

# Thioether-NHC Ligated Pd(II) Complex in Crafting of Filtration-Free Magnetically Retrievable Catalyst for Suzuki-Miyaura Coupling in Water

Kamal Nayan Sharma,\*<sup>[a]</sup> Naveen Satrawala,<sup>[a]</sup> and Raj Kumar Joshi\*<sup>[a]</sup>

Abstract: A new benzimidazolium salt, 1-[N-benzylacetamido]-3-[1-(2-phenvlsulfanvlethvl)] benzimidazolium chloride (L) which is a precursor of novel thioether functionalized NHC. was synthesized by the subjection of 1*H*-benzimidazole to a sequence of reactions with 1,2-dichloroethane, sodium thiophenolate, and N-benzyl-2chloroacetamide, successively. Moisture/air insensitive complex  $[Pd(L-HCI)Cl_2]$  (1), was prepared by a palladium promoted reaction of L with PdCl<sub>2</sub>. The molecular structure of 1 established with X-ray crystallography reveals the square planar geometry around Pd. Complex 1 was screened for Suzuki-Miyaura coupling for various aryl/hetero-aryl bromides (Yield up to 94% in 2 h) at rt in water. Furthermore, the complex 1 was immobilized onto the surface of the aminopropyl functionalized silica-coated magnetite NPs [Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-(CH<sub>2</sub>)<sub>3</sub>-NH<sub>2</sub>] through linking the amide functionality present on sidearm of NHC within the NHC-Pd(II) complex and a heterogeneous magnetically retrievable catalyst (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1') achieved. The magnetic nano-support, novel thioether based NHCs, easily separable catalyst and aqueous aerobic medium of reaction level up the properties of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1' and make the most desirable catalyst for Suzuki-Miyaura coupling. It was noticed that the catalyst activated up to 7 cycles and easily separated by use of an external magnet. This put extra stars and highly raised the efficiency of the catalyst.

## Introduction

Suzuki-Miyaura reaction<sup>[1]</sup> is the premier C-C cross-coupling process, widely applied in synthetic chemistry.<sup>[2]</sup> Lenience for the various functional groups, commercially availability and ease in handling of boron-based compounds, are the key advantages of Suzuki-Miyaura coupling. The industrial applications of Suzuki-Miyaura coupling for construction of biaryl units of pharmaceuticals<sup>[3]</sup> and fine chemicals<sup>[4]</sup> are also remarkable. Large numbers of homogeneous catalytic systems such as Pd(II) complexes with bulky and electron-rich phosphines,<sup>[5]</sup> carbenes,<sup>[6]</sup> and palladacycles<sup>[7]</sup> have been reported as efficient

[a]	Dr. Kamal Nayan Sharma,* Mr. Naveen Satrawala, Dr. Raj Kumar Joshi*
	Department of Chemistry
	Malaviya National Institute of Technology Jaipur
	J.L.N. Marg, Jaipur 302017, Rajasthan, India
[*]	Corresponding authors
	E-mail: rkjoshi.chy@mnit.ac.in (R. K. Joshi)
	http://www.mnit.ac.in/dept_chemistry/preprofile.php
	kamalnayaniitd@gmail.com (K. N. Sharma)
	Supporting information for this article is given via a link at the end of the document

catalytic systems for Suzuki-Miyaura cross-coupling. The reported methods have certain limitations with their uses like difficulty in product separation, recycling of the catalysts, and contamination of the desired product with heavy metal traces which reduce the applications potential of homogeneous catalytic systems. In light of increasing environmental ethics and sustainability, the development of recyclable catalysts is highly desirable which can efficiently beat the challenges of homogeneous catalysis. For reuse the catalyst, heterogenization of the homogeneous version of the catalysts on to the solid support material could be a logical possibility, it also shows new ways for design and synthesis of efficient, stable and recyclable catalysts.<sup>[8]</sup> Several solid supports which includes the silica,<sup>[9]</sup> silica-coated magnetite,<sup>[10]</sup> graphene oxide nanohybrid,<sup>[11]</sup> maghemite,<sup>[12]</sup> zeolites,<sup>[13]</sup> hydrogel,<sup>[14]</sup> porous glass<sup>[15]</sup> are reported with palladium based heterogeneous recyclable catalyst. However, the heterogeneous catalyst based on the solid support of magnetic core-shell NPs, particularly have achieved new horizons in catalysis due to easily separable magnetic properties. Moreover, the coating of the magnetite NPs within a silica-shell enhances the stability of core-shell NPs and prevents the magneto-static agglomeration.<sup>[16]</sup> The coordination capability of ligand supported on to the surface of the solid with palladium has been employed in the strategy for the development of a solid supported catalyst for Suzuki coupling. The ligand frameworks designed using pyridine,  $^{[17]}$  O $^{-}/N, ^{[18]}$ NHC,<sup>[19]</sup> amine functionalized NHC,<sup>[20]</sup> and/or phosphine<sup>[21]</sup> derived donor functionalities, have been used frequently for this purpose. Due to the unique two-electron σ-donor and weak лacceptor properties, NHCs are known to increases the electron density on metal centre and consequently favors the oxidative addition step with providing longer lifetime to real catalytic species.<sup>[22]</sup> Moisture/air insensitive Pd(II) complexes of chalcogen donor containing ligands have been found very efficient catalyst for C-C coupling reactions.<sup>[23]</sup> The NHCs,<sup>[24]</sup> as well as chalcogen donors with N, or O donor chelating functions, are well explored,<sup>[23]</sup> However, the chelating ligands contains NHC and chalcogen donors are rare<sup>[25]</sup> and not much explored. Therefore, in the quest of air/moisture insensitivity, efficiency and recyclability of catalyst for Suzuki coupling, the incorporation of chelating chalcogen donor based functions in NHC, and palladium coordination of such ligand for build up a magnetically retrievable heterogeneous catalytic system is worth exploring. In the best of our mind, till date, neither the magnetite NPssupported nor the other solids supported palladium complex of (S, C<sub>NHC</sub>) type bidentate ligand has been reported for catalysis of any organic transformation.

In present paper, we report a novel, homogeneous Pd(II) catalyst chelating with thioether-NHC ligand, heterogeneous

## WILEY-VCH

version of the catalyst was also synthesised through immobilizing the catalyst on the silica encapsulated magnetite NPs and developed a filtration-free, magnetically retrievable and efficient palladium catalyst which is effectively working (up to seventh cycles) for Suzuki-Miyaura reaction.

### **Results and Discussion**

The strategy used for the syntheses of the benzimidazolium salt (L) and Pd(II) complex  $[Pd(L-HCI)CI_2]$  (1), is depicted in Scheme 1.



Scheme 1. Strategy Used in Preparation of Benzimidazolium Chloride (L) and Pd(II)-NHC Complex (1).

1-(2-Chloroethyl)-1H-benzimidazole (A) was prepared by a modified synthetic procedure reported previously.<sup>[26]</sup> The presented procedure involved the use of K<sub>2</sub>CO<sub>3</sub> with tetra-nbutyl ammonium bromide in a reaction of 1H-benzimidazole with 1,2-dichloroethane and exclusively produced the desired product (A) rather than an impure mixture containing the dehydrohalogenated product.<sup>[26]</sup> The thioether functionalized benzimidazole (B) was formed when ethanolic solution of A was added to the in situ generated sodium thiophenolate in refluxing ethanol. The proton and <sup>13</sup>C NMR and mass spectra authenticating the formation of A, B, L and 1, are provided in Figures S1-S12 of Supporting Information (SI). The NMR spectra of B (SI, Figure S4 and S5) indicate a typical resonance for aliphatic substituted benzimidazoles in the range 7.16-7.76 ppm for  $H_{3-6}$  protons, a singlet at 7.80 ppm for  $H_1$  proton and 142.6 ppm for  $C_1$  carbon of **B**. The intense peak in the mass spectrum (See SI, Figure S6) at (m/z) 255.1145 corroborating the presence of [M+H]<sup>+</sup>, also supports the structure. The FT-IR spectrum of B indicates the disappearance of C-Cl stretching band (664 cm<sup>-1</sup>) of A and slightly shifted (red shifted) bands observed due to the less electronegative S than Cl. An efficient atom economy reaction of **B** with N-benzyl-2-chloroacetamide, afforded air-stable thio-ether functionalized NHC ligand precursor (L) in nearly quantitative yield (92%). Thereafter, the palladium(II) complex (1), was prepared by palladium metal promoted direct reaction between the NHC ligand precursor (L) and PdCl<sub>2</sub> without using any base.<sup>[27]</sup> The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of L (SI, Figure S7 and S8) and the complex 1 (SI, Figure S10 and S11) supported the proposed molecular structures shown in Scheme 1. A singlet at 10.54 ppm in <sup>1</sup>H NMR spectrum of L, related to the highly deshielded proton (H<sub>1</sub>) attached with the pre-carbene carbon (C<sub>1</sub>), is in the range reported previously for imidazolium salts ( $\delta$  9.5-12.0 ppm),<sup>[25]</sup> and suggests its high acidity. This <sup>1</sup>H NMR signal was not observed in the proton NMR of complex 1, which indicates the deprotonation of C<sub>1</sub> proton followed by the coordination with Pd(II). Furthermore, a most intense peak at (*m*/*z*) 402.1635 and 542.0305 in mass spectra of L and 1, respectively, correspond to [M–CI]<sup>+</sup>.

### **Crystal Structure**

The suitable quality single crystals of **1** were grown by slow evaporation of concentrated solution of **1** in CHCl<sub>3</sub>-CH<sub>3</sub>OH (4:1) at 0 °C. X-ray diffraction was recorded to establish the molecular structure of **1** (details of crystal data and refinements, see Table S1 of SI). The molecular structure of **1** with thermal ellipsoid is depicted in Figure 1 (for more detail, see Table S2 of SI). The geometry is nearly square planar and ligand is coordinated with metal centre in a bidentate ( $C_{NHC}^{-}S$ ) mode forming a sixmembered chelate ring. In complex **1**, the Pd-C<sub>NHC</sub> and Pd-S bond lengths, are found 1.970(3) and 2.2838(8) Å, respectively, and also in close agreement with the reported 1.976(4) and 2.2823(11) Å values, respectively.<sup>[25]c</sup>



Figure 1. Molecular Structure of 1 with Thermal Ellipsoids Set at the 30% Probability Level. H Atoms and a Molecule of  $CHCl_3$  are omitted for Clarity. Bond Lengths (Å): Pd(1)-C(1) 1.970(3), Pd(1)-S(1) 2.284(8), Pd(1)-Cl(1) 2.357(8), Pd(1)-Cl(2) 2.313(8); Bond angles (°): C(1)-Pd(1)-S(1) 91.91(8), S(1)-Pd(1)-Cl(1) 84.99(3), Cl(1)-Pd(1)-Cl(2) 92.25(3), Cl(2)-Pd(1)-Cl(1) 80.768).

# Evaluation of Catalytic Potential of 1 for Suzuki-Miyaura Coupling

The Pd(II) complex (1) was explored for catalytic investigation of Suzuki-Miyaura coupling and found efficient under aqueous and aerobic reaction conditions in water. 4-Bromobenzaldehyde was selected as a model substrate for preliminary investigations of catalysis. The solvents used in reaction also influence the course of reaction and yield of the product. After performing a series of reactions (Entries 1-5, Table 1), it was observed that water is the best solvent. It was found that 0.01 mol% of 1 is ideal for the reaction while further lowering in mol% of 1,

significantly reduced the yield of product (Entries 6-9, Table 1). The initial formation of desired products was detected after 20-30 minutes of the reaction, however, the best yield was obtained in 2 h.

while slight warming (up to 55 °C) was required to activate the inactivated aryl bromides.

	<b>Table</b> PhB(O	<ol> <li>Scope of Suzuki-Miya</li> <li>H)<sub>2</sub> + Br-aryl / heteroit</li> </ol>	aryl $coupling Reactions Usincomplex 1, K2CO3water, T °C Ph$	g 1 as Catalyst. —aryl / heteroaryl
1iyaura Coupling	Entry	Arvl/Heteroarvl	Coupling	[4]
	No.	Bromides	Products	Yield <sup>[a]</sup> (%)
<i>—</i> сно	1	Br-CHO	С-Сно	94 <sup>[b]</sup>
Yield (%) <sup>a</sup>	2			92 <sup>[b]</sup>
94	3	Br-CN		94 <sup>[b]</sup>
94				
75	4	BrNO2		86 <sup>[b]</sup>
85	_			<b>1</b> -3
25	5	Br-(COOH	COOH	82 <sup>[0]</sup>
94 65	6	Br		93 <sup>[b]</sup>
25 NC	7	Br-CH3		88 <sup>[c]</sup>
NC	8			83 <sup>[c]</sup>
88	9	Br		88 <sup>[c]</sup>
68 35	10	Br		85 <sup>[b]</sup>
nyde (1.0 mmol, me 2 h. NC (no	11	Br - N		85 <sup>[c]</sup>
	12	Br		88 <sup>[b]</sup>
aldehyde, 4- num reaction	13	Br		92 <sup>[b]</sup>
hat maximum her increasing	14	Br		93 <sup>[c]</sup>
r parameters, product.	15	Br-NO2		91 <sup>[b]</sup>
oserved in the of the base is	16	Br-NO2		82 <sup>[b]</sup>
Table 1). The as Na <sub>2</sub> CO <sub>3</sub> ,	17	Br-NO2		85 <sup>[c]</sup>

Table 1. Solvent, Base and Catalyst Optimization for Suzuki-M Catalyzed by 1.

-B(OH) <sub>2</sub> + Br - CHO complex 1 base, solvent - CHO				
Entry	Base	Solvent	<b>1</b> (mol%)	Yield (%) <sup>a</sup>
1	K <sub>2</sub> CO <sub>3</sub>	Water	0.01	94
2	K <sub>2</sub> CO <sub>3</sub>	DMF-water	0.01	94
3	K <sub>2</sub> CO <sub>3</sub>	DMF	0.01	75
4	K <sub>2</sub> CO <sub>3</sub>	Ethanol-water	0.01	85
5	K <sub>2</sub> CO <sub>3</sub>	THF	0.01	25
6	K <sub>2</sub> CO <sub>3</sub>	Water	0.05	94
7	K <sub>2</sub> CO <sub>3</sub>	Water	0.005	65
8	K <sub>2</sub> CO <sub>3</sub>	Water	0.001	25
9	K <sub>2</sub> CO <sub>3</sub>	Water	0.0005	NC
10	No base	Water	0.01	NC
11	Na <sub>2</sub> CO <sub>3</sub>	Water	0.01	85
12	Cs <sub>2</sub> CO <sub>3</sub>	Water	0.01	88
13	КОН	Water	0.01	65
14	NaOAc	Water	0.01	68
15	TEA	Water	0.01	35

Phenylboronic acid (1.3 mmol, 0.158 g), 4-bromobenzaldeh 0.185 g), base (2.0 mmol), solvent (5 mL), Temp. 55 °C, Tir conversion), <sup>a</sup> Isolated yield

The time profile of reaction for some r aryl/heteroaryl bromides such as 4-bromobenz bromoanisole, and 2-bromopyridine with optim conditions was studied (SI, Figure S13). It reveals the conversion can be achieved in 2 h, moreover furth the time of the reaction with maintaining the similar does not bring any significant change in the yield of

The formation of cross-coupled product was not ob absence of the base, it indicates that the presence an essential requisite for the reaction (Entry 10, reaction was optimized using various bases such Cs<sub>2</sub>CO<sub>3</sub>, KOH, and CH<sub>3</sub>COONa, and triethylamine (TEA). Of these, K<sub>2</sub>CO<sub>3</sub> was found most suitable (Yield 94%, Table 1, Entry 1). Other bases also work for the reaction but demand comperatively long time to bring the admirable conversions (Entry 11-15, Table 1).

The scope of the present coupling reaction was further explored for the several aryl and heteroaryl bromides with phenyl, substituted phenyl and nephthyl boronic acids and a high conversion of the coupling product was observed (Table 2). A significant transformation was also observed with deactivated substrates i.e. 4-bromoanisole (Entry 8, Table 2). For activated aryl bromides, the catalyst worked well at room temperature Catalyst loading (0.01 mol%, 1.0×10<sup>-4</sup> mmol); phenylboronic acid (1.3 mmol); Aryl/heteroaryl bromide (1.0 mmol); base (2.0 mmol); water (5 ml); time (2 h); [a] isolated yield, [b] at room temperature, [c] at 55 °C. (Entries 15-19; p-tolylboronic acid, 2-naphthylboronic acid and fluorophenylboronic acid were used)

CH<sub>3</sub>

75<sup>[c]</sup>

77<sup>[b]</sup>

During the catalytic investigations, the formation of black particles was experienced after 20-30 min of the reaction. The decomposition of Pd(II) complexes of sulfur-containing ligands to

18

19

## WILEY-VCH

Accepted Manuscrip

Pd(0) species and an equilibrium stage between NPs of Pd and the actual active species during the catalytic reaction, reported previously.<sup>[28-30]</sup> Here, we assumed that complex **1** is dispensers of real catalytic species, either directly or via some intermediate formation of nanophase.

To explore furthermore about the active catalyst, a typical reaction of 4-bromobenzaldehyde with phenylboronic acid catalyzed with 1 under optimum conditions was studied in detail and the black particles were isolated and subjected for detailed analysis with HR-TEM and TEM-EDX. The HR-TEM images (Figure 2) of the black material indicates the uniformly dispersed spherical NPs and the size of 70% particles are in the range of ~1.5-2.0 nm (inset Figure 2b). These NPs can be formulated as Pd<sub>2</sub>S on the basis of quantitative % determined through TEM-EDX analysis (SI, Figure S14).<sup>[25]a</sup>



Figure 2. HR-TEM Images of Pd-S NPs Formed From 1 at Some Stage of Present Suzuki-Miyaura Coupling (a) at 100 nm Scale Bar (b) at 10 nm Scale Bar and Size Distribution (Inset) (c) at 5 nm Scale Bar (d) Zoom In Image of Focused Area by a Red Square Shape (See SI, Figure S14 For TEM-EDX Analysis).

The catalytic potential of isolated NPs was also investigated for some of the typical Suzuki-Miyaura coupling substrates *i.e.*, 4bromobenzaldehyde and PhB(OH)<sub>2</sub> under similar reaction conditions, the average yield (55%) of the product was obtained with 10 mg of Pd<sub>2</sub>S NPs. Moreover, the NPs deactivated in one cycle and failed to couple 4-bromoanisole (deactivated substrate), it might be due to the probable leaching of active discrete Pd in the solution during catalysis.

# Immobilization of 1 onto the surface of $Fe_3O_4@SiO_2$ core/shell NPs

To overcome the reusability issue of catalyst, **1** was immobilized onto the surface of silica coated magnetite NPs, and heterogeneous magnetically retrievable catalyst (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-

1') was obtained. The amide functionality, present on the side arm of NHC ligand of 1 served as a linker to connect the NHC-Pd(II) complex with amino propyl functionalized silica coated magnetite NPs  $[Fe_3O_4@SiO_2-(CH_2)_3-NH_2]$ . A stepwise modification strategy onto the surface of the silica coated magnetite NPs was affianced for developing a heterogeneous Pd(II)-NHC catalyst (Scheme 2).



Scheme 2. Schematic Illustration of Synthesis of Solid Supported Magnetically Retrievable Pd(II)-NHC Catalyst ( $Fe_3O_4@SiO_2$ -1').

Fe<sub>3</sub>O<sub>4</sub> NPs were synthesized using a previously reported procedure.<sup>[31]</sup> Because of the aggregation tendency of free magnetic NPs and corroding tendency with acids; their coating with silica seems favourable. Moreover, the shell of silica around Fe<sub>3</sub>O<sub>4</sub>, also helps in providing active sites (Si-OH groups) for further surface modification. Therefore, the silica-coating of freshly synthesized Fe<sub>3</sub>O<sub>4</sub> NPs was performed by a known method (sol-gel approach).<sup>[32]</sup> Thereafter, the introduction of amine functionalities onto the surface of the core-shell NPs (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>), was obtained using 3-aminopropyl triethoxysilane.[33] The aminopropyl functionalized silica-coated magnetite NPs (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-amine) were further reacted with chloroacetyl chloride that lead to the covalent immobilization of chloromethyl-amide onto the surface of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-amine resulted in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-amide-CH<sub>2</sub>CI NPs. Further, the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-amide-CH<sub>2</sub>Cl NPs on reaction with 1-(2phenylsulfanyl-ethyl)-1H-benzimidazole (B) resulted in covalent immobilization of N-heterocyclic carbene ligand on the modified NPs. Finally, the supported NHC ligand precursor (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-L') were treated with PdCl<sub>2</sub> (using the analogous procedure

## WILEY-VCH

Accepted Manuscrip

employed in the synthesis of 1) to produce the solid supported palladium catalyst (Fe $_3O_4@SiO_2-1'$ ).

In the powder X-ray pattern (Figure 3) of core/shell NPs (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>), six characteristic Bragg's peaks centered at 30.2°, 35.6°, 43.3°, 53.7°, 57.1° and 62.7° (20) were observed, which corroborate the crystal planes (220), (311), (400), (422), (511) and (440) reported in standard JCPDS card No. 019-0629. Additionally, the appearance of a broad peak centered at 21.2° is attributed to the presence of amorphous SiO<sub>2</sub> shell around the Fe<sub>3</sub>O<sub>4</sub> core.<sup>[32]</sup>



Figure 3. Powder X-ray of Silica Coated Magnetite NPs.

FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-amine, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-amide-CH<sub>2</sub>Cl, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-L' and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1' found in close aggreement with the qualitative identifications of functional groups present in the various NPs (Figure 4).



Figure 4. FT-IR Spectra of (i) Fe<sub>3</sub>O<sub>4</sub>, (ii) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, (iii) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-amine, (iv) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-amide-CH<sub>2</sub>Cl, (v) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-L' and (vi) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1'.

The distinguished Fe-O stretching vibrations at 593 cm<sup>-1</sup> and a broad band at 3344 cm<sup>-1</sup> are attributable to OH groups present on the surface of magnetite NPs.<sup>[34]</sup> Furthermore, the Si-O-Si symmetric, Si-O symmetric and Si-O-Si asymmetric stretching vibration of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> observed at 802, 959 and 1103 cm<sup>-1</sup> respectively.<sup>[32]</sup> A considerably decreased less intense band of Fe-O stretching was recorded for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>. It establishes the structural differences between the pure and silica-coated magnetite NPs and also supports the presence of silica-shell around Fe<sub>3</sub>O<sub>4</sub> core. The subsequent modification on to the surface of core-shell magnetic nanosupport by 3aminopropyltriethoxysilane (APTES) is identified by the appearance of two distinct bands 2925 cm<sup>-1</sup> and 1630 cm<sup>-1</sup> of CH<sub>2</sub> and NH<sub>2</sub> groups, respectively. An intense band appearing at 1640 cm<sup>-1</sup> indicates the C=O stretching vibrations of amido functional group present in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-amide-CH<sub>2</sub>CI NPs. The FT-IR spectrum of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-L' shows the significant blue shift in C=O stretching vibration and supports its formation. Additionally, the noticeable shift in all bands was found in order to suggest a coordinate bond formation between the metal and ligand. The size and shape of the final solid supported palladium catalyst was analyzed by transmission electron microscopy (TEM). The TEM micrograph of freshly prepared Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1' shows the range of 20-25 nm sized NPs with a dark nano-Fe<sub>3</sub>O<sub>4</sub> core surrounded by a grey spongy silica shell [Figure 5(b)].



Figure 5. (a) TEM Images of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1' NPs and Size Distribution Plot (inset) and (b) Zoom In Image of the Red Square Focused Area Showing Presence of Core-Shell Morphology (See SI, Figure S15 for TEM-EDX analysis).

No separate silica aggregates were seen in the TEM image of SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>-1' NPs, which confirmed the coating of silica NPs on the surface of the magnetic core. The Debye Scherrer formula was used for the determination of average crystallite size of the Fe<sub>3</sub>O<sub>4</sub> NPs using the peak of highest intensity observed in powder X-ray patterns (Figure 3) *i.e.*, the (311) peak in present case and estimated to be 24 nm which is also consistent with the size observed in TEM of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> NPs. The TEM-EDX analysis confirmed the availability of all the constituent elements in the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1' NPs, and also revealed a successful immobilization of NHC-Pd(II) complex 1 on to the surface of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> NPs (SI, Figure S15). Moreover, there was no occurrence of Pd in the NPs form was found on the surface of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1' NPs; this supports the fact that the available Pd in the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1' NPs is in the molecular complex form. The ICP-AES analysis indicates the

5

0.128 mmol/g (1.369% Pd by weight) of Pd content in the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1'. The core-level XPS analysis of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1' was also performed to ascertain the oxidation state of Pd (SI, Figure S16). The XPS spectrum of Pd shows the two characteristic peaks at binding energy of 339.3 eV and 344.7 eV due to the  $3d^{5/2}$  and  $3d^{3/2}$  states, respectively, this confirmed the +2 oxidation state of palladium in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1' NPs.<sup>[35]</sup>

# Evaluation of Supported Palladium Catalyst (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1') for Suzuki-Miyaura Coupling

The catalytic potential of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1' was explored for Suzuki-Miyaura coupling of several aryl/heteroaryl bromides and the results are summarized in Table 3. A systematic evaluation of the results revealed that 20 mg of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1' is an ideal amount to produce the best results in 2 h at 55 °C in water. The magnetically active Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1' NPs fully recovered after completion of the reaction by an external magnet; moreover, catalyst still maintained its efficiency. After isolation of catalyst, the obtained liquid was cooled down to room temperature and analytically pure coupling product was extracted in diethyl ether.

### Recyclability of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1'

After completion of the reaction, the catalyst was separated by an external magnet. The isolated catalyst was washed with water followed by methanol and then dried under vacuum and reused for the present reaction. We have continuously explored the catalyst up to the seven cycles. The experimental details and %yield of each run is separately provided in SI, Table S3. The 85% transformation was recorded in the 7<sup>th</sup> cycle, hence, it indicates the high potential and robustness of the catalyst towards the Suzuki-Miyaura coupling.

### Nature of Catalysis: Homogeneous or Heterogeneous

The heterogeneity of the catalyst Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1' was examined using a hot filtration test. The Suzuki reaction of 4bromobenzaldehyde with phenyl boronic acid under optimum conditions was executed. When formation of cross coupled product in the reaction reached up to ~42% (NMR yield after 50 min of reaction), the reaction was stopped and the catalyst was magnetically separated. The clear reactions mixture was divided in two halves; one half was transferred into another round bottom flask for reaction to run while the isolated NPs were added into the remaining half. Both reactions were allowed to run under same reaction conditions for another 2 h and product formation was estimated by proton NMR. The conversion exceed up to 94%, in the flask containing the catalyst, while in the catalyst-free flask yield of desired product reached only to 49%. Here, we assumed, the palladium complex immobilized onto the surface of magnetic NPs generates palladium-sulfide NPs followed by the deposition onto the surface of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> NPs. There are reports available where the metal coordinated onto the surface of the solid material becomes stabilized after forming the metal NPs through the deposition-reduction process.[36]

## WILEY-VCH

Accepted Manuscrip

Table 3.	Catalytic	Investigation	of	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -1'	for	Suzuki-Miyaura
Coupling of Aryl/hetero-aryl Bromides with Aryl Boronic Acids.						

Entry	Aryl/Heteroaryl	Coupling	Yield <sup>[a]</sup>
No	Bromides	Products	(%)
1	Br-CHO	СНО	93 <sup>[b]</sup>
2	Br-COCH3		91 <sup>[b]</sup>
3	Br		94 <sup>[b]</sup>
4	Br-NO2		88 <sup>[b]</sup>
5	Br-COOH	С-соон	80 <sup>[b]</sup>
6	Br		92 <sup>[b]</sup>
7	Br-CH3		90 <sup>[c]</sup>
8			78 <sup>[c]</sup>
9	Br		85 <sup>[c]</sup>
10	Br		83 <sup>[b]</sup>
11	Br — N		82 <sup>[c]</sup>
12	Br		91 <sup>[b]</sup>
13	Br		92 <sup>[b]</sup>
14	Br		94 <sup>[c]</sup>
15	Br-NO2	H <sub>3</sub> C-	92 <sup>[b]</sup>
16	Br-NO2		85 <sup>[b]</sup>
17	Br-NO2		88 <sup>[c]</sup>
18	Br-NO2		78 <sup>[c]</sup>
19	Br-CH3		84 <sup>[b]</sup>

Catalyst (0.02 g, Wt% of Pd 1.369%, 0.128 mmol/g, 0.002 mmol Pd, 0.2 mol% Pd); aryl/heteroaryl bromide (1.0 mmol); phenylboronic acid (1.3 mmol); base (2.0 mmol), solvent (5 mL), time (2 h); [a] isolated yield, [b] at room temperature, [c] at 55 °C. (Entries 15-19; *p*-tolylboronic acid, 2-naphthylboronic acid and 4-fluorophenylboronic acid were used)

Moreover, the leaching of discrete Pd(0) was tested using ICP-AES analysis of  $Fe_3O_4@SiO_2-1'$  before and after the three catalytic cycles. Wt% of Pd in the catalyst was recorded before the catalysis (1.369%) and after three cycles it was slightly reduced to 1.110%. However, no further significant changes in Pd content was noticed even after seventh catalytic cycle. This

WILEY-VCH

observation favors a largely heterogeneous nature of catalysis. A two phase test<sup>[37]</sup> (SI, Page No. S21, Scheme S1) was also conducted to establish the heterogeneous or homogeneous nature of the catalysis. A mixture of 4-bromoacetophenone and 4-bromobenzoic acid immobilized on silica (as amide) and phenylboronic acid, were allowed to react under optimum reaction conditions. The liquid part of the reaction was filtered, desired product was extracted in diethylether and ~95% yield of 4-acetylbiphenyl was recored in <sup>1</sup>H NMR. Furtheromore, the remaining solid residue of reaction mixture was hydrolyzed, and after workup the resulting products were analyzed with <sup>1</sup>H NMR. It indicates ~15% of the immobilized 4-bromobenzoic acid (as amide) was converted to the cross-coupled product. These observations suggest the minor leaching of homogeneous Pd species (molecular or colloidal, responsible for homogeneous catalysis) from the nanocatalyst. Thus, it proved that coupling catalyzed with the solid supported Pd catalyst Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1', is significantly in heterogeneous manner.

Furthermore, based on various reaction parameters (optimum catalyst loading, reaction temperature, time, or atmosphere), a comparison of catalytic performance of 1 with the previously reported N or P donor functionalized NHC-Pd(II) catalysts has been made and provided in supporting informations (SI, Table S4). It appears that the present Pd(II) complex 1 can be labeled as efficent catalyst; since, 94% yield in 2 h under aqueous/aerobic reaction conditions was recorded. The noted superior catalytic activity of 1 is attributed to the unique  $\sigma$ -donor and weak *n*-acceptor properties of NHCs along with the air/moisture insensitivity and ease of handling and synthesis of thioether functionalized ligands which have made them viable alternatives to classical air/moisture sensitive phosphine based Pd-catalysts.<sup>[5]</sup> The catalytic activity of NHC-Pd(II) (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1') was also found either superior or comparable with the previously reported solid supported NHC-Pd catalysts (See SI, Table S5). However, the homogeneous version (complex 1) of the catalyst Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1' has higher catalytic activity in term of catalyst loading but unfortunately deactivated after one cycle. The solid supported catalyst Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1' was found excellent due to the intact feature of reusability and recyclability upto 7<sup>th</sup> cycles. It has been assumed, the excessive binding capabilities of free amines or amide present onto the surface of core-shells Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-amide-NH<sub>2</sub> NPs with PdCl<sub>2</sub> at some stage of immobilization are responsible to raised the Pd content in TEM-EDX anaylsis.

## Conclusions

Synthesis of general and silica encapsulated magnetic solid supported Pd(II) complexes of thioether containing NHC and their comparative study of catalytic activity for Suzuki-Miyaura coupling was explored with the homo- and heterogeneous version of the catalyst. The structure of homogeneous catalyst 1 was established with X-ray crystallography. Both homogeneous and heterogeneous catalytic systems are easy to handle, synthesize, and stable in air/moisture. We are the first to report the silica encapsulated magnetic NPs supported Pd(II) complex using thioether based NHC. The two-phase test indicates, the Pd(0) leaching makes the catalytic process of **1**, homogeneous while in case of solid supported catalyst **2**, leaching of Pd(0) is negligible and catalytic process is largely heterogeneous. The catalyst recovery by an external magnet and continuously reuse for 7 cycles without losing catalytic strength are the novel and highly desirable features in the development of sustainable processes. At last, the formation of a novel thioether based NHC-Pd(II) catalyst works in feasible reaction conditions at low temperature in aqueous green solution which further make the process more effective and economical benign.

## **Experimental Section**

#### Synthesis of 1-(2-Chloroethyl)-1H-benzimidazole (A)

A mixture of benzimidazole (1.772 g, 15.0 mmol), potassium carbonate (4.146 g, 30.0 mmol) and tetra-n-butylammonium bromide (1.612 g, 5.0 mmol) in 50 mL of 1,2-dichloroethane was stirred under reflux for 24 h. A light yellow suspension observed was extracted in dichloromethane (50 mL). The solvent was completely removed on rotary evaporator and resulting residue was purified by column chromatography on silica gel. which affords the off-white crystalline solid of the product. Off-white solid, Yield: 2.298 g (85%). Mp: 78 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.91 (s, 1H, H<sub>1</sub>), 7.84-7.80 (m, 1H, H<sub>3</sub>), 7.34-7.28 (m, 3H, H<sub>5</sub>, H<sub>4</sub> and H<sub>6</sub>), 4.40 (t, J = 6.0 Hz, 2H, H<sub>8</sub>), 3.77 (t, J = 6.0 Hz, 2H, H<sub>9</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm): 143.7 (C<sub>7</sub>), 143.2 (C<sub>1</sub>), 133.2 (C<sub>2</sub>), 123.1 (C<sub>4</sub>), 122.3 (C5), 120.5 (C6), 109.0 (C3), 46.4 (C8), 42.0 (C9). Mass (CH3CN)  $[M+H]^+$  (*m/z*) Found: 181.0753; Calc. value for  $[C_9H_{10}CIN_2]^+$ : 181.0527. FT-IR (KBr, v<sub>max</sub>/cm<sup>-1</sup>): 3057 (m, v<sub>C-H aromatic</sub>), 2961 (m, v<sub>C-H aliphatic</sub>), 1614 (s,  $v_{C=N \text{ aromatic}}$ ), 1493 (s,  $v_{C=C \text{ aromatic}}$ ), 1257 (m,  $v_{C=N \text{ aliphatic}}$ ), 742 (s,  $v_{C-H}$ aromatic), 664 (s, V<sub>C-Cl aliphatic</sub>).

#### Synthesis of 1-(2-Phenylsulfanyl-ethyl)-1H-benzimidazole (B)

The ethanolic solution 30 ml of sodium hydroxide (0.200 g, 5.0 mmol) and thiophenol (0.551 g, 5.0 mmol) was refluxed for 30 minutes. 20 mL solution of 1-(2-Chloroethyl)-1H-benzimidazole (0.903 g, 5.0 mmol) in ethanol was added to it and further allowed to stirred under reflux for 12 h. Thereafter, extraction in chloroform (4  $\times$  25 mL), the extract was washed with water (3 × 40 mL) and dried over anhydrous sodium sulphate. The solvent removed under reduced pressure and obtained product was purified by column chromatography on silica gel. Yellow oil, Yield: 1.079 g (85%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.80 (s, 1H, H<sub>1</sub>), 7.76–7.69 (m, 1H, H<sub>3</sub>), 7.34–7.16 (m, 8H, H<sub>5</sub>, H<sub>4</sub>, H<sub>13</sub>, H<sub>12</sub>, H<sub>11</sub> and H<sub>6</sub>), 4.27 (t, J =6.9 Hz, 2H, H<sub>8</sub>), 3.24 (t, J = 6.9 Hz, 2H, H<sub>9</sub>). <sup>13</sup>C{<sup>1</sup>H}NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 142.9 (C<sub>7</sub>), 142.6 (C<sub>1</sub>), 133.4 (C<sub>10</sub>), 132.7 (C<sub>2</sub>), 129.5 (C11), 128.6 (C12), 126.4 (C13), 122.4 (C5), 121.6 (C4), 119.6 (C6), 108.9 (C<sub>3</sub>), 43.3 (C<sub>8</sub>), 32.9 (C<sub>9</sub>). Mass (CH<sub>3</sub>CN) [M+H]<sup>+</sup> (*m/z*) Found: 255.1145; Calc. value for [C<sub>15</sub>H<sub>15</sub>N<sub>2</sub>S]<sup>+</sup>: 255.0950. FT-IR (KBr, v<sub>max</sub>/cm<sup>-1</sup>): 3055 (m,  $v_{C-H \text{ aromatic}}$ ), 2929 (m,  $v_{C-H \text{ aliphatic}}$ ), 1613 (s,  $v_{C=N \text{ aromatic}}$ ), 1582 (s,  $v_{C=C}$ aromatic), 1248 (m, v<sub>C-N aliphatic</sub>), 738 (s, v<sub>C-H aromatic (bending)</sub>).

#### Synthesis of 1-[*N*-Benzylacetamido]-3-[1-(2-phenylsulfanylethyl)]benzimidazolium Chloride (L)

Mixture of 1-(2-phenylsulfanylethyl)-1*H*-benzimidazole (0.254 g, 1.0 mmol) and *N*-benzyl-2-chloroacetamide (0.183 g, 1.0 mmol) in 10 mL of toluene was stirred under reflux in an inert atmosphere to give **L** as white solid which was precipitated in reaction medium after 12 h. The reaction mixture was filtered; the obtained residue was washed with toluene and

dried *in vacuo* yielding L as white solid. White solid, Yield: 0.402 g (92%). Mp: 128 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 10.54 (s, 1H, H<sub>1</sub>), 9.92 (t, J = 5.8 Hz, 1H, N<u>H</u>), 7.88 (dd, J = 6.0, 3.1 Hz, 1H, H<sub>5</sub>), 7.62-7.48 (m, 2H, H<sub>6</sub>, H<sub>3</sub>), 7.40 (dd, J = 5.9, 3.1 Hz, 1H, H<sub>4</sub>), 7.29 (dd, J = 8.6, 4.9 Hz, 4H, H<sub>12</sub>, H<sub>19</sub>), 7.24-7.14 (m, 5H, H<sub>18</sub>, H<sub>11</sub>, H<sub>20</sub>), 7.11 (d, J = 7.1 Hz, 1H, H<sub>13</sub>), 5.59 (s, 2H, H<sub>14</sub>), 4.62 (t, J = 6.3 Hz, 2H, H<sub>8</sub>), 4.37 (d, J = 5.9 Hz, 2H, H<sub>16</sub>), 3.50 (t, J = 6.3 Hz, 2H, H<sub>9</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 164.41 (C<sub>15</sub>), 143.11 (C<sub>1</sub>), 138.02 (C<sub>17</sub>), 132.98 (C<sub>10</sub>), 131.77 (C<sub>7</sub>), 130.86 (C<sub>2</sub>), 130.72 (C<sub>18</sub>), 129.33 (C<sub>19</sub>), 128.38 (C<sub>11</sub>), 127.82 (C<sub>12</sub>), 127.51 (C<sub>6</sub>), 127.37 (C<sub>3</sub>), 127.05 (C<sub>13</sub>, C<sub>20</sub>), 114.59 (C<sub>5</sub>), 112.16 (C<sub>4</sub>), 49.89 (C<sub>14</sub>), 46.97 (C<sub>8</sub>), 43.53 (C<sub>16</sub>), 33.45 (C<sub>9</sub>). Mass (CH<sub>3</sub>CN) [M–CI]<sup>+</sup> (*m*/*z*) Found: 402.1635; Calc. value for [C<sub>24</sub>H<sub>24</sub>N<sub>3</sub>OS]<sup>+</sup>: 402.1635. FT-IR (KBr, v<sub>max</sub>/cm<sup>-1</sup>): 3199 (m, v<sub>N+H amide</sub>), 3045 (m, v<sub>C-H atomatic</sub>), 2817 (m, v<sub>C-H atomatic</sub>), 753 (s, v<sub>C-H atomatic</sub>)).

### Synthesis of [Pd(L-HCI)Cl<sub>2</sub>] (1)

A mixture of L (0.219 g, 0.5 mmol), PdCl<sub>2</sub> (0.089 g, 0.5 mmol) in 10 mL of DMF was stirred under inert atmosphere at 90 °C for 12 h. Thereafter, the volatiles were removed by a rotary evaporator. The residue was dissolved in minimum amount of dichloromethane. After addition of diethyl ether, a pale yellow solid precipitated which was isolated by filtration and dried under vacuum. The product was dissolved in CH2CI2- $CH_3OH$  (4:1) and suitable quality single crystals were grown by slow evaporation. Pale yellow solid, Yield: 0.263 g, 91%. Mp: 195 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ (ppm): 9.25-8.98 (br m, 1H, N<u>H</u>), 7.79-7.63 (br m, 4H,  $H_{3^{-6}}),\,7.36$  (br m, 10H,  $H_{18^{-20}},\,and$   $H_{11^{-13}}),\,5.71$  (br s, 2H,  $H_{14}),\,5.00$ (br s, 1H, H\_8), 4.89 (br s, 1H, H\_8), 4.38 (br s, 2H, H\_{16}), 3.80-3.56 (br m, 1H, H<sub>9</sub>), 3.17-3.09 (br m, 1H, H<sub>9</sub>).  $^{13}C$  NMR (101 MHz, DMSO-d\_R)  $\delta$ (ppm): 166.0 ( $C_{15}$ ), 138.8 ( $C_{17}$ ), 134.23 ( $C_{10}$ ), 132.75 ( $C_7$ ), 132.53 ( $C_2$ ), 129.51 (18), 128.36 (C19), 127.86 (C11), 127.36 (C12), 126.89 (C6), 125.73 (C<sub>3</sub>), 124.16 (C<sub>20</sub>), 123.93 (C<sub>13</sub>), 112.01 (C<sub>5</sub>), 111.72 (C<sub>4</sub>), 50.34 (C<sub>14</sub>), 46.58 (C<sub>8</sub>), 42.51 (C<sub>16</sub>), 30.33 (C<sub>9</sub>). Mass (CH<sub>3</sub>CN) [M-CI]<sup>+</sup> (*m/z*) Found: 542.0305; Calc. value for [C24H23CIN3OPdS]+: 542.0302. FT-IR (KBr, v<sub>max</sub>/cm<sup>-1</sup>): 3324 (m, v<sub>N-H amide</sub>), 3059 (m, v<sub>C-H aromatic</sub>), 2944 (m, v<sub>C-H aliphatic</sub>), 1687 (s,  $v_{C=O}$ ), 1622 (s,  $v_{C=C \text{ aromatic}}$ ), 1248 (m,  $v_{C-N \text{ aliphatic}}$ ), 745 (s,  $v_{C-H}$ aromatic (bending)).

#### Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-amide-CH<sub>2</sub>CI

After the dropwise addition of chloroacetyl chloride (excess) to a solution of nanostructured Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-amine (1.00 g) dispersed in 25 mL of 1,2-dichloroethane and triethylamine (10 mmol) with maintaining the temperature between 0-5 °C, the mixture was overnight stirred at room temperature. A brownish material was observed which was isolated from the reaction mixture by means of an external magnet. It was washed several times with water, saturated solution of sodium chloride and again with water. Finally, it was dried under vacuum and NPs of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-amide-CH<sub>2</sub>Cl obtained.

### Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-L'

 $Fe_3O_4@SiO_2$ -amide-CH\_2Cl (1.00 g) dispersed in 10 mL of toluene through 30 min. sonication, further it was stirred for next 12 h under reflux with 1-(2-phenylsulfanylethyl)-1*H*-benzimidazole (0.254 g, 1.0 mmol). A brownish material was formed which was isolated from the mixture by use of an external magnet. It was washed with toluene (25 mL), and dried under *vacuo* to obtain Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-L' NPs.

### Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1'

A mixture of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-L' (1.0 g) NPs dispersed in dry DMF (10 mL) and PdCl<sub>2</sub> (0.089 g, 0.5 mmol) was stirred at 90 °C for 12 h under nitrogen atmosphere. The Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1' formed and isolated by using

Accepted Manuscript

an external magnet, washed with methanol (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and dried *in vacuo*.

#### General Procedure for Suzuki-Miyaura Coupling Reaction

A mixture of phenylboronic acid (0.159 g, 1.3 mmol),  $K_2CO_3$  (0.276 g, 2.0 mmol), aryl/hetero aryl bromide (1.0 mmol) and palladium catalyst in appropriate solvent (5 mL) was stirred under ambient conditions. The reaction was monitored with TLC until maximum conversion of aryl bromide to the desired product observed. On completion, the reaction mixture was extracted with diethyl ether (2 × 20 mL). The solvent was removed in vacuo, the residue was considered chromatographic work up on silica gel column, and desired cross-coupled product was isolated.

#### Isolation of in situ Generated Nanoparticles from Pd(II)-complex (1) During Suzuki-Miyaura Coupling

A mixture of 4-bromoanisole (0.185 g, 1.0 mmol), phenylboronic acid (0.159 g, 1.3 mmol), K<sub>2</sub>CO<sub>3</sub> (0.276 g, 2.0 mmol) and Pd(II)-complex 1 (0.288 g, 0.5 mmol) in water (5.0 mL) was stirred under ambient conditions for 2 h. Thereafter, the solvent was decanted and the black residue was thoroughly washed with water-acetone (1:3) and subjected to further analytical characterization.

## **Supporting Information**

Physical measurements, chemical/reagents used, NMR spectra; mass spectra; crystal and refinement data; bond lengths and angles; CIF of 1 (CCDC No. 1585446); TEM-EDX, XPS and the two-phase test.

### Acknowledgements

R.K.J. thanks to Council of Scientific and Industrial Research (CSIR) for financial support (01(2760)/13/EMR-II). K.N.S. thanks to Science and Engineering Research Board (SERB), New Delhi for start-up research grant (YSS/2015/000698). Authors acknowledge the MRC, MNIT Jaipur for characterization facilities. SIC, IIT Indore for single crystal X-ray and SAIF, IIT Bombay for ICP-AES analyses.

**Keywords:** Thioether-NHC • core/shell NPs • magnetically retrievable • Heterogeneous Catalysis • Suzuki-Miyaura Coupling

- a) A. Suzuki, Angew. Chem. Int. Ed. 2011, 50, 6722-6737; b) A. Suzuki, J. Organomet. Chem. 1999, 576, 147-168.
- a) C. Valente, M. Organ, Boronic Acids: Preparation and Applications in Organic Synthesis and Medicine (D. G. Hall, Ed.) Wiley-VCH, vol. 2, 2005, chap. 4, pp. 213-262; b) J. Liu, J. J. Lavigne Boronic Acids: Preparation and Applications in Organic Synthesis and Medicine (D. G. Hall, Ed.) Wiley-VCH, vol. 2, 2005, chap. 14, pp. 612-676; c) J.-P. Wan, C. Wang, R. Zhou, Y. Liu, RSC Advances 2012, 2, 8789-8792.
- [3] J. Magano, J. R. Dunetz, Chem. Rev. 2011, 111, 2177-2250.
- [4] M. Beller, H. U. Blaser Organometallics as Catalysts in the Fine Chemical Industry Springer Berlin Heidelberg, 2012.
- [5] C. A. Fleckenstein, H. Plenio, Chem. Soc. Rev. 2010, 39, 694-711.
- [6] V. Calo, A. Nacci, A. Monopoli, J. Organomet. Chem. 2005, 690, 5458-5466.

- [7] a) F. Bellina, A. Carpita, R. Rossi, *Synthesis* 2004, *15*, 2419-2440; b) R.
   B. Bedford, C. S. J. Cazin, D. Holder, *Coord. Chem. Rev.* 2004, *248*, 2283-2321; c) A. F. Littke, G. C. Fu, *Angew. Chem., Int. Ed.* 2002, *41*, 4176-4211; d) J. Dupont, C. S. Consorti, J. Spencer, *Chem. Rev.* 2005, *105*, 2527-2572.
- [8] a) N. T. S. Phan, D. H. Brown, H. Adams, S. E. Spey, P. Styring, *Dalton Trans.*, **2004**, 1348-1357; b) L. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133-173; c) V. Polshettiwar, R. S. Varma, *Chem.-Eur. J.* **2009**, *15*, 1582-1586; d) A. E. C. Collis, I. T. Horváth, *Catal. Sci. Technol.* **2011**, *1*, 912-919.
- [9] V. Polshettiwar, C. Len, A. Fihri, Coord. Chem. Rev. 2009, 253, 2599-2626.
- [10] D. Wang, D. Astruc, Chem. Rev., 2014, 114, 6949-6985.
- [11] S. J. Hoseini, V. Heidari, H. Nasrabadi, J. Mol. Catal. a. Chem. 2015, 396, 90-95.
- [12] E. Nehlig, B. Waggeh, N. Millot, Y. Lalatonne, L. Motte, E. Guenin, *Dalton Trans.* 2015, 44, 501-505.
- [13] A. Papp, G. Galbács, Á. Molnár, Tetrahedron Lett. 2005, 46, 7725-7728.
- [14] S. Paul, Md. M. Islam, S. M. Islam, RSC Adv. 2015, 5, 42193-42221.
- [15] C. Schmöger, T. Szuppa, A. Tied, F. Schneider, A. Stolle, B. Ondruschka, *ChemSusChem* 2008, *1*, 339-347.
- [16] H. L. Ding, Y. X. Zhang, S. Wang, J. M. Xu, S. C. Xu, G. H. Li, *Chem. Mater.* 2012, 24, 4572-4580.
- [17] Z. Yan-Qi, W. Xian-Wen, Y. Rui, *Catal. Lett.* **2010**, *135*, 256-262.
- [18] X. Jin, K. Zhang, J. Sun, J. Wang, Z. Dong, R. Li, *Catal. Commun.* 2012, 26, 199-203.
- [19] P. D. Stevens, J. Fan, H. M. R. Gardimalla, M. Yen, Y. Gao, Org. Lett. 2005, 7, 2085-2088.
- [20] J. Wang, B. Xu, H. Sun, G. Song, Tetrahedron Lett. 2013, 54, 238-241.
- a) P. Li, L. Wang, L. Zhang, G.-W. Wang, *Adv. Synth. Catal.* 2012, *354*, 1307-1318; b) A. Schätz, T. R. Long, R. N. Grass, W. J. Stark, P. R. Hanson, O. Reiser, *Adv. Funct. Mater.* 2010, *20*, 4323-4328; c) S. Shylesh, L. Wang, W. R. Thiel, *Adv. Synth. Catal.* 2010, *352*, 425-432.
- [22] W. A. Herrmann, Angew. Chem., Int. Ed. 2002, 41, 1290-1303.
- [23] a) A. Kumar, G. K. Rao, S. Kumar, A. K. Singh, *Dalton Trans.* 2013, 42, 5200-5223; b) A. Kumar, G. K. Rao, F. Saleem, A. K. Singh, *Dalton*

*Trans.* **2012**, *41*, 11949-11977; c) A. Kumar, G. K. Rao, A. K. Singh, *RSC Adv.* **2012**, *2*, 12552-12574; d) L. Luconi, Z. Gafurov, A. Rossin, G. Tuci, O. Sinyashin, D. Yakhvarov, G. Giambastiani, *Inorg. Chim. Acta* **2018**, *470*, 100-105.

- [24] O. Kühl, Chem. Soc. Rev. 2007, 36, 592-607.
- [25] a) K. N. Sharma, H. Joshi, A. K. Sharma, O. Prakash, A. K. Singh, *Organometallics* 2013, *32*, 2443-2451; b) C. Fliedel, P. Braunstein, *Organometallics* 2010, *29*, 5614-5626; c) C. Fliedel, A. Sabbatini, P. Braunstein, *Dalton Trans.* 2010, *39*, 8820-8828; d) P. Dubey, S. Gupta, A. K. Singh, *Dalton Trans.* 2017, *46*, 13065-13076.
- [26] D. Bogdal, K. Jaskot, Synth. Commun. 2000, 30, 3341-3352.
- [27] H. M. Lee, J. Y. Zeng, C.-H. Hu, M.-T. Lee, *Inorg. Chem.* 2004, 43, 6822-6829.
- [28] D. Zim, S. M. Nobre, A. L. Monteiro, J. Mol. Catal. A: Chem. 2008, 287, 16-23.
- [29] K. N. Sharma, H. Joshi, V. V. Singh, P. Singh, A. K. Singh, Dalton Trans. 2013, 42, 3908-3918.
- [30] F. Saleem, G. K. Rao, P. Singh, A. K. Singh, Organometallics 2013, 32, 387-395.
- [31] S. Wang, Z. Zhang, B. Liu, J. Li, Catal. Sci. Technol. 2013, 3, 2104-2112.
- [32] Q. Zhang, H. Su, J. Luo, Y. Wei, Green Chem. 2012, 14, 201-208.
- [33] F. Liu, F. Niu, N. Peng, Y. Su, Y. Yang, RSC Adv. 2015, 5, 18128-18136.
- [34] K. Petcharoena, A. Sirivat, Mater. Sci. Eng., B 2012, 177, 421-427.
- [35] Q. Deng, Y. Shen, H. Zhu, Chem. Commun. 2017, 53, 13063-13066.
- [36] a) N. J. S. Costa, L. M. Rossi, *Nanoscale* 2012, *4*, 5826-5834; b) A.
   Fihri, M. Bouhrara, B. Nekoueishahraki, J.-M. Basset, V. Polshettiwar, *Chem. Soc. Rev.* 2011, *40*, 5181-5203; c) S. Natour, R. Abu-Reziq,
   *RSC Adv.* 2014, *4*, 48299-48309; d) J. Manna, S. Akbayrak, S. Özkar,
   *RSC Adv.* 2016, *6*, 102035-102042.
- [37] a) J. Rebek, F. Gavina, J. Am. Chem. Soc. 1974, 96, 7112-7114; b) J.
   Rebek, D. Brown, S. Zimmerman, J. Am. Chem. Soc. 1975, 97, 454-455; c) I. W. Davies, L. Matty, D. L. Hughes, P. J. Reider, J. Am. Chem. Soc. 2001, 123, 10139-10140.

## WILEY-VCH

# Entry for the Table of Contents



Dr. Kamal Nayan Sharma,\* Mr. Naveen Satrawala, and Dr. Raj Kumar Joshi\*

Page No. - Page No.

Thioether-NHC Ligated Pd(II) Complex in Crafting of Filtration-Free Magnetically Retrievable Catalyst for Suzuki-Miyaura Coupling in Water

A new benzimidazolium chloride (L), precursor of novel thioether functionalized NHC, and complex  $[Pd(L-HCI)Cl_2]$  (1) were synthesized. Structure of 1 was established with X-ray crystallography. 1 was found an efficient pre-catalyst for Suzuki-Miyaura coupling of aryl/hetero-aryl bromides (Yield up to 94% in 2 h) at rt in water. To avoid the deactivation of catalyst in reuse, 1 was immobilized on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core/shell NPs to develop heterogeneous magnetically retrievable catalyst (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-1'). The magnetic nano-support and novel thioether-NHC make the catalyst easily separable and reusable up to 7 cycles.

ccepted Manuscri