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A Highly Efficient, Recyclable Catalyst for C−C Coupling Reactions in Ionic Liquids: Pyrazolyl-Functionalized N-Heterocyclic Carbene Complex of Palladium(II)

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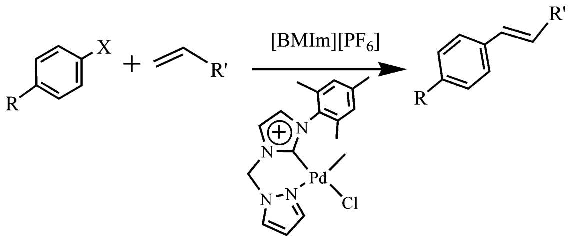

A hemilabile pyrazolyl-functionalized N-heterocyclic carbene complex of palladium(II) has been synthesized. It is an excellent catalyst for Heck and Suzuki cross-coupling reactions in ionic liquids.

The initial isolation of a free carbene in 1991[1] has encouraged much interest in the chemistry of *N*-heterocyclic carbenes (NHCs) and their metal complexes.[2] NHCs behave like typical strong σ-donor ligands with negligible π-acceptor abilities. Because these electronic characteristics are similar to those of phosphines,[3,4] they have played the same roles as well-studied phosphine ligands in catalytic cycles. In addition, NHCs show superior performance in many aspects over traditional phosphine ligands, including ready preparation, air and moisture stability, nontoxicity, low loading, and high efficency.[4] Many metal complexes of NHCs behave as highly efficient catalysts in organic synthesis. However, facile reductive elimination with hydrocarbyl ligands from Ni(II) and Pd(II) NHC complexes was observed in some cases.[5] The process suggested a potentially important route to deactivation of catalysts. Subsequent experimental and theoretical investigations revealed that this disadvantage could be prevented if the chelating coordination groups containing P, O, or N donor atoms were attached to the carbene as hemilabile arms resulting in more stable and efficient catalysts.[6−9]

Recently, there have been a few reports of metal complexes containing pyridyl-functionalized NHCs and their applications as catalyst precursors for C−C coupling,[7] copolymerization of CO/norbornene,[8] and polymerization of olefins.[9] Their excellent properties encouraged us to develop new types of phosphine-free hemilabile catalysts. Since it is well-known that the pyrazolyl ring is more weakly coordinating to metal centers than the pyridyl ring,[10] we reasoned that transition-metal complexes of pyrazolyl-functionalized NHCs may facilitate oxidative additions in a catalytic cycle and may form more efficient catalyst precursors than those from a corresponding pyridyl ring. However, these kinds of hemilabile compounds have not been reported.

Organic reactions that employed palladium(II) complexes of pyridyl-functionalized hemilabile NHCs as catalysts were typically carried out in nonreusable organic solvents, such as toluene, THF, DMF, and dioxane,[7−9] and the expensive catalysts could not be recovered and recycled. However, when the reactions were performed in ionic liquids (ILs), important advantages in immobilization and recycling of the catalyst were available.[11] The capacity of ILs to solvate both polar and nonpolar species allows the dissolution of a wide range of organic, inorganic, and organometallic compounds favoring the formation of a homogeneous catalytic system. The organic products can be readily separated from the palladium(II) catalysts in the ionic liquids through simple distillation or extraction with ether or hexane. Most importantly, the carbene ligands do not readily dissociate from the metal center.[3,7] Therefore, this means that an excess of ligand is unnecessary and the catalyst can easily be immobilized in ILs. However, many palladium(II)-catalyzed coupling reactions are carried out in ILs in the presence of bulky phosphine ligands.[12] The latter are sensitive to oxygen and moisture, which can lead to catalyst

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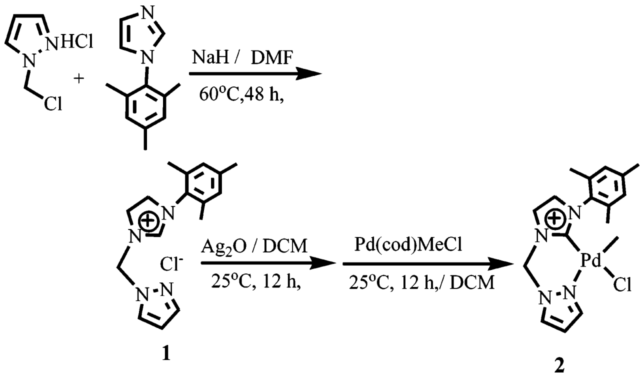
10.1021/jo052098b CCC: $33.50

SCHEME 1. Synthesis of Pyrazolyl-Functionalized Imidazolium Chloride and Catalyst 2



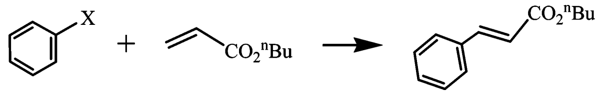
decomposition. Thus, the development of phosphine-free recyclable catalysts is of great importance.[13,14]

As an extension of our research work in recyclable phosphine-free catalytic systems,[14] we were interested in the use of conventional and functionalized room-temperature ionic liquids as reaction media. We now report the synthesis of a palladium (II) catalyst precursor from a pyrazolyl-functionalized hemilabile NHC, {[Pd(Me)(3-mesityl-1-(pyrazolylmethylene)imidazolium)] chloride (**2**)}, which exhibited good activity in Heck and Suzuki cross-coupling reactions in an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate [(BMIm)(PF_6)].

The pyrazolyl-functionalized imidazolium salt **1** was synthesized by reaction of 1-chloromethylpyrazole hydrochloride, NaH, and 1-mesitylimidazole in DMF at 60 °C (Scheme 1). Since attempts to prepare the methylpalladium(II) catalyst **2** by in situ deprotonation of **1** with an external strong base followed by reaction with Pd(cod)MeCl failed, a strategy based on use of a silver (I) *N*-heterocyclic carbene complex as a ligand transfer reagent for the synthesis of the desired palladium(II) complex was adopted.[6b,7a,c,8,1515] The formation of **2** was confirmed by the absence of the ^{1}H NMR resonance for the imidazolium C2-H at 9.93 ppm, where the signal of its precursor (**1**) is found. In the ^{13}C NMR spectrum, the signal for the carbene carbon atom of **2** appears at 170.6 ppm which is a characteristic peak for a metal carbene complex.[7a,9] The chemical shifts for the methylpalladium group were found at −0.21 ppm in the ^{1}H NMR and at −12.4 ppm in the ^{13}C NMR spectra, respectively, which are similar to those reported for methylpalladium(II) NHC compounds.[6b,7a]

Crystals of **2** were obtained by slow evaporation of the CH_2Cl_2 solution. As shown in Figure 1 (Supporting Information), the palladium(II) center has a distorted square-planar geometry. Ligand **1** serves as a chelating ligand coordinating to palladium(II) through its carbene carbon and pyrazolyl nitrogen. The resulting six-membered ring is puckered to release conformational strain. The imidazolium ring is not coplanar with the mesityl ring and the pyrazolyl ring with the dihedral angles between them being 76.1° and 63.9°, respectively. The chloride ion is *trans* to the carbene carbon atom with the Cl(1)−Pd(1) bond distance and the C(11)−Pd(1)−Cl(1) bond angle at 2.3699(7) Å and 176.31(8)°, respectively.

TABLE 1. Heck Cross-Coupling Reactions of Aryl Halides with *n*-Butyl Acrylate in ILs under Various Reaction Conditions[a]



entry	X	base	time (h)	(cycle) yield[b]		
1	I	Et_3N	8	(1) 91	(2) 91	(3) 89
2	I	Et_3N	8	(4) 92	(5) 87	(6) 93
3[c]	I	Et_3N	8	(1) 91	(2) 83	(3) 73
4[d]	I	Et_3N	8	(1) 89	(2) 91	(3) 87
5	I	Et_3N	1	(1) 83	(2) 88	(3) 85
6	I	Na_2CO_3	8	(1) 90	(2) 91	
7	I	NaOAc	8	(1) 91	(2) 93	
8	Br	Et_3N	12	(1) 49	(2) 54	
9	Br	Na_2CO_3	12	(1) 29	(2) 24	
10	Br	NaOAc	12	(1) 32	(2) 29	

[a] All reactions were carried out using 1 mmol of aryl halides, 1.25 mmol of *n*-butyl acrylate, 1.5 mmol of base, 2 mol % of catalyst, and 3 g of ILs at 120 °C. [b] Isolated yield (%). [c] The reaction was exposed to air. [d] Performed with 0.2 mol % of catalyst.

Compound **2** is stable in air and moisture and is moderately soluble in [BMIm][PF_6]. The catalytic activity of **2** was first examined in Heck cross-coupling reactions. Initially, we screened the base for the Heck reaction at 120 °C. The reactions of iodobenzene and *n*-butyl acrylate occurred completely with a catalyst loading of 2 mol % in the presence of different bases, such as triethylamine, Na_2CO_3, and NaOAc. No side products were formed and only *n*-butyl (*E*)-cinnamate was obtained in an excellent isolated yield. When the reaction was carried out for 1 h, iodobenzene was completely converted into the target product, which suggested that the pyrazolyl-functionalized palladium(II) catalyst is highly efficient for Heck reactions. It should be emphasized that the catalyst still remains active after the initial coupling reaction of iodobenzene and *n*-butyl acrylate in the presence of triethylamine. The reaction was performed a total of six times (Table 1, entries 1 and 2) using the same catalyst, and high yields were obtained consistently. Moreover, the reactions of bromobenzene and *n*-butyl acrylate under identical conditions showed that triethylamine is an ideal base in the absence of other additives. Sodium carbonate and NaOAc have also been employed successfully, but lower isolated yields were obtained. In our work, the Heck reactions were run with triethylamine as a base. The observations were in agreement with the catalytic reactions of pyridyl-functionalized hemilabile NHCs in THF[7b] and other phosphine-free catalysts in ILs.[16] It should be mentioned that palladium black or an insoluble solid formed when the coupling reaction of iodobenzene and *n*-butyl acrylate was run under similar conditions in an open system. Although no unreacted iodobenzene was observed at the end of the time period and a high isolated yield was found, the yield in the second run is slightly lower (entry 3). Therefore, all of the reactions were carried out in an atmosphere of nitrogen.

The stability and recyclability of the catalyst at very low concentrations were also examined. The reactions proceeded well at a catalytic loading of 0.2 mol %. In this case, excellent

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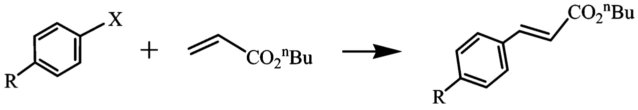
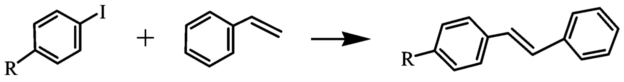
TABLE 2. Heck Cross-Coupling Reactions of Aryl Halides with *n*-Butyl Acrylate under Optimized Reaction Conditions[a]



entry	R	X	(cycle) yield[b]		
1	Me	I	(1) 92	(2) 89	(3) 94
2	MeO	I	(1) 94	(2) 90	(3) 91
3	NO$_2$	I	(1) 93	(2) 91	(3) 91
4	F	I	(1) 95	(2) 90	(3) 94
5[c]		I	(1) 86	(2) 88	(3) 81
6	NO$_2$	Br	(1) 80	(2) 72	(3) 76
7	F	Br	(1) 72	(2) 77	(3) 68
8	CF$_3$	Br	(1) 77	(2) 84	(3) 74
9	CH$_3$CO	Br	(1) 77	(2) 73	(3) 81

[a] All reactions were carried out using 1.0 mmol of aryl halides, 1.25 mmol of *n*-butyl acrylate, 1.5 mmol of Et$_3$N, 2 mol % of catalyst, and 3.0 g of ILs at 120 °C for 8 h. [b] Isolated yield (%). [c] 2-iodothiophene acts as a substrate.

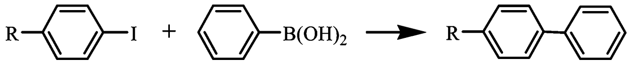
TABLE 3. Recyclable Heck Cross-Coupling Reactions of Aryl Halides with Styrene[a]



	R =				
	H	Me	MeO	F	NO$_2$
cycle	1	2	3	4	5
yield[b]	89	93	90	91	93

[a] All reactions were carried out using 1 mmol of aryl halides, 1.25 mmol of styrene, 1.5 mmol of Et$_3$N, 2 mol % of catalyst, and 3 g of ILs at 120 °C for 8 h. [b] Isolated yield (%).

TABLE 4. Recyclable Suzuki Coupling Reactions[a]



	R				
	H	Me	MeO	F	NO$_2$
cycle	1	2	3	4	5
yield[b]	90	91[c]	88	90	87

[a] All reactions were carried out using 1.0 mmol of aryl iodide, 1.1 mmol of phenylboronic acid, 2.0 mmol of Na$_2$CO$_3$, 1 mL of H$_2$O, 2 mol % of catalyst, and 3.0 g of ILs at 110 °C for 1 h. [b] Isolated yield (%). [c] Containing ∼3% biphenyl.

stability and high activity have been achieved as shown in Table 1 (entry 4). Furthermore, the reaction could be recycled three times without evident loss of catalytic efficiency. As shown in Table 2, the reactions of *n*-butyl acrylate with aryl iodides containing electron-withdrawing groups, such as fluoro and nitro, or electron-donating groups, such as methyl and methoxyl, progressed smoothly under optimized coupling conditions. The corresponding *n*-butyl (*E*)-cinnamates were obtained in very high yields with complete regioselectivity at the β-position. In addition, no *cis* olefin products were observed. A heteroaromatic compound, 2-iodothiophene, also reacted with *n*-butyl acrylate to give the desired product in a satisfactory yield (entry 5). The side product of the reaction, 1,1′-bisthiophene, has not been observed in the system.[13a] To determine the scope of this catalyst with aryl bromide substrates, the reactions of *n*-butyl acrylate with electron-poor 1-bromo-4-nitrobenzene, 4-bromofluorobenzene, 4-bromobenzene trifluroride, and 4-bromoacetophenone were run under identical conditions, and satisfactory yields were obtained (entries 6−10). All coupled products were easily separated from the catalyst and ILs by extraction with ether. After extracting the products from ionic liquids which contained the palladium(II) catalyst, the resulting solution was washed with water to remove ammonium salts and dried under vacuum before reusing.

To test the scope and recyclability of the catalyst further in [BMIm][PF$_6$], a more versatile and practical method was applied to the coupling reactions between iodoarenes and styrene under similar conditions (Table 3). When iodobenzene was treated with styrene with a catalyst loading of 2 mol % at 120 °C for 8 h, the desired coupling product was obtained in an 89% isolated yield. After separation of the product and the recovery of ionic liquids containing the palladium(II) catalyst, different substrates were charged into the reaction system. The reactions still proceeded well and no unreacted aryl iodide was detected at the end of the reaction period. The ILs containing the palladium(II) catalyst were recycled five times with different reactants, and no loss of catalytic activity was detected.

To evaluate the present reaction system further, Suzuki coupling reactions were also evaluated according to the reported protocol.[17] In this system, Na$_2$CO$_3$ was used as a base rather than Et$_3$N. To increase the solubility of the inorganic salt, water was added as cosolvent. Excellent results were observed in the reactions of aryl iodides with phenylboronic acid with Na$_2$CO$_3$ and the catalyst loading of 3% at 110 °C for 1 h. The ILs containing the palladium (II) catalyst were recycled five times using different reactants, and no detectable loss of activity was observed (Table 4). Moreover, no appreciable difference in yields between activated and deactivated iodoarenes was found, thus demonstrating the high activity of the catalytic system.

The excellent catalytic activity and recyclability of **2** in ILs arise from its strong Pd(II)−carbene bond and the weak Pd(II)−nitrogen bond. On one hand, the weak coordination of the pyrazolyl nitrogen to Pd(II) made it easy to dissociate from the Pd(II) center to form the Pd(0) intermediate. Such dynamic behavior generates a vacant coordination site that allows complexation of substrates during the catalytic process facilitating oxidative addition of organic halides. Concomitantly, the strong σ bond between the carbene electron pair and Pd(II) stabilizes and activates the zerovalent palladium center. This is especially true when an alkyl group coordinates to the Pd(II) center in the hemilabile ligands, where the alkyl group might accelerate catalysis through olefin insertion into the Pd−alkyl bond with subsequent β-hydride elimination.[7] Consequently, the catalyst may be activated. On the other hand, the pyrazolyl ring can coordinate to the palladium(II) center after the catalytic reaction which will result in recovery of the catalyst. Perhaps most importantly, ionic liquids, as an excellent supporting medium, can further immobilize the catalyst and enhance the recovery and recycling of the palladium(II) catalyst.[18] This mechanism can also be used to explain excellent efficiency in Suzuki cross-coupling reactions.

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In summary, we have synthesized a new type of palladium(II) complex from a pyrazolyl-functionalized hemilabile NHC. The Pd(II) compound not only exhibits high stability and efficient activity as catalyst precursor for Heck and Suzuki cross-coupling reactions in ionic liquids, but it can also be recovered and recycled at least three times without significant loss in activity. This work has demonstrated that organic reactions catalyzed by a functionalized hemilabile Pd(II) complex proceed efficiently in ionic liquids.

Experimental Section

Synthesis of 3-Mesityl-1-(pyrazolylmethylene)imidazolium Chloride Hydrate (1). 1-(Chloromethyl)pyrazole hydrochloride (1.52 g, 10.0 mmol) was added slowly to a solution of sodium hydride (0.40 g, 10.0 mmol) in dry DMF (50 mL) at 0 °C and then stirred for 30 min. 1-Mesitylimidazole (2.05 g, 11 mmol) in 10 mL of DMF was added to the reaction mixture and heated at 60 °C for 48 h. After the mixture was cooled to 25 °C, the inorganic salt was removed by filtration and washed with acetone several times. After removal of the solvent in the combined washings under reduced pressure, the residue was purified by flash chromatography on silica gel to give a colorless solid: yield 1.9 g (63%); ^{1}H NMR δ 9.93 (s, 1H), 8.28 (d, $J = 2.0$ Hz, 1H), 8.17 (d, $J = 2.0$ Hz, 1H), 7.95 (d, $J = 1.8$ Hz, 1H), 7.68 (d, $J = 1.8$ Hz, 1H), 7.15 (s, 2H), 6.73 (s, 2H), 6.42 (t, $J = 1.9$ Hz, 1H), 2.34 (s, 3H), 1.97 (s, 6H); ^{13}C NMR δ 141.7, 140.3, 138.2, 134.0, 131.6, 130.9, 129.2, 124.3,-122.4 107.0, 61.7, 20.5, 16.7; IR (KBr pellet) 3560 (w), 3146 (m), 2967 (s), 2876 (m), 1610 (m), 1583 (s), 1515 (s), 1467 (m), 1447 (m), 1351 (s), 1192 (s), 1057 (s), 936 (w), 781 (m), 701 (w), 654 (w), 615 (m), 571 (w), 511(m). Anal. Calcd for $C_{16}H_{21}ClN_4O$ (320.14): C, 59.90; H, 6.60; N 17.46. Found: C, 60.17; H, 6. 53; N, 17.71. Compound **1** decomposed before melting.

Synthesis of [Pd(Me)(3-mesityl-1-(pyrazolylmethylene)imidazolium) Chloride (2). A mixture of **1** (0.60 g, 2.0 mmol) and silver(I) oxide (0.24 g, 1.05 mmol) in dichloromethane (20 mL) was stirred at 25 °C for 12 h. The reaction mixture was filtered through Celite and washed twice with CH_2Cl_2 (10 mL). The solvent volume was reduced to ~10 mL under vacuum. The Pd(cod)MeCl (0.53 g, 2 mmol) in CH_2Cl_2 (10 mL) was added to the resulting solution and stirred at 25 °C for 12 h. It was filtered through Celite and washed twice with CH_2Cl_2 (2 × 10 mL). The combined solution was evaporated under reduced pressure to leave a white solid which was recrystallized from CH_2Cl_2/Et_2O (3 mL/10 mL), washed with hexane (2 × 5 mL), and dried in vacuo to produce a white power: yield 0.65 g (77%); ^{1}H NMR 8.06 (d, $J = 2.0$ Hz, 1H), 7.69 (d, $J = 2.0$ Hz, 2H), 7.29 (d, $J = 1.8$ Hz, 1H), 7.00 (s, 2H), 6.56 (s, 2H), 6.40 (t, $J = 2.2$ Hz, 1H), 5.74 (s, 1H), 2.29 (s, 3H), 2.00 (s, 6H), −0.21 (s, 3H); ^{13}C NMR 170.6, 141.1, 138.1, 134.4, 131.8, 128.5, 123.0, 121.4, 106.3, 62.6, 54.8, 20.5, 16.7, −12.4; IR (KBr pellet) 3500 (s, br), 1637 (s), 1561 (m), 1446 (w), 1354 (s), 1288 (w), 1198 (vs), 1143 (m), 1094 (w), 1058 (s), 984 (vw), 764 (m), 615 (m), 570 (w), 511 (w) cm^{-1}. Anal. Calcd for $C_{17}H_{21}ClN_4Pd\cdot$ (422.05): C, 48.24; H, 5.00; N 13.24. Found: C, 48.04; H, 5.04; N, 13.17. Colorless single crystals of **2** suitable for X-ray diffraction were obtained by slow evaporation in CH_2Cl_2. Compound **2** decomposed before melting.

General Procedure for Heck Reactions in Ionic Liquid. Palladium(II) complex **2** (8.44 mg, 0.02 mmol) was dissolved in [BMIm][PF_6] (3 g), and the solvent was degassed under reduced pressure at 60 °C for 1 h. Aryl halide (1.0 mmol), olefin (1.25 mmol), and base (1.5 mmol) were subsequently added at 25 °C. The resulting mixture was stirred for an appropriate time under nitrogen at 120 °C. The product was extracted from the reaction mixture with ethyl ether (3 × 3 mL). The combined organic layer was concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the desired product. The products were confirmed by comparison with literature spectroscopic data. The IL solutions containing Pd(II) catalyst were washed three times with water (3 × 3 mL) to remove excess of base and its salt, dried under reduced pressure at 60 °C for 4 h to remove traces of ethyl ether and water, and employed for the next cycle.

General Procedure for the Suzuki Reactions in Ionic Liquid. The aryl iodide (1.0 mmol), phenylboronic acid (0.13 g, 1.1 mmol), and Na_2CO_3 (0.21 g, 2.0 mmol) and water (1 mL) were added to the ionic liquid solution of Pd(II) catalyst **2** (8.44 mg, 0.02 mmol). The resulting mixture was stirred for 1 h at 110 °C. The product was extracted from the reaction mixture by addition of ethyl ether (4 × 3 mL). The combined organic layer was concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the desired product. The identity of the products was confirmed by comparison with literature spectroscopic data. The ILs containing the Pd(II) catalyst were recycled as above.

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Supporting Information Available: Experimental procedures and spectroscopic data for new compounds, packing diagram of compound **2**, and X-ray crystallographic data for **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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