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Pd complexes with trans-chelating ligands composed of two pyridyl groups and rigid π -conjugated backbone

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ABSTRACT

1,2-Bis(2-pyridylethynyl)benzene derivatives, having two pyridyl groups and π -conjugated backbone, were prepared from the 1:2 Sonogashira reaction of 1,2-diiodobenzene with 2-alkynyl pyridines. The obtained ligands react with the palladium(II) complexes such as [PdCl₂(cod)] and [PdCl₂(MeCN)₂] to form the complexes with the ligands coordinated in a trans-chelating bidentate mode. The ligand obtained from 1,3-diiodobenzene and 2-alkynyl pyridine bridges two Pd(II) centers, yielding a dipalladium complex. A dichloropalladium complex with the trans-chelating ligand, containing two methoxy groups in the central arylene group, promotes coupling of phenyl lithium and of phenyl acetylene to yield the respective homo-coupling products. The ligand displacement reactions of {bis(2-pyridylethynyl)benzene}palladium(II) complex with phosphine and dinitrogen ligands, such as PPh₃, dppe, dppb, en, tmeda, bpy and phen, takes place smoothly to release the trans-chelating ligand.

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1. Introduction

Palladium(II) complexes with cis-chelating dinitrogen ligands such as 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), and N, *N*,*N'*,*N'*-tetramethyl-1,2-ethylenediamine (tmeda), are commonly known because of their high stability as well as various chemical properties [1,2]. The complexes with cis-chelating dinitrogen ligands catalyze homo-coupling reaction of thiophene [3], cyclizative hydrosilylation of 1,6-dienes [4] and oxidative cyclocarbonylation of β -aminoalcohols [5] as well as the cyclization and polymerization of dienes [6,7]. The dinitrogen ligands are employed for the Pd-catalyzed copolymerization of olefin and CO to yield the polyketone [8]. Brookhart et al. discussed detailed mechanism of the [PdCl₂(bpy)]-catalyzed co-polymerization, which includes alternating insertion of the two different monomers [9]. Organopalladium(II) complexes having the ligand with extended π -conjugated system were reported to show fluorescence in solution as well as in the solid state [10]. Recent interest in the oligopyridine ligand for Pd(II) complex is in its use as the building blocks of the supramolecules [11]. The amphiphilic (1,2-ethylenediamine)palladium(II) bearing N-alkylbipyridinium ligands were reported to form micelle and [5] rotaxanes with α -cyclodextrins in water [12]. The Pd complexes with trans-chelating dinitrogen ligands are much less common than that of the cis-chelating ligands. Gelman et al. reported that 1,8-bis(diisopropylphosphino)tripty-1,8-bis(p-(diphenylphosphino)phenyl)anthracenes cene and

* Corresponding author. *E-mail address:* kosakada@res.titech.ac.jp (K. Osakada). coordinate with palladium(II) as the trans bidentate ligand [13]. Addition of 1.8-bis(*p*-(diphenylphosphino)phenyl)anthracene to the palladium-catalyzed Mizoroki-Heck reaction of cyclohexene and aryl bromides results in high regioselectivity of the product. 1,2-Bis(2-pyridylethynyl)benzene is a dinitrogen ligand first employed by Bosch et al. [14], and is used as the ligand for mononuclear and oligonuclear complexes of Ag [14], Cu [15], Co [16], Zn [16], Rh [17] and Pd [14,18]. Recently we reported the dipalladium complexes with a [3]rotaxane structure, composed of the crown ethers bearing palladium(II)(dichloro){1,2-bis(2-pyridylethynyl) benzene} unit and its catalytic properties for the cyclizative Mizoroki-Heck reactions of difunctionalized substrates [19]. Here we report the synthesis of the substituted 1,2-bis(2-pyridylethynyl)benzene derivatives and their palladium(II) complexes as well as their reactivity. Formation of a dinuclear Pd(II) complex of 1,3bis(2-pyridylethynyl)benzene is also mentioned.

2. Results and discussion

2.1. Preparation of bis(2-pyridylethynyl)benzene ligands and their Pd(II) complexes

Chart 1 lists the palladium(II) complexes, **1a–1h**, **3**, and their ligands **2a**, **2d**, **2f–2h**, **4**.

Ligands, **2d** and **2f–2h**, have the substituents on the pyridyl or phenylene group.

Table 1 summarizes the synthesis of *o*-{bis(2-pyridylethynyl)arene}, **2a** and **2d**, by Sonogashira coupling reaction. Reaction of 1,2-diiodobenzene (**5a**) and 2-ethynylpyridine in 0.5 M



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Chart 1. Pd(II) complexes 1a-1h and 3 and their ligands 2a, 2d, 2f-2h and 4.

Table 1

Synthesis of 1,2-bis(2-pyridylethynyl)benzene 2a, 2b.ª



Run	5a-5c	Base/solvent	Temp./time	Yield
1	5a	0.5 M NH ₃ (aq)/THF	r.t./94 h	2a , >99%
2	5a	Ethanolamine/THF	50 °C/14 h	2a , 83%
3	5b	0.5 M NH ₃ (aq)/THF	r.t./24 h	2d , 92%
4 ^b	5c	Ethanolamine/THF	r.t./24 h	2a , 0%
5°	5c	Et ₃ N/DMF	100 °C/46 h	2a , 5%
6 ^d	5c	Et ₃ N/DMF	100 °C/18 h	2a , 16%

^a [PdCl₂(PPh₃)₂], 2 mol%; CuI, 4 mol%.

^b [PdCl₂(PPh₃)₂], 3 mol%; CuI, 2 mol%.

^c [PdCl₂(MeCN)₂], 5 mol%; CuI, 10 mol%; P(C₆H₄-2-Me)₃, 15 mol%.

 d [PdCl₂(MeCN)₂], 5 mol%; Cul, 10 mol%; P-tBu₂(C₆H₄-2-C₆H₄-2,4,6-iPr) (tBu-X-phos) 15 mol%.

 $NH_3(aq)/THF$ [20] at room temperature or in ethanolamine/THF at 50 °C gave **2a** in good yields (run 1, 2). A similar reaction using 1,2-

diiodo-4,5-dimethoxybenzene (**5b**) yields **2d** in 92% yield (run 3). 1,2-Dibromobenzene (**5c**) showed much lower reactivity than **5a** and its reaction with 2-ethynylpyridine yielded **2a** in low yields (0–16%, run 4–6). The Pd/tBu-X-Phos (X-Phos = 2-di-tert-butyl-phosphino-2',4',6'-triisopropylbiphenyl) catalyst (run 6) led to better yield than the reaction using triarylphosphines.

Eq. (1) shows synthesis of 1,2-{bis(2-pyridylethynyl)benzene} derivatives, **2f**-**2h**, having substituents on the pyridyl groups from Sonogashira reaction of 1,2-dialkynylbenzene with 2-bromopyridines, **6f**-**6h**.



2h: R¹ = Br, R² = H (87%)

1,3-{Bis(2-pyridylethynyl)benzene}, **4**, is synthesized from 1,3-diiodobenzene and 2-ethynylpyridine by a similar procedure to that of **2a** (Eq. (2)).



Table 2 summarizes synthesis of palladium(II) complexes 1a-**1h**. [PdCl₂(MeCN)₂], [PdCl₂(cod)], [PdBr₂(cod)], and Pd(OAc)₂ were employed as the starting complexes. Reaction of 2a and [PdCl₂(MeCN)₂] in CH₂Cl₂/MeCN yields **1a** in 60%, while using [PdCl₂(cod)] results in quantitative formation of the product (99%). 1,2-Bis(2-pyridylethynyl)benzene palladium(II) complex, bearing bromo and acetoxy ligands, 1b and 1c, were similarly synthesized from the reaction of 2a with [PdBr2(cod)], and with Pd(OAc)₂, respectively. Fig. 1 depicts molecular structures of 2a, 1f, and 1g determined by X-ray crystallography. 1,2-{Bis(2-pyridylethynyl)benzene} (2a) adopts a distorted planar conformation with torsion angle C7-C8-C13-C14 of 2.9° (Fig. 1A). Complex 1f was determined as a square planar four-coordinated complex bearing trans-chelating-1,2-{bis(2-pyridylethynyl)benzene}. Palladium, carbon, and nitrogen atoms of 1f are included in a plane with C8-C9-C14-C15 torsion angle of 0.2°. Complex 1g contains a crystallographic 2-fold axis in the molecule and its dinitrogen ligand has conformation of the backbone to the ligand of 1f.

Fig. 2A and B compares ¹H NMR spectra of **2f** and **1f**. The pyridyl (δ 7.57, 7.74, 7.95) and phenylene (δ 7.69, 7.90) hydrogen peaks of

Table 2

Synthesis of {1,2-bis(2-pyridylethynyl)benzene}palladium(II) complexes.



Run	Ligand, 2a , 2d , 2f–2h			PdX ₂ L ₂	Solvent	Temp./time	Yield	
		R1	R2	R3				
1	2a	Н	Н	Н	[PdCl ₂ (MeCN) ₂]	CH ₂ Cl ₂ /MeCN	r.t./24 h	1a , 60%
2	2a	Н	Н	Н	[PdCl ₂ (cod)]	CHCl ₃	50 °C/42 h	1a , 99%
3	2a	Н	Н	Н	[PdBr ₂ (cod)]	dmso	50 °C/2 h	1b , 80%
4	2a	Н	Н	Н	$Pd(OAc)_2$	Toluene	r.t./15 min	1c, 77%
5	2d	Н	Н	OMe	[PdCl ₂ (MeCN) ₂]	CH ₂ Cl ₂ /MeCN	r.t./72 h	1d, 60%
6	2d	Н	Н	OMe	[PdCl ₂ (cod)]	CHCl ₃	50 °C/98 h	1d, 99%
7	2d	Н	Н	OMe	$Pd(OAc)_2$	Toluene	r.t./10 min	1e, 75%
8	2f	Н	Me	Н	[PdCl ₂ (MeCN) ₂]	CH ₂ Cl ₂ /MeCN	r.t./48 h	1f, 93%
9	2g	Н	CH ₂ OPh	Н	[PdCl ₂ (MeCN) ₂]	CH ₂ Cl ₂ /MeCN	r.t./13 h	1g , 96%
10	2h	Br	Н	Н	[PdCl ₂ (MeCN) ₂]	CH ₂ Cl ₂ /MeCN	r.t./3 h	1h , 90%





Fig. 2. ¹H NMR spectra of (A) **2f**, (B) **1f** and (C) **3** (300 MHz, r.t., dmso- d_6). The labeling assigned to the hydrogens of compound **3** is given in the Eq. (3).

Fig. 1. Molecular structures of (A) **2a**, (B) **1f** and (C) **1g** with 50% of probability. The hydrogen atoms and incorporated solvent molecule of **1f** are omitted.

1f are observed at lower magnetic field position than those of **2f** (δ 7.11, 7.33, 7.55, 7.64).

Reaction of **4** with $[PdCl_2(cod)]$ in CHCl₃ yields dinuclear complex **3** in 55% yield (Eq. (3)). The structure of **3** was determined by NMR and mass spectroscopy as well as elemental analysis. FAB mass spectrum of **3** contains peaks at m/z 878 and 703, assigned to $[\mathbf{3}\text{-}Cl^{-}]^{+}$ (Calc. 876.9) and $[\mathbf{3}\text{-}PdCl_{3}^{-}]^{+}$ (Calc. 702.5), respectively.



¹H NMR spectrum of **3** (Fig. 2C) shows seven signals each of which is assigned to the hydrogen of two equivalent 1,3-{bis(2-pyridylethynyl)benzene} ligands. Peak due to the hydrogen at 6-position of the pyridyl group of **3** (δ 9.06) is observed at lower magnetic field position than that of **4** (δ 8.59).



Scheme 1. Reactions of 1d with phenyllithium and with phenylacetylene.

Table 3Ligand exchange of 1d.



Run	L ₂	Temp./time	Yield of PdCl ₂ L ₂
1	2PPh ₃	r.t./22 h	74% ^a
2	$Ph_2P(CH_2)_2PPh_2$ (dppe)	r.t./30 min	>99%
3	Ph ₂ P(CH ₂) ₄ PPh ₂ (dppb)	r.t./30 min	75%
4	Me ₂ N(CH ₂) ₂ NMe ₂ (tmeda)	100 °C/30 min	95%
5	$H_2N(CH_2)_2NH_2$ (en)	100 °C/10 min	97%
6	2,2'-bpy	100 °C/50 min	64%
7	1,10-phen	100 °C/10 min	87%
8	1a	100 °C/65 h	57%
9	Pyridine (py)	100 °C/6 days	No reaction
10	cod	50 °C/30 h	No reaction ^b
11	dmso-d ₆	100 °C/47 h	No reaction ^c

^a Reaction in CH₂Cl₂.

^b Reaction in CDCl₃.

^c Reaction in dmso-d₆.

2.2. Reactions of phenyllithium and phenylacetylene with bis(2pyridylethynyl)benzene palladium(II) complex

The homo-coupling reaction of aryl-metal reagents and of terminal alkynes were studied by using various transition metal catalysis [21,22]. Previously, we reported the quantitative formation of biaryls from the intermolecular reaction of the cationic arylpalladium and arylnickel complexes with 2,2'-bipyridine ligand [23,24]. The reaction of PhLi with **1d** also takes place to produce biphenyl as shown in Scheme 1. The reaction of phenylacetylene with **1d** under basic conditions yields the corresponding diyne in 10%. Although the trans-chelating ligand of **1d** may prevent smooth reductive elimination of the homocoupling product from a diorganopalladium(II) intermediate generated from the reaction of **1d** with the organometallic reagent, the products are obtained in considerable yields.

2.3. Reactions of auxiliary cis-coordinating ligands with 1,2-bis(2pyridylethynyl)benzene palladium(II) complexes

Ligand displacement reactions starting from the Pd(II) complexes such as [PdCl₂(cod)] and [PdCl₂(MeCN)₂] bearing relatively labile ligands were widely employed as the synthesis of the corresponding dichloropalladium complexes with other auxiliary ligands. The ligand displacement reaction provides information on the stability of the coordination bonds of these ligands.

The reaction of PPh₃ with **1d** yields a mixture of **2d** (74%) and [PdCl₂(PPh₃)₂] (Table 3, run 1). Similar reactions using Ph₂P(CH₂)₂PPh₂ (dppe) and Ph₂P(CH₂)₄PPh₂ (dppb) form [PdCl₂(dppe)] and [PdCl₂(dppb)], respectively (run 2, 3). The reactions of dinitrogen ligands, such as tmeda (*N*,*N*,*N'*,*N'*-tetramethyl-ethylenediamine), en (ethylenediamine), 2,2'-bpy and phen with **1d** at 100 °C yield the corresponding Pd(II) complexes with the cis-chelating ligand in high yield (95–97%). The reaction of **1d** with **2a** at 100 °C gave a mixture of **1a**, **1d**, **2a** and **2d** after 65 h (run 8). No replacement was observed in the reaction of py, cod and dmso with **2d**. These results indicate that 1,2-bis(2-pyridylethynyl)benzene coordinates to Pd(II) more strongly than with py, cod and dmso and less strongly than with phosphine and dinitrogen ligands, as shown in Table 3.

3. Conclusion

Palladium(II) complexes bearing 1,2- and 1,3-bis(2-pyridylethynyl)benzene ligands were obtained and their structure and reactivity have been studied. The ligand exchange reaction starting from [PdCl₂(cod)] and 1,2-bis(2-pyridylethynyl)benzenes yields corresponding dichloropalladium (II) complex in high yield. The reaction of [PdCl₂(MeCN)₂] and 1,3-bis(2-pyridylethynyl)benzenes causes 2:2 complexation to generate the dinuclear Pd(II) complex. {1,2-Bis(2-pyridylethynyl)benzene}palladium complex reacts with PhLi and with phenylacetylene to give biphenyl and diyne, respectively. The ligand displacement reactions revealed that the 1,2bis(2-pyridylethynyl)benzene is a weaker ligand than the phosphine and the cis-chelating dinitrogen ligands, such as PPh₃, dppe, dppb, en, tmeda, bpy and phen.

4. Materials and methods

4.1. General

[PdX₂(cod)] (X = Cl, Br) [25] and 1,2-diethynylbenzene [26] were prepared according to the literature method. The other chemicals were commercially available and used without further purification. ¹H and ¹³C{¹H} NMR spectra were recorded on Varian

MERCURY300 and JEOL EX-400 spectrometers. IR absorption spectra were recorded on Shimadzu FT/IR-8100 spectrometers. Fast atom bombardment mass spectrum (FABMS) was obtained from JEOL JMS-700 (matrix, glycerol or *m*-nitrobenzyl alcohol). Elemental analysis was carried out with a LECO CHNS-932 CHNS or Yanaco MT-5 CHN autorecorder at the Center for Advanced Materials Analysis, Technical Department, Tokyo Institute of Technology.

4.1.1. Dichloro-(1,2-bis(2'-pyridylethylnyl)benzene)palladium (1a) [14]

A solution of $[trans-PdCl_2(MeCN)_2]$ (87.9 mg, 0.34 mmol) in MeCN (10 mL) was carefully layered over a solution of **2f** (76.8 mg, 0.27 mmol) in CH₂Cl₂ (3 mL). The mixture was sealed and allowed to stand in the dark. Clear yellow precipitate was formed after 24 h. The resulting solid was collected by filtration, washed with MeCN and dried in vacuo to form **1a** as yellow solid. Yield: 75 mg (60%). IR (KBr disk, r.t.) ν 3060, 3023, 2221 (C=C), 1596, 1495 cm⁻¹.

4.1.2. Dibromo-{1,2-bis[(2-pyridyl)ethynyl]benzene}palladium (1b)

A mixture of **1a** (280 mg, 1.0 mmol) and [PdBr₂(cod)] (187 mg, 0.50 mmol) in dmso (4.0 mL) was stirred for 2 h at 50 °C. A yellow solid, separated from the solution, was collected by filtration. The product was washed with toluene and hexane and then dried under reduced pressure to give **1b**. Yield: 218 mg (80%). ¹H NMR (300 MHz, CDCl₃, r.t.) δ = 7.36 (ddd, C₅H₄N, 2 H, *J* = 7.4, 5.8, 1.7 Hz), 7.51 (dd, C₆H₄, 2 H, *J* = 5.8, 3.3 Hz), 7.66 (d, C₅H₄N, 2 H, *J* = 7.7 Hz), 7.75-7.81 (m, 4 H, C₅H₄N, C₆H₄), 8.89 (d, 2 H, C₅H₄N, *J* = 5.8 Hz). MS (ESI pos): *m/z* = 466.9 ([M-Br]⁺). IR (KBr disk, r.t.) *v* 3058, 3021, 2220 (C=C), 1596, 1494, 759 cm⁻¹.

4.1.3. Diacetoxy-{1,2-bis[(2-pyridyl)ethynyl]benzene}palladium (1c)

A toluene (13 mL) solution of Pd(OAc)₂ (140 mg, 0.62 mmol) was added to a toluene (8.0 mL) solution of **1a** (179 mg, 0.64 mmol), and the mixture was stirred for 1 h at room temperature. The brown solid, separate from the solution, was collected by filtration, washed with toluene and hexane, and then dried under reduced pressure to give **1c**. Yield: 241 mg (77%). ¹H NMR (300 MHz, CDCl₃, r.t.) δ = 1.67 (s, Me, 6 H), 7.34 (ddd, C₅H₄N, 2 H, *J* = 7.4, 5.5, 1.6 Hz), 7.53 (dd, C₆H₄, 2 H, *J* = 5.8, 3.3 Hz), 7.63 (d, C₅H₄N, 2 H, *J* = 7.1 Hz), 7.76 (ddd, C₅H₄N, 2 H, *J* = 7.7, 7.7, 1.7 Hz), 7.80 (dd, 2 H, C₆H₄, *J* = 5.8, 3.3 Hz), 9.51 (d, 2 H, C₅H₄N, *J* = 5.8 Hz). MS (FAB pos): *m/z* = 446 ([M–Cl⁻]⁺). IR (KBr disk, r.t.) ν 3105, 3070, 2222 (C=C), 1628, 1327 cm⁻¹. *Anal.* Calc. for C₂₄H₁₈N₂O₄Pd·H₂O: C, 55.13; H, 3.86; N, 5.36. Found: C, 55.01; H, 3.81; N, 5.01%.

4.1.4. Dichloro-{1,2-dimethoxy-4,5-bis(2'-

pyridylethynyl)benzene}palladium (1d) [18c]

Ligand **2d** (510 mg, 1.5 mmol) was dissolved in 21 mL of CH_2Cl_2 . A solution of $[PdCl_2(MeCN)_2]$ (580 mg, 2.2 mmol) in MeCN (68 mL) was prepared separately, and was carefully layered over the CH_2Cl_2 solution of **2d**. The reaction mixture was placed in the dark. Clear yellow precipitate was formed after 72 h. The resulting solid was collected by filtration, washed with MeCN and dried in vacuo to form **1d** as yellow solid. Yield: 500 mg (60%).

4.1.5. Diacetoxy-{1,2-dimethoxy-4,5-bis(2'pyridylethynyl)benzene}palladium (**1e**)

A toluene (15 mL) solution of Pd(OAc)₂ (140 mg, 0.62 mmol) was added to a toluene (10 mL) solution of **1b** (218 mg, 0.64 mmol), and the mixture was stirred for 10 min at room temperature. The brown solid, separated from the solution, was collected by filtration, washed with acetone and Et₂O, and then dried under reduced pressure to give **1e**. Yield: 272 mg (75%). ¹H NMR (300 MHz, CDCl₃, r.t.) δ = 1.67 (s, OAc, 6 H), 4.02 (s, OMe, 6

H), 7.22 (s, 2 H, C₆H₂), 7.28 (dd, C₅H₄N, 2 H, J = 8.1, 7.4 Hz), 7.59 (d, C₅H₄N, 2 H, J = 7.4 Hz), 7.74 (dd, C₅H₄N, 2 H, J = 8.1, 7.7 Hz), 9.50 (m, 2 H, C₅H₄N). *Anal.* Calc. for C₂₆H₂₂N₂O₆Pd·(H₂O)_{0.5}: C, 54.41; H, 4.04; N, 4.88. Found: C, 54.45; H, 4.03; N, 4.73%.

4.1.6. Dichloro-{1,2-bis[(6-methyl-2-

pyridyl)ethynyl]benzene}palladium (1f)

The ligand **2f** (30.8 mg, 0.10 mmol) was dissolved in CH₂Cl₂ (1.0 mL). A solution of [PdCl₂(MeCN)₂] (39 mg, 0.15 mmol) in MeCN-CH₂Cl₂ (1:1) (4.0 mL) was prepared separately. The MeCN-CH₂Cl₂ (1:1) solution was carefully layered over the CH₂Cl₂ solution, and the reaction mixture was placed in the dark. After 2 days yellow crystals of **1f** were formed which were collected by filtration, washed with CHCl₃ and dried in the atmosphere. Yield: 46 mg (93%). ¹H NMR (300 MHz, dmso-*d*₆, r.t.) δ = 3.51 (s, 6 H), 7.57 (d, 2 H, *J* = 6.6 Hz), 7.69 (dd, 2 H, *J* = 5.8, 3.6 Hz), 7.74 (d, 2 H, *J* = 6.6 Hz), 7.90 (dd, 2 H, *J* = 5.8, 3.6 Hz), 7.95 (t, 2 H, *J* = 7.7 Hz). MS (FAB pos): *m/z* = 452 ([M-Cl⁻]⁺). IR (KBr disk, r.t.) *v* 3066, 2211 (C=C), 1566, 1467, 1238 cm⁻¹.

4.1.7. Dichloro-{1,2-bis[(6-phenoxymethyl-2-

pyridyl)ethynyl]benzene}palladium (1g)

Ligand **2g** (19 mg, 0.04 mmol) was dissolved in CH₂Cl₂ (1.0 mL), and a solution of [PdCl₂(MeCN)₂] (16 mg, 0.059 mmol) in 2.0 mL of MeCN–CH₂Cl₂ (1:1) was prepared, separately. The MeCN–CH₂Cl₂ (1:1) solution was carefully layered over the CH₂Cl₂ solution and the vial capped and placed in the dark. After 13 h, the yellow crystals of **1g**, formed were collected by filtration, washed with CH₂Cl₂ and dried in the atmosphere. Yield: 26 mg (96%). MS (FAB pos) *m*/ *z* = 635 ([M–Cl⁻]⁺). Anal. Calc. for C₃₄H₂₆Cl₂N₂Pd·H₂O: C, 59.36; H, 3.81; N, 4.07. Found: C, 60.12; H, 4.06; N, 4.21%.

4.1.8. Dichloro-{1,2-bis[(5-bromo-2-

pyridyl)ethynyl]benzene}palladium (1h)

The ligand **2h** (131 mg, 0.29 mmol) was dissolved in CH₂Cl₂ (3.0 mL) and a separate solution of $[PdCl_2(MeCN)_2]$ (104 mg, 0.39 mmol) in MeCN (13 mL) was prepared. The MeCN solution was carefully layered over the CH₂Cl₂ solution and the vial capped and placed in the dark. Clear yellow precipitate was formed after 3 h. The resulting solid was collected by filtration, washed with CHCl₃ and dried in vacuo to form **1h** as brown solid. Yield: 170 mg (90%). MS (FAB pos) m/z = 581 ($[M-Cl^{-}]^{+}$). ¹H NMR (400 MHz, CD₂Cl₂, r.t.) $\delta = 6.96$ (t, 2 H, J = 7.2 Hz), 7.12 (dd, 2 H, J = 8.0, 2.4 Hz), 7.23 (t, 4 H, J = 7.6 Hz), 7.64-7.60 (m, 6 H), 7.65 (d, 2 H, J = 6.8 Hz), 7.59 (dd, 2 H, J = 3.2, 6.0 Hz), 7.83 (t, 2 H, J = 4.8 Hz), 7.86 (dd, 2 H, J = 3.2, 5.6 Hz). MS (FAB pos): m/z = 461 ($[M-2(Cl)]^{+}$). IR (KBr disk, r.t.) ν 3055, 2223 (C=C), 1494, 1230, 759 cm⁻¹.

4.1.9. 1,2-Bis(2'-pyridylethynyl)benzene (2a) [14]

A mixture of 1,2-diiodobenzene (3.3 g, 10 mmol), 2-ethynylpyridine (2.3 g, 22 mmol), [PdCl₂(PPh₃)₂] (140 mg, 0.20 mmol) and Cul (76 mg, 0.40 mmol) in THF (120 mL) and 0.5 M aqueous ammonia (80 mL) was stirred under argon at room temperature for 94 h. After evaporation of the solvent, the obtained oily residue was dissolved in CH₂Cl₂, The solution was washed with water, and was dried over MgSO₄. After removing MgSO₄ and subsequent evaporation of the solvent, the obtained residue was purified by chromatography on silica gel eluting with CH₂Cl₂. Yield: 3.6 g (>99%). IR (KBr disk, r.t.) ν 3057, 2220 (C=C), 1579, 1460, 773 cm⁻¹.

4.2. 1,2-Dimethoxy-4,5-bis(2'-pyridylethynyl)benzene (2d) [18c]

A mixture of 1,2-diiodo-4,5-dimethoxybenzene (1.2 g, 3.0 mmol), 2-ethynylpyridine (680 mg, 12 mmol), $[PdCl_2(PPh_3)_2]$ (42.0 mg, 0.059 mmol) and CuI (23.0 mg, 0.12 mmol) in THF

(36 mL) and 0.5 M aqueous ammonia (24 mL) was stirred at room temperature for 24 h. After evaporation of the solvent, the oily residue was dissolved in CH_2Cl_2 . The organic layer was washed with water, dried over MgSO₄ and filtered, and the solvent was evaporated. The residue was purified by chromatography on silica gel eluting with CH_2Cl_2 . Yield: 940 mg (92%).

4.3. 1,2-Bis[(6-methyl-2-pyridyl)ethynyl]benzene (2f)

A Et₃N solution (15 mL) of 6-bromo-2-picoline (**6f**) (69 mg, 4.0 mmol), CuI (13 mg, 0.068 mmol), [PdCl₂(PPh₃)₂] (48 mg, 0.068 mmol), 1,2-diethynylbenzene (200 mg, 1.7 mmol) was stirred for 12 h at 80 °C. The resulting solid was removed by filtration, which was followed by evaporation of the filtrate. The obtained solid was washed with hexane to give **2f** as white solid. Yield: 267 mg (52%). ¹H NMR (400 MHz, CDCl₃, r.t.) δ = 2.59 (s, 6 H), 7.11 (dd, 2 H, *J* = 5.6, 3.2 Hz), 7.33 (dd, 2 H, *J* = 5.6, 3.2 Hz), 7.55 (m, 4 H), 7.64 (dd, 2 H, *J* = 5.6, 3.2 Hz). ¹³C NMR (75.5 MHz, CDCl₃, r.t.): δ 24.5, 87.4, 93.1, 122.6, 124.8, 125.5, 128.5, 132.0, 136.2, 142.6, 158.8. *Anal.* Calc. for C₂₂H₁₆N₂: C, 85.69; H, 5.23; N, 9.08. Found: C, 85.81; H, 5.04; N, 9.06%. MS (ESI pos): *m*/*z* = 331.1 ([M+Na]⁺). IR (KBr disk, r.t.) *v* 3046, 2210 (C==C), 1580, 1449, 788 cm⁻¹. *Anal.* Calc. for C₂₂H₁₆N₂: C, 85.69; H, 5.23; N, 9.08. Found: C, 85.81; H, 5.04; N, 9.06%.

4.4. 1,2-Bis[(6-phenoxymethyl-2-pyridyl)ethynyl]benzene (2g)

A Et₃N solution (11 mL) of 2-bromo-6-(phenoxymethyl)pyridine (**6g**) (528 mg, 2.0 mmol), CuI (7.0 mg, 0.037 mmol), [PdCl₂(PPh₃)₂] (24.0 mg, 0.034 mmol), 1,2-diethynylbenzene (100 mg, 0.78 mmol) was stirred at 50 °C for 24 h, the reaction mixture was cooled to room temperature. The resulted solid was removed by filtration. The filtrate was evaporated to dryness under reduced pressure to give crude product. The oily residue was dissolved in AcOEt, and the resulting solution was washed with saturated aqueous NH₄Cl, H₂O and brine. The organic layer was dried over MgSO₄ and filtered, and the solvent was evaporated. The oily residue was purified by chromatography on silica gel eluting with AcOEt–hexane to give **2g**. Yield: 336 mg (88%). ¹H NMR (300 MHz, CDCl₃, r.t.) δ = 5.24 (s, 4 H), 6.96-6.99 (m, 6 H), 7.30 (t, 4 H, *J* = 8.0 Hz), 7.39 (dd, 2 H, *J* = 5.8, 3.3 Hz), 7.50 (dd, 2 H, *J* = 6.3, 2.2 Hz), 7.63–7.70 (m, 6 H).

4.5. 1,2-Bis[(5-bromo-2-pyridyl)ethynyl]benzene (2h)

A Et₃N solution (15 mL) of 2,5-dibromopyridine (6h) (948 mg, 4.0 mmol), CuI (13.0 mg, 0.068 mmol), [PdCl₂(PPh₃)₂] (48.0 mg, 0.068 mmol), 1,2-diethynylbenzene (200 mg, 1.7 mmol) was stirred at 80 °C for 24 h, the reaction mixture was cooled to room temperature, and then filtration was applied. The filtrate was evaporated to dryness under reduced pressure to give an oily residue. The oily residue was dissolved in AcOEt, and the resulting solution was washed with saturated aqueous NH₄Cl and brine. The organic layer was dried over MgSO₄ and filtered, and the solvent was evaporated. The oilv residue was purified by chromatography on silica gel eluting with AcOEt-hexane to give **2h**. Yield: 627 mg (87%). ¹H NMR (300 MHz, CDCl₃, r.t.) δ = 7.38 (dd, 2 H, *I* = 5.8, 3.3 Hz), 7.59 (d, 2 H, *I* = 8.3 Hz), 7.63 (dd, 2 H, *I* = 5.8, 3.3 Hz), 7.81 (dd, 2 H, J = 8.3, 2.5 Hz), 8.68 (d, 2 H, J = 2.5 Hz). ¹³C NMR (75.7 MHz, CDCl₃, r.t.): δ 88.8, 92.1, 120.1, 125.1, 128.6, 129.0, 132.2, 138.9, 141.7, 151.2. IR (KBr disk, r.t.) v 3030, 2223 $(C \equiv C)$, 1456, 1003, 750 cm⁻¹. MS (ESI pos): m/z = 460.9 ([M+Na]⁺).

4.6. Complex 3 [27]

A CHCl₃ solution (30 mL) of **4** (168 mg, 0.60 mmol) and [PdCl₂(cod)] (155 mg, 0.60 mmol), was stirred at 50 °C for 24 h. The resulting solid was collected by filtration, washed with CHCl₃ and dried in vacuo to form **3** as yellow solid. Yield: 298 mg (55%). ¹H NMR (300 MHz, dmso-*d*₆, r.t.) δ = 7.44 (t, 2 H, *J* = 8.3 Hz), 7.62 (t, 4 H, *J* = 7.4 Hz), 7.72 (d, 4 H, *J* = 7.7 Hz), 7.87 (d, 4 H, *J* = 7.7 Hz), 8.04 (t, 4 H, *J* = 7.7 Hz), 8.30 (s, 2 H), 9.06 (d, 4 H, *J* = 5.2 Hz). MS (FAB pos): *m/z* = 878 ([M–Cl⁻]⁺). IR (KBr disk, r.t.) ν 3063, 2219 (C=C), 1487, 1362 cm⁻¹. Anal. Calc. for C₄₀H₂₄Cl₄N₄Pd₂: C, 52.49; H, 2.64; N, 6.12; Cl, 15.49. Found: C, 52.71; H, 2.87; N, 6.10; Cl, 15.51%.

4.7. 1,3-Bis(3'-pyridylethynyl)benzene (4)

A mixture of 1,3-diiodobenzene (3.30 g, 10 mmol), 2-ethynylpyridine (113 mg, 22 mmol), $[PdCl_2(PPh_3)_2]$ (140 mg, 0.10 mmol) and Cul (76.0 mg, 0.39 mmol) in THF (120 mL) and 0.5 M aqueous ammonia (80 mL) was stirred under argon at room temperature for 30 h. After evaporation of the solvent, the oily residue was dissolved in AcOEt and washed with saturated aqueous NH₄Cl and brine. The organic layer was dried over MgSO₄ and filtered, and the solvent was evaporated. The residue was purified by chromatography on silica gel eluting with CH₂Cl₂–AcOEt to give **4** as brown solid. Yield: 2.67 g (96%). ¹H NMR (300 MHz, CDCl₃, r.t.) δ = 7.22 (dd, 2 H, *J* = 7.4, 4.9 Hz), 7.33 (t, 1 H, *J* = 7.7 Hz), 7.50 (d, 2 H, *J* = 7.7 Hz), 7.57 (d, 2 H, *J* = 7.7 Hz), 7.66 (dt, 2 H, *J* = 7.7, 1.4 Hz), 7.79 (s, 1 H), 8.59 (d, 2 H, *J* = 4.9 Hz). IR (KBr disk, r.t.) *v* 3049, 2214 (C=C), 1579, 1458, 781 cm⁻¹.

4.8. Reaction of phenyllithium with 1d

A cyclohexane–diethylether solution of PhLi (1.09 M, 0.42 mL) was added to the $CHCl_3$ (20 mL) solution of **1d** (26 mg, 0.05 mmol). The mixture was stirred for 24 h at 50 °C then cooled to room temperature. The reaction was stopped by addition of water and $CHCl_3$ to the mixture. Separated organic phase was washed with water, dried over MgSO₄, and dried under reduced pressure to form biphenyl (35 mg, 0.022 mmol, 44%). The product was determined by ¹H NMR spectroscopy.

4.9. Reaction of ethynylbenzene with 1d

Et₃N (2.0 mL, 0.014 mmol), CuI (2.0 mg, 1.0×10^{-3} mmol) and ethynylbenzene (0.022 mL, 0.20 mmol) was added to the THF (2.0 mL) solution of **1d** (52 mg, 0.10 mmol). The mixture was stirred for 20 h at room temperature. The solid separated from the solution was removed by filtration. The solvent was evaporated to from the crude product which is dissolved in Et₂O then washed with water. The separated organic phase was dried over MgSO₄ then evaporated to form the product which is analyzed by ¹H NMR spectroscopy. The product contains 1,4-diphenylbutadiene (10%) and **2d** (30%).

4.10. Typical procedure of the ligand displacement reaction of 1d

In an NMR tube was charged a dmso- d_6 (0.60 mL) solution of **1d** (4.2 mg, 6.0×10^{-3} mmol), the dinitrogen ligand (6.0×10^{-3} mmol) and 1,2-diphenylethane (1.1 mg, 6.0×10^{-3} mmol, Internal standard). ¹H NMR spectra (r.t.) were checked occasionally. The reactions were monitored by integration of the ¹H NMR signal of **2d**.

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4.11. X-ray crystallography

Crystals of **2a**, **1f** and **1g** suitable for X-ray diffraction study were obtained by recrystallization from $CH_2Cl_2/hexane$, $CH_2Cl_2/$ MeCN, and $CH_2Cl_2/MeCN$, respectively. All measurements were made on a Rigaku Saturn70 diffractometer using graphite monochromated Mo K α radiation. The data were collected at a temperature of $-160 \,^{\circ}$ C to a maximum 2θ value of 55°. A total of 720 oscillation images were collected. The structures were solved by direct methods and refined against all data by full matrix leastsquare on F^2 using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were included in the refinement at geometrically ideal positions and refined with a riding model. A program package CRYSTAL STRUCTURE for Windows [28] were used for calculations and for generating the structures.

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Appendix A. Supplementary data

CCDC 851271, 851272 and 851273 contains the supplementary crystallographic data for **1a**, **2f** and **2g**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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