A Concept of Supported Amino Acid Ionic Liquids and Their Application in Metal Scavenging and Heterogeneous Catalysis

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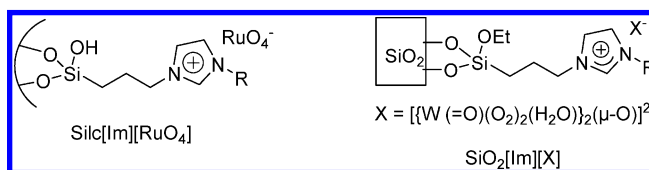
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Abstract: Novel supported task-specific ionic liquids have been developed for the first time via the ionic-pair coupling of imidazolium cation of the modified polystyrene support with L-proline. The materials have shown an efficient metal scavenging ability (e.g., CuI, Pd(OAc)$_2$, Pd^0, and IrCl$_3$) without the aid of a nonimmobilized ionic liquid, which relies on the highly synergistic effect of the coordination with the nitrogen atom and the COO$^-$ group of the L-proline moiety, electrostatic forces, and steric protection. The resulting metal-soaked supported ionic liquids can be used as efficient heterogeneous catalysts. These materials have been investigated in the CuI-catalyzed *N*-arylation of nitrogen-containing heterocycles and exhibit much higher catalytic activity and a more extensive structural range of aryl and heteroaryl halides than those exhibited by free L-proline in combination with CuI both in the ionic liquid ([BMIM][BF$_4$]) and in the corresponding homogeneous reaction conditions. The CuI-soaked catalyst **4a-2** can be recycled for nine runs at least without any considerable loss of activity. To the best of our knowledge, our catalytic process is among the most efficient approaches to the *N*-arylation of imidazoles with aryl halides so far reported. Furthermore, the Pd-soaked material **4a-2** also shows higher catalytic activity in the solvent-free hydrogenation of styrene to ethylbenzene. This new concept is generally applicable and may easily be extended to other supported task-specific ionic liquids.

Introduction

Ionic liquids (ILs) have received great attention in a variety of different areas reaching from material synthesis to separation science as well as alternative reaction media.[1] However, despite promising results, their widespread use in process chemistry is still hampered by the following practical drawbacks: (i) product isolation, (ii) catalyst recovery, and (iii) the use of relatively large amounts of ionic liquids in biphasic systems which is costly and may cause possible toxicological concerns.[2] To overcome these drawbacks, the concept of supported ionic liquid catalysis (SILC) has recently been established to combine the advantages of ionic liquids with those of heterogeneous support materials.[3]

Task-specific ionic liquids (TSILs) can provide a facile and promising route to multifunctional compounds.[4] So far, the majority of these ionic liquids have focused on the derivatization of the cationic component due to their convenient chemical modification. Although ILs containing functional anions are starting to attract interest,[5] there is little information about the

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supported ones, in which the functional anions have been designed for the catalytically active species. Typically, among these outstanding examples reported so far, the anions mainly involve peroxometalates and polyoxometalates (e.g., RuO_4^-, $[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]^{2-}$, and $[PW_{12}O_{40}]^{3-}$, etc.).[6] These materials have been prepared by ionically coupling peroxometalates or polyoxometalates with the imidazolium cations in a simple anion-exchange reaction (e.g., Silc[Im][RuO₄][6a] and SiO₂[Im][X][6b]). More surprisingly, despite the extensive application of organic ligands in catalysis, the supported ionic liquid catalysis attributed to organic anions has received much less attention to date. Natural amino acids, especially for L-proline, have proved to be an outstanding class of ligands in organocatalysis and organometallic catalysis. Quite recently, task-specific ionic liquids with amino acids as anions (e.g., 1-ethyl-3-methylimidazolium amino acids ([Emim][AA]),[7a] tetrabutylphosphonium amino acids ([P(C₄)₄][AA]),[7b] and phosphonium trifluoromethanesulfonyl amino acids ([P4448][Tf-AA])[7c]) have been synthesized from natural amino acids. Herein,

[Emim][AA]

[P(C₄)₄][AA]

[P4448][Tf-AA]
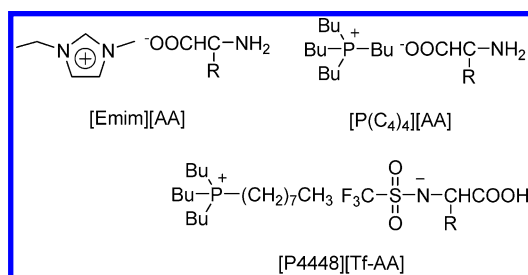
we illustrate a novel concept for the preparation of multifunctional materials by using an IL-modified polystyrene backbone, in which the imidazolium cations deliberately couple amino acids via the ionic-pair interaction, and thus various characteristics of amino acids would easily be delivered into the resulting materials. To the best of our knowledge, amino acids have never been immobilized as the supported task-specific ILs.

Results and Discussion

Generally, it is assumed that ionic liquids are noncoordinating solvents and stable toward many organic and inorganic substances. However, the deprotonation at the C2 position of the imidazolium nucleus can generate *N*-heterocyclic carbenes due to the relatively high acidity ($pK_a = 21-23$) of the H2 hydrogen and may further result in the formation of metal−carbene complexes.[8] Therefore, in this article both 1,2-dimethyl-3-(4-vinylbenzyl)imidazolium chloride (**1a**) and 1-methyl-3-(4-vinylbenzyl)imidazolium chloride (**1b**) have been chosen as the monomers for comparison of the physical and chemical properties of the resulting materials. The synthetic route of imidazolium-modified polymers **4** is illustrated in Scheme 1. The polymer **2a** (PS[DMVBIM][Cl]) was synthesized by the free radical copolymerization of **1a**, styrene, and 1,4-divinylbenzene

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Scheme 1. Preparation of the Polymer-Supported Task-Specific ILs PS[DMVBIM][Pro] (**4a**) and PS[MVBIM][Pro] (**4b**)

4a R = CH₃
4b R = H
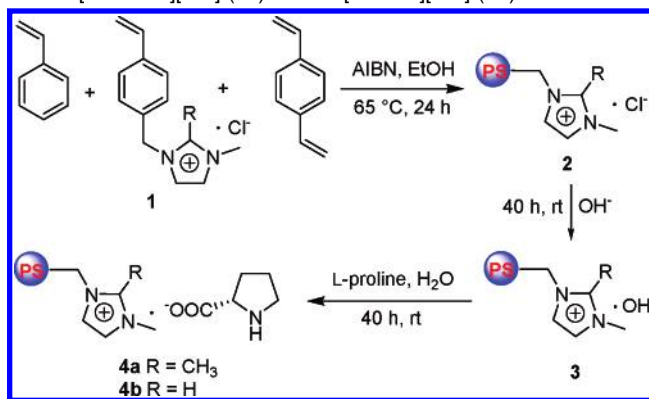
Table 1. Loading Level of the Imidazolium Unit on the Material **2** and the L-Proline Moiety on the Material **4**[a]

| entry	monomer **1** used in the free radical copolymerization (mol %)	loading of the imidazolium unit on the resin **2** (mmol/g)	loading of L-proline on the resin **4** (mmol/g)
1	31.07	1.96	1.55 (**4a-1**)
2	18.56	1.35	0.69 (**4a-2**)
3	5.03	0.32	0.14 (**4a-3**)
4	18.98	1.46	0.44 (**4b**)

[a] The loading amount of the L-proline moiety on the material **4** was calculated from the nitrogen content of **2** and **4**.

(DVB) using azobisisobutyronitrile (AIBN) as an initiator and polyvinylpyrrolidone (PVP) as a dispersant in ethanol at 65 °C for 24 h. Further treatment of **2a** with either aqueous NaOH or KOH for 40 h, followed by neutralization with a large excess of L-proline, afforded the PS[DMVBIM][Pro] (**4a**).[7] The PS-[MVBIM][Pro] (**4b**) was prepared from **1b** according to the same procedure as described above. In sharp contrast, all attempts to prepare the supported TSILs were unsuccessful by attachment of the free L-proline to **2** containing the halide anions. The supported TSILs **4** were analyzed by elemental analysis to quantify the amount of L-proline by measuring the nitrogen content of **2** and **4**. This loading level of L-proline could be adjusted by changing the amount of the monomer **1** in the free radical copolymerization. In this work, four supported TSILs **4a**-1, **4a**-2, **4a**-3, and **4b** with different loading levels of the L-proline unit were prepared as shown in Table 1.

The supported ionic liquid catalysts have been prepared by using two different approaches involving the covalent attachment of ionic liquids to the support surface and the simple physisorption of the catalytically active species.[3a] Among various types of catalysts described so far, a thin film of the free ionic liquid phase is most commonly required to hold the catalytically active species on the surface of the support.[3,9] From a practical and environmental viewpoint, it is highly desirable to develop an interesting variation of the supported ionic liquid catalysis,

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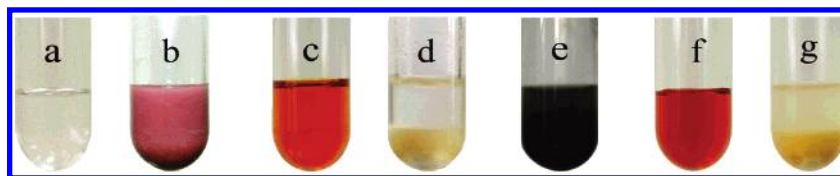
Figure 1. View of scavenging of metal salts: (a) CuI (0.035 mmol) in DMSO; (b) **4a-2**/CuI in DMSO (1:2 molar ratio of CuI/L-proline); (c) Pd(OAc)$_2$ (0.0086 mmol) in DMF; (d) **4a-2**/Pd(OAc)$_2$ in DMF (1:8 molar ratio of Pd(OAc)$_2$/L-proline); (e) the formation of Pd^0 particles after hydrogenation; (f) IrCl$_3$ (0.0086 mmol) in DMF; (g) **4a-2**/IrCl$_3$ in DMF (1:8 molar ratio of IrCl$_3$/L-proline).

Figure 2. Representative SEM and TEM images of the polymers. (a) **4a-2** (SEM); (b) ionic liquid-soaked Pd(OAc)$_2$ on **4a-2** (0.53 mmol/g Pd(OAc)$_2$ loading level) (TEM); and (c) ionic liquid-stabilized Pd nanoparticles on **4a-2** after hydrogenation (TEM).

in which the ionic liquid-modified materials can carry out their catalysis in the absence of a nonimmobilized ionic liquid. In comparison with the former, however, only very few examples have appeared in the literature to date.[6a,b,10] For instance, a polymer-supported ionic liquid prepared via the covalent anchoring of an imidazolium salt to a polystyrene resin (PS-[Hmim][X]) showed much higher activity for nucleophilic substitution reactions including fluorinations.[10a,b] Ru nanoparticles immobilized on montmorillonite-supported ionic liquids demonstrated a highly efficient heterogeneous catalyst for the hydrogenation of benzene.[10c] Recently, Mioskowski et al. reported that polyionic gels (PGELs) were employed as efficient heterogeneous media for metal stabilization and catalysis.[11] Herein, we found that our supported TSILs displayed considerable ability for metal scavenging onto their surface (e.g., CuI, Pd(OAc)$_2$, Pd^0, and IrCl$_3$) without the aid of a nonimmobilized ionic liquid.
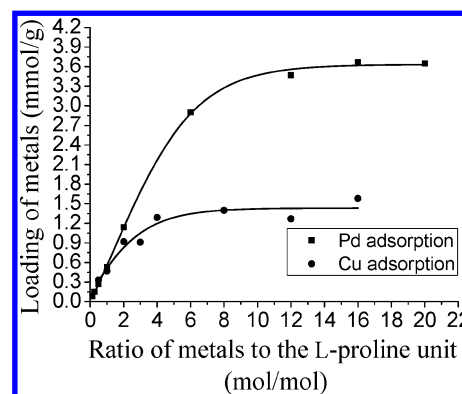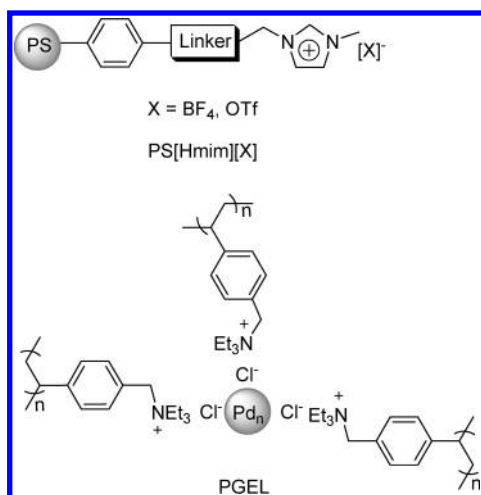
Figure 3. Loadings of CuI and Pd(OAc)$_2$ on **4a-2**.

While a suspension of **4a-2** was stirred in a solution of metal salt at room temperature, an obvious color change was observed, which clearly illustrated the high affinity ability with metal precursors (Figure 1). For example, more than 97% of CuI was soaked on **4a-2** in DMSO, and the loading level of CuI was *ca.* 0.34 mmol/g, which was determined by the ICP-AES analysis as a CuI/L-proline molar ratio was maintained at 1:2 (Figure 1a,b). An SEM image depicts that the surface of **4a-2** is composed of nanoscale beads with *ca.* 60−80 nm in diameter (Figure 2a) and could not be differentiated by sight after soaking CuI. The scavenging ability of **4a-2** for CuI was investigated and shown in Figure 3. The CuI loading level on **4a-2** could be controlled by the molar ratios of CuI used and the L-proline unit during the soaking process. The experimental results on the adsorption of CuI are clearly indicative of Langmuir type adsorption. The adsorption constant and the adsorption capacity are 18.4 dm^3 mol^{-1} and 1.6 mmol/g, respectively.[12]

We next investigated the scavenging ability of **4a-2** for Pd-(OAc)$_2$. Similarly, the experimental results indicate that the adsorption of Pd(OAc)$_2$ corresponds to Langmuir type adsorp-
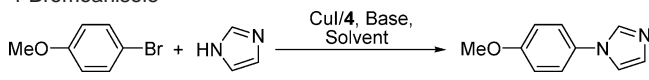
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tion (Figure 3), and the adsorption constant and the adsorption capacity are 19.0 dm^3 mol^{-1} and 3.8 mmol/g, respectively.[12] For instance, the orange supernatant became colorless after **4a-2** was stirred in a solution of Pd(OAc)$_2$ with a metal/L-proline molar ratio of 1:8 in DMF to afford a loading of 0.085 mmol/g, which roughly corresponds to the total absorption of Pd(OAc)$_2$ in solution (Figure 1c,d). The use of a 1:1 molar ratio of Pd-(OAc)$_2$/L-proline resulted in a Pd^{2+} content of *ca.* 0.53 mmol/g. A color change of the Pd-soaked precatalyst from orange to black was observed by hydrogen reduction in water for 30 min, indicating that the formation of Pd^0 particles (Figure 1e). The TEM analysis clearly demonstrated that some Pd nanoparticles are distributed on the outer PS surfaces with the size of the particles ranging *ca.* 2 ± 1 nm (Figure 2b,c).[9e,11,13] It is well-known that metallic particles are kinetically unstable with respect to agglomeration to the bulk metal. To our delight, the resin **4a-2** has considerable ability for stabilizing Pd^0 nanoparticles on its surface, which should stem from the highly synergistic effect of the coordination with the nitrogen atom and the COO$^-$ group of the L-proline moiety, electrostatic forces, and steric protection.[14] Furthermore, we found that **4a-2** also showed the ability for IrCl$_3$ scavenging onto its surface using the straightforward procedure described above (Figure 1f,g). Thus, it is reasonable to assume that other classes of transition metals (e.g., Co, Zn, Rh, Ru, and La, etc.) may also be scavenged using this method and the resulting materials can be used as heterogeneous catalysts.

Recently, the economic attractiveness of copper has led to a resurgence of interest in the Cu-catalyzed *N*-arylation of nitrogen-containing heterocycles with aryl halides in the presence of amino ligands to afford the corresponding *N*-arylazoles, which are ubiquitous in biochemical, biological, and medicinal structure and function.[15] Despite significant progress, however, the coupling with respect to imidazoles is still a long-standing problem, which is far from being satisfactorily solved.[16] The majority of aryl halides investigated to date, already limited in examples, are aryl iodides. There are only a few examples

Table 2. Some Representative Results from the Screening of Reaction Conditions for the *N*-Arylation of Imidazole with 4-Bromoanisole[a]

entry	amount of L-proline salt (mol %)	amount of CuI (mol %)	base	solvent	time (h)	temp (°C)	yield[b] (%)
1	**4a-2** (10)	10	K$_2$CO$_3$	DMF	60	120	41
2	**4a-2** (20)	10	K$_2$CO$_3$	DMF	60	120	68
3	**4a-2** (30)	10	K$_2$CO$_3$	DMF	60	120	66
4	**4a-2** (40)	10	K$_2$CO$_3$	DMF	60	120	59
5	**4a-2** (20)	10	K$_2$CO$_3$	DMSO	60	120	97
6	**4a-2** (20)	10	K$_2$CO$_3$	*n*-BuOH	60	120	53
7	**4a-2** (20)	10	K$_2$CO$_3$	*i*-PrOH	60	80	trace
8	**4a-2** (20)	10	K$_3$PO$_4$	DMSO	60	120	76
9	**4a-2** (20)	10	Cs$_2$CO$_3$	DMSO	60	120	87
10	**4a-2** (10)	5	K$_2$CO$_3$	DMSO	60	120	46
11	**4a-2** (20)	10	K$_2$CO$_3$	DMSO	24	120	38
12	**4a-2** (20)	10	K$_2$CO$_3$	DMSO	48	120	81
13	**4a-1** (20)	10	K$_2$CO$_3$	DMSO	60	120	84
14	**4a-3** (20)	10	K$_2$CO$_3$	DMSO	60	120	53
15	**4b** (20)	10	K$_2$CO$_3$	DMSO	60	120	trace
16	L-proline (20) (in ILs)	10	K$_2$CO$_3$	DMSO	60	120	54[c]

[a] Reaction conditions: 4-bromoanisole (0.6 mmol), imidazole (0.5 mmol), and base (1.2 mmol) in the presence of **4** and CuI in 2.0 mL of solvent under a N$_2$ atmosphere. [b] Isolated yields (average of two runs) based on imidazole. [c] 20 mol % of the free L-proline in 2.0 mL of ionic liquid ([BMIM][BF$_4$]).

describing the coupling of imidazoles with aryl bromides or of functional substrates or of hindered substrates, and in some cases the electron-withdrawing groups and/or higher reaction temperatures even have to be required. Following our continuing interest in the development of the *N*-arylation of imidazoles,[17] we therefore chose to focus initial studies on evaluation of the behavior of **4** doped with CuI as catalyst in the synthesis of *N*-arylimidazoles.

A preliminary survey of reaction conditions was conducted using 4-bromoanisole and imidazole as model arylating agents (Table 2, entries 1−15). As shown in Table 2, the best results were obtained in DMSO at 120 °C for 60 h under N$_2$ using 2.4 equiv of K$_2$CO$_3$ as base in the presence of a catalyst system generated in situ from 10 mol % of CuI and the supported IL **4a-2** containing 20 mol % of L-proline unit (Table 2, entry 5). The **4a-2** doped with CuI could smoothly prompt the cross-coupling reaction, and show much higher catalytic activity than the free L-proline catalyst performed both in the ionic liquid (compare entries 5 and 16 in Table 2)[18] and in the corresponding homogeneous analogue.[19] For instance, the coupling reaction of 4-bromoanisole with imidazole afforded only 22% yield of product in the homogeneous catalytic system.[19] The catalytic performance, however, proved to be significantly influenced by the catalyst composition and could be fine-tuned by adjusting the structure and the L-proline loading of the supported TSILs (Table 2, entries 5, 13−15). Interestingly, the catalyst system that was prepared from **4b** attaching to 1-methyl-3-(4-vinyl-benzyl)imidazolium salt did not display any catalytic activity (Table 2, entry 15), whereas high catalytic activity was observed

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Table 3. Catalytic *N*-Arylation of Imidazole with Aryl Halides by CuI/**4a-2**[a]

entry	Ar–X	product	yield[b] (%)
1	4-bromoanisole	**6a**	97
2	2-bromoanisole	**6b**	90
3	4-bromobenzonitrile	**6c**	95[c]
4	1-(4-bromophenyl)ethanone	**6d**	92[c]
5	ethyl 4-bromobenzoate	**6e**	91[d]
6	4-bromotoluene	**6f**	98
7	2-bromotoluene	**6g**	89
8	1-bromonaphthalene	**6h**	62
9	2-bromophenol	**6i**	74
10	4-bromophenol	**6j**	97
11	4-bromoaniline	**6k**	86
12	3-bromoaniline	**6l**	99
13	1-chloro-4-nitrobenzene	**6m**	97[c]
14	4-chlorobenzonitrile	**6c**	87[e]

[a] Reaction conditions: aryl halide (0.6 mmol), imidazole (0.5 mmol), 1.2 mmol of K₂CO₃ in the presence of 20 mol % of entrapped L-Pro⁻, and 10 mol % of CuI in 2.0 mL of DMSO at 120 °C under a N₂ atmosphere for 60 h. [b] Isolated yields (average of two runs) based on imidazole. [c] 90 °C. [d] 90 °C, 1.5 equiv of aryl halide. [e] 30 h, 1.5 equiv of aryl halide.

for **4a-2** containing 1,2-dimethyl-3-(4-vinylbenzyl)imidazolium. We speculated that the lack of turnover was a consequence of the formation of copper–carbene complexes in the copolymer **4b**.[8]

Next, a series of aryl halides were employed to investigate the scope of the reaction as shown in Table 3. We were delighted to find that the *N*-arylation of imidazole with a broad range of aryl bromides (e.g., electron-rich, electron-deficient, electron-neutral, sterically hindered, and functionalized bromoarenes) could be conducted smoothly to afford the corresponding products in good to excellent yields (Table 3, entries 1–12). Notably, our catalyst system showed very high activity with regard to electron-rich aryl halides although transition-metal-catalyzed reactions involving these electron-rich arylating agents are traditionally less straightforward (Table 3, entries 1–2, 9–12). The reaction of the notoriously recalcitrant-hindered and deactivated 2-bromoanisole even gave an excellent yield of 90%, to the best of our knowledge, demonstrating the best result reported so far.

Substrates that contain certain functional groups have proven to be persistently problematic in the *N*-arylation of imidazoles. First, some functional groups themselves might be decomposed at higher temperatures, for example, the partial hydrolysis of the ester to benzoic acid and of the nitrile to amide.[16d,g] Our catalytic system could tolerate a variety of functional groups such as ester, nitrile, ketone, and nitro (Table 3, entries 3–5, 13–14). Another problematic situation is the competition from the formation of a C(aryl)–N and C(aryl)–O bond when there is a free OH or NH directly bound to the aromatic ring that contains the halide.[15a] Generally, free hydroxyl and primary amine groups should be protected before carrying out the *N*-arylation of imidazoles.[20] It is important to stress that our method could almost exclusively undergo the selective *N*-

arylation to provide the corresponding *N*-arylimidazoles in excellent yields (Table 3, entries 9–12, and Table 4, **6n**), avoiding the formation of diarylethers and diarylamines. This is particularly interesting as nature amino acids have been reported as ligands in the Cu-catalyzed syntheses of aryl ethers and arylamines from aryl halides.[19,21] Hence our protocols have offered new opportunities for the synthesis of highly functionalized azoles.

Preliminary results suggest that the current system could be applied to aryl chlorides to a less extent (Table 3, entries 13–14, and Table 4, **6r**). Further exploration revealed that some heteroaryl halides (Table 4, **6n–6r**) were compatible with these reaction conditions, giving satisfactory yields (60%–99%).[22] Notably, to date the development of chemistry that could emanate from a single method for each of the major classes of nitrogen-containing heterocycles has been seriously inhibited. To our delight, this new catalytic system could also be applied to other π-electron-rich nitrogen heterocycles (Table 4, **6s–6y**).

Compared to the corresponding homogeneous system, which prefers aryl iodides and aryl bromides activated by an electron-withdrawing group,[19,23] our protocol showed higher activity and a more extensive structural range of aryl or heteroaryl halides. It is reasonable to assume that the significantly improved catalytic activity may stem from a highly polyionic polar microenvironment.[24] Such ionic binding of amino acids to the support should offer the advantage of a strong yet reversible interaction with the polymer. Consequently, the spatial array of the polymer-bound amino acids could be expected to modulate more freely to the steric requirement for coordination at the metal center. Furthermore, the polyelectrolyte could prevent leaching of the metal salts and thus ensure the multiple usage of the catalysts.

Further, the supported ionic liquid catalyst was easily separated from the reaction system by simple filtration and could also be stored several months without loss of activity. The **4a-2**/CuI system had shown a remarkable recyclability as the corresponding yields started at 95% and reached 73% after nine runs in the *N*-arylation of imidazole with 4-bromobenzonitrile at 90 °C. The ICP-AES analysis of the supernatant indicated a negligible leaching of CuI from every run. Despite this minimal loss, reduced catalyst activity was observed in consecutive runs, which was likely attributed to the presence of air and the loss of reactants. Further, we investigated the pH sensitivity of the materials. After being soaked in a series of aqueous hydrochloric acid or sodium hydroxide solutions of different pH values for at least 24 h, the **4a-2** in combination with CuI was employed to promote the *N*-arylation of imidazole with 4-bromobenzonitrile at 90 °C. The results indicate that the catalytic performance could remain at a high level in the range of pH values from 6 to 10. Otherwise, the catalytic activity would be decreased slightly. For example, the yields of product were 79% and 81% at the pH values of 0 and 14, respectively.

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Table 4. Catalytic *N*-Arylation of Azoles with Aryl and Heteroaryl Halides by CuI/**4a-2**[a,b]
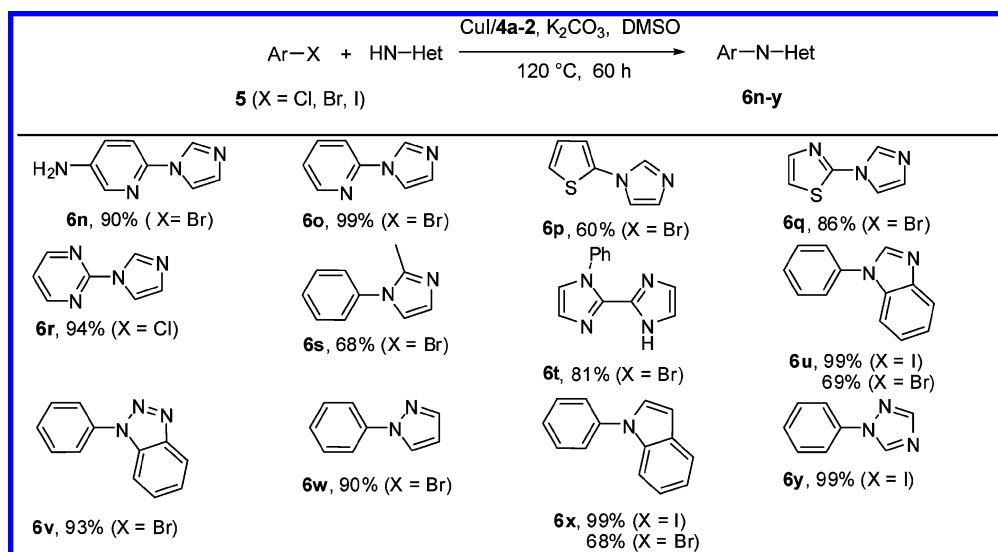
[a] Reaction conditions: see Table 3. [b]Isolated yields (average of two runs) based on azole.

Finally, the Pd-soaked **4a**-**2** with *ca.* 0.53 mmol/g Pd loading was used in the "green" solvent-free hydrogenation of styrene to ethylbenzene (eq 1). As expected, the catalyst showed remarkable activity at room temperature under a constant pressure of H_2 (1 atm), and a TON of 5000 and a turnover frequency (TOF) of 250 h^{-1} were obtained using 0.02 mol % of Pd with >99% of conversion in 20 h. Furthermore, we also
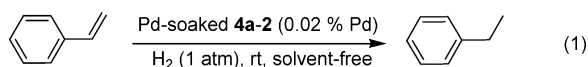
tested the hydrogenation of 1,2-diphenyl-1-propene using the chiral Pd-L-proline IL catalyst, but the racemic product was afforded under our standard conditions although the high TON and TOF were achievable.

Conclusion

In summary, we have developed novel supported task-specific ILs via the ionic-pair coupling of imidazolium cations of the modified polystyrene support with amino acid anions, which display an efficient metal-soaking ability as "metal sponges". The concept of supported ionic liquid catalysis has successfully been used for the first time in the CuI-catalyzed *N*-arylation of nitrogen-containing heterocycles without the aid of additional immobilized ionic liquid, demonstrating that the homogeneous catalyst could be heterogenized with dramatic improvement of the catalyst performance by supporting itself on the ionic liquid-modified polymer. The supported ionic liquid catalyst can be recycled for nine runs at least without any considerable loss of activity. Furthermore, the Pd-soaked material has also shown remarkable activity for the solvent-free hydrogenation of styrene to ethylbenzene. This new concept is generally applicable and may easily be extended to other supported task-specific ILs. Further studies for the preparation of other catalytic systems are currently underway in our laboratory.

Experimental Section

General Remarks. ^{1}H NMR spectra were obtained with a Bruker AV-300 (300 MHz), a Varian Inova-400 (400 MHz), or a Varian Inova-600 (600 MHz) spectrometer, while ^{13}C NMR spectra were recorded with a Bruker AV-300 (75 MHz), a Varian Inova-400 (100 MHz), or a Varian Inova-600 (150 MHz). The ^{1}H chemical shifts were measured relative to tetramethylsilane as the internal reference, while the ^{13}C NMR chemical shifts were recorded with CDCl$_3$ and CD$_3$OD as the internal standard. Elemental analyses were performed with a CARLO ERBA1106 instrument. The low-resolution mass spectra (ESI) were obtained by a Finnigan-LCQ^{DECA} spectrometer, and the GC−MS spectra were recorded with an Agilent 6890-5973 machine. The TEM analysis was performed on a JEM-100CXII transmission electron microscope. The SEM images were acquired with a JSM-5900 LV.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by refluxing for at least 24 h over CaH$_2$ (DMF, DMSO, or CHCl$_3$) and sodium/benzophenone (THF or toluene) and freshly distilled prior to use. CuI should be washed with THF using a Soxhlet extractor before it is used to ensure satisfactory catalytic activity. Unless otherwise indicated, all syntheses and manipulations were carried out under dry N$_2$ atmosphere.

Sample Preparation for TEM Studies. A drop of suspension was placed onto a carbon-coated 300 mesh copper grid. After adsorption, the excess of liquid was removed with a piece of filter paper and the grid was dried under air. Transmission electron microscopy (TEM) observation was performed with a JSM 100CX II microscope operating at 100 kV. The images were taken at a nominal magnification of 270 000 times.

Preparation of the Ionic Liquid Monomer 1a,b[8c] **1,2-Dimethyl-3-(4-vinylbenzyl)imidazolium Chloride (1a), [DMVBIM][Cl].** A mixture of 1,2-dimethyl imidazole (8.30 g, 86.5 mmol) and 4-chloromethyl styrene (17.12 g, 112.2 mmol) was stirred in 50 mL of CHCl$_3$ for 8 h at 50 °C. The resulting white solid was filtered and washed with ethyl acetate to afford the desired product in 95% yield. ^{1}H NMR (400 MHz, D$_2$O): δ 2.55 (s, 3H), 3.77 (s, 3H), 5.31 (s, 2H), 5.34 (d, *J* = 10.8 Hz, 1H), 5.85 (d, *J* = 17.6 Hz, 1H), 6.74−6.81 (m, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.35 (s, 2H), 7.51 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (75 MHz, D$_2$O): δ 9.1, 34.7, 51.2, 115.3, 121.1, 122.4, 126.9, 128.2, 133.3, 135.9, 138.0, 144.6. MS (ESI$^+$) *m/z* 213 [M−Cl] $^+$. Anal. Calcd for C$_{14}$H$_{17}$ClN$_2$: C, 67.60; H, 6.89; N, 11.26. Found: C, 67.44; H, 6.92; N, 11.24.

1-Methyl-3-(4-vinylbenzyl)imidazolium Chloride (1b), [MVBIM]-[Cl]. This compound was prepared from 1-methyl imidazole following the same procedure as that described above (**1a**). Compound **1b** was obtained in 90% yield as a pale yellow semisolid. ^{1}H NMR (400 MHz,

D$_2$O): δ 3.82 (s, 3H), 5.28 (s, 2H), 5.30 (d, J = 11.2 Hz, 1H), 5.79 (d, J = 18 Hz, 1H), 6.66–6.73 (m, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 0.8 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H) 8.72 (s, 1H). ^{13}C NMR (75 MHz, D$_2$O): δ 35.8, 52.5, 115.4, 122.2, 123.9, 126.9, 129.0, 133.1, 135.8, 138.2. MS (ESI$^+$) m/z 199 [M–Cl] $^+$. Anal. Calcd for C$_{13}$H$_{15}$-ClN$_2$: C, 66.52; H, 6.44; N, 11.93. Found: C, 66.38; H, 6.46; N, 11.90.

General Procedure for the Polymerization. A mixture of **1**, styrene, 1,4-divinylbenzene (DVB), azobisisobutyronitrile (AIBN), and poly-vinylpyrrolidone (PVP) as a dispersant was stirred in ethanol for 24 h at 65 °C under a nitrogen atmosphere. The resulting resin was filtered and washed with distilled water, ethanol, and dichloromethane. The resulting white polymer was dried in *vacuo* for 24 h and then was analyzed by elemental analysis to quantify the amount of imidazolium groups by measuring the nitrogen content. This loading level could be adjusted by changing the amount of ionic liquid monomer **1**. In this work, four polymers with different loadings of the imidazolium group were used as shown in Table 1.

Poly[1,2-dimethylimidazoliummethyl styrene chloride]-*co*-PS Resin (PS[DMVBIM][Cl], 2a-1). The ionic liquid monomer **1a** (9.9 g, 39.8 mmol), styrene (6.3 g, 60.6 mmol), divinylbenzene (3.6 g, 27.7 mmol), PVP (1.1 g), and AIBN (173 mg, 1.1 mmol) were used in EtOH (88 mL). Elemental analysis (%): C, 78.02; H, 7.43; N, 5.48. The loading of the imidazolium on the resin: 1.96 mmol/g.

Poly[1,2-dimethylimidazoliummethyl styrene chloride]-*co*-PS Resin (PS[DMVBIM][Cl], 2a-2). The ionic liquid monomer **1a** (9.9 g, 39.8 mmol), stryene (12.4 g, 119.2 mmol), divinylbenzene (7.2 g, 55.4 mmol), PVP (1.6 g), and AIBN (265 mg, 1.6 mmol) were used in EtOH (135 mL). Elemental analysis (%): C, 80.81; H, 7.53; N, 3.79. The loading of the imidazolium on the resin: 1.35 mmol/g.

Poly[1,2-dimethylimidazoliummethyl styrene chloride]-*co*-PS Resin (PS[DMVBIM][Cl], 2a-3). The ionic liquid monomer **1a** (9.9 g, 39.8 mmol), stryene (53.6 g, 515.4 mmol), divinylbenzene (30.6 g, 235.4 mmol), PVP (6.7 g), and AIBN (1.12 g, 6.8 mmol) were used in EtOH (572 mL). Elemental analysis (%): C, 89.49; H, 7.39; N, 0.89. The loading of the imidazolium on the resin: 0.32 mmol/g.

Poly[1-methylimidazoliummethyl styrene chloride]-*co*-PS Resin (PS[MVBIM][Cl], 2b). The ionic liquid monomer **1b** (9.6 g, 40.9 mmol), stryene (12.4 g, 119.2 mmol), divinylbenzene (7.2 g, 55.4 mmol), PVP (1.6 g), and AIBN (265 mg, 1.6 mmol) were used in EtOH (135 mL). Elemental analysis (%): C, 81.97; H, 7.17; N, 4.10. The loading of the imidazolium on the resin: 1.46 mmol/g.

General Procedure for the Preparation of 4a,b. The polymer **2** (10.0 g) was stirred in aqueous NaOH (1 M, 100 equiv based on the imidazolium group) for 40 h at room temperature. The resulting polymer **3** was separated and washed with distilled water, followed by a stirring in an aqueous solution of L-proline (1 M, 100 equiv based on the imidazolium group) for 40 h at room temperature. The solid was separated and washed with distilled water and then dried in *vacuo* for 24 h. The polymer was analyzed by an elemental analyzer to quantify the amount of the L-proline unit by measuring the nitrogen content **2** and **4** as shown in Table 1.

Poly[1,2-dimethylimidazoliummethyl styrene L-proline salt]-*co*-PS Resin (PS[DMVBIM][Pro], 4a-1). A pale yellow solid. Elemental analysis of **4a-1** (%): C, 75.08; H, 7.64; N, 6.98. The loading of L-proline on the resin: 1.55 mmol/g.

Poly[1,2-dimethylimidazoliummethyl styrene L-proline salt]-*co*-PS Resin (PS[DMVBIM][Pro], 4a-2). A pale yellow solid. Elemental analysis of **4a-2** (%): C, 79.00; H, 7.66; N, 4.55. The loading of L-proline on the resin: 0.69 mmol/g.

Poly[1,2-dimethylimidazoliummethyl styrene L-proline salt]-*co*-PS Resin (PS[DMVBIM][Pro], 4a-3). A pale yellow solid. Elemental analysis of **4a-3** (%): C, 88.38; H, 7.98; N, 1.08. The loading of L-proline on the resin: 0.14 mmol/g.

Poly[1-methylimidazoliummethyl styrene L-proline salt]-*co*-PS Resin (PS[MVBIM][Pro], 4b). A pale yellow solid. Elemental analysis

of **4b** (%): C, 80.50; H, 7.60; N, 4.57. The loading of l-proline on the resin: 0.44 mmol/g.

Metal Salt Scavenging Experiment. CuI scavenging. A mixture of **4a-2** (100 mg, 0.069 mmol of the L-proline unit), CuI (6.6 mg, 0.035 mmol, 0.5 equiv), and DMSO (2 mL) was stirred overnight under N$_2$ at room temperature, and an obvious color change of the resin from pale yellow to red was observed. The ICP-AES analysis of the supernatant indicated that the content of copper was 32.81 ppm, demonstrating more than 97% of CuI was soaked on the resin **4a-2** and the loading level of CuI was *ca.* 0.34 mmol/g. Other CuI-soaked **4a-2** materials with different CuI loadings were prepared according to the same procedure, and their CuI loading levels are shown in Figure 3.

Pd(OAc)$_2$ Scavenging. A mixture of **4a-2** (100 mg, 0.069 mmol of the L-proline unit), Pd(OAc)$_2$ (1.9 mg, 0.0086 mmol, 0.125 equiv), and DMF (1 mL) was stirred overnight at room temperature, and the supernatant became colorless. The ICP-AES analysis of the supernatant showed that the content of Pd^{2+} was 3.22 ppm, demonstrating more than 99% of Pd(OAc)$_2$ was soaked on the resin **4a-2**, and the loading level of Pd(OAc)$_2$ was *ca.* 0.085 mmol/g. Other Pd(OAc)$_2$-soaked **4a-2** materials with different Pd loadings were prepared according to the same procedure, and their Pd(OAc)$_2$ loading levels are shown in Figure 3.

IrCl$_3$ Scavenging. A mixture of **4a-2** (100 mg, 0.069 mmol of the L-proline unit), IrCl$_3$ (2.6 mg, 0.0086 mmol, 0.125 equiv), and DMF (1 mL) was stirred overnight at room temperature, and the supernatant became colorless. The ICP-AES analysis of the supernatant showed that the content of Ir^{3+} was 16.3 ppm, demonstrating more than 99% of IrCl$_3$was soaked on the resin **4a-2**, and the loading level of IrCl$_3$ was *ca.* 0.085 mmol/g.

General Procedure for the Catalytic *N*-Arylation of Nitrogen-Containing Heterocycles with Aryl and Heteroaryl Halides. A flame-dried Schlenk test tube with a magnetic stirring bar was charged with CuI (9.5 mg, 0.05 mmol), **4a-2** (145 mg, 0.1 mmol of the L-proline unit), K$_2$CO$_3$ (165 mg, 1.2 mmol), nitrogen-containing heterocycle (0.5 mmol), aryl or heteroaryl halide (0.6 mmol), and DMSO (2 mL) under N$_2$. A rubber septum was replaced with a glass stopper, and the system was then evacuated three times and backfilled with N$_2$. The reaction mixture was stirred for 30 min at room temperature and then heated at 120 °C for 60 h. The resulting mixture was cooled to ambient temperature, diluted with 2–3 mL of ethyl acetate, filtered through a plug of silica gel, and washed with 10–20 mL of ethyl acetate. The filtrate was concentrated, and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

Recycling Experiments. These experiments were performed according to the representative procedure described above. The organic solvent was filtrated after every run, and the resulting residue was extracted with degassed ethyl acetate, washed with degassed water, and then dried in *vacuo*. The recycled catalyst was used directly for the next cycle after the addition of 2.4 equiv of K$_2$CO$_3$.

General Procedure for Solvent-Free Hydrogenation of Styrene. A mixture of **4a-2** (100 mg, 0.069 mmol of the L-proline unit), Pd-(OAc)$_2$ (15.5 mg, 0.069 mmol), and DMF (8 mL) was stirred overnight at room temperature. The ICP-AES analysis of the supernatant showed that the content of Pd^{2+} was 218.43 ppm, demonstrating the loading level of Pd(OAc)$_2$ was *ca.* 0.53 mmol/g. The resulting solid was separated and washed with DMF, followed by hydrogenation in 4 mL of water under H$_2$ (1 atm) overnight at room temperature. The resulting black solid was filtrated and washed with water and dried in *vacuo*. A Schlenk test tube with a magnetic stirring bar was then charged with the black solid (2.2 mg, 0.0012 mmol of Pd) and styrene (0.641 g, 6.2 mmol). The mixture was stirred for 20 h under H$_2$ (1 atm) at room temperature to afford the hydrogenated product (GC analysis: >99% yield).

Supporting Information Available: Detailed experimental procedures for the syntheses of *N*-arylazoles, characterizational NMR spectral data (^{1}H and ^{13}C) of *N*-arylazoles **6a**−**6y**; copies of ^{1}H and ^{13}C NMR spectra for compounds **1a,b** and **6a**−**y**. This material is available free of charge via the Internet at http://pubs.acs.org.

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