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Benzene benzimidazole containing Pd(II) metallacycle: Synthesis, X-ray crystallographic characterization and its use as an efficient Suzuki coupling catalyst

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Abstract

A first example of a highly stable benzimidazole N-donor dinuclear palladacycle complex is reported. X-ray diffraction analysis showed that two ligands assembled through complexation to two palladium(II) ions to give a compressed rectangular shaped metallamacrocycle. This complex catalyzed Suzuki coupling reaction effectively in MeOH at room temperature. Hg(0) poisoning test supports the formation of L-Pd(0) species in the catalytic reaction.

Keywords: Benzimidazole; Dinuclear Pd(II) metallacycle; Suzuki coupling reaction

1. Introduction

C–C bond formation reactions have played an important role in organic chemistry [1]. They have found wide application in the design of pharmaceutical drugs and in the synthesis of natural products [2]. Palladacyclic catalysts have been reputed as the most active catalysts for C–C and C-heteroatom bond formations [3].

Coupling reactions like Suzuki–Miyura, Sonogashira, Stille and Heck reactions are the most important methods reported so far for the formation of C–C bond using palladacycle. The use of organoboron compounds and their relative stability to air and water, combined with the relatively mild conditions for the reaction as well as the formation of non-toxic by-products, makes the Suzuki reaction a most useful tool to the synthetic chemist [1]. To search for an environmental friendly reaction is one of the central themes in organic reactions. The use of inexpensive, non-toxic, easily handleable and recyclable catalyst is desirable. In the past decades phosphine ligands based palladium catalysts were extensively used due to their extreme donor ability. Although their toxicity, Pd(II) catalysts with phosphine ligands have shown very high TONs even at room temperature [1b,4]. Recently Herrmann et al., Nolan et al., Arduengo et al. and others have designed five [5] and six members [6] N-heterocyclic carbene (NHC) ligands and used them to prepare efficient Pd(II) catalyst for cross coupling reactions. Apart from this, the use of a C-N/S/O donor ligand system [7] as a catalyst was also suggested for the same. Some of these are highly reactive in cross-coupling reactions but their preparation needs several steps with extreme caution involving a skillful hand. Miura et al. [1b] and Buchwald et al. [4k] reported that besides bulkiness and electron-richness an important factor that imparts a high catalytic performance is the π-systems of the ortho-aromatic groups on the ligands which interact with the Pd center. This interaction may also orient the arene ring of the substrate perpendicularly to the Pd–N bond, placing it in the stereochemically optimum arrangement for reductive elimination to take place [4k].

Recently, Pd(II) catalyst with diversed N-donor [8] ligands became attractive for catalytic application, because these strong σ-donor ligands favor both the oxidative addition and reductive-elimination steps in the catalytic cycle [8a]. The N-donor ligands that have been used so far for the synthesis of palladium complexes are given in Scheme 1. The use of benzimidazole as nitrogen donor ligand, however, has not been tested.

We have aimed to prepare Pd(II) complexes of a benzimidazole ligand 1,4-dibenzimidazolylbenzene (H_2DBImB), which

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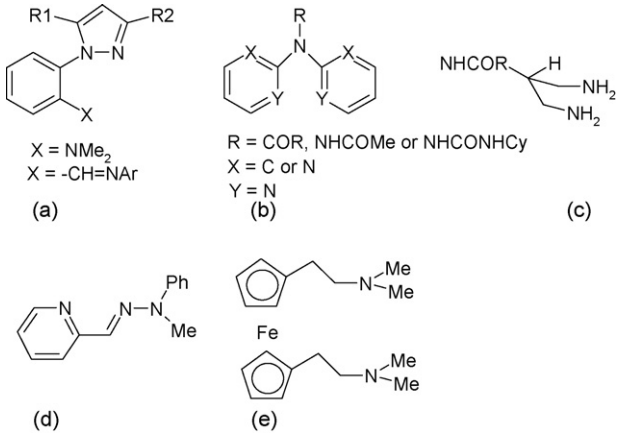


Scheme 1.

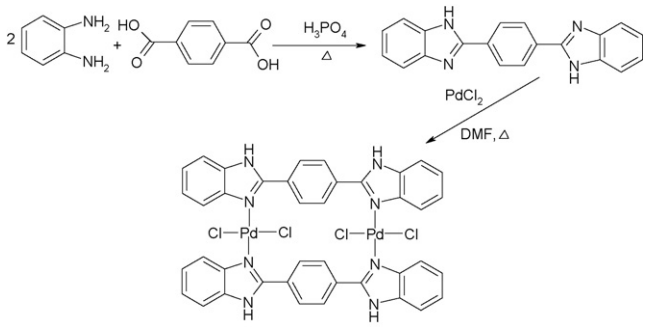
interlocked two metal centers in close proximity and showed good activity for Suzuki coupling reaction under mild reaction conditions.

2. Results and discussion

2.1. Preparation of ligand and complex

The preparation of the 1,4-di-benzimidazolylbenzene (H_2DBImB) ligand and $Pd_2(H_2DBImB)_2Cl_4$ complex are given in Scheme 2.

The reaction of H_2DBImB with $PdCl_2$ in DMF at 120 °C yielded a light yellow air stable, neutral, metallacycle complex $[Pd_2(H_2DBImB)_2Cl_4]$ in good yield (80%). Since other analytical and spectroscopic data gave little structural information, we have attempted to prepare a single crystal by the diffusion of acetone into a DMSO solution of the complex. The X-ray quality crystals of $[Pd_2(H_2DBImB)_2Cl_4]$. 6DMSO were obtained after 15 days at room temperature.



Scheme 2.

The solid state structure of the square planar dinuclear Pd(II) complex is displayed in Fig. 1. The two ligands functioning as bridges between two Pd(II) centers facilitate the formation of a dinuclear complex. X-ray crystal structure proves that the complex is centrosymmetric and the two Pd(II) ions have joined the two ligands resulting in a compressed rectangular shaped metallacycle. It appears that the molecule contains an intermolecular π–π interactions between benzene rings of benzimidazole of different complex molecules [centroid to centroid distance 3.8521 Å, inter planar distance 3.304 Å (Fig. 2)]. This type of secondary interaction is of fundamental importance for understanding molecular recognition phenomena, biological processes and physical and chemical properties of new materials [9]. The distance between the arene planes is taken as the criterion to suggest π-stacking and this lies between 3.3 and 3.8 Å [9,10].

The N–Pd–N and Cl–Pd–Cl bond angles (171.51° and 177.48°, respectively) reveal that both the Pd(II) centers

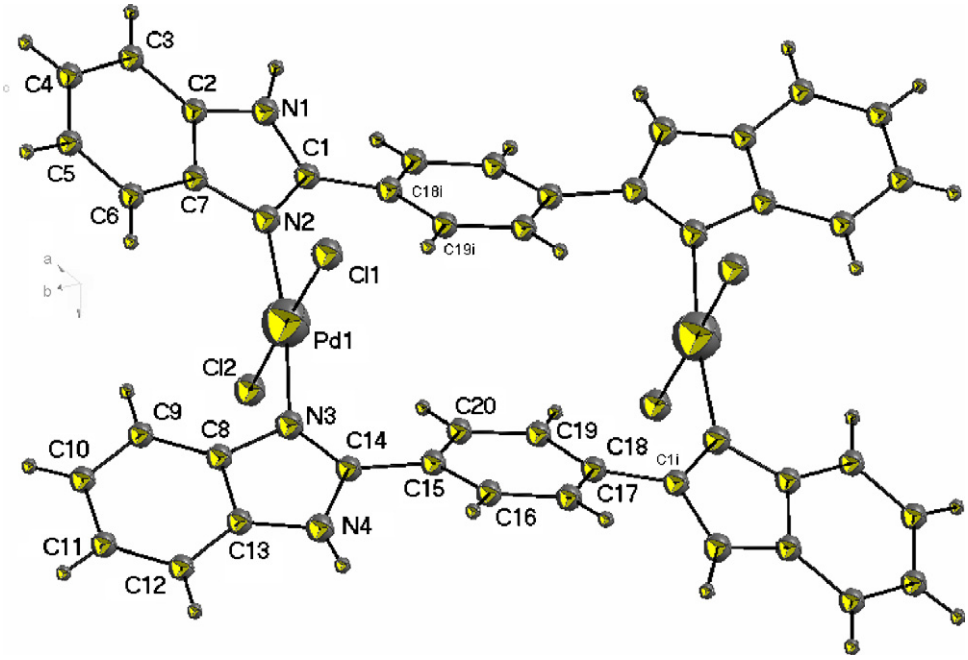


Fig. 1. ORTEP diagram of $Pd_2(H_2DBImB)_2Cl_4$ complex at the 50% probability level. Selected bond lengths (Å): Pd1-N3, 2.019(3); Pd1-N2, 2.009(3); Pd1-Cl1, 2.2915 (10); Pd1-Cl2, 2.2997(11). Bond angles (°): N3-Pd1-N2, 171.52(11); Cl1-Pd1-Cl2, 177.48(4); N3-Pd1-Cl1, 90.40(9); N3-Pd1-Cl2, 90.86(9); N2-Pd1-Cl1, 89.03(9); N2-Pd1-Cl2, 90.04(9). Symmetry codes (i) $2-x$, $2-y$, $-1-z$.

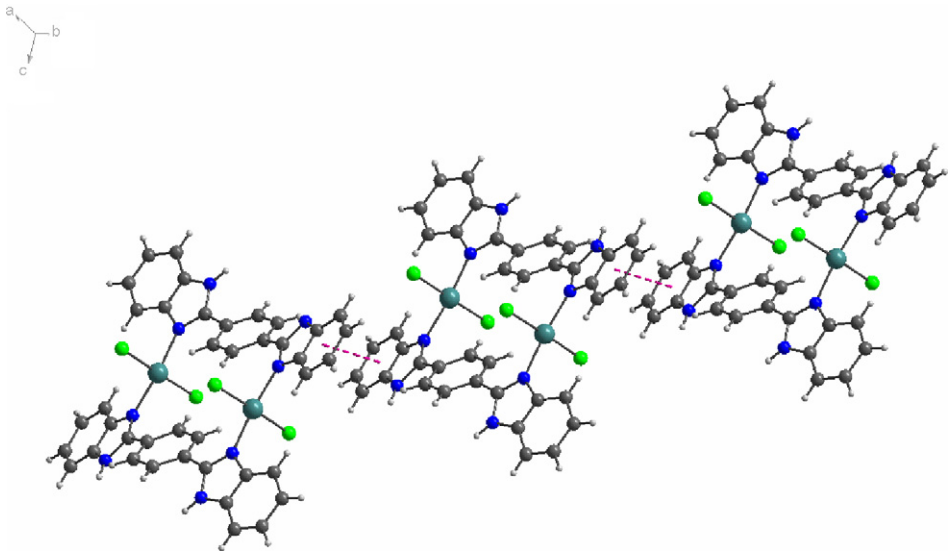


Fig. 2. Intermolecular π–π interaction in $Pd_2(H_2DBImB)_2Cl_4$ complex.

are in distorted square planar, with two trans Pd–N (average distance 2.014 Å) and two Pd–Cl (average distance 2.296 Å) bonds. The Pd–N bond distances are remarkably shorter than that of reported Pd-complex Pd_2Cl_4[Fe[η-$C_5H_4(CH_2)_2N(CH_3)_2]_2$ [8b] and are comparable with those of $Pd_2(DAniF)_4$, β-$Pd_2(TPG)_2(\eta^2$-TPG$)_2$ [11] synthesized from anion donor ligands (DAniF = *N*,*N*′-di-*p*-anisylformamidinate, TPG = *N*,*N*′*N*″-triphenylguanidinate) and Pd(L)Cl (L = glyoxal bis(*N*-methyl-*N*-phenylhydrazone)). Two dihedral angles of the ligand, one between benzene ring and benzimidazole ring of the same ligand (33.22°) and other between two benzimidazole of two ligands in the complex molecule (22.38°), have manifested their tune condition.

The complex also suffers strong H-bonding interactions with solvent molecule, DMSO. Four N–H's of benzimidazole units form strong H-bonding interaction (average N–H–O distance = 2.7455 Å) with the solvent molecules.

2.2. Suzuki cross-coupling reactions

The Suzuki cross-coupling reaction has been investigated so far with a large number of phosphene-free Pd(II) catalyst [5–8]. Among them only a few are active at room temperature [7b,8b,8c,8e], recyclable [8a,12] and tested in aerobic condition [7a,7b,8a,8e].

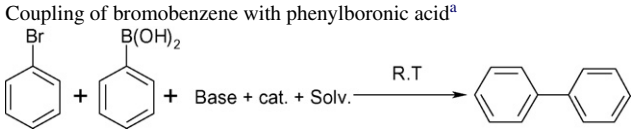
Palladium complex $[Pd_2(H_2DBImB)_2Cl_4]$ was found to be an active catalyst precursor for the Suzuki reaction. Initially unsubstituted or electronically neutral aryl bromide and phenylboronic acid were used to find out the optimized condition for the room temperature Suzuki reaction in aerobic condition. Aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol) and solvent were stirred at room temperature. After 15 min (no product was observed by TLC), $[Pd_2(H_2DBImB)_2Cl_4]$ was added with continuous stirring. The TLC showed that the reaction started within 2 min. Results of the coupling reaction are summarized in Table 1.

Since the proper combination of base and solvent is extremely important, we have examined several different bases and solvents for the Suzuki reaction. Initially many commonly available bases were used with MeOH as the solvent (Table 1, entries 1–9). In MeOH, the use of a strong base $KOBu^t$ completed the coupling reaction in a very short time (entry 6). Other bases like K_3PO_4, KOH, K_2CO_3 and Cs_2CO_3 produced slightly lower yields (entries 7, 8, 3, 5, respectively). The use of NaOAc and NEt_3 as bases gave inferior results and showed slow reaction rate (Table 1, entries 1 and 9, respectively) compared to that of the other inorganic bases. The use of DMF, H_2O/TBAB and CH_3CN as solvents with $KOBu^t$ failed to promote the Suzuki reaction (Table 1, entries 15, 17, 14, respectively) even at elevated temperature. The dioxane/H_2O solvent system with K_2CO_3, however, gave good product yield (entry 13). Therefore, $KOBu^t$ was found to be the most effective base in MeOH at room temperature. These reaction conditions also tolerated the presence of a variety of substituents in aryl bromides and produced the expected products in good yields (Table 2).

In order to gauge the further potential of our Pd(II) complex towards the Suzuki coupling methodology, we choose substituted aryl bromides, as shown in Table 2, for the reaction with arylboronic acid. The results show that both activated and deactivated aryl bromides are efficiently converted to biaryl at room temperature. This phenomenon is in line with those of reported N-donor ligand based Pd(II) complexes [7e,8b,8c,8e]. We observed ∼10% biphenyl as a homocoupling product of $ArB(OH)_2$ [13]. Recently Adamo et al. has mentioned the involvement of a palladium peroxo complex for the formation of homocoupling product, which is formed in aerobic condition [14].

Low catalyst loading tests were performed in order to find out the efficiency of the catalyst. When $KOBu^t$ was used as the base, the reaction of electronically challenging aryl bromide proceeded to completion up to 92% yield in MeOH within 2 h (Table 2, entry 1). So we choose the same base and solvent

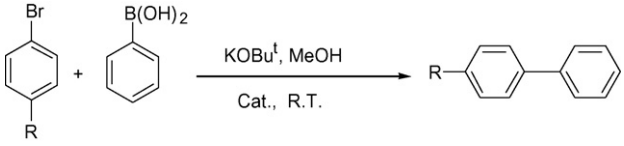
Table 1
Coupling of bromobenzene with phenylboronic acid[a]



Entry	Base	Solvent	Amount of catalyst (mol%)	Time (h)	Yield[b] (%)
1	NaOAc	MeOH	0.5	10	81
2	K_2CO_3	MeOH	0.5	1	86
3	K_2CO_3	MeOH	0.5	4	96
4	K_2CO_3	MeOH	1	1	99
5	Cs_2CO_3	MeOH	0.5	2	96
6	KOBu^t	MeOH	0.5	1.5	98
7	K_3PO_4	MeOH	0.5	1.5	97
8	KOH	MeOH	0.5	2	98
9	NEt_3	MeOH	0.5	10	83
10	K_2CO_3	DMF	0.5	18	8
11	KOH	H_2O[c]	0.5	2	10
12	K_2CO_3	CH_3CN	0.5	18	5
13	K_2CO_3	Dioxane/H_2O	0.5	3	94
14	KOBu^t	CH_3CN	0.5	12	5
15	KOBu^t	DMF	0.5	15	16
16	KOBu^t	Dioxane/H_2O	0.5	15	36
17	KOBu^t	H_2O[c]	0.5	15	3

[a] Aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol), and solvent (4.0 ml).
[b] Determined by G.C.
[c] 1.0 mmol of tetrabutylammonium bromide (TBAB) added.

Table 2
Effect of substitution on the coupling reaction[a]



Entry	R	Time (h)	Amount of catalyst (mol%)	Yield[b] (%)
1	-OMe	2	0.5	92 (88)[c]
2	-CN	5	0.5	91
3	-Me	2	0.5	89
4	-$COCH_3$	2	0.5	93 (90)[c]

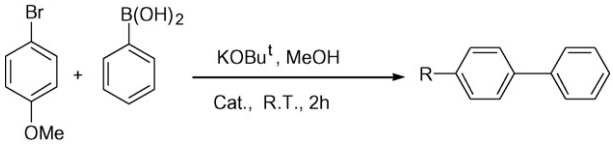
[a] Aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol), and MeOH (4.0 ml).
[b] Determined by G.C.
[c] Isolated yield.

for low catalyst loading with 4-bromoanisole and results are summarized in Table 3. In the case of 0.05 mol% catalyst loading (Table 3, entry 4), although 60% yield was obtained at 2 h, reaction went to completion (>90% yield) within 24 h.

To monitor the recyclability of this catalytic system similar reaction conditions with 0.5 mol% catalyst were employed. The results are shown in Table 4. We have observed some Pd blacks after each run and the catalyst was completely deactivated after the fourth run. For weak bases such as NaOAc, NEt_3 deactivation occurred more slowly than for strong bases; ~76% yield was obtained after the fourth run albeit consuming more time (9–10 h for each run).

Aryl halides substrates were also examined. Using KOBu^t as a base, MeOH as a solvent and 1 mol% of the catalyst, the reaction of ArCl with $ArB(OH)_2$ produced only 25% yield at room temperature after 12 h (entry 1, Table 5). The yield of the

Table 3
Effect of low catalyst loading and Hg(0) poisoning in the coupling reaction[a]



Entry	Amount of catalyst (mol%)	Yield[b] (%)
1	0. 5	92
2	0.2	89
3	0.1	85
4	0.05	60
5	5 mg catalyst + 268 mg Hg(0)	5

[a] 4-Bromoanisol (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol), and MeOH (4.0 ml).
[b] Determined by G.C.

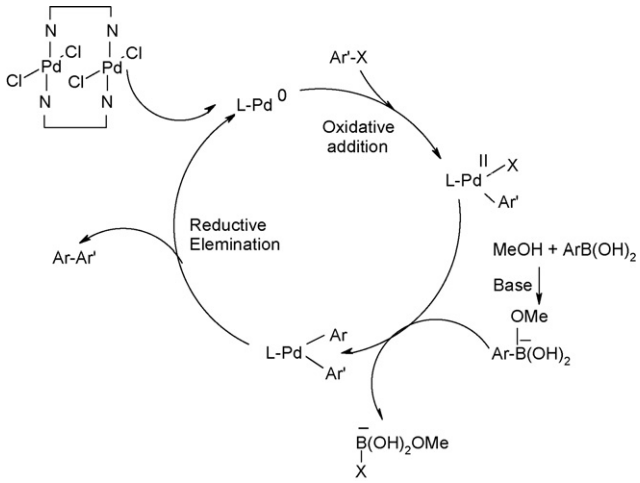
Table 4
Recyclability of catalyst in the coupling reaction with KOBu^t[a]

Run	Yield[b] (%)
1st run	92
2nd run	89
3rd run	78
4th run	<50

[a] Reaction conditions: 4-bromoanisole (1.0 mmol), phenylboronic acid (1.5 mmol), KOBu^t (2.0 mmol), MeOH (4.0 ml), Catalyst (0.5 mol%), room temperature.
[b] Determined by G.C.

above reaction was increased up to ~42%, when the temperature was raised (entry 2, Table 5). The change of solvents and bases again gave inferior results (entries 3–5). Activated aryl chlorides (entries 6 and 7) gave 53% and 46% yield respectively under similar reaction conditions, whereas an inactivated one gave only 5% yield (entry 8). The low yields obtained with aryl chloride or substituted aryl chlorides are due to the stronger Csp^2-Cl bonds of aryl chlorides than those of the heavier congeners. Namely, the oxidative addition reactions of aryl chlorides are less facile than those of aryl bromides and aryl iodides as have been reported [15].

Two different kinds of mechanisms have been proposed for the Suzuki coupling reaction: a classical Pd(0)/Pd(II) [16,17a] pathway and a Pd(II)/Pd(IV) cycle [4a,7d,17]. It has been known that Hg(0) can poison the catalytic property of a metal(0) species by amalgamating the metal or absorbing on the metal surface in a heterogeneous catalysis [18]. In our study we also found that the addition of excess Hg(0) (Hg:Pd = 150:1) indeed deactivated the reaction as shown in Table 3 (entry 5). This results therefore suggest that the actual catalytic species at room temperature is Pd(0) species as reported [19]. Therefore in our system, the catalyst precursor $Pd_2(H_2DBImB)_2Cl_4$ will be converted to L-Pd(0) *in situ*. Oxidative addition of L-Pd(0) by aryl halide will form a Pd(II) intermediate. The halide ion can then be substituted by the aryl group of $ArB(OH)_2$. This followed by reductive elimination to form a new biphenyl. A schematic representation of description is depicted in Scheme 3.



Scheme 3.

3. Conclusion

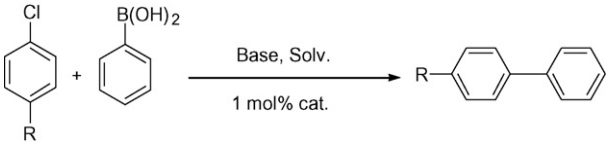
To the best of our knowledge, this is the first example of benzimidazole imine nitrogen containing metallamacrocycle, which has been structurally characterized. The catalytic system performed in this work is very efficient for the coupling reaction of aryl bromides and $ArB(OH)_2$ at room temperature. Our Hg(0) poisoning test suggest that the catalyst do not follow the Pd(II)/Pd(IV) catalytic cycle. The high catalytic activity may possibly be due to the macrocyclic structure and π-cloud interaction. This result has motivated us to use this simple catalyst in other catalytic systems.

4. Experimental

4.1. General

All the reactions were carried out in air. The solvents and reagents were purchased from general sources and were used without further purification. G.C. analyses were performed with a GL Sciences GC-353B gas chromatograph equipped with a

Table 5
Coupling reaction of aryl chlorides[a]



Entry	R	Time (h)	Base	Temperature (°C)	Solvent	Yield[b] (%)
1	-H	12	KOBu^t	RT	MeOH	25
2	-H	12	KOBu^t	80	MeOH	42
3	-H	16	KOH	80	Dioxan	10
4	-H	16	KOH	80	DMF	8
5	-H	18	NaOAc	80	MeOH	12
6	-NO_2	16	KOBu^t	80	MeOH	53
7	-COOH	24	KOBu^t	80	MeOH	46
8	-OMe	24	KOBu^t	80	MeOH	5

[a] Aryl chloride (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol), and solvent (4.0 ml).
[b] Isolated yield.

flame ionization detector and a 10 m (2.65 μm film thickness) RESTEK Rtx-2887 fused silica capillary column. ^{1}H NMR spectra were recorded on a Bruker DX-300 NMR spectrometer. Chemical shifts were referenced to TMS, and deuterated DMSO (Aldrich) was used as a solvent and as a secondary reference. Mass Spectra were measured on a Micromass Platform II spectrometer. Elemental analyses were carried out using a Perkin-Elmer 2400, 2400II elemental analyzer. The pH intervals were measured using SUNTEX pH Meter Model NO: SP-701.

4.2. Synthesis of 1,4-di(benzimidazolyl)benzene (H2DBImB)

The ligand was synthesized following the procedure described in literature [20] with some modification introduced. The 2:1 (mol proportion) mixture of terephthalic acid and *o*-phenylenediamine was heated with minimum volume of H_3PO_4 at 210 °C for 4 h. When poured into the water it has formed a green mass which when slurred with 5% sodium carbonate solution turned light pink (pH 8). The product was filtered, washed with water and dried in vacuo (yield 78%). The ligand is soluble in hot alcohol, DMF and DMSO forming a pink color. The compound behaves as an acid–base indicator (pH interval and color change in aqueous methanolic solution: 0–2 = blue–violet, 3–4 = blue, 5.5–8 = red–violet, 9.5–14 = yellow).

Anal. Calcd. for $C_{20}H_{14}N_4$: C, 77.41; H, 4.51; N, 18.06. Found: C, 77.38; H, 4.47; N, 17.97. ^{1}H NMR: δ 13.09 (s, 2H), 8.33 (s, 4H), 7.24 (m, 4H), 7.68 (d, 2H, $J_{H\text{-}H}$ = 7.2 Hz), 7.54 (d, 2H, $J_{H\text{-}H}$ = 7.5 Hz). MS (FAB): *m/z* 310 $[M]^+$.

4.3. Synthesis of $Pd_2(H_2DBImB)_2Cl_4$

To a solution of H_2DBImB (62 mg, 0.20 mmol) in 6 ml of DMF, $PdCl_2$ was added (43 mg, 0.24 mmol) and the mixture was heated at 120 °C for 24 h. After cooling, the light yellow mixture was quenched with small volume of ether in stirring condition. The light yellow product was filtered and washed with MeOH and ether, and dried in vacuo (yield 80%). Anal. Calcd for $C_{40}H_{28}N_8Pd_2Cl_4$: C, 49.23; H, 2.87; N, 11.48. Found: C, 49.11; H, 2.77; N, 11.34. ^{1}H NMR: δ 9.41 (s, 2H), 9.14 (d, 2H, $J_{H\text{-}H}$ = 8.58 Hz), 7.93 (s, 2H), 7.71 (m, 2H), 7.58 (m, 2H). MS (FAB): *m/z* 972 $[M]^+$, 310 $[L]^+$.

4.4. X-ray data collection and structure refinement

Crystals of $Pd_2(H_2DBImB)_2Cl_4$ suitable for X-ray diffraction were grown by slow diffusion of acetone into the DMSO solution of the compound. A single crystal was mounted on a glass fiber and the X-ray diffraction intensity data were measured on a Bruker Smart 1000 CCD XRD. A crystal of the complex (0.08 mm × 0.08 mm × 0.08 mm) was selected for the structural analysis. The intensity data were collected at 273 K. All data were collected with ω scan technique using graphite monochromatic Mo Kα radiation (λ = 0.71073 Å). All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were refined using a 'maXus' model. The structures were solved by direct methods using the SHELXS-97 computer program and refined by full-matrix least-squares methods on F^2 using SHELXL-97 [21]. Complete structure data have been deposited. Salient crystal data are: $C_{52}H_{64}Cl_4N_8O_6Pd_2S_6$, M_r = 144.07, monoclinic, space group $P2_1/c$, T = 273 K, a = 13.5860(9) Å, b = 20.5052(14) Å, c = 12.4364(8) Å, β = 115.7780(10)°, V = 3119.8(4) Å^3, Z = 2, D_{calc} = 1.537 g/cm^3, μ = 1.001 mm^{-1}, θ_{range} = 1.66–28.31°. Of 36,266 reflections collected, 7784 were independent, R_{int} = 0.0382, and 5709 were observed ($I > 2\sigma(I)$); final R indices: R_1 = 0.0452 ($I > 2\sigma(I)$), wR_2 = 0.1362.

4.5. General procedure for Suzuki reaction and isolation of product

Aryl bromide or substituted aryl bromide (1.0 mmol), arylboronic acid (1.5 mmol), base (2.0 mmol) and solvent (4.0 ml) were stirred. After 15 min the catalyst (amount according to the table) was added with continuous vigorous stirring at room temperature. The progress of the reaction was tested from time to time by G.C. After the reaction was completed, the mixture was extracted with ethyl acetate (EA) and washed 5 times with equal volume of water. The EA layer was filtered through Whatman filter paper and dried over anhydrous $MgSO_4$. $MgSO_4$ was filtered off and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using 5:1 *n*-hexane:EA (v/v). The procedures described here are short and representative and the yields given are average, and thus the yields may little differ from those given in the tables.

4.6. Procedure for catalyst recyclability

The above procedure was followed and the mixture was stirred vigorously for 2 h. After stirring the solvent was centrifuged and separated and the residue was washed once by solvent and once by water and centrifuged off. The residue of catalyst left was used for the next cycle and the centrifuged solvent was tested by G.C.

4.7. Hg poisoning test

4-Bromoanisole (1.0 mmol), arylboronic acid (1.5 mmol), $KOBu^t$ (2.0 mmol), MeOH (4.0 ml) and Hg(0) (268 mg) were stirred vigorously at room temperature. After 15 min 0.5 mol% catalyst was added with continuous stirring. Only very little conversion was observed after 2 h (G.C.).

5. Supporting information

CCDC 618499 contains the supplementary crystallographic data for this paper. These data can obtained free of charge from The Cambridge Crystallographic Center via www.ccdc.cam.ac.uk/data-request/cif.

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