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# NCN-Pincer palladium complexes immobilized on MCM-41 molecular sieve: Application in $\alpha$ -arylation reactions



## Kai Wang, Qian Hua\*, Liu Dabin, Ye Zhiwen

School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, 210094, Jiangsu, China

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<i>Keywords:</i> α-arylation reaction Immobilization MCM-41 Pincer complexes Catalyst recycling	Aromatic para-functionalized NCN pincer compounds tethered to a triethoxysilane moiety through a carbamate linkage were immobilized on ordered MCM-41 molecular sieve using a grafting process. The acquired im- mobilized organometallic pincer complexes were synthesized in high yields with no complex degradation and characterized by IR sprctroscopy, elemental content analysis. Nitrogen physisorption, XRD and TEM revealed that the mesoporous structure was retained during the immobilization process. The hybrid materials were ap- plied as Lewis acid catalysts in the $\alpha$ -arylation reaction between aryl ketones and aryl halides, with the yield up to 95%. The tendency to form mono- or di-arylated products was investigated and the catalyst could be easily recovered and reused in five runs without a significant loss in its activity.

#### 1. Introduction

Palladium catalyzed carbon–carbon bond formation reactions are powerful tools in organic synthesis, providing mild methods for the synthesis of valuable chemicals [1]. An important example of such reaction is  $\alpha$ -arylation reaction of aryl ketones with aryl halides. The first practical researches of palladium-catalyzed  $\alpha$ -arylation of carbonyl compounds were reported independently by Hartwig [2], Buchwald [3], and Miura [4]. Driven by their pioneering work, numerous alternative methods have emerged, and are now widely applied to synthesize pharmaceutical compounds [5]. A variety of ligands are tried in these reactions, including phosphines [6], carbenes [7], modified ferrocenes phosphine-based pincer ligands [8], to broaden the substrates, increase the reaction selectivity and provide high turnover frequency. However, it is intricate to separate catalyst from the product solution, which is an ineluctable aspect of homogeneous catalytic processes.

In view of economical and ecological respect, heterogeneous catalysts possess obvious merits on account of the easy-separation after the completion of reactions. Combination of high selectivity and activity of homogeneous catalysts with easy-separation, catalyst recovery of heterogeneous catalysts would be expectable to reach an ideal catalyst system.

Pincer organometallic complex is depicted as a terdentate ligand bound through a covalent C–M bond, and the metal center is clamped by two hetero atom containing substituents via ortho-chelation. As a subclass of cyclo-palladated compounds, pincer complex has been widely used in various carbon–carbon or carbon–hetero bond formation and material science [9]. The functionalization of the main backbone of the pincer compounds mainly took place on the *para* position of the aromatic ring, and the ideal catalyst system is of great possibility to be achieved by immobilizing complexes on an inorganic support ulteriorly [10]. Various supports have already been attempted to immobilize pincer-based metal catalysts, including hyperbranched polymers [11], oligo(ethylene glycol) [12], dendronized polymers [13], carbosilane dendrimers [14], cartwheel molecules [15], and polycationic dendrimers [16], and the synthesized hybrid catalysts are further applied and recycled from reaction products. Notably, in many cases it has been observed that functionalization in the *para* position maintains the integrity of the pincer compounds both in structure and chemical reactivity and only generates anchoring points.

The actual immobilization of a homogeneous catalyst on a heterogeneous support can be achieved mainly by two different approaches. A transition metal is either complexed to ligands already chemically bonded to a support, or a metal complex containing an appropriate coupling agent is tethered to a support. In the first approach, the coordination sphere around the metal center changes during immobilization via various ligand exchange processes and the average structural properties of this immobilized complex could be quite different from those of the homogeneous complex. In the second approach, such changes may be minimal provided that the metal ion is strongly complexed to the ligand and that this configuration remains intact during grafting [17].

E-mail address: iem\_liu@163.com (H. Qian).

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<sup>\*</sup> Corresponding author.

Table 1 Comparison of previous methods and present work for the  $\alpha$ -arylation reaction.

Entry	Catalyst system	Yield/%
1	[PdCl <sub>2</sub> (dppf)] [18]	61
2	[Ni{(iPr <sub>2</sub> Ph) <sub>2</sub> NHC}(PPh <sub>3</sub> )Cl <sub>2</sub> ] [19]	65
3	(SIPr)Pd(Py)Cl <sub>2</sub> [20]	85
4	[Pd(cin)Cl] <sub>2</sub> /DalPhos [21]	88
5	[t-BuPheBoxMe <sub>2</sub> ]PdBr [22]	96
6	Bisamide(NCN)PdBr [23]	95
7	Immobilized bisamide(NCN)PdBr (present work)	95

For this study, we have used palladium complex of so-called 'pincer' ligands of the NCN type which can be subsequently immobilized onto a MCM-41 support, and to study whether the heterogenized system formed has retained its initial metal–ligand configuration. The immobilized complexes were characterized by various techniques, such as IR spectroscopy and elemental content analysis. The activity and recyclability in catalyzing the  $\alpha$ -arylation reaction between aryl ketones and aryl bromides were also investigated. Table 1 illustrates several reported literature for the  $\alpha$ -arylation reactions. In most cases acetophenone and its derivatives were used as substrate to afford good yields of the arylated products, this study also took a further insight to see the suitability of the catalyst system for aliphatic ketones and its recyclability after the catalytic runs.

#### 2. Experimental section

#### 2.1. General procedures

Synthetic procedures were conducted under a dry nitrogen atmosphere using standard Schlenk techniques. All reagents were obtained from commercial sources with reagent grade and were used without further purification. The IR spectra were recorded on a Nicolet IS-10 spectrometer and expressed in cm<sup>-1</sup> (KBr). XRD tests of the ordered mesoporous silicas and hybrid material were carried out in Bruker D8 X-ray powder diffractometer (Bruker, Germany), using Cu Ka  $(\lambda = 0.154 \text{ nm})$  radiation at a scanning rate of 5°/min with an angle ranging from 0 to 10° of 20. Elemental analysis by ICP was performed using a JICP-PS-1000 UV spectrophotometer (Teledyne Leeman Lab., U.S.A.) Specific surface area and pore size distribution of the hybrid materials were measured by recording the nitrogen adsorption/desorption isotherms at liquid N2 temperature (77 K), with the use of a Micromeritics ASAP 2000 system. OH-functionalized NCN-pincer metal complexes [PdBr(NCN - OH)] 2 were prepared as described previously [23].

#### 2.2. Synthesis of 3-aminopropyl-1-MCM-41

MCM-41 (10.00 g, calcined at 120 °C for 8 h and cooled to room temperature) and 3-aminopropyl-1-(triethoxy)silane (9.29 g, 0.04 mol) were placed in dry toluene (150 mL, 1.41 mol) and heated at reflux for 24 h. The mixture was filtered hot, washed with toluene, EtOH, acetone, and CH<sub>2</sub>Cl<sub>2</sub>, and dried under vacuum to afford 10.1 g white powder. IR:  $\nu_{SiO-H}$  3522 cm<sup>-1</sup>.

## 2.3. Synthesis of isocyanate-functionalized MCM-41

3-aminopropyl-1-silica (5.00 g) was placed in a Schlenk with toluene (30 mL, 0.28 mol). Triphosgene (2.03 g, 6.8 mmol) was added, and the resulting mixture was heated at reflux for 24 h. The mixture was filtered hot, then washed with toluene, acetone, CH<sub>2</sub>Cl<sub>2</sub>, and pentane, and subsequently dried under vacuum affording 4.88 g white powder. IR:  $\nu_{CNO}$  2276 cm<sup>-1</sup>,  $\nu_{SiO-H}$  3522 cm<sup>-1</sup>.

#### 2.4. Grafting procedure

In a typical procedure [24], the complex **2** (49.8 mg, 0.1 mmol) was dissolved in a CH<sub>2</sub>Cl<sub>2</sub>/MeOH mixture (1:1, 10 mL) and stirred over an ion-exchange resin (DOWEX 50WX8) for 6 h. The resulting solution was filtered and the resulting solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) with NEt<sub>3</sub> (3 mL), DMAP (5 mg, 0.04 mmol), and 3-isocyanatopropyl-1-MCM-41 (1 g) and was stirred at reflux for 24 h. The mixture was filtered hot, then washed with EtOH, CH<sub>2</sub>Cl<sub>2</sub>, and pentane, and subsequently dried under vacuum. Brown powder. IR:  $\nu_{SiO-H}$  3520 cm<sup>-1</sup>,  $\nu_{carbamate}$  1725 and 1550 cm<sup>-1</sup>,  $\nu_{N-H}$  3310 and 1441 cm<sup>-1</sup>.

## 2.5. Protection of free silanol groups with trimethylsilyl groups

In a typical procedure, silica **3** (0.5 g) was treated with hexamethyldisilazane (HMDS) (5 g, 31 mmol) in hexane (25 mL). The mixture was heated at reflux for 24 h. The mixture was filtered, washed with hexane (2 × 25 mL) and dried under vacuum to yield brown powder **5**. IR:  $\nu_{\text{carbamate}}$  1750 and 1562 cm<sup>-1</sup>,  $\nu_{\text{C-H}}$  2901 cm<sup>-1</sup>,  $\nu_{\text{N-H}}$  3312 and 1450 cm<sup>-1</sup>.

#### 2.6. Synthesis of cationic organopalladium hybrid materials

In a typical procedure, silica **3** (0.5 g) and AgBF<sub>4</sub> (9.7 mg, 0.05 mmol) were stirred in dry dichloromethane (10 mL) at room temperature for 1 h in the absence of light, and the reaction mixture was filtered through Celite eluting with dichloromethane. The filtrate was evaporated to dryness to give the cationic organopalladium material as a brown solid **4**. IR:  $\nu_{carbamate}$  1725 and 1550 cm<sup>-1</sup>,  $\nu_{C-H}$  2893 cm<sup>-1</sup>,  $\nu_{N-H}$  3310 and 1451 cm<sup>-1</sup>.

## 2.7. Catalysis and recycling

The catalytic experiments were carried out using potassium tertbutoxide (1.5 mmol) as a base, functionalized silica materials (approx. Pd content 1.0 mol%) as catalyst, and ketone (1.0 mmol), and aryl halide (1.2 mmol) as reagents in acetonitrile (10 mL) at reflux temperature. After cooling the reaction mixture, the reaction vessel was centrifuged to settle the silica and the catalyst was separated from the liquid product by decanting the supernatant carefully and then filtration. The filtrate was analyzed by gas chromatography to determine the yield of the product. The recovered catalyst was washed twice with  $CH_2Cl_2$  and dried in vacuo. It was then used for the next run.

#### 3. Results and discussion

#### 3.1. Immobilization of NCN-Pincer palladium complexes on MCM-41

The immobilization process of NCN-Pincer Palladium Complexes on MCM-41 was shown in Schemes 1 and 2, and the synthesis of [(OH-NCN)PdBr] pincer complex was achieved according to our previous work [23]. The conversion of amino-propyl groups bounding to MCM-41 to active functionalities was successful and isocyanate-functionalized material 1 was synthesized from alkyl amines with excess of triphosgene in toluene. The reaction was found to be high-yielding with byproduct that can easily be removed. The material 1 and an organometallic fragment was successfully connected though a carbamate linker, however, this reaction requires relatively extreme condition, including sufficient stir in ion-exchange resin, large excess trimethylamine, catalytic amount of N, N-dimethylamino pyridine, reflux temperature, to ensure conversion of the isocyanate groups. To investigate the effect of remained silanol groups on catalysis, the synthesized hybrid material 3 was further treated with hexamethyldisilazane in hexane for 24 h at room temperature to obtain material 5, in which the remaining silanol groups were capped by trimethylsilyl groups. Finally, the material 3 and 5 were treated with AgBF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> to afford



Scheme 1. Synthesis of isocyanate-functionalized material 1: (i) 3-aminopropyl trimeth- oxysilane, toluene, reflux, 24 h; (ii) triphosgene, toluene, reflux, 24 h.

cationic Pd-aquo complexes, which are believed to be the active species in catalytic process.

#### 3.2. Characterization

## 3.2.1. IR studies

FTIR experiments were performed to demonstrate the successful loading of the pincer complex on isocyanate-functionalized MCM-41 (Fig. 1). The peak at  $3425 \text{ cm}^{-1}$  in FTIR spectrum of MCM-41 (Fig. 1a) was characteristic of  $\nu_{SiO-H}$  stretching vibrations. The bands at 1086 and  $803 \text{ cm}^{-1}$  could be attributed to the Si – O stretching vibrations, and these peaks can also be observed in the FTIR spectrum of isocyanatefunctionalized MCM-41 sample (Fig. 1b), with a characteristic  $\nu_{\rm NCO}$  at 2276 cm<sup>-1</sup>, indicating the successful functionalization of MCM-41. Comparison of the IR spectra of the isocyanate-functionalized MCM-41 (Fig. 1b), complex 2 (Fig. 1c) with those of hybrid materials 4 (Fig. 1d) pointed to a strong decrease in the number of isocyanate groups in the latter silicas, suggesting that not all isocyanate groups are tethered to a pincer complex. In addition, the complex 2 displayed absorption bands at 3450, 1649 and 1578 cm<sup>-1</sup> that correspond to N–H stretching, C=O stretching vibrations, and N-H bending vibrations of the amide groups, respectively. These peaks were partial overlapped with those of isocyanate-functionalized MCM-41 and the new formed characteristic stretches of carbamate group, which were observed at 1725 and 1550 cm<sup>-1</sup>. The features of this spectrum showed consentient results with previous reports on carbamate-tethered silica species <sup>25</sup>. The intensity of the signal for isolated free silanol groups in 4 is decreased in the spectrum of 6 (Fig. 1e), which is due to the substitution the TMS group in 6.

## 3.2.2. XRD analysis

Fig. 2 shows the XRD patterns of MCM-41 and the corresponding hybrid materials. The similar XRD patterns between the prepared



Fig. 1. FT-IR spectra of MCM-41 (a), isocyanate-functionalized MCM-41 (b), complex 2 (c), hybrid material 4 (d) and hybrid material 6 (e).

hybrid materials and the MCM-41 indicated that the anchoring process did not show significant influence on the mesoporous silica material. The pattern of blank MCM-41 revealed three well-resolved peaks located at 2.0, 3.7 and 4.5 degrees 20, that could be assigned to the (100), (110) and (200) diffraction lines, respectively, associated with a hexagonal symmetry that is typical for MCM-41 [26]. Although small variations between the d-spacing values of the (110) diffraction line of



Scheme 2. Immobilization and activation of 2 on isocyanate-functionalized material: (i) CH<sub>2</sub>Cl<sub>2</sub>/MeOH, then CH<sub>2</sub>Cl<sub>2</sub>/NEt<sub>3</sub>, DMAP, reflux, 24 h; (ii) AgBF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>; (iii) HMDS, hexane, 24 h.



Fig. 2. XRD patterns of MCM-41 (a), hybrid material 3 (b), hybrid material 6 (c) and hybrid material 6 after 5 runs (d).

the different samples were found, the XRD results demonstrated that the hexagonal symmetry was retained for the functionalized material during both the grafting treatment and after five runs of catalysis.

#### 3.2.3. Elemental analysis

Carbon, hydrogen, oxygen and silicon analysis gives little information because they are present in large excess with respect to the organometallic species (C as TMS capping groups, Si and O as polymeric support). The grafting result of hybrid material **3** showed a marked increase in nitrogen content, which is due to the introduction of a pincer organometallic complex. Notably, large quantity of free isocyanate groups still exist on the surface, suggesting that not all isocyanate groups are tethered to a pincer complex. This can be deduced via the disproportionate ratio of N/Pd, the nitrogen loading is expected to be seven times as much as Pd content (Pd, 0.31%) if all isocyanate groups had been substituted with carbamate groups during the immobilization process. However, the observed N/Pd ratio was 22:1, which was much larger than the expected proportion.

#### 3.2.4. Nitrogen physisorption

The textural properties of MCM-41 and changes in surface properties at different stages of hybrid materials were further investigated using N<sub>2</sub> sorption analysis, and the result was shown in Fig. 3. The isotherms of these four materials showed Type IV curves with a high onset at low relative pressures originating from the intra-wall microporosity, and hysteresis at higher values due to the ordered mesoporous channels. The relative pressure region (p/p<sub>0</sub> = 0.3-0.5) in which the N<sub>2</sub> adsorption capacity increased sharply along with the emergence of hysteresis ring is due to the condensation of nitrogen molecules in the mesoporous pores. The nitrogen physisorption results indicated that the textural properties of hybrid material 4 and 6, together with recycled material after 5 runs of catalysis (Fig. 3b–d) were well retained.

The BET surface area and pore volume of the samples are given in Table 2. Compared with the pure MCM-41, both materials 4 and 6 showed slight decrease in pore volumes, average pore size and specific surface area, which indicates that the nature of the mesoporous silica material was not significantly affected during the anchoring process of organometallic moiety. The observed large pore volumes of hybrid materials indicate adequate accessibility of catalyst site and further ensure that the support is unlikely to influence much on the mass transport of the catalytic reactions. The recycled material remained nearly the same physisorption results with material 6, indicating the

catalytic process had little effect on the textural properties within five runs.

#### 3.2.5. TEM analysis

Fig. 4 shows two typical TEM images of the MCM-41 and the hybrid material **6**, which further confirmed the XRD results. Although it is observed that few amount of channels in hybrid material partially collapsed, in some degree, into disordered and wormhole-like packings (Fig. 4b), the hexagonal periodicity of the mesophase of MCM-41 was basically maintained after functionalization and immobilization process, as displayed in the TEM images (Fig. 4a).

#### 3.3. Catalysis

NCN-pincer palladium complexes are known to be excellent precatalysts for the formation of Lewis acid catalysts for the  $\alpha$ -arylation reaction between aryl ketones and aryl halides [8,27]. In this study, we generated the corresponding cationic-aquo complexes, which are believed to be the real active catalytic species, to investigate how these hybrid materials work in the reaction. Table 3 shows the influences of catalyst loadings on  $\alpha$ -arylation coupling reaction of bromobenzene with acetyl benzene over the two cationic-aquo complexes immobilized on MCM-41. The model reaction was carried out at 81 °C for 2 h using potassium tert-butoxide as base in acetonitrile solvent. The reaction mediated by material **6** with 1.0 mol% Pd catalyst loadings (0.5 mol %) offered a 90% yield with 85% monoarylated product after only 2 h (enter 3). Finally, reducing the catalyst loading to 0.2 mol% delivered an 83% yield after 6 h (entry 6).

Table 4 shows typical results of the reactions of bromobenzene with various ketones over material 6. The reaction of propiophenone gave monoarylated product in 89% yield (entry 1). Aryl ketones with an electron donating group such as 4-methyl acetophenone, 4-methoxyacetophenone and 1-(4-dimethylamino-phenyl)-ethanone gave corresponding cross-coupling products with high yields, although trace amounts of diarylated coupling product were accompanied as a byproduct (entries 2-4). On the other hand, reaction of 4-fluorine acetophenone and 1-(4-trifluoromethyl-phenyl)-ethanone having an electron-withdrawing group gave only 70% and 71% monoarylated yields, respectively (entries 5 and 6). It was noteworthy that the coupling of hindered ketones, such as 1-ferrocenylethanone and 1'-acetonaphthone, could also give the desired mono-products in good yields (entries 7 and 8). When 3-pentanone was taken as a substrate, trace amount of diarylated coupling product was obtained. However, when we change the solvent to toluene, the reaction could afford a 77% diarylated yield without any monoarylated product (entry 6). This unexpected result caught our attention and we further increased the proportion of ketone/ bromobenzene to 1:1.5, the diarylated coupling product was consequently enhanced to 80%. When the ratio was 1:2, the diarylated yield was decreased to 55%, suggesting that the optimal proportion to obtain diarylated product was 1:1.5. This is probably because the mono-products have a tendency to form a thermodynamic stable enolates in polar solvent, while they tend to further transform into dynamic stable enolates in nonpolar solvent, which are the crucial intermediates to yield the diarylated product.

## 3.4. Plausible mechanism

Based on the previous efforts [28], a plausible mechanism was shown in Scheme 3 ( $-OH_2$  and  $-BF_4$  groups were omitted for clarity). The first step is the oxidative addition of the aryl halide to Pd° species generated from the precatalyst to form the organopalladium species. Reaction with base and ketones gives the corresponding enolates, which further affording the desired product via reductive elimination. The availability of a vacant site on a species generated after oxidative addition could possibly facilitate $\beta$ -hydrogen elimination.



Fig. 3. Nitrogen physisorption isotherms of MCM-41 (a), hybrid material 4 (b), hybrid material 6 (c) and hybrid material 6 after 5 runs (d).

Table 2Textural data of MCM-41 and hybrid materials samples.

Samples	$V_{meso}^{[a]}$ (cm <sup>3</sup> /g)	Pore size <sup>[b]</sup> (nm)	$S_{BET}^{[c]}(m^2/g)$
MCM-41	1.06	3.28	998
Hybrid material 4	0.95	2.84	920
Hybrid material 6	0.82	2.68	912
6 after 5 runs	0.81	2.64	910

[a]  $V_{meso}\!=\!mesopore$  volume. [b] Average pore diameter by BJH. [c]  $S_{BET}\!=\!BET$  surface area.

#### 3.5. Recycling

The recyclability of solid catalysts is a major problem for their utilities. To investigate the reusable properties of catalyst, recycle experiments were performed and the results were illustrated in Fig. 5. After cooling the reaction mixture, the reaction vessel was centrifuged to settle the silica and the catalyst was separated from the liquid product by decanting the supernatant carefully and then filtration. The recovered catalyst was washed twice with  $CH_2Cl_2$ , dried in vacuo, and then used for the next run. It was found that the reactivity of the recycled material was preserved at a high level within five runs, although



Fig. 4. Nitrogen physisorption isotherms of MCM-41 (a), hybrid material 6 (b).

#### Table 3

Optimization of catalyst species and loadings for the cross-coupling between acetyl benzene and bromobenzene<sup>[a].</sup>

Entry	Catalyst No.	Pd loading (mol %)	Yield <sup>[b]</sup>	Percentage of mono- product
1	None	_	0	0
2	4	0.5	86	78
3	6	0.5	90	85
4	4	1	93	86
5	6	1	95	88
6	6	0.2	83	77

[a] Reaction details: acetyl benzene (1.0 mmol), bromobenzene (1.2 mmol), solvent (10 mL) at 81  $^{\circ}$ C for 2 h. [b] GC yield.

Table 4

 $\alpha\text{-arylation}$  reaction of various ketones with bromobenzene over material  $\boldsymbol{6}^{[a]}$ 

Entry	Ketones Se		Yield <sup>[b]</sup>	
			mono- product	di-product
1	propiophenone	CH <sub>3</sub> CN	89	0
2	4-methyl acetophenone	CH <sub>3</sub> CN	92	4
3	4-methoxy acetophenone	CH <sub>3</sub> CN	92	3
4	1-(4-dimethylamino-phenyl)- ethanone	CH <sub>3</sub> CN	88	Trace
5	4-fluorine acetophenone	CH <sub>3</sub> CN	70	6
6	1-(4-trifluoromethyl-phenyl)- ethanone	CH <sub>3</sub> CN	71	Trace
7	1-ferrocenylethanone	CH <sub>3</sub> CN	57	Trace
8	1'-acetonaphthone	$CH_3CN$	55	Trace
9	3-pentanone	CH <sub>3</sub> CN	93	Trace
10	3-pentanone	Toluene	_	77 <sup>[c]</sup>
11 <sup>[d]</sup>	3-pentanone	Toluene	_	80 <sup>[c]</sup>
12 <sup>[e]</sup>	3-pentanone	Toluene	_	55 <sup>[c]</sup>

[a] Reaction details: ketone (1.0 mmol), bromobenzene (1.2 mmol), solvent (10 mL) at 81  $^\circ$ C for 2 h. [b] GC yield. [c] Based on bromobenzene. [d] 1.0 : 1.5 ratio of 3-pentanone: bromobenzene. [e] 1.0 : 2.0 ratio of 3-pentanone: bromobenzene.



Scheme 3. Plausible mechanism of the reaction.

it drops gradually after each run. This strongly suggested that the catalyst could be reused at least five times without appreciable decrease in yield. To understand the faith of the catalyst on decaying, specific



Fig. 5. Recycling of catalysts in  $\alpha$ -arylation of acetyl benzene and bromobenzene.

designed experiments were carried out. It is possible that leaching is produced by catalyst decomposition during catalytic process, so we simply added one more equivalent substrate to the reaction mixture without seperating the catalyst after the first run. The result showed no significant decrease in reactivity, suggesting that the active palladium sites did not change over the whole catalytic process. Other possible reasons for catalyst deactivation were that small amout of palladium sites were removed during the recycling peocedure or inseparable species were formed. To test this possibility, ICP analysis was used for the supernatants and washings of two runs, and the result showed that the molar ratio of Si/Pd in the washings was 6.4 and 8.8. It is worth noting that the theoretical value of Si/Pd is expected to be 1 for the leached but intact catalyst [25], supposing the deactivation is only caused by cleavage of Si-O-Si bonds between silica and the organiometalic fragment. In other words, small and inseparable species/particles are most likely to be formed via surface reconstitution of molecular sieve during recycling procedure. These results indicated that the surface reconstitution should account for the main decease of the catalyst activity during the recycling runs.

## 4. Conclusions

In summary, we have successfully synthesized hybrid materials immobilized with aromatic para-functionalized NCN pincer compounds tethered to a triethoxysilane moiety through a carbamate linkage. The immobilized organometallic pincer complexes were synthesized in high yields, both the inorganic support and organometallic moiety retained their structure integrity during immobilization process. It was found that hybrid material **6** showed a high catalytic activity in  $\alpha$ -arylation reaction of ketones, affording a 95% yield of product. The mono- and di-arylated product could be selectively obtained through changing the solvent and ratio of substrates. The anchoring of the active organometallic catalyst on a stable support results in an excellent heterogeneous catalyst, which can be recycled and reused up to five times without a significant loss of activity and nicely reach the purpose of combining positive properties of homogeneous and heterogeneous catalytic systems.

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