ACS Catalysis
Research Article
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Immobilized Palladium Metal-Containing Ionic Liquid-Catalyzed Alkoxycarbonylation, Phenoxycarbonylation, and Aminocarbonylation Reactions

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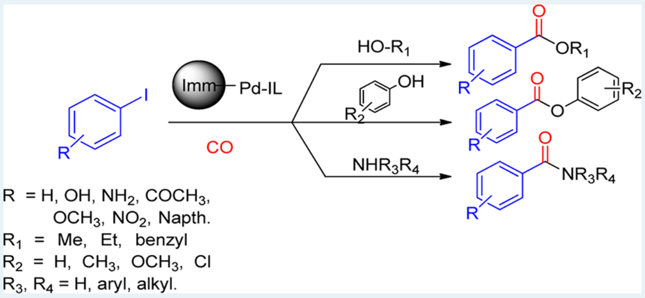
S *Supporting Information*

ABSTRACT: Immobilized palladium metal-containing ionic liquid (ImmPd-IL), a structurally well-defined transition metal complex, is explored as an immobilized, phosphine-free catalyst for carbonylation reactions, including alkoxycarbonylation, phenoxycarbonylation, and aminocarbonylation reactions. The effect of various reaction parameters, such as solvent, base, time, temperature, and CO pressure on carbonylation reactions using ImmPd-IL catalyst was investigated. The optimized protocol was applied to a wide variety of substituted aryl iodides and various alcohol/phenols and amines having different steric and electronic properties and afforded the corresponding products in good to excellent yield. The developed catalytic system circumvents the use of phosphine ligands, with an additional advantage of palladium catalyst recovery and reuse for up to four consecutive cycles. The recycled catalyst was characterized using XPS analysis.



KEYWORDS: *alkoxycarbonylation reaction, aminocarbonylation reaction, immobilization, phenoxycarbonylation reaction, palladium*

1. INTRODUCTION

Carbon monoxide (CO) is a useful C_1 building block for the synthesis of various organic molecules because of its ability to introduce a carbonyl group into the parent molecule. The CO molecule inserts into the aryl palladium bond to form an acyl palladium complex, which then reacts with various nucleophiles to give aryl carbonyl compounds. Transition metal-catalyzed carbonylation of aryl halides in the presence of an appropriate nucleophile represents a valuable tool for the selective introduction of the carbonyl moiety into aromatic derivatives.[1] Carbonylation of aryl halides with alcohols, phenols, or amines catalyzed by palladium complexes is a convergent and direct route for the synthesis of aromatic esters and amides.[2]

Aromatic esters are important building blocks for various pharmaceuticals and agrochemicals, whereas phenyl esters are widely used in liquid crystals,[3] photosensitizers,[4] and biologically active compounds.[5] Traditionally, these esters were synthesized via reaction of the carboxylic acid with alcohols or phenols.[6] Carbonylation of the aryl halides in the presence of an alcohol/phenol is an attractive alternative method that tolerates a wide range of substrates, thus demonstrating a great advantage for the synthesis of substituted aromatic esters and its derivatives.[7−9] In this regard, various palladium-based catalytic systems, such as $Pd(OAc)_2$,[10] $PdCl_2(PhCN)_2$ with ferrocenyl phosphine ligand,[11] and $Pd(OAc)_2/PPh_3$ in the presence of an ionic liquid,[12] have been explored for alkoxycarbonylation and phenoxycarbonylation reactions.

Aminocarbonylation is a constructive method for the direct synthesis of aromatic amides via coupling of aryl, heteroaryl, or alkynyl halides with primary/secondary amines. Aromatic amides are an important functional group of various natural products and designed pharmaceutical molecules. Some heterocyclic amides are potential CNS (central nervous system)-active compounds.[13] A variety of palladium-based homogeneous catalytic systems, such as $PdBr_2(PPh_3)_2/PdCl_2(PPh_3)_2$,[14] $Pd(dppp)Cl_2$,[15] palladium-1,3-bis (dicyclohexylphosphino) propane-H_2BF_4,[16] and $Pd(OAc)_2$/xantphos catalytic system,[17] were used for this reaction. Aminocarbonylation using an ionic liquid and $Pd(OAc)_2/PPh_3$[18] was explored by Kollar and co-workers.

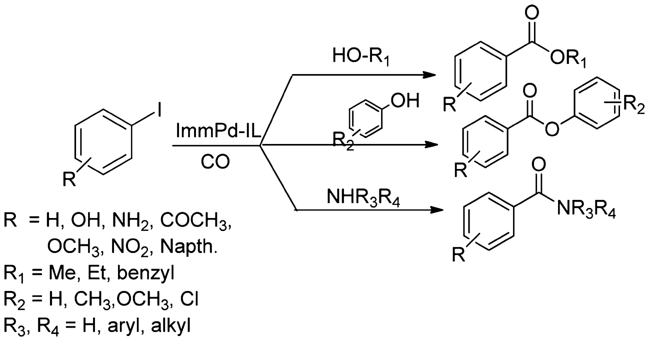
Literature reports reveal that alkoxycarbonylation, phenoxycarbonylation, and aminocarbonylation have been well explored by using a variety of homogeneous Pd complexes using various air- and moisture-sensitive N/P-containing ligands. Moreover, with these homogeneous catalytic processes, the recovery and recycling of the palladium catalyst is a challenging task.[10−12] Hence, immobilized palladium catalysts

Received: November 8, 2012
Revised: January 2, 2013
Published: January 14, 2013

are expected to solve this problem. Considering this, immobilization strategies for a metal complex wherein the metal is coordinated to a ligand grafted onto an inorganic or organic support has been developed.[19,20] Ionic liquids containing metal ions are considered catalytic precursors, and they can be immobilized on a solid support, thus facilitating the reuse of the catalyst and showing promise for use in organic transformations.[21] In this regard, an immobilized palladium metal-containing ionic liquid [ImmPd-IL] was prepared and characterized by various spectroscopic techniques, including EXAFS, UV−vis, TGA, IR, and elemental analysis.[22−24]

Inspired by all the attractive preliminary results of ImmPd-IL and in continuation of our ongoing research for the development of an efficient, phosphine-free, and recyclable protocol for carbonylation reaction,[25−28] herein we have explored the ImmPd-IL catalyst for different carbonylation reactions (Scheme 1).

Scheme 1. ImmPd-IL-Catalyzed Carbonylation Reactions



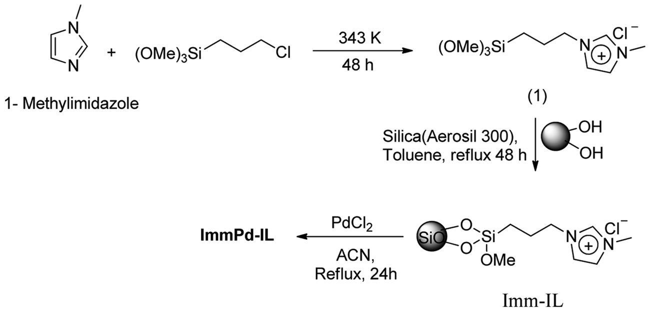
2. EXPERIMENTAL SECTION

2.1. Materials and Method. *N*-Methylimidazole (99+%) and 3-trimethoxysilylpropyl chloride (97+%) were purchased from Aldrich. $PdCl_2$ was purchased from WAKO. Anhydrous redistilled 1-methylimidazole (99+%) was purchased from Aldrich. All the dehydrated solvents were obtained from WAKO. Aerosil 300 (300 m^2/g) was obtained from Japan Aerosil Co. and calcined at 573 K for 1.5 h in air and 30 min in vacuum before use as a support. The procedures for catalyst preparation were based on our previous publication[22] with some modifications. Prepared catalyst was characterized by using IR and elemental analysis, and loading of the catalyst was calculated by XRF measurements (SEA-2010, Seiko Electronic Industrial Co.). The XPS of ImmPd-IL was measured using a PHI5000 Versa Probe with monochromatic focused (100 × 100 μm) Al Kα X-ray radiation (15 kV, 30 mA) and dual beam neutralization using a combination of argon ion gun and electron irradiation.

The products are well-known in the literature[30−37] and were compared with authentic samples. Progress of the reaction was monitored by gas chromatography (GC). The product was purified by column chromatography on silica gel (100−200 mesh). Gas chromatography analysis was carried out on Perkin-Elmer Clarus 400 GC equipped flame ionization detector with a capillary column (Elite-1, 30 m × 0.32 mm × 0.25 μm). A GC/MS-QP 2010 instrument (Rtx-17, 30 m × 25 mm i.d., film thickness 0.25 μm df) (column flow 2 mL min^{-1}, 80−240 °C at 10°/min rise.). The ^1H NMR spectra were recorded on Varian-300/400 MHz FT-NMR spectrometer in $CDCl_3$ using TMS as the internal standard. The ^{13}C NMR spectra were recorded with a JEOL FT-NMR, model-AL300 (75/100 MHz) spectrometer in $CDCl_3$. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as the internal standard. *J* (coupling constant) values were reported in hertz. Proton splitting patterns are described as s (singlet), d (doublet), t (triplet), and m (multiplet).

2.2. Preparation of ImmPd-IL. Immobilized metal ion-containing ionic liquid catalyst was prepared as shown in Scheme 2. 1-Methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride was synthesized by mixing *N*-methylimidazole (0.690 mol) and 3-trimethoxysilylpropyl chloride (0.690 mol) in a dry 300 mL flask under a nitrogen atmosphere and refluxing for 48 h. After cooling to room temperature, the resultant liquid was washed using dehydrated ethyl acetate five times and dried at room temperature under reduced pressure for 48 h. The obtained compound was stored at 253 K under dry nitrogen. Silica (Aerosil 300; surface area 300 m^2/g, calcined at 573 K for 1.5 h in air) and 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride (weight ratio 1:1) was dispersed in dehydrated toluene, and the mixture was refluxed for 48 h under nitrogen. After the reflux, toluene was removed by filtration using a glass filter, and the excess ionic liquid was removed by washing with dichloromethane several times. The resultant solid is denoted as Imm-IL.

Scheme 2. Preparation of Palladium Metal-Ion-Containing Immobilized Ionic Liquid



In the next step, Imm-IL was added to an acetonitrile solution of $PdCl_2$ and refluxed for 24 h. Acetonitrile and an excess of metal chloride were removed by washing with acetone using a glass filter several times. The metal loading of ImmPd-IL was 3.4 wt % as determined by XRF measurements (SEA-2010, Seiko Electronic Industrial Co.).

2.3. General Experimental Procedure for Alkoxycarbonylation Reaction. To a 100 mL autoclave, aryl iodide (1 mmol), alcohol (5 mL), ImmPd-IL (2 mol %), and Et_3N (3 mmol) were added. The autoclave was closed, purged three times with carbon monoxide, pressurized with 0.5 MPa of CO, and heated at 80 °C for 3 h. After the completion of the reaction, the reactor was cooled to room temperature, and the remaining CO gas was carefully vented, and the reactor was opened. The reactor vessel was thoroughly washed with ethyl acetate (2 × 10 mL) to remove any traces of product and catalyst if present. The catalyst was filtered, and the reaction mixture was evaporated under vacuum. The residue obtained was purified by column chromatography (silica gel, 100−200 mesh; petroleum ether/ethyl acetate, 95:05) to afford the desired product.

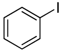
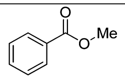
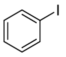
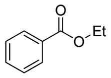
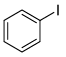
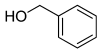
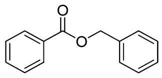
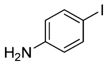
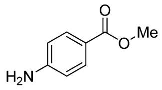
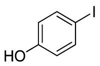
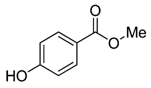
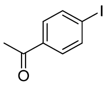
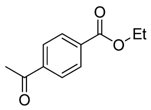
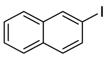
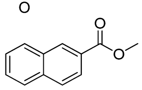
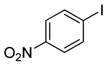
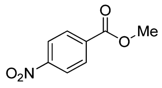
2.4. General Experimental Procedure for Recycling of ImmPd-IL. After completion of the reaction, the reaction mixture was cooled to room temperature, and the catalyst was collected by filtration. The filtered catalyst was washed with distilled water (3 × 5 mL) and methanol (3 × 5 mL) to remove all traces of product or reactant present. The filtered catalyst was then dried under reduced pressure. The dried catalyst was then used for the alkoxycarbonylation reaction of iodobenzene with methanol for the recyclability experiment.

2.5. General Experimental Procedure for Phenoxy Carbonylation Reaction. To a 100 mL autoclave, aryl iodide (1 mmol), phenol (2 mmol), ImmPd-IL (2 mol %), toluene (10 mL), and Et_3N (3 mmol) were added. The autoclave was closed, purged three times with carbon monoxide, pressurized with 1 MPa of CO, and heated at 100 °C for 8 h. After the completion of the reaction, the reactor was cooled to room temperature, and the remaining CO gas was carefully vented and the reactor was opened. The reactor vessel was thoroughly washed with ethyl acetate (2 × 10 mL) to remove any traces of product and catalyst if present. The catalyst was filtered, and the reaction mixture was evaporated under vacuum. The residue obtained was purified by column chromatography (silica gel, 100–200 mesh; petroleum ether/ethyl acetate, 95:05) to afford the desired product.

2.6. General Experimental Procedure for Aminocarbonylation Reaction. To a 100 mL autoclave, aryl iodide (1 mmol), amine (2 mmol), ImmPd-IL (2 mol %), toluene (10 mL), and Et_3N (3 mmol) were added. The autoclave was closed, purged three times with carbon monoxide, pressurized with 1 MPa of CO, and heated at 100 °C for 8 h (the ensuing procedure is the same as that discussed above for the phenoxy carbonylation reaction).

2.7. Spectral Data of the Products. *Benzyl Benzoate (Table 1, entry 3).*[30] ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 8.04–8.08 (m, 2H, ArH), 7.31–7.52 (m, 8H, ArH), 5.3 (s, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 166.48, 136.19, 133.12, 130.25, 129.81, 128.70, 128.48, 128.34, 128.27, 66.77 ppm. GC/MS (EI, 70 eV): m/z (%) = 212 [M^+] (30), 105 (100), 91(40), 77 (35), 51 (10).

Table 1. ImmPd-IL-Catalyzed Alkoxycarbonylation of Aryl Iodides with Various Alcohols[a]

Entry	Aryl iodide	Alcohol	Product	Yield (%)[b]
1		MeOH		94
2		EtOH		95
3				89
4		MeOH		80
5		MeOH		75
6		EtOH		81
7		MeOH		79
8		MeOH		70

[a]Reaction conditions: aryl iodide (1 mmol), alcohol (5 mL), ImmPd-IL (2 mol %), Et_3N (3 mmol), 0.5 MPa CO pressure, temp (80 °C), time (3 h). [b]Isolated yield.

Methyl 4-Aminobenzoate (Table 1, entry 4).[31] ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 7.83 (d, 2H, J = 8.7 Hz, ArH), 6.61 (d, 2H, J = 8.7 Hz, ArH), 4.14 (br, s, 2H, NH_2), 3.83 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 167.24, 151.07, 131.51, 119.27, 113.68, 51.55 ppm. GC/MS (EI, 70 eV): m/z (%) = 151 [M^+] (40), 120 (100), 91 (55), 65 (19), 39 (15).

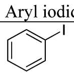
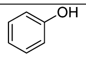
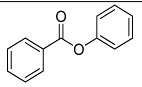
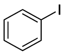
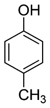
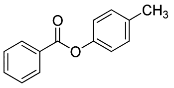
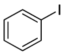
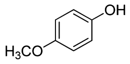
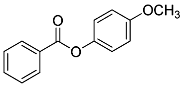
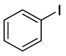
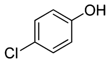
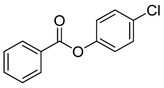
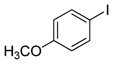
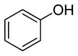
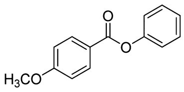
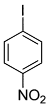
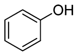
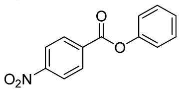
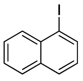
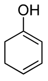
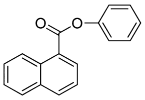
Methyl 4-Hydroxybenzoate (Table 1, entry 5).[32] ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 7.94 (d, 2H, J = 8.7 Hz, ArH), 7.22 (br, s, 1H, OH), 6.90 (d, 2H, J = 8.7 Hz, ArH), 3.90 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 167.78, 160.55, 132.03, 122.01, 115.39, 52.23 ppm. GC/MS (EI, 70 eV): m/z (%) = 152 [M^+] (40), 121 (100), 93 (55), 73 (10), 65 (19), 53 (15).

Ethyl 4-Acetylbenzoate (Table 1, entry 6).[33] ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 8.14–8.11 (m, 2H, ArH), 8.02–7.99 (m, 2H, ArH), 4.41 (q, 2H, J = 6.9 Hz, CH_2CH_3), 2.65 (s, 3H, $COCH_3$), 1.42 (t, 3H, J = 6.9 Hz, CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 197.66, 165.76, 140.12, 134.24, 129.77, 128.17, 61.47, 26.89, 14.27 ppm.

Methyl 2-Naphthoate (Table 1, entry 7).[34] ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 8.50 (s, 1H, ArH), 7.98–8.05 (m, 2H, ArH), 7.73 (t, 2H, J = 8.4 Hz, ArH), 7.54–7.61 (m, 2H, ArH), 3.96 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 166.85, 136.34, 130.87, 130.82, 130.13, 129.38, 129.01, 127.78, 127.20, 126.32, 122.60, 52.35 ppm. GC/MS (EI, 70 eV): m/z (%) = 186 [M^+] (65), 155 (100), 127 (75).

Phenyl Benzoate (Table 2, entry 1).[35] ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 8.25–8.22 (m, 2H, ArH), 7.68–8.63

Table 2. ImmPd-IL-catalyzed Phenoxycarbonylation of Aryl Iodides with Various Phenols[a]

Entry	Aryl iodide	Phenol	Product	Yield (%)[b]
1				89
2				90
3				88
4				84
5				86
6				59
7				75

[a]Reaction conditions: aryl iodide (1 mmol), phenol (2 mmol), ImmPd-IL (2 mol %), Et_3N (3 mmol), toluene (10 mL), 1 MPa CO pressure, temp (100 °C), time (8 h). [b]Isolated yield.

(m, 1H, ArH), 7.56–7.42 (m, 4H, ArH), 7.32–7.23 (m, 3H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 165.25, 151.03, 133.65, 130.23, 129.64, 129.56, 128.64, 125.96, 121.79 ppm. GC/MS (EI, 70 eV): m/z (%) = 198 [M^+] (9), 105 (100), 77 (40), 51 (9).

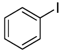
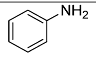
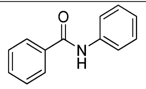
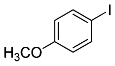
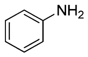
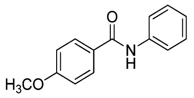
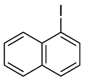
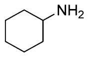
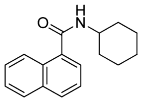
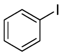
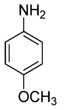
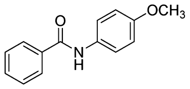
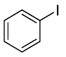
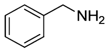
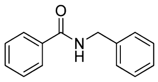
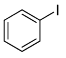
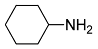
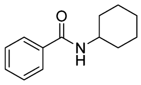
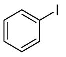
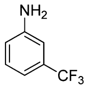
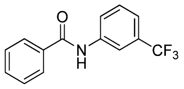
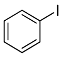
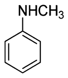
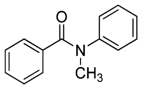
Phenyl 4-Methoxybenzoate (Table 2, entry 5).[36] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.14–8.16 (d, 2H, J = 8.7 Hz, ArH), 7.20–7.41 (m, 5H, ArH), 6.96–6.98 (d, 2H, J = 8.7 Hz, ArH), 3.86 (s, 3H, OCH_3). GC/MS (EI, 70 eV): m/z (%) = 228 [M^+] (5), 135 (100), 107 (9), 77 (20).

Phenyl 4-Nitrobenzoate (Table 2, entry 6).[35] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.37 (s, 4H, ArH), 7.23–7.48 (m, 5H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 163.47, 151.10, 150.72, 135.17, 131.44, 129.84, 126.57, 123.88, 121.57 ppm. GC/MS (EI, 70 eV): m/z (%) = 243 [M^+] (15), 150 (100), 77 (10).

Phenyl 1-Naphthoate (Table 2, entry 7).[36] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.04 (d, 1H, ArH), 8.45 (d,1H, ArH), 8.04 (d, 1H, ArH), 7.88 (d, 1H, ArH), 7.42–7.63 (m, 5H, ArH), 7.26–7.28 (m, 3H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 165.94, 151.18, 134.40, 134.08, 131.82, 131.34, 129.68, 128.83, 128.50, 128.29, 126.50, 126.05, 125.90, 124.65, 122.03 ppm. GC/MS (EI, 70 eV): m/z (%) = 248 [M^+] (10), 155 (100), 127 (60).

N-Phenylbenzamide (Table 3, entry 1).[37] ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 7.98 (br, s, 1H, NH), 7.87–8.83 (m, 2H, ArH), 7.63 (d, 2H, J = 7.6 Hz, ArH), 7.32–7.53 (m, 5H, ArH), 7.16 (t, 1H, J = 7.3, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 165.90, 137.98, 135.02, 131.86, 129.11, 128.80, 127.09, 124.61, 120.32 ppm. GC/MS (EI, 70 eV): m/z (%) = 197 [M^+] (42), 105 (100), 77 (54), 51 (14).

Table 3. ImmPd-IL-Catalyzed Aminocarbonylation of Aryl Iodides with Various Aliphatic and Aromatic Primary Amines and Secondary Amine[a]

Entry	Aryl iodide	Amine	Product	Yield (%)[b]
1				90
2				85
3				80
4				88
5				90
6				92
7				75
8				91

[a]Reaction conditions: aryl iodide (1 mmol), amine (2 mmol), ImmPd-IL (2 mol %), Et_3N (3 mmol), toluene (10 mL), 1 MPa CO pressure, temp (100 °C), time (8 h). [b]Isolated yield.

N-Benzylbenzamide (Table 3, entry 5).[37] ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 7.99–7.76 (d, 2H, J = 7.3 Hz, ArH), 7.40–7.29 (m, 8H, ArH), 6.70 (br, s, 1H, NH), 4.59 (d, 2H, J = 5.7 Hz, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 167.48, 138.30, 134.41, 131.57, 128.79, 128.60, 127.91, 127.59, 127.06, 44.11 ppm. GC/MS (EI, 70 eV): m/z (%) = 211 [M^+] (11), 210 (68), 209 (30), 105 (100), 91 (11), 77 (69), 51 (12).

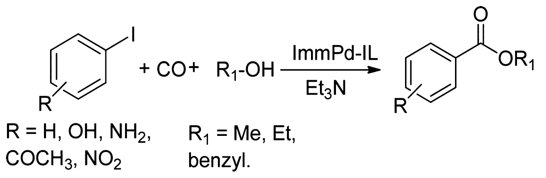
N-Cyclohexylbenzamide (Table 3, entry 6).[37] ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 7.77–7.74 (m, 2H, ArH), 7.36–7.46 (m, 3H, ArH), 6.18 (br, s, 1H, NH), 3.97–3.94 (m, 1H, CH), 2.03–1.98 (m, 2H, CH_2), 1.77–1.61 (m, 3H, CH_2), 1.43–1.15 (m, 5H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 166.69, 135.11, 131.22, 128.49, 126.91, 48.73, 33.21, 25.58, 24.98 ppm. GC/MS (EI, 70 eV): m/z (%) = 203 [M^+] (29), 122 (75), 105 (100), 79 (15), 77 (52).

3. RESULTS AND DISCUSSION

Considering the objective of the development of an efficient, phosphine-free, heterogeneous, and recyclable protocol, ImmPd-IL was developed as a common catalyst for alkoxycarbonylation, phenoxycarbonylation, and aminocarbonylation reactions, and the obtained results using this catalyst are discussed here.

3.1. Immobilized Pd-IL-Catalyzed Alkoxycarbonylation Reaction. To get the maximum yield of the desired product, we studied the effect of various reaction parameters, such as the base, temperature, time, and CO pressure, on the alkoxycarbonylation of iodobenzen and methanol as a model system using ImmPd-IL as a catalyst (Scheme 3).

Scheme 3. ImmPd-IL-Catalyzed Alkoxycarbonylation Reaction



Initially, the reaction was carried out with various inorganic bases, such as K_2CO_3 (80%) and Cs_2CO_3 (79%), and organic bases, such as DBU (85%) and Et_3N (96%). Because Et_3N provides the maximum yield of the corresponding product, it was used for further study. No profound increase in the yield of the desired product was observed when the reaction temperature was increased from 80 to 100 °C; therefore, 80 °C was considered as an optimum reaction temperature for further studies. The reaction was carried out at 0.5 MPa of CO pressure, providing an excellent yield of the desired product within 3 h. Hence, the finalized reaction conditions were the following: base, Et_3N; temperature, 80 °C; solvent, alcohol (also as a nucleophile); time, 3 h; and 0.5 MPa of CO pressure. These reaction parameters were then successfully applied for carbonylation of a variety of aryl iodides with different alcohols (Table 1, entries 1–8). Iodobenzene reacts efficiently with methyl alcohol, ethyl alcohol, and benzyl alcohol to give the corresponding products in good to excellent yields (Table 1, entries 1–3). The substituted iodobenzene derivatives, 4-iodoaniline and 4-iodophenol, furnish 80% and 75% yield of corresponding product, respectively (Table 1, entries 4–5). 4-

Acetyliodobenzene reacts with ethanol to give 81% yield of ethyl-4-acetylbenzoate (Table 1, entry 6). Iodonaphthalene provides 79% yield of the desired product (Table 1, entry 7), whereas 1-iodo-4-nitrobenzene furnishes a moderate yield (70%) of the corresponding carbonylated product (Table 1, entry 8).

It is believed that the supported palladium leaches out from the solid support into the solvent at higher temperature and the reaction was catalyzed mainly by dissolved palladium species.[29] Hence, to determine whether the catalysis was due to the ImmPd-IL complex or a leached homogeneous palladium complex that comes off the support at higher temperature during the reaction, we performed a hot filtration test.[38,39] Alkoxycarbonylation of iodobenzene with benzyl alcohol was carried out at 80 °C using ImmPd-IL catalyst, then after 1.5 h, the ImmPd-IL complex catalyst was filtered off and was allowed to react further. We found that no further reaction occurred after this hot filtration procedure; hence, this experimental finding suggests there is no palladium leaching from the ImmPd-IL complex during the progress of a reaction. In addition, to reconfirm this observation, ICP-AES analysis of the reaction mixture was carried out after 1.5 and 3 h, which revealed a below detectable level (below 0.01 ppm) of palladium in solution.

3.2. Recycle Study. It is also important to study the separation and recyclability of the catalyst. The catalyst can be separated from the reaction mixture by a simple filtration procedure, and ImmPd-IL was found to be effective up to four consecutive recycles for methoxycarbonylation reaction (Figure 1).

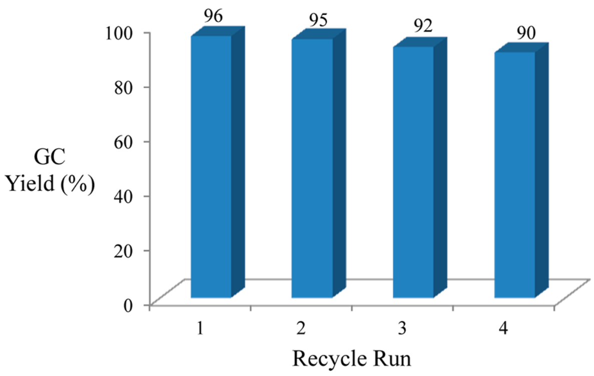


Figure 1. Recyclability study of ImmPd-IL complex catalyst.

3.3. XPS Analysis of the Catalyst. The XPS spectra of ImmPd-IL show that two peaks at 337 and 342.4 eV for fresh Imm-Pd are assigned as $3d_{5/2}$ and $3d_{3/2}$ for Pd^{2+} species, respectively (Figure 2). For the first recycle sample, new peaks appear at 334.2 and 339.2 eV, which are assigned as $3d_{5/2}$ and $3d_{3/2}$ for Pd^0 species, respectively, indicating that the reduction of tye Pd species takes place during the catalytic reaction. From the spectrum of the fourth recycle sample, it is obvious that the component of Pd^{2+} is decreasing upon recycles, although the component of Pd^0 remains constant.

3.4. Immobilized Pd-IL Catalyzed Phenoxycarbonylation Reaction. The ImmPd-IL catalyst was also tested for the phenoxycarbonylation reaction (Scheme 4). Initially, the reaction of iodobenzene with phenol was studied as a model reaction using ImmPd-IL catalyst.

The influence of various reaction parameters, such as solvent, base, temperature, CO pressure, and time, were examined on the model reaction. The role of various solvents, such as toluene (yield 90%), *N*,*N*-dimethyl formamide (DMF) (56%), 1,4-dioxane (62%), and water (0%), was studied. It was observed that the reaction was more favorable when using toluene as a solvent. Screening of a variety of bases (K_2CO_3, Cs_2CO_3, DBU, and Et_3N) showed Et_3N (90%) to be superior at 100 °C. The initial reaction was carried out at 1 MPa, at which point the CO pressure provides 90% yield of desired product; a further decrease in CO pressure up to 0.5 MPa decreased the yield of the product (80%). The optimized reaction parameters (Et_3N base in toluene, CO 1 MPa at 100 °C for 8 h) were then applied for the phenoxycarbonylation of aryl halides and phenols having different electron-donating or withdrawing groups (Table 2, entries 1−7).

Iodobenzene reacts efficiently with phenol within 8 h, providing 89% yield of phenyl benzoate (Table 2, entry1). Substituted phenols such as *p*-cresol, *p*-methoxyphenol, and *p*-chlorophenol, react with iodobenzene to provide good to excellent yields of the corresponding product (Table 2, entries 2−4). The substituted iodobenzene derivative reacts with phenol to provide 86% yields of the corresponding product (Table 2, entry 5). 1-Iodo-4-nitrobenzene furnishes moderate yield (59%) of the corresponding carbonylated product (Table 1, entry 6). Reaction of 1-iodonaphthalene with phenol gave a 75% yield of the expected product (Table 2, entry 7).

3.5. Immobilized Pd-IL Catalyzed Aminocarbonylation Reaction. The scope of ImmPd-IL was further extended for aminocarbonylation of aryl iodides with a range of aliphatic, aromatic, primary, and secondary amines (Scheme 5).

The reaction of iodobenzene with aniline was selected as a model reaction for optimization. Various solvents, such as DMF (80%), water (70%), anisole (60%), and toluene (92%), were screened for the reaction, but toluene was found to be the best solvent. Further reaction was optimized with respect to various reaction parameters, including temperature, time, and CO pressure, and the best optimized reaction conditions were then applied for the aminocarbonylation of a variety of iodoaryls and amines (Table 3, entries 1−8). Various substituted aryl halides and aromatic amines were well tolerated to give the desired amides in good to excellent yields. The model reaction of iodobenzene with aniline provides a 90% yield of the desired product under optimized reaction conditions (Table 3, entry 1), whereas iodo aryl derivatives, such as 4-iodoanisole and 2-iodonaphthalene, furnish 85% and 80% yield of the corresponding amide, respectively (Table 3, entries 2−3). 4-Methoxyaniline reacts with iodobenzene, providing 88% yield of the desired product (Table 3, entry 4). Furthermore, aliphatic amines, such as benzyl amine and cyclohexyl amine, provide good to excellent yields of the corresponding product (Table 3, entries 5−6). 3-(Trifluoromethyl)aniline provides a moderate yield of the desired product (Table 3, entry 7). An aromatic secondary amine, such as *N*-methyl aniline, reacts with iodobenzene to furnish a 91% yield of the desired product (Table 3, entry 8).

4. CONCLUSION

In conclusion, the present study reports an efficient and common protocol for alkoxycarbonylation, phenoxycarbonylation, and aminocarbonylation reactions by using a well-defined heterogeneous ImmPd-IL complex as a versatile catalyst. The reaction system was optimized with respect to various reaction

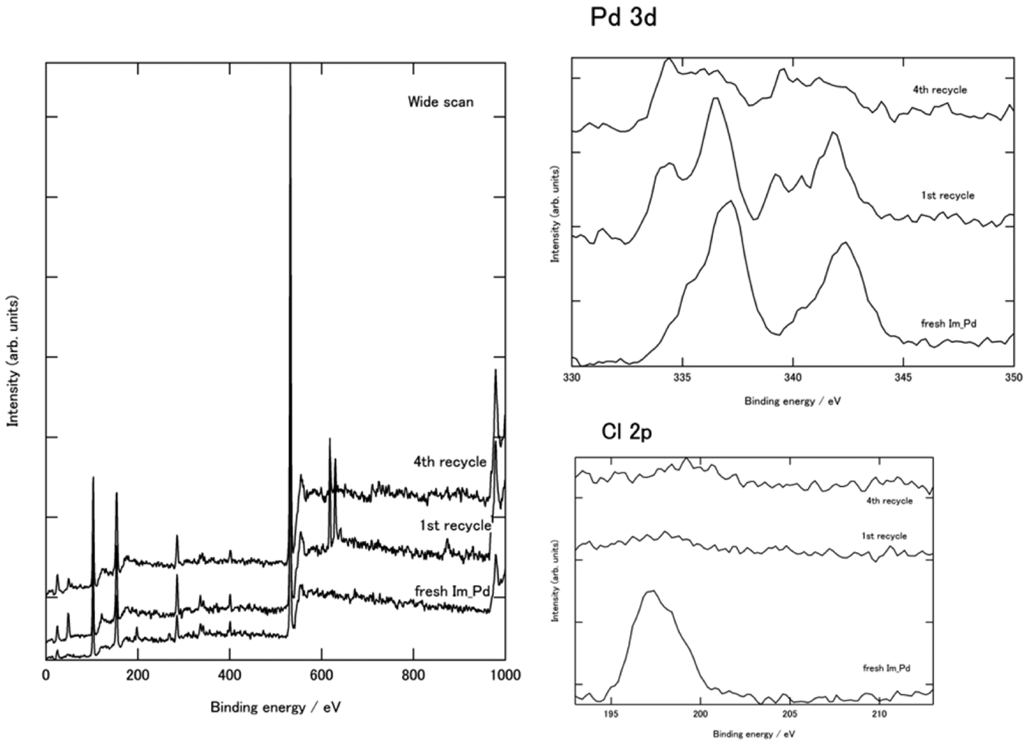
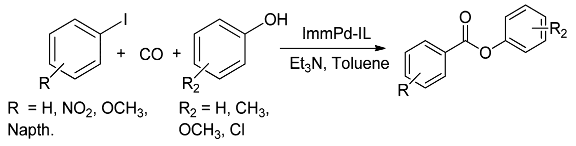
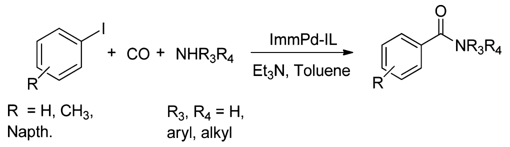


Figure 2. XPS of Pd 3d and Cl 2p for ImmPd-IL catalyst.

Scheme 4. ImmPd-IL-Catalyzed Phenoxycarbonylation Reaction



Scheme 5. ImmPd-IL-Catalyzed Aminocarbonylation Reaction



parameters and applied for carbonylation of a range of aryl iodides with different types of alcohols, phenols, and amines furnishing good to excellent yields of the corresponding products. Furthermore, the catalytic system was also recycled up to four consecutive recycles. Thus, we believe that the present protocol will be a useful contribution in the utilization of CO for synthesis of valuable chemicals from inexpensive feedstock with the use of a heterogeneous recyclable catalyst.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectral data of the products, references for the known products and copies of NMR. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The author M. V. Khedkar is greatly thankful to the University Grant Commission (UGC) India, for providing a Senior Research Fellowship (SRF). XPS measurements were conducted in the Research Hub for Advanced Nano Characterization, the University of Tokyo, supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. T.S. acknowledges the Special Coordination Funds for Promoting Science and Technology "Development of Sustainable Catalytic Reaction System using Carbon dioxide and Water" from MEXT, Japan.

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