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Borenium ionic liquids as alternative to BF_3 in polyalphaolefins (PAOs) synthesis

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KEYWORDS: Borenium, Lewis acids, ionic liquids, carbocationic oligomerization, 1-decene, polyalphaolefins (PAOs)

ABSTRACT: Lewis superacidic borenium ionic liquids of the general formula $[BCl_2(L)][M_nCl_{3n+1}]$ (L = pyridine or picoline, n = 1 or 2) were used as catalysts for the oligomerization of 1-decene to polyalphaolefins (PAOs), as a safer alternative to the conventional BF_3 catalyst, which is a toxic and corrosive gas. The catalytic activity of the borenium system could be tuned by modifying the ligand on the borenium cation, the chlorometallate anion and the reaction temperature. Following the optimization of the reaction conditions on small scale, the reaction was scaled up to 3 L. Following fractional distillation of the crude product and blending, lubricant base oils matching market specifications (viscosity index, pour point) for PAO4 and

PAO6 grades were obtained. Synthesised from inexpensive, off-the-shelf components, borenium ionic liquids are a new, cost-effective alternative to BF_3, offering substantial gains in process safety and CAPEX savings.

Introduction

Automotive lubricants are blends of a base oil and additives, which vary in proportion depending on the application.[1] Hydrocarbon base oils are divided into four groups with differing physical and chemical properties. Synthetic polyalphaolefins (PAOs), which belong to Group IV, have superior physical properties compared to those produced from crude oil refining (Groups I-III).[2] They have viscosity index (VI) above 120 units, which indicates a smaller change in viscosity with increasing temperature, a low pour point (PP) below -40°C, which makes them suitable for low temperature applications, and low Noack volatility, which contributes to better stability in higher applications. Finally, lower content of impurities and unsaturated hydrocarbons contributes to a higher oxidative stability of PAOs compared to Groups I-III base oils.[2] PAOs are divided into classes based on their kinematic viscosity at 100 °C (Kv_{100}), and are blended to fit within one of the several categories: Kv_{100} = 2, 4, 6, 8, 10, 40 and 100 cSt.[3] PAO4 and 6 are the most sought after as low-viscosity, high performance automotive lubricants. The PAO market is continuously growing, as the modern automotive market favors synthetic lubricants based on PAOs, which are instrumental in reducing wear and tear of engine parts, as well as improving fuel economy.

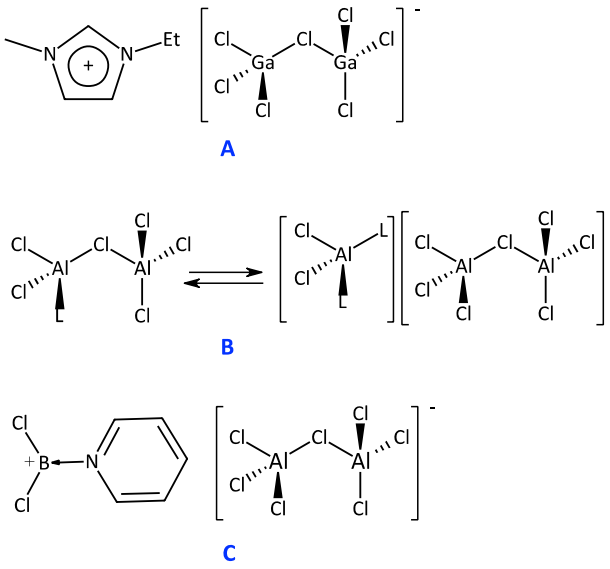
The molecular structure of PAOs (length and branching of hydrocarbon chains) determines the properties of the lubricant. In general, linear alkyl chains have favorably high VIs but also undesirably high PP, whereas highly branched hydrocarbons have low VI and PP.[4–6] Commercial PAOs require very carefully balanced degree of branching, to attain sufficiently low pour point without compromising the temperature-dependent viscosity properties. These properties depend to a largest extent on the catalyst used in PAO production.

The vast majority of PAOs are produced *via* the carbocationic oligomerization of 1-decene, using a strong Lewis acid catalyst. The Lewis acid is either promoted with a protic additive (*e.g*. an alcohol) or interacts with adventitious water, to generate Brønsted superacidic protons, capable of protonating 1-decene and initiating the oligomerization reaction.[7] Low viscosity lubricants (PAO4 and 6) contain predominantly the trimer (C30), tetramer (C40) and pentamers (C50) of 1-decene, and are industrially produced through the BF_3/*n*BuOH-catalyzed oligomerization, which gives only a small proportion of the dimer and little to no heavy oligomers in the crude product.[8–10] In contrast, conventional catalysts based on $AlCl_3$, or on metallocenes, deliver very high viscosity lubricants:[11] aluminium yielding branched chains of high molecular weight, and metallocenes - linear oligomers with high pour points.[8]

In the synthesis of PAO4 and 6, the fundamental drawback is that BF_3 is a toxic gas, which hydrolyses to release HF and subsequently fluoroboric acid. This poses significant operational hazard and – in the industrial setting - incurs very high CAPEX overhead to ensure the plant safety. The challenge lies in identifying a catalyst that would produce base oils matching exactly the same specifications as those produced with BF_3 (aligned with the needs of the automotive industry) but using a safer and economically viable catalyst. BF_3 promoted with protic additives is the only commercially used catalyst for low-viscosity PAOs, whereas Al-based catalysts ($AlCl_3$, $EtAlCl_2$, chloroaluminate ionic liquids) promoted with water or alcohols typically give heavier, high viscosity products.[8] With careful fine-tuning of conditions, medium-visocisty polymers can be accessed.[12] Metallocene catalysts, sometimes with an aluminium co-catalysts, produce very high viscosity oligomers/polymers.[8,13] Brønsted acids, in contrast, yield very light products.[14]

Chloroaluminate ionic liquids, based on an organic cation and a chloroaluminate anion, $[Al_2Cl_7]^-$,[15] which feature prominently in the patent literature as promoting the production of heavy

oligomers,[16–18] inspired our group's search for Lewis acidic ionic liquids yielding low-viscosity PAOs. Lewis acidic chlorogallate ionic liquids (exemplified in Scheme 1, A) gave favorable products distribution and good yields (up to >90%), but were much too costly for commercial use.[19] Liquid coordination complexes (LCCs) based on aluminium(III) chloride (Scheme 1, B)[20] delivered surprisingly low molecular weight oligomers with low viscosities for Al-centered Lewis acids, and were more cost effective than conventional chloroaluminate ionic liquid, having dispensed with an organic cation.[21] However, they gave lower yields (about 70-85%) and lower selectivities to PAO4 and 6 than that of BF_3. In this work we introduce a process catalyzed by borenium ionic liquids (exemplified in Scheme 1, C) which are the first reported ionic liquid systems with Lewis acidic cations.[22]



Scheme 1. Examples of structures of: chlorogallate ionic liquids (A), liquid coordination complex, where L = urea, trioctylphosphine oxide, trioctylphosphine etc. *(B) and borenium ionic liquids (C).*

Borenium cations are recognized for their high Lewis acidity,[23,24] and the systems used here are inexpensive, extremely active,[25] and give higher selectivities and conversions than any LCCs reported to date.

Experimental

Materials and methods

All experiments were carried out under inert atmosphere using a glovebox or standard Schlenk techniques. All pyridine ligands were purchased from Sigma Aldrich (>98%), purified by distillation and stored under argon over dried 3 Å molecular sieves. Boron trichloride was purchased as a 1 M solution in heptanes from Sigma Aldrich and used as received. For small-scale experiments, $AlCl_3$ (99.999%) and $GaCl_3$ (99.999%) were purchased from Alfa Aesar in sealed ampules which were transferred to the glovebox (MBraun labmaster dp, <0.3 ppm of H_2O and O_2). The materials were used as received. For large scale reaction $AlCl_3$ (98%) was purchased from Sigma Aldrich and was doubly sublimed before use, following a literature procedure.[21,26]

Syntheses of borenium ionic liquids

Borenium ionic liquids were synthesized according to literature procedures.[22] BCl_3 in heptane (5 cm^3, 5 mmol) in dichloromethane (20 cm^3) was cooled to -78 °C before dropwise addition of a dry base: pyridine (0.36 g, 4.5 mmol) or picoline (0.42 g 4.5 mmol). The resulting mixture was stirred for 1 h before the removal of the volatiles under reduced pressure. Adducts, that formed quantitatively as white powders, were dried (60 °C, 10^{-2} bar, overnight) and transferred to the glovebox.

In the glovebox, an adduct (4.5 mmol) was placed in a vial equipped with a stirring bar, and MCl_3 (M = Al, Ga, 4.5 mmol or 9 mmol) was added slowly, with little heat evolved. The mixture was then heated and stirred (50 °C, *ca*. 1 h), until a homogenous liquid was obtained. All adducts and ionic liquids were analyzed by ^{1}H, ^{11}B and, where appropriate, ^{27}Al NMR spectroscopy (Bruker

AvanceIII 400 MHz spectrometer). Adducts were measured as solutions in $CDCl_3$, whereas ionic liquids were studied neat, with d_6-dmso capillary as an external lock. Expanded experimental procedures and full NMR spectroscopic characterization is shown in the SI (Figures S1 – S30).

Small-scale oligomerization of 1-decene

Oligomerization reactions were carried out according to the earlier-established procedure.[21] On the small scale, experiments were carried out in a battery of eight glass computer-controlled H.E.L. reactors (120 cm^3) designed for high corrosion resistance, and equipped with efficient temperature control (cooling/heating) system. The reactor vessels and stirrer propellers were dried overnight in an oven (>100 °C), and then cooled in a desiccator. The remaining parts were dried with a heat gun (*ca*. 5 min) immediately prior to use, and the reactors were assembled. 1-Decene (40 cm^3) was poured into the reactors and stirred vigorously (600 rpm) at the reaction temperature (60 – 130 °C), whilst the reactors were purged with argon. The borenium ionic liquid (0.62 mmol, *ca.* 1 wt %) was loaded into a gas-tight syringe in the glovebox, transported to reactors in a syringe with tip protected from atmospheric moisture, and added to the 1-decene. The catalyst addition was performed as quick drop-wise addition, over *ca.* 10 s, resulting in a strong exotherm. After certain time (1-1.5 h), the reaction was quenched with water. The organic phase was dried over $MgSO_4$, filtered, and analyzed by SimDist GC.

Scaled-up oligomerization of 1-decene

Reactions were carried out in a computer-controlled glass H.E.L. reactor (5 L). The fully assembled reactor was dried (60 °C, 30 min, 10^{-2} mbar) prior to the reaction, and then 1-decene (3 kg, 21.4 mol) was added under positive pressure of argon; the reactor was then purged with argon (10 min). Subsequently, vigorously stirred (600 rpm) 1-decene was heated to the reaction

temperature (60 – 100 °C). The borenium ionic liquid (5.75 – 27.75 g, 12 – 60 mmol) was loaded into a dry gas-tight syringe, following the procedure analogous to that for small-scale oligomerization, albeit the syringe was placed in a syringe pump. The catalyst was subsequently added using a syringe pump, at a pace designed to prevent thermal runaway (0.2 cm^3 min^{-1}). After a given reaction time, the stirring was stopped, and the system was allowed to cool to ambient temperature. The reaction mixture was washed with deionized water (3×10^3 cm^3), and each time the reactor content was heated to 95 °C, in order to ensure dissolution of the boric acid produced by hydrolysis of the catalyst. Each wash, the bottom (aqueous) layer was removed through the tap located at the bottom of the reactor vessel. The product was dried over $MgSO_4$ and filtered through a large sintered funnel.

Simulated distillation gas chromatography (SimDist GC)

Samples for SimDist GC analysis were dissolved in toluene (100 mg cm^{-3}), dried over magnesium sulfate, filtered and analyzed according to ASTM D6352.[27] The analysis were carried out using Agilent 6890N GC, equipped with an FID detector and a high-performance HT PTV (high temperature programmable temperature vaporizing) inlet with optimized design for SIMDIST applications. Column: Agilent J&W DB-HT 5M SimDist Column. Reproducibility of the results was limited by the reproducibility of the reaction outcome, rather than the error of the analytical method, as already reported.[21] Error associated with each product fraction is shown in Table 1.

Table 1. Error in reproducibly producing each fraction of oligomers.[21]

	Conversion (%)	**C_{20} (%)**	**C_{30} (%)**	**C_{40} (%)**	**C_{50} (%)**	**C_{60} (%)**	**C_{70+} (%)**
Error	± 3	± 4	± 3	± 2	± 2	± 1	± 1

Distillation

Fractionated distillation was carried out in a computer-controlled DistriLab D5236 Crude Oil Distillation System, equipped with a $6 \cdot 10^3$ cm^3 boiling flask, according to ASTM D5236.[28] In a typical procedure, the distillation rig was dried prior to use (1 mmHg, 30 min). A sample (2 - $4 \cdot 10^3$ cm^3) was dried over $MgSO_4$, filtered and loaded into the boiling flask. Unreacted decene was distilled first (10 mmHg), then the mixture was cooled and the decene fraction was removed from the distillation rig. Subsequently, the dimer (C_{20}) fraction was distilled (0.1 mmHg, vigorous stirring). Then, the distillation rig was cleaned by distilling toluene, in order to prevent contamination of subsequent fractions. The trimer (C_{30}) was fractionally distilled (0.1 mmHg) with the C_{30} and distillation residue being blended to give PAO 4 and 6 samples. A minimum of $0.4 \cdot 10^3$ cm^3 (the heaviest fraction) was left in the boiling flask as a residue. All fractions and the residue were analyzed using SimDist GC. After blending appropriate proportions of C_{30}, heavier fractions and the residue, the pour point, Kv_{40} and Kv_{100} values were measured, and VI was calculated.

Physical properties tests

Pour point was measured according to ASTM D97-11.[29] The pour point cryostat (Stanhope-Seta, Model 93531-7) was validated against a standard gas oil sample (99851-0) according to ASTM method (pour point −15 °C, cloud point −4 °C). Each sample was placed in a glass vessel fitted with a low temperature thermometer and held in a bath heated to 45 °C until the temperature was reached, before transferring to a constant temperature bath held at 24 °C. Once cooled to 27 °C, it was transferred to a bath at 0 °C, followed by consecutive baths held at -18 °C, -33 °C, -51 °C and -69 °C (the last temperature was achieved using a dry ice bath). The samples were removed from the baths and tested for flow by tilting the glass vessel at every 3 °C temperature decrease.

Kinematic viscosities (Kv) were measured according to ASTM D445-11a.[30] The measurements were performed at 40 and 100 °C using the appropriate Cannon-Fenske kinematic viscosity glassware and a precisely-controlled heating bath. Kv was found by timing the gravitational flow of the sample through a capillary.

Viscosity index (VI) was calculated from Kv data, according to eq (1). L and H are constants based on Kv_{100}, tabularized in ASTM 2270.[31]

$$VI = 100(L-Kv_{40})(L-H)^{-1} \qquad (1)$$

Hydrogenation

Hydrogenation reactions were carried out in a 250 cm^3 stainless steel Paar reactor. Crude PAO product (100 cm^3) was loaded into the reactor with 0.5 g of Pd/C and the reactor was sealed, purged with positive pressure of argon, and then pressurized to 40 bar with H_2. Hydrogenation was carried out (100 °C, 600 rpm, 2 h), and then the mixture was filtered to yield hydrogenated PAO. Analysis by ^1H NMR showed no aromatic or olefinic peaks.

Results and Discussion

Syntheses of borenium ionic liquids

All tetracoordinate boron adducts, $[BCl_3L]$, formed readily as white powders, without observable side reactions, as reported in the literature.[22] The complexes (L = py, 3pic or 4pic) were all found to be stable in air and could be recrystallized from dry DCM/hexane, yielding ^1H and ^{11}B NMR spectra in agreement with the literature.[22]

An exception was noted for the reaction of 2-picoline and BCl_3, whereby the white powder that formed, dissolved in $CDCl_3$, gave ^{11}B NMR spectrum showing two signals at 8.65 and 7.21 ppm, in 3:1 ratio, and ^{1}H NMR spectroscopy showed two ligand environments, at 1:1 ratio. Attempts to purify by recrystallization in air resulted in decomposition of the sample. Variable temperature ^{1}H NMR spectroscopy (25 – 40 °C) showed no significant variation in the ratio of these peaks. It can be reasonably assumed that the methyl group in the alpha position with respect to the nitrogen atom induces steric hindrance and weakens the B-N bond, which is known to encourage disproportionation of the adduct (Equation 2) in chemistry of boron complexes.[32] As such, this equilibrium observed *via* NMR spectroscopy is an inherent property of the compound, rather than impurity.

$$2[BCl_3(2pic)] \rightleftarrows [BCl_2(2pic)_2][BCl_4] \qquad (2)$$

Most importantly in the context of this work, the reaction of $[BCl_3(2pic)]$ with two moles of $AlCl_3$ resulted in the reaction product analogous with other systems. The ^{1}H NMR spectrum featured a single set of signals corresponding to the 2-picoline ligand, shifted downfield indicating loss of electron density from the aromatic ring. The ^{11}B NMR spectrum features a single broad peak at $\delta\ ^{11}B$ = 45.0 ppm, indicative of the borenium cation, $[BCl_2(2pic)]^+$, as well as a small peak at $\delta\ ^{11}B$ = 7.6 ppm (<1% area), potentially a hydrolysis product caused by adventitious water. The corresponding ^{27}Al NMR spectra shows a single broad peak at $\delta\ ^{27}Al$ = 104 ppm, attributable to $[Al_2Cl_7]^-$. All this points to the formation of the borenium ionic liquid.

The addition of 1 or 2 equivalents of $AlCl_3$ or $GaCl_3$ to the $[BCl_3L]$ adducts afforded ionic liquids: either room-temperature liquids, or low-melting solids (Table 2), in agreement with the literature.[22]

Table 2. Physical state of borenium ionic liquids synthesized here, at ambient conditions, as a function of cation-anion combination.

	$[BCl_2(py)]^+$	**$[BCl_2(2pic)]^+$**	**$[BCl_2(3pic)]^+$**	**$[BCl_2(4pic)]^+$**
$[AlCl_4]^-$	Solid/Gel	Liquid	Liquid	Solid/Gel
$[Al_2Cl_7]^-$	Liquid	Liquid	Liquid	Liquid
$[GaCl_4]^-$	Solid/Gel	Liquid	Liquid	Solid/Gel
$[Ga_2Cl_7]^-$	Liquid	Liquid	Liquid	Liquid

Each ionic liquid listed in Table 2 comprises two main components: a Lewis acidic borocation, $[BCl_2L]^+$, combined with either a Lewis neutral anion, $[MCl_4]^-$, or a Lewis acidic one, $[M_2Cl_7]^-$. Since the $[MCl_4]^-$ anion is more coordinating, borenium cations in the $[BCl_2L][MCl_4]$ systems are less Lewis acidic compared to the same cations combined with $[M_2Cl_7]^-$, which manifests itself through lower AN values (where AN is Gutmann acceptor number, a quantitative measure of Lewis acidity) and more upfield ^{11}B NMR chemical shifts.[22] In contrast, $[BCl_2L][M_2Cl_7]$ ionic liquids feature two strongly Lewis acidic centres: a Lewis superacidic cation (AN > 150) and highly Lewis acidic anion (AN of *ca*. 96).[19,33]

In terms of catalytic reactivity, it has long been established that ionic liquids with organic (spectator) cations and Lewis neutral anions, $[MCl_4]^-$ (M = Al or Ga), are catalytically inactive, whereas ionic liquids with Lewis acidic anions, $[M_2Cl_7]^-$, are recognized as strong Lewis acids.[15,34] The same is true for liquid coordination complexes based on Al or Ga, which were found catalytically inactive when containing only mononuclear complexes, $[AlCl_2L_2][AlCl_4]$, but displayed high catalytic activity with dinuclear complexes, $[AlCl_2L_2][Al_2Cl_7]$ (Scheme 1, B).[21,35]Finally, in our earlier work on borenium ionic liquids as catalysts for Diels-Alder reaction, we found $[C_2mim][AlCl_4]$ catalytically inactive, in contrast to borenium ionic liquids with this anion, that were active catalysts.[25] This leads to the general conclusion that ionic liquids of a general formula $[BCl_2L][MCl_4]$ are catalytically active due to the cation, and those with formula [BCl2L][M_2Cl_7] have two Lewis acidic centres, in the cation and the anion.

Adding complexity is the fact that carbocationic oligomerisation of higher olefins with Group 13 halides is initiated by a Lewis/Brønsted acid system, rather than by a direct interaction of a Lewis acid with the double bond.[7] Upon the addition of a Lewis acidic ionic liquid to the reaction mixture, it interacts with adventitious water and generates Brønsted superacidic protons in an exothermic reaction. These protons then protonate 1-decene (initiation). Subsequently, carbocationic oligomerization occurs, with the propagating carbocation accompanied by anions present in the system. In parallel, chain isomerization takes place. The activity of both Brønsted acidic proton and propagating carbocation is considered to be more dependent on the coordinating ability of the strongest base in the system (that is, the anions), than on the initial strength of the Lewis acid. Finally, termination occurs, simultaneously through a number of routes. Therefore, the overall outcome is not dependent on a single factor, such as Lewis acidity, but on the combination of a number of variables, and is therefore difficult to predict.[7]

Small-scale oligomerization of 1-decene

From very preliminary experiments it has been known that borenium ionic liquids were capable of oligomerizing 1-decane to generate dimers, trimers, tetramers and some heavier oligomers.[36] From the process perspective, it was important to maximize conversion (ideally reaching over 90%), in order to limit recycle of the decane fraction, and to minimize the yield of low-value C_{20} fraction. Yields of C_{30} and C_{40} fractions were to be maximized, as most desirable for PAO4 and 6.

Small-scale experiments, carried out in a batch of 120 cm^3 reactors, were conducted to elucidate the influence of the anion, the cation, and the reaction conditions on conversion and products distribution.

Influence of the anion. A set of four ionic liquids, of the general formula $[BCl_2(3pic)][M_nCl_{3n+1}]$ (M = Al or Ga, n = 1 or 2), were tested under fixed reaction conditions (0.62 mmol of catalyst per 40 cm^3 of 1-decene, 1 h, 100 °C). 3-Picoline was selected as the ligand, given that it produced liquid samples for all four compositions (*viz*. Table 2). Conversions and product distributions are tabularized in Table 3; to aid interpretation, product distributions are also visualized using a stacked bar graph (Figure 1).

Table 3 Conversions, product distribution and exotherms in $[BCl_2(3pic)][M_nCl_{3n+1}]$ catalyzed oligomerization, 0.62 mmol of catalyst, 1 h, 100 °C, M = Al or Ga, n = 1 or 2, compared to Lewis acidity of the borocation, expressed as AN (from ref 18).

Anion	Conversion (± 3 %)	C_{20} (± 4 %)	C_{30} (± 3 %)	C_{40} (± 2 %)	C_{50} (± 2 %)	C_{60} (± 1 %)	C_{70+} (± 1 %)	Exotherm (°C)	AN^{22}	$\delta\ ^{11}B^{22}$ (ppm)
$[AlCl_4]^-$	82	28	35	17	9	5	7	20	124	31
$[Al_2Cl_7]^-$	81	32	33	17	9	4	6	80	170	45
$[GaCl_4]^-$	53	49	29	10	5	4	4	8	121	26
$[Ga_2Cl_7]^-$	77	43	35	13	5	2	3	55	135	44

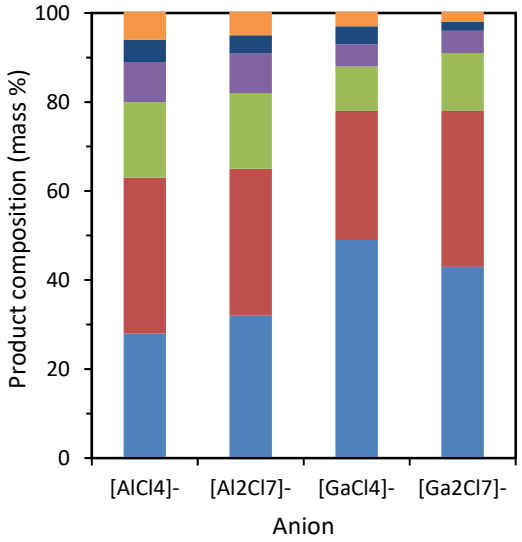


Figure 1: Product distribution from $[BCl_2(3pic)][M_nCl_{3n+1}]$ catalyzed oligomerization, 0.62 mmol of catalyst, 1 h, 100 °C, M = Al or Ga, n = 1 or 2 (blue = C_{20}, red = C_{30}, green = C_{40}, purple = C_{50}, navy = C_{60}, orange = C_{70+})

The exotherm generated by the interaction of Lewis acidic ionic liquids with adventitious water to generate Brønsted superacidic protons, was to a certain degree corresponding to both reported measures of Lewis acidity of borenium cations: AN values and ^{11}B NMR chemical shift (Table 3). However, Lewis acidity did not have a direct influence either on conversion, or selectivity to the C_{30}-C_{50} fractions (desired products). Both chloroaluminate anions gave virtually the same performance, with *ca*. 81% conversion and *ca*. 30% of dimer (C_{20}, which is too light for PAO4 or PAO6 production). Chlorogallate systems had overall worse performance, with $[BCl_2(3pic)][Ga_2Cl_7]$ giving lower conversion (77%) and more C_{20} (43%) than either of the

chloroaluminate ionic liquids, and even poorer performance when using $[BCl_2(3pic)][GaCl_4]$, with 53% conversion and 49% of C_{20}. In conclusion, borenium chloroaluminate ionic liquids perform better than chlorogallate ones. From preliminary data, there was little difference between the performance of $[BCl_2(3pic)][AlCl_4]$ and $[BCl_2(3pic)][Al_2Cl_7]$.

Influence of the cation. Ionic liquids with a variety of pyridine ligands (L) on the borenium cation, $[BCl_2L]^+$, combined with either chloroaluminate or chlorogallate anions, were screened (*viz*. Table 4 and Figure 2). Pyridine ligands were chosen because they are inexpensive (therefore present an industrially-viable option) and are already known to form borenium ionic liquids.[22] In order to have all catalysts in the liquid form at ambient conditions, only $[M_2Cl_7]^-$ anions were included in the screening.

Table 4: Conversion and product distribution achieved in $[BCl_2L][M_2Cl_7]$ catalyzed oligomerization, 0.62 mmol, 1 h, 100 °C.

Ligand	**Conversion (± 3 %)**	**C_{20} (± 4 %)**	**C_{30} (± 3 %)**	**C_{40} (± 2 %)**	**C_{50} (± 2 %)**	**C_{60} (± 1 %)**	**C_{70+} (± 1 %)**
M = Al							
py	85	29	32	19	11	5	4
2pic	76	31	34	18	9	4	5
3pic	81	32	33	17	9	4	6
4pic	86	32	33	18	9	4	4
M = Ga							
py	84	41	34	14	5	2	4
2pic	77	41	34	14	6	2	4
3pic	84	43	35	13	5	2	3
4pic	85	36	31	14	7	4	9

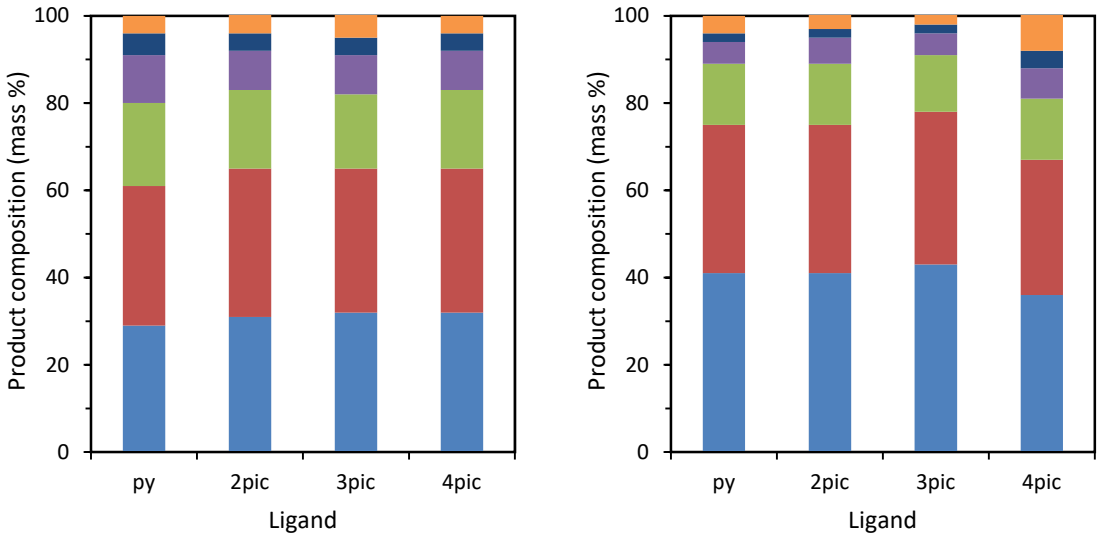


Figure 2: Product distribution from [$BCl_2(L)$][M_2Cl_7] catalyzed oligomerization, 0.62 mmol of catalyst, 1 h, 100 °C, (blue = C_{20}, red = C_{30}, green = C_{40}, purple = C_{50}, navy = C_{60}, orange = C_{70+}). M = Al (left) or Ga (right).

For the same cation, conversions achieved with $[Al_2Cl_7]^-$ and $[Ga_2Cl_7]^-$ anion were nearly identical, but ionic liquids with $[Ga_2Cl_7]^-$ produced shorter chains (more C20, less of the desired C30-C50 fraction and less heavies), indicating a greater rate of chain transfer with respect to propagation for the chlorogallate systems. This is in keeping with the anion influence screening (Table 2).

The presence and the position of the methyl group on the pyridine ligand had little effect upon the distribution of oligomers, discrepancies remaining within the error bars. However, conversion was consistently slightly lower for the $[BCl_2(2pic)]^+$ cation, when compared to other ligands. In contrast to other ligands used in this study, the methyl group in the 2-position with respect to the nitrogen is a source of steric hindrance, which may weaken the B-N bond and affect catalytic activity, but more mechanistic insight would be required to understand how this would translate to lowering the conversion.

Influence of the reaction temperature and catalyst loading. It is well-known that in the carbocationic polymerization of olefins, increase in reaction temperature results in decreased molecular weight of products (shorter chains are favored because the rate of termination processes is enhanced compared to propagation).[7] This trend has been observed in our earlier work using liquid coordination complexes (LCCs) as catalysts for the oligomerization of 1-decene.[21] The aim of this screening was to estimate the magnitude of this effect, and to study the influence of reaction temperature on conversion.

Firstly, a single catalyst, $[BCl_2(2pic)][Al_2Cl_7]$, was used at 0.62 mmol loading over a range of reaction temperatures, from 80 and 130 °C ((blue = C20, red = C30, green = C40, purple = C50, navy = C60, orange = C70+)

and Figure 3).

Table 5: Product distribution achieved during $[BCl_2(2pic)][Al_2Cl_7]$ catalyzed oligomerization, 0.62 mmol, 1 h

Temp (°C)	**Conversion (± 3 %)**	**C_{20} (± 4 %)**	**C_{30} (± 3 %)**	**C_{40} (± 2 %)**	**C_{50} (± 2 %)**	**C_{60} (± 1 %)**	**C_{70+} (± 1 %)**
130	79	39	30	14	9	4	5
120	77	37	32	15	8	5	3
110	77	33	32	16	11	5	3
100	76	31	34	18	9	4	5
90	80	25	32	18	13	6	6
80	80	22	31	19	13	8	8

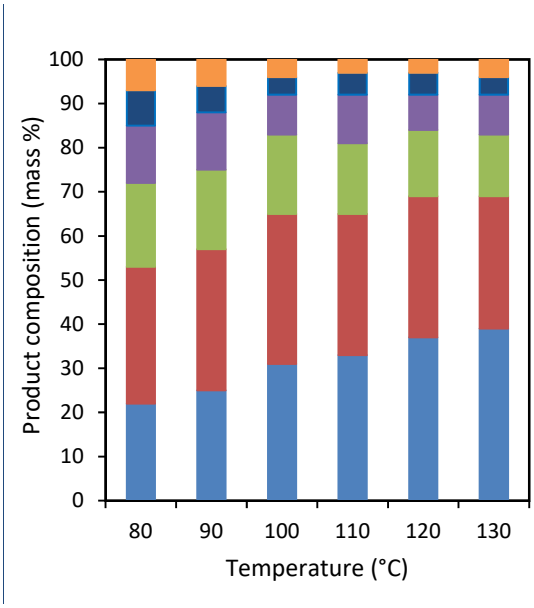


Figure 3: Product distribution from [BCl_2(2pic)][Al_2Cl_7] catalyzed oligomerization, 0.62 mmol of catalyst, 1 h, 100 °C, (blue = C_{20}, red = C_{30}, green = C_{40}, purple = C_{50}, navy = C_{60}, orange = C_{70+})

As expected, less dimer was produced at lower temperatures: its content deceased by 17%, from 39% at 130 °C to 22% at 80 °C. The proportion of C_{60+} fraction was constant for reaction temperatures of 100 °C and above, but increased notably for reactions carried out at 80 and 90 °C. From these preliminary results, the temperature of 100 °C appeared optimal, yielding relatively low proportion of both C20 (33%) and heavies (9%). Nevertheless, within the studied range, conversion appeared independent from the reaction temperature, reaching up to 80%, therefore falling short of the desired +90% mark. As such, the catalyst amount was raised from 0.62 mmol to 1.24 mmol to increase conversion. Furthermore, since [BCl_2(2pic)][Al_2Cl_7] was found to give the lowest conversions among ionic liquids that were screened here (Table 4), two other systems: [BCl_2(4pic)][Al_2Cl_7] and [BCl_2(py)][Al_2Cl_7], were used in further experiments. The studied temperature range was shifted slightly towards lower temperatures, 60-120 °C for [BCl_2(py)][Al_2Cl_7], and further reduced to 60-100 °C for [BCl_2(4pic)][Al_2Cl_7], focusing on the range that gave low C_{20} proportion and high conversion (Figure 4 and Table 6).

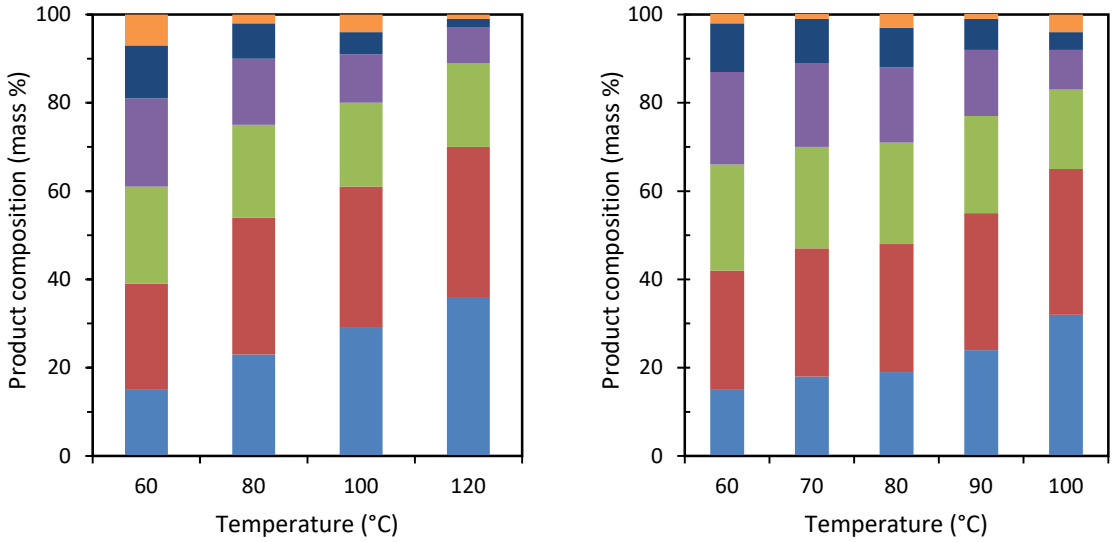


Figure 4: Product distribution from [$BCl_2(L)$][Al_2Cl_7] catalyzed oligomerization, 1.24 mmol of catalyst, 1 h, 100 °C, (blue = C_{20}, red = C_{30}, green = C_{40}, purple = C_{50}, navy = C_{60}, orange = C_{70+}). L = py (left) and 4pic (right).

Table 6: Conversions and product distributions achieved in [$BCl_2(L)$][Al_2Cl_7] catalyzed oligomerization, where L = py or 4pic, 1.24 mmol, 1 h, 100 °C

Temp (°C)	**Conversion (± 3 %)**	**C_{20} (± 4 %)**	**C_{30} (± 3 %)**	**C_{40} (± 2 %)**	**C_{50} (± 2 %)**	**C_{60} (± 1 %)**	**C_{70+} (± 1 %)**
L = py							
120	86	36	34	19	8	2	1
100	85	29	32	19	11	5	4
80	85	23	30	21	15	8	2
60	94	15	23	22	20	12	7
L = 4pic							
100	86	32	33	18	9	4	4
90	88	24	31	22	15	7	2
80	89	19	29	23	17	9	4
70	95	18	29	23	19	10	2
60	96	15	27	24	21	11	3

Increase in catalyst loading gave higher conversion, which increased up to 95% at lower reaction temperatures (60 and 70 °C), for both [BCl_2(py)][Al_2Cl_7] and [BCl_2(4pic)][Al_2Cl_7] (Table 6). At the same time, there was no noticeable change in products distribution: for example, reactions at 100 °C, irrespective of the catalyst used or its loading, yielded 29-32% of C_{20} and 8-9% of the C_{60+} fraction (*viz*. relevant data in (blue = C20, red = C30, green = C40, purple = C50, navy = C60, orange = C70+)

and Table 6). As such, increasing the catalyst loading and manipulating the reaction temperature offered a promising strategy.

Less dimer and more heavy oligomers were produced with decreasing temperature, as expected (Figure 4). For $[BCl_2(py)][Al_2Cl_7]$, there was a significant drop in C_{20} content with decreasing temperature, from 36% at 120 °C to 15% at 60 °C, but offset by increase in the heavy fraction, from only 3% at 120 °C to as high as 19% at 60 °C. Similar results were achieved with $[BCl_2(4pic)][Al_2Cl_7]$, also reaching 15% of C20 at 60 °C, but with only 14% of the C_{60+} fraction generated at that temperature. These results were found to be promising enough to motivate larger-scale lab tests, producing oligomers in a 5 L batch reactor. This quantity of sample is suitable for fractionated distillation and subsequent blending to achieve proportion of oligomers that have the potential of meeting market specification: in this work, the targets were PAO4 and 6.

Large-scale oligomerization of 1-decene

Screening reactions as a function of catalyst and reaction temperature. Scaled up reactions were performed in a 5 L batch HEL reactor, with a jacketed glass vessel, a Teflon-coated overhead stirrer and a refrigerated/heating circulator Julabo FP35. The amount of feedstock was increased to 3 L, rendering the effects of thermal runaway potentially much more dangerous. As such, the first reactions were performed with 0.25 wt% of catalyst (which was a quarter of the wt% used for the small-scale reactions). Furthermore, the catalyst was added drop-wise using a syringe pump. As expected, this reduced catalyst loading resulted in conversion drop to <70% (representative data sets are listed in Table 7). Once safe pace of addition was established, the catalyst loading was increased to 1.25 wt%, which brought the conversion back up to *ca*. 85%.

Table 7: Conversions and product distributions achieved in $[BCl_2(L)][Al_2Cl_7]$ catalyzed oligomerization, 1 h

Catalyst	Temp. (°C)	Loading (wt %)	Convers. (± 3 %)	C_{20} (± 4 %)	C_{30} (± 3 %)	C_{40} (± 2 %)	C_{50} (± 2 %)	C_{60} (± 1 %)	C_{70+} (± 1 %)
$[BCl_2(4pic)][Al_2Cl_7]$	100	0.25	69	51	32	13	3	2	0
$[BCl_2(2pic)][Al_2Cl_7]$	100	0.25	66	50	31	12	3	2	2
$[BCl_2(2pic)][Al_2Cl_7]$	100	0.25	69	51	32	13	3	2	0
$[BCl_2(py)][Al_2Cl_7]$	100	1.25	83	40	36	18	6	0	0
$[BCl_2(py)][Al_2Cl_7]$	80	1.25	86	34	33	19	10	3	1
$[BCl_2(4pic)][Al_2Cl_7]$	80	1.25	86	34	28	17	10	5	6
$[BCl_2(py)][Al_2Cl_7]$	60	1.25	86	22	33	22	16	6	1

In general, large-scale reactions gave fewer heavy oligomers than small-scale experiments carried out at the same temperature. It is known that branching and products distribution are sensitive to the amount of adventitious water (as the proton source) that is present in the system, and increase in reactor size will reduce proportion of adventitious water in the system, which may be the source of improved product distribution in this case. In contrast to small-scale experiments, large-scale screening at 80 °C gave improved selectivity for $[BCl_2(py)][Al_2Cl_7]$, when compared to $[BCl_2(4pic)][Al_2Cl_7]$, both generating the same conversion and C_{20} loading, but the former producing more heavy oligomers. Reactions with $[BCl_2(py)][Al_2Cl_7]$ were then carried out at 60 and 100 °C, confirming that it yields consistently low heavy fraction.

Potential for catalyst recycling. Throughout this work, after given reaction time the reaction mixtures were quenched with water, which resulted in hydrolysis of the catalyst. The quenching procedure is used in most industrial PAO plants, using BF_3 catalyst. However, in certain refinery alkylation processes (IONIKYLATION, ISOALKY), where Lewis acidic ionic liquids have been piloted and are about to be used commercially, they are being purified and recycled, rather than hydrolysed.[15] This offers hope for borenium ionic liquids used in this work to be potentially recycled in a cost-efficient manner; however, such purification and recycling process requires a separate study, which is outside of the scope of this work.

Preparation of base oil samples. Prior to distillation of the large-scale samples, reaction mixtures were dried using magnesium sulfate. Base oil samples were produced by the removal of the decene and then of C_{20} by distillation under reduced pressure, and subsequent distillation of C_{30} and C_{30}-C_{40} fractions, leaving C_{50+} residue. These were blended to give samples of PAO4 and PAO6, following proportions suggested by commercial Group 4 base oils, such as Durasyn PAOs manufactured by INEOS in a commercial BF_3-catalysed process, which were used as a benchmark in this work.

Key physical properties tested for blended samples were: kinematic viscosity at 40 and 100 °C (Kv_{40} and Kv_{100}), which were used to derive viscosity index (VI) and pour point (PP). To match market specification, PP must be below -40 °C, and preferably < -60 °C. VI must be at least 120, and as high as possible. Finally, the values of Kv_{100} must closely match 4 cSt for PAO4 and 6 cSt for PAO6. It is also important for samples to be colourless; any color is typically removed along with double bond presence through hydrogenation. Since there is a small risk of worsening PP during hydrogenation, it is important to test representative PAOs after hydrogenation, to assess any changes in physical properties.

The first rather surprising finding was that, in large-scale experiments, PAOs produced using $[BCl_2(py)][Al_2Cl_7]$ precipitated a fine white powder after >24 h. The product, identified as boric acid, was possible to remove by repeated high-temperature water washing, but not by filtration. Furthermore, these PAOs were found to have exceptionally low VIs, consistently below 100 units. In consequence, these PAOs have not been tested for further physical properties.

Representative results for several blends of PAO4 and 6, produced using $[BCl_2(2pic)][Al_2Cl_7]$ and $[BCl_2(4pic)][Al_2Cl_7]$, are listed in Table 8, and compared to benchmark products. These two

catalysts yielded VI>120 and low pour points (-57 °C for the hydrogenated samples), matching commercial requirements.

Table 8: Composition and physical properties of PAO samples produced using borenium ionic liquids, LCCs and compared to commercial PAO samples

Catalyst	Temperature (°C)	KV100 (cSt)	KV40 (cSt)	VI	PP (°C)	C_{30} (%)	C_{40} (%)	C_{50+} (%)
PAO6 blends								
$[BCl_2(2pic)][Al_2Cl_7]$	100	6.18	33.35	136	< -60	39	36	25
$[BCl_2(2pic)][Al_2Cl_7]$[a]	100	6.45	35.30	137	-57	39	36	25
$[BCl_2(4pic)][Al_2Cl_7]$	80	5.88	32.40	127	< -60	37	39	24
$[BCl_2(4pic)][Al_2Cl_7]$[a]	80	6.22	35.50	122	-57	37	39	24
Ur-$AlCl_3$ (χ_{AlCl3} = 0.60)[21]	120	5.79	31.46	126	< -60	42	63	22
Durasyn PAO6	-	5.76	30.22	135	-57	37	42	21
PAO4 blends								
$[BCl_2(2pic)][Al_2Cl_7]$	100	4.23	18.87	132	< -60	80	14	6
$[BCl_2(4pic)][Al_2Cl_7]$	80	3.95	17.34	125	< -60	76	15	9
Durasyn PAO 4	-	3.92	17.25	137	< -60	80	19	1
Ur-$AlCl_3$ (χ_{AlCl3} = 0.60)[21]	100	4.31	20.08	124	< -60	77	16	7

[a] Samples after hydrogenation

Branching. In order to understand the performance differences between borenium ionic liquids bearing pyridine or picoline ligands, a quick method to compare the degree of branching was used. VI is related to degrees of chain branching, and chain branching originates from double bond migration/isomerization. The degree of branching can be approximated from ^{1}H NMR spectroscopy, because linear alpha olefins have distinctive spectra with two multiplets at *ca*. 5.8 and 4.9 ppm, in a 1:2 ratio, whereas internal olefins have a multiplet at *ca.* 5.4 ppm. Thus, the degree of isomerization can be approximated by the 5.8 to 5.4 ppm signal ratio. The largest percentage of double bonds to the alkyl chain was expected in decene fraction, recovered after the oligomerization process. ^{1}H NMR spectra of decene fractions recovered post-oligomerization, carried out with different catalysts, at different loadings and temperatures, are shown in Table 9.

Table 9. Ratio of isomerized to linear decene present in decene fraction recovered from selected post-reaction mixtures, using a range of borenium catalysts, at various loadings and temperatures.

Catalyst	Catalyst (wt %)	Temperature of reaction (°C)	Conversion (%)	5.8ppm : 5.4ppm Peak Ratio
Feedstock (virgin)	-	-	-	33:1
$[BCl_2(2pic)][Al_2Cl_7]$	1	100	79	1 : 21
$[BCl_2(4pic)][Al_2Cl_7]$	1	100	86	1 : 6

[BCl_2(py)][Al_2Cl_7]	1	100	85	1 : 95
[BCl_2(py)][Al_2Cl_7]	2	80	85	1 : 84
[BCl_2(py)][Al_2Cl_7]	2	60	96	1 : 33

In all post-reaction decene fractions, there was a significant degree of double bond isomerization, but the result was largely dependent on both the catalyst and the reaction temperature. Using [BCl_2(py)][Al_2Cl_7] resulted in a much higher degree of double bond isomerization in the residual decene, compared to the other two catalysts, and lower temperature aided to decrease branching. It is apparent that relatively small modification to the *N*-donor ligand, that is the presence and position of the methyl substituent, have quite significant influence on the physical properties of the products. It is unclear at this stage why using pyridine results in high branching and in the presence of boric acid in the product, and why using 4pic gives significantly lower branching than either of the other ligands. Elucidating this will require in-depth mechanistic studies, combining *in operando* spectroscopic techniques and computer modeling. However, these results bear promise of impressive tuneability of the product properties by altering the reaction temperature and the ligand on the borenium cation.

The same samples were also studied using ^{11}B and ^{13}C NMR spectroscopy. Whereas ^{13}C spectra offered no additional insight into structural differences between PAO samples, it has been impossible to detect any ^{11}B signals, suggesting that boron has not been incorporated in the PAO product (at least not within the detection limit of ^{11}B NMR spectroscopy).

Conclusions

Through this work, we demonstrate the potential of non-volatile, fluoride-free borenium ionic liquid to replace BF_3 (toxic and corrosive gas), as a safer catalyst for PAO syntheses, capable of delivering the same yield and quality of low-viscosity lubricant base oil grades (PAO4 and 6).

Borenium ionic liquids of the general formula $[BCl_2(L)][M_2Cl_7]$ (M = Ga, Al), were shown to be effective 1-decene oligomerization catalysts, and a possible alternative to BF_3/*n*BuOH catalyzed 1-decene oligomerization. They were successfully employed on a 3 L scale to produce 1-decene oligomers which, were fractionated and blended to give PAO 4 and PAO 6 matching commercial specifications. Increase in reaction scale from 40 mL to 3 L had significant effect on product distribution and properties, which was expected for carbocationic oligomerization. Hydrogenation of selected blended PAO6 samples was shown to slightly increase the viscosity and the pour point, but all parameters remained within specifications, and these changes could be taken into consideration in future blending exercises. Temperature and ligand choice had large influence on the quality of PAOs; methypyridines produced samples with VI>120, but pyridine did not, which was apparent only from large-scale experiments. This opens up the potential for further optimization, based on modifying ligands on the boron center. Considering complicated mechanism of carbocationic oligomerisation, in-depth understanding on the relationship between the ligand and the reaction outcome calls for a separate mechanistic study. Finally, since all components of borenium ionic liquids are inexpensive, off-the-shelf reactants, and the catalyst can be synthesized through a one-pot process, it presents itself as an economically-viable alternative to BF_3. Furthermore, very significant CAPEX (capital expenditure) savings are expected from switching from toxic gas to an ionic liquid, in analogy to the ISOALKY process by Chevron, where HF was replaced by a Lewis acidic ionic liquid.[15]

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Supporting Information

Detailed synthetic procedure for borenium ionic liquids, ^{1}H and ^{11}B NMR spectra of the products

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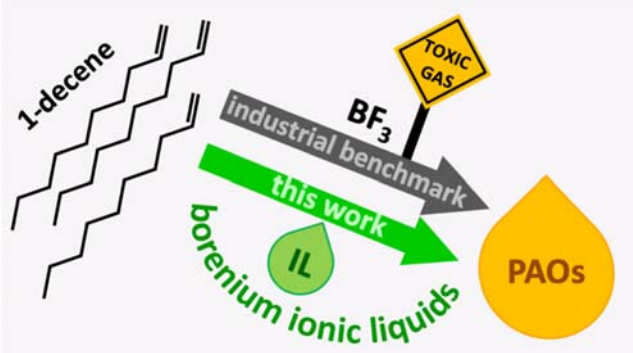
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Non-volatile, fluoride-free borenium ionic can replace BF_3 (toxic and corrosive gas) as a safer catalyst for the syntheses of low-viscosity polyalphaolefins.