Transition Met Chem
DOI 10.1007/s11243-015-9942-1

Two fluorescent cyclopalladated arylpyrazine complexes: synthesis, crystal structures and application in the double Suzuki coupling of *N*-heteroaryl halides with 1,4-benzenediboronic acid

Zhi-Qiang Xiao[1] · Chen Xu[2] · Hong-Mei Li[2] · Xin Han[1] · Zhi-Qiang Wang[2] · Wei-Jun Fu[2] · Xin-Qi Hao[1] · Mao-Ping Song[1]

Received: 5 March 2015 / Accepted: 10 April 2015

Abstract Two 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (Sphos) adducts of cyclopalladated arylpyrazine complexes have been synthesized and characterized. Additionally, the structures of both complexes were determined by single-crystal X-ray analysis. These palladacycles are fluorescent in CH_2Cl_2 at room temperature. They have been applied to the double Suzuki coupling of *N*-heteroaryl halides with 1,4-benzenediboronic acid, giving the desired products in good yields.

Introduction

Palladacycles have received considerable attention due to their interesting physical properties and have been extensively used as highly efficient precatalysts for coupling reactions [1, 2]. Generally, phosphine or *N*-heterocyclic carbene (NHC) adducts of palladacycles are far more active than the corresponding dimeric palladacycles. The active species are thought to be Pd(0)–PR_3 or Pd(0)–NHC species, and it was shown that the cyclopalladated ligand was released from the metal center during the activation of the Pd(II) precatalyst [3, 4]. For example, the groups of Buchwald [5–7] and Nolan [8, 9] have reported the use of dialkylbiarylphosphine-palladacycles and NHC-palladacycles as highly efficient catalysts for C–C and C–N coupling reactions. We have also developed several adducts of ferrocenyl palladacycle-based catalyst systems for such coupling reactions [10–12]. Palladacycles are also emerging as versatile candidates for luminescent devices [1]; a wide variety of luminescent palladacycles have been synthesized and their photochemical properties determined [13–16]. Recently, we reported fluorescent NHC-cyclopalladated 2-(4-bromophenyl)pyridine (bpp) [Pd(bpp)(NHC)Cl] [17] and 2-(4-ethylphenyl)pyrazine (epp) [Pd(epp)(NHC)Cl] complexes [18] which show purple to blue emissions. As a continuation of our interest in the synthesis and properties of cyclopalladated complexes, we decided to investigate the luminescent and catalytic properties of phosphine-cyclopalladated arylpyrazine complexes. In this work, we report the synthesis and crystal structures of two Sphos adducts of cyclopalladated arylpyrazine complexes **3** and **4** (Scheme 1), which exhibit fluorescence in CH_2Cl_2 at room temperature. The ability of complexes **3** and **4** to catalyze the double Suzuki coupling of 1,4-benzenediboronic acid was also investigated.

Experimental

All chemicals were commercially available except for dimers **1** and **2** [18], 4-chloro-6-*p*-tolylpyrimidine [19] and 4-chloro-6-pyrimidinylferrocene [20], which were prepared according to the published procedures. Elemental analyses were determined with a Carlo Erba 1160 Elemental Analyzer. IR spectra were collected on a Bruker VECTOR22 spectrophotometer in KBr pellets. Mass spectra were measured on a LC-MSD-Trap-XCT instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker

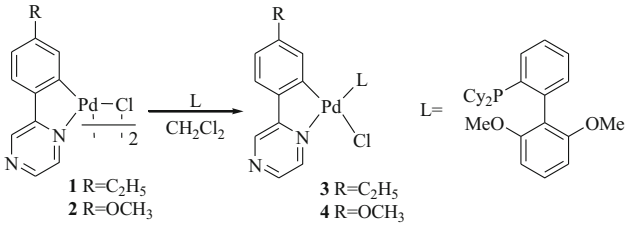
✉ Chen Xu
xubohan@163.com

✉ Xin-Qi Hao
xqhao@zzu.edu.cn

[1] College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450052, Henan, China

[2] College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471022, Henan, China

Published online: 24 April 2015



Scheme 1 Synthesis of complexes **3** and **4**

DPX-400 spectrometer (400 and 100 MHz, respectively) in $CDCl_3$ with TMS as an internal standard. The absorption and photoluminescence spectra were recorded on a Hitachi U-3010 UV–Vis spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively, at room temperature.

Synthesis of complexes 3 and 4

A solution of palladacyclic dimer **1** or **2** (0.1 mmol) and Sphos (0.21 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 30 min. The product was separated by passing through a short silica gel column with CH_2Cl_2 as eluent. The second band was collected to afford the corresponding complex **3** or **4** after the evaporation of the solvent. Complex **3**: Yellow solid, yield 85 %. Anal. Calcd. for $C_{38}H_{46}ClN_2O_2PPd$: C, 62.0; H, 6.3; N, 3.8. Found: C, 62.2; H, 6.1; N, 4.0 %. MS–ESI$^+$ [m/z]: 699.2 $(M–Cl)^+$. IR (KBr, cm^{-1}): 2922, 1587, 1516, 1470, 1365, 1248, 1157, 1105, 1053, 923, 822, 782. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (s, 1H), 8.66 (s, 1H), 7.98 (s, 1H), 7.97 (d, $J = 6.4$ Hz, 2H), 7.43–7.47 (m, 2H), 7.33–7.38 (m, 3H), 7.10–7.17 (m, 1H), 6.62 (d, $J = 6.8$ Hz, 2H), 3.69 (s, 6H), 2.75 (q, 2H), 1.62–1.87 (m, 12H), 1.13–1.38 (m, 13H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 139.1, 139.7, 132.4, 129.1, 129.0, 124.9, 119.2, 111.3, 103.4, 55.1, 33.2, 30.5, 28.8, 27.5, 26.9, 26.4. Complex **4**: Yellow solid, yield 88 %. Anal. Calcd. for $C_{37}H_{44}ClN_2O_3PPd$: C, 60.3; H, 6.0; N, 3.8. Found: C, 60.4; H, 5.9 N, 3.9 %. MS–ESI$^+$ [m/z]: 701.2 $(M–Cl)^+$. IR (KBr, cm^{-1}): 2924, 1608, 1584, 1516, 1469, 1396, 1249, 1179, 1107, 1034, 922, 825, 761. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (s, 1H), 8.42 (s, 1H), 8.05 (m, 1H), 7.53 (d, $J = 6.4$ Hz, 1H), 7.44 (t, $J = 6.0$ Hz, 1H), 7.37 (s, 1H), 7.16–7.25 (m, 3H), 6.50–6.63 (m, 4H), 3.50 (s, 6H), 3.34 (s, 3H), 1.58–1.73 (m, 22H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 143.1, 140.3, 133.5, 129.8, 129.6, 126.1, 123.2, 119.0, 103.7, 103.4, 64.9, 55.1, 29.7, 27.3, 27.2, 26.9.

General procedure for Suzuki coupling reactions

A 10-mL round-bottom flask was charged with the prescribed amount of catalyst, 1,4-benzenediboronic acid (0.5 mmol), *N*-heteroaryl halides (1.5 mmol), the selected base (1.5 mmol) and solvent (4 mL). The flask was placed in an oil bath and heated at 80 °C for 6 h, then cooled to room temperature and extracted with CH_2Cl_2. The crude products obtained from evaporation were purified by flash chromatography on silica gel. The products **5b–c**, **5f**, **5m** [21], **5d** [22], **5e** [23], **5l** [24] were known compounds and characterized by the comparison of data with those in the literature. The products **5a**, **5g–k**, **5n–o** were new compounds and characterized by elemental analysis, IR, MS, ^{1}H and ^{13}C NMR.

1,4-Bis(6-methylpyridin-2-yl)benzene **5a**. Anal. Calcd. for $C_{18}H_{16}N_2$: C, 83.0; H, 6.2; N, 10.8. Found: C, 83.2; H, 6.1; N, 10.9 %. MS–ESI$^+$ [m/z]: 261.1 $(M + H)^+$. IR (KBr, cm^{-1}): 2917, 1575, 1558, 1449, 1417, 1263, 1163, 1090, 1030, 971, 808, 740. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 4H), 7.67 (t, $J = 6.2$ Hz, 2H), 7.60 (d, $J = 6.2$ Hz, 2H), 7.13 (d, $J = 6.0$ Hz, 2H), 2.67 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 158.4, 156.5, 139.9, 136.9, 127.3, 121.8, 117.7, 29.7.

1,4-Bis(4-methylpyridin-2-yl)benzene **5g**. Anal. Calcd. for $C_{18}H_{16}N_2$: C, 83.0; H, 6.2; N, 10.8. Found: C, 83.2; H, 6.1; N, 10.9 %. MS–ESI$^+$ [m/z]: 261.1 $(M + H)^+$. IR (KBr, cm^{-1}): 2923, 1609, 1567, 1464, 1420, 1389, 1334, 1272, 1146, 1120, 1084, 834, 739. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, $J = 4.0$ Hz, 2H), 8.12 (s, 4H), 7.64 (s, 2H), 7.10 (d, $J = 3.9$, 2H), 2.45 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 156.8, 149.5, 147.9, 139.8, 127.2, 123.3, 121.6, 21.3.

1,4-Bis(6-methoxypyridin-2-yl)benzene **5h**. Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 74.0; H, 5.5; N, 9.6; found: C, 74.1; H, 5.4; N, 9.7 %. MS–ESI$^+$ [m/z]: 293.1 $(M + H)^+$. IR (KBr, cm^{-1}): 2924, 1600, 1577, 1467, 1420, 1393, 1326, 1284, 1254, 1162, 1083, 1024, 985, 874, 788. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 4H), 7.68 (t, $J = 6.0$ Hz, 2H), 7.43 (d, $J = 6.0$ Hz, 2H), 6.74 (d, $J = 6.0$ Hz, 2H), 4.10 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 163.8, 154.2, 139.4, 139.2, 126.9, 112.9, 109.4, 53.3.

1,4-Bis(3-hydroxy-6-methylpyridin-2-yl)benzene **5i**. Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 74.0; H, 5.5; N, 9.6. Found: C, 74.1; H, 5.4; N, 9.7 %. MS–ESI$^+$ [m/z]: 293.1 $(M + H)^+$. IR (KBr, cm^{-1}): 3236, 2922, 1447, 1377, 1269, 1236, 1211, 1143, 1029, 938, 823, 739. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, $J = 6.8$ Hz, 2H), 7.48 (d, $J = 6.8$ Hz, 2H), 7.19 (d, $J = 4.0$ Hz, 2H), 6.99 (d, $J = 4.0$, 2H), 2.53 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 149.7, 148.4, 145.0, 137.4, 128.8, 124.4, 123.1, 29.5.

1,4-Bis(5-trifluoromethylpyridin-2-yl)benzene **5j**. Anal. Calcd. for $C_{18}H_{10}F_6N_2$: C, 58.7; H, 2.7; N, 7.6. Found: C, 58.9; H, 2.6; N, 7.7 %. MS–ESI$^+$ [m/z]: 369.1 $(M + H)^+$. IR (KBr, cm^{-1}): 2921, 1601, 1558, 1465, 1421, 1255, 1107, 1025, 991, 859, 815, 790. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (d, $J = 4.0$ Hz, 2H), 8.21(s, 4H), 8.03 (s, 2H), 7.51 (d,

Table 1 Crystallographic data for complexes **3** and **4**

Empirical formula	$C_{38}H_{46}ClN_2O_2PPd$ **3**	$C_{37}H_{44}ClN_2O_3PPd$ **4**
F_w	735.59	737.56
Crystal system	Triclinic	Monoclinic
Space group	P-1	C2/c
a (Å)	13.7417(5)	39.235(3)
b (Å)	15.2756(4)	13.6389(3)
c (Å)	19.6874(7)	20.2376(14)
α (°)	109.462(3)	90.00
β (°)	93.616(3)	139.738(14)
γ (°)	113.256(43)	90.00
Volume (Å^3)	3488.4(2)	6998.9(7)
Z	4	8
D_c (g/cm^3)	1.401	1.400
GOF	1.029	1.030
F(000)	1528.0	3056.0
Reflections	28,915	24,967
Independent reflections	14,228	6255
Observed reflections	10,545	5333
Final R indices [$I > 2$sigma(I)]	$R1 = 0.0428$, $wR2 = 0.0886$	$R1 = 0.0349$, $wR2 = 0.0900$
R indices (all data)	$R1 = 0.0679$, $wR2 = 0.0990$	$R1 = 0.0432$, $wR2 = 0.0962$

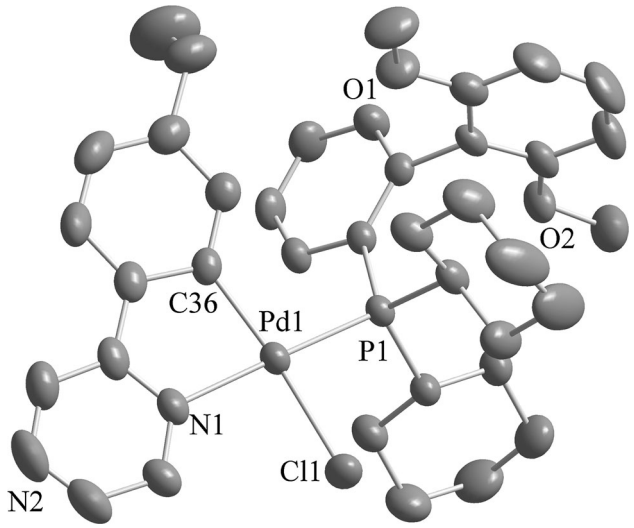


Fig. 1 Molecular structure of complex **3**. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are as follows (corresponding values for the unshown second structure are given in *brackets*): Pd(1)–C(36) 2.017(3) [2.023(4)], Pd(1)–P(1) 2.2935(8) [2.2912(8)], Pd(1)–N(1) 2.114(3) [2.105(3)], Pd(1)–Cl(1) 2.4015(10) [2.3876(4)], and C(36)–Pd(1)–N(1) 80.98(12) [81.12(14)], C(36)–Pd(1)–P(1) 98.75(10) [99.09(11)], N(1)–Pd(1)–Cl(1) 90.16(8) [89.74(10)], P(1)–Pd(1)–Cl(1) 91.07(3) [90.51(3)]

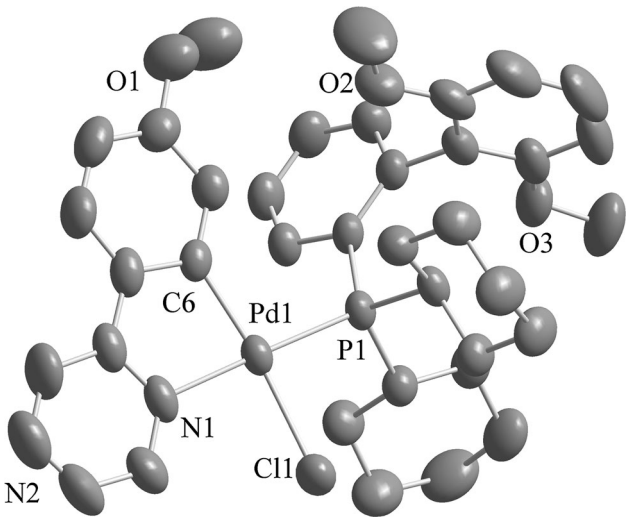


Fig. 2 Molecular structure of complex **4**. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–C(6) 2.019(3), Pd(1)–P(1) 2.2946(7), Pd(1)–N(1) 2.106(2), Pd(1)–Cl(1) 2.4029(9), and C(6)–Pd(1)–N(1) 81.19(12), C(6)–Pd(1)–P(1) 99.84(9), N(1)–Pd(1)–Cl(1) 88.50(9), P(1)–Pd(1)–Cl(1) 90.66(3)

$J = 4.0$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 157.9, 150.8, 139.2, 127.6, 124.3, 121.6, 117.9, 116.2.

1,4-Bis(5-acetylpyridin-2-yl)benzene **5k**. Anal. Calcd. for $C_{20}H_{16}N_2O_2$: C, 75.9; H, 5.1; N, 8.9. Found: C, 76.1; H, 5.0; N, 9.0 %. MS–ESI$^+$ [m/z]: 316.2 $(M + H)^+$. IR (KBr, cm^{-1}): 2923, 1671, 1588, 1562, 1456, 1369, 1279, 1146, 1011, 965, 829, 758. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.27 (s, 2H), 8.34 (d, $J = 7.6$ Hz, 2H), 8.24 (s, 4H), 7.94 (d, $J = 7.6$ Hz, 2H), 2.69 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 198.2, 165.2, 150.7, 148.1, 140.4, 129.3, 124.6, 122.5, 26.8.

1,4-Bis(6-*p*-tolylpyrimidin-4-yl)benzene **5n**. Anal. Calcd. for $C_{28}H_{22}N_4$: C, 81.1; H, 5.4; N, 13.5. Found: C, 81.2; H, 5.2; N, 13.7 %. MS–ESI$^+$ [m/z]: 415.2 $(M + H)^+$. IR

(KBr, cm^{-1}): 2926, 1576, 1510, 1459, 1366, 1235, 1187, 1112, 991, 822, 758. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.34 (s, 2H), 8.32 (s, 2H), 7.99 (d, $J = 7.2$ Hz, 4H), 7.36 (d, $J = 7.2$ Hz, 4H), 7.32 (d, $J = 7.2$ Hz, 4H), 2.45 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 159.2, 157.5, 141.7, 134.2, 133.9, 130.0, 127.9, 127.2, 116.8, 112.8, 29.8.

1,4-Bis(6-ferrocenylpyrimidin-4-yl)benzene **5o**. Anal. Calcd. for $C_{34}H_{26}Fe_2N_4$: C, 67.8; H, 4.4; N, 9.3. Found: C, 68.0; H, 4.2; N, 9.4 %. MS–ESI^+ [m/z]: 603.1 $(M + H)^+$. IR (KBr, cm^{-1}): 2921, 1574, 1456, 1377, 1259, 1159, 1105, 1057, 1012, 909, 812, 722. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.15 (d, $J = 6.0$ Hz, 2H), 8.29 (s, 2H), 7.85 (d, $J = 8.0$ Hz, 2H), 7.76 (d, $J = 6.0$, 2H), 5.09 (s, 4H), 4.58 (s, 4H), 4.12 (s, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): 156.8, 142.8, 139.5, 137.2, 127.8, 112.5, 80.1, 71.6, 70.3, 68.2.

Crystal structure determination

Crystallographic data for complexes **3** and **4** were collected on an Oxford Diffraction Gemini E diffractometer with Mo–Ka radiation ($\lambda = 0.71073$ Å) at ambient temperature. The data were corrected for Lorentz polarization factors as well as for absorption. Structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 with the SHELX-97 program [25]. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions. Crystal data as well as details of data collection and refinements of complexes **3** and **4** are summarized in Table 1. The CCDC deposition numbers are 1042713 and 1042714 for complexes **3** and **4**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

Results and discussion

Synthesis and structures of complexes 3 and 4

Bridge-splitting reactions of the palladacyclic dimers **1** or **2** with Sphos in CH_2Cl_2 at room temperature readily afforded the corresponding complexes **3** or **4,** respectively, in good yields (Scheme 1). They are air and moisture stable, both in the solid state and in solution. Complexes **3** and **4** were characterized by elemental analysis, IR, MS, ^{1}H and C^{13} NMR. The ^{1}H NMR spectra of the free arylpyrazine ligands show two doublets for the benzene ring protons [18], while complexes **3** and **4** exhibit only a corresponding doublet showing that they are *ortho*-cyclopalladated complexes. Single-crystal structure analyses reveal that **3** and **4** both have *trans* geometries and the Pd atom in each complex is in a slightly distorted square-planar environment provided by a Cl ligand, the P atom of the Sphos ligand, and the C and N atoms of the arylpyrazine ligand. The molecules are shown in Figs. 1 and 2. Complex **3** crystallizes in the triclinic P-1 space group with two mononuclear molecules in each asymmetric unit. The Pd–N (2.105(3)–2.114(3) Å) and Pd–P (2.2912(8)–2.2946(7) Å) bond lengths of the two complexes are similar to those of the related Sphos adducts of palladacycles (2.124(3)–2.126(4) Å and 2.2786(9)–2.2848(12) Å) [26, 27]. The crystal structure packing of **3** consists of inversion-related pairs of molecules with π–π interactions involving the neighboring pyrazine rings (the interplane distance is 3.544 Å). There are also C–H···Cl hydrogen bonds (Cl···H = 3.068 Å). By the virtue of these π–π interactions and complex hydrogen bonds, the crystal structure of **3** is extended into a 1D architecture. Complex **4** also has a one-dimensional chain structure involving C–H···N (N···H = 2.658 Å) hydrogen bonds and π–π interactions between the neighboring pyrazine rings (the interplane distance is 3.504 Å). However, in the crystal structure of **4**, no obvious C–H···Cl hydrogen bonds can be found.

Luminescent properties

The UV–Vis absorption and fluorescence spectra of these complexes have been measured in CH_2Cl_2 at room temperature (Fig. 3). Unlike the related NHC-cyclopalladated complexes [Pd(epp)(NHC)Cl] [18], complexes **3** and **4** do not exhibit luminescent emission in the solid state at room temperature. Strong absorption bands at 241 and 291 nm in the ultraviolet region are assigned to ligand-localized π–π* transitions, while weak bands

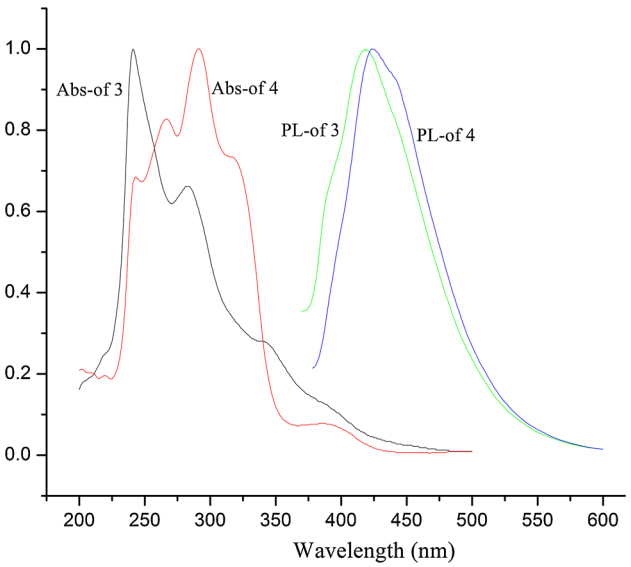
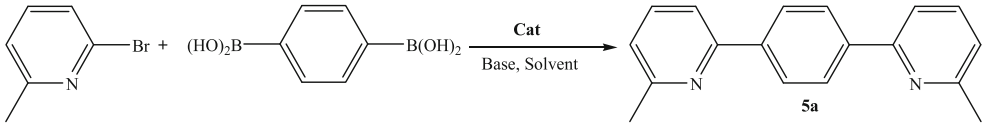


Fig. 3 Normalized absorption and emission spectra of **3** and **4** in CH_2Cl_2 at room temperature

Table 2 Optimization of reaction conditions for the coupling of 2-bromo-6-methylpyridine with 1,4-benzenediboronic acid

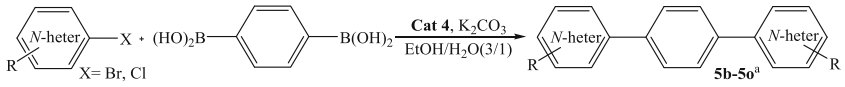


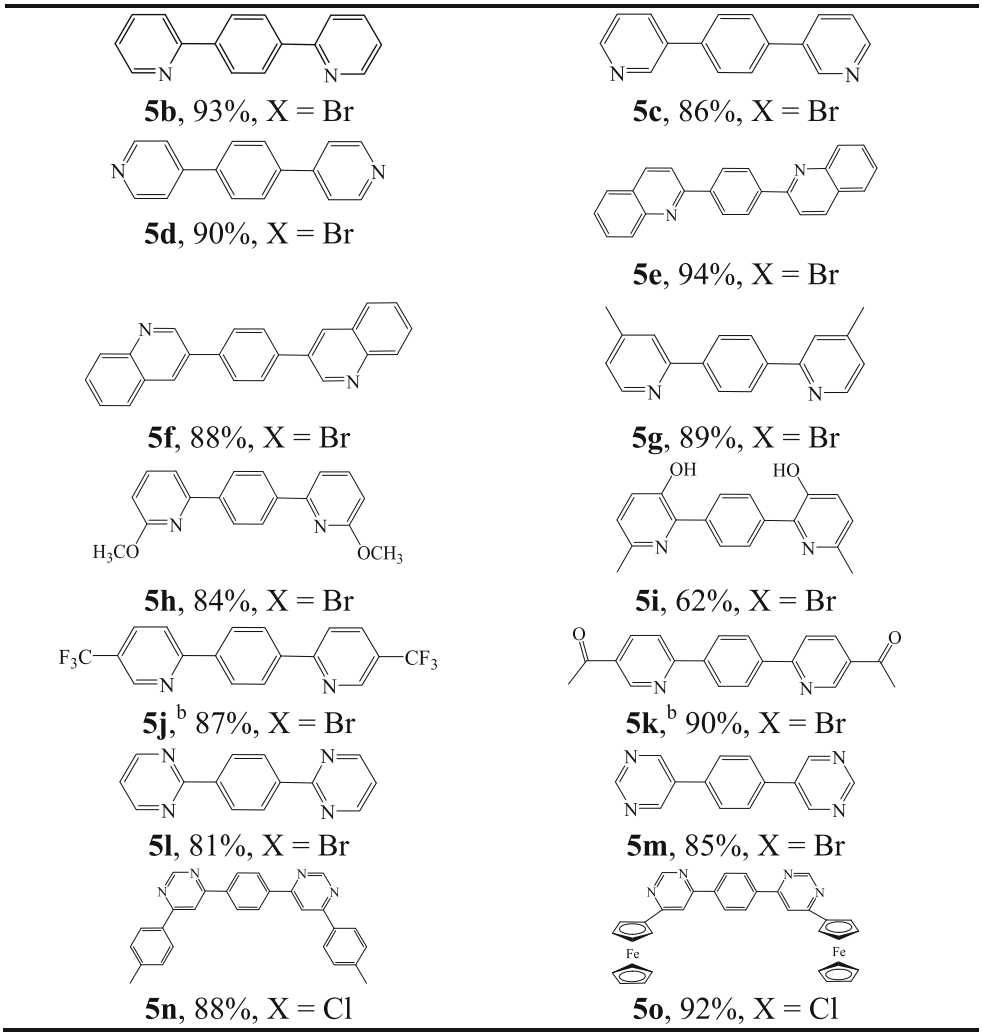
Entry	Base	Solvent	Catalyst (mol%)	Yield (%)[a]
1	K_2CO_3	H_2O	**3**(0.5)	46
2	K_2CO_3	C_2H_5OH/H_2O(3/1)	**3**(0.5)	91
3	K_2CO_3	C_2H_5OH/H_2O(3/1)	**4**(0.5)	92
4	K_2CO_3	C_2H_5OH/H_2O(3/1)	**3**(0.2)	78
5	K_2CO_3	C_2H_5OH/H_2O(3/1)	**4**(0.2)	80
6	K_2CO_3	1,4-Dioxane	**3**(0.2)	72
7	K_2CO_3	1,4-Dioxane	**4**(0.2)	75
8	K_2CO_3	C_2H_5OH	**4**(0.5)	59
9	Na_2CO_3	C_2H_5OH/H_2O(3/1)	**4**(0.5)	87
10	Cs_2CO_3	C_2H_5OH/H_2O(3/1)	**4**(0.5)	90
11	KOAc	C_2H_5OH/H_2O(3/1)	**4**(0.5)	56
12	K_3PO_4	C_2H_5OH/H_2O(3/1)	**4**(0.5)	70
13	$NaHCO_3$	C_2H_5OH/H_2O(3/1)	**4**(0.5)	85
14	K_2CO_3	C_2H_5OH/H_2O(3/1)	**1**(0.25)	42
15	K_2CO_3	C_2H_5OH/H_2O(3/1)	**2**(0.25)	45
16	K_2CO_3	C_2H_5OH/H_2O(3/1)	**2**/Sphos (0.25/0.5)	68

Reaction conditions: 2-bromo-6-methylpyridine (1.5 mmol), 1,4-benzenediboronic acid (0.5 mmol), base (1.5 mmol), solvent (4 mL), 80 °C, 6 h

[a] Isolated yield

Table 3 Coupling of *N*-heteroaryl halides with 1,4-benzenediboronic acid catalyzed by **4**





Reaction conditions: *N*-heteroaryl halides (1.5 mmol), 1,4-benzenediboronic acid (0.5 mmol), **4** (0.5 mol%), K_2CO_3 (1.5 mmol), EtOH/H_2O(3/1) (4 mL), 80 °C, 6 h

[a] Isolated yield

[b] Catalyst **4** (0.2 mol%)

between 342 and 396 nm are assigned to metal-to-ligand charge transfer (MLCT) transitions. An obvious red shift of these bands in comparison with the fluorescence spectra of the free ligands [18] is typical upon ligand coordination, indicating that the ligand-centered (LC) levels are involved in the observed emission. The palladacycles **3** and **4** display strong emission peaks at 419 and 426 nm, suggesting that the inductive effect of the substituent on the cyclometalated ligand has an effect on the luminescence.

Suzuki coupling reactions

Palladium-catalyzed Suzuki coupling has become an extremely powerful method for the formation of biaryl compounds. It is of particular interest to utilize Suzuki couplings of heteroaryl halides for the synthesis of substituted heterocyclic compounds [28–30]. In contrast to Suzuki coupling of aryl monoboronic acids, the double coupling of aryl diboronic acids for the synthesis of teraryl compounds has been relatively less reported [31–33].

Ideally, such reactions should be carried out in environmentally benign solvents such as water and alcohol [34–36]. In the present study, we investigated the use of palladacycles **3** and **4** as catalysts for the double couplings of *N*-heteroaryl halides with 1,4-benzenediboronic acid (Table 2). Initially, the coupling of 2-bromo-6-methylpyridine with 1,4-benzenediboronic acid was selected as a model reaction to probe the optimal conditions using **3** and **4** as catalysts in the presence of K_2CO_3 at 80 °C for 6 h under air. The isolated yield of the product **5a** was only 46 % with 0.5 mol% of **3** in pure water (entry 1). However, the addition of ethanol led to a very rapid increase in the reactivity [36]; the yields increased to 91–92 % when the volume ratio of ethanol to water was 3:1 (entries 2–3). Using 0.2 mol% of **3** and **4** afforded **5a** in 78 and 80 %, respectively (entries 4–5). Organic solvents such as 1,4-dioxane and EtOH gave only moderate yields (entries 6–8). Upon screening, a variety of bases (entries 9–13), K_2CO_3 and Cs_2CO_3 were found to give the best results. The dimers **1** and **2** generated the products in low yields under the same reaction conditions (entries 14–15), but the yield was improved to 68 % by the addition of Sphos (entry 16).

In the following experiments, the double coupling of a variety of electronically and structurally *N*-heteroaryl halides with 1,4-benzenediboronic acid was investigated using **4** as catalyst under the optimized reaction conditions (K_2CO_3, C_2H_5OH/H_2O(3/1), 80 °C, 6 h) (Table 3). For unsubstituted pyridinyl and quinolinyl bromides, 2-bromopyridine and 2-bromoquinoline afforded the products **5b** and **5e** in excellent yields (93–94 %) and the results were slightly better than those (86–88 %) for the corresponding 3-bromo-substituted derivatives. Similar to the results with 2-bromo-6-methylpyridine, good yields (84–89 %) were obtained for 2-bromo-4-methylpyridine and 2-bromo-6-methoxypyridine. 2-Bromo-3-hydroxy-6-methylpyridine also provided a moderate yield (62 %) under the same reaction conditions. For electron-deficient 2-bromopyridine derivatives, the yields of the coupled products **5j** and **5k** could reach 87–90 % when using 0.2 mol% of **4**. Couplings of bromo-substituted pyrimidine also gave the products **5l** and **5m** in good yields (81–85 %). Finally, we investigated the couplings of 1,4-benzenediboronic acid with 2-chloro-substituted pyrimidines; they were found to be efficient coupling partners in this system, giving **5n** and **5o** in excellent yields (88–92 %).

Conclusion

In summary, two Sphos adducts of cyclopalladated arylpyrazine complexes have been synthesized and characterized. These complexes exhibit blue emission in CH_2Cl_2 at room temperature. They were found to be efficient catalysts for the coupling of *N*-heteroaryl halides with 1,4-benzenediboronic acid in $EtOH/H_2O$ under air. These results provide a practical method for the synthesis of *N*-heterocyclic teraryl compounds.

Acknowledgments We are grateful to the Innovation Scientists and Technicians Troop Construction Projects of Henan Province, the Aid Project for the Leading Young Teachers in Henan Provincial Institutions of Higher Education of China (2013GGJS–151), and the Science Foundation of Henan Education Department (14A150049 and 15B150008).

References

1. Dupont J, Pfeffer M (2008) Palladacycles. Wiley-VCH, Weinheim
2. Selander N, Szabó KJ (2011) Chem Rev 111:2048
3. Bedford RB, Cazin CSJ, Holder D (2004) Coord Chem Rev 248:2283
4. Wang LH, Li JY, Cui XL, Wu YS, Zhu ZW, Wu YJ (2010) Adv Synth Catal 352:2002
5. Fors BP, Davis NR, Buchwald SL (2009) J Am Chem Soc 131:5766
6. Bruno NC, Tudge MT, Buchwald SL (2013) Chem Sci 4:916
7. Bruno NC, Niljianskul N, Buchwald SL (2014) J Org Chem 79:4161
8. Marion N, Navarro O, Mei JG, Stevens ED, Scott NM, Nolan SP (2006) J Am Chem Soc 128:4101
9. Navarro O, Marion N, Oonishi Y, Kelly RA III, Nolan SP (2006) J Org Chem 71:685
10. Xu C, Wang ZQ, Fu WJ, Lou XH, Li YF, Cen FF, Ma HJ, Ji BM (2009) Organometallics 28:1909
11. Xu C, Li HM, Yuan XE, Xiao ZQ, Wang ZQ, Fu WJ, Ji BM, Hao XQ, Song MP (2014) Org Biomol Chem 12:3114
12. Li HM, Xu C, Duan LM, Lou XH, Wang ZQ, Li Z, Fan YT (2013) Transition Met Chem 38:313
13. Kozlov VA, Aleksanyan DV, Nelyubina YV, Lyssenko KA, Gutsul EI, Puntus LN, Vasilev AA, Petrovskii PV, Odinets IL (2008) Organometallics 27:4062
14. Díez Á, Forniés J, Fuertes S, Lalinde E, Larraz C, López JA, Martín A, Moreno MT, Sicilia V (2009) Organometallics 28:1705
15. Sicilia V, Forniés J, Fuertes S, Martín A (2012) Inorg Chem 51:10581
16. Yamada M, Tashiro S, Miyake R, Shionoya M (2013) Dalton Trans 3300
17. Xu C, Li HM, Xiao ZQ, Wang ZQ, Tang SF, Ji BM, XQ Hao, Song MP (2014) Dalton Trans 10235
18. Xu C, Wang ZQ, Yuan XE, Han X, Xiao ZQ, Fu WJ, Ji BM, Hao XQ, Song MP (2015) J Organomet Chem 777:1
19. Hartung CG, Backes AC, Felber B, Missio A, Philipp A (2006) Tetrahedron 62:10055
20. Xu C, Zhang YP, Wang ZQ, Fu WJ, Hao XQ, Xu Y, Ji BM (2010) Chem Commun 6852
21. Mandali PK, Chand DK (2013) Catal Commun 31:16
22. Culp JT, Madden C, Kauffman K, Shi F, Matranga C (2013) Inorg Chem 52:4205
23. Buu-Hoi NP, Perin F, Jacquignon P (1965) J Heterocycl Chem 2:7
24. Begouin JM, Gosmini C (2009) J Org Chem 74:3221
25. Sheldrick GM (2008) Acta Crystallogr A 64:112
26. Biscoe MR, Fors BP, Buchwald SL (2008) J Am Chem Soc 130:6686

27. Vicente J, Saura-Llamas I, Oliva-Madrid MJ, García-López JA (2011) Organometallics 30:4624
28. Billingsley K, Buchwald SL (2007) J Am Chem Soc 129:3358
29. Wu XF, Anbarasan P, Neumann H, Beller M (2010) Angew Chem Int Ed 49:9047
30. Rossi R, Bellina F, Lessi M (2012) Adv Synth Catal 354:1181
31. Todd MH, Balasubramanian S, Abell C (1997) Tetrahedron Lett 38:6781
32. Chaumeil H, Le Drian C, Defoin A (2002) Synthesis 6:757
33. Zotto AD, Amoroso F, Baratta W, Rigo P (2009) Eur J Org Chem 110
34. Li CJ, Chan TH (1998) Organic reaction in aqueous media. Wiley, New York
35. Diallo AK, Ornelas C, Salmon L, Aranzaes JR, Astruc D (2007) Angew Chem Int Ed 46:8644
36. Xiao XF, Liu C, Qiu JS, Jin ZL (2012) Org Biomol Chem 10:7875