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Acyclic Palladium(II)-*N*-heterocyclic Carbene Metallacrown Ether Complexes: Synthesis, Structure and Catalytic Activity

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Novel acyclic Pd(II)-*N*-heterocyclic carbene (NHC) metallacrown ethers **5a**, **5b** have been synthesized. Reaction of the imidazolium salts bearing a long polyether chain with Ag_2O afforded Ag-NHC complexes, which then reacted as carbene transfer agent with $PdCl_2(MeCN)_2$ to give the desired acyclic Pd(II)-NHC metallacrown ether complexes **5a** and **5b**. The ^1H NMR and ^{13}C NMR spectra show **5a** and **5b** exist as mixtures of *cis* and *trans* isomers in solution. The *trans* isomer of **5a** was characterized by X-ray diffraction, which clearly demonstrated two pseudo-crown ether cavities in *trans*-**5a**. Pd(II)-NHC complexes **5a** and **5b** have been shown to be highly effective in the Suzuki-Miyaura reactions of a variety of aryl bromides in neat water without the need of inert gas protection.

Keywords palladium, *N*-heterocyclic carbene, carbene ligands, acyclic metallacrown ether, C—C coupling

Introduction

N-Heterocyclic carbenes (NHCs) in recent years have been employed with considerable success in coordination chemistry and various catalytic transformations.[1-3] Substitution of phosphine donor in phosphine metallacrown ether, which combines the two features of transition metal complex and crown ether in the same molecule,[4-7] with NHCs has led to several examples of NHC metallacrwon ether. For example, Cavell *et al*. prepared an oxoether-bridged Ag-containing dimetallacrown rings of smaller size.[8] Rogers *et al*. reported a mercury(II) carbene complex containing a three-ether spacer which revealed the possibility of a carbene extraction mechanism.[9-11] Zhang *et al*. described bidentate NHC-bridged dinuclear Ag(I), Au(I) and Cu(I) cationic metallacrown ethers.[12-14] These publications were mainly focused on the synthesis and characterization. Nielsen *et al*. reported a Pd(II)-NHC complex containing one ether spacer which was an active catalyst for Heck reaction in the presence of *n*-Bu_4NBr.[15] We reported Pd(II)-NHC metallacrown ether complexes which were shown to be effective catalysts for the Suzuki-Miyaura reaction.[16]

Acyclic crown ether which has more flexible polyether chain compared to common crown ether can easily adopt itself to different ions. Flexibility of the acyclic nature allows acyclic crown ether to engage in multiple bridging and helical binding modes when are not possible with crown ethers.[17,18] When aromatic groups, especially those with donor groups in *ortho* position of aromatic residue are located at the end of the polyether chain,[19-22] overall organization is enhanced.[23] In these acyclic crown ethers, the flexible polyether units provide basic requirement for complexation and aromatic groups control the structure elements,[24] such as π-electron, steric influence, hydrophobic interaction or donor groups in *ortho* position of aromatic residue.[25-27] Hence, acyclic crown ethers with aromatic end groups fill the gap between linear oligoethylene glycol methyl ether and the common crown ether.[24] Nevertheless, very few examples appending acyclic crown ether to NHC ligands have appeared,[28-32] and NHC transition metal-complexes which have acyclic crown ether with aromatic donor end groups in the molecule are unprecedented to date. We hereby present the synthesis and characterization of acyclic Pd-NHC metallacrown ethers with aromatic donor end groups. Their application as catalysts for Suzuki-Miyaura coupling in neat water is also described.

Results and Discussion

Ligand and metal complex synthesis

The synthetic route to desired acyclic Pd-NHC metallacrown ether **5** is shown in Scheme 1. Compound **1** was prepared by the classical method from catechol and 1,2-bis(2-chloroethoxy)ethane.[33] Reaction of **1** with 2-chloroethanol using the same procedure gave compound **2**. Chlorination of **2** with thionyl chloride was

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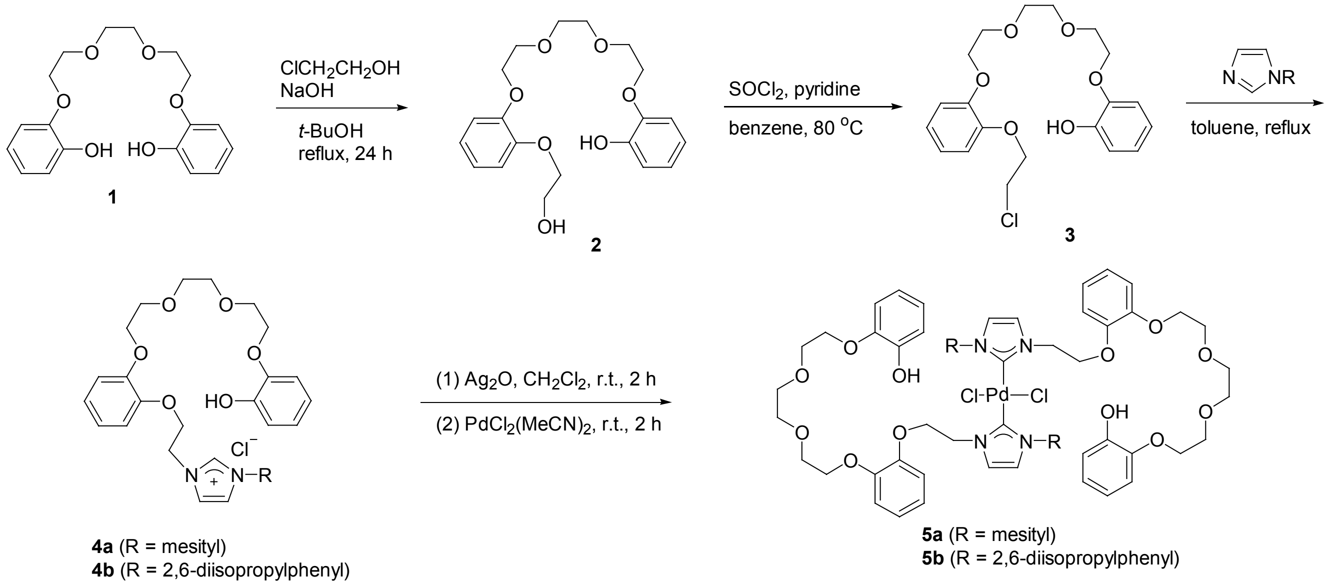
Scheme 1 Synthesis of acyclic Pd(II)-NHC metallacrown ether



optimized to give **3** in good isolated yield. Compound **3** was subsequently treated with substituted imidazoles to give the corresponding imidazolium salt **4**. In the ^{1}H NMR spectra, characteristic signals of the imidazolium salt NC(H)N protons were observed at δ 10.28 and 10.11. These values fall in the range observed for related imidazolium salts.[34-36]

The choice of base for the synthesis of palladium complex **5** was found to be crucial. Attempts to prepare the palladium complexes by *in situ* deprotonation of **4** with external strong base followed by reaction with $PdCl_2$ or $Pd(OAc)_2$ were unsuccessful. Transmetalation has proved to be a promising procedure[16,37,38] to obtain metal-NHC complexes, which typically involves treatment of the imidazolium salt with silver oxide to form the Ag-NHC complex, followed by transmetalation to a species such as $[PdCl_2(MeCN)_2]$ to give the metal-carbene complexes. We then turned to the synthesis of **5** by transmetalation from the corresponding Ag-NHC complexes. Although it was clearly observed that the reactions of imidazolium salt **4** with silver oxide occurred when the dark reaction mixture turned pale, the corresponding pure Ag-NHC complex was not isolated. We found it best to add $PdCl_2(MeCN)_2$ directly to the Ag-NHC solutions after filtering off the unreacted silver oxide and insoluble residues. The addition of $[PdCl_2(MeCN)_2]$ immediately gave a white precipitate of silver chloride and the desired product in good isolated yield. The formation of **5** was confirmed by the appearance of the signals around δ 170 which are characteristic resonances for palladium carbene complexes in the ^{13}C NMR spectra.[39,40] The appearance of two carbenoid carbon signals in the ^{13}C NMR spectra of **5a** and **5b** indicate that they exist as a mixture of *cis* and *trans* isomers in solution. Two sets of resonances corresponding to the *cis* and *trans* isomers in the ^{1}H NMR spectra of **5a** and **5b** are also observed. The ^{1}H NMR spectra indicate that the two isomers of **5a** are present in a *ca.* 1 : 1.15 ratio and the two isomers of **5b** in a *ca.* 1 : 1.35 ratio. Similar *cis-trans* isomer equilibrium mixtures of Pd-NHC complex in solution had been described in literature.[37,41-44]

The pale yellow crystals of the *trans* isomer (*trans*-**5a**) of complex **5a** suitable for an X-ray diffraction study were obtained by evaporating slowly its CH_2Cl_2/hexane solution at room temperature. Slowly precipitation of the *trans* isomer during evaporation of solvents presumably helps to drive the equilibrium between the *cis* and *trans* isomers to *trans*-**5a**. The molecular structure of complex *trans*-**5a** is depicted in Figure 1.[45] The two NHC ligands are coordinated to palladium in a *trans*-positioned fashion, with the palladium-carbene distances of Pd—C10 = 2.024 Å and Pd—C10' = 2.024 Å which are very similar to the $Pd—C_{carbene}$ bond distances found for complexes with two *trans*-positioned imidazolin-2-ylidene donor groups.[41-44] X-ray diffraction analysis of *trans*-**5a** reveals the square-planar arrangement of the ligands at the metal center, with a C10-Pd-C10' angle of 180.00° and a Cl1-Pd-Cl1' angle of 180.00°. The two NHC planes are parallel to each other and approximately orthogonal to the coordination plane. These definitely result from the space group symmetry of *P*-1.

It is noteworthy that the X-ray single crystal diffraction analysis of *trans*-**5a** reveals clearly the formation of the pseudo-crown ether cavity at each ethylene glycol chain, with a water molecule inside the cavity. In the cavity, weak hydrogen bonds are found between the protons of water and the oxygen of acyclic crown ether [Ow—H1w···O1, Ow—H1w···O2, Ow—H2w···O4]. The hydrogen bonds between the acidic proton of the phenolic hydroxyl and oxygen of water [O6—H6···Ow] are also observed. The distances[46] between donor

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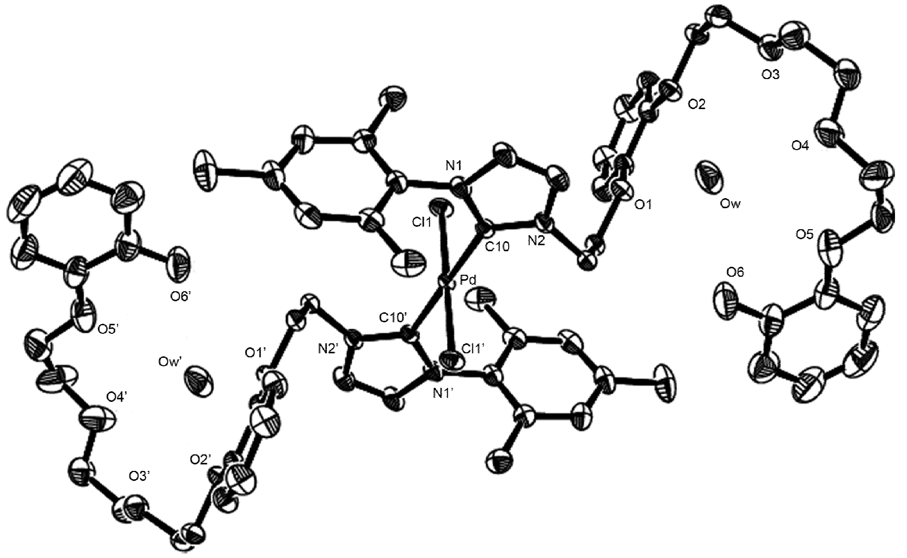


Figure 1 Molecular structure of complex *trans*-**5a**•$2H_2O$. Hydrogen atoms have been omitted for clarity; thermal ellipsoids are drawn at the 20% probability level. Selected interatomic distances (Å) and angles (°): Pd—C10 = 2.024, Pd—C10' = 2.024, Pd—Cl1 = 2.3075, Pd—Cl1' = 2.3075, C10-Pd-C10' = 180.00°, Cl-Pd-Cl' = 180.00°.

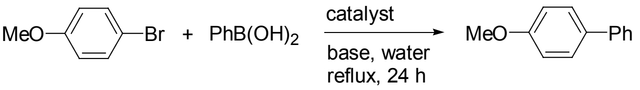
and acceptor of these hydrogen bonds are similar to the length of known hydrogen bonds.[47-51] We presume that the adventitious water may come from air and/or the CH_2Cl_2/hexane solution and stabilize the pseudo-crown cavity resulting in the formation of single crystal of *trans*-**5a**.

Application as catalyst

Water which is abundant, non-toxic, inexpensive and nonflammable can undoubtedly be considered as the cleanest solvent for chemical reaction.[52] Much effort has recently been directed towards using water as solvent for organic and organometallic reactions. The palladium-catalyzed Suzuki-Miyaura reaction, which involves the coupling of aryl halides and arylboronic acids, has become one of the most powerful and convenient synthetic tools for the synthesis of biaryl compounds. Intensive research efforts are being directed to perform the Suzuki-Miyaura coupling either via aqueous biphasic catalysis or in neat water.[32,53-65]

The acyclic Pd-NHC metallacrown ethers **5a** and **5b** are thermally stable and inert toward air and moisture in the solid state. The application of them as catalysts was then examined by catalyzing the Suzuki-Miyaura reactions under aerobic and aqueous conditions. Based on our recent experience,[16] the catalytic activities of **5a** and **5b** were firstly tested at a catalyst loading of 0.001 mol% in neat water. It is well known that the base can improve the reaction efficiency for some catalytic system. Subsequently, the reaction was investigated in the presence of different bases. As summarized in Table 1, the reaction conditions involving KOBu-*t* appeared to be superior to the others. K_2CO_3, Na_2CO_3 and Cs_2CO_3 were less effective, and K_3PO_4, NaOMe, NaOH and Et_3N gave moderate yields. We found **5a** and **5b** showed high activity in the coupling reaction of 4-bromoanisole with phenylboronic acid under the optimized reaction conditions, and **5b** was slightly superior to **5a**.

Table 1 Effect of base on the Suzuki-Miyaura cross-coupling of 4-bromoanisole with phenylboronic acid[a]



Entry	Base	Yield[b]/%	TON
1[c]	KOBu-*t*	86	86000
2	KOBu-*t*	91	91000
3	K_3PO_4	83	83000
4	KOH	63	63000
5	K_2CO_3	33	33000
6	Na_2CO_3	32	32000
7	NaOMe	79	79000
8	NaOH	64	64000
9	Cs_2CO_3	*trace*	0
10	Et_3N	60	60000

[a] Reaction conditions: 0.25 mmol of 4-bromoanisole, 0.5 mmol of phenylboronic acid, 0.5 mmol of base, 10 μL of **5b** as catalyst in dioxane (0.25 mmol/L), 1.0 mL of water, 100 ℃, 24 h, under air. [b] Isolated by silica gel column chromatography and based on 4-bromoanisole. [c] **5a** as catalyst.

The above optimized conditions were used to examine the representative range of aryl bromides for the reaction. The results are summarized in Table 2. A variety of aryl bromides and arylboronic acids containing both electron-donating (methoxyl, methyl) and electron-withdrawing substitutents (fluoro, nitro, formyl, acetyl, trifluoromethyl) tolerated well the reaction conditions, affording the corresponding biaryl products in good to excellent yields. It is noteworthy that all cross-couplings

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listed in Table 1 and Table 2 were carried out in air, and no visible palladium black formation was observed during the catalytic process. Though various catalysts have been developed for the Suzuki-Miyaura reactions, very few examples[32,58-63] can be used at a low catalyst loading of 0.001 mol% in neat water without the need of inert gas protection.

Table 2 Catalytic Suzuki-Miyaura cross-coupling reactions of aryl bromides with arylboronic acids[a]

$$\mathrm{Ar^1\text{-}X} + \mathrm{Ar^2\text{-}B(OH)^2} \xrightarrow[\text{KOBu-}t,\ \mathrm{H_2O},\ 100\ ^\circ\mathrm{C}]{\text{catalyst } \mathbf{5b}} \mathrm{Ar^1\text{-}Ar^2}$$

Entry	Ar^1	Ar^2	Catalyst/mol%	Yield[b]/%
1	3-MeOPhBr	Ph	0.005	96
2	4-CF_3PhBr	Ph	0.005	80
3	3-NO_2PhBr	Ph	0.001	83
4	4-MeCOPhBr	Ph	0.001	97
5	4-CHOPhBr	Ph	0.001	98
6	4-MeOPhBr	4-CF_3Ph	0.001	86
7	4-MeOPhBr	3-NO_2Ph	0.005	84
8	3-MeOPhBr	4-MePh	0.005	93
9	3-NO_2PhBr	4-MePh	0.001	96
10	4-MeOPhBr	4-MePh	0.001	93
11	4-MeOPhBr	4-FPh	0.001	95

[a] Reaction conditions: 0.25 mmol of aryl bromide, 0.5 mmol of arylboronic acid, 0.5 mmol of KOBu-*t*, 10 μL of **5b** in dioxane (0.25 mmol/L), 1.0 mL of water, 100 ℃, under air. The reactions were monitored by TLC. [b] Isolated by silica gel column chromatography and based on aryl bromides.

Conclusions

In summary, we have synthesized and characterized two novel acyclic Pd(II)-NHC metallocrown ethers (**5a**, **5b**) from the corresponding imidazolium salts by transmetallation. NMR spectra indicated that **5a** and **5b** existed as mixtures of *cis* and *trans* isomers in solution. The molecular structure of *trans*-**5a** was successfully determined by X-ray structural analysis which clearly showed the formation of the pseudo-crown ether cavity at each ethylene glycol chain, with a water molecule inside the cavity. Complexes **5a** and **5b** have been shown to be highly effective in the Suzuki-Miyaura reactions of a variety of aryl bromides and arylboronic acids in neat water without the need of inert gas protection. Typically the use of 0.001—0.005 mol% of Pd catalyst gave the biaryl products in good to excellent yields.

Experimental

General

Unless otherwise noted, all manipulations were performed under an argon atmosphere using standard Schlenk techniques. All solvents were dried according to standard procedures. 1,8-Bis(2-hydroxyphenoxy)-3,6-dioxaoctane (**1**)[33] was prepared according to literature procedure. All other reagents are commercially available and were used without further purification. ^1H (400 MHz, 600 MHz) and ^{13}C (100 MHz, 150 MHz) NMR spectra were recorded using Bruker instruments. Chemical shifts are reported relative to TMS as an internal standard. All NMR spectra were acquired at room temperature. GC-MS were recorded on an Agilent Technologies 6890-5973N. Mass spectra were obtained by using Bruker Daltonics Data Analysis 3.2. Elemental analyses were performed on a Carlo Erba-1106 instrument.

1-Hydroxy-15-(2-hydroxyphenyl)-4,5-dibenzo-3,6,9,12,15-pentaoxapentadecane (2)[66] To a solution of dissolved 1,8-bis(2-hydroxyphenoxy)-3,6-dioxa-octane (**1**) (9.00 g, 27 mmol) and sodium hydroxide (2.75 g, 67 mmol) in butanol (60 mL) was added dropwise in 15 min 2-chloroethanol (2.50 mL, 37.5 mmol), and the mixture was refluxed for 24 h. The solvent was removed under vacuum. The resultant oil was dissolved in CH_2Cl_2, washed with aqueous sodium hydroxide and water, and dried over Na_2SO_4. The product was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, $V∶V=3∶1$) to give a yellow oil. Yield: 6.5 g (64%). ^1H NMR (400 MHz, $CDCl_3$) δ: 6.83—6.91 (m, 7H, Ar-H), 6.77—6.79 (m, 1H, Ar-H) 4.14—4.18 (m, 4H, OCH_2CH_2O), 4.09—4.11 (m, 2H, OCH_2CH_2O), 3.91—3.93 (m, 2H, OCH_2CH_2O), 3.82—3.89 (m, 6H, OCH_2-CH_2O), 3.74—3.77 (m, 2H, OCH_2CH_2O); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.2, 149.1, 147.2, 146.1, 122.5, 122.2, 121.9, 119.7, 115.7, 115.3, 115.1, 114.0, 71.6, 70.8, 69.9, 69.7, 69.5, 68.8, 61.2; HRMS (MALDI) calcd for $C_{20}H_{26}O_7$ ($[M+Na]^+$) 401.1576, found 401.1527.

1-Chloro-15-(2-hydroxyphenyl)-4,5-dibenzo-3,9,12,15-pentaoxapentadecane (3) To a solution of **2** (0.700 g, 1.85 mmol) in dry benzene (15 mL) were added thionyl chloride (0.34 mL, 4.6 mmol) and pyridine (0.3 mL, 3.7 mmol). The mixture was refluxed for 8 h and poured into water after cooling. The solution was extracted three times with ethyl acetate. The organic phase was dried over Na_2SO_4. The product was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, $V∶V=1∶1$) to a give yellow oil. Yield: 0.68 g (93%). ^1H NMR (400 MHz, $CDCl_3$) δ: 6.90—6.95 (m, 7H, Ar-H), 6.77—6.81 (m, 1H, Ar-H), 4.24—4.28 (m, 2H, OCH_2), 4.15—4.20 (m, 4H, OCH_2), 3.88—3.90 (m, 2H, OCH_2), 3.79—3.84 (m, 6H, OCH_2), 3.76—3.73 (m, 2H, $ClCH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.2, 148.2, 147.5, 146.0, 122.9, 122.5, 121.7, 119.8, 115.8, 115.7, 115.2, 114.8, 70.8, 70.7, 69.9, 69.8, 69.7, 69.6, 68.9, 42.1; HRMS (MALDI) calcd for $C_{20}H_{25}ClO_6$ ($[M+K]^+$) 435.0977, found 435.0981.

1-(3-Mesitylimidazolium)-15-(2-hydroxyphenyl)-4,5-dibenzo-3,6,9,12,15-pentaoxapentadecane chloride (4a) A solution of **3** (0.317 g, 0.8 mmol) and 1-mesitylimidazole (0.446 g, 2.4 mmol) in xylene (1 mL) was heated to 150 ℃ for 50 h. After removal of the solvent, the residue was washed with ethyl acetate to give a yellow oil. Yield: 0.4 g (95%). ^1H NMR (400 MHz,

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$CDCl_3$) *δ*: 10.28 (s, 1H, NCHN), 8.48 (s, 1H, imi-H), 7.12 (s, 1H, imi-H), 6.89—6.96 (m, 9H, Ar-H), 6.71 (d, *J*=2.4 Hz, 1H, Ar-H), 5.29—5.30 (m, 2H, $\mathrm{NC\mathbf{H}_2CH_2O}$), 4.51—4.53 (m, 2H, $\mathrm{OC\mathbf{H}_2CH_2N}$), 4.15—4.17 (m, 2H, $\mathrm{OC\mathbf{H}_2CH_2O}$), 4.04—4.07 (m, 2H, $\mathrm{OC\mathbf{H}_2CH_2O}$), 3.78—3.83 (m, 4H, $\mathrm{OC\mathbf{H}_2CH_2O}$), 3.65—3.72 (m, 4H, $\mathrm{OC\mathbf{H}_2CH_2O}$), 2.33 (s, 3H, CH_3), 1.97 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 148.4, 147.7, 147.4, 142.9, 141.1, 138.4, 134.3, 130.8, 129.7, 125.2, 123.6, 122.7, 122.5, 122.4, 121.9, 121.1, 114.9, 113.6, 70.5, 70.1, 69.8, 69.5, 69.3, 68.3, 67.9, 49.9, 21.1, 17.4; HRMS (ESI) calcd for $C_{32}H_{39}ClN_2O_6$ ($[M-Cl]^+$) 547.2803, found 547.2789.

1-[3-(2,6-Diisopropylphenyl)imidazolium]-15-(2-hydroxyphenyl)-4,5-dibenzo-3,6,9,12,15-pentaoxapentadecane chloride (4b) A solution of **3** (0.635 g, 1.6 mmol) and 1-(2,6-diisopropyl)phenylimidazole (0.925 g, 4.0 mmol) in xylene (1 mL) was heated to 150 ℃ for 60 h. Then addition of ethyl acetate resulted in precipitation of a white powder, which was collected and washed with ethyl acetate (5 mL×3) to afford the product. Yield: 0.96 g (97%). ^1H NMR (400 MHz, $CDCl_3$) *δ*: 10.11 (s, 1H, NCHN), 8.61 (s, 1H, imi-H), 7.51 (t, *J*=7.8 Hz, 1H, Ar-H), 7.27 (d, *J*=3.2 Hz, 1H, Ar-H), 7.12 (t, *J*=1.8 Hz, 1H, imi-H), 6.82—6.96 (m, 8H, Ar-H), 6.12—6.76 (m, 1H, Ar-H), 5.28—5.30 (m, 2H, $\mathrm{NC\mathbf{H}_2CH_2O}$), 4.49—4.51 (m, 2H, $\mathrm{NCH_2C\mathbf{H}_2O}$), 4.12—4.14 (m, 2H, $\mathrm{OC\mathbf{H}_2CH_2O}$), 4.06—4.08 (m, 2H, $\mathrm{OC\mathbf{H}_2CH_2O}$), 3.76—3.79 (m, 4H, $\mathrm{OC\mathbf{H}_2C\mathbf{H}_2O}$), 3.70—3.71 (m, 4H, $\mathrm{OC\mathbf{H}_2C\mathbf{H}_2O}$), 2.21—2.24 [m, 2H, $\mathrm{(CH_3)_2C\mathbf{H}}$], 1.11 (d, *J*=6.4 Hz, 6H, CH_3), 1.05 (d, *J*=6.4 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 148.5, 147.9, 147.5, 146.1, 145.6, 138.7, 131.7, 130.4, 125.5, 124.5, 123.2, 123.0, 122.5, 121.9, 119.7, 116.3, 115.5, 115.0, 113.8, 70.5, 70.3, 69.8, 69.6, 68.4, 67.9, 50.1, 28.6, 24.4, 24.0; HRMS (ESI) calcd for $C_{35}H_{45}ClN_2O_6$ ($[M-Cl]^+$) 589.3121, found 589.3088.

[Pd{1-(3-arylimidazolin-2-yliden-1-yl)-15-(2-hydroxyphenyl)-4,5-dibenzo-3,6,9,12,15-pentaoxapentadecane}$_2$Cl$_2$] (5) A mixture of imidazolium salt **4** (0.40 mmol) and silver(I) oxide (48.3 mg, 0.21 mmol) in 5 mL of CH_2Cl_2 was stirred at room temperature for 2 h. The reaction mixture was filtered and washed with CH_2Cl_2 (5 mL×2). The combined filtrate was reduced to 5 mL under vacuum. $[PdCl_2(MeCN)_2]$ (25.8 mg, 0.10 mmol) in CH_2Cl_2 (3 mL) was added to the resulting solution and stirred at room temperature for 2 h. The reaction mixture was filtered and washed with CH_2Cl_2 (5 mL×2). The combined solution was evaporated under reduced pressure to leave a raw product, which was purified by flash chromatography on silica gel (CH_2Cl_2) to give a yellow solid.

[Pd{1-(3-mesitylimidazolin-2-yliden-1-yl-)-15-(2-hydroxyphenyl)-4,5-dibenzo-3,6,9,12,15-pentaoxapentadecane}$_2$Cl$_2$] (5a) Yield: 0.15 g (21%). ^1H NMR [400 MHz, $CDCl_3$; two isomers in a *ca*. 1∶1.15 ratio (a∶b)] *δ*: 7.48 (d, *J*=1.6 Hz, 2H, imi-H_a), 7.36 (d, *J*=2.0 Hz, 2H, imi-H_b), 6.95 (s, 4H, Ar-H), 6.85—6.89 (m, 30H, Ar-H), 6.78—6.79 (m, 6H, Ar-H), 6.67 (d, *J*=2.0 Hz, 2H, imi-H_b), 6.63 (d, *J*=1.6 Hz, 2H, imi-H_a), 5.07—5.09 (m, 4H, $\mathrm{NC\mathbf{H}_{2a}CH_2O}$), 4.67—4.69 (m, 4H, $\mathrm{NC\mathbf{H}_{2b}CH_2O}$), 4.55—4.57 (m, 4H, $\mathrm{NCH_2C\mathbf{H}_{2a}O}$), 4.24—4.26 (m, 4H, $\mathrm{NCH_2C\mathbf{H}_{2b}O}$), 4.09—4.18 (m, 16H, OCH_2CH_2O), 3.87—3.90 (m, 8H, OCH_2CH_2O), 3.73—3.80 (m, 24H, OCH_2CH_2O), 2.46 (s, 6H, CH_{3a}), 2.29 (s, 6H, CH_{3b}), 2.17 (s, 12H, CH_{3b}), 1.88 (s, 12H, CH_{3a}); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 171.7 (NCN_b), 170.0 (NCN_a) ($C_{carbene}$), 148.7, 148.5, 148.4, 148.3, 147.5, 146.1, 138.4, 137.5, 136.7, 135.9, 135.5, 128.8, 128.6, 123.0, 122.8, 122.5, 122.4, 122.0, 121.9, 121.3, 119.8, 115.8, 114.8, 114.4, 114.2, 113.9, 70.6, 69.9, 69.7, 69.4, 69.2, 68.9, 68.7, 68.4, 50.6, 50.3, 21.3, 21.1, 18.9, 18.5; HRMS (MALDI) calcd for $C_{64}H_{76}Cl_2N_4O_{12}Pd$ (M^+) 1268.3872, found 1268.3927. Anal. calcd for $C_{64}H_{76}Cl_2N_4O_{12}Pd$: C 60.50, H 6.03, N 4.41; found C 60.39, H 5.92, N 4.56.

[Pd{1-(3-(2,6-diisopropylphenyl)imidazolin-2-yliden-1-yl-)-15-(2-hydroxyphenyl)-4,5-dibenzo-3,6,9,12,15-pentaoxapentadecane}$_2$Cl$_2$] (5b) Yield: 0.12 g (50%). ^1H NMR [400 MHz, $CDCl_3$; two isomers in a *ca*. 1∶1.35 ratio (a∶b)] *δ*: 7.47—7.27 (m, 12H, Ar-H, imi-H), 7.06 (d, *J*=7.6 Hz, 4H, Ar-H), 6.87—6.89 (m, 26H, Ar-H), 6.74—6.79 (m, 8H, Ar-H, imi-H_b), 6.66 (s, 2H, imi-H_a), 5.25—5.27 (m, 4H, $\mathrm{NC\mathbf{H}_{2(a+b)}CH_2O}$), 4.62—4.66 (m, 8H, $\mathrm{NC\mathbf{H}_{2(a+b)}CH_2O}$, $\mathrm{NCH_2C\mathbf{H}_{2(a+b)}O}$), 4.10—4.16 (m, 20H, OCH_2CH_2O), 3.87—3.90 (m, 8H, OCH_2CH_2O), 3.72—3.80 (m, 24H, OCH_2CH_2O), 2.85—2.55 [m, 8H, $(CH_3)_2CH_{(a+b)}$], 1.31 (d, *J*=6.4 Hz, 12H, $CH_{3(a+b)}$), 0.85—0.91 (m, 36H, $CH_{3(a+b)}$); ^{13}C NMR (100 MHz, DMSO-d_6) *δ*: 171.6 (NCN_a), 170.9 (NCN_b) ($C_{carbene}$), 148.8, 148.7, 148.6, 147.4, 147.2, 147.0, 146.2, 135.9, 135.3, 129.9, 124.9, 124.8, 123.7, 123.5, 122.8, 122.0, 121.8, 119.7, 116.2, 115.3, 114.7, 70.4, 69.7, 69.5, 68.9, 68.6, 50.4, 50.3, 28.2, 27.8, 26.8, 26.4, 23.1, 22.8; HRMS (MALDI) calcd for $C_{70}H_{88}Cl_2N_4O_{12}Pd$ (M^+) 1352.4811, found 1352.4842. Anal. calcd for $C_{70}H_{88}Cl_2N_4O_{12}Pd$: C 61.06, H 6.55, N 4.14; found C 61.08, H 6.48, N 4.68.

X-ray crystal structure determination and refinement

X-ray single-crystal diffraction data for *trans*-**5a** were collected on an Enraf-Nonius CAD-4 diffractometer at 294(2) K with Mo K*α* radiation ($\lambda=0.71073$ Å) by $\omega/2\theta$ scan mode. The structures were solved with direct methods using SHELXS-97 and refined by full-matrix least-squares refinement on F^2 with SHELXL-97. All atoms except hydrogen atoms were refined with anisotropic displacement parameters. In general, hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model.

General procedure for the Suzuki-Miyaura cross-coupling reaction

In a typical run, aryl bromide (0.25 mmol), arylboronic acid (0.50 mmol), KOBu-*t* (0.50 mmol), and Pd-NHC metallacrown ether complex **5b** in dioxane (10 μL, 0.0025 μmol) were charged in a reaction tube with a stirring bar. Water (1 mL) was then added to the mixture

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using a syringe. The reaction mixture was vigorously stirred at reflux in air. After 24 h, the reaction was stopped. CH_2Cl_2 (10 mL) was added to the reaction mixture. The organic phase extracted from water was dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography to obtain the final products. All of the cross-coupling products have been identified by comparing their ^1H NMR and ^{13}C NMR spectra with those reported in literature.

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