

# Green Chemistry

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## ARTICLE

# Liquid coordination complexes: a new class of Lewis acids as safer alternatives to $\text{BF}_3$ in synthesis of polyalphaolefins

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

James M. Hogg, Fergal Coleman, Albert Ferrer-Ugalde, Martin P. Atkins and Małgorzata Swadźba-Kwaśny\*

Liquid coordination complexes (LCCs) are a new class of liquid Lewis acids, prepared by combining excess of a metal halide (e.g.  $\text{GaCl}_3$ ) with a basic donor molecule (e.g. amides, amines or phosphines). LCCs were used to catalyse oligomerisation of 1-decene to polyalphaolefins (PAOs). Molecular weight distribution and physical properties of the produced oils were compliant with those required for low viscosity synthetic (Group IV) lubricant base oils. Kinematic viscosities at 100 °C of ca. 4 or 6 cSt were obtained, along with viscosity indexes above 120 and pour points below -57 °C. To achieve such physical properties, PAOs are commercially produced using  $\text{BF}_3$  gas as a catalyst. LCCs are proposed as a safer and economically attractive alternative to  $\text{BF}_3$  gas for the production of polyalphaolefins.

## Introduction

### Polyalphaolefins

Polyalphaolefins (PAOs) are oligomers of higher  $\alpha$ -olefins, predominantly of 1-decene. They are used as base stock oils for synthetic (Group IV) lubricants, destined mainly for automotive and industrial applications.<sup>1,2</sup> PAOs are commonly considered to have superior properties compared to mineral (Group I-III) base stocks,<sup>3,4</sup> allowing for formulation of high-performance engine oils, e.g. low-viscosity automotive oils, which can yield >2% fuel savings. PAOs are classified and marketed depending on their kinematic viscosity at 100 °C,  $K_{V100}$ , which has to fall within a specific bracket for each PAO grade.<sup>5</sup> Furthermore, they are required to have excellent thermal properties. They must have a viscosity index (VI) value of at least 120, which indicates small changes in viscosity as a function of temperature. In addition, pour points (PP) must be below -40 °C, ensuring that PAOs flow at extremely low temperatures. Finally, they must be characterised by low volatility and high oxidative stability.<sup>4</sup>

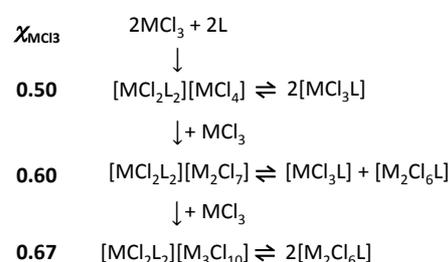
There is a strong relationship between molecular structure of PAOs and their physical properties.<sup>6,7</sup> Linear oligomers have high VI (desired), but also high pour point (undesired in many applications); increase in chain branching decreases both the VI and PP. Achieving optimum physical properties requires a finely-tuned catalyst and reaction conditions during PAO synthesis, followed by fractionated distillation, blending and formulation with additives.

The catalytic syntheses of PAOs have been expertly discussed by Ray *et al.*<sup>4</sup> Boron trifluoride, promoted with water,

alcohol or acids, is the only known catalyst used commercially to produce low viscosity PAOs ( $K_{V100} = 4$  cSt or 6 cSt), characterised by moderately high VI > 120 and low pour points (as low as -66 °C). In contrast,  $\text{AlCl}_3$  and  $\text{EtAlCl}_2$ , typically promoted with water or alcohols, give heavier products of very high  $K_{V100}$  (> 40 cSt), with VI > 130 and PP > -42 °C. Similar results were obtained when chloroaluminate ionic liquids, [cation][ $\text{Al}_2\text{Cl}_7$ ], were used as catalysts. Lighter products were obtained using chlorogallate(III) ionic liquids,<sup>8</sup> but no physical properties have been reported. Among other catalysts, those based on low-valent chromium,  $\text{TiCl}_4$  or Zr-based metallocenes promote the formation of highly linear PAOs with high viscosities and VIs,<sup>4</sup> whilst solid Brønsted acids (e.g. zeolites) yield very light products.<sup>9</sup>

### Liquid coordination complexes (LCCs)

LCCs are a new class of liquid Lewis acid, comprising of equilibrated cationic, anionic and neutral coordination complexes (Scheme 1).<sup>10</sup>



Scheme 1. Main equilibria in LCCs, inferred from spectroscopic studies for the key compositions ( $\text{M} = \text{Al}^{\text{III}}$  or  $\text{Ga}^{\text{III}}$ ,  $\chi_{\text{MCl}_3}$  – mol fraction of metal chloride in LCC).<sup>10</sup>

LCCs are prepared by a one-step, solventless reaction of a simple donor molecule with an anhydrous metal halide, typically with the metal halide in excess. Donor molecules may include *O*-, *N*-, *S*- or *P*-donors, such as ureas,<sup>11</sup> thioureas, trialkylphosphines, trialkylphosphine oxides or some amines; metal is typically, but not exclusively, Al<sup>III</sup> or Ga<sup>III</sup>. The mol fraction of metal halide to neutral ligand in an LCC, of metal halide in an LCC,  $\chi_{\text{MCl}_3}$ , is of key importance: LCCs with  $\chi_{\text{MCl}_3} = 0.50$  are considered neutral, as they do not contain oligonuclear, Lewis acidic anions,  $[\text{M}_x\text{Cl}_{(3x+1)}]$ . Compositions where  $\chi_{\text{MCl}_3} > 0.50$  have been shown to be Lewis acidic,<sup>10</sup> as they contain oligonuclear anions, which readily react with bases following Eqn 1.



LCCs are promising Lewis acidic catalysts in industrial applications; they combine ease of preparation, low price, and high Lewis acidity. Gutmann Acceptor Numbers (AN, a quantitative measure of Lewis acidity) reported for some LCCs (AN = *ca.* 102)<sup>10</sup> were slightly higher than values in chloroaluminate(III) ionic liquids (AN = *ca.* 96).<sup>12</sup> Moreover, certain donor-AlCl<sub>3</sub> mixtures have already been demonstrated to act as Lewis acidic catalysts: dimethylformamide-AlCl<sub>3</sub> and tetrahydrofuran-AlCl<sub>3</sub> were reported to catalyse Friedel-Crafts alkylation<sup>13</sup> and Diels-Alder cycloaddition,<sup>14</sup> respectively.

#### Rationale for this work

The physical properties of PAOs depend strongly on the catalyst used in their synthesis; to date, boron trifluoride has been the only industrially viable catalyst yielding low viscosity PAOs. BF<sub>3</sub> is a colourless, toxic gas (classified as poisonous gas) and pulmonary irritant.<sup>15</sup> In contact with moisture it hydrolyses to release HF, which in turn dissolves in water to form hydrofluoric acid. Hydrofluoric acid is an acute poison, able to permeate human/animal tissue and react with Ca<sup>2+</sup>/Mg<sup>2+</sup> ions to form fluorides, potentially causing cardiac arrest and tissue poisoning leading to death.<sup>16</sup>

In contrast, LCCs are non-volatile liquids, which do not contain fluorine. Furthermore, they are easier to handle, less expensive, and versatile in terms of structure. In this work, LCCs were tested as a safer and economically viable alternative to BF<sub>3</sub> in the oligomerisation of 1-decene to polyalphaolefins.

## Experimental

#### Purification of starting materials

Unless otherwise mentioned, all chemicals were purchased from Sigma-Aldrich. 1-Decene, +96%, was sourced from both AlfaAesar and Sigma-Aldrich and used as received. Trioctylphosphine, trihexyl(tetradecyl)phosphonium chloride and tetrabutylphosphonium chloride were provided by Cytec Industries. 1-Ethyl-3-methylimidazolium chloride<sup>17</sup> and 1-octyl-3-methylimidazolium chloride<sup>18</sup> were synthesised as described in the literature.

Trioctylphosphine, supplied in an air-tight gas cylinder, was used as received. Urea, thiourea, acetamide and trioctylphosphine oxide were dried under reduced pressure (overnight, 80 °C, 10<sup>-2</sup> mbar) and stored in the glovebox (MBraun labmaster dp, <0.3 ppm of H<sub>2</sub>O and O<sub>2</sub>). Octanenitrile was dried over 3 Å molecular sieves and stored under argon. Dimethylacetamide was stirred with calcium hydride (1 h), distilled under reduced pressure and stored under argon.

For small-scale experiments, anhydrous metal chlorides were purchased: AlCl<sub>3</sub>, 99.99%; GaCl<sub>3</sub>, 99.999%, both packed in ampoules under argon. The ampoules were opened in a glovebox and used as received. For scale-up experiments, aluminium(III) chloride, 98% anhydrous, was doubly sublimed, transferred to glovebox and stored there.

In a typical sublimation procedure, aluminium(III) chloride, dry sodium chloride and aluminium wire (each at 2.5 wt % per mass of AlCl<sub>3</sub>) were, in the glovebox, transferred into a round-bottomed flask. The flask was then fitted with a condenser, removed from the glovebox and placed on a hotplate. The sublimation was carried out under a flow of nitrogen (190 °C, 2 h). The setup was cooled, closed with a stopper and transferred to the glove box. Sublimed AlCl<sub>3</sub> (off-white solid) was crushed using a mortar and pestle and the process was repeated to obtain white doubly-sublimed aluminium chloride.

#### Synthesis of liquid coordination complexes (LCCs)

LCCs were prepared in the glovebox. Donor was added slowly, in small portions, with stirring, to metal(III) chloride. Heat was evolved. Afterwards, the mixture was stirred (0.5-24 h, 30-80 °C) to complete the reaction. All LCCs were stored in the glovebox until used.

#### Synthesis of chloroaluminate(III) ionic liquids

Chloroaluminate(III) ionic liquids were prepared in the glovebox. Aluminium(III) chloride (2 mol eq.) was added slowly, in small portions, with stirring, to organic chloride salt (1 mol eq.). Heat was evolved. Afterwards, the mixture was stirred (0.5-24 h, 60 °C) to complete the reaction. All ionic liquids were stored in the glovebox until used.

#### Oligomerisation – small scale

Experiments were carried out in a battery of eight glass computer-controlled H.E.L. reactors (120 cm<sup>3</sup>) designed for high corrosion resistance.

The reactor vessels and stirrer propellers were dried overnight in an oven, and then cooled in a desiccator, over phosphorus(V) oxide. The remaining parts were dried with a heat gun, and the reactors were assembled. The feedstock (1-decene, dry by Karl-Fisher analysis) was poured into the reactors and stirred vigorously (600 rpm) at the reaction temperature, whilst the reactors were purged with dry argon.

The LCC catalyst was loaded, in the glovebox, into a dry gas-tight syringe. The tip of the needle was sealed, the loaded syringe was removed from the glovebox and immediately plunged through a septum into the reactor. The catalyst addition to the vigorously stirred feedstock, equilibrated at the reaction

temperature, was carried out drop-wise, as fast as possible without thermal runaway.

After a given reaction time, the reaction was quenched by stirring with deionised water (600 rpm, 10 min, ambient temperature) and centrifuged to enhance phase separation. All products were analysed using SimDist GC.

### Oligomerisation – scale-up

Scale-up reactions were carried out in a computer-controlled glass H.E.L. reactor (5 L). The reactor was dried (60 °C, 30 min, 10<sup>-2</sup> mbar) and then 1-decene was added under positive pressure of argon; the remaining air was purged by the flow of argon. Subsequently, vigorously stirred (500 rpm) 1-decene was equilibrated at the reaction temperature.

The LCC catalyst (0.25-3.00 wt % per mass of the feedstock) was loaded into a dry syringe as described for the small-scale oligomerisation. The catalyst was added using a syringe pump (>0.2 cm<sup>3</sup> min<sup>-1</sup>), slow enough to prevent thermal runaway. 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 deionised water (3 x 1 L). Each batch was analysed using SimDist GC.

### Simulated Distillation GC (SimDist GC)

Samples for SimDist GC analysis were dissolved in toluene (100 mg cm<sup>-3</sup>), dried over magnesium sulfate, filtered and analysed according to ASTM D6352. The analysis were carried out using Agilent 6890N GC, equipped with an FID detector and a high-performance HT PTV (high-temperature programmable temperature vaporising) inlet with optimized design for SIMDIS applications. Column: Agilent J&W DB-HT Sim Dis Column.

### Fractionated distillation

Fractionated distillation was carried out in a computer-controlled Distilab D5236 Crude Oil Distillation System with 6 L boiling flask, according to ASTM D5236.

In a typical procedure, the distillation rig was dried prior to use (1 mmHg, 30 min). A sample (2 to 4 L) was dried over MgSO<sub>4</sub>, filtered and loaded into the boiling flask. The conditions required to remove each fraction were programmed into the software; the expected mass of each fraction was predicted from SimDist GC. Firstly, the decene fraction was removed (10 mmHg, vigorous stirring) at a carefully controlled heating rate. After the decene removal and cooling of the apparatus, the dimer (C<sub>20</sub>) fraction was distilled (0.1 mmHg, vigorous stirring). Then, the distillation rig was cleaned with toluene to prevent contamination of subsequent fractions and higher oligomers (mainly the trimer, C<sub>30</sub>) were fractionally distilled (0.1 mmHg) to obtain PAO6. A minimum of 0.4 L (the heaviest fraction) was left in the boiling flask as residue.

All fractions and the residue were analysed using SimDist GC. After blending, pour point, K<sub>v40</sub> and K<sub>v100</sub> were measured, and VI was calculated.

### Physical properties tests

**POUR POINT** was measured according to ASTM D97-11. 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).

**KINEMATIC VISCOSITY (Kv)** was measured according to ASTM D445 – 11a. The measurements were performed at 40 and 100 °C using the appropriate Cannon-Fenske kinematic viscosity glassware and a dedicated, precisely-controlled heating bath. Kv was found by timing the gravitational flow of the sample through a capillary; temperature was maintained using a high-accuracy heating bath.

**VISCOSITY INDEX (VI)** was calculated according to Eqn (2), where L and H are constants based on K<sub>v100</sub>, tabularised in ASTM 2270.

$$VI = 100(L - K_{v40})(L-H)^{-1} \quad (2)$$

## Results and discussion

### Synthesis and properties of LCCs

LCCs used in this work were based on aluminium(III) chloride or gallium(III) chloride, and on a range of ligands, listed with abbreviations in Table 1.

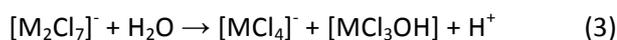
Table 1. Abbreviations and systematic of donor molecules used in this work

L	name
P <sub>888</sub>	trioctylphosphine
P <sub>888</sub> O	trioctylphosphine oxide
Ur	urea
SUr	thiourea
AcA	acetamide
DMA	dimethylacetamide
C <sub>7</sub> CN	octanenitryl

Ligands were selected from off-the-shelf chemicals, and represented a selection of donor atoms (*O*, *S*, *P* and *N*-donors) and different affinity to olefins (from urea to trioctylphosphine). Noteworthy, in all cases miscibility of LCCs and olefins was limited, and biphasic mixtures were formed.

In selecting the metal halide to ligand ratio,  $\chi_{MCl_3}$ , care was taken to form mobile liquids. LCCs based on AlCl<sub>3</sub> formed homogenous liquids around  $\chi_{AlCl_3} = 0.60$ .<sup>10</sup> Some LCCs based on GaCl<sub>3</sub> were liquid within a wide compositional range ( $\chi_{GaCl_3} = 0.50$  to 0.75), but to ensure all GaCl<sub>3</sub>-based LCCs being liquid, the composition of  $\chi_{GaCl_3} = 0.67$  was required. The C<sub>7</sub>CN-AlCl<sub>3</sub> combination did not form a homogenous liquid and hence wasn't further studied.

As a consequence of their high Lewis acidity, LCCs are hydrolytically unstable, which makes them active catalysts in carbocationic processes. In oligomerisation of olefins, LCCs react with adventitious water in the system (Eqn 3), and generates a Brønsted superacidic proton, which reacts with an olefin to form a carbocation.



### Distribution of oligomers in commercial PAO samples

Figure 1 depicts SimDist GC analysis of commercial PAO4 and PAO6 samples. Oligomers of 1-decene,  $C_n$  ( $n$  - number of carbons in the alkyl chain) are easily identifiable in the chromatograms (Figure 1a). Starting material (C10) or dimers (C20) are absent in either chromatogram. PAO4 contains mainly the trimer (C30), with small amounts of tetramer (C40), whereas PAO6 contains similar quantities of C30 and C40, with significant amounts of pentamer (C50) and some hexamers and heavier oligomers (C60 and C70+).

The amount of each fraction in SimDist chromatogram can be precisely quantified. The chromatograms can be processed

into simulated distillation curves (Figure 1b), where the mass percentage of hydrocarbon fractions in the sample is plotted against their boiling points. This allows for the construction of Figure 1c, where distribution of oligomers can be plotted as a function of a selected factor (here, PAO grade).

From analysis of the commercial PAO samples, it transpires that, to maximise PAO yield, high yields of C30 and C40 fractions are desired. Some heavier oligomers are needed for PAO6, but excessive amount would detrimentally affect pour point, hence must be avoided. Monomer and C20 can be recycled, but recycling of large volumes may not be economically viable.

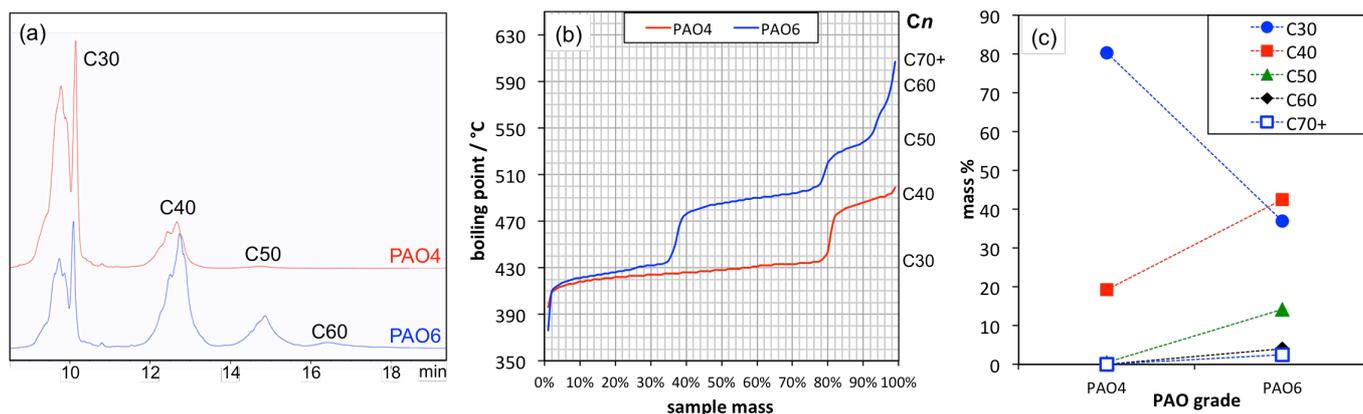


Figure 1. SimDist GC analysis of commercial PAO samples: (a) chromatograms, (b) simulated distillation curves, and (c) distribution of oligomer fractions as a function of PAO grade. Dashed lines in graph (c) are only guidelines for the eye.

### Small-scale screening

The carbocationic mechanism relies on traces of adventitious water for carbocation generation; consequently, the variation in the amount of adventitious water is the main source of variation in the results. It is therefore essential to rigorously maintain consistent experimental procedure, and to assess the error before drawing any conclusions based on gathered data. Moreover, experimental error is inversely proportional to the scale of reaction; hence, error estimation was of particular importance in small-scale studies.

**ERROR ESTIMATION.** Ideally, all experiments should be carried out in several replicates; however, considering the large number of experiments in this work, this would not be practical. Instead of repeating all experiments, two model oligomerisation reactions: with  $Ur-AlCl_3$ ,  $\chi_{AlCl_3} = 0.60$ , and with  $Ur-GaCl_3$ ,  $\chi_{GaCl_3} = 0.67$ , were carried out in several replicates. Two different batches of each catalyst were used. Conversions and products distribution for each run, with calculated standard deviations, are shown in Table 2. The higher of the two standard deviations calculated for each fraction, rounded to the nearest integer, was assumed as error for this fraction in subsequent experiments.

Table 2. Conversions and oligomer distributions, obtained using two LCCs (120 °C, 1 h, 1 wt % of LCC). Values measured for each reaction replicate are given, along with calculated averages and standard deviations.

no.	conversion (%)	product distribution (%)					
		C20	C30	C40	C50	C60	C70+
$Ur-GaCl_3$ , $\chi_{GaCl_3} = 0.67$							
1	74	40	35.9	13.8	6.9	2.8	0.7
2	72	33	35.5	17.0	8.5	4.3	2.1
3	76	32	34.4	17.2	10.6	4.0	2.0
4	72	32	35.0	16.8	9.8	4.2	2.1
<i>aver</i>	<b>74</b>	<b>34</b>	<b>35.2</b>	<b>16.2</b>	<b>9.0</b>	<b>3.8</b>	<b>1.7</b>
<i>st dev</i>	<b>2</b>	<b>4</b>	<b>0.6</b>	<b>1.6</b>	<b>1.6</b>	<b>0.7</b>	<b>0.7</b>
$Ur-AlCl_3$ , $\chi_{AlCl_3} = 0.60$							
1	78.5	35	37	15.5	5.2	5.2	2.0
2	80.5	30	37	17.6	8.8	3.8	3.1
3	77.5	38	34	15.7	7.8	2.6	2.0
4	78.5	37	30	14.2	9.0	5.2	4.5
5	78.5	36	31	16.8	9.0	3.9	3.2
<i>aver</i>	<b>78.7</b>	<b>35</b>	<b>34</b>	<b>16.0</b>	<b>8.0</b>	<b>4.1</b>	<b>3.0</b>
<i>st dev</i>	<b>1.1</b>	<b>3</b>	<b>3</b>	<b>1.3</b>	<b>1.7</b>	<b>1.0</b>	<b>1.0</b>
<b>error assumed for all experiments (%)</b>							
	<b>±2</b>	<b>±4</b>	<b>±3</b>	<b>±2</b>	<b>±2</b>	<b>±1</b>	<b>±1</b>

**INFLUENCE OF THE CATALYST** was investigated by varying the metal halide, the ligand, and their molar ratio ( $\chi_{MCl_3}$ ), in catalysts used for oligomerisation of 1-decene under identical conditions.

The influence of the  $\chi_{MCl_3}$  value on conversion and products distribution could be studied only for selected  $Ga^{III}$ -based

systems, which were liquid for a wide range of  $\chi_{\text{GaCl}_3}$  values. The DMA-GaCl<sub>3</sub> system, at four compositions:  $\chi_{\text{GaCl}_3} = 0.50, 0.60, 0.67$  and  $0.75$ , was investigated. In each reaction, equal amounts of GaCl<sub>3</sub> equivalent (1.707 mmol) were used. The results are compared in Table 3 and, to facilitate the analysis, product distributions for successful experiments are plotted against  $\chi_{\text{GaCl}_3}$  in Figure 2.

In a control experiment with the neutral composition,  $\chi_{\text{GaCl}_3} = 0.50$ , no conversion of 1-decene was observed, as anticipated. For Lewis acidic compositions, conversion obtained for compositions,  $\chi_{\text{GaCl}_3} = 0.60$  and  $0.67$ , was the same within experimental error, but for the composition of highest acidity ( $\chi_{\text{GaCl}_3} = 0.75$ ) it increased slightly. Product distribution remained unaffected by changes in  $\chi_{\text{GaCl}_3}$ , taking into consideration 4% and 3% error bars on C20 and C30 content (Figure 2).

In conclusion, the catalyst composition ( $\chi_{\text{MCl}_3}$ ) had negligible impact on the reaction outcome, provided, that the catalyst was Lewis acidic (*e.g.*  $\chi_{\text{MCl}_3} > 0.50$ ).

Table 3. Conversions and products distributions, obtained using LCCs based on Ur-GaCl<sub>3</sub>, where  $\chi_{\text{GaCl}_3} = 0.60, 0.67$  or  $0.75$  (120 °C, 1 h, 1.707 mmol of GaCl<sub>3</sub> equivalent in each catalyst loading).

$\chi_{\text{GaCl}_3}$	conversion (%)	product distribution (%)					
		C20	C30	C40	C50	C60	C70+
0.50	-	-	-	-	-	-	-
0.60	71.5	36.9	36.9	15.6	7.1	3.5	-
0.67	73.5	34.1	35.2	16.2	8.9	3.8	1.7
0.75	78.5	38.7	33.5	15.5	7.7	4.5	-

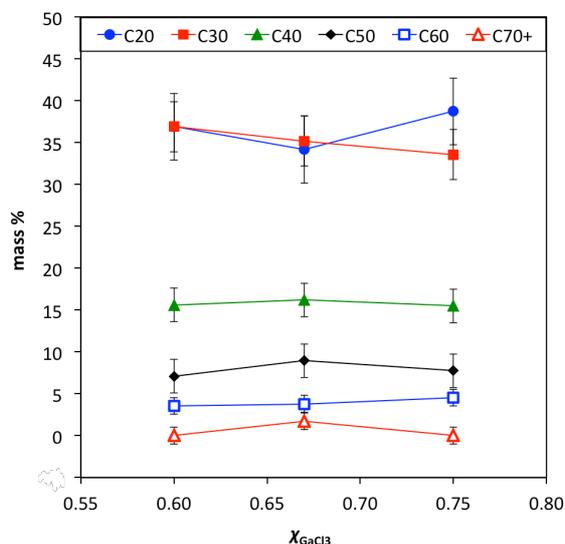


Figure 2. Distributions of 1-decene oligomers, obtained using LCCs based on Ur-GaCl<sub>3</sub>, where  $\chi_{\text{GaCl}_3} = 0.60, 0.67$  or  $0.75$  (120 °C, 1 h, 1.707 mmol of GaCl<sub>3</sub> in each catalyst loading).

The influence of changes in LCC metal and ligand on the oligomerisation outcome was investigated by testing L-AlCl<sub>3</sub> systems at  $\chi_{\text{AlCl}_3} = 0.60$  and L-GaCl<sub>3</sub> systems at  $\chi_{\text{GaCl}_3} = 0.67$ ,

under identical reaction conditions. Equal amounts of MCl<sub>3</sub> equivalents (1.707 mmol) were used.

Conversions (Table 4) were consistently high, between 75.5 and 87.5%. Although this discrepancy lies outside of the error bars assumed for conversion, no simple correlation between the LCC structure and conversion could be proposed.

Table 4. Conversions and distributions of 1-decene oligomers, obtained using LCCs based on GaCl<sub>3</sub> and AlCl<sub>3</sub>, and a range of ligands (120 °C, 1 h, 1.707 mmol of LCC).

L	conversion (%)	product distribution (%)					
		C20	C30	C40	C50	C60	C70+
L-GaCl <sub>3</sub> , $\chi_{\text{GaCl}_3} = 0.67$							
P <sub>888</sub>	76.5	43.7	35.8	14.6	5.3	0.7	-
P <sub>888</sub> O	81.5	46.0	33.5	14.9	5.0	0.6	-
Ur	75.5	32.2	33.6	17.5	9.4	5.4	2.0
AcA	82.5	32.0	34.4	17.2	9.8	4.9	1.8
SUr	80.5	39.0	40.3	15.1	5.0	0.6	-
C <sub>7</sub> CN	86.5	42.1	33.9	15.2	5.9	2.3	0.6
L-AlCl <sub>3</sub> , $\chi_{\text{AlCl}_3} = 0.60$							
P <sub>888</sub>	81.5	33.5	37.3	18.6	7.5	2.5	0.6
P <sub>888</sub> O	82.5	39.3	34.4	18.4	6.1	1.8	-
Ur	78.5	37.4	29.7	14.2	9.0	5.2	4.5
AcA	79.5	28.0	33.1	17.8	11.5	5.1	4.5
SUr	87.5	30.1	35.8	19.7	9.3	3.5	1.7

Product distribution (Table 4, Figure 3) changed moderately with changes in LCC. In general, slightly lower MW oligomers were produced using L-GaCl<sub>3</sub> systems, than using analogous L-AlCl<sub>3</sub> systems. This was most evident when comparing C20 content in both graphs in Figure 3. Moreover, distribution shifted towards lighter products (C20) for LCCs with hydrophobic ligands: P<sub>888</sub> and P<sub>888</sub>O (three long alkyl chains per ligand) and C<sub>7</sub>CN (one long chain per ligand). In contrast, small and hydrophilic ligands gave less C20 and slightly more heavy oligomers; which was particularly visible for DMA-MCl<sub>3</sub>. This is rather surprising; increased miscibility with olefin was expected to result in longer contact of propagating carbocation with the catalyst phase, whereas lower miscibility should result in phase-separation from LCC of relatively short oligomers, such as C20 or C30. Here, however, a reverse trend was observed.

For comparison, oligomerisation of 1-decene has been carried out using a range of chloroaluminate(III) ionic liquids and aluminium(III) chloride powder, with equal mol equivalents of AlCl<sub>3</sub> in each reaction. The selected cations ranged from very hydrophilic (1-ethyl-3-methylimidazolium, [C<sub>2</sub>mim]<sup>+</sup>), through moderately hydrophilic (1-octyl-3-methylimidazolium, [C<sub>8</sub>mim]<sup>+</sup> and tetrabutylphosphonium, [P<sub>4444</sub>]<sup>+</sup>), to hydrophobic (trihexyl(tetradecyl)phosphonium, [P<sub>66614</sub>]<sup>+</sup>). The main anion in chloroaluminate(III) ionic liquids at  $\chi_{\text{AlCl}_3} = 0.67$  is [Al<sub>2</sub>Cl<sub>7</sub>]<sup>-</sup>, the same as in LCCs at  $\chi_{\text{AlCl}_3} = 0.60$  (see Scheme 1). However, in ionic liquids there are no ligands other than chloride coordinating to Al<sup>III</sup>, whereas in LCCs the [Al<sub>2</sub>Cl<sub>7</sub>]<sup>-</sup> anion remains in a dynamic equilibrium with other coordination complexes (Scheme 1).

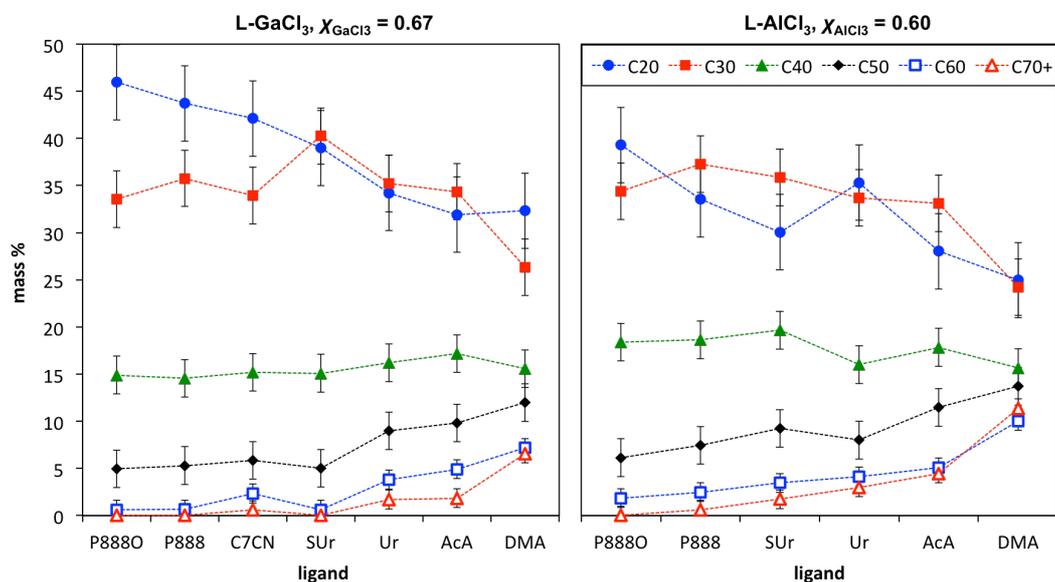


Figure 3. Distributions of 1-decene oligomers, obtained using LCCs based on  $\text{GaCl}_3$  or  $\text{AlCl}_3$ , and a range of ligands (120 °C, 1 h, 1.707 mmol of LCC). Dashed lines are only guidelines for the eye.

Miscibility of ionic liquids and olefin phase was limited; biphasic mixtures were formed in all cases. Unlike in LCCs, both conversions and products distributions were closely related to expected miscibility of ionic liquids with olefin.

As shown in Table 5,  $\text{AlCl}_3$  gave the lowest conversion. Conversions achieved with ionic liquids were higher (on par with those obtained with LCCs), and increased with lipophilicity of the cation. The distribution of products (Figure 4) also corresponded well to the cation lipophilicity:  $[\text{P}_{66614}][\text{Al}_2\text{Cl}_7]$  gave the most heavies and the least C20, whereas  $[\text{C}_2\text{mim}][\text{Al}_2\text{Cl}_7]$  produced more C20 and less C60 and C70+. Noteworthy, products obtained with ionic liquids were heavier than those synthesised using  $\text{Al}^{\text{III}}$ -based LCCs (see Figure 4 vs. Figure 3).

Table 5. Conversions and distributions of 1-decene oligomers, obtained using chloroaluminate(III) ionic liquids,  $\chi_{\text{AlCl}_3} = 0.67$  (120 °C, 1 h, 1.707 mmol of  $\text{AlCl}_3$  equivalent).

catalyst	conversion (%)	product distribution (%)					
		C20	C30	C40	C50	C60	C70+
$\text{AlCl}_3$	55.5	18.4	29.4	23.8	20.2	8.3	-
$[\text{C}_2\text{mim}][\text{Al}_2\text{Cl}_7]$	79.5	31.9	24.2	15.3	14.0	8.9	5.7
$[\text{P}_{4444}][\text{Al}_2\text{Cl}_7]$	85.5	20.1	27.2	20.1	16.6	9.5	6.5
$[\text{C}_8\text{mim}][\text{Al}_2\text{Cl}_7]$	86.5	17.5	19.9	16.4	15.2	11.7	19.3
$[\text{P}_{66614}][\text{Al}_2\text{Cl}_7]$	95.5	5.3	12.7	14.8	19.0	19.1	29.1

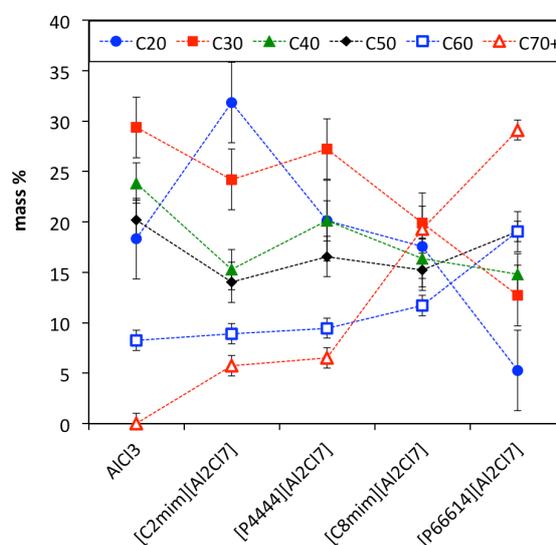


Figure 4. Distributions of oligomers obtained using chloroaluminate(III) ionic liquids,  $\chi_{\text{AlCl}_3} = 0.67$  (120 °C, 1 h, 1.707 mmol of  $\text{AlCl}_3$  equivalent).

It is apparent that structural factors have different effect on the products distribution in ionic liquids and in LCCs. In chloroaluminate(III) ionic liquids, lipophilic cations produced heavier oligomers, by enhancing longer contact of propagating carbocation with the ionic liquid. In contrast, for LCCs, lipophilic ligands gave lighter products and small hydrophilic

ligands gave more heavies, for both Ga<sup>III</sup> and Al<sup>III</sup>-based LCCs. Furthermore, ionic liquids based on [Al<sub>2</sub>Cl<sub>7</sub>]<sup>-</sup> gave heavier products than LCCs containing the same anion. This indicates that factors other than solubility govern products distribution in LCC-catalysed oligomerisation.

Considering the carbocationic mechanism,<sup>19</sup> distribution of oligomers depends on the rate of propagation (chain growth) vs. rate of termination. Under identical physical conditions (reaction temperature *etc.*), propagation depends on complex interactions between all charged species present in the reaction mixture. In both ionic liquids and LCCs, this interaction may be limited by mass transport, governed by factors such as solubility of olefin in the droplet of catalyst, or viscosity of the catalyst. Provided good mass transport, the chemical structure of interacting ions may be the crucial factor: 'hardness' of the anion, as well as competitive interactions of the anion with carbocation and with cations in ionic liquid/LCC. Understanding what governs products distribution when using LCCs, which would exceed beyond phenomenological observations, requires in-depth physico-chemical and mechanistic studies, supported by computational modelling. These studies are currently under way in our group.

At this stage, however, it can be stated that there is a qualitative difference between Al<sup>III</sup>-based LCCs and other Al<sup>III</sup> based catalysts; the introduction of a non-halide ligand altered the way in which the catalyst affects product distribution. This suggests that LCCs may promote the formation of different classes of PAOs than older Al<sup>III</sup>-based catalyst, which led to high-viscosity, heavy products.

**INFLUENCE OF THE REACTION CONDITIONS** was investigated by varying reaction temperature and amount of LCC catalyst.

The Ur-AlCl<sub>3</sub> ( $\chi_{\text{GaCl}_3} = 0.60$ ) system was used to catalyse oligomerisation of 1-decene at a wide range of temperatures, from 40 to 160 °C. Conversions and product distributions are compared in Table 6; conversions and yields of selected fractions are plotted against reaction temperature in Figure 5.

Conversions were independent of temperature, and levelled at 79±4%, except for the reaction carried out at the lowest temperature, 40 °C, which reached only 70.5% conversion.

Table 6. Conversions and distributions of 1-decene oligomers, obtained using Ur-AlCl<sub>3</sub>,  $\chi_{\text{AlCl}_3} = 0.60$ , at a range of temperatures (1 h, 1 wt % of LCC).

reaction temperature (°C)	conversion (%)	product distribution (%)					
		C20	C30	C40	C50	C60	C70+
160	83.5	49.7	31.5	13.3	3.6	1.8	0.0
140	78.5	47.7	31.0	11.6	6.5	1.3	1.9
130	77.5	41.8	30.1	13.1	7.8	3.9	3.3
120	78.5	37.4	29.7	14.2	9.0	5.2	4.5
110	78.5	31.0	31.0	16.8	10.3	5.2	5.8
100	79.5	24.2	31.8	17.8	11.5	7.6	7.0
90	77.5	23.5	34.0	18.3	10.5	7.8	5.9
80	76.5	18.5	29.1	18.5	15.9	9.3	8.6
60	83.5	4.8	18.2	13.3	19.4	14.5	29.7
40	70.5	1.4	8.6	8.6	17.3	15.8	48.2

As expected for carbocationic process, distribution of oligomers depended strongly on the reaction temperature: as the temperature increased, the distribution shifted towards lighter

products. Because termination rate increases with temperature more rapidly than propagation rate, oligomeric chains are shorter at higher temperatures. From 80 to 160 °C, yields in all fractions change gradually, but for <80 °C the amount of heavy oligomers increases rapidly. At high reaction temperatures the amount of heavy products is negligible, but the amount of C20 increases to nearly 50% of the sample. Consequently, temperatures around 120 °C appear to offer a good balance of heavy oligomers (<5%) and relatively low level of the C20 fraction, whilst maintaining the highest possible yield of the middle fractions.

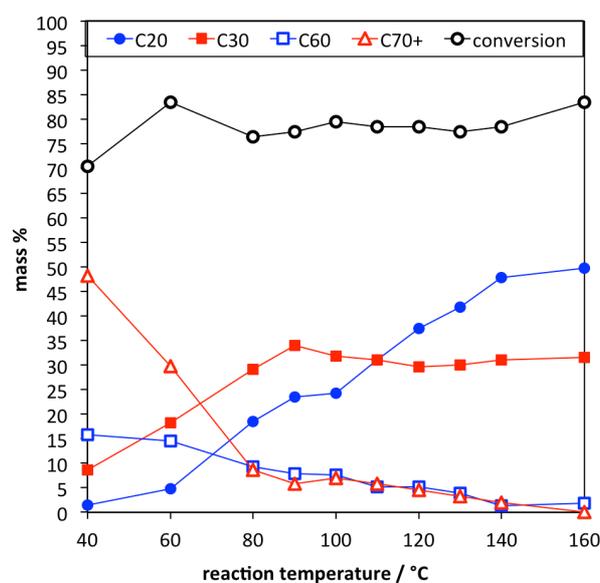


Figure 5. Distributions of 1-decene oligomers, obtained using Ur-AlCl<sub>3</sub>,  $\chi_{\text{AlCl}_3} = 0.60$ , at a range of temperatures (1 h, 1 wt % of LCC).

The influence of catalyst amount was investigated using two catalytic systems: P<sub>888</sub>O-AlCl<sub>3</sub>,  $\chi_{\text{AlCl}_3} = 0.60$ , and Ur-AlCl<sub>3</sub>,  $\chi_{\text{AlCl}_3} = 0.60$ . The amount of former LCC was varied from 0.86 to 5.12 mmol of AlCl<sub>3</sub> eq.; however, for <1.00 mmol of AlCl<sub>3</sub> eq., small amount of catalyst hindered reproducibility of the results. Therefore, the latter system was used at 1.71 to 5.12 mmol of AlCl<sub>3</sub> eq. Conversions and product distributions are compared in Table 7.

Table 7. Conversions and distributions of 1-decene oligomers, obtained using two LCC catalysts: L-AlCl<sub>3</sub>,  $\chi_{\text{AlCl}_3} = 0.60$ , where L = P<sub>888</sub>O or Ur, at different quantities, expressed as mmol of AlCl<sub>3</sub> eq. (120 °C, 1 h).

catalyst amount (AlCl <sub>3</sub> mmol)	conversion (%)	product distribution (%)					
		C20	C30	C40	C50	C60	C70+
P <sub>888</sub> O-AlCl <sub>3</sub> , $\chi_{\text{AlCl}_3} = 0.60$							
0.86	75.5	45.6	34.9	14.8	4.7	-	-
1.71	82.5	39.3	34.4	18.4	6.1	1.8	-
3.41	88.5	25.1	35.4	24.0	10.3	4.6	0.6
5.12	85.5	28.4	36.7	22.5	9.5	2.4	0.6
Ur-AlCl <sub>3</sub> , $\chi_{\text{AlCl}_3} = 0.60$							
1.71	79.0	36.5	30.1	15.4	9.0	4.5	4.5
3.41	86.5	33.3	37.4	18.1	7.6	2.3	1.2
5.12	91.5	29.3	37.0	19.9	8.8	2.8	2.2

For  $P_{888}O-AlCl_3$ , conversion was slightly lower for the minimum catalyst amount, but for 1.71 to 5.12 mmol of  $AlCl_3$  eq., it oscillated at *ca.* 85%. In contrast, for  $Ur-AlCl_3$ , a significant increase in conversion as a function of catalyst loading was observed, up to 91.5%. Yields of all fractions are

plotted against the reaction temperature in Figure 6. For both LCCs, there was a small but observable decrease in C20 content, in favour of C40, with increasing catalyst amount, which levelled out for higher contents of the  $P_{888}O-AlCl_3$  system.

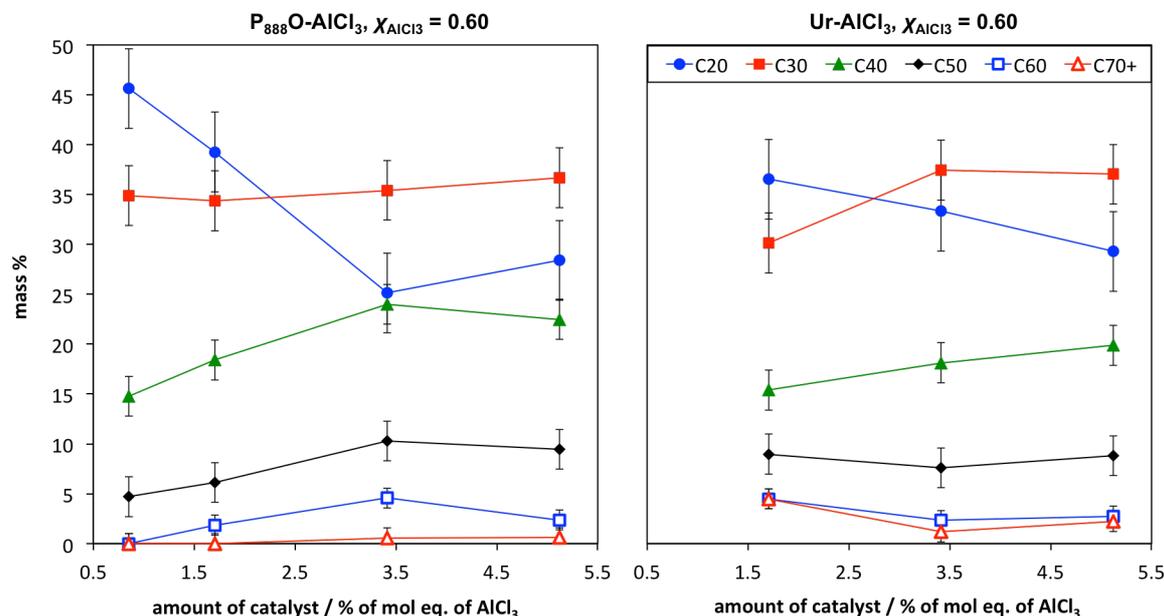


Figure 6. Distributions of 1-decene oligomers, obtained using two LCC catalysts:  $L-AlCl_3$ ,  $\chi_{AlCl_3} = 0.60$ , where  $L = P_{888}O$  (left) or  $Ur$  (right), at different quantities, expressed as mol % of  $AlCl_3$  (120 °C, 1 h).

In conclusion, optimising the reaction temperature is the key to manipulating the distribution of oligomers. Increasing the catalyst amount could also aid to increase conversion and slightly decrease C20 amount, but tripling the catalyst amount may be more expensive solution than recycling an additional few per cent of the feedstock.

### Scale-up

In order to test physical properties, such as kinematic viscosity (Kv), viscosity index (VI) and pour point (PP), it was necessary to scale-up the reaction. The products could then be distilled into fractions, and blended with the aim to achieve marketable PAO4 or PAO6 (viscosity brackets of 4 or 6 cSt, respectively).

SCALE-UP REACTION CONDITIONS were chosen to strike balance between achieving optimum conditions and project economy. Urea was selected as a very cheap ligand, offering a balanced oligomers distribution: limited amounts of C20 and heavies.  $Al^{III}$ -based LCC was chosen over the  $Ga^{III}$  equivalent due to much lower price. Reaction temperature of *ca.* 120 °C was chosen to balance C20 and heavies in the product.

Reproducibility of scale-up reactions was superior to that in the small scale. Products prepared at the same conditions contained slightly less heavies. The catalyst amount was reduced to 0.25 wt %, whilst maintaining good conversion.

REACTION KINETICS. Preliminary small-scale studies suggested that after 1 h the reaction did not progress. However, frequent sampling of the reaction mixture at that scale

introduced significant amounts of moisture, compromising data quality. This problem has been eliminated at the scale-up. Conversion and products distribution were studied as a function of the reaction time, in a reaction catalysed with  $Ur-AlCl_3$ ,  $\chi_{AlCl_3} = 0.60$ , carried out for 2 h (Table 8 and Figure 7).

Table 8. Conversions and distributions of 1-decene oligomers, obtained using  $Ur-AlCl_3$ ,  $\chi_{AlCl_3} = 0.60$ , as a function of reaction time (100 °C, 1 wt % LCC).

reaction time (min)	conversion (%)	product distribution (%)					
		C20	C30	C40	C50	C60	C70+
5	55.0	37.0	38.9	14.8	5.6	1.9	1.9
10	66.0	40.0	36.9	12.3	6.2	3.1	1.5
15	68.0	38.8	37.3	13.4	6.0	3.0	1.5
20	69.0	39.7	35.3	14.7	5.9	2.9	1.5
25	69.0	38.2	36.8	14.7	5.9	2.9	1.5
30	69.0	38.2	36.8	14.7	5.9	2.9	1.5
35	71.0	38.6	35.7	15.7	5.7	2.9	1.4
40	72.0	38.0	36.6	14.1	7.0	2.8	1.4
45	72.0	38.0	36.6	14.1	7.0	1.4	2.8
50	72.0	36.6	38.0	14.1	7.0	1.4	2.8
55	74.0	37.0	37.0	15.1	6.8	1.4	2.7
60	74.0	37.0	37.0	15.1	6.8	1.4	2.7
100	78.0	36.4	36.4	15.6	6.5	2.6	2.6
120	78.0	35.1	37.7	15.6	6.5	2.6	2.6

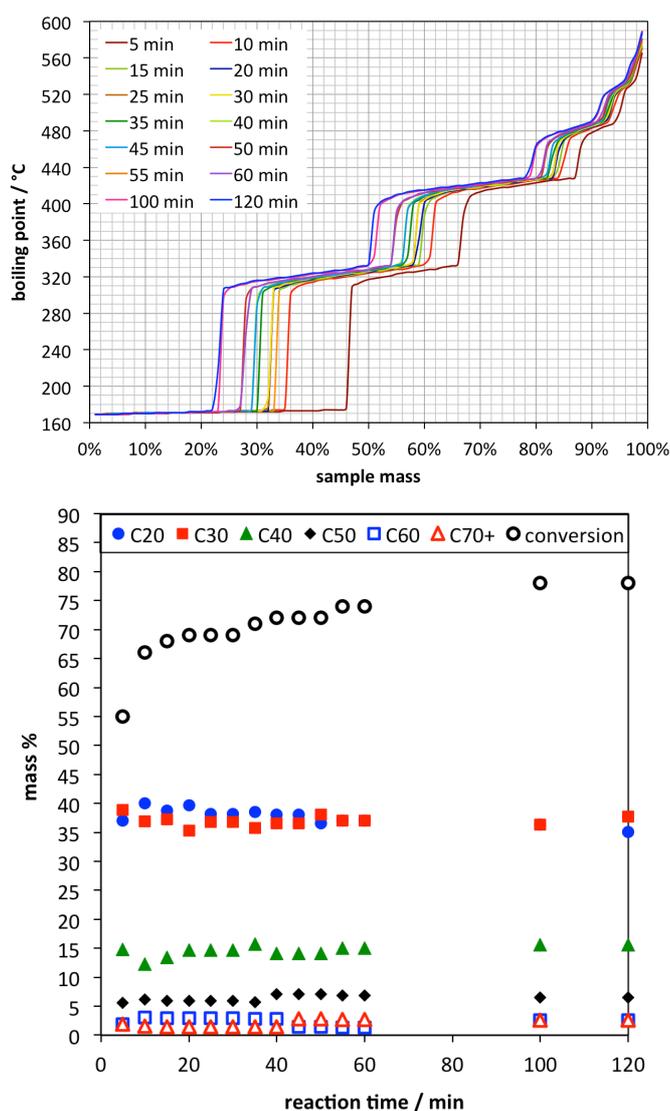


Figure 7. SimDist GC chromatograms (top) and corresponding graph (bottom), depicting conversions and distributions of 1-decene oligomers as a function of reaction time (100 °C, 0.25 wt % of LCC: Ur-AlCl<sub>3</sub>,  $\chi_{\text{AlCl}_3} = 0.60$ )

The initial reaction rate was very high, with 55% conversion after 5 min and 66% after 10 min; afterwards the conversion of C10 increased slowly to plateau at 78% after 100 min. Product distribution was remarkably independent from reaction time and from conversion.

In conclusion, it has been demonstrated that the oligomerisation could be carried out using as little as 0.25 wt % of the catalyst, achieving >75% conversion and favourable product distribution (Figure 7). Alternatively, the catalyst amount could be increased, which would increase the conversion and decrease the volume of the recycled fraction: C10 and C20 (Figure 6). To make an informed decision, techno-economical evaluation of the process would be required. Moreover, at 0.25 wt %, considering the low catalyst price and benign products of hydrolysis (urea and oxo/hydroxoaluminium species, mildly acidified water), recycling of the catalyst is not required. Upon increasing the catalyst amount, it may be

beneficial to attempt recycling: LCC would be purified from acid soluble oils (ASO), which accumulate in the catalyst phase during carbocationic processes,<sup>20</sup> and then returned to the reaction. This methodology is currently studied in our group. However, the recycle conditions (solvents, energy demand) may render the decomposition and disposal of the catalysts a more sustainable option, as practiced in comparable industrial processes (*viz.* BF<sub>3</sub>-based oligomerisation).<sup>4</sup>

**PHYSICAL PROPERTIES OF PAOS.** Scale-up reactions were performed at four temperatures, 100-160 °C, with several runs at each temperatures. C10 and C20 fractions were removed at reduced pressure. C30 and some C40 were separated by fractionated distillation, leaving heavy products as a residue. Then, these fractions were blended at various proportions, with aim to achieve marketable PAO grades: Kv<sub>100</sub> = *ca.* 4 or 6 cSt, VI >120 and PP < -40 °C. The catalyst and process conditions were different from the commercial ones, hence different degree of branching could be anticipated. Consequently, proportion of oligomers typically found in the commercial samples could only be a rough guideline. *N.B.*, unlike the commercial samples, PAOs produced in this work have not yet been hydrogenated, which is anticipated to slightly increase Kv values, but should not affect other physical properties.

All tested samples had very low pour points, PP < -57 °C. Other physical parameters of PAOs blended at various proportions, from oligomers synthesised at different temperatures, are listed in Table 9. Achieving Kv<sub>100</sub> = *ca.* 4 or 6 cSt was feasible by adjusting the ratio of oligomers. The main challenge lied in accessing VI > 120, which could not be obtained, at any fractional composition, with products made at 140 or 160 °C. However, it was possible to obtain satisfactory VI for PAO6 produced at 100 and 120 °C, and for PAO4 produced at 100 °C. This clearly suggests that the degree of branching in the studied samples is higher than that in commercial samples. Moreover, degree of branching can be controlled, and decreased to a satisfactory level, by lowering the reaction temperature.

Table 9. Physical properties of unhydrogenated PAO blends, produced using Ur-AlCl<sub>3</sub>,  $\chi_{\text{AlCl}_3} = 0.60$ , at a range of temperatures (1 h, 0.25 wt % of LCC).

Blend no.	reaction temperature (°C)	products distribution (%)			Kv <sub>100</sub> (cSt)	Kv <sub>40</sub> (cSt)	VI (-)
		C30	C40	C50+			
1	160	86.9	13.1	-	4.11	20.28	102
2	160	47.0	36.0	17.0	5.84	35.16	108
3	160	48.5	35.4	16.2	5.68	32.32	115
4	160	29.3	45.5	25.3	6.72	43.87	106
5	160	14.1	54.5	31.3	7.79	53.93	109
6	140	77.8	22.2	-	4.13	19.88	109
7	140	47.0	35.0	18.0	6.39	39.61	111
8	120	46.5	31.3	22.2	5.22	26.88	127
9	120	42.0	36.0	22.0	5.79	31.46	126
10	120	42.0	37.0	21.0	5.74	31.35	126
11	100	93.9	6.1	-	3.10	12.58	105
12	100	45.5	32.3	22.2	5.27	26.19	137
13	100	77.0	16.0	7.0	4.31	20.08	124

Chromatogram of the unhydrogenated PAO6 sample produced in this work (Table 9, entry 10) was compared to the

chromatogram of a commercial PAO6 (Figure 8). In the former chromatogram, peaks corresponding to different oligomers were slightly broader and shifted towards lower retention times, which again suggested a higher degree of isomerisation and more branching.

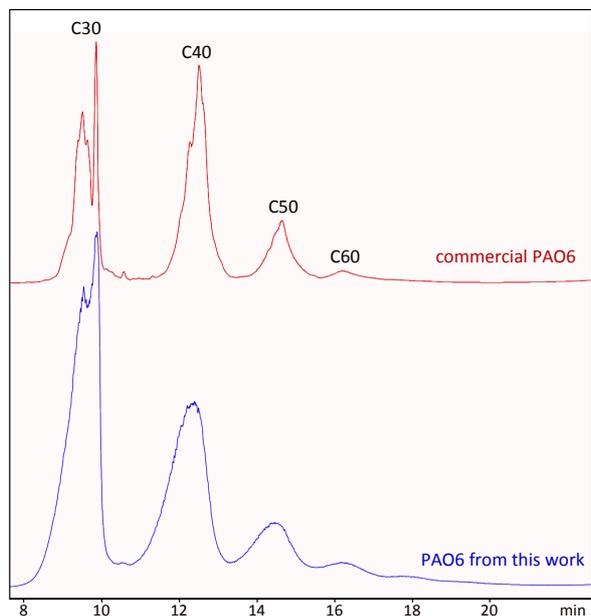


Figure 8. SimDist GC chromatograms of unhydrogenated PAO6 blend, produced using  $Ur-AlCl_3$ ,  $\chi_{AlCl_3} = 0.60$ , compared to commercial PAO6 sample.

PAO samples synthesised using LCCs differ in degree of branching from the commercial products. Nevertheless, they were demonstrated to meet all major specifications for low viscosity synthetic base oils, in both PAO4 and PAO6 grades.

## Conclusions

A new class of liquid Lewis acidic catalysts, Liquid Coordination Complexes, were successfully used as a sustainable and inexpensive alternative to the industrially used  $BF_3/nBuOH$  catalyst.

Oligomers distribution and physical properties of the products could be modified by altering reaction temperature. Lipophilicity of LCC ligand and the amount of the catalyst used had lesser, but significant, effects on products distribution. Conversion could be influenced by changing reaction time and the amount of the catalyst.

It has been demonstrated that  $Al^{III}$ -based LCCs acted in the oligomerisation process distinctly different to other  $Al^{III}$ -based catalysts, such as  $AlCl_3$  or chloroaluminate(III) ionic liquids. This enabled the production of low-viscosity PAO4 and PAO6 base oils, in contrast to high-viscosity base oils accessible with other  $Al^{III}$ -based catalysts.

After fractionated distillation and blending, it has been possible to prepare PAO4 and PAO6 samples matching commercial specifications. The combination of  $AlCl_3$  and inexpensive ligands, such as urea or acetamide, makes a safer

and economically attractive alternative to the extant process, based on poisonous and corrosive  $BF_3$  gas.

## Acknowledgements

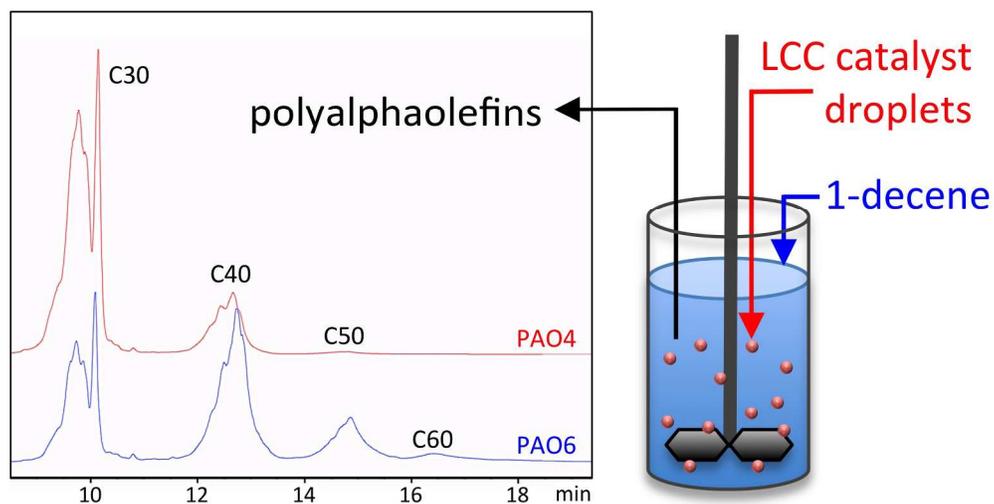
Petronas is kindly acknowledged for funding this project. Cytec is acknowledged for providing trioctylphosphine and phosphonium chloride salts.

## Notes and references

The QUILL Research Centre, The Queen's University of Belfast, David Keir Building, Stranmillis Road, BT9 5AG, Belfast, UK; email: m.swadzba-kwasny@qub.ac.uk

- 1 J. R. Dickey, *Lubrication and Lubricants*, in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 2005, **15**, 1–82.
- 2 *API 1509, Engine Oil Licensing and Certification System*, 17<sup>th</sup> Ed., September 2012, *Appendix E – API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils*, September 2011.
- 3 R. Benda, J. Bullen, and A. Plomer, *J. Synth. Lubr.*, 1996, **13**, 41.
- 4 S. Ray, P. V. Rao and N. V. Choudary, *Lubr. Sci.*, 2012, **24**, 23.
- 5 G. R. Lapin, L. H. Nemeč, J. D. Sauer, and D. Wagner, *Olefins, Higher*, in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley and Sons, Inc., 2010, **17**, 709–728.
- 6 L. I. Kioupis and E. J. Maginn, *J. Phys. Chem. B*, 1999, **103**, 10781.
- 7 S. S. Scheuermann, S. Eibl and P. Bartl, *Lubr. Sci.*, 2011, **23**, 221.
- 8 M. P. Atkins, K. R. Seddon and M. Swadzba-Kwasny, *Pure Appl. Chem.*, 2011, **83**, 1391.
- 9 E. T. Marquis, J. R. Sanderson and J. F. Knifton, *Us Pat. 5053569*, 1991.
- 10 F. Coleman, G. Srinivasan, and M. Swadzba-Kwasny, *Angew. Chem. Int. Ed. Engl.*, 2013, **52**, 12582.
- 11 H. M. A. Abood, A. P. Abbott, A. D. Ballantyne and K. S. Ryder, *Chem Commun*, 2011, **47**, 3523.
- 12 (a) T. A. Zawodzinski Jr and R. A. Osteryoung, *Inorg Chem*, 1989, **28**, 1710; (b) J. Estager, A. A. Oliferenko, K. R. Seddon and M. Swadzba-Kwasny, *Dalton Trans*, 2010, **39**, 11375.
- 13 (a) H. Aichaoui, J. H. Poupaert, D. Lesieur and J. P. Hélichart, *Bull. Soc. Chim. Belg.*, 1992, **101**, 1053; (b) H. A. Derbala, *J. Heterocycl. Chem.*, 2012, **49**, 700.
- 14 F. Fringuelli, R. Girotti, F. Pizzo and L. Vaccaro, *Org. Lett.*, 2006, **8**, 2487.
- 15 F. Alam, F. Evans, G. Mani and J. R. Papcun, *Boron Halides*, in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley and Sons, Inc., 2003, **4**, 138-168.
- 16 R. A. Smith, *Fluorine Compounds, Inorganic, Hydrogen*, in *Kirk-Othmer Encyclopedia of Chemical Technology*, 2003, **13**, 1-26.
- 17 J.S. Wilkes, J.A. Levisky, C.L. Hussey and M.L. Druehlinger, *Proc. Int. Symp. Molten Salts*, 1980, **81-89**, 245.
- 18 D. C. Apperley, C. Hardacre, P. Licence, R. W. Murphy, N. V. Plechkova, K. R. Seddon, G. Srinivasan, M. Swadzba-Kwasny and I. J. Villar-Garcia, *Dalton Trans*, 2010, **39**, 8679.

- 19 (a) I. Majoros, A. Nagy and J. P. Kennedy, in *Advances in Polymer Science*, Springer Berlin Heidelberg, 1994, **112**, 1, (b) I. Majoros, T. M. Marsalko and J. P. Kennedy, *J. Polym. Sci. A Polym. Chem.*, 1996, **34**, 1675.
- 20 (a) L. F. Albright, M. A. Spalding, C. G. Kopser and R. E. Eckert, *Ind. Eng. Chem. Res.*, 1988, **27**, 386; (b) L. F. Albright, *Ind. Eng. Chem. Res.*, 2002, **41**, 5627.



Low-viscosity polyalphaolefins were synthesised using  $\text{AlCl}_3$ -based liquid coordination complexes (LCCs), in a sustainable and economically competitive process  
902x453mm (72 x 72 DPI)