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A Magnetic Nanoparticle-Supported *N*-heterocyclic Carbene-Palladacycle: An Efficient and Recyclable Solid Molecular Catalyst for Suzuki-Miyaura Cross-Coupling of 9-Chloroacridine

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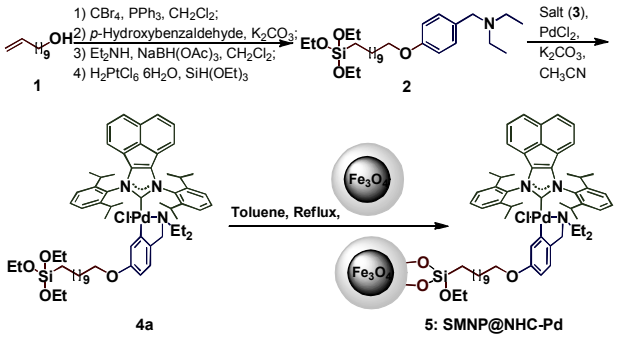
A robust magnetic nanoparticle-supported *N*-heterocyclic carbene-palladacycle has been readily synthesized by directly anchoring the structrual defined acenaphthoimidazolylidene palladacycle with long tail on the magnetic nanoparticles (MNPs), which functioned as a solid molecular catalyst and exhibited extremely high catalytic activity towards the challenging Suzuki-Miyaura cross-coupling reactions between less-studied heterocyclic 9-chloroacridine and diverse boronic acids. Remarkably, the catalyst could be used 5 times without obvious loss of activity highlighing the efficiency of our strategy on the immobilization of the previledge catalysts.

As strong σ-donors and weak π-acceptors, *N*-heterocyclic carbenes (NHCs) represent one type of important robust ligands.[1] Numerous transition-metal NHC complexes have been successfully developed and unveiled excellent catalytic activity towards a broad number of transformations.[2] Among them, NHC-Pd complexes have been demonstrated extremely high catalytic activity especially in the Suzuki-Miyaura cross-coupling reactions, accessing bi-phenyl derivatives with potential applications in pharmaceuticals and functional organic materials.[3] However, the consumption and leaching of the noble metals of the catalysts lead to numerous waste and environmental problems. Therefore, the immobilization of privileged catalysts based on NHC-M complexes on various organic matrixes or solid supports constitute one of potential solutions.[4] Amongst, magnetic nanoparticles (MNPs) have drawn great attention because the supported catalysts could be readily recovered by magnetically separation.[5]

The general approach for NHC-Pd catalyst immobilization is anchoring firstly the imidazolium salts with terminal triethoxysilyl groups on the MNPs' surface via hydrosilation reactions.[6b] After further metalation/coordination with suitable palladium precursors, the MNPs supported NHC-Pd (MNP@NHC-Pd) catalysts were therefore obtained.[6,7] The catalysts could also be fabricated directly from MNP, NHCs and palladium precursors in one pot manner.[8] However, these conventional immobilization approaches always suffered from various negative effects such as lower stability, reduced catalytic activity and/or selectivity as a result of the poor accessibility, random anchoring, or disturbed geometry of the active sites in the solid matrix of these recyclable catalysts.



Scheme 1. Synthesis of MNPs-supported *N*-heterocyclic carbene-palladacycle **5**.

Very recently, we demonstrated novel NHC-based palladacycles exhibited high catalytic activity towards challenging amination of heteroaryl chlorides.[9] Notably, the extremely high thermal stability of the structure defined palladacycles during the transformations make them as suitable candidates for the direct immobilization on MNPs.[10] Following our recent research interests in the design, synthesis and application of various types of solid molecular catalysts,[11] herein, we synthesized an acenaphthoimidazolyildene palladacycle with long chain triethoxysilyl tail and successfully immobilized it on the surface of MNPs. The resulting structural defined recyclable MNPs-supported NHC-palladacycle exhibited extremely high catalytic activity towards challenging Suzuki-Miyaura cross-coupling reactions between heterocyclic 9-chloroacridine and diverse boronic acids.

As shown in Scheme 1, the key linker **2** was synthesized from inexpensive and commercial available 10-undecene-1-ol

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(**1**) after simple bromination, etherification, ammoniation and hydrosilation steps. Then the corresponding triethoxysilyl-functionalized NHC-palladacycle **4a** was readily prepared from $PdCl_2$, readily available acenaphthoimidazolium salt (**3**) and the linker **2** in toluene in a good yield.[12] Subsequently, the palladacycle with long tail (**4a**) was straightforward anchored on the surface of the core-shell silica coated magnetic nanoparticles (SMNPs) via hydrolysis[13] to produce the desired supported NHC-palladacycle (**5**, SMNP@NHC-Pd), in which tertiary amine moiety may function as a hemilabile ligand[14] and benefit the active Pd(0) species formation.[15] The loading of Pd in SMNP@NHC-Pd is 0.01 mmol/g, which is quite consistent from batch-to-batch and determined by inductively coupled plasma atomic emission spectrometry (ICP-AES).

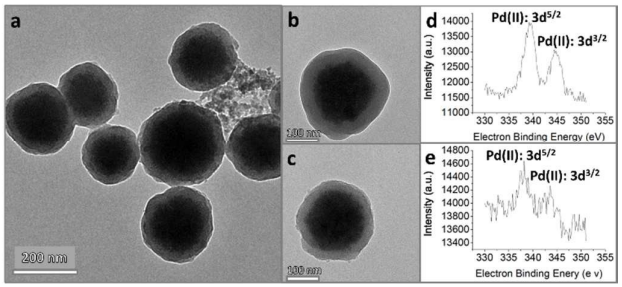
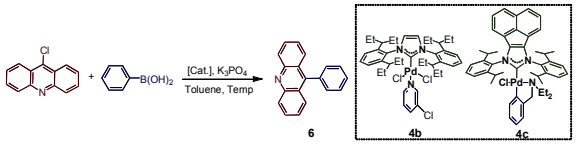


Fig. 1 TEM images of SMNP@NHC-Pd **5**: (a) full image, (b) fresh prepared and (c) recovered single particle; XPS spectra of (d) fresh prepared and (e) recovered SMNP@NHC-Pd **5**.

With the desired supported SMNP@NHC-Pd **5** in hand, transmission electron microscopy was applied to investigate their morphologies. As shown in Fig. 1, in comparison with SMNPs precursors, particles of SMNP@NHC-Pd **5** are slightly bigger with an average diameter of 150 nm (Fig 1a vs. Fig S1b, †ESI). The thickness of the out layer of SMNP@NHC-Pd **5** is ca. 40 nm (Fig 1b), which is quite uniform with the observed particles. In order to further confirm the immobilization of palladacycles **4a** on the surface of SMNPs, energy-dispersive X-ray (EDX) study was also carried out. To our delighted, EDX quantification of the SMNP@NHC-Pd particles **5** indicates the presence of all expected elements including Fe, Pd, O and Si (Fig. S2, †ESI). Notably, the formation of agglomerated palladium black nanoparticles on SMNP was not observed. The XPS studies also support this observation. Only Pd(II) signals are found at 337.26 ($3d^{5/2}$) and 342.57 ($3d^{3/2}$), corresponding to two oxidation states of palladium, which clearly indicates the accomplishments of immobilization of palladcycles on the surface of SMNPs. Finally, the differential scanning calorimetry-thermogravimetric analysis (DSC-TGA) study further highlights good thermal stability of the obtained SMNP@NHC-Pd particles (Fig. S3, †ESI), which could be stored under ambient condition for years.

Due to palladacycle **4c** exhibited very high catalytic activity towards challenging amination reactions between heteroaryl chlorides in our recent study.[9] With the structure defined supported palladacycle **5** (SMNP@NHC-Pd) in hand, we would like to further investigate its catalytic activity and recyclability toward challenging Suzuki-Miyaura coupling reactions of heteroaryl chlorides with vairious boronic acids. Nowadays, acridine derivatives have been found various potentials in material sciences and pharmaceuticals.[16,17] Despite the broad-spectrum utility of this motif, only one approach had been developed to synthetize aryl or alkyl substituted acridines with active organozinc reagents.[17] Therefore, we would like to using less-studied Suzuki-Miyaura coupling reactions of heterocyclic 9-chloroacridine and phenylboronic acid as a model reaction to explore the catalytic activity and recyclability of newly developed SMNP@NHC-Pd.

Table 1. Optimization of reaction conditions[a]



Entry	[Cat.](mol%)	Temp (^oC)	Yield (%)[b]
1	**5** (1)	80	89
2	**5** (1)	90	98
3	**5** (1)	100	99
4	**5** (0.5)	100	99
5	**5** (0.4)	100	94
6	**5** (0.2)	100	87
7	**4a** (0.5)	100	99
8[c]	**$Pd(OAc)_2$** (0.5)**/PPh_3** (1.0)	100	23
9[c]	**$Pd(OAc)_2$** (0.5)**/Sphos** (1.0)	100	79
10[c]	**4b**	100	95
11[c]	**4c**	100	99

[a] Reaction was carried out with 0.15 mmol 9-chloroacridine, 3.0 equiv. K_3PO_4 in 4 mL toluene with catalyst under N_2 at 100 ^oC for 24 h; [b] Isolated yield; [c] Reaction was carried out with 0.5 mmol scale.

In the presence of 1 mol% SMNP@NHC-Pd (150 mg, **5**), the coupling reaction between 9-chloroacridine and phenylboronic acid was carried out with K_3PO_4 in toluene at 80 ^oC, the desired product 9-phenylacridine **6** was formed in 89% yield (Table 1, entry 1). Further increasing the reaction temperature, the yield was also increased (98% and 99% for 90 ^oC and 100 ^oC, respectively, Table 1, entries 2 and 3). When other organic solvents and bases were screened, no better results were produced (Table S2, †ESI). To our delighted, even with 0.5 mol% catalyst loading, a quantitative yield was still obtained (Table 1, entry 4). Especially, no difference was observed with yields for the SMNP@NHC-Pd **5** from batch-to-batch. Further decreasing the catalyst loading, only slightly lower yields were observed (94% and 87% for 0.4 mol% and 0.2 mol% catalyst loadings, respectively, Table 1, entries 5 and 6), which further confirmed the catalytic efficiency of the supported catalyst **5**. In comparison, the palladcycle **4a**, the precursor for immobilization, was also applied as a homogenous molecular catalyst in the model reaction. Similar as SMNP@NHC-Pd **5**, at least 0.5 mol% catalyst loading was required to achieve the quantitative yield (Table 1, entry 7). In contrast, in the case of homogenous catalysts generated *in situ* from selected palladium precursors,[16a] such as $Pd(OAc)_2$, $PdCl_2$ and $Pd_2(dba)_3$,and readily avaiable phosphine ligands (PPh_3, BINAP and dppf), only up to 23% isolated yield could be obtained

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under the standard reaction conditions (Table 1, entry 8 and Table S2, entries 36-39).[18] When more bulky viable catalysts including **SPhos** and **4b**, which showed extremely high catalytic activities in a broad number of coupling reactions,[18b-d] were applied, the yields of 79% and 95% could be obtained, respectively (Table 1, Entries 9 and 10). In contrast, when homogenous palladacycle **4c** was used instead, a compatible isolated yield with supported catalyst **5** and its precursor **4a** was produced (Table 1, Entry 11), further highlighting the efficiency of our immobilization strategy.

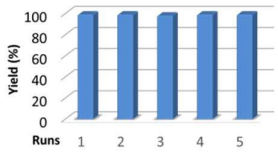


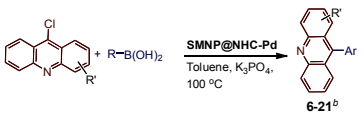
Fig. 2 Reusability of SMNP@NHC-Pd **5** in the Suzuki reaction of 9-chloroacridine and phenylboronic acid (0.15 mmol scale)

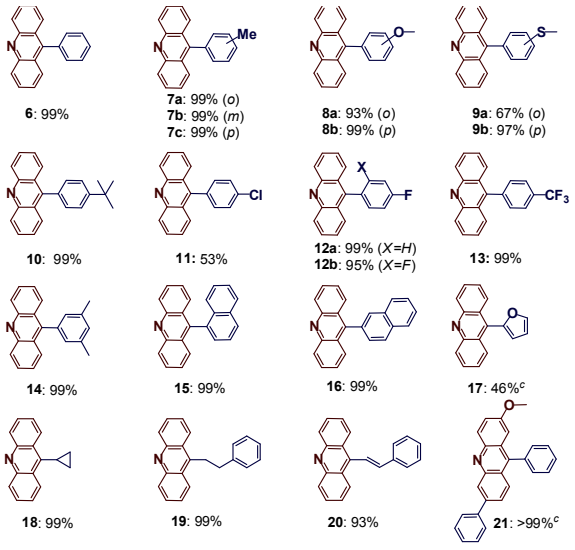
With this good result in hand, the reusability of the catalyst SMNP@NHC-Pd was then carried out. After the reaction completion, the supported catalyst **5** in the model reaction could be readily fully recovered by magnetic separation (99%, confirmed by ICP-AES). After washing by ethanol and H_2O successively, the recovered supported catalyst could be reused directly in the second run, by simply adding the substrates, solvent and base. To our delighted, SMNP@NHC-Pd could be recovered and reused for 5 consecutive trials without loss of its catalytic activity, and almost quantitative yield was found for each run (Fig. 2). The TEM image and XPS spectra of the recovered SMNP@NHC-Pd also further support these outcomes. The recovered SMNP@NHC-Pd particles after 5 runs still kept core-shell spherical morphology with ca. 35-40 nm out layer (Fig. 1c vs. 1b). The absorption peaks of Pd(II) of the recovered SMNP@NHC-Pd particles basically remain unchanged (Figure 1e vs. 1d). This is also agreed with the ICP-AES study of the filtrates (Table S3). After each run, almost no leaching palladium species was detected in the filtrate and products. All these data clearly indicate the excellent stability and reusability of the newly developed SMNP@NHC-Pd **5**.

In order to further confirm the reaction was catalyzed by the SMNP@NHC-Pd catalyst, but not Pd(0) nanoparticles formed *in situ,* a set of mercury tests was performed under the optimal conditions. In the presence of 0.5 mol % SMNP@NHC-Pd, one drop of Hg was added after 0, 2, and 4 hours, corresponding product could be obtained in 82 %, 83 %, and 91 % yields, respectively (Table S5). These outcomes clearly indicated the molecular catalyst property of SMNP@NHC-Pd **5**.

With the results obtained so far, the substrate scope on various (hetero-)arylboronic acids was then explored (Table 2). Delightedly, the relative positions (**7a-c**) and electronic properties (**7-14**) of substituents hardly affect coupling efficiency. Even with *ortho*-methylthio substitute, usually toxic to Pd catalysts, a moderate yield was still presented (**9**). In the case of 4-chlorophenylboronic acid, although there was a competition between the self-coupling reactions, a 53% isolated yield of the corresponding acridine derivative (**11**) was still obtained. Furthermore, the naphthylboronic acids successfully coupled and delivered corresponding products (**15** and **16**) in quantitative yields, too. Heterocyclic aryl boronic acid was also a suitable substrate; whereas, slightly low yield was observed (**17**). In general, alkyl boronic acids are regarded as rather poor partners in the previously homogeneous Suzuki-Miyaura studies.[19] To our delighted, all selected alkyl and even alkenyl boronic acids resulted in excellent to quantitative yields (**18-20**). The protocol is readily extended to the double Suzuki-Miyaura coupling of challenging 6,9-dichloro-2-methoxyacridine, and a quantitative yield was obtained. In consideration the catalytic activity of such type of NHC-palladacycles has not been investigated in the routine Suzuki-Miyaura coupling of chlorobenzene, a number of boronic acids were involved. The relative positions (**S1a-c**), electronic properties (**S2-S4**) of substituents and heterocyclic properties of boronic acids showed less impact on the coupling efficiency, good to quantitative yields were achieved (72-99%, Table S6, †ESI) which further highlighted the catalytic efficiency of SMNP@NHC-Pd **5**.

Table 2. Substrate scope





[a] Reaction was carried out with 0.15 mmol acridine, 0.5 mol% **5** (SMNP@NHC-Pd), 3.0 equiv. K_3PO_4 in 4 mL toluene under N_2 at 100 °C for 24 h; [b] Isolated yield; [c] With 1.0 mol% **5** (SMNP@NHC-Pd)

In summary, a robust magnetic nanoparticle-supported *N*-heterocyclic carbene-palladacycle has been readily developed by directly anchoring the structural defined acenaphthoimidazolyildene palladacycle with long chain triethoxysilyl tail on the magnetic nanoparticles (MNPs), which functioned as a solid molecular catalyst and exhibited extremely high catalytic activity towards challenging Suzuki-

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Miyaura coupling reactions between heterocyclic 9-chloroacridine and diverse boronic acids. In comparison with homogenous catalysts derived from viable ligands, the protocol well tolerated a broad range of aryl, alkyl, alkenyl and even heterocyclic boronic acids under mild reaction conditions at 0.5 mol% catalyst loading and afforded the corresponding functional acridine derivatives in excellent yields. Remarkably, the catalyst could be used 5 times without obvious loss of activity highlighting our strategy efficiency on the immobilization of the privileged catalysts.

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Conflicts of interest

There are no conflicts to declare

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