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(NHC)-Pd(II) complexes with hydrophilic nitrogen ligands: catalytic properties in neat water

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Abstract: The cleavage reactions of the dimers $[(NHC)PdX_2]_2$ with hydrophilic N-donors, L, afforded the mixed-ligand complexes of the type *trans*-$[(NHC)LPdX_2]$ (X = Cl or Br; NHC = 1,3-dialkylbenzimidazol-2-ylidene (BIm) or bis(imino)acenaphthene-annulated bis(2,6-diisopropylphenyl)imidazol-2-ylidene (BIAN-IPr); L = diethanolamine (DEA), morpholine (MOR), and 3-pyridinecarboxylic acid (3-PCA)). The new complexes (**1**–**3**) were characterized by elemental analysis and spectroscopic methods and the molecular structure of **1a** was determined by X-ray diffraction studies. These complexes were applied in the Suzuki–Miyaura cross-coupling reaction of phenylboronic acid with aryl halides in neat water. The activities of catalysts were monitored by gas chromatography–flame ionization detector and nuclear magnetic resonance. Whereas the complexes with DEA or 3-PCA ligands did not show significant difference in the activity, the BIAN-IPr complexes **1b** and **3b** bearing DEA and 3-PCA, displayed the highest catalytic activity at 100 °C.

Key words: Palladium, diethanolamine, N-heterocyclic carbene, water soluble complexes, cross-coupling

1. Introduction

Palladium-catalyzed carbon–carbon coupling reactions constitute a category of the most frequently employed organic reactions.[1] Among these transformations, the coupling of aryl and alkyl halides with arylboronic acids (Suzuki–Miyaura [S–M] reaction) is an interesting example of unsymmetrical biaryl formation.[2] These reactions are generally carried out in the presence of various ligands, such as tertiary phosphine, which could stabilize the active palladium intermediates.[3] However, traditional phosphines have some drawbacks and, consequently, N-heterocyclic carbene (NHC)-ligated Pd complexes have also received considerable attention as a class of moisture- and air-stable catalyst precursors for the coupling reactions. NHC is considered as a strong σ donor with a weak π-accepting ability; however, the π-acceptor properties of the NHC might influence the catalytic behavior of these complexes considerably.[4] One of the focal points of current research concerns the development of (NHC)-Pd(II) complexes with a nitrogen ligand, which has been described as a "throw-away" ligand.[5] In these catalysts, steric hindrance of NHC is of crucial importance. For example, the IPent complex in PEPPSI (pyridine-enhanced precatalyst preparation stabilization and initiation) complexes display higher activity than IPr.[6] Some related Pd(II) complexes bearing triethylamine and IPr or SIPr ligands were reported as active

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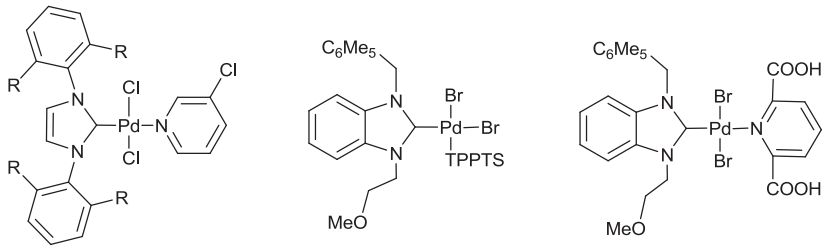
This article is dedicated to the memory of Prof Dr A.S. Demir, who was one of the pioneers of frequently used novel catalysts in organic synthesis.

S–M coupling catalysts.[5c,d] Most of the catalytic reactions involving these catalysts were carried out in organic media due to the hydrophobic nature of the ligands surrounding the Pd center.



Recently, a great deal of attention has been paid to the search for water-soluble metal complexes because, in principle, the advantages of homogeneous and heterogeneous catalysts can be combined.[7] Furthermore, water has a number of favorable properties, such as nontoxicity, nonflammability, and availability in large quantities. Despite this interest, almost all published aqueous chemistry studies concentrate on tertiary phosphines, and triphenylphosphine-3,3,3-trisulfonic acid trisodium salt (TPPTS) is the most favored hydrophilic phosphine.[7,8] This concept has been successfully extended to the NHC ligands by introducing polar functionalities such as $-SO_3^-$, $-COO^-$, -OH, or $-(CH_2CH_2O)_n$-H, $-NR_4^+$ by various research groups.[9] In this context, we have, very recently, reported the synthesis and catalytic activity of water-soluble complexes A and B obtained by cleavage of the dimer $[(NHC)PdBr_2]_2$ with TPPTS and pyridine-2,6-dicarboxylic acid, respectively.[8b,10] However, a sophisticated ligand design mostly resulted in increasingly expensive complexes. Therefore, we have focused on hydrophilic throw-away ligands analogous to that of PEPPSI catalysts and obtained good results with B, using aryl halides as substrates. Furthermore, the way they act during the catalytic process remains unknown. Herein, we attempt to find some information in order to get a better understanding of this question by applying alternative commercially available and cheap nitrogen ligands. A related objective is to study the role of the size of the NHC ligand in determining the efficiency in the S–M reaction.

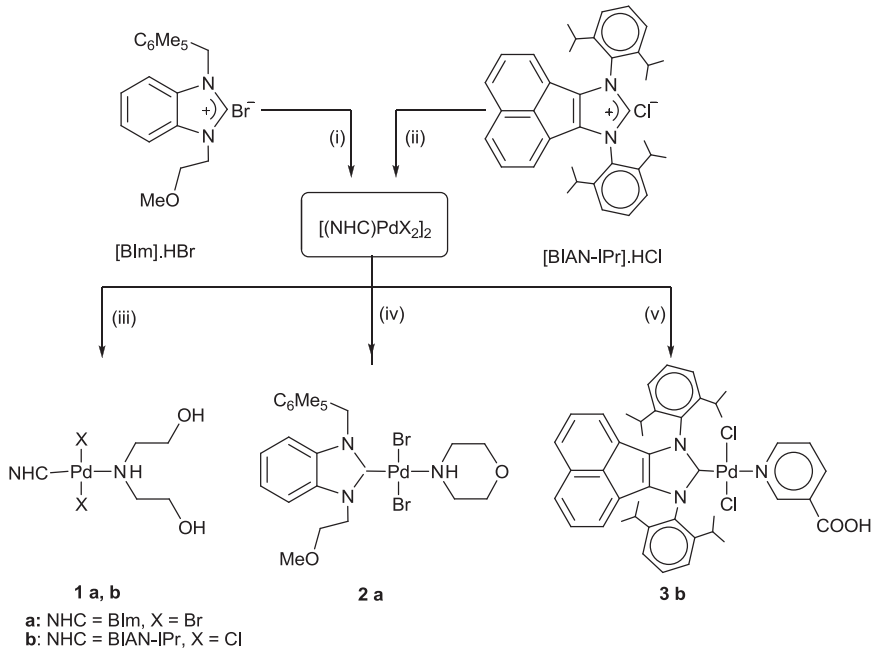
2. Results and discussion

2.1. Synthesis and cleavage of (NHC)-palladium dimers with hydrophilic N ligands

NHCs are not purely σ-donors; π-back donation represents approximately 10%–30% of the character of the bond.[11] The percentage of π-back bonding could significantly increase for more electronrich species such as (NHC)-Pd(0), which are believed to play an important role in the catalytic cycle.[12] Previous studies have shown that, for the S–M reaction, 4,5-annulation and bulky N-substituents are crucial for high catalytic performances. In view of this information and for comparative purposes, we have focused on 4,5-annulated imidazolium salts [BIm].HBr and [BIAN-IPr].HCl as NHC precursors. Rh(I), Ir(I), Ru(II), Ag(I), Au(I), and Pd(II) complexes bearing the BIAN-IPr ligand have been reported while this work was in progress.[13] We previously employed a saturated version of the BIAN-IMes ligand in Ag(I), Rh(I), and Pd(II) complexes.[14] We have chosen surface-active DEA as a hydrophilic coligand akin to diethylamine, which has been found to inhibit the S–M reaction at 40 °C, and this inhibition has been attributed to the intramolecular H-bonding between diethylamine and a chloride attached to the Pd center.[5d] However, at higher temperatures and longer reaction times, the catalysts were effective.

The targeted mixed-ligand complexes, **1**–**3**, were obtained as yellow-orange solids from the dimers $[(NHC)PdX_2]_2$ according to the synthetic route presented in Scheme. The dimer $[(BIm)PdBr_2]_2$ has been prepared using the literature method,[15] whereas $[(BIAN\text{-}IPr)PdCl_2]_2$ was obtained via an NHC transfer reaction of [(BIAN-IPr)-Ag-Cl].[13b] Pyridinecarboxylic (PCA)-derived Pd(II) complexes (such as B) were successfully used as water-soluble catalysts in the S–M reaction. Our initial attempt to cleave $[(BIAN\text{-}IPr)PdCl_2]_2$ with 2,6-PDCA failed, but 3-PCA readily reacted to give the expected **3b** in high yield. Owing to its easy accessibility and formal similarity to 3-chloropyridine, 3-PCA was the ligand of choice for the cleavage reaction to prepare **3b**. The coligands DEA and MOR, a dehydrated form of DEA, are completely soluble/miscible with water. They are electronically and sterically different from 3-PCA and afforded **1**–**3** in high yields. Due to their ability to form strong H-bonds, the DEA complexes **1a** and **1b** are water-soluble at 100 °C, **3b** is soluble in its deprotonated form (basic conditions) at 25 °C and **2a** is the least soluble. The sharp contrast in the water solubility of complexes **1a** and **2a** clearly reflects diminished H-bonding characteristics of MOR complex.

The palladium complexes can be stored in air for a long period of time. In some cases, the stabilities of NHC complexes in water have been described as being low.[9i] Therefore, we gradually heated and monitored the solutions of the new complexes by ^{1}H NMR in wet DMSO-d_6, but no significant changes were observed ((ESI) electronic supporting information). They were characterized by ^{1}H NMR, ^{13}C NMR, and elemental analyses. The NMR spectra of complexes **1a 1b 2a** and **3b** show that the amine ligands are coordinated to the palladium center. The ^{1}H NMR spectra of complexes **1a** and **2a** clearly indicate benzylic protons at 6.11 and 6.06 ppm, respectively. The signals of the carbene of **1b** (δ 163.8) in the ^{13}C NMR spectrum are slightly shifted to higher field as compared to their signals from pyridine derivative **3b** (δ 168.4).



Scheme. Synthesis of (NHC)-Pd(II) complexes' conditions and reagents: (i) $Pd(OAc)_2$, DMSO, 90 °C; (ii) a) Ag_2O, CH_2Cl_2, 25 °C, b) $PdCl_2(MeCN)_2$, 40 °C; (iii) DEA, CH_2Cl_2, 25 °C; (iv) MOR, CH_2Cl_2, 25 °C; (v) 3-PCA, CH_2Cl_2, 25 °C.

2.2. X-ray structural analyses of the complex

Diffraction data for the complex were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 296(2) K using graphite monochromated Mo Kα radiation at $\lambda = 0.71073$ Å. Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART[16] program package. For further crystal and data collection details, see Table 1. Structure solution was found with the SHELXS-97[17] package using the direct methods and were refined with SHELXL-97[18] against F^2 using first isotropic and later anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were added to the structure model at calculated positions. Geometric calculations were performed with PLATON.[19]

2.3. Description of structure

The molecular structure of complex **1a** was determined by single-crystal structure X-ray diffraction studies. The ORTEP view of the complex is shown in the Figure and the crystallographic data are summarized in Table 1. The complex crystallizes in a monoclinic system with Z = 4 in space group P21/n. The structure determination of complex **1a** reveals a mononuclear square-planar Pd(II) atom coordinated by the NHC, 2 bromide ligands, and 1 diethanolamine ligand in a *trans* arrangement (Figure).

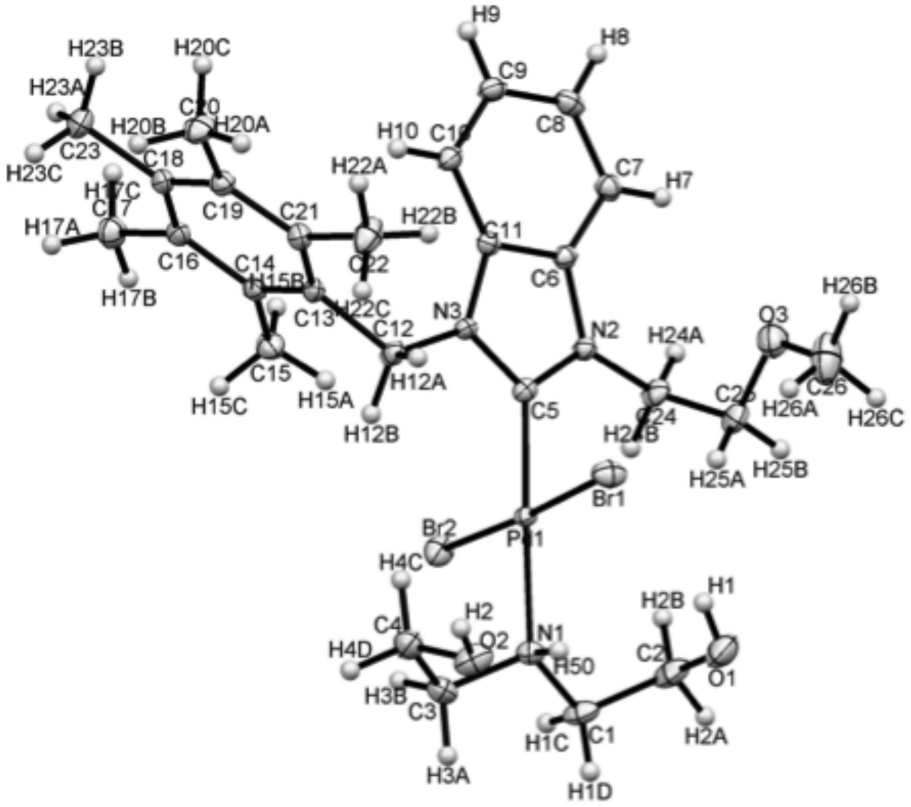


Figure. A view of the complex **1a**, showing 50% probability displacement ellipsoids and the atom-numbering scheme; selected bond lengths (Å) and angles (°) for complex **1a**: Pd(1)-C(5) 1.959(18), Pd(1)-N(1) 2.134(16), Pd(1)-Br(1) 2.431(2), Pd(1)-Br(2) 2.431(2), C(5)-Pd(1)-N(1) 177.3(7), C(5)-Pd(1)-Br(1) 88.33(5), N(1)-Pd(1)-Br(1) 89.06(5), C(5)-Pd(1)-Br(2) 88.85(5), N(1)-Pd(1)-Br(2) 93.77(5).

The palladium ion has slightly disordered square planar geometry, principally due to Br_1-Pd-Br_2 [176.94 (8)°], and C5-Pd-N1 [177.34°]. The bromide ligands are bent towards the NHC ligand for steric reasons. Pd-Br bond length [2.431 (2) Å] is similar to the equivalent value found in the related complexes *trans*-[(NHC)LPd(Br_2] (L = PCy_3, PPh_3).[2] The Pd (II)-$C_{carbene}$ [1.959 (18) Å] and the Pd-N [2.134 (16) Å] bond lengths are slightly shorter than other similar types of Pd(II)-NHC complexes[21–24] and also reported Pd-C bonds[25], and this result is attributed to the π-back bonding interaction of the Pd (II)-carbene bonds for the latter types.

Table 1. Crystal data and structure refinement parameters for complex **1a**.

Empirical formula	$C_{26}H_{39}Br_2N_3O_3Pd$
Formula weight	707.80
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21/n
Unit cell dimensions	a = 18.7767(3) Å alpha = 90° b = 7.51130(10) Å beta = 100.3250(10)° c = 19.9073(3) Å gamma = 90°
Volume	2762.21(7) $Å^3$
Z, Calculated density	4, 1.702 Mg/m^3
Absorption coefficient	3.597 mm^{-1}
F(000)	1424
Crystal size	0.53 × 0.27 × 0.18 mm
Theta range for data collection	1.65° to 28.41°
Limiting indices	$-25 \le h \le 23$, $-7 \le k \le 10$, $-25 \le l \le 26$
Reflections collected / unique	25988 / 6932 [R(int) = 0.0251]
Completeness to theta	28.41 99.4%
Absorption correction	Integration
Max. and min. transmission	0.524 and 0.325
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6891 / 0 / 328
Goodness-of-fit on F^2	1.035
Final R indices [I > 2sigma(I)]	R1 = 0.0218, wR2 = 0.0532
R indices (all data)	R1 = 0.0277, wR2 = 0.0553
Largest diff. peak and hole	0.519 and –0.467 e.$Å^{-3}$

2.4. Catalytic studies

Early experiments established that coupling reactions proceeded in water at 100 °C in the presence of 1 mol% NHC-Pd complexes with KOH as a base.[8b,10] In this work, we first carried out a catalyst screening by comparing the activity of **1a**, **1b**, **2a**, and **3b** in the coupling of 4-chloroacetophenone and 4-chlorobenzaldehyde with phenylboronic acid. The reactions were carried out in neat water at 100 °C with 1 mol% palladium complexes loading in the presence of KOH. Among the complexes, **1a** and **1b** containing DEA gave the highest yield, while **2a** with MOR gave moderate yields. The results from the screening of aryl chlorides with phenylboronic acid are summarized in Table 2. These observations showed that the presence of DEA ligands in complexes provided the catalytic enhancement. In separate experiments, we used DEA as a base, which showed higher efficiencies than KOH (Table 2). It is assumable that DEA increases the rate of the reaction catalyzed by water soluble catalysts to stabilize catalytically active species in water or/and to act as a mass transfer promoter. Mono- and triethanolamines were less efficient. Therefore, the rest of the tests were carried out with DEA. Efficiency of

1b over **3b** suggests that DEA may stabilize the active species in **1b** due to the "NHC Pd^b" intermediate via hydrophilic OH groups.

In order to evaluate the role of NHC ligands, we included other water-soluble palladium complexes. In this context, we decided to examine *trans*-[$PdCl_2(DEA)_2$], **4**.[24] However, the efficiency of **4** was much lower (45% yield), and therefore further experiments were abandoned. This observation clearly suggests that NHC ligands play an important role in the catalysis. In the catalytic studies, phenyldioxazaboracane was also used as a substrate (Table 2, entry 1), because DEA and $PhB(OH)_2$ are known to form phenyldioxazaboracane.[26] However, a lower yield was observed.

Table 2. Palladium-catalyzed C-C coupling reaction of phenylboronic acid with aryl halides.

	Cat.				
R	**1a**	**1b**	**2a**	**3b**	**4**
$COCH_3$	$85^a(97)^b(62)^{b,c}$	$100^{b,d}$	34^b	91^b	45^b
CHO	$82^a(89)^b$	$100^{b,d}$	16^b	97^b	37^b
CN	$80^a(91)^b$	$100^{b,d}$	-	100^b	-
NO_2	$78^a(89)^b$	$100^{b,d}$	-	100^b	-
OMe	$61^a(70)^b$	$94^b(85)^{b,d}$	-	$87^b(78)^{b,d}$	-
CH_3	$53^a(67)^b$	$91^b(82)^{b,d}$	-	$89^b(76)^{b,d}$	-

Yields were determined by gas chromatography for an average of 2 runs. [a] KOH was used as a base. [b] Diethanolamine was used as a base. [c] Phenyldioxazaboracane was used instead of phenylboronic acid. [d] Reaction time is 2 h.

2.5. Catalyst recycling

We examined the possibility of reusing catalysts **1a** **1b** or **3b** for the S–M reaction of 4-chloroacetophenone and phenylboronic acid and the reactions were conducted under the same conditions. After the first reaction, the solid product was separated by filtration (100% yield). To the filtrate containing **1b** fresh substrates DEA (2.0 mmol) and sufficient distilled water were added to bring the volume to 6.0 mL. The yields for the 2nd, 3rd, and 4th cycles were 92%, 87%, and 77% respectively (Table 3). Catalyst **1b** appears to be reusable for 6 cycles for the reaction of 4-chloroacetophenone; however, on the sixth cycle, the yield dropped to 54%.

Table 3. Reusability of catalyst **B**, **1a**, **1b**, and **3b** for the S–M reaction of 4-chloroacetophenone and phenylboronic acid.

Cat./Cycles	1st	2nd	3rd	4th	5th	6th
B	99	67	63	48	41	30
1a	97	88	83	70	65	40
1b	100	92	87	77	69	54
3b	91	84	79	71	63	50

Yields (%) at 100 °C for 4 h; DEA used as base.

3. Conclusion

We showed that the cleavage reaction of $[(NHC)PdX_2]_2$ is a suitable synthetic procedure for the incorporation of hydrophilic ligands such as DEA, MOR, or 3-PCA onto the Pd-center to prepare water-soluble complexes. The DEA coordinates to palladium through its N, while the ethanolic groups are pendant and ready to interact with phenylboronic acids or to give H-bonds with water.

The attempt to improve the catalytic efficiency of the S–M reaction by combining bulky BIAN-IPr with DEA or 3-PCA is highly successful, particularly in view of the commercial availability of these hydrophilic ligands and ease of synthesis of the (BIAN-IPr).HCl precursor. Again, the combination of BIAN-IPr and DEA as ligands is found to be beneficial in water for the S–M reaction. The strategy may have further implications in large-scale operations. Work is also in progress to extend this system to other C-C and C-N cross-coupling reactions catalyzed by (NHC)Pd complexes.

4. Experimental

4.1. General procedures

The complexes [BIm].HBr, [BIAN-IPr].HCl, and **4** were prepared according to the literature methods.[13b,14,24] NMR spectra were recorded at 297 K on a Varian Mercury AS 400 at 400 MHz (^{1}H) and 100.56 MHz (^{13}C). Elemental analyses were carried out by the analytical service of the Scientific and Technological Research Council of Turkey with a Carlo Erba Strumentazione Model 1106 apparatus. The yields of C-C coupling products were determined using GC and NMR.

4.2. General procedure for the preparation 1a, 1b, 2a, and 3b; cleavage of the [(NHC)PdX$_2$]$_2$ with DEA, MOR, or 3-PCA

A sample of [(NHC)PdX$_2$]$_2$ (0.5 mmol) and DEA, MOR, or 3-PCA (1.0 mmol) were dissolved in 10 mL of CH_2Cl_2. The mixture was stirred at ambient temperature for 1 h. The volume of the solution was reduced to about 5 mL in vacuo. Diethyl ether (10 mL) was added to the solution to obtain a bright cream precipitate, which was collected by filtration, washed with 10 mL of diethyl ether, and dried in vacuo. The product was recrystallized from CH_2Cl_2/Et_2O. Complexes **1a**, 1**b**, **2a**, and **3b** were synthesized according to this procedure.

[(BIAN-IPr)PdCl$_2$]$_2$, b: To a solution of (BIAN-IPr).HCl (500 mg, 0.9 mmol) in CH_2Cl_2 (20 mL), Ag_2O (310 mg, 1.35 mmol) was added. The mixture was stirred at 35 °C for 48 h in the dark and filtered through Celite. [Pd(CH_3CN)$_2$Cl$_2$] (468 mg, 1.8 mmol) was added and, after stirring for 24 h at 35 °C, the product was separated by column chromatography (CH_2Cl_2). The product was recrystallized from CH_2Cl_2/Et_2O, yield: 404 mg, 65%. ^{1}H NMR ($CDCl_3$): δ 7.75–7.62 (m, 4 H, Naph-*H*, Ar-*H*), 7.44 (d, J = 7.6 Hz, 4 H, Ar-*H*), 7.27 (dd, J = 14.5, 7.2 Hz, 2 H, Naph-*H*), 6.71 (d, J = 7.6 Hz, 2 H, Naph-*H*), 3.00 (dt, J = 13.4, 6.7 Hz, 4 H, -C*H*), 1.29 (d, J = 6.5 Hz, 12 H, -CH_3), 0.80 (d, J = 6.5 Hz, 12 H, -CH_3). ^{13}C NMR: δ 153.2 (*C*-Pd), 147.2, 140.5, 133.4, 130.9, 129.7, 129.1, 128.4, 127.4, 126.0, 125.1, 122.4 (Ar-*C*, Naph-*C*), 29.0 (-*C*H$_3$), 25.8 (-*C*H), 24.3 (-*C*H$_3$). Anal. Calc. for $C_{74}H_{80}Cl_4N_4Pd_2$ (1380,11): C 64.40, H 5.84, N 4.06; Found C 64.37, H 5.80, N 4.01%.

1a: Yield: 0.57 g, 80%. ^{1}H NMR ($CDCl_3$): δ 7.46 (d, J = 8.4 Hz, 1 H, Benz-*H*), 7.12 (t, J = 7.2 Hz, 1 H, Benz-*H*), 6.85 (t, J = 8.0 Hz, 1 H, Benz-*H*), 6.18 (d, J = 8.4 Hz, 1 H, Benz-*H*), 6.11 (s, 2 H, CH_2C$_6$(CH$_3$)$_5$), 4.96 (t, J = 5.6 Hz, 2 H, NCH_2CH$_2$OCH$_3$), 4.83 (t, J = 10.4 Hz, 2 H, NH(CH$_2$CH_2OH)$_2$), 4.12 (t, J = 5.6 Hz, 2 H, NCH$_2$CH_2OCH$_3$), 3.93 (d, J = 11.2 Hz, 2 H, NH(CH_2CH$_2$OH)$_2$), 3.51 (br, 1 H, N*H*(CH$_2$CH$_2$OH)$_2$), 3.36 (s, 3 H, CH$_2$CH$_2$OCH_3), 2.61 (m, 2 H, NH(CH$_2$CH_2OH)$_2$), 2.27 (m, 2 H, NH(CH_2CH$_2$OH)$_2$), 2.33 (s, 3 H, CH$_2$C$_6$(CH_3)$_5$*p*), 2.28 (s, 6 H, CH$_2$C$_6$(CH_3)$_5$*m*), 2.26 (s, 6 H, CH$_2$C$_6$(CH_3)$_5$*o*). ^{13}C NMR: δ 164.6 (C-Pd), 136.4, 135.7, 134.6, 134.7, 133.3, 127.3, 123.1, 122.6, 111.7, 111.0 (Benz-*C*, CH$_2$*C*$_6$(CH$_3$)$_5$), 71.3 (NH(CH$_2$*C*H$_2$OH)$_2$), 60.6 (NH(*C*H$_2$CH$_2$OH)$_2$), 59.3 (NCH$_2$CH$_2$O*C*H$_3$),

54.3 ($NCH_2CH_2OCH_3$), 52.5 ($CH_2C_6(CH_3)_5$), 48.6 ($NCH_2CH_2OCH_3$), 17.6 ($CH_2C_6(CH_3)_5m$), 17.3 ($CH_2C_6(CH_3)_5o$), 16.8 ($CH_2C_6(CH_3)_5p$). Anal. Calc. for $C_{26}H_{39}Br_2N_3O_3Pd$ (707.83): C 44.12, H 5.55, N 5.94; Found C 44.11, H 5.51, N 5.97%.

1b: Yield: 0.72 g, 91%. ^{1}H NMR ($CDCl_3$): δ 7.74–7.64 (m, 4 H, Naph-*H*, Ar-*H*), 7.50 (d, J = 7.8 Hz, 4 H, Ar-*H*), 7.36 (dd, J = 8.3, 7.1 Hz, 2 H, Naph-*H*), 6.95-6.93 (m, 2 H, Naph-*H*), 4.08 (t, J = 11.7 Hz, 2 H, $NH(CH_2CH_2OH)_2$), 3.41 (br, 1 H, $NH(CH_2CH_2OH)_2$), 3.24 (dt, J = 13.4, 6.7 Hz, 4 H, -C*H*), 3.08 (br, 2 H, $NH(CH_2CH_2OH)_2$), 2.73 (t, J = 11.5 Hz, 2 H, $NH(CH_2CH_2OH)_2$), 2.53 (t, J = 10.5 Hz, 2 H, $NH(CH_2CH_2OH)_2$), 2.26 (d, J = 11.5 Hz, 2 H, $NH(CH_2CH_2OH)_2$), 1.39 (d, J = 6.6 Hz, 12 H, -CH_3), 0.93 (d, J = 6.6 Hz, 12 H, -CH_3). ^{13}C NMR: δ 163.8 (*C*-Pd), 147.5, 140.6, 133.7, 131.0, 129.8, 129.4, 128.4, 127.5, 126.2, 124.7, 122.6 (Ar-*C*, Naph-*C*), 60.3 ($NH(CH_2CH_2OH)_2$), 53.3 (NCH_2CH_2OH), 29.1 (-*C*H_3), 26.1 (-*C*H), 24.0 (-*C*H_3). Anal. Calc. for $C_{41}H_{51}Cl_2N_3O_2Pd$ (795,19): C 61.93, H 6.46, N 5.28; Found C 61.89, H 6.42, N 5.24%.

2a: Yield: 0.62 g, 90%. ^{1}H NMR ($CDCl_3$): δ 7.46 (d, J = 8.4 Hz, 1 H, Benz-*H*), 7.11 (t, J = 8.0 Hz, 1 H, Benz-*H*), 6.87 (t, J = 8.0 Hz, 1 H, Benz-*H*), 6.23 (d, J = 8.4 Hz, 1 H, Benz-*H*), 6.06 (s, 2 H, $CH_2C_6(CH_3)_5$), 4.94 (t, J = 6.0 Hz, 2 H, $NCH_2CH_2OCH_3$), 4.13 (t, J = 6.0 Hz, 2 H, $NCH_2CH_2OCH_3$), 3.84 (d, J = 7.2 Hz, 2 H, $NH(CH_2CH_2)_2O$), 3.46 (m, 4 H, $NH(CH_2CH_2)_2O$), 2.94 (d, J = 7.2 Hz, 2 H, $NH(CH_2CH_2)_2O$), 2.53 (br, 1 H, $NH(CH_2CH_2)_2O$), 2.31 (s, 3 H, $CH_2C_6(CH_3)_5p$), 2.26 (s, 6 H, $CH_2C_6(CH_3)_5m$), 2.24 (s, 3 H, $CH_2C_6(CH_3)_5o$). ^{13}C NMR: δ 164.5 (*C*-Pd), 136.3, 135.9, 135.0, 134.9, 133.3, 127.8, 123.2, 122.7, 111.6, 111.3 (Benz-*C*, $CH_2C_6(CH_3)_5$), 71.5 ($NH(CH_2CH_2)_2O$), 68.3 ($NH(CH_2CH_2)_2O$), 59.3 ($NCH_2CH_2OCH_3$), 54.4 ($NCH_2CH_2OCH_3$), 52.4 ($CH_2C_6(CH_3)_5$), 48.9 ($NCH_2CH_2OCH_3$), 17.8 ($CH_2C_6(CH_3)_5m$), 17.5 ($CH_2C_6(CH_3)_5o$), 17.1 ($CH_2C_6(CH_3)_5p$). Anal. Calc. for $C_{26}H_{37}Br_2N_3O_2Pd$ (689.82): C 45.27, H 5.41, N 6.09; Found C 45.22, H 5.37, N 6.17%.

3b: Yield: 0.73 g, 90%. ^{1}H NMR ($CDCl_3$): δ 9.30 (s, 1 H, C_5H_4NCOOH), 8.86 (d, J = 5.5 Hz, 1 H, C_5H_4NCOOH), 8.20 (d, J = 7.9 Hz, 1 H, C_5H_4NCOOH), 7.73–7.58 (m, 4 H, (2 H + 2 H) Naph-*H*, Ar-*H*), 7.49 (d, J = 7.7 Hz, 4 H, Ar-*H*), 7.33 (t, J = 7.6 Hz, 2 H, Naph-*H*), 7.25 (d, J = 1 Hz, 1 H, C_5H_4NCOOH), 6.80 (d, J = 7 Hz, 2 H, Naph-*H*), 4.51 (br, 1 H, C_5H_4NCOOH), 3.42 (sept, 4 H, -C*H*), 1.47 (d, J = 6.5 Hz, 12 H, -CH_3), 0.93 (d, J = 6.8 Hz, 12 H, -CH_3). ^{13}C NMR: δ 168.4 (*C*-Pd), 159.7, 155.7, 153.5, 147.5, 140.6, 139.1, 134.1, 130.9, 129.8, 129.3, 128.2, 127.4, 126.3, 126.1, 124.9, 123.9, 122.4 (Ar-*C*, Naph-*C*, C_5H_4NCOOH), 29.1 (-*C*H_3), 26.0 (-*C*H), 24.5 (-*C*H_3). Anal. Calc. for $C_{43}H_{46}Cl_2N_3O_2Pd$ (814.17): C 63.43, H 5.69, N 5.16; Found C 63.38, H 5.66, N 5.21%.

Supplementary data: Crystallographic data can be obtained from the Cambridge Crystallographic Data Centre by quoting the reference number CCDC - 798814. The data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif.

4.3. General procedure for the Suzuki coupling reactions

Catalytic studies were performed under aerobic conditions. A 2-necked 25-mL flask was charged with aryl chlorides (1.0 mmol), 2 mmol KOH or DEA, phenylboronic acid (1.5 mmol), and 1.0% **1a**, **1b**, **2a**, **3b**, or **4** in 6 mL of H_2O. The flask was placed in a preheated oil bath under air atmosphere and temperature of 100 °C for 2 or 4 h.

4.4. Recycling of catalyst

The flask was charged with catalyst **1a**, **1b**, **3b** 4-chloroacetophenone (1.0 mmol), 2 mmol DEA, phenylboronic acid (1.5 mmol), and diethyleneglycol-*di-n*-butylether (0.6 mmol, internal standard). The reaction was carried out in water at 100 °C. After cooling to room temperature, the organic products were removed by filtration. The aqueous phase was then transferred to a new reaction flask for the next cycle. Yields were determined by gas chromatography for an average of 2 runs.

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