Are Ionic Liquids and Liquid Coordination Complexes Really Different? - Synthesis, Characterization, and Catalytic Activity of AlCl$_3$/Base Catalysts

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Experimental

Chemicals

Anhydrous AlCl$_3$ (99% purity) and triethylammonium hydrochloride (HN$_2$Cl) (98% purity) were purchased from Alfa Aesar (Ward Hill, MA); while 1-methyl imidazole (N-Mim) (99% purity), N-methyl-2-pyrrolidone (O-NMP) (99% purity), and Benzyl chloride (99% purity) were purchased from VWR Life Science (Amresco, OH), and anhydrous benzene and acetonitrile were purchased from Sigma-Aldrich (St. Louis, MO). Dimethyl sulfoxide-$d_6$ (99.9% purity), used as NMR solvent, was purchased from Cambridge Isotope Laboratory, Inc (Andover, MA).

Characterization

Neat nuclear magnetic resonance spectroscopy (NMR) ($^1$H, $^{13}$C, $^{27}$Al): The AlCl$_3$/base catalysts were characterized by neat NMR. The $^1$H, $^{13}$C, and $^{27}$Al NMR spectra were obtained utilizing a 500 MHz Bruker Avance NMR spectrometer (Karlsruhe, Germany). Each sample was loaded neat in a flame-sealed capillary, and the spectra were collected at 100 °C using dimethyl sulfoxide-$d_6$ (DMSO-$d_6$) as an external lock solvent. The $^{27}$Al NMR spectra were obtained with a tuned Al probe, using AlCl$_3$·6H$_2$O/D$_2$O solution as the external lock.
Infrared spectroscopy (FT-IR): The spectra were recorded on a Bruker Alpha FT-IR instrument, Brucker Optics Inc. (Billerica, MA) equipped with an attenuated total reflectance (ATR) sample accessory in the range of 400–4000 cm$^{-1}$ (number of scans = 24). The measurements were done under Ar atmosphere. The Lewis acidity measurements were conducted by mixing 25 mg each of ionic liquids (ILs) or liquid coordination complexes (LCCs) and acetonitrile as a probe molecule, and then spreading them on the ATR window for spectra collection.

Single crystal X-ray diffraction (SCXRD): The data were collected on a Bruker diffractometer equipped with a Platform 3-circle goniometer and an Apex II CCD area detector (Bruker-AXS, Madison, WI) using graphite-monochromated Mo-Kα radiation. Suitable crystals were isolated under an optical polarizing microscope, mounted on a nylon loop, and cooled to the collection temperature under a stream of N₂ gas using an Oxford N-helix cryostat (Oxford Cryosystems, Oxford, UK). A hemisphere of unique data was collected using a strategy of 0.5° scans about omega and phi. Unit cell determination, data collection, integration, absorption correction, and scaling were done using the Bruker Apex2 software suite.

Experimental Section

Synthesis of AlCl₃/N-Mim and AlCl₃/O-NMP catalysts: In an Ar-filled glove bag, a 10-mL borosilicate glass screw-top vial equipped with a Teflon coated magnetic stir bar was loaded with ligand followed by addition of white solid AlCl₃ with different molar fractions ($\chi_{\text{AlCl}_3}$) (here $\chi_{\text{AlCl}_3}$ represents mole fraction of AlCl₃) of 0.2, 0.33, 0.4, 0.5, 0.6, 0.67, and 0.8. The vials were covered with a cap having a Teflon/silicon (10/90) septum and sealed with Parafilm. The vials were then removed from the glove bag, and heated with magnetic stirring in a temperature-controlled oil bath at 100 °C. After 4 h the vials were removed from the oil bath and left to cool on the bench top. The solid catalyst of AlCl₃/N-Mim at 0.4, 0.5, and 0.6 were crystallized by heating a sample at 100 °C to liquefy it, followed by very slow cooling to room temperature, where it was left for more than 10 days after which crystals of neutral AlCl₃(N-Mim) were obtained at all ratios. The solid AlCl₃/O-NMP catalyst at 0.5 was crystallized by following a similar procedure and crystals of [AlCl₂(O-NMP)₂][AlCl₄] were obtained.

AlCl₃/O-NMP catalyst at $\chi_{\text{AlCl}_3}$ 0.5 prepared in benzene: In an Ar-filled glove bag, a 5-mL borosilicate glass screw-top vial equipped with a Teflon coated magnetic stir bar was loaded with O-NMP (1 mmol) and benzene (2 g) followed by addition of solid AlCl₃ (1 mmol). After addition,
the heterogeneous mixture with white solid and colorless liquid was heated at 75 °C for 4 h and the reaction mixture became a homogeneous colorless liquid. After 20 days, crystals of [Al(O-NMP)₆][AlCl₄]₃·(C₆H₆)₃ were obtained.

The ILs [HN₂₂₂][AlCl₄], mixture of [HN₂₂₂][AlCl₄] and [HN₂₂₂][Al₂Cl₇] at χₐlCl₃ 0.6, and [HN₂₂₂][Al₂Cl₇] were prepared by following reported procedures.

Conductivity measurements: The conductivity was measured using a YSI 3200 conductivity instrument (Model 3200-115V). The LCC sample was loaded neat in the glass tube and heated to 100 °C under Ar atmosphere. As sample attained temperature of 100 °C, the electrode was inserted in the sample and conductivity was recorded.

Catalysis

For a typical experiment, in an Ar-filled glove bag, a 5-mL borosilicate glass screw-top vial equipped with a Teflon coated magnetic stir bar was loaded with 2 mol% of catalyst followed by addition of a mixture of 10 mmol of benzene and 2 mmol of benzyl chloride. The vial was capped using a rubber septum, sealed with Parafilm, and stirred at room temperature for 3 min. After 3 min, a small aliquot of mixture was withdrawn from the reaction mixture and monitored by using a gas chromatographer coupled to a mass spectrometer (GC-MS, HP 6890 GC series connected to a Water Micromass AutoSpec-Ultima™ NT Mass spectrometer, Waters, Milford, MA). The following conditions were utilized: Initial temperature of 40 °C and a hold time of 1 min, ramp rate of 10 °C min⁻¹, and a final temperature of 200 °C, with a hold time of 10 min; Zebron ZB-5MS column (30 m length, 250 µm internal diameter, column coating thickness of 25 µm), electron ionization (EI) source temperature 220 °C. The conversion was calculated based on peak area integration of the unreacted benzyl chloride. The diphenylmethane product selectivity was determined by calculating area under the peak of diphenyl methane and di-benzyl benzene.
Figure S1. $^1$H (left) and $^{13}$C (right) NMR of AlCl$_3$/N-Mim catalysts at $\chi_{\text{AlCl}_3}$ 0.33, 0.4, 0.5, and 0.6 (100 °C, neat, DSMO-$d_6$ lock), compared to N-Mim.

Figure S2. $^1$H (left) and $^{13}$C (right) NMR of AlCl$_3$/O-NMP catalysts at $\chi_{\text{AlCl}_3}$ 0.33-0.6 (100 °C, neat, DSMO-$d_6$ lock) compared to O-NMP.
Figure S3. Portion of the IR spectra of AlCl$_3$/N-Mim catalysts at $\chi_{\text{AlCl}_3}$ 0.33, 0.4, 0.5, and 0.6.

Figure S4. Asymmetric unit (left) and crystal packing (right) of [(AlCl$_2$(O-NMP)$_2$)$_2$][(AlCl$_4$)$_2$] crystal isolated by slow cooling of liquid AlCl$_3$/O-NMP catalyst at $\chi_{\text{AlCl}_3}$ 0.5. The whole O-NMP ligands of [AlCl$_2$(O-NMP)$_2$] show significant positional disordered which are unmodeled.
Figure S5. Portion of the IR spectra of AlCl₃/O-NMP catalysts at \( \chi_{\text{AlCl}_3} \) 0.33, 0.4, 0.5, and 0.6 compared to pure O-NMP.

Figure S6. Variation in the CN IR stretch in acetonitrile solutions as a function of mole fraction of AlCl₃ in the IL and LCCs.

Table S1. Variation in C=O and Al-Cl stretching frequencies in AlCl₃/O-NMP catalysts.

<table>
<thead>
<tr>
<th>Molar Fraction</th>
<th>C=O Stretch (cm⁻¹)</th>
<th>Al-Cl Stretch (cm⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>1693</td>
<td>-</td>
</tr>
<tr>
<td>0.33 and 0.4</td>
<td>1634</td>
<td>482</td>
</tr>
<tr>
<td>0.5</td>
<td>1636</td>
<td>482</td>
</tr>
<tr>
<td>0.6</td>
<td>1654</td>
<td>500</td>
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Table S2. Ionic conductivity measurement of LCCs

<table>
<thead>
<tr>
<th>LCCs System</th>
<th>Temperature (°C)</th>
<th>Conductivity (mS/cm)</th>
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<tbody>
<tr>
<td>AlCl₃(O-NMP) $\chi_{AlCl3}$ 0.6</td>
<td>100</td>
<td>2.57</td>
</tr>
<tr>
<td>AlCl₃(N-Mim) $\chi_{AlCl3}$ 0.6</td>
<td>100</td>
<td>0.77</td>
</tr>
</tbody>
</table>

References

1. APEX 2 AXScale and SAINT, version 2010; Bruker AXS, Inc.: Madison, WI.