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Heck Arylation of Conjugated Alkenes with Aryl Bromides or Chlorides Catalyzed by Immobilization of Palladium in MCM-41

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Abstract A new 3-(2-aminoethylamino)propyl-functionalized MCM-41-immobilized palladium(II) complex [MCM-41-2N-$PdCl_2$] was conveniently synthesized from commercially available and cheap 3-(2-aminoethylamino) propyltrimethoxysilane via immobilization on MCM-41, followed by reacting with palladium chloride. It was found that this heterogeneous palladium complex is a highly efficient catalyst for Heck arylation of conjugated alkenes with aryl bromides or chlorides using tetrabutylammonium bromide as additive and can be reused for at least six consecutive trials without any decreases in activity.

Keywords Supported palladium catalyst · Bidentate nitrogen palladium complex · Functionalized MCM-41 · Heck arylation · Heterogeneous catalysis

1 Introduction

The palladium-catalyzed reaction of aryl and alkenyl halides with alkenes (the Heck reaction) represents one of the most versatile tools in modern synthetic chemistry and has great potential for industrial applications [1–4]. The Heck reaction is generally catalyzed by soluble palladium complexes such as $Pd(OAc)_2$ and $PdCl_2$ with phosphine ligands. However, industrial applications of homogeneous palladium complexes remain a challenge because they are expensive, cannot be recycled, and difficult to separate from the product mixture, which is a particularly significant drawback for their application in the pharmaceutical industry. The immobilization of catalytically active species, i.e. organometallic complexes, onto a solid support to produce a molecular heterogeneous catalyst is one potential solution to the latter two problems [5].

The high costs of the transition metal catalysts coupled with toxic effects associated with many transition metals has led to an increased interest in immobilizing catalysts onto a support. Heterogeneous catalysis also helps to minimize wastes derived from reaction workup, contributing to the development of green chemical processes [6, 7]. Although a number of heterogeneous palladium catalysts were reported to be effective for Heck reaction [8–11], very few catalysts were shown to have good catalytic activity for Heck arylation of alkenes with unactivated bromoarenes [12–14] and chloroarenes [15]. Among these reported heterogeneous palladium catalysts, most of them are the supported phosphine palladium complexes which suffer from severe disadvantages that have so far precluded their practical applications. It is known that catalysts containing phosphine ligands are unstable at high temperatures [16–18]. Furthermore, the procedure for preparing the polymer-supported phosphine palladium complexes is rather complicated since the non-crosslinked poly(chloromethylstyrene) is not commercially available and the chloromethylation requires the use of carcino-genic chloromethyl methyl ether. Therefore, the development of phosphine-free heterogeneous palladium catalysts having a high activity and stability is a topic of enormous importance.

Recent developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilization of homogeneous catalysts [19–21].

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MCM-41 has a regular pore diameter of ca.5 nm and a specific surface area >700 m^2/g [22]. Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach to the surface of the channel [23–25]. In addition, the regular pore size of MCM-41 can provide shape selectivity not provided by silica gel. To date, some palladium complexes on functionalized MCM-41 support have been prepared and successfully used in Heck reactions [26–29], however, they exhibited poor catalytic activity for unactivated bromoarenes as the substrates and no activity for chloroarenes. In continuing our efforts to develop greener synthetic pathways for organic transformations, our new approach, described in this paper, was to design and synthesize a novel 3-(2-aminoethylamino)propyl-functionalized MCM-41-immobilized palladium(II) complex, which was used as an effective, phosphine-free and recyclable palladium catalyst for the Heck arylation of conjugated alkenes with aryl bromides or chlorides.

2 Experimental

All chemicals were reagent grade and used as purchased. The mesoporous material MCM-41 was prepared according to a literature procedure [30]. All reactions were performed under an inert atmosphere of dry argon using distilled dried solvents. All arylation products were characterized by comparison of their spectra and physical data with authentic samples. IR spectra were determined on a Perkin-Elmer 683 instrument. ^1H NMR (400 MHz) spectra were recorded on a Bruker Avance 400 MHz spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ as solvent. Palladium content was determined with inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA Corporation). X-ray photoelectron spectra were recorded on XSAM 800 (Kratos). X-ray powder diffraction patterns were obtained on Damx-rA (Rigaka).

2.1 Preparation of MCM-41-2N

A solution of 1.54 g of 3-(2-aminoethylamino)propyltrimethoxysilane in 18 mL of dry chloroform was added to a suspension of 2.2 g of the MCM-41 in 180 mL of dry toluene. The mixture was stirred for 24 h at 100 °C. Then the solid was filtered and washed by $CHCl_3$ (2 × 20 mL), and dried in vacuum at 160 °C for 5 h. The dried white solid was then soaked in a solution of 3.1 g of Me_3SiCl in 100 mL of dry toluene at room temperature under stirring for 24 h. Then the solid was filtered, washed with acetone (3 × 20 mL) and diethyl ether (3 × 20 mL), and dried in vacuum at 120 °C for 5 h to obtain 3.49 g of hybrid material MCM-41-2N. The nitrogen content was found to be 1.84 mmol/g by elemental analysis.

2.2 Preparation of MCM-41-2N-$PdCl_2$

In a small Schlenk tube, 3.3 g of the above-functionalized MCM-41 (MCM-41-2N) was mixed with 0.226 g (1.27 mmol) of $PdCl_2$ in 50 mL of dry acetone. The mixture was refluxed for 72 h under an argon atmosphere. The solid product was filtered by suction, washed with acetone, distilled water and acetone successively and dried at 70 °C/26.7 Pa under Ar for 5 h to give 3.47 g of a yellow palladium complex [MCM-41-2N-$PdCl_2$]. The nitrogen and palladium content was found to be 1.63 and 0.33 mmol/g, respectively.

2.3 General Procedure for the Arylation of Styrene with Aryl Bromides or Chlorides

A mixture of aryl halide (2.0 mmol), styrene (3.0 mmol), Bu_3N (3.0 mmol), TBAB (1.2 g), and the MCM-41-2N-$PdCl_2$ complex (18 mg, 0.006 mmol of Pd) was stirred under Ar in an oil bath at 110–135 °C for 6–36 h. The mixture was cooled, extracted with Et_2O (3 × 20 mL). The ammonium salt and the palladium catalyst were reused in the next run. The combined ether solution was washed with 5N HCl (2 × 10 mL), brine (3 × 10 mL), and dried over $MgSO_4$ and concentrated under a reduced pressure. The crude product was recrystallized from EtOH.

2.4 General Procedure for the Arylation of Butyl Acrylate with Aryl Bromides or Chlorides

A mixture of aryl halide (2.0 mmol), butyl acrylate (3.0 mmol), Bu_3N (3.0 mmol), TBAB (1.2 g), and the MCM-41-2N-$PdCl_2$ complex (18 mg, 0.006 mmol of Pd) was stirred under Ar in an oil bath at 120–140 °C for 5–48 h. The mixture was cooled, extracted with Et_2O (3 × 20 mL). The ammonium salt and the palladium catalyst were reused in the next run. The combined ether solution was washed with 5N HCl (2 × 10 mL), brine (3 × 10 mL), and dried over $MgSO_4$ and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 19/1).

2.5 General Procedure for the Arylation of Acrylamide with Aryl Bromides or Chlorides

A mixture of aryl halide (2.0 mmol), acrylamide (3.0 mmol), Bu_3N (3.0 mmol), TBAB (1.2 g), and the MCM-41-2N-$PdCl_2$ complex (18 mg, 0.006 mmol of Pd) was stirred under Ar in an oil bath at 120–140 °C for 10–48 h. The mixture was cooled, extracted with hot EtOH

(3 × 20 mL). The ammonium salt and the palladium catalyst were reused in the next run. The combined extract was poured into water (50 mL), the precipitated product was isolated by suction and washed with water (3 × 10 mL). The crude product was recrystallized from EtOH.

3 Results and Discussion

A new 3-(2-aminoethylamino)propyl-functionalized MCM-41-immobilized palladium complex [MCM-41-2N-$PdCl_2$] was very conveniently synthesized from commercially available and inexpensive 3-(2-aminoethylamino) propyltrimethoxysilane via immobilization on MCM-41, followed by reacting with palladium chloride (Scheme 1). The X-ray powder diffraction (XRD) analysis of the MCM-41-2N-$PdCl_2$ indicated that, in addition to an intense diffraction peak (100), two higher order peaks (110) and (200) with lower intensities were also detected, and therefore the chemical bonding procedure did not diminish the structural ordering of the MCM-41. Elemental analyses and X-ray photoelectron spectroscopy (XPS) were used to characterize the 3-(2-aminoethylamino)propyl-functionalized MCM-41-immobilized palladium(II) complex. The N : Pd mole ratio of the MCM-41-2N-$PdCl_2$ was determined to be 4.94. The XPS data for MCM-41-2N-$PdCl_2$, MCM-41-2N, $PdCl_2$ and metal Pd are listed in Table 1. It can be seen that the binding energies of Si_{2p} and O_{1s} of MCM-41-2N-$PdCl_2$ are similar to those of MCM-41-2N and the binding energy of Cl_{2p} of MCM-41-2N-$PdCl_2$ is similar to that of $PdCl_2$. However the difference of N_{1s} binding energies between MCM-41-2N-$PdCl_2$ and MCM-41-2N is 0.9 eV. The binding energy of $Pd_{3d5/2}$ in MCM-41-2N-$PdCl_2$ is 0.7 eV less than that in $PdCl_2$, but 2.2 eV larger than that in metal Pd. These results show that a coordination bond between N and Pd is formed.

The arylation reaction of styrene with bromobenzene was chosen as a model reaction, and the influences of various reaction parameters such as solvent, base, additive, reaction temperature, and palladium catalyst quantity on the reaction were tested. The results are summarized in Table 2. The arylation reactions of styrene with bromobenzene in solvents such as *p*-xylene, DMF and NMP afforded (*E*)-stilbene in low yields (entries 1–3). However, in the presence of tetrabutylammonium bromide (TBAB), the arylation reactions proceeded effectively to give (*E*)-stilbene in moderate to good yields (entries 4–6). Jeffery and Calo [31, 32] also reported that the catalytic activity of homogeneous palladium catalysts could be enhanced in the presence of TBAB in the Heck reactions. We were pleased to find that the reaction proceeded very smoothly in the absence of organic solvent using TBAB (1.2 g) as the additive to afford (*E*)-stilbene in excellent yield (entry 7). For the temperatures tested [100, 110, and 130 °C], 110 °C gave the best result. We then turned our attention to investigate the effect of bases on the arylation reaction. For the bases evaluated [Bu_3N, DBU, NaOAc, Na_2CO_3, and Cs_2CO_3], Bu_3N was found to be the most effective. Other bases such as DBU, NaOAc, Na_2CO_3 and Cs_2CO_3 were substantially less effective. The amount of supported palladium catalyst was also screened, and 0.3 mol% loading of palladium was found to be optimal (entry 14), a lower yield was observed and a longer reaction time was required when the amount of the catalyst was decreased (entries 15 and 16). Thus, the optimized reaction conditions for this arylation reaction are the MCM-41-2N-$PdCl_2$ (0.3 mol%) with TBAB as additive and Bu_3N as base at 110 °C under Ar for 8 h (entry 14).

Table 1 XPS data for MCM-41-2N-$PdCl_2$, MCM-41-2N, $PdCl_2$ and metal Pd

Sample	$Pd_{3d5/2}$	N_{1s}	Si_{2p}	O_{1s}	Cl_{2p}
MCM-41-2N-$PdCl_2$	337.4	400.5	103.4	533.1	199.1
MCM-41-2N		399.6	103.2	533.1	
$PdCl_2$	338.1				199.2
Metal Pd	335.2				

The binding energies are referenced to C_{1s} (284.6 eV) and the energy differences were determined with an accuracy of ±0.2 eV

Scheme 1 Preparation of the MCM-41-2N-$PdCl_2$ complex

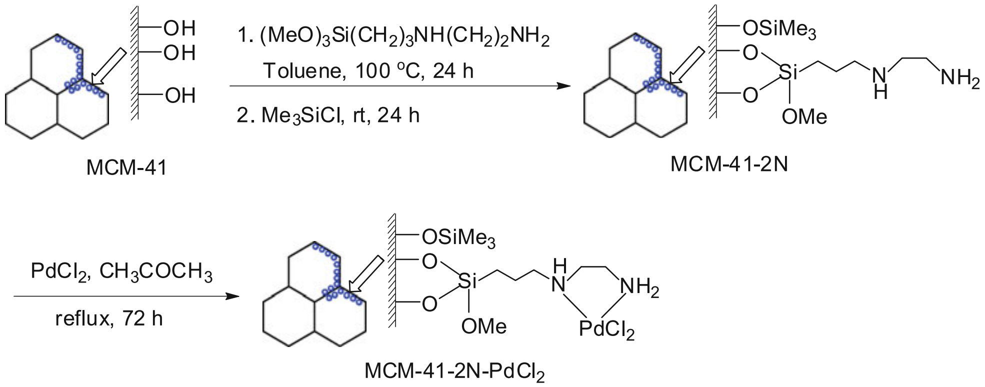

Table 2 Reaction condition screening for the arylation reaction of styrene with bromobenzene

Entry	Solvent	Base	Additive (g)	Pd catalyst (mol%)	Temp. (°C)	Time (h)	Yield (%)[a]
1	*p*-Xylene	Bu_3N	None	0.6	130	24	25
2	DMF	Bu_3N	None	0.6	130	24	36
3	NMP	Bu_3N	None	0.6	130	24	39
4	*p*-Xylene	Bu_3N	TBAB (0.6)	0.6	130	24	64
5	DMF	Bu_3N	TBAB (0.6)	0.6	130	24	73
6	NMP	Bu_3N	TBAB (0.6)	0.6	130	24	82
7	None	Bu_3N	TBAB (1.2)	0.6	130	2	92
8	None	Bu_3N	TBAB (1.2)	0.6	110	3	96
9	None	Bu_3N	TBAB (1.2)	0.6	100	24	68
10	None	DBU	TBAB (1.2)	0.6	110	24	79
11	None	NaOAc	TBAB (1.2)	0.6	110	24	60
12	None	Na_2CO_3	TBAB (1.2)	0.6	110	24	51
13	None	Cs_2CO_3	TBAB (1.2)	0.6	110	24	57
14	None	Bu_3N	TBAB (1.2)	0.3	110	8	96
15	None	Bu_3N	TBAB (1.2)	0.2	110	16	90
16	None	Bu_3N	TBAB (1.2)	0.1	110	30	79

All reactions were performed using 2.0 mmol of PhBr, 3.0 mmol of styrene, 3.0 mmol of base in 1.0 mL of solvent under Ar

[a] Isolated yield

To examine the scope for this heterogeneous Heck arylation reaction, we have investigated the reaction of conjugated alkenes with a variety of aryl bromides or chlorides under the optimized reaction conditions (Scheme 2) and the results are outlined in Table 3. As shown in Table 3, the Heck arylation reactions of styrene with a variety of aryl bromides proceeded smoothly using TBAB as additive and Bu_3N as base at 110 °C to afford the corresponding (*E*)-stilbenes in excellent yields (entries 1–7). The *trans*-selectivity was always near quantitative and no *cis*-product was observed. The reactivity of aryl bromides with electron-withdrawing groups was higher than that of aryl bromides with electron-donating groups, but the reaction of 4-bromoanisole having strong electron-donating group could also give (*E*)-4-methoxystilbene in 92 % yield (entry 7). The results above prompted us to investigate the arylation reactions of aryl chlorides with styrene. It is well known that aryl chlorides are not reactive in Heck arylation reactions of olefins unless a special and expensive ligand is present. However, with our catalytic system, the reactions of aryl chlorides having either electron-withdrawing or electron-donating groups also proceeded effectively at 130–135 °C to afford the corresponding (*E*)-stilbenes in good yields on longer reaction times (entries 8–11).

This catalytic system was also applied to the arylation reactions of other conjugated alkenes such as butyl acrylate and acrylamide with a variety of aryl bromides or chlorides, the results are also summarized in Table 3. The Heck arylation of butyl acrylate with various aryl bromides proceeded smoothly at 120 °C to give the corresponding butyl (*E*)-cinnamates in good to excellent yields (entries 12–15). Both electron-withdrawing and electron-donating substituents on aryl bromides were well tolerated. The reactivity of aryl chlorides was obviously lower than that of aryl bromides. The reactions of aryl chlorides having electron-withdrawing groups at 140 °C could afford moderate yields of desired coupled products (entries 16 and 17), but the reaction of aryl chloride with electron-donating group was very slow and only trace of desired product was formed (entry 18). For the arylation of acrylamide, the results similar to those with butyl acrylate were observed. The reactions of acrylamide with a variety of aryl bromides could also proceed smoothly at 120 °C to afford the corresponding (*E*)-cinnamamides in good to excellent yields (entries 19–23). The reactions of only aryl chlorides with strong electron-withdrawing substituents such as 4-nitro or 4-trifluoromethyl groups could take place at 140 °C to give the desired coupled products in moderate yields on longer reaction times (entries 24 and 25). The high catalytic activity of our system may be attributed to the combination of MCM-41-supported bidentate nitrogen palladium complex with TBAB as an efficient additive. It is generally believed that high surface area of heterogeneous catalyst results in high catalytic activity. Considering the fact that MCM-41 support has an extremely high surface area and the catalytic palladium species is anchored on the inner surface of the mesopore of MCM-41 support, we expect that MCM-41-supported bidentate nitrogen palladium catalyst will exhibit high activity and good reusability. It was observed by Herrmann et al. [33], Reetz et al. [34] and

Scheme 2 Heterogeneous arylation of conjugated alkenes with aryl bromides or chlorides

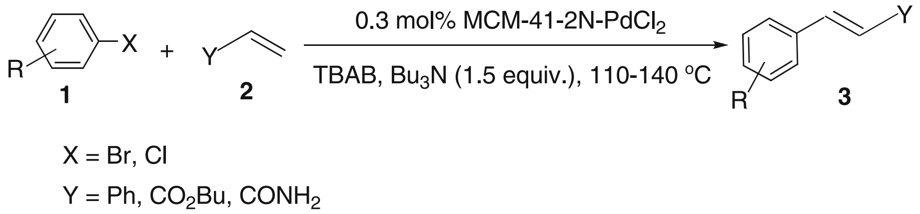

Table 3 Arylation of conjugated alkenes with aryl bromides or chlorides catalyzed by MCM-41-2N-PdCl$_2$

Entry	R	X	Y	Temp. (°C)	Time (h)	Product	Yield (%)[a]
1	H	Br	Ph	110	8	**3a**	96
2	4-CHO	Br	Ph	110	6	**3b**	98
3	3-NO$_2$	Br	Ph	110	6	**3c**	98
4	4-Cl	Br	Ph	110	6	**3d**	97
5	4-CN	Br	Ph	110	6	**3e**	98
6	4-Me	Br	Ph	110	16	**3f**	95
7	4-MeO	Br	Ph	110	24	**3g**	92
8	H	Cl	Ph	130	30	**3a**	78
9	4-CHO	Cl	Ph	135	24	**3b**	81
10	4-NO$_2$	Cl	Ph	135	20	**3h**	84
11	4-Me	Cl	Ph	135	36	**3f**	73
12	H	Br	CO$_2$Bu	120	8	**3i**	87
13	4-Cl	Br	CO$_2$Bu	120	6	**3j**	91
14	4-MeO	Br	CO$_2$Bu	120	24	**3k**	84
15	4-NO$_2$	Br	CO$_2$Bu	120	5	**3l**	95
16	4-CHO	Cl	CO$_2$Bu	140	48	**3m**	51
17	4-NO$_2$	Cl	CO$_2$Bu	140	40	**3l**	59
18	4-Me	Cl	CO$_2$Bu	140	48	**3n**	Trace
19	H	Br	CONH$_2$	120	12	**3o**	85
20	3-NO$_2$	Br	CONH$_2$	120	10	**3p**	90
21	4-Cl	Br	CONH$_2$	120	10	**3q**	92
22	4-Me	Br	CONH$_2$	120	24	**3r**	83
23	4-MeO	Br	CONH$_2$	120	30	**3s**	81
24	4-NO$_2$	Cl	CONH$_2$	140	48	**3t**	64
25	4-F$_3$C	Cl	CONH$_2$	140	48	**3u**	61

All reactions were performed using 2.0 mmol of aryl halide, 3.0 mmol of alkene, 3.0 mmol of Bu$_3$N, 0.006 mmol of MCM-41-2N-PdCl$_2$, 1.2 g of TBAB as additive under Ar

[a] Isolated yield

Buchwald et al. [35] that in the Heck reaction, the addition of tetraalkylammonium salts to conventional solvents led to higher catalytic activities. The ammonium salts effects are multiple. A possible explanation for TBAB acting as such a good additive is that the bulkiness of tetrahedral n-Bu$_4$N$^+$, by forcing the bromide ion away from the cation, renders the bromide ion more nucleophilic and available for catalyst activity and stability than the planar ammonium cation can.

Table 4 Arylation reaction of bromobenzene with styrene catalyzed by recycled catalyst

Cycle	Yield (%)[a]	Cycle	Yield (%)[a]
1	96	2	96
3	94	4	95
5	95	6	94

Reaction conditions: 2.0 mmol of bromobenzene, 3.0 mmol of styrene, 3.0 mmol of Bu$_3$N, and 0.3 mol% MCM-41-2N-PdCl$_2$, 1.2 g of TBAB as additive at 110 °C for 8 h under Ar

[a] Isolated yield

We also investigated the possibility to reuse of the catalyst by using the arylation reaction of bromobenzene with styrene. After carrying out the reaction, the mixture was cooled, extracted with diethyl ether for three times. The ammonium salt and the palladium catalyst were reused directly in the next run without further purification and almost consistent activity was observed for six consecutive cycles (Table 4, entries 1–6). In addition, palladium leaching in the supported catalyst was also determined. The palladium content of the catalyst was determined by ICP analysis to be 0.33 mmol/g after six consecutive runs, no palladium had been lost from the MCM-41 support. In general, the continuous recycle of resin-supported palladium catalysts is difficult owing to leaching of the palladium species from the polymer supports, which often reduces their activity within a five-recycle run. The high stability and excellent reusability of this heterogeneous palladium catalyst should result from the chelating action of bidentate 2-aminoethylamino ligand on palladium and the mesoporous structure of the MCM-41 support. The result is important from a practical point of view. The high catalytic activity, excellent reusability and the easy accessibility of the MCM-41-2N-PdCl$_2$ complex make it a highly attractive heterogeneous palladium catalyst for the parallel solution phase synthesis of diverse libraries of compounds.

4 Conclusions

In summary, we have developed a novel, practical and environmentally friendly catalyst system for the Heck arylation of conjugated alkenes with aryl bromides or chlorides by using 3-(2-aminoethylamino)propyl-functionalized

MCM-41-supported palladium complex [MCM-41-2N-PdCl$_2$] as catalyst and tetrabutylammonium bromide (TBAB) as additive with Bu$_3$N as base. The Heck arylation reactions generated the corresponding *trans*-coupled products stereoselectively in good to excellent yields. This novel heterogeneous palladium catalyst can be conveniently prepared from commercially available and inexpensive reagents and exhibits high catalytic activity and can be reused at least six times without any decreases in activity. The Heck arylation reactions of styrene, butyl acrylate and acrylamide with aryl bromides or chlorides catalyzed by the MCM-41-2N-PdCl$_2$ complex provide a better and practical procedure for the stereoselective synthesis of a variety of (*E*)-stilbenes, butyl (*E*)-cinnamates and (*E*)-cinnamamides, respectively.

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