Subscriber access provided by Stony Brook University | University Libraries

Letter

Enhanced Acidity and Activity of Aluminum/Gallium Based Ionic Liquids Resulting from Dynamic Anionic Speciation

Kai Li, Hemant Choudhary, Manish Kumar Mishra, and Robin D Rogers

ACS Catal., **Just Accepted Manuscript** • DOI: 10.1021/acscatal.9b03132 • Publication Date (Web): 26 Sep 2019

Downloaded from pubs.acs.org on September 30, 2019

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Enhanced Acidity and Activity of Aluminum/Gallium Based Ionic Liquids Resulting from Dynamic Anionic Speciation

Kai Li,[a,‖] Hemant Choudhary,[a,ξ] Manish Kumar Mishra[a,§] and Robin D. Rogers[a,b,*]

[a] College of Arts & Sciences, The University of Alabama, Tuscaloosa, Alabama 35487, United States

[b] 525 Solutions, Inc., P.O. Box 2206, Tuscaloosa, Alabama 35403, United States

---

ABSTRACT: To explore if the catalytic activity of single metal species in halometallate catalysts can be enhanced with mixed metal species, aluminum and gallium were simultaneously introduced to prepare a mixed metal ionic liquids (IL) through a one-pot reaction of $[HN_{222}]Cl$, $AlCl_3$, and $GaCl_3$ in various amounts. The Lewis acidity in Friedel-Crafts acylation and alkylation reactions of these IL compositions were evaluated and all mixed metal $[HN_{222}][xAlCl_3+(2\text{-}x)GaCl_3]Cl$ ILs exhibited higher catalytic activity than $AlCl_3$, $GaCl_3$, $[HN_{222}][Al_2Cl_7]$, or $[HN_{222}][Ga_2Cl_7]$. The broadening in ^{27}Al NMR of these ILs indicates the presence of dynamic anionic species, whereas MALDI-TOF and acetonitrile-probed FT-IR analyses correlates the structure-activity relationship, for instance, identifying the presence of mixed metal containing $[Cl_2GaOClAlClOGaCl_2]^-$ species in the better performing ILs.

KEYWORDS. Double salt ionic liquids, Friedel-Crafts acylation/alkylation, Lewis acid catalyst, chloroaluminate, chlorogallate

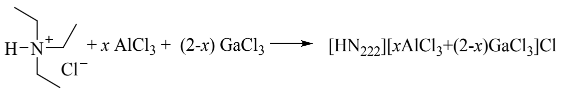
Ionic liquids (ILs, salts with melting points below 100 °C[1]), have aroused extensive attention in different areas, such as biomass processing,[2, 3] active pharmaceutical ingredients,[4] process development,[5] materials sciences,[6] *etc*., due to their easily accessible and tunable properties.[1, 7] The ease of combining different cations and anions in IL structures to tune their catalytic properties has also been a promising and active area in the search for alternatives to traditional catalysts. For instance, halometallate ILs (a subclass of ILs possessing metal halide(s) in/as anion[8]) have been utilized as reaction media or active acidic catalysts in many different reactions.[8a, 9]

Chauvin's pioneering work with chloroaluminates for catalytic olefin dimerization and metathesis was awarded the 2005 Noble Prize in Chemistry.[10] Since then, these ILs have been exploited to replace traditional toxic and corrosive Lewis acids *e.g.*, aluminum chloride ($AlCl_3$) or boron trifluoride (BF_3), and Brønsted acids, such as hydrofluoric acid (HF) or concentrated sulfuric acid (H_2SO_4), *etc*., as catalysts in industrially relevant chemical transformations,[11] such as Friedel-Crafts reactions, esterifications, and oxidations, among others. In fact, Chevron recently announced a scaled-up facility for liquid-phase alkylation using chloroaluminate ILs replacing the toxic HF.[12]

The field of ILs has experienced extensive growth and development in the past few years, and recently attention is starting to focus on more complex liquids containing more than two types of ions, variously named binary mixtures, high ionicity ionic liquids, and double salt ionic liquids (DSILs).[13] Compared to single metal halometallate ILs, these multiple metal center containing ILs can allow fine tuning of the physical and chemical properties of the *final* IL composition. ILs based on chloroaluminates and CuCl have been used as a catalyst for industrial isobutane alkylation.[14] Very recently, we have also reported superior catalytic performances of an Al-Zn IL system ($[HN_{222}]_{2x}[(1-x)AlCl_3+xZnCl_4]$) in Beckman rearrangement reactions when compared to the individual single metal catalysts.[15] The results suggested that this approach could be a unique methodology for the design of highly pertinent catalysts. Motivated by these results and with an urge to develop highly active acidic catalyst, we sought to strategically design new multiple metal center containing IL catalytic systems, which could be prepared in straightforward one-pot reactions.

Both $AlCl_3$ and gallium chloride ($GaCl_3$) are established Lewis acids, belonging to the same group and having similar coordination environments. Aluminum is more electronegative than Ga indicating more electrostatic attraction, while Ga has a larger size that can help electron/charge delocalization. Both chloroaluminate and chlorogallate ILs have been separately reported to be active in acid-catalyzed reactions.[7, 16] We hypothesized that ILs containing both Al^{3+} and Ga^{3+} would possess an ideal Lewis acidity leading to synergistic activity. Interestingly, despite the ease of making mixed-metal ILs of this type, the combination of both Al and Ga into one IL has not yet been reported.

In our work, Al/Ga-based ILs were easily synthesized in a one-pot approach by direct mixing, under an inert (Ar) atmosphere and without additional solvents. Solid triethylammonium chloride ($[HN_{222}]Cl$), $AlCl_3$, and $GaCl_3$ were mixed in a 10 mL vial where the molar ratio of total metal chlorides to ammonium salt was 2:1. The Al:Ga molar ratio was varied to give systems of the following formulas $[HN_{222}][xAlCl_3+(2\text{-}x)GaCl_3]Cl$, where x = 2.0, 1.5, 1.33, 1.0, 0.67, 0.5, or 0 (**ESI**, **Scheme 1**). Mixing of the solid reactants led to an exothermic reaction immediately yielding transparent liquids in all molar ratios studied. These systems were then sealed and heated at 50 °C for 24 h.



Scheme 1. One pot synthesis of [HN$_{222}$][xAlCl$_3$+(2-x)GaCl$_3$]Cl liquids from solid precursors.

The Lewis acidity of the [HN$_{222}$][xAlCl$_3$+(2-x)GaCl$_3$]Cl, ILs was investigated by FT-IR spectroscopy with acetonitrile (CH$_3$CN) as probe,[17] and compared with AlCl$_3$ and GaCl$_3$. The ILs, AlCl$_3$, and GaCl$_3$ were treated with CH$_3$CN in 1:1 molar ratio and the FT-IR spectra were recorded (**Figure 1**). Pure CH$_3$CN has two characteristic bands at 2292 and 2252 cm^{-1}, originating from its C≡N stretching vibrations. For AlCl$_3$, GaCl$_3$, and [HN$_{222}$][xAlCl$_3$+(2-x)GaCl$_3$]Cl, two new bands at ca. 2320 and 2300 cm^{-1} appeared after mixing with acetonitrile, confirming coordination of CH$_3$CN and allowing an evaluation of the overall Lewis acidity of the metal centers.

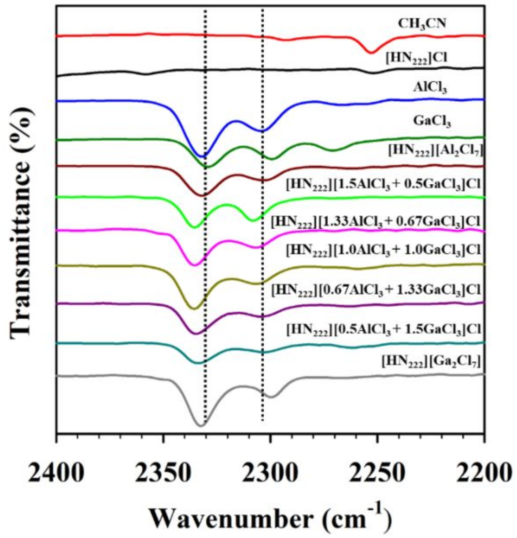


Figure 1. FT-IR spectra of the ILs and starting materials after treatment with acetonitrile.

In these spectra, the higher the wavenumber of the coordinated CH$_3$CN bands, the stronger the coordination and the higher the Lewis acidity. Compared to AlCl$_3$ and GaCl$_3$, all [HN$_{222}$][xAlCl$_3$+(2-x)GaCl$_3$]Cl ILs exhibited higher CH$_3$CN band wavenumbers (around 2330 cm^{-1}; **Figure 1**) indicating each IL was more Lewis acidic than either pure metal chloride. Of the ILs, [HN$_{222}$][1.33AlCl$_3$+0.67GaCl$_3$]Cl, was found to be the most acidic (υ = 2335 cm^{-1}).

Interestingly, during this study crystals were formed overnight from the 1:1 solution of [HN$_{222}$][xAlCl$_3$+(2-x)GaCl$_3$]Cl and acetonitrile. Single crystal X-ray diffraction of these crystals revealed them to be the previously reported [Al(CH$_3$CN)$_5$Cl][AlCl$_4$]$_2$•CH$_3$CN[18] and [Al(CH$_3$CN)$_5$Cl][GaCl$_4$]$_2$•CH$_3$CN (**Figure 2**). The crystal structure of the latter is isostructural with the former,[18] with one [Al(CH$_3$CN)$_5$Cl]$^{2+}$ cation and two [GaCl$_4$]$^-$ anions. In the cation, the Al atom is bonded to one Cl atom and five CH$_3$CN molecules in a distorted octahedral geometry (**Figure 2**). The four equatorial acetonitrile ligands in the cation are in the plane perpendicular to A1-C1(1) bond. This bond slightly bends away from the equatorial acetonitrile ligands plane with a mean C1-A1-N angle of 94.6° due to the consequence of steric effects generated by Cl. The [GaCl$_4$]$^-$ anions have approximate tetrahedral geometry.

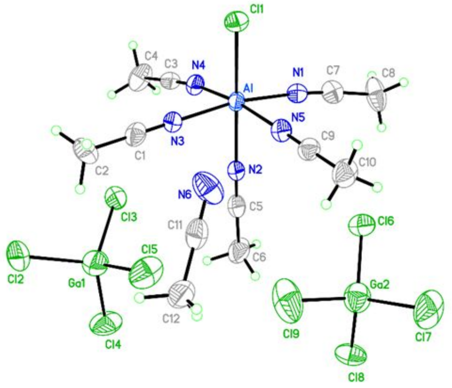


Figure 2. Probability ellipsoid (50%) plot of the formula unit of [Al(CH$_3$CN)$_5$Cl][GaCl$_4$]$_2$•CH$_3$CN.

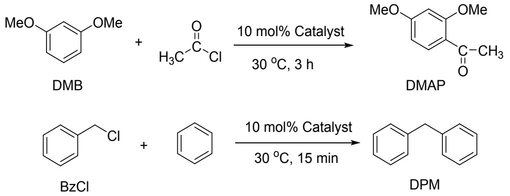
Overall, these results confirmed that the ILs with double metal centers had higher Lewis acidity compared with the Lewis acid precursors, confirming our hypothesis. We next tested their catalytic performance in the classic Lewis acid catalyzed Friedel-Crafts acylation reaction of 1,3-dimethoxybenzene (DMB) and acetyl chloride. **Table 1** summarizes the results for acylation of DMB with 10 mol% [HN$_{222}$][xAlCl$_3$+(2-x)GaCl$_3$]Cl, AlCl$_3$, and GaCl$_3$ in benzene at 30 °C for 3 h. The only product observed under our employed reaction conditions was the monoacylated product 2',4'-dimethoxyacetophenone (DMAP). Among all of the acid catalysts, [HN$_{222}$][1.33AlCl$_3$+0.67GaCl$_3$]Cl resulted in the highest yields of DMAP (25.4%; **Table 1**, entry 6).

Interestingly, the well-established state-of-the-art Lewis acidic catalysts, AlCl$_3$ and GaCl$_3$, afforded DMAP in only 7.3% and 3.6% yield, respectively, under identical conditions (**Table 1**, entries 3-4). The all Al-based IL, [HN$_{222}$][Al$_2$Cl$_7$], could not convert DMB efficiently and offered only 3.7% DMAP yield under the employed reaction conditions, even lower than AlCl$_3$ (**Table 1**, entry 5). The all Ga-based IL, [HN$_{222}$][Ga$_2$Cl$_7$], on the other hand, had a decent DMB conversion to form 16.6% DMAP (**Table 1**, entry 11). Nevertheless, all of the Al/Ga ILs could convert 48-70% DMB to afford DMAP yields of 13-25% (**Table 1**, entries 6-10).

The catalytic activity of the mixed metal ILs was also evaluated for the alkylation of benzyl chloride (BzCl) using benzene under inert atmosphere at 30 °C for 15 min (**Table 1)**. Diphenylmethane (DPM) was the only product detected. The trend in catalytic activities was similar to that observed for the acylation reaction, with [HN$_{222}$][1.33AlCl$_3$+0.67GaCl$_3$]Cl exhibiting the highest DPM yield (72%, **Table 1**, entry 7). DPM yields with AlCl$_3$ and GaCl$_3$ under identical conditions were 63.6% an 64.1%, respectively (**Table 1**, entries 3-4). The all Al- or Ga-based ILs afforded only 65.5% and 57.8% DPM, respectively (**Table 1**, entries 5 and 11). The [HN$_{222}$][xAlCl$_3$+(2-

x)GaCl$_3$]Cl ILs have better or similar catalytic performance considering the yields, compared with the well-established Lewis acids catalyst, *e.g.*, AlCl$_3$, GaCl$_3$, [HN$_{222}$][Al$_2$Cl$_7$], and [HN$_{222}$][Ga$_2$Cl$_7$].

Table 1. Acylation and alkylation reactions studied



Entry	Catalyst	DMAP[a]		DPM[b]	
		Yield (%)	Sel. (%)	Yield (%)	Sel. (%)
1	None	0	0	0	0
2	[HN$_{222}$]Cl	0	0	0	0
3	AlCl$_3$	7.3	34.1	63.6	63.6
4	GaCl$_3$	3.6	32.0	64.1	64.1
5	[HN$_{222}$][Al$_2$Cl$_7$]	3.7	12.3	65.5	65.5
6	[HN$_{222}$][1.5AlCl$_3$ +0.5GaCl$_3$]Cl	18.7	36.0	69.3	69.3
7	[HN$_{222}$][1.33AlCl$_3$ + 0.67GaCl$_3$]Cl	25.4	20.9	72.0	72.0
8	[HN$_{222}$][1.0AlCl$_3$ +1.0GaCl$_3$]Cl	20.3	31.6	71.7	71.7
9	[HN$_{222}$][0.67AlCl$_3$ +1.33GaCl$_3$]Cl	13.7	28.5	68.0	68.0
10	[HN$_{222}$][0.5AlCl$_3$ +1.5GaCl$_3$]Cl	19.1	31.1	62.5	62.5
11	[HN$_{222}$][Ga$_2$Cl$_7$]	16.6	33.7	57.8	57.8

[a]DMB: Acetyl Chloride: Catalyst = 1:1:0.1 (molar ratio), benzene (1 mL), 30 °C, 3 h. [b]BzCl: Catalyst = 1:0.1 (molar ratio), benzene (5 mL), 30 °C, 15 min. Product yield and selectivity were determined by GC-MS using naphthalene as an internal standard.

Having shown [HN$_{222}$][1.33AlCl$_3$+0.67GaCl$_3$]Cl to be the best catalyst, we sought to understand what species was responsible for the synergistic catalytic activity. ^{1}H, ^{13}C, ^{27}Al, and ^{71}Ga NMR spectra were recorded for all of the ILs studied (see **Figures 3, S1, S2**). ^{1}H and ^{13}C NMR confirmed the presence of [HN$_{222}$]$^+$ rather than any N-coordinated species. ^{27}Al NMR (**Figure 3**) showed a broad peak centered at 106 ppm for[HN$_{222}$][Al$_2$Cl$_7$] which was assigned to the [Al$_n$Cl$_{3n+1}$]$^-$ anion in dynamic equilibrium based on previous reports (**Figure S3**).[19] The spectrum for Ga containing ILs, exhibited a clear hump at 98 ppm and also the broader peak for [Al$_n$Cl$_{3n+1}$]$^-$. This suggests that the chemical environment of Al in the anion is not the same in these ILs compared with [HN$_{222}$][Al$_2$Cl$_7$]. The peak shapes of these ILs are also different, which is possibly due to the dynamic equilibrium of the anion species and their different concentrations[20] We believe the presence of Ga modifies the chemical environment leading to stronger acidic species, which could explain the higher activity of these ILs compared with [HN$_{222}$][Al$_2$Cl$_7$]. ^{71}Ga NMR was attempted to characterize the ILs, however no signal was obtained, which is consistent with the reported absence of a ^{71}Ga signal in studies where polynuclear anions containing Ga were studied.[21]

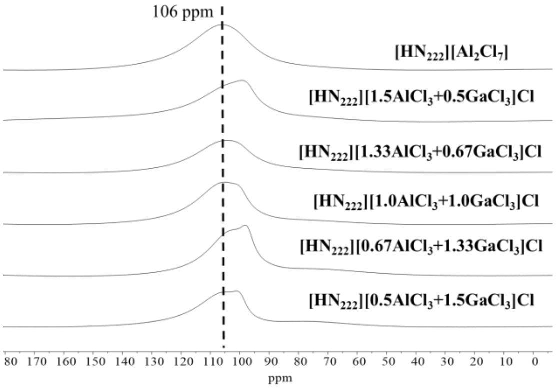


Figure 3. ^{27}Al NMR spectra of [HN$_{222}$][xAlCl$_3$+(2-x)GaCl$_3$]Cl ILs at 300 K, DMSO-d_6 as external lock solvent in a capillary.

To further understand the speciation in [HN$_{222}$][xAlCl$_3$+(2-x)GaCl$_3$]Cl, these ILs were analyzed with matrix-assisted laser-desorption ionization time-of-flight (MALDI-TOF). All of the ILs have the expected peak at m/z 102 in the positive-ion spectra (**Figure S4**), indicating the existence of the [HN$_{222}$]$^+$ cation. The negative-ion spectrum of [HN$_{222}$][Al$_2$Cl$_7$] (**Figure 4**) has two signals at m/z 168 and 302 that can be assigned to [AlCl$_4$]$^-$ and [Al$_2$Cl$_7$]$^-$. This is in agreement with the broad signal assigned to [Al$_n$Cl$_{3n+1}$]$^-$ in the ^{27}Al NMR.[22] For [HN$_{222}$][Ga$_2$Cl$_7$], GaCl$_3$ and [GaCl$_4$]$^-$ were observed, confirming the dynamic equilibrium between GaCl$_3$, [GaCl$_4$]$^-$, and [Ga$_2$Cl$_7$]$^-$.[21]

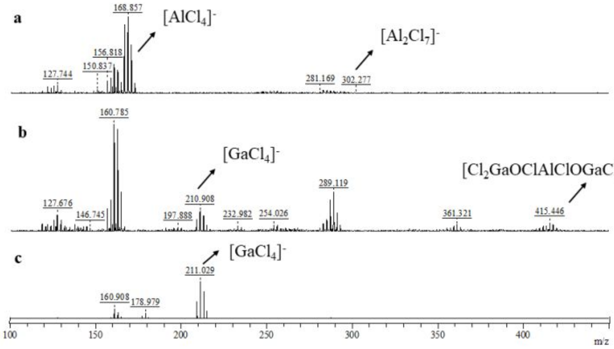


Figure 4. Negative-ion MALDI-TOF mass spectra of (a) [HN$_{222}$][Al$_2$Cl$_7$], (b) [HN$_{222}$][1.33AlCl$_3$+0.67GaCl$_3$]Cl, and (c) [HN$_{222}$][Ga$_2$Cl$_7$].

When [HN$_{222}$][1.33AlCl$_3$+0.67GaCl$_3$]Cl was studied by MALDI-TOF, a [GaCl$_4$]$^-$ peak at m/z 211 was observed, however, a peak corresponding to [AlCl$_4$]$^-$ was not found. Instead, a new peak at m/z 415 appeared suggesting the presence of an anion containing both Al and Ga. This peak was also observed for [HN$_{222}$][1.0AlCl$_3$+1.0GaCl$_3$]Cl and [HN$_{222}$][0.67AlCl$_3$+1.33GaCl$_3$]Cl (**Figure S5**) and suggests the presence of a complex polynuclear species consisting of Al, Ga, O, and Cl atoms based on the mass and charge, which could possibly be [Cl$_2$GaOClAlClOGaCl$_2$]$^-$ (**Figure S6**), where the oxygen and chloride atoms are shared by both Al and Ga. The presence of oxygen is likely due to the highly hygroscopic nature of the metal chlorides employed in this study, likely resulting in the formation of AlOCl or GaOCl type units. Such a coordination mode could account for the higher catalytic activity observed, however, it must be noted that under the conditions of our experiment such large dynamic anions are highly unstable, and thus a lower concentration should be anticipated. The formation of the polynuclear $[Cl_2GaOClAlClOGaCl_2]^-$ (and similar) anions could explain why there is no signal in the ^{71}Ga NMR.[21] In some cases, such as $[HN_{222}][1.33AlCl_3+0.67GaCl_3]Cl$ (**Figure 4)** and $[HN_{222}][0.67AlCl_3+1.33GaCl_3]Cl$ (**Figure S7**), we also observed a peak at m/z 361 that also suggests the presence of the oxygen atom in the system.[19, 23] Even, without definitive proof of the $[Cl_2GaOClAlClOGaCl_2]^-$ ion and its concentration, overall, however, the data suggests that the ions in these ILs are in dynamic equilibrium and we thus anticipate exact identification of all species present will turn out to be quite difficult.

In summary, room temperature ILs containing both Al and Ga could be easily synthesized by simply mixing solids of $[HN_{222}]Cl$, $AlCl_3$, and $GaCl_3$ in desired molar ratios using a one-pot strategy. The ILs $[HN_{222}][xAlCl_3+(2-x)GaCl_3]Cl$ have enhanced Lewis acidity compared with their precursors. Among these, $[HN_{222}][1.33AlCl_3+0.67GaCl_3]Cl$ has the strongest Lewis acidity, which resulted in the highest catalytic activities in Friedel-Craft acylation and alkylation reactions, even higher than $AlCl_3$, $GaCl_3$, $[HN_{222}][Al_2Cl_7]$, or $[HN_{222}][Ga_2Cl_7]$. Studies of the speciation (NMR and MALDI-TOF) suggested the existence of $[Al_nCl_{3n+1}]^-$ and $[Ga_nCl_{3n+1}]^-$ transient anions, and a possible complex polynuclear species of $[Cl_2GaOClAlClOGaCl_2]^-$, which would be the most acidic species. The synergism of having two metal centers or multiple metal centers into a catalytic IL appears to be a reasonable strategy to tune IL catalysts by design and the ease of the one-pot reaction to prepare them provides a versatile platform making and investigating the ILs. However, more work is needed to fully define the complex speciation in these systems whose anions appear to be in transient equilibrium.

AUTHOR INFORMATION

Corresponding Author

* Robin D Rogers: rdrogers@ua.edu.

‖ Current address: Chemical Sciences Division, Oak Ridge National Laboratory, 1 Bethel Valley Road, Knoxville, Oak Ridge, Tennessee 37831, United States.

ξ Current address: Joint BioEnergy Institute, Emeryville, California 94608, United States

§ Current address: Pharmaceutical Materials Science and Engineering Laboratory, Department of Pharmaceutics, College of Pharmacy, University of Minnesota, 9-127B Weaver-Densford Hall, 308 Harvard Street S.E., Minneapolis, Minnesota 55455, United States

Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information

Experimental and characterization details including preparation of ILs, Single crystal X-ray diffraction (SCXRD) details, ORTEP diagram, Lewis acidity tests, catalyst activity, nuclear magnetic resonance, gas chromatography, and matrix-assisted laser-desorption ionization time-of-flight (MALDI-TOF) can be found in the supporting information.

ACKNOWLEDGMENTS

The authors would like to thank Qiaoli Liang for MALDI-TOF data collection.

REFERENCES

(1) Welton, T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem. Rev.* **1999,** *99*, 2071-2084.

(2) Li, K.; Berton, P.; Kelley, S. P.; Rogers, R. D. Singlet oxygen production and tunable optical properties of deacetylated chitin-porphyrin crosslinked films. *Biomacromolecules* **2018,** *19*, 3291–3300.

(3) Shamshina, J. L.; Zavgorodnya, O.; Berton, P.; Chhotaray, P. K.; Choudhary, H.; Rogers, R. D. Ionic liquid platform for spinning composite chitin–poly(lactic acid) fibers. *ACS Sustainable Chem. Eng.* **2018,** *6*, 10241-10251.

(4) Choudhary, H.; Li, K.; Rogers, R. D. Active Pharmaceutical Ingredient Ionic Liquid: A New Platform for the Pharmaceutical Industry. In *Encyclopedia of Ionic Liquids*, Zhang, S., Ed. Springer Singapore: Singapore, 2019; pp 1-14.

(5) Choudhary, H.; Berton, P.; Gurau, G.; Myerson, A. S.; Rogers, R. D. Ionic liquids in cross-coupling reactions: "Liquid" solutions to a "solid" precipitation problem. *Chem. Commun.* **2018,** *54*, 2056-2059.

(6) Kang, X.; Sun, X.; Han, B. Synthesis of functional nanomaterials in ionic liquids. *Adv. Mater.* **2016,** *28*, 1011-1030.

(7) Hallett, J. P.; Welton, T. Room-temperature ionic liquids: Solvents for synthesis and catalysis. 2. *Chem. Rev.* **2011,** *111*, 3508-3576.

(8) (a) Brown, L. C.; Hogg, J. M.; Swadźba-Kwaśny, M. Lewis acidic ionic liquids. *Top. Curr. Chem.* **2017,** *375*, 78; (b) Li, K.; Choudhary, H.; Rogers, R. D. Ionic liquids for sustainable processes: Liquid metal catalysis. *Curr. Opin. Green Sustain. Chem.* **2018,** *11*, 15-21.

(9) (a) Estager, J.; Oliferenko, A. A.; Seddon, K. R.; Swadzba-Kwasny, M. Chlorometallate(iii) ionic liquids as Lewis acidic catalysts-A quantitative study of acceptor properties. *Dalton Trans.* **2010,** *39*, 11375-11382; (b) Lee, C. W. Diels-Alder reactions in chloroaluminate ionic liquids: acceleration and selectivity enhancement. *Tetrahedron Lett.* **1999,** *40*, 2461-2464.

(10) https://www.nobelprize.org/nobel_prizes/chemistry/laureates/2005/ (accessed April 09, 2019).

(11) (a) Corma, A.; Garcia, H. Lewis acids: From conventional homogeneous to green homogeneous and heterogeneous catalysis. *Chem. Rev.* **2003,** *103*, 4307-65; (b) Akiyama, T.; Itoh, J.; Fuchibe, K. Recent progress in chiral Brønsted acid catalysis. *Adv. Synth. Catal.* **2006,** *348*, 999-1010.

(12) McCoy, M. Chevron embraces ionic liquids. *Chem. Eng. News* **2016,** *94*, 16.

(13) (a) Chatel, G.; Pereira, J. F. B.; Debbeti, V.; Wang, H.; Rogers, R. D. Mixing ionic liquids - "simple mixtures" or "double salts"? *Green Chem.* **2014,** *16*, 2051-2083; (b) Niedermeyer, H.; Hallett, J. P.; Villar-Garcia, I. J.; Hunt, P. A.; Welton, T. Mixtures of ionic liquids. *Chem. Soc. Rev.* **2012,** *41*, 7780-7802; (c) Oliveira, F. S.; Pereiro, A. B.; Araújo, J. M.; Bernardes, C. E.;

Lopes, J. N. C.; Todorovic, S.; Feio, G.; Almeida, P. L.; Rebelo, L. P.; Marrucho, I. M. High ionicity ionic liquids (HIILs): comparing the effect of ethylsulfonate and ethylsulfate anions. *Phys. Chem. Chem. Phys.* **2013,** *15*, 18138-18147; (d) Pereiro, A. B.; Araújo, J. M.; Oliveira, F. S.; Bernardes, C. E.; Esperança, J. M.; Lopes, J. N. C.; Marrucho, I. M.; Rebelo, L. P. Inorganic salts in purely ionic liquid media: the development of high ionicity ionic liquids (HIILs). *Chem. Commun.* **2012,** *48*, 3656-3658.

(14) (a) Gan, P.; Tang, S. Research progress in ionic liquids catalyzed isobutane/butene alkylation. *Chin. J. Chem. Eng.* **2016,** *24*, 1497-1504; (b) Rogers, R. D.; Gurau, G.; Kelley, S. P.; Kore, R.; Shamshina, J. L. Mixed metal double salt ionic liquids with tunable acidity. US20170209858A1, 2017.

(15) Kore, R. K.; Kelley, S. P.; Aduri, P.; Rogers, R. D. Mixed metal double salt ionic liquids comprised of $[HN_{222}]_2[ZnCl_4]$ and $AlCl_3$ provide tunable Lewis acid catalyst related to the ionic environment. *Dalton Trans.* **2018,** *47*, 7795-7803.

(16) (a) Estager, J.; Holbrey, J. D.; Swadzba-Kwasny, M. Halometallate ionic liquids-revisited. *Chem. Soc. Rev.* **2014,** *43*, 847-886; (b) Kore, R.; Berton, P.; Kelley, S. P.; Aduri, P.; Katti, S. S.; Rogers, R. D. Group IIIA halometallate ionic liquids: Speciation and applications in catalysis. *ACS Catal.* **2017,** *7*, 7014-7028.

(17) Yang, Y. L.; Kou, Y. Determination of the Lewis acidity of ionic liquids by means of an IR spectroscopic probe. *Chem Commun (Camb)* **2004,** *2*, 226-227.

(18) Junk, P. C.; Raston, C. L.; Skelton, B. W.; White, A. H. The trans-$[py_2AlCl_4]^-$ ('py' = pyridine) Anion, Structurally Characterized in Two Pyridinium Salts. *Aust. J. Chem.* **2004,** *57*, 503-506.

(19) Abbott, A. P.; Qiu, F.; Abood, H. M. A.; Ali, M. R.; Ryder, K. S. Double layer, diluent and anode effects upon the electrodeposition of aluminium from chloroaluminate based ionic liquids. *Phys. Chem. Chem. Phys.* **2010,** *12*, 1862-1872.

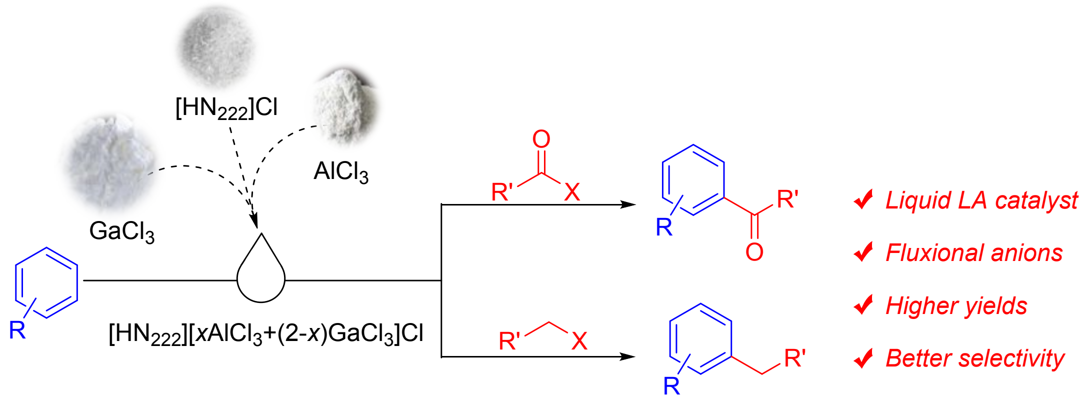
(20) Wilkes, J. S.; Frye, J. S.; Reynolds, G. F. Aluminum-27 and carbon-13 NMR studies of aluminum chloride-dialkylimidazolium chloride molten salts. *Inorg. Chem.* **1983,** *22*, 3870-3872.

(21) Hardacre, C.; Murphy, R. W.; Seddon, K. R.; Srinivasan, G.; Swadźba-Kwaśny, M. Speciation of chlorometallate ionic liquids based on Gallium (III) and Indium (III). *Aust. J. Chem.* **2010,** *63*, 845-848.

(22) Karpinski, Z. J.; Osteryoung, R. A. Determination of equilibrium constants for the tetrachloroaluminate ion dissociation in ambient-temperature ionic liquids. *Inorg. Chem.* **1984,** *23*, 1491-1494.

(23) Wicelinski, S. P.; Gale, R. J.; Pamidimukkala, K. M.; Laine, R. A. Fast atom bombardment mass spectrometry of low temperature chloroaluminate and chlorogallate melts. *Anal. Chem.* **1988,** *60*, 2228-2232.

For Table of Content Only



Synopsis: Dynamic anionic species in ionic liquids generated from the combination of [HN$_{222}$]Cl, AlCl$_3$, and GaCl$_3$ provide synergistically-enhanced Lewis acid catalysis.