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Special Issue: Organometallic Chemistry in Ionic Liquids

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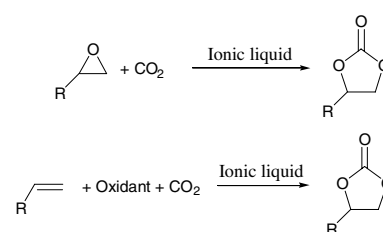
Reviews

**Jianmin Sun, Shin-ichiro Fujita,
Masahiko Arai**

J. Organomet. Chem. 690 (2005) 3490

Development in the green synthesis of cyclic carbonate from carbon dioxide using ionic liquids

A short review is given on the synthesis of cyclic carbonates from CO₂ using ionic liquids as catalyst and/or reaction medium: chemical and electrochemical cycloaddition of CO₂ to epoxides and oxidative carboxylation of olefins. The reaction systems using ionic liquids will contribute to the development of green processes of CO₂ fixation and production of valuable organic compounds.

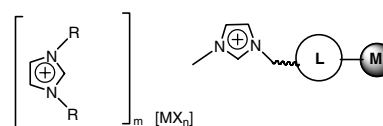


Ivan J.B. Lin, Chandra Sekhar Vasam

J. Organomet. Chem. 690 (2005) 3498

Metal-containing ionic liquids and ionic liquid crystals based on imidazolium moiety

This review evaluates the advantages and the future scope for metal containing ionic liquids and ionic liquid crystals based on imidazolium moiety in various branches of chemistry.



M-ILs and MILCs

R = short alkyl chain for MILs
R = long alkyl chain for MILCs

IL-supported metal catalyst

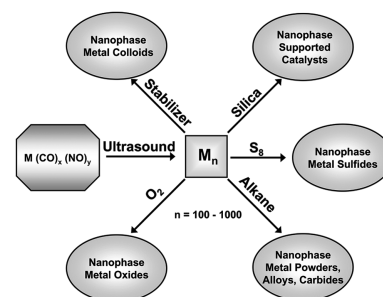
L = ligand
M = metal

**David J. Flannigan, Stephen D. Hopkins,
Kenneth S. Suslick**

J. Organomet. Chem. 690 (2005) 3513

Sonochemistry and sonoluminescence in ionic liquids, molten salts, and concentrated electrolyte solutions

Recent interest in using ultrasound to accelerate chemical reactions conducted in ionic liquids necessitates an understanding of the effects of acoustic cavitation on these solvents. Here, we review our previous results on the effects of cavitation on some room-temperature ionic liquids, including the sonoluminescence spectra of molten salt eutectics and concentrated aqueous electrolyte solutions.



Note

**Steven J. Craythorne, Alan R. Crozier,
Fabio Lorenzini, Andrew C. Marr,
Patricia C. Marr**

J. Organomet. Chem. 690 (2005) 3518

The preparation of silica entrapped homogeneous hydrogenation catalysts by conventional and ionic liquid mediated sol-gel routes

[RhCl(PPh₃)₃] has been entrapped inside silica matrices. The activity of these heterogenised catalysts has been tested for the hydrogenation of styrene. The catalyst prepared in an ionic liquid was found to be more active and have low Rh leaching. In addition the catalyst prepared via the ionic liquid route showed a 10 times recycling with no loss of activity or selectivity.



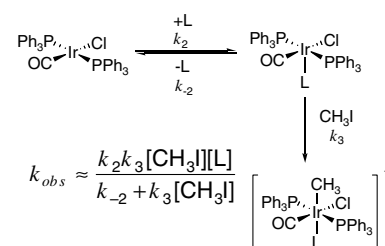
Regular papers

**Steven J. P'Pool, Marc A. Klingshirn,
Robin D. Rogers, Kevin H. Shaughnessy**

J. Organomet. Chem. 690 (2005) 3522

Kinetic study of the oxidative addition of methyl iodide to Vaska's complex in ionic liquids

Oxidative addition of methyl iodide to Vaska's complex in the ionic liquids gave rates that were 5–10 times slower than the rate seen in DMF. Saturation in the methyl iodide dependence was observed in the ILs. A ligand-promoted mechanism is proposed to account for the saturation kinetics.

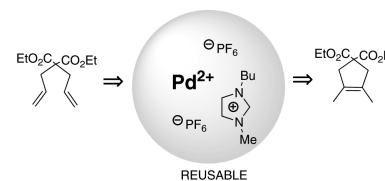


**Avelino Corma, Hermenegildo García,
Antonio Leyva**

J. Organomet. Chem. 690 (2005) 3529

Palladium catalyzed cycloisomerization of 2,2-diallylmalonates in imidazolium ionic liquids

Palladium salts and complexes catalyze the cycloisomerization of diethyl 2,2-diallylmalonate in imidazolium ionic liquids. The system comprising Pd species dissolved in ionic liquid can be reused several times without loss of the selectivity to the symmetric cyclopentene. The products coming from 1,10-undecadiene derivative show that the cycloisomerization is specific for the formation of five-member rings.

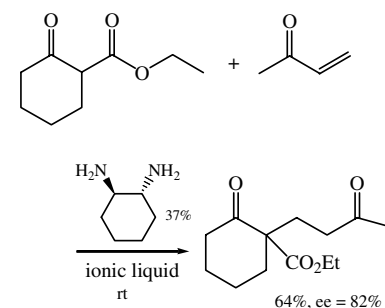


**Vito Gallo, Daniela Giardina-Papa,
Piero Mastrorilli, Cosimo Francesco Nobile,
Gian Paolo Suranna, Yaquan Wang**

J. Organomet. Chem. 690 (2005) 3535

Asymmetric Michael addition promoted by (*R,R*)-*trans*-1,2-diaminocyclohexane in ionic liquids

In ionic liquids, (*R,R*)-*trans*-1,2-diaminocyclohexane acts as chiral auxiliary for the addition of ethyl cyclohexanone-2-carboxylate to methyl vinyl ketone giving enantiomeric excesses up to 91%. The reaction can be performed catalytically.

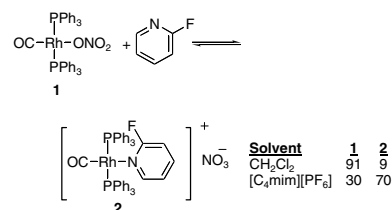


Michael D. Sliger, Steven J. P'Pool, Rachel K. Traylor, James McNeill III, Sidney H. Young, Norris W. Hoffman, Marc A. Klingshirn, Robin D. Rogers, Kevin H. Shaughnessy

J. Organomet. Chem. 690 (2005) 3540

Promoting effect of ionic liquids on ligand substitution reactions

Ionic liquid solvents promoted the displacement of anionic ligands by pyridine derivatives in *trans*-(Ph₃P)₂Rh(CO)X (X = NO₃⁻, C₆F₅CO₂⁻). Thus, addition of a slight excess of 2-fluoropyridine to *trans*-(Ph₃P)₂Rh(CO)-NO₃ in [C₄mim][PF₆] gave a 30:70 product mixture of *trans*-(Ph₃P)₂Rh(CO)NO₃:[*trans*-(Ph₃P)₂Rh(CO)(2-fluoropyridine)][NO₃], while the ratio was 91:9 in dichloromethane.

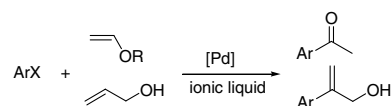


Wen Pei, Jun Mo, Jianliang Xiao

J. Organomet. Chem. 690 (2005) 3546

Highly regioselective Heck reactions of heteroaryl halides with electron-rich olefins in ionic liquid

The Heck reactions of heteroaryl halides with the electron-rich olefins vinyl ethers and allyl alcohol afforded essentially only the branched products in an imidazolium ionic liquid, whereas in molecular solvents a mixture of regioisomers was formed.

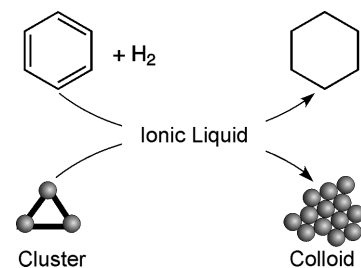


Tilman J. Geldbach, Paul J. Dyson

J. Organomet. Chem. 690 (2005) 3552

Searching for molecular arene hydrogenation catalysis in ionic liquids

Ionic liquids are excellent solvents for conducting hydrogenation reactions and also facilitate catalysis by intact molecular clusters. Our attempts to prove arene hydrogenation by homogeneous catalyst, including molecular clusters, are described.

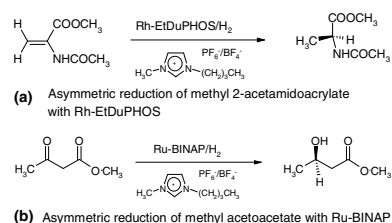


Adi Wolfson, Ivo F.J. Vankelecom, Pierre A. Jacobs

J. Organomet. Chem. 690 (2005) 3558

The role of additional solvents in transition metal complex catalyzed asymmetric reductions in ionic liquid containing systems

When ionic liquids are employed as solvents for transition metal complex catalyzed reductions, a second solvent can be added to increase the efficiency of the catalytic cycle and the solubility of the reactant in the IL phase. Product separation and TMC recycling is then performed by adding an excess of the second solvent or by adding a third solvent.

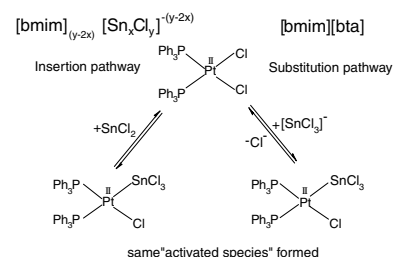


**Peter Illner, Achim Zahl, Ralph Puchta,
Nico van Eikema Hommes,
Peter Wasserscheid, Rudi van Eldik**

J. Organomet. Chem. 690 (2005) 3567

Mechanistic studies on the formation of Pt(II) hydroformylation catalysts in imidazolium-based ionic liquids

The kinetics and mechanism of the formation of the active species *cis*-[Pt^{II}(PPh₃)₂-Cl(SnCl₃)] and *cis*-[Pt^{II}(PPh₃)₂(SnCl₃)₂] from the hydroformylation catalyst precursor *cis*-[Pt^{II}(PPh₃)₂Cl₂] in the presence of SnCl₂, was studied in two different imidazolium-based ionic liquids.



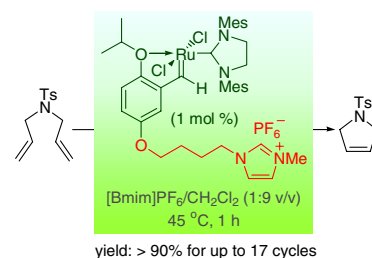
Change in mechanism in different ionic liquids

Qingwei Yao, Matthew Sheets

J. Organomet. Chem. 690 (2005) 3577

An ionic liquid-tagged second generation Hoveyda–Grubbs ruthenium carbene complex as highly reactive and recyclable catalyst for ring-closing metathesis of di-, tri- and tetrasubstituted dienes

A Ru catalyst bearing an ionic liquid tag was prepared and shown to be highly reactive for the RCM of a variety of diene and enyne substrates in minimally ionic solvents ([Bmim]PF₆/CH₂Cl₂, 1:9–1:1 v/v). Both the catalyst and the ionic liquid can be conveniently recycled and repeatedly reused (up to 17 cycles).

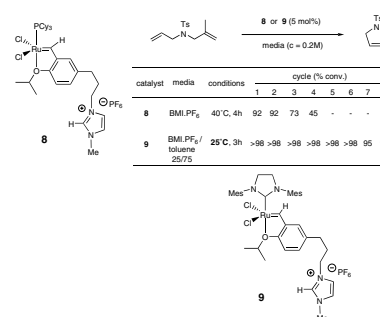


**Hervé Clavier, Nicolas Audic,
Jean-Claude Guillemin, Marc Mauduit**

J. Organomet. Chem. 690 (2005) 3585

Olefin metathesis in room temperature ionic liquids using imidazolium-tagged ruthenium complexes

This work reports the development of efficient imidazolium-tagged ruthenium catalysts to perform metathesis reactions in ionic liquids. Whereas a high level of recyclability combined with a high reactivity were obtained with the first generation catalyst **8**, the second generation of *N*-heterocyclic carbene ruthenium complex **9** appeared to be more suitable to perform ring-closing metathesis reactions of less reactive substrates.

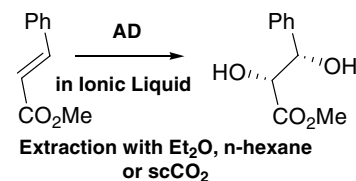


**Ana Serbanovic, Luis C. Branco,
Manuel Nunes da Ponte, Carlos A.M. Afonso**

J. Organomet. Chem. 690 (2005) 3600

Osmium catalyzed asymmetric dihydroxylation of methyl *trans*-cinnamate in ionic liquids, followed by supercritical CO₂ product recovery

The combination of ionic liquids as a solvent in the asymmetric Sharpless dihydroxylation (AD) of methyl *trans*-cinnamate and the use of *sc*CO₂ in the separation process allows a very simple, efficient, clean and robust system for the reuse of the AD catalytic system.



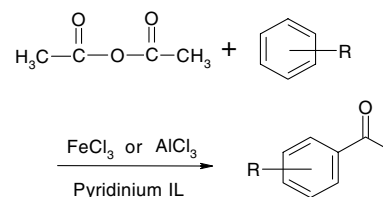
- * High yields and enantioselectivities
- * Osmium in the product lower than ICP detection limit
- * Catalytic system reused 6 times

Ying Xiao, Sanjay V. Malhotra

J. Organomet. Chem. 690 (2005) 3609

Friedel-Crafts acylation reactions in pyridinium based ionic liquids

The Friedel-Crafts acylations of representative aromatics was studied in pyridinium based ionic liquids (ILs). Suitable reaction conditions were developed in these 'environmentally friendly' medium. The ILs could also be recycled and reused effectively.



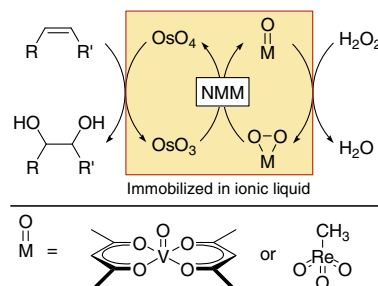
IL : [EtPy]⁺[CF₃COO]⁻ or [EtPy]⁺[BF₄]⁻

Mikael Johansson, Auri A. Lindén, Jan-E. Bäckvall

J. Organomet. Chem. 690 (2005) 3614

Osmium-catalyzed dihydroxylation of alkenes by H₂O₂ in room temperature ionic liquid co-catalyzed by VO(acac)₂ or MeReO₃

A practical and useful catalytic system for dihydroxylation of alkenes by H₂O₂ was obtained by immobilization of OsO₄ and a co-catalyst (VO(acac)₂ or MeReO₃ (MTO)) in an ionic liquid. The presence of *N*-methylmorpholine (NMM) as an additional co-catalyst (electron transfer mediator) increased the efficiency of the dihydroxylation in most cases. In a preliminary experiment an enantioselective dihydroxylation with this system was obtained.

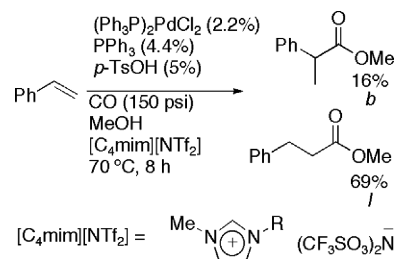


Marc A. Klingshirn, Robin D. Rogers, Kevin H. Shaughnessy

J. Organomet. Chem. 690 (2005) 3620

Palladium-catalyzed hydroesterification of styrene derivatives in the presence of ionic liquids

Hydroesterification of styrene derivatives and 1-octene was achieved in good yield in ionic liquid solvents. Both styrenes and 1-octene gave good linear:branch product selectivities. The catalyst/IL phase could be recycled up to 5 times with an average yield of 68%.



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