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An Ionic Liquid-Coordinated Palladium Complex: A Highly Efficient and Recyclable Catalyst for the Heck Reaction

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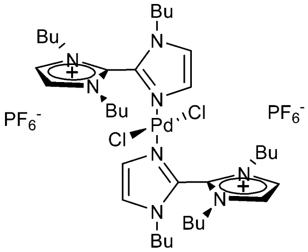
ABSTRACT



The monoquaternary product of 2,2′-biimidazole with iodobutane is an ionic liquid that acts as both the solvent and ligand for catalytic reactions. A new palladium complex was prepared by adding PdCl$_2$ to this ionic liquid to form a catalytic solution that is effective for Heck reactions with good recyclability.

The design of ionic liquids for use as solvents that can serve for both immobilization and as coordinating ligands for the catalyst in processes involving homogeneous catalysis is a worthwhile objective. Such a system would be useful in avoiding catalyst leaching from the ionic layer. However, the coordinating abilities of ordinary ionic liquids are often very poor.[1,2] One of the predominant applications of ionic liquids[3] as solvents focuses on homogeneous catalysis since ionic liquids have been demonstrated to be ideal immobilizing agents for various classical transition-metal catalyst precursors in hydrogenation,[4] hydroformylation,[5] and carbon−carbon coupling reactions.[6] However, in certain cases, the transition-metal catalysts are often removed from the ionic liquid catalyst solution by polar products. When this occurs it is necessary to use specially designed polar ligands to avoid catalyst leaching.[3c,7] To date, some efforts have been made to address this by introducing functional groups into the ionic liquid which can complex the metal centers.[2,8] Such func-

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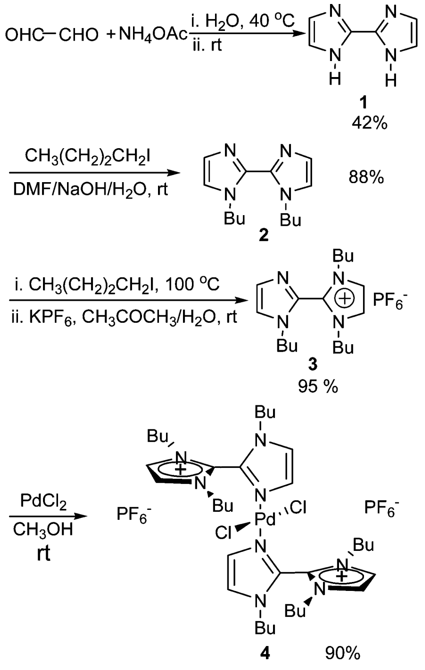
tional groups include thiourea, thioether, and urea which were employed for the extraction of metal ions from aqueous solutions,[9] amines,[9a,10] amides,[11] phosphines,[2c] nitriles,[2a] and alkynes.[8,12] Recently, metal complexes with pending imidazolium tags have also been reported.[2b,13] These incorporated functional groups are sometimes play a role in the reaction. Herein, we report a new type of ionic liquid-coordinated palladium complex for the Heck reaction. This catalytic ionic liquid solution can be recovered and recycled without significant loss in activity.

In some molecules with multiple centers available for quaternization, such as 4,4′-bipyridine, a coordination center remains after monoquaternization. In our earlier work, it was shown that the monoquaternary products of 4,4′-bipyridine are not room temperature ionic liquids although they are relatively low melting salts, 52−109 °C.[14] We now have extended our research to 2,2′-biimidazole, **1**, which was prepared from glyoxal and ammonium acetate.[15] Treatment of **1** with 1-iodobutane in the presence of base leads readily to 1,1′-dibutyl-2,2′-biimidazole, **2**.[16] Reaction with 1 equiv of 1-iodobutane at 100 °C quaternizes one of the two basic nitrogens of **2** to give the monoquaternary salt. Subsequent metathetical reaction with potassium hexafluorophosphate resulted in the formation of **3** (95% yield), which can be classified as a room-temperature ionic liquid with a glass transition temperature of −42.76 °C (Scheme 1).

Scheme 1. Synthesis of Complex **4**



The coordination ability of **3** was then tested. Dissolution of $PdCl_2$ in 2 equiv of **3** in methanol for 6 h at room temperature afforded a yellow palladium complex, **4**, in 90% yield. A crystal suitable for X-ray single-crystal diffraction analysis was obtained from a 1:3 $CH_3OH/(C_2H_5)_2O$ mixture (Figure 1). This complex is insensitive to oxygen or moisture and is completely soluble in the coordinating ligand−ionic liquid **3**. We believe that this is the first example of a complex formed between an ionic liquid with more than one center available for quaternization and a transition metal.

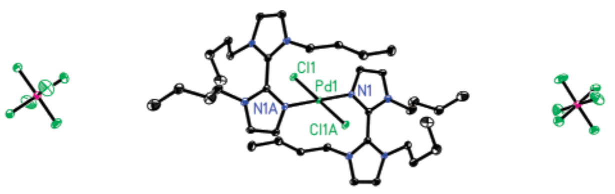


Figure 1. Single-crystal X-ray structure of **4**. Compound **4** crystallizes in the triclinic space group *P*-1 with the Pd atom on the inversion center. The other half of the molecule and the extra anion for charge balance are symmetry generated. The bi-imidazole ligands are oriented trans to each other, and they are tilted out of the $PdCl_2$ plane by 53.4°. There is also a twist between the two imidazole rings of 68°. Both tilting and twisting are seen in other imidazole−$PdCl_2$ complexes[17] and bi-imidazole systems.[18] In this case, the tilt is relatively large, probably due to the steric influence of the Bu arms. These pendant Bu arms wrap around the Cl atoms and encapsulate the $PdCl_2$ group in a hydrocarbon shell. This may have some bearing on the catalyst recovery rate seen for **4** in the Heck reaction (vide infra).

The palladium-catalyzed coupling of olefins with aryl or vinyl halides, known as the Heck reaction, is one of the most important, reliable, and general reactions for carbon−carbon bond formation in organic synthesis.[19] Various strategies are

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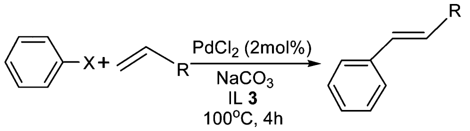
employed to recover and reuse the palladium catalyst for the Heck reaction. Many studies on the Heck reaction by immobilizing the palladium−bulky phosphine complexes in ionic liquids have been reported,[20] and only a few phosphine-free Heck reactions are known.[21]

Since the ionic liquid **3** could coordinate well with $PdCl_2$ to form a stable phosphine-free complex, **4**, it was interesting to investigate its catalytic activity. Moreover, as mentioned above, it was envisaged that **3** might be used both as the solvent and as the ligand. Therefore, we tried the Heck coupling reaction of iodobenzene with methyl acrylate (Table 1). Sodium carbonate, iodobenzene and methyl acrylate were added directly to a preformed solution of 2 mol % $PdCl_2$ in **3**. Complete formation of the coupled product was obtained after heating at 100 °C for 4 h under ambient laboratory conditions. The product, (*E*)-methyl cinnamate,[22] was easily separated from the reaction mixture by simple extraction and decantation with ethyl ether. The desired product was isolated in 92% yield by column chromatography on silica gel using hexanes−ethyl acetate (40:1) as eluent.

Table 1. Recyclable Heck Coupling Reaction of Aryl Halide with Vinyl Compounds[a]



X	R	cycle	yield[a] (%)	cycle	yield[a] (%)
I	CO_2Me	1	92	4	91
		2	90	5	91
		3	94		
Cl	CO_2Me	6	70	8	75
		7	78		
Cl	Ph	9	86	11	83
		10	81		

[a] All reactions were carried out using 2 mmol of aryl halide, 1.25 equiv of the vinyl compound, 1.5 equiv of Na_2CO_3, 2 mol % **4**, and 2 g of **3**, at 100 °C, 4 h. [b] Isolated yield.

These results prompted us to examine the reuse of this catalytic system. The catalyst−ionic liquid solution was recovered by washing with water to remove the sodium salt and drying under vacuum before using. The same amounts of starting materials were added to the recovered ionic liquid solution again. A similarly high conversion was obtained after 4 runs (cycle 5), showing that this catalytic ionic liquid system remained active. Further, this recovered catalyst-ionic liquid solution was used for a second substrate, the nonactive chlorobenzene, leading to the same product in 75% yield after two runs (cycle 8). Then, the recycled catalytic system was employed in the reaction of chlorobenzene with styrene. Two runs later, it was possible to obtain the product in 83% yield (cycle 11). These observations show that this catalyst−ionic liquid solution could be recycled at least 10 times without significant decrease in catalytic performance. The most important feature of the catalytic system is that this catalyst is part of the ionic liquid and therefore not easily lost during extraction of the product.

In conclusion, we present a new type of ionic liquid-coordinated palladium complex as catalyst for the Heck reaction. This catalytic ionic liquid solution can be recovered and recycled without significant loss in activity. From these results, it seems likely that many other transition-metal-catalyzed reactions could be performed equally well in this catalytic ionic liquid solution.

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Supporting Information Available: Experimental procedures and analytical data for the work described. X-ray crystallographic data for **4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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