



Abstract Listing

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414940: Palladium catalyzed coupling reactions in room-temperature ionic liquids

IEC 0 [414940]: Palladium catalyzed coupling reactions in room-temperature ionic liquids

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ACCEPTED

Topic Selection: *Green (or Greener) Industrial Applications of Neoteric Solvents: Ionic and Supercritical Fluids: Catalysis I*

Invited: *Y*

Preferred Presentation Format: *OralOnly*

Consider for Sci-Mix: *N*

Conforms to Bylaw 6: *Y*

Last Modified: *2000-11-24*

Abstract

The stereo- and regiospecific generation of carbon-carbon bonds is one of the most important reactions in organic synthesis. Recently, with the modern preference for catalytic processes, the palladium-mediated coupling reactions of organic electrophiles (halides or equivalents) with organoboron (Suzuki), organotin (Stille) alkynyl (Sonogashira) or alkenyl (Heck) reagents have come to the fore. Room-temperature ionic liquids have been illustrated to dramatically effect these reactions, which in some cases have lead to unprecedented catalytic activities, selectivities and catalyst stabilities compared to conventional solvent systems. Other benefits include immobilisation of the active palladium species, novel product isolation and solvent/catalyst recycling protocols. In this paper, we concentrate on the various ways in which the ionic liquids can effect the palladium catalysed coupling reactions and assess their contribution to the overall improvements in reactivity.

418583: Palladium-catalyzed carbonylation of aryl halides in ionic liquids

IEC 0 [418583]: Palladium-catalyzed carbonylation of aryl halides in ionic liquids

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Abstract

Palladium-catalyzed carbonylation of aryl halides proceeded in ionic liquids (1-butyl-3-methylimidazolium hexafluorophosphate and tetrafluoroborate). Carbonylation of iodobenzene with isopropanol forming isopropyl benzoate was greatly accelerated by the use of ionic liquid when a palladium-triphenylphosphine catalyst system was used under 150 kg/cm² of CO pressure. In the case of the reaction with methanol under 30 kg/cm² of CO pressure, the catalyst/solvent mixture could be recycled, after separation of the product by distillation. The catalytic activity was sustainable in the ionic liquid media to allow recycling at least twice without significant decrease in the yield. Total turnovers after the seventh recycling reached approximately 1100. Double carbonylation of iodobenzene also proceeded smoothly in ionic liquids to give keto amide in the presence of diethylamine.

419294: Catalytic oxidations in ionic liquids

IEC 0 [419294]: Catalytic oxidations in ionic liquids

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Abstract

A pressing issue for chemists in the twenty-first century is the development of 'cleaner' chemical reactions and processes. One of the major sources of chemical waste which is often taken for granted is the use of volatile organic solvents. Molten salts are not only novel alternatives to traditional volatile and carcinogenic solvents, but they also permit catalyst recovery and recycling. The net result is a combination of the high activity and selectivity of homogeneous catalysis, and the ease of separation that distinguishes heterogeneous catalysis. We have employed successfully transition-metal catalysts (rhenium and vanadium) in alkene and alcohol oxidations with room-temperature ionic liquids as solvents. The stoichiometric oxidant is either hydrogen peroxide or t-butyl hydroperoxide. The advantages and limitations of performing oxidations in ionic media will be highlighted. Kinetics and mechanistic aspects of the catalytic systems will be discussed along with selectivity and application issues.

419596: Biphasic catalysis using supercritical carbon dioxide and ionic liquids**IEC 0 [419596]: Biphasic catalysis using supercritical carbon dioxide and ionic liquids**

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Abstract

Biphasic or phase-separable catalysis combines the selectivity and catalyst/ligand design advantages of homogeneous catalysis with the product recovery and catalyst recycle advantages of heterogeneous catalysis. We will report on recent results from work in our laboratory aimed at exploring opportunities for phase-separable catalysis using mixtures of supercritical carbon dioxide (sc CO₂) and room temperature ionic liquids (IL), particularly substituted imidazolium salts. We will present examples of catalytic hydrogenation and other reactions, where homogeneous transition metal complexes can be immobilized in the IL phase, facilitating catalyst separation and recycle. For example, we have found that a biphasic scCO₂/IL system can be used to hydrogenate carbon dioxide to dialkyl formamides or esters in the presence of dialkylamines or alcohols, respectively. We will compare reactivities and selectivities for this reaction and other transformations in this biphasic medium to other solvent systems, including neat supercritical fluids and organic solvents.

423070: Ionic liquids-polar, weakly coordinating solvents for the biphasic oligomerisation of ethylene to α -olefins with cationic Ni-complexes**IEC 0 [423070]: Ionic liquids-polar, weakly coordinating solvents for the biphasic oligomerisation of ethylene to α -olefins with cationic Ni-complexes**

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Abstract

Cationic Ni-complexes have attracted some attention as highly active catalyst for ethylene oligomerisation to higher α -olefins (HAOs). In comparison to neutral complexes, they usually possess higher electrophilicity of the nickel centre which often results in a higher oligomerisation activity of the system. However, to our knowledge, there is no example of an active biphasic ethylene oligomerization to HAOs with cationic nickel complexes in the literature. Obviously, the high affinity of the electrophilic nickel centre towards polar solvent such as e.g. 1,4-butanediol is a limiting factor. In our contribution, we demonstrate the use of hexafluorophosphate ionic liquids as novel solvents for the biphasic ethylene oligomerisation to HAOs with cationic nickel complexes. Activation of the cationic catalyst in the ionic liquid and selectivity effects are discussed in detail.

438954: Transition metal catalyzed hydrosilylation and hydroboration of acetylenes in ionic liquids

IEC 0 [438954]: Transition metal catalyzed hydrosilylation and hydroboration of acetylenes in ionic liquids

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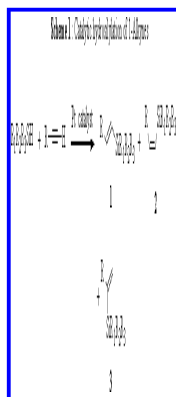
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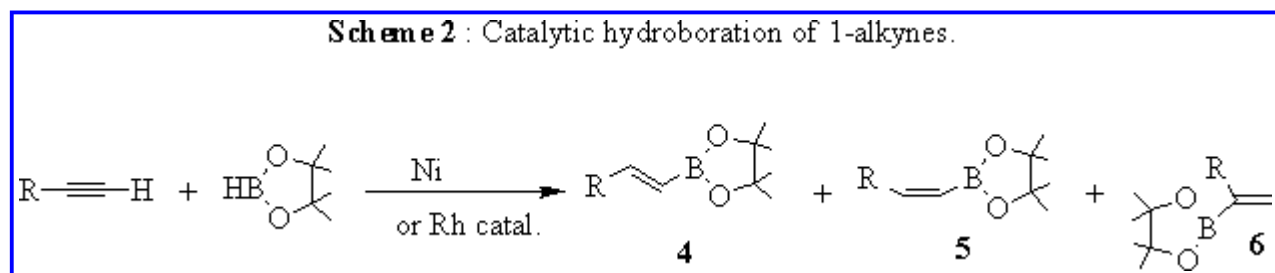
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Abstract

The associations of N,N'-dialkylimidazolium and N-alkylpyridinium cations with common weakly coordinating anions such as AlCl_4^- , BF_4^- , PF_6^- , CF_3SO_3^- , $^- \text{N}(\text{SO}_2\text{CF}_3)_2$ etc... are liquids at or near room temperature and can dissolve either organic or inorganic salts including ionic transition metal complexes. Moreover, the miscibility of ionic liquids with organic liquids can be adjusted allowing catalytic reactions to be performed in a biphasic system with recycling of the solution catalyst. We have applied these simple ideas to the transition metal catalyzed hydrosilylation (scheme 1) and hydroboration (scheme 2) of acetylenes in ionic liquids.



These reactions have been studied in ionic liquids in the presence of catalytic amounts of platinum catalysts including $[\text{H}_2\text{PtCl}_6, 6 \text{H}_2\text{O}]$, $[\text{K}_2\text{PtCl}_4]$ and $[\text{K}_2\text{PtCl}_6]$. Mixtures of vinylsilanes **1** and **3** were obtained in excellent yields. Selectivity and reactivity depend very much on the ionic liquid used for the reaction. Under certain conditions, the isomerization of vinylsilanes into allylsilanes was observed. These results will be presented in details. Hydroboration of 1-alkynes with pinacolborane in ionic liquids leading to vinylboronates **4** and **6** has also been studied (scheme 2).



The reaction rates and selectivities depend very much on catalysts and the nature of ionic liquids and very good results could be obtained under appropriate conditions.

Vinylsilanes and vinylboronates could be purified by a simple bulb to bulb distillation of the crude mixture under vacuum. In both cases, the solutions of catalyst in the ionic liquids could be reused without any further treatment.

445125: Intermission

0 [445125]: Intermission

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445126: Discussion**0 [445126]: Discussion****ACCEPTED**

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