Ionic Liquids (IL's): An Ionic Liquid-Supported Ruthenium Carbene Complexes for RCM in Ionic Liquids

J. Am. Chem. Soc. 2003, 125, 9248-49
Angew. Chem. Int. Ed. 2003, 42, 3395-3398

Literature presentation

By

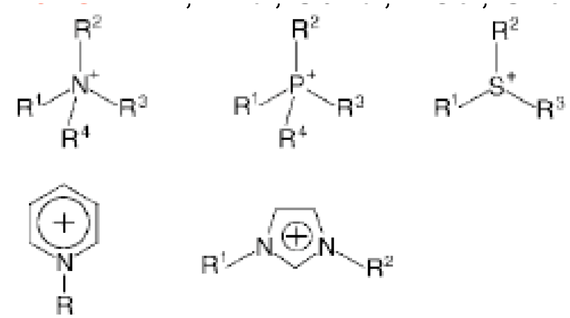
P. V. Reddy

What are ionic liquids?

Quite simply, they are liquids that are entirely composed by ions.

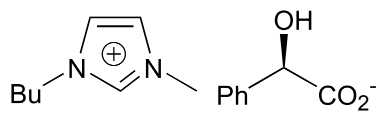
The term ionic liquid, in contrast, implies a material that is fluid at (or close to) ambient temperature, is colorless, has a low viscosity and is easily handled, i.e. a material with attractive properties for a solvent.

cations:

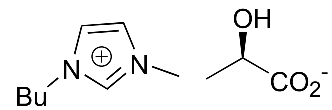


anions: BF_4^-, PF_6^-, SbF_6^-, NO_3^-, $CF_3SO_3^-$, $(CF_3SO_3)_2N^-$, $ArSO_3^-$, $CF_3CO_2^-$, $CH_3CO_2^-$, $Al_2Cl_7^-$

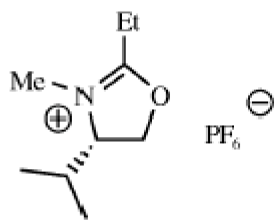
Fig. 1 Structure of ionic liquids



[bmim][mandelate]-**1**



2 [bmim][lactate]



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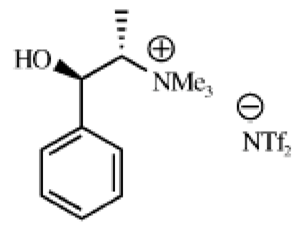

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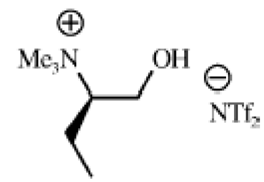

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Catalysis in ionic liquids: general considerations:

Room temperature ionic liquids (**RTIL's**) exhibit many properties which make them potentially attractive media for homogeneous catalysis:

* They have essentially no vapour pressure, *i.e.* they do not evaporate and are easy to contain.

* They generally have reasonable thermal stability. (upto 300-400 ^{o}C)

* They are able to dissolve a wide range of organic, inorganic and organometallic compounds.

* The solubility of gases, *e.g.* H_2, CO and O_2, is generally good which makes them attractive solvents for catalytic hydrogenations, carbonylations, hydroformylations, and aerobic oxidations.

* They are immiscible with some organic solvents, *e.g.* alkanes, and, hence, can be used in two-phase systems. Similarly, lipophilic ionic liquids can be used in aqueous biphasic systems.

* Polarity and hydrophilicity/lipophilicity can be readily adjusted by a suitable choice of cation/anion and ionic liquids have been referred to as **'designer solvents'**.

* They are often composed of weakly coordinating anions, *e.g.* BF_4 and PF_6 and, hence, have the potential to be highly the ionic liquid.

Historical Background:

* They are known since 1914 – [($Et_3N(NO_3)$)] – but contains a small amount of water (200-600ppm)

* First ionic liquid with chloroaluminates – 1948 by Hurly and Wier at the Rice Institute, Texas

* In 1967, 'Swain et al – tetra-*n*-hexylammonium benzoate as a solvent for kinetic and electrochemical studies

* 1980s the group of Seddon and Hussey-used chloroaluminate melts as a nonaqueous, polar solvents for –transition metal complexes

* 1980s-used for Friedal-Crafts reactions

* 1990 by Chauvin et al. and by Wilkes et al. dissolved Ni catalysts in weakly acidic chloroaluminate melts –used it for dimerization of propene, ethylene and Ziegler-Natta catalysts

* 1995--

Synthesis of BMIM.PF_6:

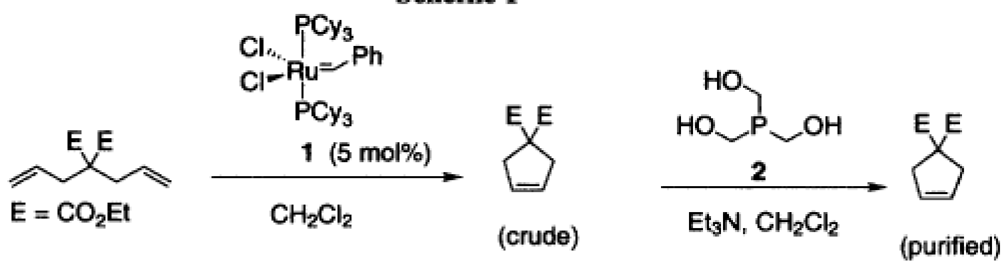
(1)

Purification Technique for the Removal of Ruthenium from Olefin Metathesis Reaction Products

Heather D. Maynard and Robert H. Grubbs*

The Arnold and Mabel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125

Scheme 1



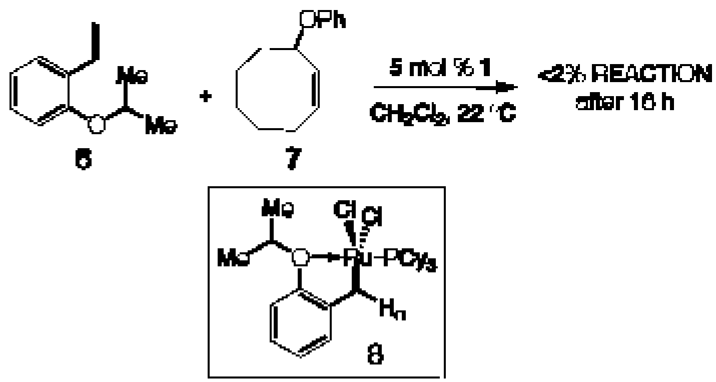
Tetrahedron Letters 40 (1999) 4137–4140

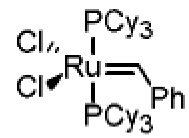
A Recyclable Ru-Based Metathesis Catalyst

Jason S. Kingsbury, Joseph P. A. Harrity,# Peter J. Bonitatebus, Jr., and Amir H. Hoveyda*

Contribution from the Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467

Scheme 2





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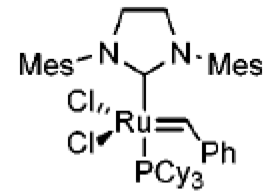

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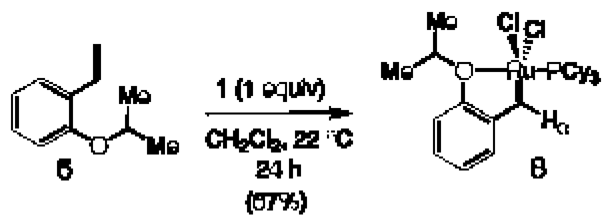
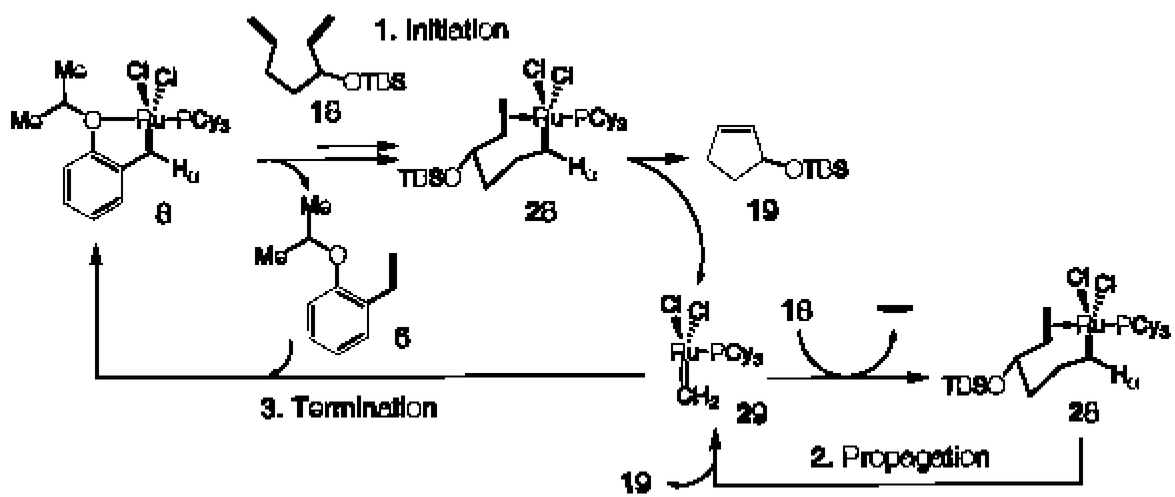


(1)

J. Am. Chem. Soc. **1999,** *121,* 791-799

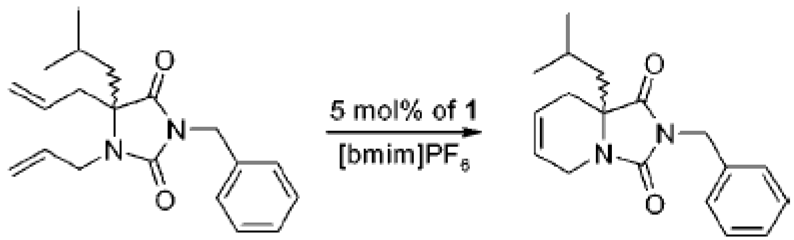
General Mechanism:



Ruthenium-Catalyzed Olefin Metathesis in Ionic Liquids

Rogier C. Buijsman,* Elizabeth van Vuuren, and Jan Gerard Sterrenburg
Lead DiscoVery Unit, N.V. Organon, P.O. Box 20, 5340 BH Oss, The Netherlands

Scheme 1



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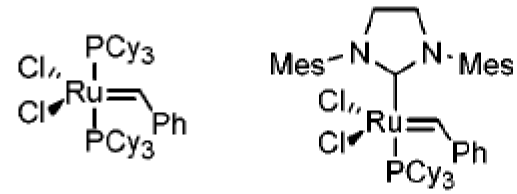
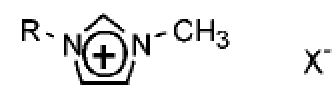


1 2



3a R=butyl, X=BF_4
3b R=butyl, X=PF_6
3c R=octyl, X=BF_4
3d R=octyl, X=PF_6
3e R=octyl, X=SbF_6

Table 1. Conversions of RCM[a] in Different (Mixtures of) Ionic Liquids and Ru Contaminant Level in RCM Product **5**

entry	solvent	ratio (v:v)	convn (%)[b]	Ru residue, μg/mg
1[c]	DCM		100	1.7
2	**3b**		98	3.2
3	**3b**:**3a**	1:1	95	9.7
4	**3b**:**3d**	1:1	77	5.2
5	**3b**:**3c**	2:1	77	6.3
6	**3b**:**3e**	2:1	81	5.4
7	**3b**:**3c**	3:1	92	5.2
8	**3b**:**3e**	3:1	69	3.6

[a] All reactions were performed at 50 °C, a substrate concentration of 55 mg/mL, and 5 mol % of **1** for 24 h. [b] Conversions were measured after extraction with diethyl ether and subsequent HPLC analysis. [c] Reaction in DCM was evaporated after 1 h, and product was purified using silica column chromatography.

*OL, 2001, **3**, 3785*

Table 2. Influence of Temperature on RCM in [bmim]PF_6[a]

entry	temp (°C)	convn (%)[b]
1	50	30
2	60	68
3	70	88
4	80	100
5	90	100
6	100	100

[a] Reactions were performed using **4** with a concentration of 55 mg/mL and 5 mol % of **1** for 1 h. [b] Conversions were measured after extraction with diethyl ether and subsequent HPLC analysis.

Table 3. Recycling of **1** and **2** and Ru Contaminant Level in RCM Product **5**[a]

entry	catalyst	recycling	convn (%)[b]	Ru residue, μg/mg
1	**1**		97	3.9
2	**1**	entry 1	94	4.8
3	**1**	entry 2	61	5.3
4	**2**		95	1.6
5	**2**	entry 4	88	1.6
6	**2**	entry 5	74	1.3

[a] All reactions were performed at 80 °C, a substrate concentration of 30 mg/mL, and 5 mol % of catalyst for 1 h. [b] Conversions were measured after extraction with ether and subsequent HPLC analysis.

An Ionic Liquid-Supported Ruthenium Carbene Complex: A Robust and Recyclable Catalyst for Ring-Closing Olefin Metathesis in Ionic Liquids

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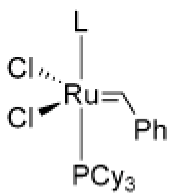
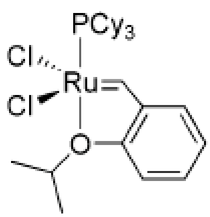
Laboratoire de Synthe`ses et ActiVations de Biomole´cules, UMR CNRS 6052,
Ecole Nationale Supe´rieure de Chimie,
Institut de Chimie de Rennes, 35700 Rennes, France



1 L = PCy_3

2 L = 

3 L = 



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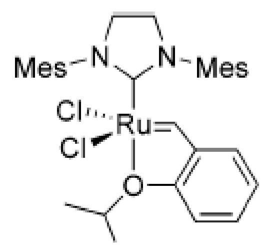

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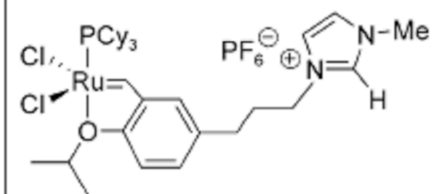
Mes = 2,4,6-trimethylphenyl
Cy = cyclohexyl



IL-cat **10**

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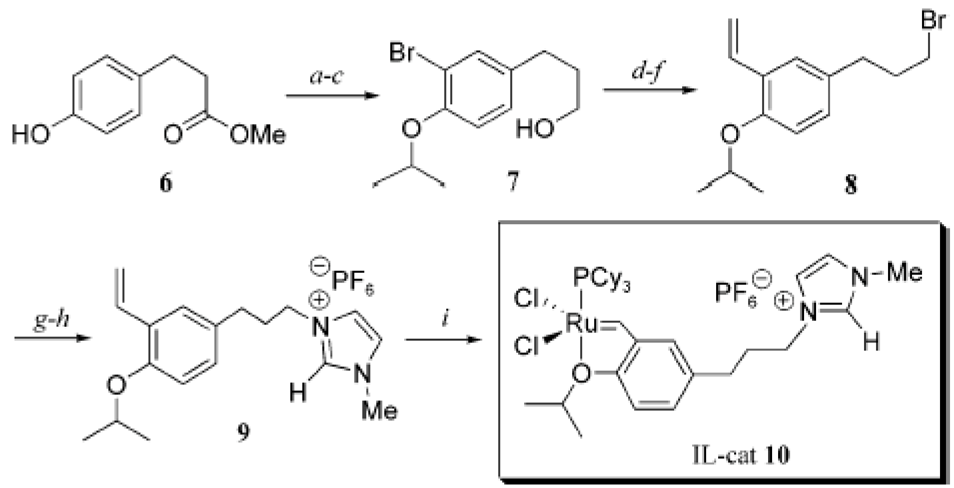
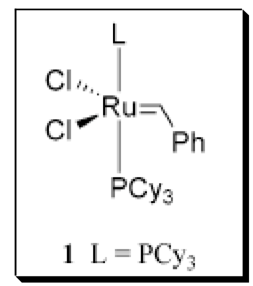
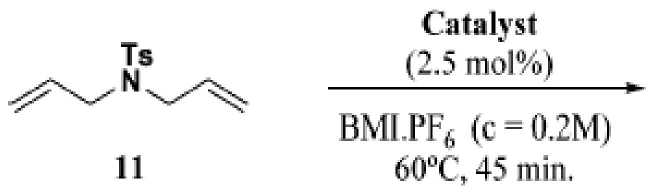
Scheme 1. Synthesis of IL Catalyst **10**[a]





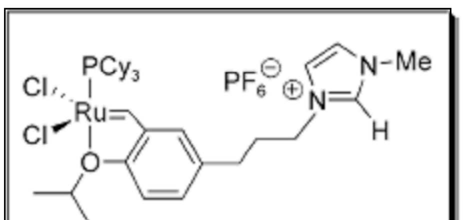
[a] Reaction conditions: (*a*) 2.2 equiv NaH, 2.2 equiv i-PrI, DMF, THF, rt, 90%. (*b*) 1.05 equiv Br_2, 0.04 equiv HOAc, CH_2Cl_2, rt, 98%. (*c*) 1 equiv $LiAlH_4$, THF, 0 °C, 95%. (*d*) 1.5 equiv $Bu_3SnCHCH_2$, 3 mol % $Pd(PPh_3)_4$, toluene, 110 °C, 75%. (*e*) 1.5 equiv Et_3N, CH_2Cl_2, 0 °C to rt. (*f*) 2 equiv LiBr, THF, DMF, rt, 74% overall for two steps. (*g*) 2 equiv 1-methylimidazole, toluene 110 °C. (*h*) HPF_6, H_2O, 0 °C, 87% overall for two steps. (*i*) 1.5 equiv **1**, 1.25 equiv CuCl, CH_2Cl_2, rt, 78%.

Table 1. Comparative Recycling and Reuse in BMI.PF_6 of IL Catalyst **10** and Catalysts **1** and **4** in the RCM of Diene **11**

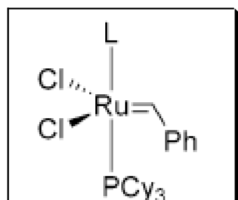


catalyst	cycle (% conv.[a]) 1	2	3	4	5	6	7	8	9	10[b]
10	>98	>98	>98	>98	>98	96	92	92	92	95
1	>98	20	–	–	–	–	–	–	–	–
4	>98	40	20	–	–	–	–	–	–	–

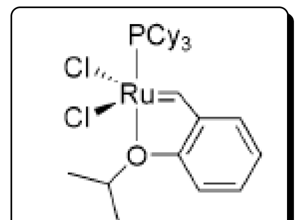
[a] Determined by ^{1}H NMR spectroscopy analysis. [b] **13** as starting material.



IL-cat **10**



1 L = PCy_3



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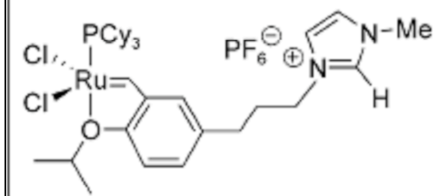
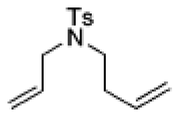
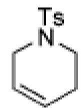
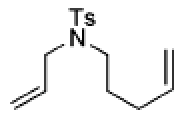
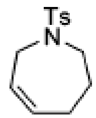
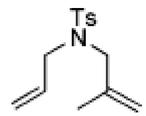
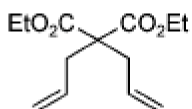
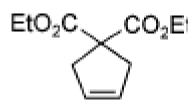
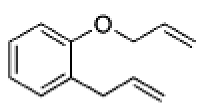
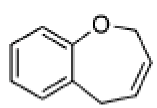
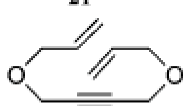
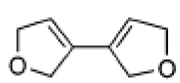


IL-cat **10**

Table 2. Recyclability of IL-cat **10** in Various RCM Reactions

Substrate	Product	Cycle	Conv.(%)[b]		
 **13**[a]	 **14**	1	>98	5	>98
		2	>98	6	>98
		3	>98	7	97
		4	>98	8	92
 **15**[a]	 **16**	1	>98	5	93
		2	>98	6	91
		3	>98	7	80
		4	96		
 **17**[c]	 **18**	1	92		
		2	92		
		3	73		
 **19**[d]	 **20**	1	98		
		2	98		
		3	90		
		4	74		
 **21**[d]	 **22**	1	94		
		2	78		
		3	48		
 **23**[d]	 **24**	1	>98		
		2	>98		
		3	92		
		4	69		

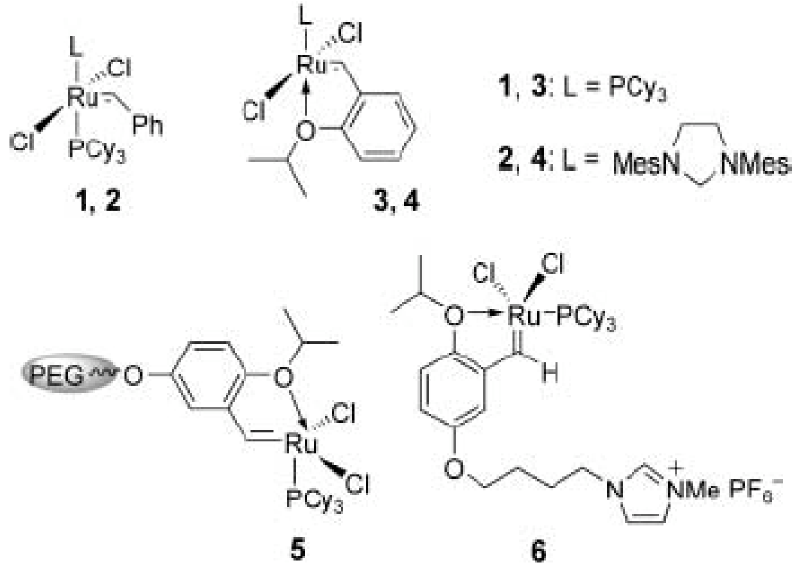
[a] **10** (2.5 mol %), BMI·PF_6 (0.2M), 60 °C, 45 min. [b] Determined by ^1H NMR spectroscopic analysis. [c] **10** (5 mol %), BMI·PF_6 (0.2 M), 60 °C, 4 h. [d] **10** (2.5 mol %), BMI·PF_6 (0.2M), 60 °C, 2 h.

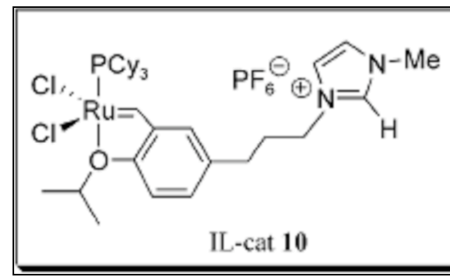
Olefin Metathesis in the Ionic Liquid 1-Butyl-3-methylimidazolium Hexafluorophosphate Using a Recyclable Ru Catalyst: Remarkable Effect of a Designer Ionic Tag

Qingwei Yao* and Yiliang Zhang

Department of Chemistry and Biochemistry, The Michael Faraday Laboratories

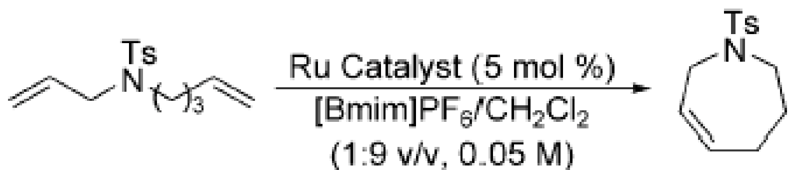
Northern Illinois University, DeKalb, IL 60115-2862 (USA)



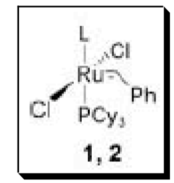

IL-cat **10**

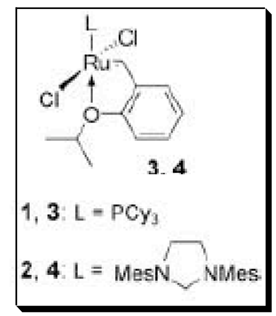
Angew. Chem. Int. Ed. 2003, 42, 3395-3398

Table 1: Recycling and reuse of Ru catalysts **1** and **3** in the ring-closing metathesis of diene **7**.[a]



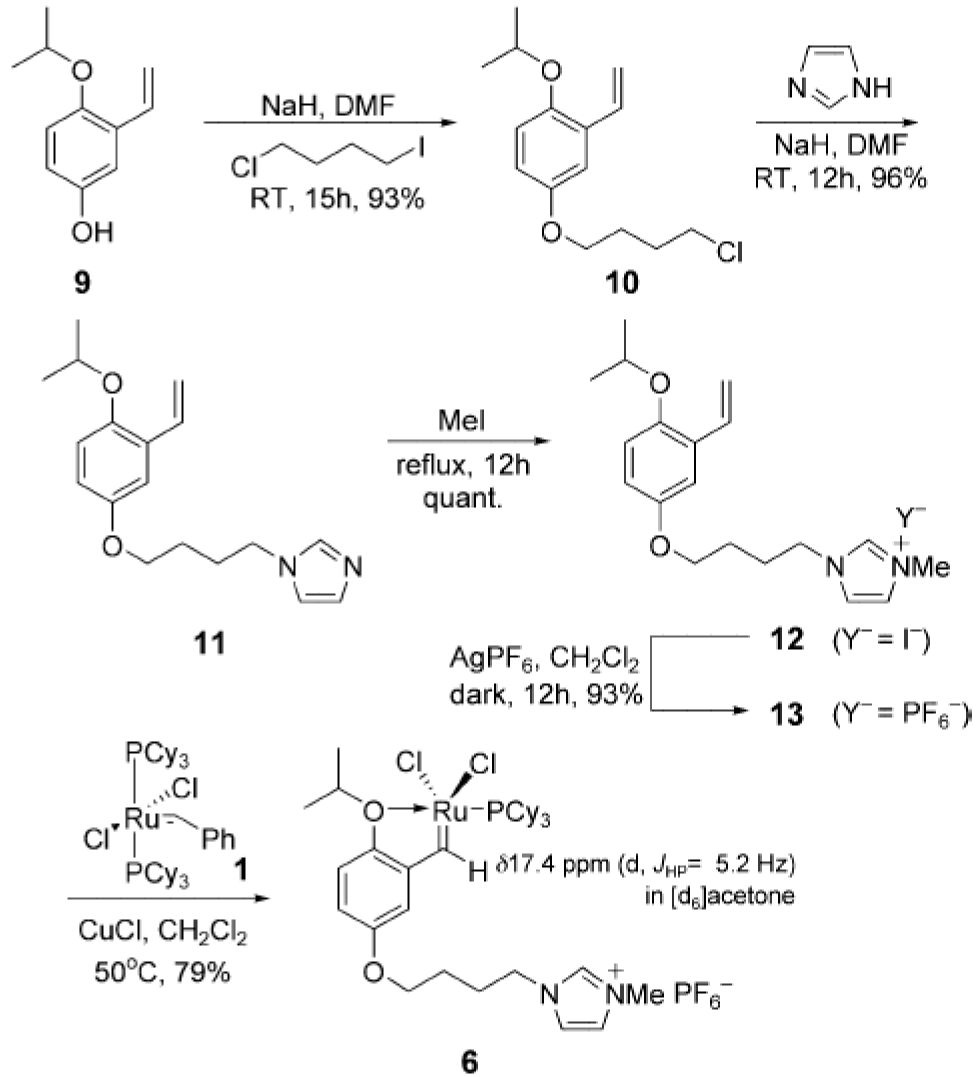
7 **8**





	Catalyst **1**			Catalyst **3**		
Cycle	1	2	3	1	2	3
reaction time [h]	3	3	6	3	3	6
conversion [%][b]	> 98	54	41	> 98	75	37

[a] All reactions were performed with 0.5 mmol of the substrate in the solvent system [Bmim]PF_6/CH_2Cl_2 (1:9 v/v, 10 mL) at 50 °C under an Ar atmosphere. [b] Determined by ^{1}H NMR spectroscopy at 500 MHz.



Scheme 1. Preparation of Ru carbene complex **6**.

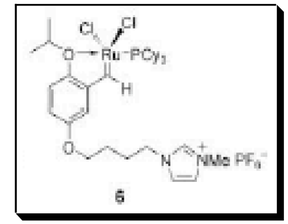
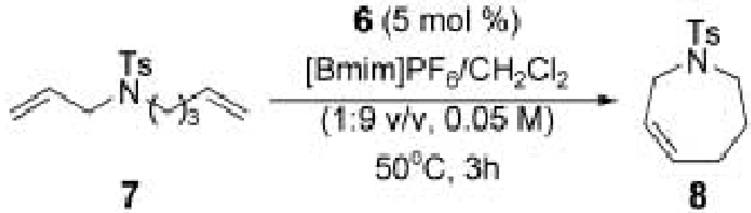


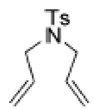
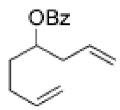
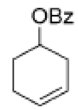
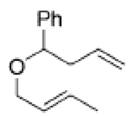
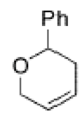
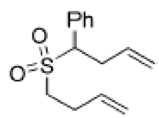
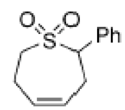
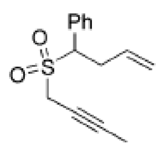
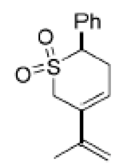
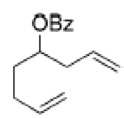
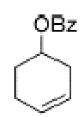
Table 2: Recycling and reuse of Ru catalyst **6** in the ring-closing metathesis of diene **7**.[a]



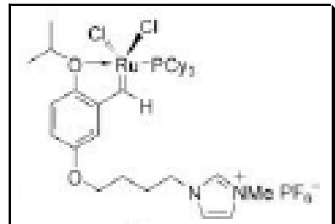
Cycle	1	2	3	4	5	6	7	8	9	10
conversion [%][b]	>98	>98	97	96	95	94	92	92	91	90

[a] The reactions were performed with 0.5 mmol of the substrate in the solvent system [Bmim]PF_6/CH_2Cl_2 (1:9 v/v, 10 mL) at 50 °C under an Ar atmosphere. [b] Determined by ^{1}H NMR spectroscopy at 500 MHz .

Table 3: Ring-closing metathesis catalyzed by Ru complex **6** in [Bmim]PF_6/CH_2Cl_2.[a]

Entry	Substrate	(conc)	Product	Catalyst [mol%]	Conditions	Conversion [%][b] (yield [%][c])
1	 **14**	(0.05 M)	 **15**	5	50 °C, 3 h	98(95)
2		(0.05 M)		5	50 °C, 3 h	97(94)
3[d]		(0.1 M)		2.5	RT, 12 h	>98(96)
4[d]	 **16**[e]		 **17**[e]	2.5	50 °C, 4 h	95(89)
1	 **18**[e]	(0.05 M)	 **19**[e]	5	50 °C, 3 h	98(90)
2		(0.05 M)		5	50 °C, 3 h	96(89)
3[g]	 **20**[f]	(0.02 M)	 **21**[f]	5	50 °C, 6 h	92(70)
4	 **22**[f]	(0.05 M)	 **23**[f]	5	50 °C, 6 h	78(72)
5	 **16**[e]	(0.05 M)	 **17**[e]	5	50 °C, 4 h	87(83)

[a] Unless otherwise indicated, all reactions were performed under the following standard conditions: 0.5 mmol of substrate in the solvent system [Bmim]PF_6/CH_2Cl_2 (1:9 v/v, 10 mL) under an Ar atmosphere at the indicated temperature. [b] Determined by ^1H NMR spectroscopy at 500 MHz. [c] Yield of pure product after chromatography on silica gel. [d] Performed with 1.0 mmol of substrate. [e] Ref. [8]. [f] Ref. [17]. [g] Performed with 0.5 mmol of substrate in the solvent system [Bmim]PF_6/CH_2Cl_2 (1:24 v/v, 25 mL). Bz = benzyl.


6

Aziridination in Ionic Liquids

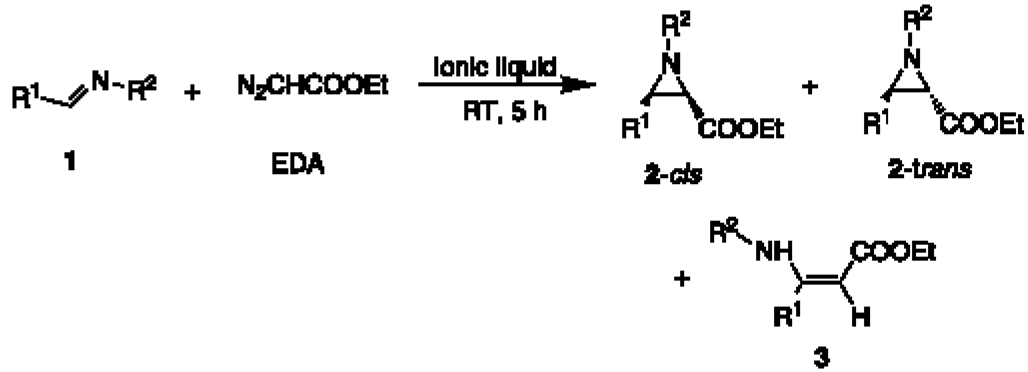


Table 1. Formation of azridines **2a–h** from imines **1a–h** and EDA in room temperature ionic liquids[a]

Entry	Ionic liquid	Imine	R^1	R^2	Product (yield%)[b]	
1[c]	$bmimBF_4$	**1a**	Ph	Ph	**2a** (82, *cis*:*trans* = 29.6:1)	**3a** (3)
2[c]	$bmimPF_6$	**1a**	Ph	Ph	**2a** (95, *cis* only)	**3a** (2)
3	$bmimPF_6$	**1a**	Ph	Ph	**2a** (93, *cis* only)	**3a** (3)
4[d]	$bmimPF_6$	**1a**	Ph	Ph	0	0
5[e]	$bmimPF_6$	**1a**	Ph	Ph	0	0
6	$bmimPF_6$	**1b**	*p*-Me-Ph	Ph	**2b** (83, *cis* only)	**3b** (8)
7	$bmimPF_6$	**1c**	*p*-Me-Ph	*p*-Me-Ph	**2c** (91, *cis* only)	
8	$bmimPF_6$	**1d**	*o*-MeO-Ph	Ph	**2d** (85, *cis* only)	
9	$bmimPF_6$	**1e**	*p*-Cl-Ph	Ph	**2e** (98, *cis* only)	
10	$bmimPF_6$	**1f**	*o*-Cl-Ph	Ph	**2f** (97, *cis* only)	
11	$bmimPF_6$	**1g**	*p*-NO_2-Ph	Ph	**2g** (98, *cis*:*trans* = 33.7:1)	
12	$bmimPF_6$	**1h**	*p*-Br-Ph	Ph	**2h** (98, *cis* only)	

[a] All reactions were carried out using 0.5 mmol of imine and 0.5 mmol of EDA in 1.5 ml of ionic liquid at room temperature for 5 h.
[b] Isolated yield, the ratio of *cis* and *trans* isomers was determined by GC–MS and ^1H NMR.
[c] 1 mmol of imine and 0.5 mmol of EDA.
[d] 0.5 mmol of imine, 0.5 mmol of EDA and 0.1 mmol of $bmimPF_6$ in 3 ml of CH_2Cl_2 at room temperature for 7 h.
[e] 0.5 mmol of imine, 0.5 mmol of EDA and 0.1 mmol of $bmimPF_6$ in 3 ml of hexane at room temperature for 7 h.

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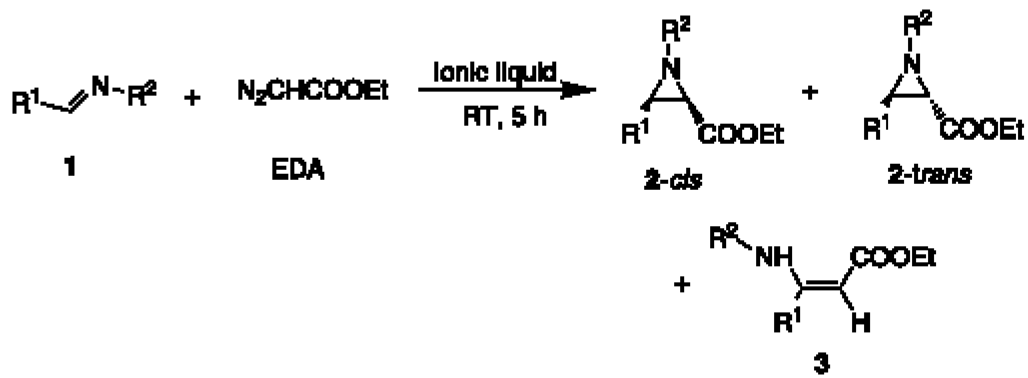

Table 2. Formation of azridines **2a** from imine **1a** and EDA in $bmimPF_6$ recycling[a]

Entry	Recycle no.	Product (yield%)[b]	
1	1	**2a** (93, *cis* only)	**3a** (3)
2	2	**2a** (93, *cis* only)	**3a** (3)
3	3	**2a** (93, *cis* only)	**3a** (3)
4	4	**2a** (94, *cis* only)	**3a** (2)
5	5	**2a** (91, *cis* only)	**3a** (4)

[a] 0.5 mmol of imine and 0.5 mmol of EDA in 1.5 ml of $bmimPF_6$ at room temperature for 5 h.

[b] Isolated yield, the ratio of *cis* and *trans* isomers was determined by GC–MS and ^{1}H NMR.