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# Nickel-Catalyzed Propene Dimerization Reactions in Triphenylbismuth-Buffered Chloroaluminate Ionic Liquids: High Performance with Unconventional Cations

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Dedicated to Professor Peter Morys on the occasion of his 70th birthday

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**Abstract:** The addition of triphenylbismuth ($BiPh_3$) efficiently buffers Lewis acidic chloroaluminate ionic liquids over a wide range of compositions. Since the melting points of these ternary mixtures are lower compared to unbuffered chloroaluminate systems, the scope of cations for the formation of buffered room temperature ionic liquids is greatly extended. The buffered ionic liquids were used to activate nickel complexes for selective biphasic propene dimerization reactions. Lifetimes, selectivities and productivities of such dimerization catalysts could be adjusted by the choice of the cation and the composition. At lower reaction temperatures, the selectivities to give dimers increased significantly. Propene dimers were obtained with selectivities of up to 98%. A cation screening with 100 ammonium and phosphonium halide salts was performed. *N*-Methylpyrrolidine hydrochloride gave the best results in terms of selectivity and lifetime. Propene dimerization reactions in $BiPh_3$-buffered chloroaluminate melts were catalyzed by various soluble nickel compounds with similar performances. The introduction of basic, sterically demanding tricyclohexylphosphine ligands led to higher degrees of branching, however, at the expense of lower dimer selectivities.

**Keywords:** biphasic catalysis; chloroaluminates; dimerization; ionic liquids; nickel; triphenylbismuth

## Introduction

Selective dimerization reactions of α-olefins attracted a lot of attention in the second half of the 20th century, after Ziegler described the “nickel effect” in 1955.[1] Nickel impurities from previous hydrogenation reactions were found to catalyze selective ethene dimerization reactions to give butenes in the presence of alkylaluminum compounds. Ziegler was originally interested in chain growth and polymerization reactions. However, his discovery also launched an intensive research on selective nickel-catalyzed dimerization reactions of short chain olefins in the following decades.[2]

The DIMERSOL® process of the Institut Français du Pétrole Énergies Nouvelles (IFPEN) is the largest industrial process based on nickel complexes activated by alkylaluminum cocatalysts. It was developed by Chauvin et al. in the 1970s[3] to dimerize propene (DIMERSOL® G) or 1-butene (DIMERSOL® X) selectively. Currently, 35 licensed DIMERSOL® units with typical capacities between 20,000 and 90,000 tons per year are in use for selective dimerization reactions of short chain olefins.[4]

About 30 years ago, Wilkes et al. and Osteryoung et al. reported the first room temperature ionic liquids based on aluminum chloride.[5] In the 1980s, these chloroaluminate ionic liquids were thoroughly investigated in terms of their physical and electrochemical properties.[6] It took about ten more years until chloroaluminate ionic liquids started to attract attention as new media for biphasic catalysis.[7]

Initially, Lewis acidic chloroaluminate melts were used as catalysts for Friedel–Crafts alkylation reactions.[8] In the 1990s, Chauvin et al. developed nickel-catalyzed biphasic dimerization reactions of α-olefins in organochloroaluminate ionic liquids.[9] Ethylaluminum groups were found to suppress uncontrolled cationic olefin oligomerization reactions, which occur in solely $AlCl_3$-based ionic liquids.[10] The IFPEN brought this so-called DIFASOL® process to industrial application by retrofitting it to their existing DIMERSOL® units.[4a,11]

Besides alkylaluminum groups, the addition of weak Lewis bases also reduces the "latent acidity"[12] of chloroaluminate melts. While Wasserscheid et al. used pyrrole, pyridine, and quinoline derivatives to prevent undesired cationic olefin oligomerization reactions,[13] we recently reported that triphenylphosphine and triphenylbismuth efficiently buffer even highly acidic chloroaluminate ionic liquids.[14] These buffered chloroaluminate melts were successfully employed to activate nickel complexes for selective propene dimerization reactions.

Buffering with Lewis base additives is advantageous compared to the commercial DIFASOL® system. First, buffering with $EtAlCl_2$ is restricted to only slightly acidic compositions. If higher acidities are chosen, the dimer selectivities decrease. Second, at higher alkylaluminum contents, leaching of neutral chloroalkylaluminum compounds formed by disproportionation reactions[15] becomes a major problem.[11b] Also, alkylaluminum cocatalysts contribute to the deactivation of Ni(II) catalysts by reducing Ni(II) to its zero oxidation state.[16] Usually, the melting points of aluminum chloride-based ionic liquids display a minimum for highly acidic melts, while a local maximum is observed around equimolar compositions.[6b,17] Therefore, DIFASOL® systems are limited to cations intrinsically forming low-melting liquids, for example, *N*,*N'*-alkylmethylimidazolium or *N*-alkylpyridinium salts.[13b]

In a recent paper, we described that the melting points of acidic chloroaluminate systems are reduced upon addition of $BiPh_3$. Thus, it was possible to obtain buffered room temperature ionic liquid compositions from aluminum chloride and cations which would only yield solids at ambient temperature without $BiPh_3$.[14a] Furthermore, the scope of potential cations became even larger since low-melting highly acidic systems could be used for nickel-catalyzed selective olefin dimerization reactions. Because no reactive alkylaluminum groups were present in $BiPh_3$-buffered chloroaluminate ionic liquids, these systems were not limited to quaternary ammonium cations. Instead, cheap halide salts like amine hydrochlorides could be used, which can be recovered easily upon hydrolysis and a subsequent drying step.

In this paper, we report nickel-catalyzed propene dimerization reactions in $BiPh_3$-buffered chloroaluminate melts with 100 mostly unconventional cation compositions. Only two out of 100 mixtures did not form liquids at ambient temperature. Furthermore, the effects of Lewis acidities, buffer contents and reaction temperatures on the dimer selectivities were investigated. Finally, several nickel complexes were tested for their performances in $BiPh_3$-buffered chloroaluminate melts.

## Results and Discussion

### Variation of Buffering and Acidity Levels

As described in our recent paper, not only slightly acidic chloroaluminate melts but also highly acidic $[cation]^+[Al_2Cl_7]^-$ systems could be buffered with $BiPh_3$.[14a] Therefore, the effects of different acidities

**Table 1.** Nickel-catalyzed propene dimerization reactions in $BiPh_3$-buffered chloroaluminate melts with different compositions.[a]

| No. | $[AlCl_3]/[BMIMCl]$ | $[BiPh_3]/[BMIMCl]$ | Productivity[b] | $C_6$ [%] |
|---|---|---|---|---|
| 1 | 1.20 | 0.05 | $>15.8$[c] | oil[d] |
| 2 | 1.20 | 0.07 | $>10.8$[c] | 89.2 |
| 3a | 1.20 | 0.12 | $>8.0$[c] | 93.1 |
| 3b[e] | 1.20 | 0.12 | 0 | – |
| 4 | 1.20 | 0.30 | 6.7 | 96.0 |
| 5 | 1.30 | 0.12 | $>8.0$[c] | 81.8 |
| 6 | 1.50 | 0.12 | $>10.6$[c] | 74.1 |
| 7 | 1.50 | 0.18 | $>12.0$[c] | 83.2 |
| 8 | 2.00 | 0.12 | $>11.4$[c] | 74.8 |
| 9 | 2.00 | 0.18 | $>12.3$[c] | 79.5 |
| 10 | 2.00 | 0.24 | $>7.4$[c] | 83.3 |
| 11 | 2.00 | 0.30 | $>9.3$[c] | 85.5 |
| 12 | 2.00 | 0.60 | $>11.5$[c] | 90.6 |

[a] *Reaction conditions:* 2.5–3.5 g buffered ionic liquid; catalyst precursor **A**; $[cat]=10^{-5}$ mol/$g_{ionic\ liquid}$; $T=25\,°C$; stirring rate $=1200\ min^{-1}$; $t=60$ min; 300-mL glass autoclave; 40–70 mL liquid propene.

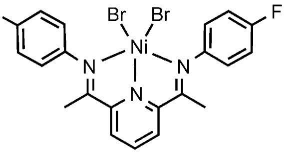
[b] $g_{product}/g_{ionic\ liquid} \times h$.

[c] Complete conversion.

[d] Higher oligomers derived from a cationic oligomerization reaction.

[e] No catalyst precursor **A** was added.

and $BiPh_3$ contents in chloroaluminate ionic liquids on nickel-catalyzed propene dimerization reactions were investigated in detail (Table 1). For the screening experiments, we used our standard nickel complex **A** as the catalyst precursor (Figure 1).



**A**

**Figure 1.** Catalyst precursor **A** used for biphasic propene dimerization reactions.

We chose a system based on the commercially available 1-butyl-3-methylimidazolium (BMIM) tetrachloroaluminate, to which the corresponding amounts of $AlCl_3$ were added. With slightly acidic $AlCl_3$/BMIMCl $= 1.20$ systems, which were used by Wasserscheid et al.[13b] and for DIFASOL® systems,[9c] dimers were obtained starting with 0.07 equivalents of $BiPh_3$ (Table 1, No. 2). With increasing buffer content, selectivities increased. Employing 0.30 equivalents of $BiPh_3$, already 96% dimers were obtained (No. 4), however, at the expense of a reduced productivity. Such highly selective systems almost exclusively produced dimers and trimers. Only traces of higher oligomers were formed. For systems with lower dimer selectivities, the product curve is shifted to higher oligomers.

In the absence of a nickel catalyst, no dimerization reaction occurred (No. 3b). Instead, this system was completely inactive. The buffer fully suppressed uncontrolled cationic oligomerization reactions, which are usually initiated by acidic chloroaluminate melts.[10]

Due to mass transfer limitations,[13d] the term "activity" was replaced by "productivity". Thus, above a catalyst concentration of about $10^{-6}$ mol/$g_{\text{ionic liquid}}$,[14a] the product yield per hour is proportional to the amount of ionic liquid and independent from the catalyst concentration. As expected, increasing acidities with a constant buffer level reduced the dimer selectivities. However, from an $AlCl_3$/BMIMCl ratio of 1.50 to 2.00, the selectivities dropped only a few percent if the buffer level was held constant. Thus, the advantage of low melting points at highly acidic compositions did not have to be paid by disproportional high amounts of buffer. With only 0.12 equivalents of buffer, the maximum acidic system still yielded about 75% dimers (No. 8).

## Cation Screening

Considering these results, we were curious if our system could be extended to rather unusual and cheap cations. In the literature, only a few chloroaluminate systems were mentioned which do not rely on standard imidazolium or pyridinium cations. Trimethylammonium heptachlorodialuminate was used for cationic oligomerization reactions of 1-decene.[18] The use of triethylamine hydrochloride, dibutylamine hydrochloride, ethylamine hydrochloride, and dimethylamine hydrochloride was reported for Friedel–Crafts alkylation reactions.[7e] Dimethylaniline hydrochloride,[19] and several quaternary asymmetrical benzyl-substituted melts were described, too.[20] However, none of these were used for nickel-catalyzed olefin dimerization reactions due to the above-mentioned melting point and acidity restrictions. Friedel–Crafts alkylation reactions or cationic olefin oligomerization reactions employ the Lewis acidic ionic liquid itself as catalyst. Thus, in these cases a variation of the cation should only result in minor changes in the results of the reactions. In contrast, the performances of nickel-catalyzed olefin dimerization reactions in $BiPh_3$-buffered chloroaluminate melts should strongly depend on the cation. The reactions are catalyzed by a nickel complex, not by the ionic liquid itself. It is necessary that the $BiPh_3$ buffer dissolves well in the ionic liquids to minimize leaching effects. Also, the cation determines the viscosities and the solubilities of the substrate olefin within the ionic liquids. Both the viscosity and the solubility of the substrate are crucial since biphasic nickel-catalyzed dimerization reactions in chloroaluminate melts suffer from a mass transport limitation of the olefin.[13d] Therefore, we decided to perform a systematic screening of cations including quaternary ammonium salts, hydrochlorides of primary, secondary and tertiary amines, phosphonium salts, heterocyclic ammonium salts, and cations with more than one heteroatom. One hundred different halide salts and their $AlCl_3$/halide salt $= 2.00$ compositions were synthesized. These compositions were buffered with 0.30 equivalents of $BiPh_3$ and tested for nickel-catalyzed propene dimerization reactions. The screening reactions were performed in batch experiments. Furthermore, the lifetime of each system was investigated qualitatively. After each experiment, the product phase was decanted until the dimer selectivity dropped significantly. In Table 2, 34 selected cations and the corresponding $C_6$ selectivities obtained in the first batch experiment are shown. The complete dataset can be found in the Supporting Information.

Since the reference complex **A** had no effect on the branching of the hexene dimers,[14a] all $C_6$ fractions consisted of ($\pm 2\%$) 25% *n*-hexenes, 69% 2-methylpentenes, and 6% 2,3-dimethylbutenes. This correlated to the typical product distribution obtained from

**Table 2.** Selected results of the cation screening for nickel-catalyzed propene dimerization reactions in $BiPh_3$-buffered chloroaluminate melts (sorted by $C_6$ selectivity within quaternary, tertiary, secondary, primary amines and phosphonium salts).[a]

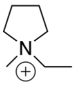
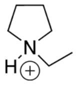
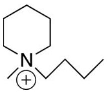
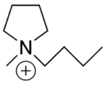
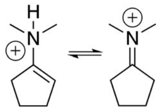
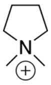
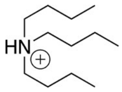
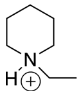
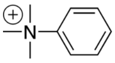
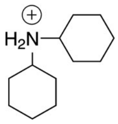
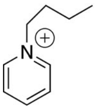
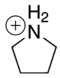
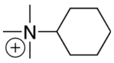
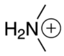
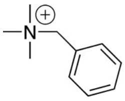
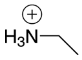
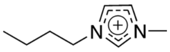
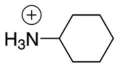
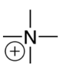
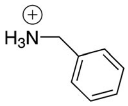
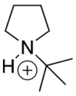
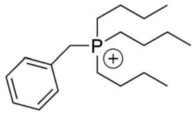
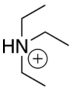
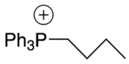
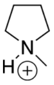
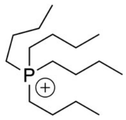
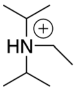
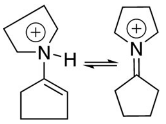
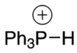
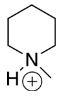
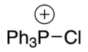
| No. | Cation | $C_6$ [%] | No. | Cation | $C_6$ [%] |
|---|---|---|---|---|---|
| 13 |  | 92.0 | 30 |  | 89.6 |
| 14 |  | 91.2 | 31 |  | 89.6 |
| 15 |  | 90.9 | 32 |  | 89.6 |
| 16 |  | 90.1 | 33 |  | 89.4 |
| 17 |  | 90.0 | 34 |  | 89.1 |
| 18 |  | 89.7 | 35 |  | 90.4 |
| 19 |  | 89.3 | 36 |  | 83.0 |
| 20 |  | 89.3 | 37 |  | 73.3 |
| 21 |  | 89.2 | 38 |  | 79.0 |
| 22 |  | 86.2 | 39 |  | 76.1 |
| 23 |  | 75.9 | 40 |  | 66.1 |
| 24 |  | 93.1 | 41 |  | 92.5 |
| 25 |  | 92.5 | 42 |  | 91.0 |
| 26 |  | 91.6 | 43 |  | 85.4 |
| 27 |  | 90.7 | 44 |  | 78.1 |
| 28 |  | 90.0 | 45 |  | 68.6 |

**Table 2.** (Continued)

| No. | Cation | $C_6$ [%] | No. | Cation | $C_6$ [%] |
|---|---|---|---|---|---|
| 29 |  | 89.9 | 46 |  $\overset{\oplus}{Ph_3P}-Cl$ | 49.5 |

[a] *Reaction conditions:* 2.5–4.0 g buffered ionic liquid; composition $[BiPh_3]/[cation]^+[Al_2Cl_7]^- = 0.30$; catalyst precursor **A**; $[cat] = 10^{-5}$ mol/$g_{ionic\ liquid}$; $T = 25\,°C$; stirring rate = 1200 min$^{-1}$; $t = 60$ min; 300-mL glass autoclave; 40–60 mL liquid propene.

ligand free nickel salts.[13d] Because the productivities of such buffered systems mainly depended on the buffering level,[14a] the productivities of different cations should not be compared directly. Cations yielding compositions with a good $BiPh_3$ efficiency automatically displayed higher dimer selectivities and subsequently lower productivities. Therefore, the goal was to identify systems, which kept high selectivities over many repetitions.

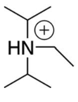
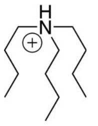
Surprisingly, 95 of 100 compositions produced dimers. Only two cations, formamidine hydrochloride and 1,4-diazabicyclo[2.2.2]octane hydrochloride, yielded solids at ambient temperature (see Supporting Information). Even the pentavalent triphenylphosphine dichloride based system (No. 46) successfully dimerized propene to give 50% dimers. However, the systems displayed big differences in their overall performances. The best results were obtained with quaternary ammonium salts and hydrochlorides of tertiary amines. In general, hydrochlorides of primary and secondary amines were less selective. However, even small changes on the cation could have severe effects on the lifetimes and selectivities of the systems. For example, the 1-butyl-3-methylimidazolium chloride cation, which was used for the initial acidity screening experiments, was found to be among the worst quaternary ammonium cations (No. 22). Introduction of an ethyl (No. 17) instead the butyl chain significantly improved the selectivity as well as the lifetime of the system (see Supporting Information). As already reported, the system based on *N*-methylpyrrolidine hydrochloride (No. 26) displayed the best performance in terms of selectivity and qualitative lifetime.[14a] In the case of the $BiPh_3$ buffer, there appears to be an optimum range of carbon atoms for ammonium salts, roughly between five and nine. Ionic liquids derived from cations with more or less carbon atoms dropped much faster in terms of selectivity than those within that range.

## Temperature Effect on Dimer Selectivities

Furthermore, we investigated the effect of the reaction temperature on dimer selectivities with 0.30 and 0.60 equivalents of $BiPh_3$ (Table 3). The reactions were performed either at ambient temperature or at 0 °C.

While the selectivity of an ethyldiisopropylamine (Hünig's base) hydrochloride-based system with 0.30 equivalents of $BiPh_3$ increased from 91% at 25 °C (No. 47) to 96% at 0 °C (No. 48) the mixture containing 0.60 equivalents of $BiPh_3$ solidified at 0 °C (No. 50). Thus, the series was repeated with tributylamine

**Table 3.** Nickel-catalyzed propene dimerization reactions in $BiPh_3$-buffered chloroaluminate melts at 0 °C and 25 °C.[a]

| No. | Cation | [Buffer]/[Cation] | Temp.[°C] | Productivity[b] | $C_6$ [%] |
|---|---|---|---|---|---|
| 47 |  | 0.30 | 25 | $>10.1$[c] | 90.7 |
| 48 | | 0.30 | 0 | $>6.7$[c] | 95.5 |
| 49 | | 0.60 | 25 | 4.6 | 93.8 |
| 50 | | 0.60 | 0 | –[d] | – |
| 51 |  | 0.30 | 25 | $>10.6$[c] | 89.4 |
| 52 | | 0.30 | 0 | $>12.9$[c] | 96.0 |
| 53 | | 0.60 | 25 | $>7.6$[c] | 90.8 |
| 54 | | 0.60 | 0 | 1.8 | 98.0 |

[a] *Reaction conditions:* 3.2–5.2 g buffered ionic liquid; composition $[BiPh_3]/[cation]^+[Al_2Cl_7]^- = 0.30$; catalyst precursor **A**; $[cat] = 10^{-5}$ mol/$g_{ionic\ liquid}$; stirring rate = 1200 min$^{-1}$; $t = 60$ min for $T = 25\,°C$; $t = 120$ min for $T = 0\,°C$; 300 mL glass autoclave; 40–60 mL liquid propene.

[b] Productivity given in $g_{product}/g_{ionic\ liquid} \times h$.

[c] Complete conversion.

[d] Composition solid at 0 °C.

hydrochloride. By lowering the temperature to 0 °C, the dimer selectivity could be increased by 7% to 96% (No. 52) and 98% (No. 54), respectively. The same effect was reported by Chauvin et al. for $EtAlCl_2$-buffered systems.[9c] An explanation for the increased selectivities at lower reaction temperatures might be the lower olefin solubility in combination with a slower rate of olefin insertion in the catalytic cycle. Both increase the probability for the elimination step to occur. The experiments also showed that above a certain buffer concentration, the addition of more $BiPh_3$ only resulted in minor improvements of the dimer selectivity. Thus, a cation screening was mandatory to identify halide salts which display high lifetimes combined with high selectivities.

## Effect of Different Nickel Catalyst Precursors on Dimer Selectivities

So far, only catalyst precursor **A** was used as a reference in all screening experiments. Now, a series of typical nickel(II) halides and complexes was tested for their performances in combination with $BiPh_3$-buffered chloroaluminate melts (Table 4). Considering the results of our previous cation screening, *N*-methylpyrrolidine hydrochloride mixed with two equivalents of aluminum chloride and buffered with 0.30 equivalents of $BiPh_3$ was chosen as reference system.

Since propene dimerization reactions in buffered chloroaluminate melts are limited by mass transfer of the olefin,[13d] the productivities of all nickel compounds should be the same if a sufficiently high catalyst concentration was chosen. In a recent paper, we determined the minimum catalyst concentration necessary to exclude catalyst concentration restrictions to be around $10^{-6}\ mol_{Ni}/g_{ionic\ liquid}$.[14a] We applied a concentration of $10^{-5}\ mol_{Ni}/g_{ionic\ liquid}$ to ensure that the catalyst concentration was not the rate-determining factor.

**Table 4.** Catalyst screening for nickel-catalyzed propene dimerization reactions in $BiPh_3$ buffered chloroaluminate melts.[a]

| No. | Catalyst Precursor | $C_6$ [%] | Conversion [%] | Productivity[b] |
|---|---|---|---|---|
| 55 | $NiF_2$ | 90.9 | 69 | 24.9 |
| 56 | $NiCl_2$ | 95.4 | 7 | 2.5 |
| 57 | $NiBr_2$ | 92.6 | 43 | 14.7 |
| 58 | $NiI_2$ | 93.0 | 47 | 16.1 |
| 59 | $(PPh_3)_2NiCl_2$ | 90.8 | 80 | 28.8 |
| 60 | $(PPh_3)_2NiBr_2$ | 91.0 | 81 | 28.2 |
| 61 | $Ni(hfacac)_2$ | 91.8 | 75 | 23.1 |
| 62 | $NiL_2$[c] | 90.6 | 75 | 27.0 |

[a] *Reaction conditions:* 4.4 g buffered ionic liquid; composition $[BiPh_3]/[N\text{-methylpyrrolidinium}]^+[Al_2Cl_7]^- = 0.30$; $[cat] = 10^{-5}\ mol/g_{ionic\ liquid}$; $T = 40\,°C$; stirring rate = $600\ min^{-1}$; $t = 60$ min; stirred 300-mL Parr stainless steel autoclave; 130–160 g liquid propene; hfacac = hexafluoroacetylacetonate.

[b] $g_{product}/g_{ionic\ liquid} \times h$.

[c] $NiL_2$ = bis(*N*-isopropylsalicylaldimine)Ni(II).

First, the four binary nickel halides were tested. All of them yielded very high selectivities of more than 90%. However, the productivities were quite different. Nickel fluoride produced 24.9 g product per gram buffered ionic liquid (No. 55). The other halides displayed lower productivities. This behaviour might be explained by the low solubility of these ligand free halide salts. Although $10^{-5}\ mol_{Ni}/g_{ionic\ liquid}$ were added to the liquid, the salts did not dissolve completely. Nickel chloride seemed to be almost insoluble in the buffered liquid. The bromide and iodide salts did not dissolve very well, either. Thus, the amount of catalyst which had actually dissolved in the ionic liquid, might have been below $10^{-6}\ mol_{Ni}/g_{ionic\ liquid}$. In this case, not only the mass transfer of the olefin but also the catalyst concentration determined the productivity.

To prove this theory, the triphenylphosphine adducts of nickel chloride and nickel bromide were tested, too (Nos. 59 and 60). Indeed, both complexes readily dissolved in the ionic liquid and yielded almost the same productivity of around 28 $g_{product}/g_{ionic\ liquid} \times h$ with a selectivity around 91% to give $C_6$. The productivities of nickel hexafluoroacetylacetonate (No. 61) and bis(*N*-isopropylsalicylaldimine)nickel(II) (No. 62) were only slightly lower.

The compositions of all $C_6$ fractions were consistent with those of ligand-free nickel salts. Hydrogenation showed that the hexenes consisted of 25% *n*-hexenes, 69% 2-methylpentenes, and 6% 2,3-dimethylbutenes (±2%). Either the triphenylphosphine ligands were abstracted from the Lewis acidic ionic liquids, or they did not influence the degree of branching.

## Effect of Tricyclohexylphosphine Ligands on the Dimer Structure

Finally, nickel chloride complexed by two sterically demanding tricyclohexylphosphine ligands was employed as catalyst precursor for olefin dimerization reactions in $BiPh_3$-buffered chloroaluminate ionic liquids (Table 5). Sterically hindered phosphines bound to a catalytically active nickel center in propene dimerization reactions are known to favour the formation of highly branched dimers.[2c,e,f] Especially 2,3-dimethylbutenes are interesting feedstocks for the production of various fine chemicals.[21] Due to their high research octane number (RON), they can also be used as octane booster to increase the RON of low octane motor fuel.[5]

**Table 5.** Effect of tricyclohexylphosphine on the degree of branching in nickel-catalyzed propene dimerization reactions in $BiPh_3$ buffered chloroaluminate melts.[a]

| Catalyst Precursor | $[BiPh_3]/[Cation]$ | $C_6$ [%] | HEX [%] | MP [%] | DMB [%] | Productivity[b] |
|---|---|---|---|---|---|---|
| **A** | 0.30 | 93.7 | 25 | 69 | 6 | 18.5 |
| $(PCy_3)_2NiCl_2$ | 0.30 | 78.5 | 16 | 54 | 30 | 26.3 |
| $(PCy_3)_2NiCl_2$ | 0.60 | 83.9 | 13 | 48 | 39 | 13.3 |

[a] *Reaction conditions:* 3.5–4.4 g buffered ionic liquid; composition $[AlCl_3]/[N\text{-methylpyrrolidine}\cdot HCl]=2.00$; $[cat]=10^{-5}$ mol/$g_{ionic\ liquid}$; $T=40\,°C$; stirring rate = 600 $min^{-1}$; $t=60$ min; stirred 300-mL Parr stainless steel autoclave; 250 mL liquid propene; HEX = *n*-hexenes; MP = 2-methylpentenes; DMB = 2,3-dimethylbutenes.

[b] Productivity given in $g_{product}/g_{ionic\ liquid}\times h$.

Indeed, the tricyclohexylphosphine ligands increased the 2,3-dimethylbutene (DMB) content from 6% to 30% when applying the same buffer level of 0.30 equivalents triphenylbismuth. However, the overall dimer selectivity dropped from more than 90% to 79% if tricyclohexylphosphine ligands were present. With 0.60 equivalents of $BiPh_3$, the DMB yield could be increased to 39%. The higher buffer level also increased the dimer selectivity slightly to 84%.

## Conclusions

We have shown that $BiPh_3$ efficiently buffered Lewis acidic chloroaluminate melts over a wide range of compositions. The ratio between cation, aluminum chloride, and $BiPh_3$ can be tuned to obtain tailor-made dimerization systems. Lifetimes, selectivities, and productivities can be adjusted by the choice of the cation and the composition. The addition of triphenylbismuth reduced the melting points of the resulting chloroaluminate mixtures and, thus, allowed the use of almost any ammonium or phosphonium halide cation. By performing a cation screening with 100 halide salts, we found that *N*-methylpyrrolidine hydrochloride gave the best catalytic results in terms of selectivity and lifetime. We further showed that olefin dimerization reactions in buffered chloroaluminate melts can be catalyzed by various nickel compounds with similar performances. The introduction of basic, sterically demanding tricyclohexylphosphine ligands led to higher degrees of branching, however, at the expense of lower dimer selectivities.

## Experimental Section

### General Remarks

All chemical manipulations were carried out using standard Schlenk techniques under an argon atmosphere. The products of the dimerization experiments were characterized by gas chromatography (Agilent 6850) and GC-MS (FOCUS DSQ™ Thermo Scientific). Propene (99.3%) was purchased from Riessner Gase, Lichtenfels, and was dried over a column packed with $P_4O_{10}$. Triphenylbismuth was purchased from ABCR and used without further purification. 1-Butyl-3-methylimidazolium tetrachloroaluminate (BASF), $AlCl_3$ (ReagentPlus®), $Ni(hfacac)_2$, $(PPh_3)_2NiCl_2$, $(PPh_3)_2NiBr_2$, $(PCy_3)_2NiCl_2$, and all nickel halides were purchased from Sigma–Aldrich and used as received. Complex **A**[14a] and bis(*N*-isopropylsalicylaldimine)Ni(II) were synthesized according to a literature procedure.[22] Details about the used ammonium and phosphonium salts can be found in the Supporting Information.

### Synthesis of Buffered Ionic Liquid Catalyst Compositions

The ionic liquids were synthesized by directly mixing the corresponding amount of $AlCl_3$ and halide salt in a cooled Schlenk tube. In the case of BMIM-based liquids, $AlCl_3$ was added to commercial 1-butyl-3-methylimidazolium tetrachloroaluminate. A few mL of an ionic liquid were filled into another Schlenk tube, and the corresponding amount of $BiPh_3$ was dissolved in the liquid by stirring. After the nickel catalyst precursor had been added, the homogeneous solution was syringed into the reaction vessel. Its amount was determined by the weight difference of the syringe.

### Procedure for Biphasic Propene Dimerization Reactions

For the Lewis acidity, cation, and temperature screening experiments, a 300-mL glass autoclave equipped with a stirring bar and a magnetic stirrer with a stirring rate of 1200 $min^{-1}$ was used. The glass autoclave was kept in a drying oven at 150 °C for several hours before an experiment. After the addition of the active ionic liquid, propene (40 to 60 mL) was condensed into the glass autoclave by liquid nitrogen cooling. Then, the autoclave was placed in a metal box for safety reasons, and the temperature was regulated by an external water bath. After the experiment, the pressure was slowly released by opening a valve. The product fraction was filtered through a short plug of silica and analyzed by gas chromatography.

For the catalyst screening experiments, a stirred 300-mL Parr stainless steel autoclave equipped with an internal thermocouple inside a thermowell was used. The steel vessel was kept in a drying oven at 150 °C for several hours before an experiment, and it was filled with argon. The catalyst-containing vessel was evacuated, and liquid propene (200 mL) was soaked into it at 77 K. The reaction was started by quickly heating the vessel to 40 °C with boiling water.

Cooling of the highly exothermic reaction was achieved manually by an external liquid nitrogen cooled acetone bath. After the experiment, the vessel was cooled to 0°C, and the pressure was slowly released. After reaching ambient temperature, the weight difference of the vessel was determined, and the product phase was analyzed by gas chromatography. To determine the content of *n*-hexenes, 2-methylpentenes, and 2,3-dimethylbutenes, the product fraction was hydrogenated with palladium on activated carbon and analyzed by gas chromatography.

### Supporting Information

Experimental procedures, the preparation of halide salts and ionic liquids as well as the detailed results of the cation screening experiments for this article are available in the Supporting Information

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## References

[1] a) K. Ziegler, E. Holzkamp, H. Breil, H. Martin, *Angew. Chem.* **1955**, *67*, 541–547; b) K. Fischer, K. Jonas, P. Misbach, R. Stabba, G. Wilke, *Angew. Chem.* **1973**, *85*, 1001–1012.

[2] a) N. Gene, H. D. Lyons, U.S. Patent 2,969,408, **1961**; b) E. H. Drew, U.S. Patent 3,390,201, **1968**; c) G. G. Eberhardt, W. P. Griffin, *J. Catal.* **1970**, *16*, 245–253; d) H. E. Swift, C.-Y. Wu, U.S. Patent 3,622,649, **1971**; e) B. Bogdanovic, *Selectivity Control in Nickel-Catalyzed Olefin Oligomerization*, in: *Advances in Organometallic Chemistry*, Vol. 17, (Eds.: F. G. A. Stone, R. West), Academic Press, New York, **1979**, pp 105–140; f) C. Carlini, M. Marchionna, A. M. R. Galletti, G. Sbrana, *J. Mol. Catal. A: Chem.* **2001**, *169*, 19–25; g) G. Wilke, U.S. Patent 3,379,706, **1968**.

[3] a) Y. Chauvin, J. F. Gaillard, D. V. Quang, J. W. Andrews, *Chem. Ind.* **1974**, 375–378; b) D. Commereuc, Y. Chauvin, G. Leger, J. Gaillard, *Oil & Gas Science and Technology – Rev. IFP* **1982**, *37*, 639–649; c) Y. Chauvin, A. Hennico, G. Leger, J. L. Nocca, *Erdoel Erdgas Kohle* **1990**, *106*, 7.

[4] a) H. Olivier-Bourbigou, F. Favre, A. Forestière, F. Hugues, *Ionic Liquids and Catalysis: the IFP Biphasic Difasol Process*, in: *Handbook of Green Chemistry*, (Eds.: P. T. Anastas, R. H. Crabtree), Wiley-VCH, Weinheim, **2010**, pp 101–126; b) A. Forestière, H. Olivier-Bourbigou, L. Saussine, *Oil & Gas Science and Technology – Rev. IFP* **2009**, *64*, 649–667.

[5] a) J. Robinson, R. C. Bugle, H. L. Chum, D. Koran, R. A. Osteryoung, *J. Am. Chem. Soc.* **1979**, *101*, 3776–3779; b) J. S. Wilkes, J. A. Levisky, R. A. Wilson, C. L. Hussey, *Inorg. Chem.* **1982**, *21*, 1263–1264; c) R. J. Gale, B. Gilbert, R. A. Osteryoung, *Inorg. Chem.* **1978**, *17*, 2728–2729.

[6] a) A. A. Fannin, L. A. King, J. A. Levisky, J. S. Wilkes, *J. Phys. Chem.* **1984**, *88*, 2609–2614; b) A. A. Fannin, D. A. Floreani, L. A. King, J. S. Landers, B. J. Piersma, D. J. Stech, R. L. Vaughn, J. S. Wilkes, L. Williams John, *J. Phys. Chem.* **1984**, *88*, 2614–2621; c) C. L. Hussey, T. B. Scheffler, J. S. Wilkes, J. A. A. Fannin, *J. Electrochem. Soc.* **1986**, *133*, 1389–1391; d) T. A. Zawodzinski, R. T. Carlin, R. A. Osteryoung, *Anal. Chem.* **1987**, *59*, 2639–2640; e) C. L. Hussey, *Pure Appl. Chem.* **1988**, *60*, 1763–1772; f) G. P. Smith, A. S. Dworkin, R. M. Pagni, S. P. Zingg, *J. Am. Chem. Soc.* **1989**, *111*, 525–530; g) F. Taulelle, A. I. Popov, *Polyhedron* **1983**, *2*, 889–894; h) J. S. Wilkes, J. S. Frye, G. F. Reynolds, *Inorg. Chem.* **1983**, *22*, 3870–3872; i) R. H. Dubois, M. J. Zaworotko, P. S. White, *Inorg. Chem.* **1989**, *28*, 2019–2020.

[7] a) J. D. Holbrey, K. R. Seddon, *Clean Technol. Environ. Policy* **1999**, *1*, 223–236; b) T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2084; c) J. H. Clark, K. Martin, A. J. Teasdale, S. J. Barlow, *J. Chem. Soc. Chem. Commun.* **1995**, 2037–2040; d) C. J. Adams, M. J. Earle, G. Roberts, K. R. Seddon, *Chem. Commun.* **1998**, 2097–2098; e) F. G. Sherif, L.-J. Shyu, U.S. Patent 5,824,832, **1998**; f) A. K. Abdul-sada, M. P. Atkins, B. Ellis, P. K. G. Hodgson, M. L. M. Morgan, K. R. Seddon, U.S. Patent 5,994,602, **1999**.

[8] J. A. Boon, J. A. Levisky, J. L. Pflug, J. S. Wilkes, *J. Org. Chem.* **1986**, *51*, 480–483.

[9] a) Y. Chauvin, B. Gilbert, I. Guibard, *J. Chem. Soc. Chem. Commun.* **1990**, 1715–1716; b) Y. Chauvin, D. Commereuc, I. Guibard, A. Hirschauer, H. Olivier, L. Saussine, U.S. Patent 5,104,840, **1992**; c) Y. Chauvin, S. Einloft, H. Olivier, *Ind. Eng. Chem. Res.* **1995**, *34*, 1149–1155; d) Y. Chauvin, H. Olivier, C. N. Wyrvalski, L. C. Simon, R. F. de Souza, *J. Catal.* **1997**, *165*, 275–278.

[10] a) O. Stenzel, R. Brüll, U. M. Wahner, R. D. Sanderson, H. G. Raubenheimer, *J. Mol. Catal. A: Chem.* **2003**, *192*, 217–222; b) M. Goledzinowski, V. I. Birss, J. Galuszka, *Ind. Eng. Chem. Res.* **1993**, *32*, 1795–1797.

[11] a) F. Favre, A. Forestiere, F. Hugues, H. Olivier-Bourbigou, J. A. Chodorge, *Oil Gas Eur. Mag.* **2005**, *31*, 83–91; b) B. Gilbert, H. Olivier-Bourbigou, F. Favre, *Oil & Gas Science and Technology – Rev. IFP* **2007**, *62*, 745–759.

[12] a) I. C. Quarmby, R. A. Mantz, L. M. Goldenberg, R. A. Osteryoung, *Anal. Chem.* **1994**, *66*, 3558–3561; b) I. C. Quarmby, R. A. Osteryoung, *J. Am. Chem. Soc.* **1994**, *116*, 2649–2650.

[13] a) P. Wasserscheid, *Patent* WO 9847616, **1998**; b) B. Ellis, W. Keim, P. Wasserscheid, *Chem. Commun.* **1999**, 337–338; c) P. Wasserscheid, M. Eichmann, *Catal. Today* **2001**, *66*, 309–316; d) M. Eichmann, W. Keim, M. Haumann, B. U. Melcher, P. Wasserscheid, *J. Mol. Catal. A: Chem.* **2009**, *314*, 42–48; e) D. S. McGuinness, W. Mueller, P. Wasserscheid, K. J. Cavell, B. W. Skelton, A. H. White, U. Englert, *Organometallics* **2001**, *21*, 175–181.

[14] a) M. Dötterl, H. G. Alt, *ChemCatChem* **2011**, *3*, 1799–1804; b) M. Dötterl, H. G. Alt, *Adv. Synth. Catal.* **2012**, *354*, 389–398.

[15] a) B. Gilbert, Y. Chauvin, I. Guibard, *Vib. Spectrosc.* **1991**, *1*, 299–304; b) H. Olivier, Y. Chauvin, F. Di Marco-Van Tiggelen, *J. Chem. Soc. Dalton Trans.* **1995**, 3867–3871.

[16] F. Peruch, H. Cramail, A. Deffieux, *Macromolecules* **1999**, *32*, 7977–7983.

[17] F. H. Hurley, J. T. P. Wier, *J. Electrochem. Soc.* **1951**, *98*, 203–206.

[18] a) K. D. Hope, M. S. Driver, T. V. Harris, U.S. Patent 6,395,948, **2002**; b) K. D. Hope, D. A. Stern, E. A. Benham, U.S. Patent 7,309,805, **2007**; c) K. D. Hope, D. W. Twomey, M. S. Driver, D. A. Stern, B. J. Collins, T. V. Harris, U.S. Patent 7,259,284, **2007**.

[19] S. G. Park, P. Trulove, R. T. Carlin, R. A. Osteryoung, *J. Am. Chem. Soc.* **1991**, *113*, 3334–3340.

[20] a) K. Kim, C. M. Lang, P. A. Kohl, *J. Electrochem. Soc.* **2005**, *152*, E56–E60; b) K. Kim, C. Lang, R. Moulton, P. A. Kohl, *J. Electrochem. Soc.* **2004**, *151*, A1168–A1172.

[21] a) H. Sato, H. Tojima, K. Ikimi, *J. Mol. Catal. A: Chem.* **1999**, *144*, 285-293; b) H. Sato, H. Tojima, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3079–3084; c) M. Itagaki, G. Suzukalo, K. Nomura, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 79–82.

[22] R. H. Holm, K. Swaminathan, *Inorg. Chem.* **1963**, *2*, 181–186.