Denmark Group Meeting

January 23, 2001

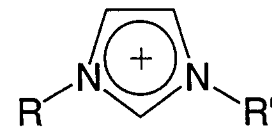
By

Tyson A. Miller

Ionic Liquids: Structure, Properties, & Applications

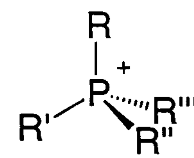
Ionic Liquid vs. Molten Salt

NaCl



X^-

KCl



X^-

Molten Salt

Liquid comprised of ions

High melting (100°C and up)

Highly viscous

Corrosive medium

Rarely useful for organic synthesis

Ionic Liquids

Liquid comprised of ions

Low melting (0 - 10°C)

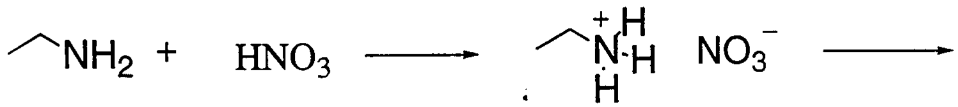
Variable viscosity

Designed reactivity

Becoming useful for organic synthesis

Ionic Liquids: A Brief History

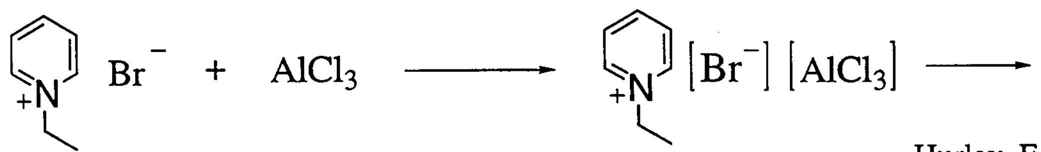
In 1914 . . . .



mp = +8°C, studying conductance of liquids

Sugden, S.; Wilkins, H. JCS (1929) 1291.

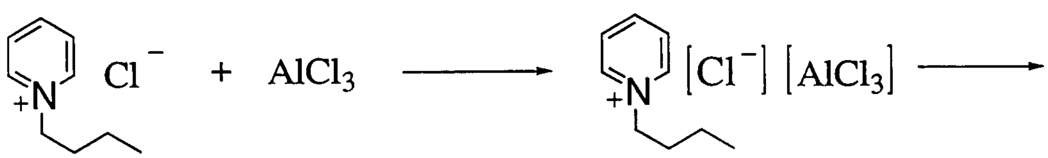
In 1948 . . . .



electroplating aluminum

Hurley, F.H.; Wier, Jr., T.P. J. Electrochem. Soc. (1951) 98 207.

In the 70's . . . .



mp = +40°C, electrochemical oxidation
discovered $Al_2Cl_7^-$ spectroscopically

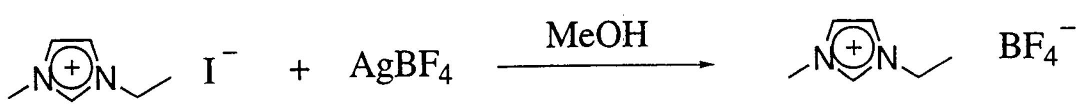
Robinson, J.; Osteryoung, R.A. JACS (1979) 101 323.

In the 80's . . . .

Seddon and Hussey used chloroaluminate melts as nonaqueous, polar solvents to investigate electrochemical and spectroscopic aspects of various transition metal complexes . . .

Scheffler, T.B.; Hussey, C.L.; Seddon, K.R.; Kear, C.M.; Armitage, P.D. Inorg. Chem. (1983) 22 2099.

In the 90's . . . .



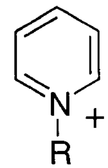
mp = +15°C, hygroscopic

Wilkes, J.S.; Zaworotko, M.J. JCS CC (1992) 965.

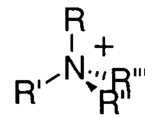
Synthesizing Ionic Liquids

Typical cation types . . .

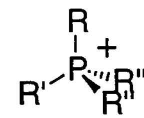
Imidazolium ion



Pyridinium ion



Ammonium ion



Phosphonium ion

Typical anion types . . .

Cl^-, Br^-, BF_4^-, PF_6^-, SbF_6^-, NO_3^-, $CH_3CO_2^-$, $CF_3CO_2^-$, HSO_4^-

Step 1: NR_3 —(+R'X)→ $[R'R_3N]^+X^-$

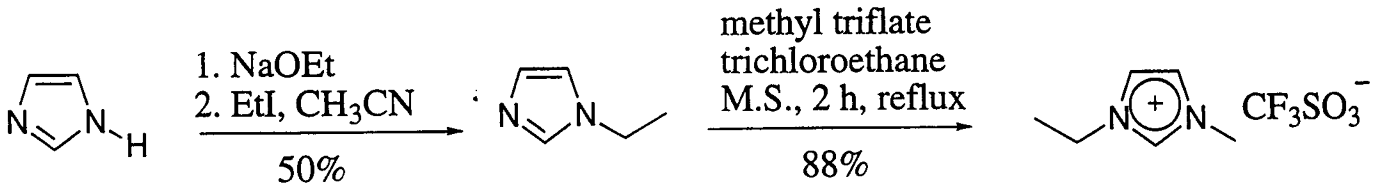
Step 2a: + Lewis Acid MX_y → $[R'R_3N]^+[MX_{y+1}]^-$

Step 2b: → $[R'R_3N]^+[A]^-$

1. + Metal Salt M^+A^-
   - MX (precipitation)
2. + Brønsted acid H^+A^-
   - HX (evaporation)
3. Ion Exchange Resin

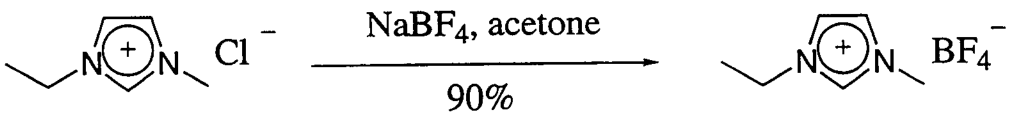
Wasserscheid, P.; Keim, W. ACIEE (2000) 39 3772.

Synthesizing Ionic Liquids



mp = -9°C

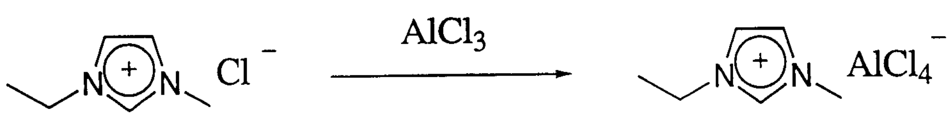
Bonhôte, P.; et al. Inorg. Chem. (1996) 35 1168.



mp = 15°C

Suarez, P.A.Z.; et al. Polyhedron (1996) 15 1217.

Other ionic exchanged anions include: PF_6^-, SbF_6^-, NO_3^-, $CH_3CO_2^-$, HSO_4^-, $B(Et_3Hex)^-$



Ions detected by FABMS:
Cl^-, $AlCl_4^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$

Abdul-Sada, A.K.; Greenway, A.M.; Seddon, K.R.; Welton, T. Org. Mass Spectrom. (1993) 28 759.

Other recent Lewis acids that have been added include: $AlEtCl_2$, BCl_3, CuCl, $SnCl_2$

Anions Observed in Chloroaluminate Melts

$$[Cat]^+X^- + MX_y \rightleftharpoons [Cat]^+ [MX_{y+1}]^-$$

$$[Cat]^+AlCl_4^- + AlCl_3 \rightleftharpoons [Cat]^+ Al_2Cl_7^-$$

$$[Cat]^+Al_2Cl_7^- + AlCl_3 \rightleftharpoons [Cat]^+ Al_3Cl_{10}^-$$

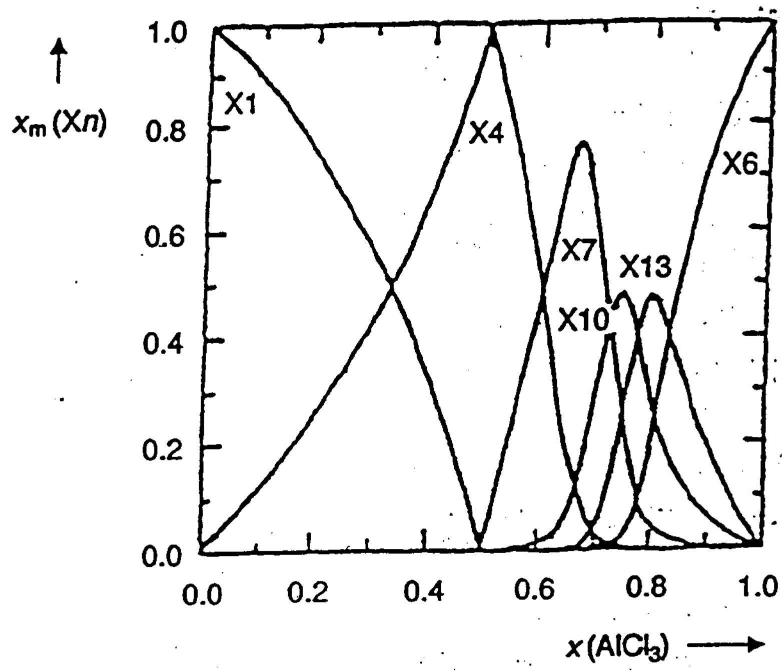


Figure 1. Mole fraction x_m of different anion species Xn in chloroaluminate melts (X1 = Cl^-; X4 = $AlCl_4^-$; X7 = $Al_2Cl_7^-$; X10 = $Al_3Cl_{10}^-$; X13 = $Al_4Cl_{13}^-$; X6 = Al_2Cl_6).

Øye, H.A.; Jag‹‹ven, M.; Oksefjell, T.; Wilkes, J.S. Mater. Sci. Forum (1991) 73-75 183.

"Designer Solvents" - Melting Point

Table 4. Melting points of various chlorides.

Salt		M. p. [°C]
NaCl		803
KCl		772
 Cl^-	R = R′ = methyl ([MMIM]Cl)[a]	125
	R = methyl, R′ = ethyl ([EMIM]Cl)	87
	R = methyl, R′ = *n*-butyl ([BMIM]Cl)	65

[a] MMIM = 1,3-dimethylimidazolium.

Table 5. Influence of different anions on the melting point of imidazolium salts.

Imidazolium salt	M. p. [°C]	Ref.
[EMIM]Cl	87	[6c]
$[EMIM]NO_2$	55	[14]
$[EMIM]NO_3$	38	[14]
$[EMIM]AlCl_4$	7	[40]
$[EMIM]BF_4$	6[a]	[17d]
$[EMIM]CF_3SO_3$	−9	[16a]
$[EMIM]CF_3CO_2$	−14	[16a]

[a] Glass transition.

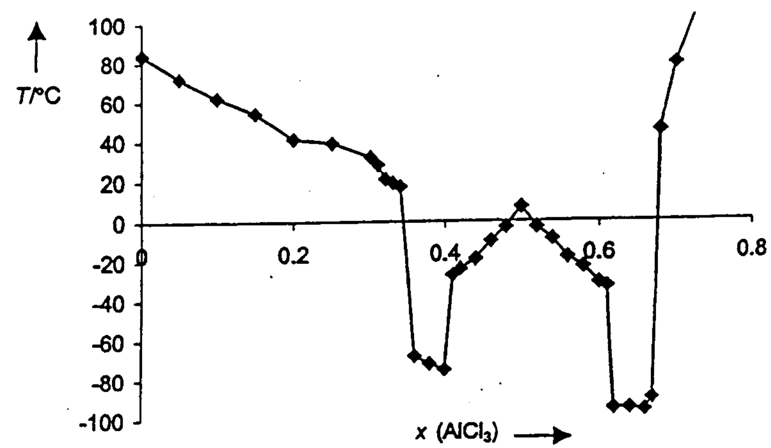


Figure 2. Experimental phase diagram in the system $[EMIM]Cl/AlCl_3$ (EMIM = 1-ethyl-3-methylimidazolium ion).

Good cation features: 1) Low symmetry
2) Weak intermolecular interactions (lack of H-bonding)
3) Good distribution of charge in the cation

Good anion features: 1) Increasing size of anion
2) Variety of anions

Wilkes, J.S.; et al. Inorg. Chem. (1982) 21 1263.
Fannin, Jr., A.A.; et al. J. Phys. Chem. (1984) 88 2614.

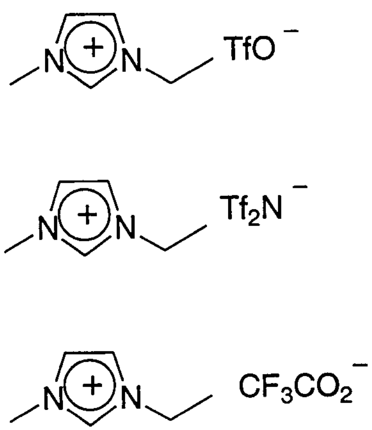
Vapor Pressure and Thermal Stability

Ionic liquids have no measurable vapor pressure ⟶ Distillation of product effective

In addition, azeotrope formation between solvent and product does not arise.

However . . . .

thermal stability is limited by strength of C-X and X-H bonds (X = N, P)



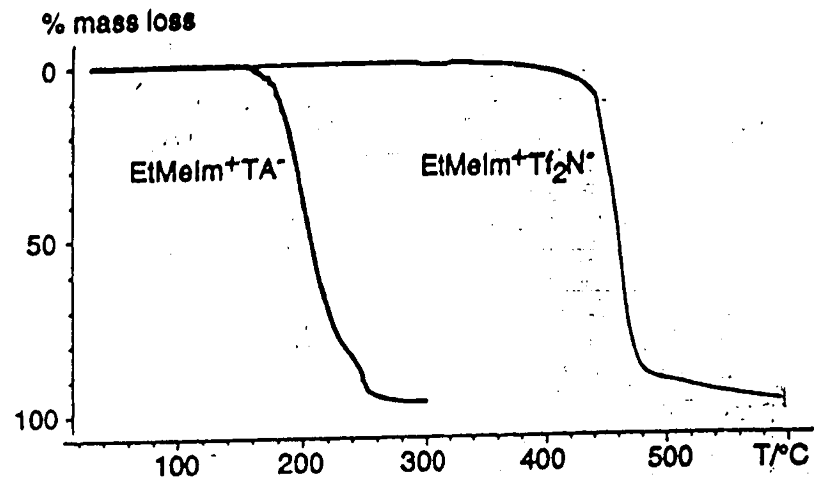


Figure 3. Thermogravimmetry in air of $EtMeIm^+Tf_2N^-$ and $EtMeIm^+TA^-$.

Quaternary ammonium and phosphonium salts tend undergo transalkylation or dealkylation reactions (related to the anion). 150°C is the maximum working temperature for these.

Bonhôte, P.; et al. Inorg. Chem. (1996) 35 1168.

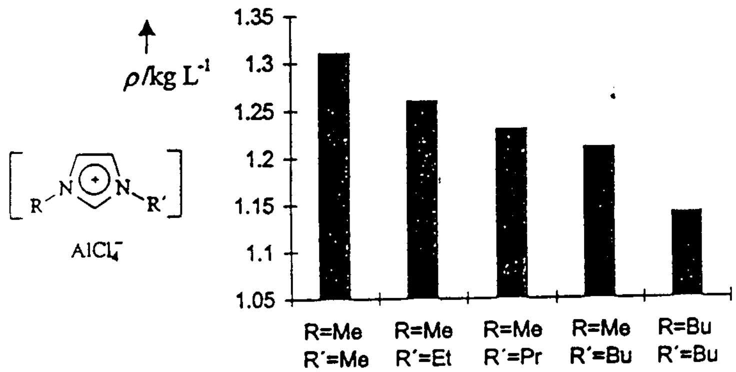


Figure 3. Dependence of the density ρ of 1,3-dialkylimidazolium tetrachloroaluminate melts on the type of both alkyl groups; measurement temperature at 60 °C, $x(AlCl_3) = 0.5$.

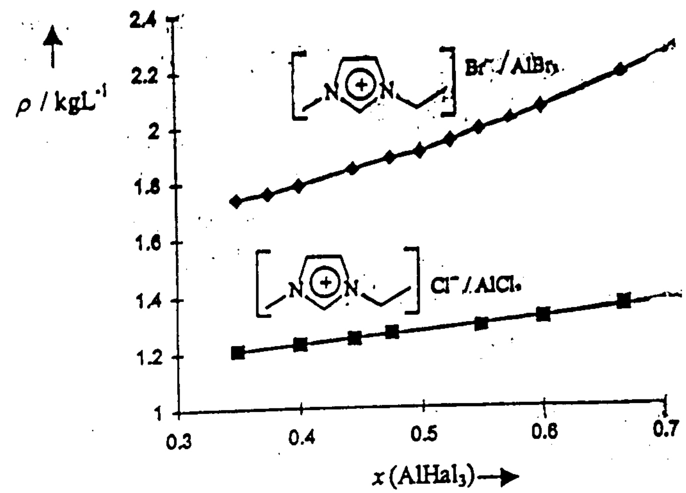


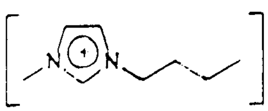
Figure 4. Dependence of the density ρ of two 1-ethyl-3-methylimidazolium tetrahaloaluminate melts on the mole fraction of aluminum trihalide at 60 °C.

Table 6. Density at 22 °C (or at the Indicated Temperature) (g cm^{-3}) of the Imidazolium Salts Which Are Liquids or Supercooled Liquids at that Temperature

Im^+	TfO^-	NfO^-	Tf_2N^-	TA^-	HB^-
3-Me					
1-Me			1.559		
1-Et	1.390		1.520	1.285	1.450
1-Bu	1.290[20]	1.473[18]	1.429[19]	1.209[21]	1.333
1-*i*-Bu			1.428[20]		
1-MeOC$_2$H$_4$	1.364		1.496		
1-CF$_3$CH$_2$			1.656[20]		
3-Et					
1-Et	1.330		1.452[21]	1.250	
1-Bu		1.427[18]	1.404[19]	1.183[23]	
1-Et-2-Me					
3-Me			1.495[21]		
1-Et-5-Me					
3-Me	1.334[20]		1.470		
3-Et			1.432[23]		

Fannin, Jr., A.A.; et al. J. Phys. Chem. (1984) 88 2614.
Sanders, J.R.; et al. J. Electrochem. Soc. (1986) 133 325.
Bonhôte, P.; et al. Inorg. Chem. (1996) 35 1168.

Table 6. Dynamic viscosities η of various 1-*n*-butyl-3-methylimidazolium (BMIM) salts at 20 °C.

	Anion [A]⁻	η [cP]
 [A]⁻	$CF_3SO_3^-$	90
	$n\text{-}C_4F_9SO_3^-$	373
	CF_3COO^-	73
	$n\text{-}C_3F_7COO^-$	182
	$(CF_3SO_2)_2N^-$	52

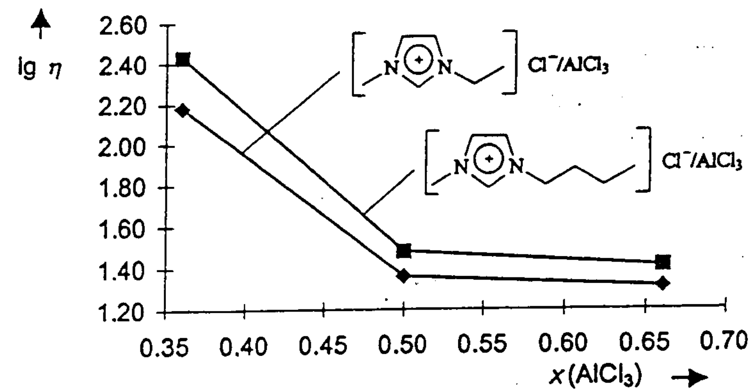


Figure 5. Dependence of the dynamic viscosity η [cP] of two 1,3-dialkylimidazolium tetrachloroaluminate melts on the mole fraction of aluminum trichloride at 25 °C.

Fannin, Jr., A.A.; et al. J. Phys. Chem. (1984) 88 2614.
Bonhôte, P.; et al. Inorg. Chem. (1996) 35 1168.

ıble V. Comparison of Peak Frequency (cm^{-1}) and Intensity Changes Occurring with Melt Acidity

	aromatic C–H str		aliphatic C–H str		–C=N– str		ring str		ring i/p b		ring o/p b	
mole ratio $AlCl_3$/ImCl	peak freq	abs	peak freq	abs	peak freq	abs	peak freq	abs	peak freq	abs	peak freq	abs
0.40:1	3148	0.63	2981	1.43	1590	0.29	1178	1.48	834	0.34	760	0.46
0.55:1	3154	0.73	2983	1.25	1590	0.38	1175	1.44	838	0.45	758	0.60
0.70:1	3156	0.85	2985	1.05	1591	0.48	1172	1.55	837	0.58	754	0.84
0.85:1	3157	0.90	2987	0.76	1592	0.64	1170	1.98	837	0.76	751	1.04
0.95:1	3158	1.08	2988	0.52	1592	0.67	1168	1.57	837	0.95	747	1.05
1.0:1	3159	1.02	2990	0.40	1595	0.72	1170	1.87	838	1.19	747	1.20
1.20:1	3159	0.98	2991	0.40	1595	0.71	1169	2.15	837	1.09	747	1.30
1.50:1	3161	1.00	2992	0.39	1595	0.78	1169	2.14	836	0.98	747	1.42
1.75:1	3161	1.03	2993	0.40	1595	0.85	1169	2.46	835	1.08	747	1.62
peak shift between 0.4:1 and 1.0:1 melts	−11		−9		5		8		4		13	
peak shift between 2.0:1 and 1.0:1 melts	2		3		0		1		3		0	

Table 1. ^{1}H-NMR Chemical Shifts (δ/ppm Relative to TMS) of MeEtIm$^+$ Salts as a Function of the Concentration, in Acetone-d_6

a. Triflate (TfO^-)

[salt]/M	H(2)	H(4)	H(5)	CH_3	CH_2	CH_2CH_3
0.028	9.112	7.791	7.721	4.413	4.065	1.573
0.070	9.107	7.785	7.713	4.404	4.055	1.567
0.188	9.101	7.782	7.707	4.395	4.046	1.562
0.307	9.093	7.780	7.705	4.389	4.040	1.559
0.543	9.077	7.776	7.699	4.379	4.032	1.553
0.988	9.056	7.775	7.695	4.370	4.025	1.549
1.629	9.032	7.774	7.692	4.362	4.020	1.548
1.797	9.028	7.775	7.692	4.360	4.019	1.548

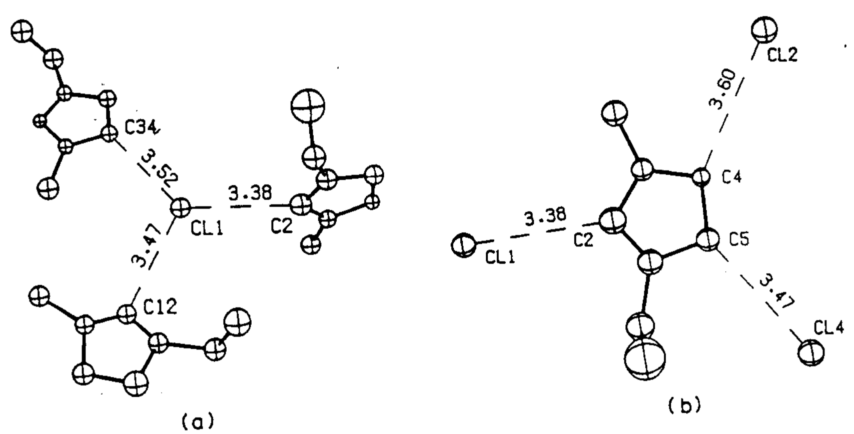


Fig. 4. (a) Representative triple interaction of Cl1 with three nearest MEI$^+$ ions, (b) interaction of MEI$^+$ (1) with three nearest Cl^- ions. Distances (Å) shown are C···Cl^- contacts.

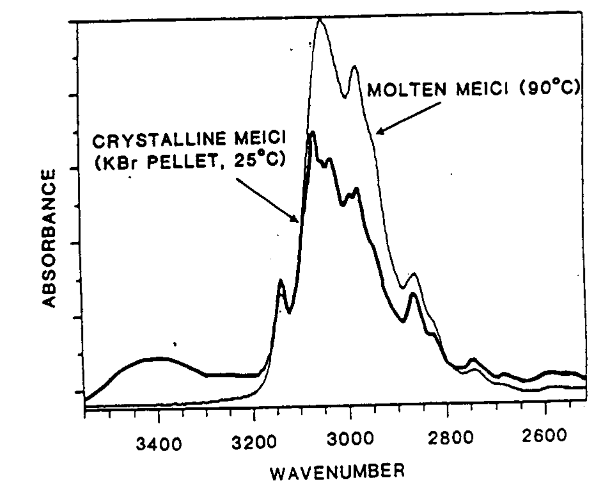


Fig. 5. FTIR spectra of solid and liquid MEICl [7].

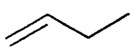
Bonhôte, P.; et al. Inorg. Chem. (1996) 35 1168.
Tait, S.; Osteryoung, R.A. Inorg. Chem. (1984) 23 4352.
Dymek, C.J.; et al. J. Mol. Struct. (1989) 213 25.

Acidity and Coordination Ability

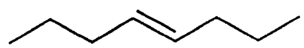
Cl^- > Ac^-, NO_3^- > SO_4^{-2} > $AlCl_4^-$, $CuCl_2^-$ > SbF_6^-, BF_4^-, PF_6^- > $Al_2Cl_7^-$, $Cu_2Cl_3^-$ > $Al_3Cl_{10}^-$, $Cu_3Cl_4^-$

Strongly Coordinating (Basic) | Weakly Coordinating (Neutral) | Non-Coordinating (Acidic)

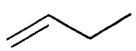
Latent Acidity



toluene, 90°C
Ni cat.

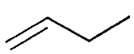


85% dimer selectivity*
75% linear dimer product*
TOF = 500 h^{-1}



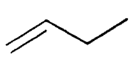
$4\text{-}MBPCl/AlCl_3$
(45:55), 25°C
Ni cat. (1 g %)

8% d.s.*
41% l.d.p.*



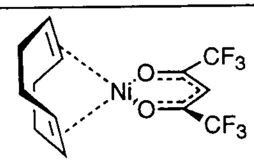
$4\text{-}MBPCl/AlCl_3$
(45:55), 25°C
Ni cat. (1 g %)
xs LiCl

75% d.s.*
30% l.d.p.*
TOF = 7500 h^{-1}



$4\text{-}MBPCl/AlCl_3$
(43:53), 25°C
Ni cat. (1 g %)
N-Me-pyrrole

98% d.s.*
51% l.d.p.*
TOF = 2100 h^{-1}



(cod)Ni(hfacac)
(1 g % = 0.01 g cat/g of ionic liquid)

Superacidity

$$HCl + Al_2Cl_7^- \rightleftharpoons [H]^+_{nonsolvated} + 2\ AlCl_4^-$$

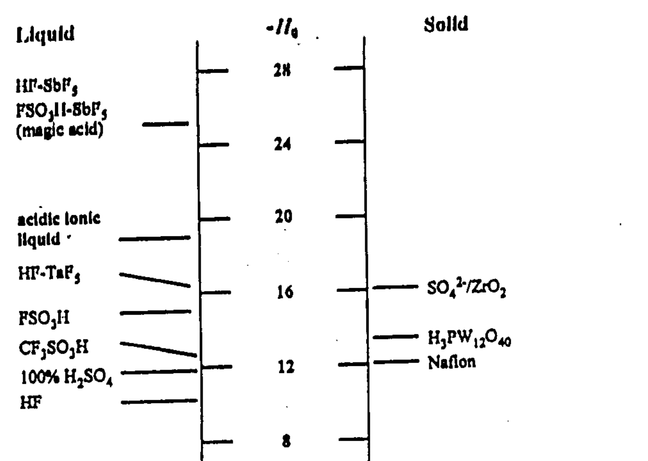


Figure 7. Comparison of the acid strength of superacid ionic liquids with those of conventional superacids.

Chauvin, Y.; et al. CHEMTECH (1995) 25 26.
Ellis, B.; et al. Chem. Comm. (1999) 337.
Wasserscheid, P.; Keim, W. ACIEE (2000) 39 3772.

Solvation Strength and Solubility

Table 7.: Miscibility of various ionic liquids with the 1-ethyl-3-methylimidazolium (EMIM) ion in organic solvents with the dielectric constant ε.[a]

Solvent	ε	[EMIM]CF_3SO_3	[EMIM]CF_3COO	[EMIM]n-C_3F_7COO	[BMIM]CF_3COO[b]	[BMIM]n-C_3F_7COO
CH_2Cl_2	8.93	m	m	m	m	m
THF	7.58	m	m	m	m	m
ethyl acetate	6.02	m	pm	pm	m	m
toluene	2.38	im	im	im	im	im
1,4-dioxane	2.01	im	im	im	im	im

[a] m: miscible; pm: partially miscible; im: immiscible.

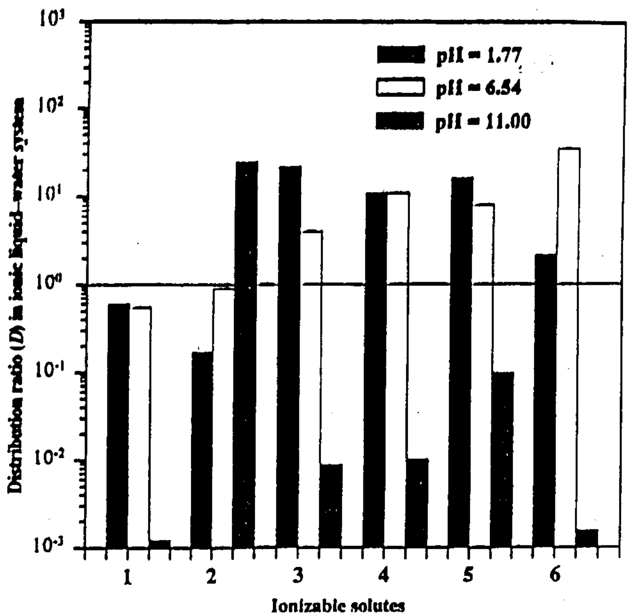


Fig. 2 The solutes studied include: 1 phthalic acid ($pK1$ = 2.89, $pK2$ = 5.51), 2 aniline (pK_b = 9.42), 3 4-hydroxybenzoic acid ($pK1$ = 4.48, $pK2$ = 9.32), 4 benzoic acid (pK_a = 4.19), 5 salicylic acid ($pK1$ = 2.97, $pK2$ = 13.40), 6 p-toluic acid ($pK1$ = 2.27)

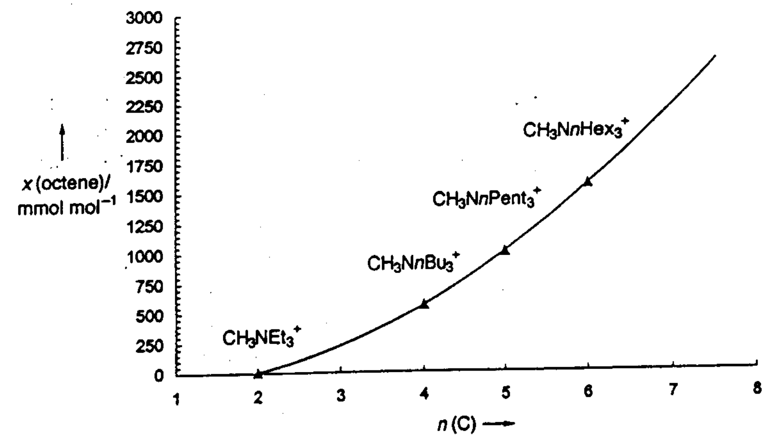
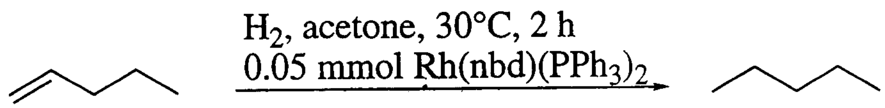


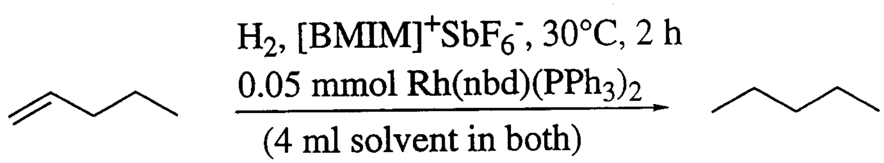
Figure 6. Solubility of 1-octene in four different tri-n-alkylmethylammonium tosylate melts at 80 °C. n(C) = number of C atoms of the alkyl residue.

Chauvin, Y.; et al. CHEMTECH (1995) 25 26.
Ellis, B.; et al. Chem. Comm. (1999) 337.
Wasserscheid, P.; Keim, W. ACIEE (2000) 39 3772.

Hydrogenations in Ionic Liquids

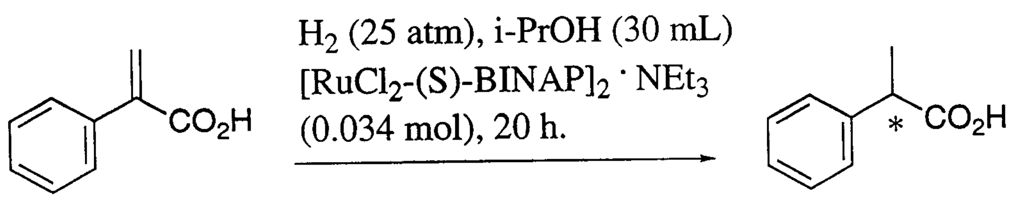


38% yield, TOF = 0.55 min^{-1}

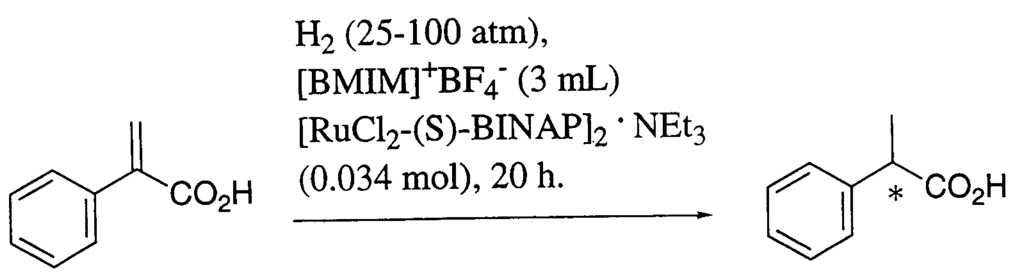


83% yield, TOF = 2.54 min^{-1}

Chauvin, Y.; et al. ACIEE (1995) 34 2698.



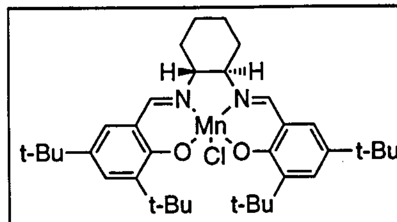
100% conv.; 64% ee (S)



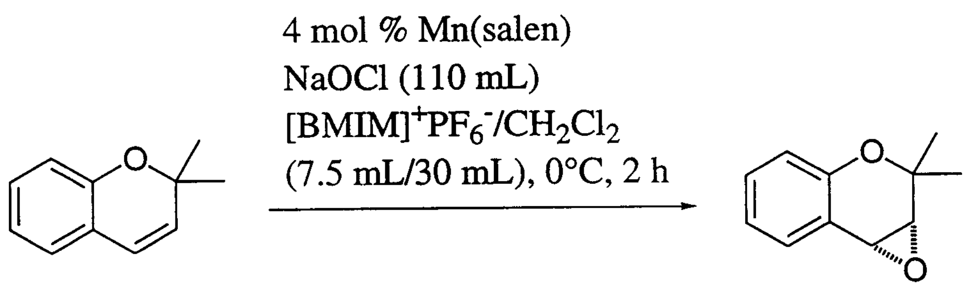
used 4 times
90-100% conv.; 67-84% ee (S)

Monteiro, A.L.; et al. Tet. Asym. (1997) 8 177.

Oxidations and Reductions in Ionic Liquids

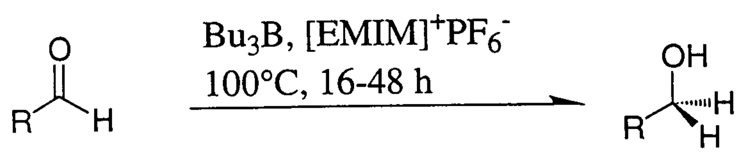


(R,R)-(salen)-Mn^{III}



Run 1: 86% Yield, 96% ee
Run 2: 73% Yield, 90% ee
Run 3: 73% Yield, 90% ee
Run 4: 60% Yield, 89% ee
Run 5: 53% Yield, 88% ee

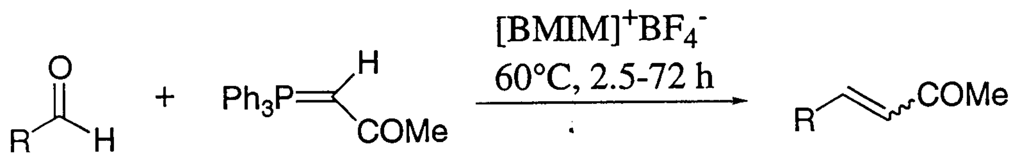
Song, C.E.; Roh, E.J. Chem. Comm. (2000) 837.



R = Ph, p-BrPh, m-BrPh, o-FPh, p-FPh, C_9H_{19}, t-Bu - 100% Yield
R = o-MePh - 98% Yield
R = p-MePh - 96% Yield
R = p-MeOPh - 40% Yield

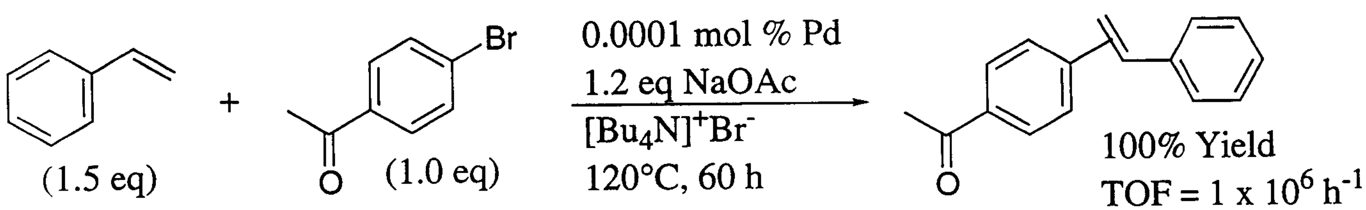
Kabalka, G.W.; Malladi, R.R. Chem. Comm. (2000) 2191.

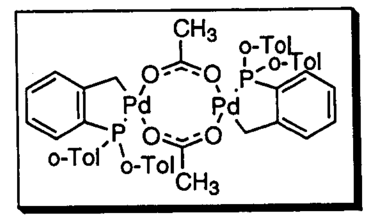
Coupling Reactions in Ionic Liquids



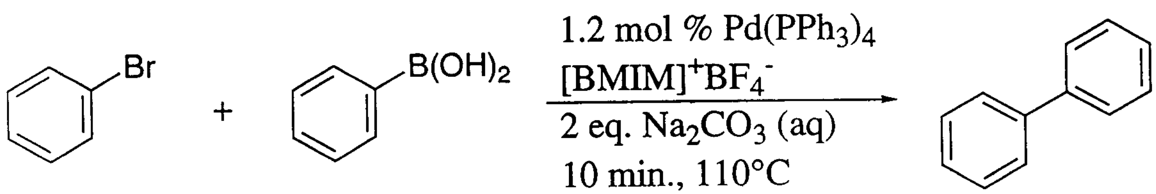
44-95% Yield
85:15 - 98:2 E:Z Ratios
R = alkyl, aryl
product in TBME, Ph_3PO in toluene

Le Boulaire, V.; Grée, R. Chem. Comm. (2000) 2195.



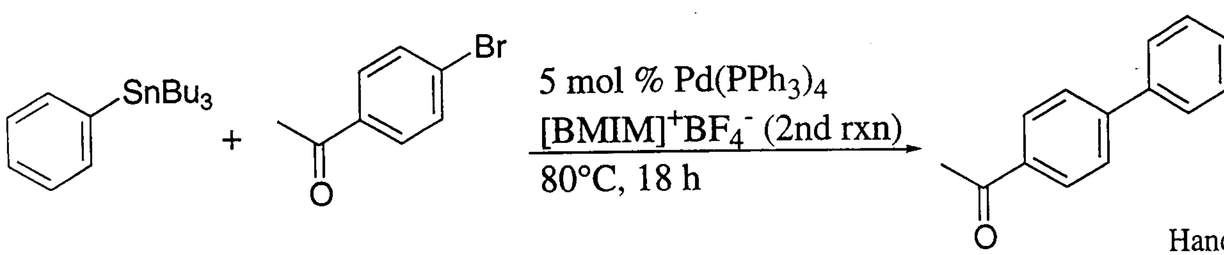


Böhm, V.P.W.; Herrmann, W.A. Chem. Eur. J. (2000) 6 1017.



93% Yield, TOF = 465 h^{-1}
Orig. Cond. - 88% Yield
6 h, TOF = 5 h^{-1}

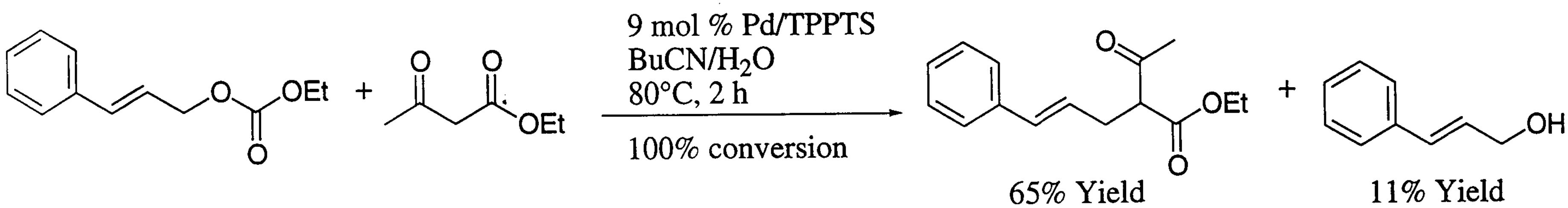
Mathews, C.J.; Smith, P.J.; Welton, T. Chem. Comm. (2000) 1249.

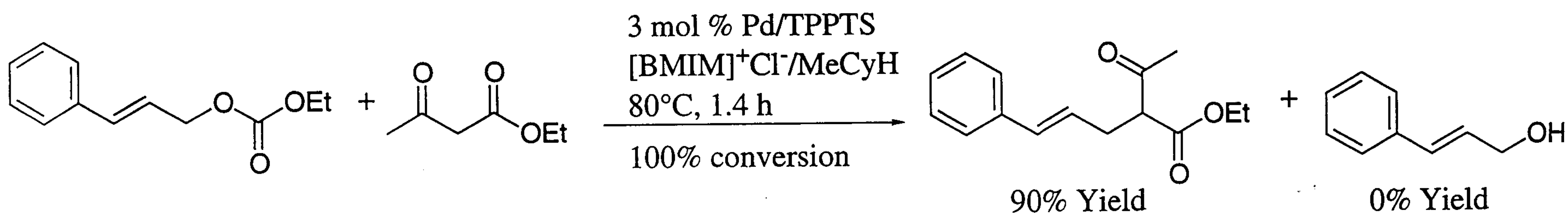


93% Yield

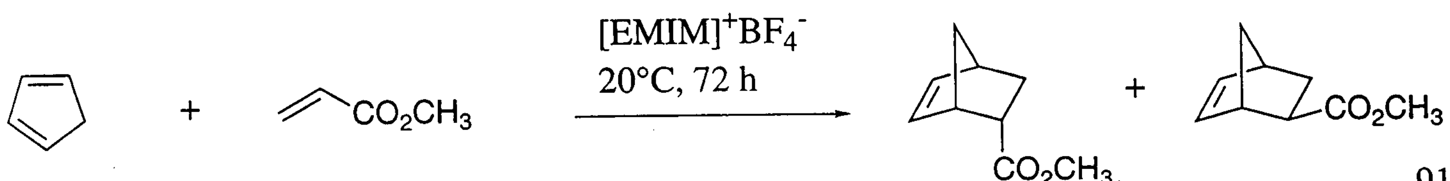
Handy, S.T.; Zhang, X. OL (2001) 3 233.

Trost-Tsuji and Diels-Alder Reactions





de Bellefon, C.; Pollet, E.; Grenouillet, P. J. Molec. Catal. A : Chem. (1999) 145 121.



91% Yield
Product : Dicyclopentadiene = 98 : 2
endo : exo = 81 : 19

Fischer, T.; et al. TL (1999) 40 793.

Conclusions

1) Ionic liquids can be used in lieu of aqueous or polar solvents

2) Ionic liquids can be used with polar organic or aqueous sensitive substrates

3) Ionic liquids typically have a wide liquid temperature range to work with in organic synthesis

4) Solvents can be "designed" to accommodate numerous reaction factors

5) Ionic liquids are slightly expensive, yet recyclable from most reactions

6) Ionic liquids enhance reactivity and stability of many transition metal catalysts

7) Ionic liquids have demonstrated an unprecedented catalyst recycling ability

8) Ionic liquids have the potential to allow transition metal coupling reactions of many types to be utilized for industrial processes

9) The surface has been scratched in terms of what is known about the utility and versatility of ionic liquids