimers and tetramers. In further preferred embodiments, the process of the present invention is selective for the preparation of dimers and trimers.

As noted above, the formation of higher oligomers may be further suppressed, if required, by the inclusion of paraffins in the olefinic feedstock.

The oligomerised products produced according to the process of the present invention have a range of desirable properties.

In some embodiments, the oligomerised products produced according to the process of the present invention have a Kv40 of from 5 to 60 cSt, preferably from 10 to 40 cSt.

In some embodiments, the oligomerised products produced according to the process of the present invention have a Kv100 of from 1 to 15 cSt, preferably from 1.5 to 10 cSt,

5 more preferably from 1.5 to 8.5 cSt (such as 2, 4, 5, 6, 7 or 8), still more preferably from 3.5 to 8.5 cSt (such as 4, 5, 6, 7 or 8), and most preferably from 3.5 to 6.5 cSt (such as 4, 5 or 6).

- 5 In some embodiments, the oligomerised products produced according to the process of the present invention have a pour point of -40°C or less, preferably of -60°C or less (in accordance with ASTM D97-11).

- 10 In some embodiments, the oligomerised products produced according to the process of the present invention have a viscosity index (VI) of 100 or greater, more preferably from 120 to 160 (according to ASTM D2270).

- 15 It is believed that the borenium ionic liquids described hereinbefore will also exhibit selectivity in other reactions comprising a carbocation mechanism, including Friedel-Crafts alkylation and alkane isomerisation reactions. Thus, in another aspect, the present invention provides a use of the borenium ionic liquids described hereinbefore as a selective Lewis acid catalyst in Friedel-Crafts alkylation and alkane isomerisation reactions.

- 20 The present invention will now be illustrated by way of the following examples and with reference to the following figures:

FIGURE 1 shows the SimDist GC chromatograph for the products of oligomerisation of 1-decene in the presence of $[\text{BCl}_2(4\text{pic})][\text{Al}_2\text{Cl}_7]$;

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FIGURE 2 shows the SimDist analysis of the product distribution obtained by oligomerising 1-decene in the presence of $[\text{C}_2\text{mim}][\text{Al}_2\text{Cl}_7]$ (not of the invention) and $[\text{BCl}_2(4\text{pic})][\text{Al}_2\text{Cl}_7]$ (according to the invention);

- 30 FIGURE 3 shows the SimDist GC chromatograph for the products of oligomerisation of 1-hexadecene in the presence of $[\text{BCl}_2(4\text{pic})][\text{Al}_2\text{Cl}_7]$; and

FIGURE 4 shows the SimDist analysis of the product distribution obtained by oligomerising 1-hexadecene in the presence of $[\text{BCl}_2(4\text{pic})][\text{Al}_2\text{Cl}_7]$ and $[\text{BCl}_2(4\text{pic})][\text{Al}_2\text{Cl}_7]\cdot\text{HCl}$.

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Examples

Unless otherwise mentioned, all chemicals were purchased from Sigma-Aldrich. 1-Hexadecene was purchased from TCI. All starting materials used were dried (for at least 24 hours prior to use) over 3 Å molecular sieves. All glassware, stirring bars, syringes *etc.* were oven-dried (*ca.* 140 °C, for at least 24 hours prior to use).

Preparation of Ionic Liquids

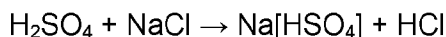
- 10 All borenium (b) ionic liquids were prepared following a similar method to that described Ryschkewitsch *et al.*, J. Am. Chem. Soc., **92:6**, 1790-1791 (1970), involving B-X bond heterolysis reactions.

15 In a typical experiment, a boron halide solution was transferred into a dry Schlenk flask, under argon. The solution was cooled to -78 °C and subsequently a dry base (or its solution in dichloromethane) was added dropwise to the vigorously stirred solution. Subsequently, the solvent was removed under reduced pressure and the [BX₃(base)] complex was purified by recrystallization. Two equivalents of AlCl₃ were added in small portions to dry [BX₃(base)] complex, to form [BX₂(base)][Al₂Cl₇] ionic liquid in an exothermic reaction. As an example of an alternative, alkyl triflate was added slowly using a dry gas-tight syringe or a dry pressure-equalising dropping funnel to a vigorously stirred solution of the [BX₃(base)] complex in dichloromethane under argon, at 0 °C. Alkyl chloride gas was evolved before the removal of solvent under reduced pressure, affording the dry ionic liquid.

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Saturation of ionic liquids with HCl

30 In a typical experiment, the apparatus for HCl generation comprised of a dropping funnel containing sulfuric acid, mounted on top of a two-necked round-bottomed flask containing sodium chloride. Drop-wise addition of the acid to the salt resulted in generation of HCl, following the reaction:



- 35 The second neck of the two-necked flask was connected (*via* bubbler with H₂SO₄) to a

dry Schlenk flask, containing vigorously stirred borenium ionic liquid (e.g. $[\text{BCl}_2(4\text{pic})][\text{Al}_2\text{Cl}_7]$). Excess of HCl gas was captured in a bubbler filled with a basic solution, placed after the Schlenk flask with the ionic liquid. The ionic liquid was stirred under flow of HCl gas for 30 min. The resulting liquid was more viscous than the starting ionic liquid, the mass balance indicated absorption of nearly equimolar amount of HCl.

Experimental procedure for oligomerisation reactions

In a typical experiment, olefin (40 cm^3) was placed in a dry, glass reactor (AutoMATE H.E.L. Reactor system), equipped with an overhead stirrer (Hastelloy®), a thermocouple, a heating coil, a cooling mantle, argon inlet and a septum inlet. The reactor was purged with argon, and maintained under positive pressure of argon throughout the experiment. The olefin was stirred vigorously (1000 rpm) and equilibrated at the temperature of reaction ($120\text{ }^\circ\text{C}$).

Ionic liquid (1.0 wt %) was added drop-wise to the vigorously stirred olefin, via a gas-tight syringe through the septum of the reactor, which resulted in a strong exotherm. After the addition, the mixture was allowed to react (30 min, $120\text{ }^\circ\text{C}$). Afterwards, stirring and heating was stopped, and the reaction was quenched with deionised water. A sample from the top (hydrocarbon) layer was dissolved in toluene, dried over magnesium sulfate, and analysed using gas chromatography (SimDist).

Example 1

Oligomerisation of 1-decene

Oligomerisation of 1-decene was carried out according to the general procedure described above. Catalysis was conducted with conventional chloroaluminate ionic liquids, $[\text{C}_2\text{mim}][\text{Al}_2\text{Cl}_7]$, $[\text{C}_8\text{mim}][\text{Al}_2\text{Cl}_7]$ and $[\text{P}_{66614}][\text{Al}_2\text{Cl}_7]$ (Entries 1, 2 and 3 in Table 1 below), as well as various borenium ionic liquids in accordance with the present invention (Entries 3 to 13 in Table 1 below). Borenium ionic liquids tested either contained one Lewis acidic centre (the borenium cation) (Entries 4 and 11) or two Lewis acidic centres (the second centre associated with the anion) (Entries 5 to 10, 13 and 13). Results of the oligomerisation reactions are provided in Table 1 below.

Table 1 - Product distribution for oligomerisation of 1-decene

Entry	IL	Feed	Product Appearance	Product distribution
1	[C ₂ mim][Al ₂ Cl ₇]	C10	Yellow oil	C10 - C20 - C30 3.0% C40 4.0% C50 8.0% C60 10.0% C70+ 75.0%
2	[C ₈ mim][Al ₂ Cl ₇]	C10	Yellow oil	C10 20.3% C20 16.0% C30 14.0% C40 13.0% C50 13.0% C60+ 23.7%
3	[P ₆₆₆₁₄][Al ₂ Cl ₇]	C10	Yellow oil	C10 9.3% C20 23.0% C30 17.0% C40 15.0% C50 15.0% C60+ 20.7%
4	[BCl ₂ (4pic)][AlCl ₄]	C10	Yellow oil	C10 38.3% C20 37.0% C30 19.0% C40 4.00% C50 1.7%
5	[BCl ₂ (4pic)][Al ₂ Cl ₇]	C10	Yellow oil	C10 13.3% C20 31.0% C30 28.0% C40 14.0% C50 7.0% C60 3.0% C70+ 3.7%
6	[BCl ₂ (DMA)][Al ₂ Cl ₇]	C10	Yellow oil	C10 27.3% C20 24.0% C30 21.0% C40 10.0% C50 6.0% C60 5.0% C70 3.0% C80+ 3.7%
7	[BCl ₂ (mim)][Al ₂ Cl ₇]	C10	Pale yellow oil	C10 19.3% C20 35.0% C30 29.0% C40 10.0% C50 3.0% C60 1.0% C70 1.7% C80+ 1.7%
8	[BCl ₂ (SUr)][Al ₂ Cl ₇]	C10	Yellow oil	C10 14.3%

				C20 26.0% C30 27.0% C40 15.0% C50 7.0% C60 4.0% C70 3.0% C80+ 3.7%
9	[BCl ₂ (P ₈₈₈)] [Al ₂ Cl ₇]	C10	Yellow oil	C10 29.3% C20 32.0% C30 24.0% C40 9.0% C50 4.0% C60+ 1.7%
10	[BCl ₂ (P ₈₈₈ O)] [Al ₂ Cl ₇]	C10	Yellow oil	C10 25.3% C20 38.0% C30 23.0% C40 9.0% C50+ 4.7%
11	[BCl ₂ (P ₈₈₈)] [AlCl ₄]	C10	Yellow oil	C10 50.3% C20 23.0% C30 17.0% C40 8.0% C50+ 1.7%
12	[BCl ₂ (mim)] [Ga ₂ Cl ₇]	C10	Pale-yellow oil	C10 24.3% C20 36.0% C30 27.0% C40 9.0% C50 3.7%
13	[BCl ₂ (P ₈₈₈ O)] [Ga ₂ Cl ₇]	C10	Yellow oil	C10 72.3% C20 20.0% C30 5.0% C40+ 2.7%

As illustrated in the results of Table 1 above, in the absence of the borenium cation (Entries 1, 2 and 3), the amount of highly oligomerised products (hexamers and higher oligomers) is significant. Hexamers and higher oligomers for Entries 1, 2 and 3 amount to 85%, 23.7% and 20.7% of the oligomerisation products respectively, which far exceeds the amount of (hexamers and higher oligomers) produced as a result of catalysis with ionic liquids comprising a borenium cation.

For example, replacing [C₂mim] of [C₂mim][Al₂Cl₇] (Entry 1) with [BCl₂(4pic)] (Entry 5) reduces the level of highly oligomerised products dramatically. Hexamers and higher oligomers for Entry 5 amount to only 6.7% of the oligomerisation products, compared with 85% for Entry 1. A SimDist GC chromatograph for the products of oligomerisation of 1-decene in the presence of [BCl₂(4pic)][Al₂Cl₇] (Entry 5) are shown in Figure 1. A

comparison of the product distributions for the oligomerisation of 1-decene in the presence of $[\text{BCl}_2(4\text{pic})][\text{Al}_2\text{Cl}_7]$ (Entry 5) and $[\text{C}_2\text{mim}][\text{Al}_2\text{Cl}_7]$ (Entry 1) is provided in Figure 2 in the form of overlaid SimDist curves (simulated distillation curves derived from SimDist GC chromatogram).

5

The results in Table 1 also demonstrate that ionic liquids comprising a single Lewis acidic centre in the form of the borenium ion (Entries 3 and 10) also result in good selectivity, with little formation of highly oligomerised products (1.7% in each case). Where two Lewis acidic centres are present (one in the cation and one in the anion), catalytic activity is increased. For example, replacing neutral anion $[\text{AlCl}_4]$ of $[\text{BCl}_2(4\text{pic})][\text{AlCl}_4]$ (Entry 3) with Lewis acidic anion $[\text{Al}_2\text{Cl}_7]$ (Entry 4) reduces the level of C10 starting materials, from 38.3% to 13.3%, indicating increased catalytic activity, without loss of selectivity.

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The borenium cation is thus an active Lewis acidic species which confers favourable selectivity in an oligomerisation reaction, whilst also mitigating against a lack of selectivity associated with the Lewis acidic anion, when present. This is especially advantageous since it means that a catalytic system comprising two Lewis acidic centres having particularly high activity can be used whilst retaining favourable selectivity, which has not previously been realised.

20

Example 2

Oligomerisation of 1-Hexadecene

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Oligomerisation of 1-hexadecene was carried out according to the general procedure described above. Catalysis was conducted with borenium ionic liquids in accordance with the present invention, $[\text{BCl}_2(4\text{pic})][\text{Al}_2\text{Cl}_7]$ (Entry 14) and $[\text{BCl}_2(4\text{pic})][\text{Al}_2\text{Cl}_7]\cdot\text{HCl}$ (Entry 15). $[\text{BCl}_2(4\text{pic})][\text{Al}_2\text{Cl}_7]\cdot\text{HCl}$ was prepared in accordance with the procedure described above. Results of the oligomerisation reactions are provided in Table 2 below.

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Table 2 - Product distribution for oligomerisation of 1-hexadecene

Entry	IL	Feed	Product Appearance	Product distribution
14	$[\text{BCl}_2(4\text{pic})][\text{Al}_2\text{Cl}_7]$	C16	Pale yellow oil	C16 25.3%

				C32	35.0%
				C48	23.0%
				C64	16.7%
15	$[\text{BCl}_2(4\text{pic})][\text{Al}_2\text{Cl}_7]\cdot\text{HCl}$	C16	Pale orange oil	C16	20.2%
				C32	35.0%
				C48	25.0%
				C64	19.7%

The results in Table 2 demonstrate the selectivity of borenium ionic liquids for the formation of dimers (C32), trimers (C48) and tetramers (C64) over highly oligomerised products in the oligomerisation of 1-hexadecene. A SimDist GC chromatograph for the products of oligomerisation of 1-hexadecene in the presence of $[\text{BCl}_2(4\text{pic})][\text{Al}_2\text{Cl}_7]$ (Entry 14) are shown in Figure 3.

Furthermore, the results in Table 2 demonstrate the effect of the presence of a Brønsted acid (HCl), which increases catalytic activity, as shown by the decrease in C16 starting material from 25.3% for Entry 14 to 20.2% for Entry 15. The effect of the presence of a Brønsted acid is illustrated in Figure 4 which provides a comparison of the product distributions for the oligomerisation of 1-hexadecene in the presence of $[\text{BCl}_2(4\text{pic})][\text{Al}_2\text{Cl}_7]$ (Entry 14) and $[\text{BCl}_2(4\text{pic})][\text{Al}_2\text{Cl}_7]\cdot\text{HCl}$ (Entry 15) in the form of overlaid SimDist curves (simulated distillation curves derived from SimDist GC chromatogram).

Example 3

Oligomerisation of a mixture of 1-Hexadecene and 1-Octadecene

Oligomerisation of a 1:1 weight ratio mixture of 1-hexadecene/1-octadecene was carried out according to the general procedure described above. Catalysis was conducted with borenium ionic liquids in accordance with the present invention, $[\text{BCl}_2(\text{P}_{888}\text{O})][\text{Al}_2\text{Cl}_7]$ (Entry 16) and $[\text{BCl}_2(\text{P}_{888})][\text{Al}_2\text{Cl}_7]$ (Entry 17). Results of the oligomerisation reactions are provided in Table 3 below.

Table 3 - Product distribution for oligomerisation of 1-hexadecene/1-octadecene mixture

Entry	IL	Feed	Product Appearance	Product distribution
16	$[\text{BCl}_2(\text{P}_{888}\text{O})][\text{Al}_2\text{Cl}_7]$	C18+16	Yellow oil	C34 34.3% C68 35.0% C102 23.0% C136 7.7%
17	$[\text{BCl}_2(\text{P}_{888})][\text{Al}_2\text{Cl}_7]$	C18+16	Yellow oil	C34 25.3% C68 36.0% C102 28.0% C136 10.7%

- 5 The results in Table 3 demonstrate the selectivity of further borenium ionic liquids for the formation of dimers (C68), trimers (C102) and tetramers (C136) over highly oligomerised products in the oligomerisation of a blend of 1-hexadecene and 1-octadecene. No oligomerisation products aside from dimers, trimers and tetramers were observed.

10 Example 4

Oligomerisation of 1-Octadecene

- Oligomerisation of 1-octadecene was carried out according to the general procedure described above. Catalysis was conducted with borenium ionic liquids in accordance with the present invention, $[\text{BCl}_2(\text{P}_{888}\text{O})][\text{Al}_2\text{Cl}_7]$ (Entry 18) and $[\text{BCl}_2(\text{P}_{888})][\text{Al}_2\text{Cl}_7]$ (Entry 19). Results of the oligomerisation reactions are provided in Table 4 below.

Table 4 - Product distribution for oligomerisation of 1-octadecene

Entry	IL	Feed	Product Appearance	Product distribution
18	$[\text{BCl}_2(\text{P}_{888}\text{O})][\text{Al}_2\text{Cl}_7]$	C18	Yellow oil	C18 20.3% C36 37.0% C54 27.0% C72 12.0% C90+ 3.7%
19	$[\text{BCl}_2(\text{P}_{888})][\text{Al}_2\text{Cl}_7]$	C18	Yellow oil	C18 22.3% C36 36.0% C54 28.0% C72 11.0% C90+ 2.7%

The results in Table 4 demonstrate the selectivity of borenium ionic liquids for the formation of dimers (C36), trimers (C54) and tetramers (C72) over highly oligomerised products in the oligomerisation of 1-octadecene. Higher oligomerisation products
5 amounted to only 3.7% or 2.7% of the oligomerisation reaction products for Entries 18 and 19 respectively.

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CLAIMS

1. A process for the preparation of alpha-olefin oligomers, comprising contacting an olefinic feedstock comprising C₅ to C₂₀ alpha-olefins with an ionic liquid comprising:
 - (i) at least one borenium cation of the formula [BX₂L]⁺, wherein L is a Lewis basic donor ligand containing a donor atom selected from oxygen, sulphur, selenium, nitrogen, phosphorus, arsenic, and each X is independently selected from fluorine, chlorine and bromine; and
 - (ii) at least one non-coordinating anion.
2. A process according to Claim 1 wherein each X is independently selected from fluorine or chlorine, preferably chlorine.
3. A process according to Claim 1 or Claim 2 wherein the Lewis basic donor ligand is selected from ligands containing a donor atom selected from oxygen, sulphur, nitrogen and phosphorus, preferably nitrogen.
4. A process according to any of the preceding claims, wherein the Lewis basic donor ligand is selected from the group of compounds consisting of ketones, sulfoxides, phosphine-oxides, ureas, esters, amides, ethers, thioketones, thioureas, thioamides, thioethers, amines, nitriles and phosphines.
5. A process according to Claim 4, wherein the Lewis basic donor ligand is selected from amides and amines, preferably amines.
6. A process according to Claim 4, wherein the Lewis basic donor ligand is selected from compounds having a formula selected from R₁-C(O)-R₁, R₁-S(O)-R₁, R₂NH-C(O)-NHR₂, R₂NH-C(S)-NHR₂, R₁-C(O)-NR₂, R₁-C(O)-OR₁, (R₃)₃P, (R₃)₃P(O) and R₁-CN;
wherein: each R₁ independently represents a C₁ to C₁₀ alkyl group, preferably a C₁ to C₆ alkyl group, more preferably a C₁ to C₃ alkyl group and most preferably a methyl group; R₂ is selected from hydrogen or a C₁ to C₁₀ alkyl group, more preferably from hydrogen or a C₁ to C₆ alkyl group, still more preferably from hydrogen or a C₁ to C₃ alkyl group, and most preferably from hydrogen or a

methyl group; and R₃ represents a C₄ to C₁₀ alkyl group; wherein any of R₁, R₂ and R₃ may optionally be substituted by one or more fluorine atoms.

- 5 7. A process according to Claim 6, wherein the at least one Lewis basic donor ligand is selected from urea, *N,N'*-dimethylurea, *N,N'*-dimethylthiourea, acetamide, dimethylacetamide, acetone, ethyl acetate dimethylsulfoxide, trioctylphosphine and trioctylphosphine oxide.
- 10 8. A process according to any of Claims 1 to 4, wherein the Lewis basic donor ligand is selected from a heterocyclic group comprising one or more of O, N, NH and S in the ring.
- 15 9. A process according to Claim 8, wherein the heterocyclic group is selected from ethylene oxide, azetidiny, pyrrolidiny, pyrrolyl, pyrazolyl, oxetanyl, pyrazolinyl, imidazolyl, imidazolinyl, imidazolidinyl, oxazolyl, oxazolidinyl, isoxazolinyl, isoxazolyl, thiazolyl, thiadiazolyl, thiazolidinyl, isothiazolyl, isothiazolidinyl, furyl, tetrahydrofuryl, thienyl, oxadiazolyl, piperidiny, piperazinyl, azepiny, pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl, triazinyl, triazolyl, tetrazolyl, tetrahydropyranyl, morpholinyl, thiamorpholinyl, preferably selected from imidazolyl, pyridyl and
- 20 pyrrolyl.
10. A process according to Claim 9, wherein the heterocyclic group is selected from picoline, lutidine, pyridine, collidine, dimethylaminopyridine (DMAP), 1-alkyl-imidazole, preferably 1-methyl-imadazole (mim).
- 25 11. A process according to any of the preceding claims wherein the at least one non-coordinating anion is selected from a) halometallate anions of the formula [MX₄]⁻ or [M₂X₇]⁻, where M is Al or Ga, preferably Al, and X is independently Cl or Br, preferably Cl; b) bis(triflamide) ([NTf₂]⁻) or triflate ([OTf]⁻); c)
- 30 bis(perfluoroalkylsulphonyl)imides (preferably methyl, ethyl, butyl and nonyl) d) tetrafluoroborate ([BF₄]⁻) or tetrachloroborate ([BCl₄]⁻); e) hexafluorophosphate ([PF₆]⁻); f) [SnX₃]⁻ or [Sn₂X₅]⁻, where X is independently Cl or Br; g) dichlorocuprate ([CuCl₂]⁻); h) hexafluoroantimonate ([SbF₆]⁻); i) hexafluoroarsenate ([AsF₆]⁻); j) fluorosulphonate ([F-SO₂-O]⁻) and perfluoroalkyl

sulphonates (preferably methyl); and k) chlorozincate(II) anions, preferably $[\text{ZnCl}_4]^{2-}$ or $[\text{Zn}_2\text{Cl}_6]^{2-}$.

12. A process according to Claim 11 wherein the at least one non-coordinating anion is selected from a) halometallate anions of the formula $[\text{MX}_4]^-$ or $[\text{M}_2\text{X}_7]^-$, where M is Al or Ga, preferably Al, and X is independently Cl or Br, preferably Cl; b) bis(trifluoromethyl)amides ($[\text{NTf}_2]^-$); c) bis(perfluoroalkylsulfonyl)imides (preferably methyl, ethyl, butyl or nonyl); d) tetrafluoroborate ($[\text{BF}_4]^-$); e) hexafluorophosphate ($[\text{PF}_6]^-$); and f) $[\text{SnX}_3]^-$ or $[\text{Sn}_2\text{X}_5]^-$ where X is independently Cl or Br.

13. A process according to Claim 12 wherein the at least one non-coordinating anion is selected from halometallate anions of the formula $[\text{MX}_4]^-$ or $[\text{M}_2\text{X}_7]^-$, where M is Al or Ga and X is independently Cl or Br.

14. A process according to Claim 13 wherein the at least one non-coordinating anion is selected from halometallate anions of the formula $[\text{M}_2\text{X}_7]^-$, where M is Al or Ga, preferably Al, and X is independently Cl or Br, preferably Cl.

15. A process according to Claim 11, wherein the at least one non-coordinating anion is Lewis acidic and selected from the group consisting of $[\text{Al}_2\text{Cl}_7]^-$, $[\text{Ga}_2\text{Cl}_7]^-$, $[\text{Sn}_2\text{Cl}_5]^-$ and $[\text{Zn}_2\text{Cl}_6]^{2-}$.

16. A process according to any one of the preceding claims, wherein the olefinic feedstock comprises at least 50 wt% of one or more C_5 to C_{20} alpha-olefins, more preferably at least 60 wt% of one or more C_5 to C_{20} alpha-olefins, more preferably at least 70 wt% of one or more C_5 to C_{20} alpha-olefins, more preferably at least 80 wt% of one or more C_5 to C_{20} alpha-olefins, more preferably at least 90 wt% of one or more C_5 to C_{20} alpha-olefins, and most preferably at least 95 wt% of one or more C_5 to C_{20} alphaolefins.

17. A process according to Claim 16, wherein the olefinic feedstock comprises at least 50 wt% C_6 to C_{18} alpha-olefins, more preferably at least 60 wt% C_6 to C_{18} alphaolefins, more preferably at least 70 wt% C_6 to C_{18} alpha-olefins, still more preferably at least 80 wt% C_6 to C_{18} alpha-olefins, and most preferably at least 90 wt% C_6 to C_{18} alpha-olefins.

18. A process according to any one of the preceding claims, wherein the olefinic feedstock comprises at least 30 wt% C₈ to C₁₄ alpha-olefins, preferably at least 50 wt% C₈ to C₁₄ alpha-olefins, more preferably at least 70 wt% C₈ to C₁₄ alpha-olefins, still more preferably at least 80 wt% C₈ to C₁₄ alpha-olefins, and most preferably at least 90 wt% C₈ to C₁₄ alpha-olefins.

19. A process according to Claim 18, wherein the olefinic feedstock comprises at least 30 wt% C₁₀ to C₁₄ alphaolefins, more preferably at least 50 wt% C₁₀ to C₁₄ alpha-olefins, more preferably at least 70 wt% C₁₀ to C₁₄ alpha-olefins, still more preferably at least 80 wt% C₈ to C₁₄ alpha olefins, and most preferably at least 90 wt% C₁₀ to C₁₄ alpha-olefins.

20. A process according to Claim 18 or Claim 19, wherein the olefinic feedstock comprises at least 30 wt% C₁₀ to C₁₂ alpha-olefins, preferably at least 50 wt% C₁₀ to C₁₂ alpha-olefins, more preferably at least 70 wt% C₁₀ to C₁₂ alpha-olefins, still more preferably at least 80 wt% C₁₀ to C₁₂ alpha-olefins, and most preferably at least 90 wt% C₁₀ to C₁₂ alphaolefins.

21. A process according to Claim 20, wherein the olefinic feedstock comprises at least 30 wt% 1-decene, preferably at least 50 wt% 1-decene, more preferably at least 70 wt% 1-decene, still more preferably at least 80 wt% 1-decene, and most preferably at least 90 wt% 1-decene.

22. A process according to Claim 20, wherein the olefinic feedstock comprises at least 30 wt% 1-dodecene, preferably at least 50 wt% 1-dodecene, more preferably at least 70 wt% 1-dodecene, still more preferably at least 80 wt% 1-dodecene and most preferably at least 90 wt% 1-dodecene.

23. A process according to any one of Claims 1 to 17, wherein the olefinic feedstock comprises at least 30 wt% C₁₆ to C₁₈ alpha-olefins, more preferably at least 50 wt% C₁₆ to C₁₈ alpha-olefins, more preferably at least 70 wt% C₁₆ to C₁₈ alpha-olefins, still more preferably at least 80 wt% C₁₆ to C₁₈ alpha-olefins, and most preferably at least 90 wt% C₁₆ to C₁₈ alpha-olefins.

24. A process according to Claim 23, wherein the olefinic feedstock comprises at least 30 wt% 1-hexadecene, more preferably at least 50 wt% 1-hexadecene, more preferably at least 70 wt% 1-hexadecene, still more preferably at least 80 wt% 1-hexadecene, and most preferably at least 90 wt% 1-hexadecene.

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25. A process according to Claim 23, wherein the olefinic feedstock comprises at least 30 wt% 1-octadecene, more preferably at least 50 wt% 1-octadecene, more preferably at least 70 wt% 1-octadecene, still more preferably at least 80 wt% 1-octadecene and most preferably at least 90 wt% 1-octadecene.

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26. A process according to any one of the preceding claims, wherein the olefinic feedstock comprises a minor amount of paraffins.

27. A process according to any one of the preceding claims, wherein the olefinic feedstock is contacted with the ionic liquid at a temperature of from 0 to 160 °C, more preferably 40 to 140 °C, more preferably 80 to 140 °C, still more preferably 100 to 140 °C, and most preferably about 120 °C.

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28. A process according to any one of the preceding claims, wherein the olefinic feedstock is contacted with the ionic liquid at a pressure of from 10 to 1000 kPa, preferably from 20 to 500 kPa, more preferably from 50 to 200 kPa, still more preferably from 80 to 120 kPa, and most preferably about 100 kPa.

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29. A process according to any one of the preceding claims, wherein the olefinic feedstock is contacted with at least 0.01 wt% of the ionic liquid, more preferably at least 0.05 wt% of the ionic liquid, still more preferably at least 0.1 wt% of the ionic liquid, and most preferably at least 0.2 wt% of the ionic liquid, based on the total weight of the ionic liquid and olefinic feedstock.

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30. A process according to Claim 29, wherein the olefinic feedstock is contacted with from 0.01 to 5 wt% of the ionic liquid, preferably from 0.05 to 2 wt% of the ionic liquid, still more preferably from 0.1 to 1 wt% of the ionic liquid and still more preferably from 0.2 to 0.8 wt% of the ionic liquid, based on the total weight of the ionic liquid and olefinic feedstock.

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31. A process according to Claim 30, wherein the olefinic feedstock is contacted with about 0.5 wt% of the ionic liquid, based on the total weight of the ionic liquid and olefinic feedstock.
- 5 32. A process according to any one of the preceding claims which is selective for the preparation of dimers, trimers and tetramers.
- 10 33. Use of an ionic liquid as defined in any of Claims 1 to 15 as a selective Lewis acid catalyst for selectively forming dimers, trimers and tetramers in an oligomerisation reaction of a feed stock comprising C₅ to C₂₀ alpha-olefins.
34. Use of an ionic liquid as defined in any of Claims 1 to 15 as a selective Lewis acid catalyst in Friedel-Crafts alkylation and alkane isomerisation reactions.

Figure 1

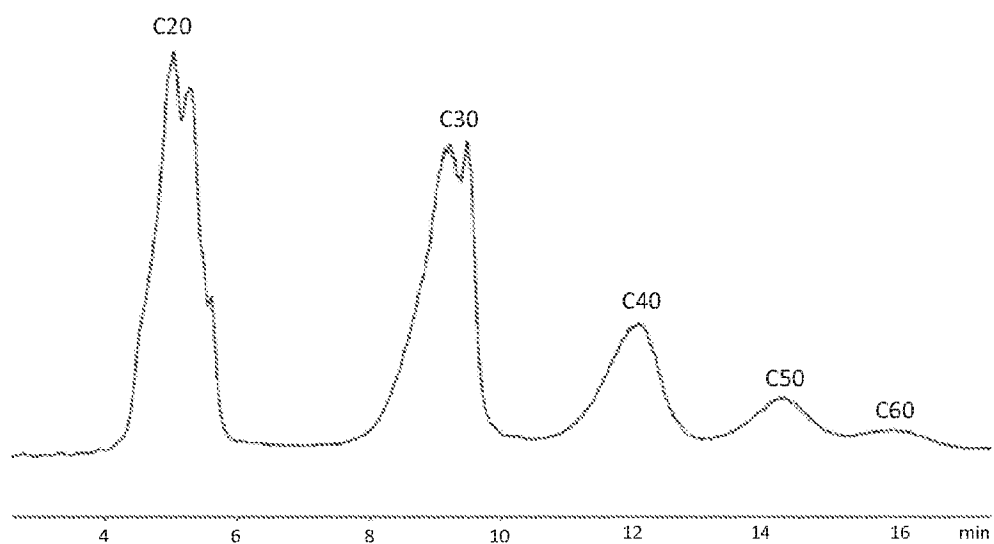


Figure 2

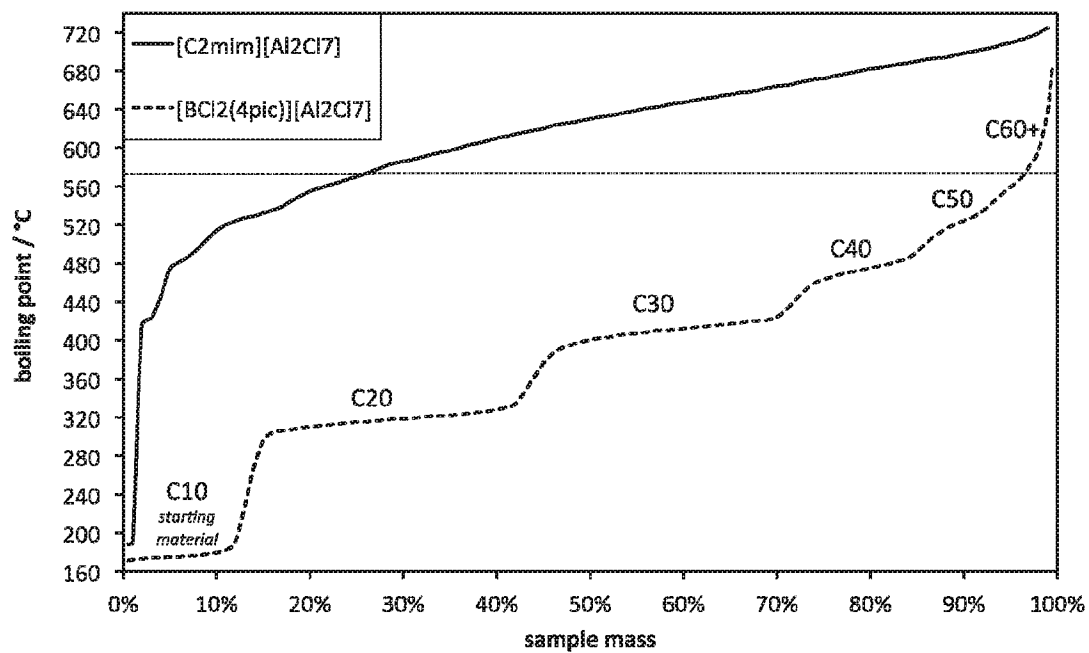


Figure 3

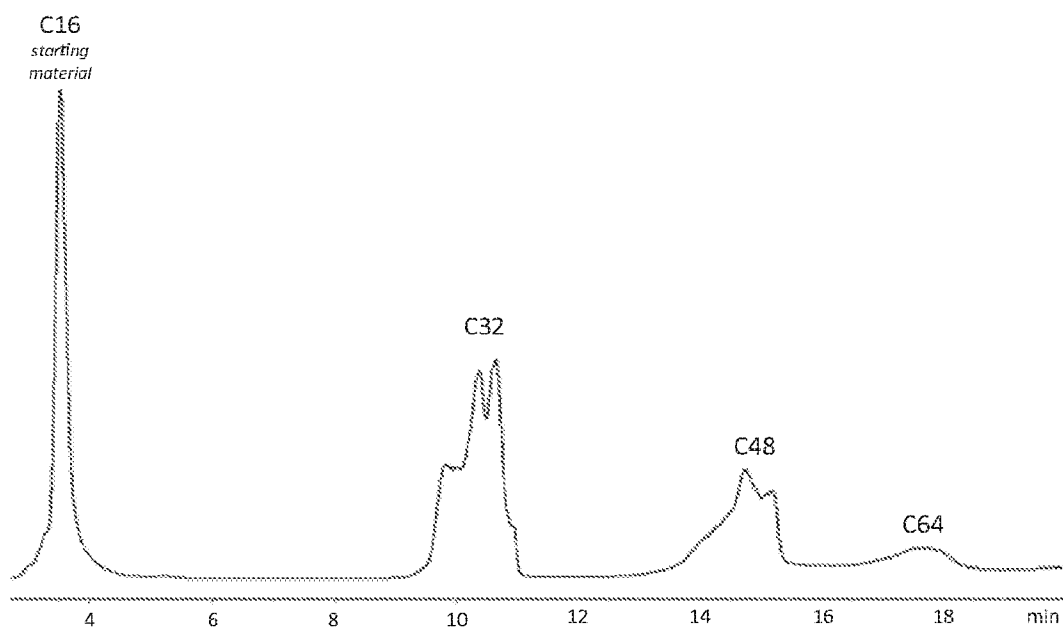
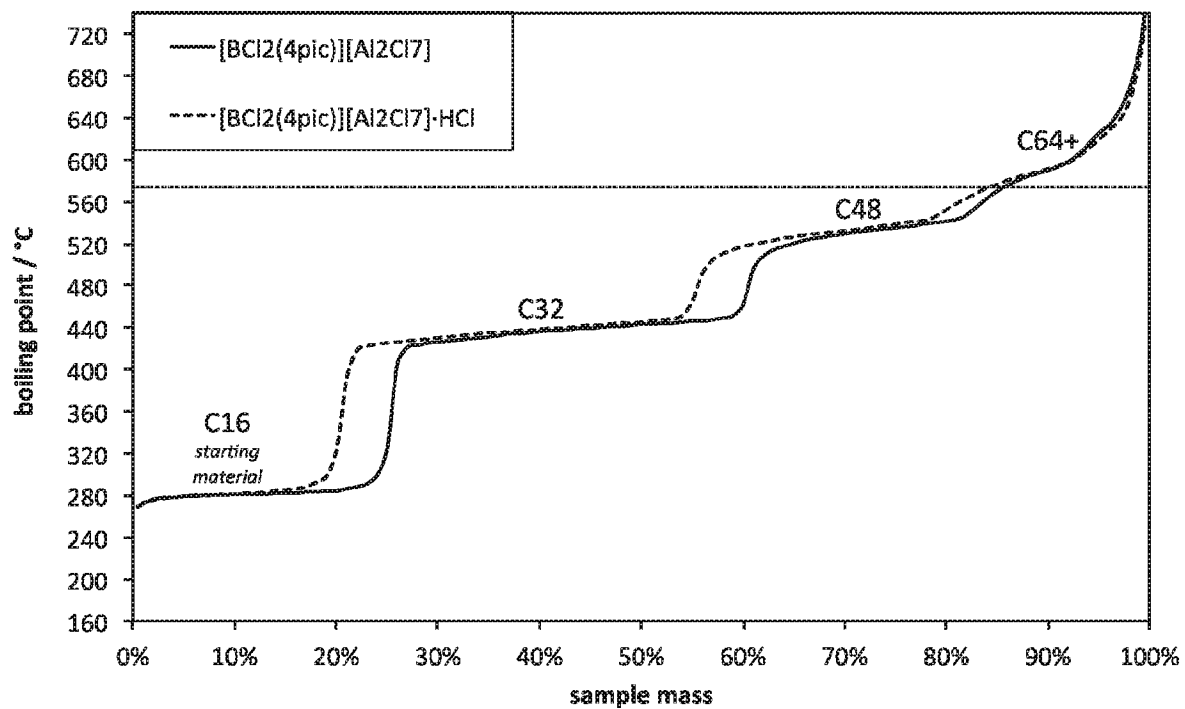


Figure 4



INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2015/052007

A. CLASSIFICATION OF SUBJECT MATTER INV. C07C2/32 C07C11/02 B01J31/02 B01J31/14 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C07C B01J C10M		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 7 572 944 B2 (S. ELOMARI, ET AL.) 11 August 2009 (2009-08-11) cited in the application claim 1; examples 1, 2, 4-6 -----	1-34
A	US 6 395 948 B1 (K.D. HOPE KENNETH, ET AL.) 28 May 2002 (2002-05-28) claim 1; examples -----	1-34
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A	JP 2000 202299 A (TOSOH CORP) 25 July 2000 (2000-07-25) abstract -----	1-34
<div style="display: flex; justify-content: space-between;"> <div> ☐ Further documents are listed in the continuation of Box C. </div> <div> ☒ See patent family annex. </div> </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-size: 1.2em;">3 September 2015</div>		Date of mailing of the international search report <div style="text-align: center; font-size: 1.2em;">22/09/2015</div>
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-size: 1.2em;">English, Russell</div>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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