Transition Met Chem (2014) 39:691–698
DOI 10.1007/s11243-014-9851-8

Synthesis of binuclear palladium complexes with a rigid phenylene bridge linker

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Received: 6 May 2014 / Accepted: 13 June 2014 / Published online: 15 July 2014

Abstract The complexes $[PdX_2Py]_2$(di-NHC) (X = Br or Cl) in which di-NHC represents a di-*N*-heterocyclic carbene, featuring a rigid phenylene spacer between the carbene units, have been prepared from reactions of the corresponding diimidazolium halide salts with $PdCl_2$ in pyridine. The molecular structures of three of the complexes were determined by X-ray diffraction studies. The influences of different substitutions and of the halide ligand (Br or Cl) on the structure and reactivity of the complexes have been studied. The catalytic activity of the binuclear palladium complexes was tested in the Mizoroki–Heck reaction of styrene with bromobenzene.

Introduction

The chemistry of *N*-heterocyclic carbenes (NHCs) has been intensively studied in recent years, and they have been successfully employed in a variety of applications such as ligands in catalytically active metal complexes [1–5], organocatalysis [6], biologically active compounds [7], and the construction of molecular devices [8]. A large number of bidentate bis-NHC ligands and their complexes have been studied. In these ligands, a pair of NHC moieties are connected mostly by flexible alkyl [9], ether [10], benzyl [11], or picolyl [12] linkers, whereas only a few reports have featured rigid liners [13–16]. An interesting feature of metal complexes with rigid linkers, especially having π conjugating systems, is their potential for metal–metal interactions, which could also have an impact on the catalytic activity of the metal centers.

Palladium is one of the most versatile metals in catalyzing reactions involving C–C bond formation [17]. For example, the Heck coupling reaction, involving the palladium-catalyzed arylation of olefins, has found a wide application in organic synthesis. In continuation of our previous research into di-NHC dipalladium complexes with flexible alkyl bridges [18–21], in this paper we describe the synthesis of a series of dipalladium di-NHC complexes bridged with a rigid phenylene spacer (Scheme 1), and their use as catalysts for the Heck reaction. The effects of different substituents and choice of halide (X = Br or Cl) on the catalytic activity were studied.

Experimental

Materials and methods

All reactions were performed under an argon atmosphere using standard Schlenk or glovebox techniques. 1,4-Bis(1-imidazolyl)benzene was synthesized according to a literature procedure [22]. Pyridine was distilled from calcium hydride under argon atmosphere, and potassium carbonate was ground to a fine powder prior to use. All other chemicals were obtained from common suppliers and used without further purification. ^{1}H and ^{13}C spectra were

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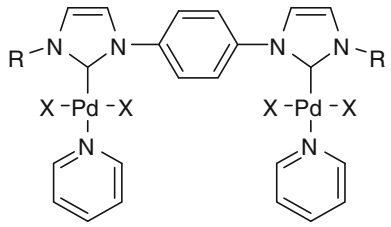


Scheme 1 Stucture of the dipalladium di-NHC complexes with a phenylene linkers. X = Cl or Br; R = Bn, *n*-Bu or *i*-Pr

recorded on a Bruker AV 400 MHz spectrometer at room temperature and referenced to the residual signals of the solvent. GC–MS was performed on an Agilent 6,890–5,973N system with electron ionization (EI) mass spectrometry. Elemental analyses were performed on a EuroVektor Euro EA-300 elemental analyzer. X-ray crystallography was conducted with a Rigaku Mercury CCD device using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Absorption correction was performed by the SADABS program. The structures were solved by direct methods using the SHELXS-97 program and refined by full-matrix least-square techniques on F^2.

Synthesis of bisimidazolium dihalides

In a typical run, a 10 mL thick wall pressure tube was charged with 1,4-di(1H-imidazol-1-yl)benzene (0.210 g, 1 mmol), the corresponding alkyl halide (2.5 mmol) and acetonitrile (2 mL). The reaction mixture was heated at 100–120 °C for 6–12 h. After the completion of the reaction, the solid was filtered off and rinsed with CH_2Cl_2 (5 mL) to give the product as a white powder.

1,1′-Dibenzyl-3,3′-(1,4-phenylene)bisimidazolium dibromide

Yield: 0.52 g (95 %). ^{1}H NMR (d_6-DMSO, 400 MHz): 10.27 (s, 2H, NC*H*N), 8.48 (t, J = 1.6 Hz, 2H, NC*H*), 8.16 (s, 4H, Ar), 8.12 (t, J = 2.0 Hz, 2H, NC*H*), 7.56 (m, 4H, Ar), 7.44 (m, 6H, Ar), 5.56 (s, 4H, CH_2). ^{1}H NMR (D_2O, 400 MHz): 7.93 (s, 2H), 7.82 (s, 4H), 7.68 (s, 2H), 7.46 (s, 10H), 5.48 (s, 4H) (two H of 2,2′-CH are not observed due to H/D exchange in D_2O). ^{13}C NMR (100 MHz, d_6-DMSO): 137.3, 136.5, 134.7, 131.2, 131.1, 130.5, 125.8, 125.0, 123.7, 123.6, 55.1. Anal. Calc. for $C_{26}H_{24}Br_2N_4$ (552.3 g/mol): C, 56.5; H, 4.4; N, 10.1. Found: C, 56.1; H, 4.0; N, 9.8 %.

1,1′-Dibenzyl-3,3′-(1,4-phenylene)bisimidazolium dichloride

Yield: 0.41 g (90 %). ^{1}H NMR (d_6-DMSO, 400 MHz): 10.37 (s, 2H, NC*H*N), 8.48 (t, J = 1.6 Hz, 2H, NC*H*), 8.16 (s, 4H, Ar), 8.12 (t, J = 2.0 Hz, 2H, NC*H*), 7.54 (m, 4H, Ar), 7.44 (m, 6H, Ar), 5.55 (s, 4H, CH_2). ^{1}H NMR (D_2O, 400 MHz): 8.00 (s, 2H), 7.89 (s, 4H), 7.76 (s, 2H), 7.54 (s, 10H), 5.56 (s, 4H) (two H of 2,2′-CH are missing due to H/D exchange in D_2O). ^{13}C NMR (100 MHz, d_6-DMSO): 137.3, 136.5, 134.7, 131.2, 131.1,130.5, 125.8, 125.0, 123.7, 123.6, 55.1. Anal. Calc. for $C_{26}H_{24}Cl_2N_4$ (463.4 g/mol): C, 67.4; H, 5.2; N, 12.1. Found: C, 67.2; H, 5.2; N, 12.2 %.

1,1′-Di-n-butyl-3,3′-(1,4-phenylene)bisimidazolium dibromide

Yield: 0.42 g (87 %). ^{1}H NMR (D_2O, 400 MHz): 9.35 (s, 2H, NC*H*N), 7.92 (s, 2H, NC*H*), 7.85 (s, 4H, Ar), 7.69 (s, 2H, NC*H*), 4.28 (t, J = 7.6 Hz, 4H, CH_2), 1.89 (m, 4H, CH_2), 1.33(m, 4H, CH_2), 0.89 (t, J = 7.2 Hz, 6H,CH_3). ^{13}C NMR (100 MHz, D_2O-DMSO): 137.3, 136.3, 125.7, 125.0, 123.3, 123.2, 51.6, 32.8, 20.4, 14.3. Anal. Calc. for $C_{20}H_{28}Br_2N_4$ (484.3 g/mol): C, 49.6; H, 5.8; N, 11.6. Found: C, 49.3; H, 5.3; N, 12.0 %.

1,1′-Di-n-butyl-3,3′-(1,4-phenylene)bisimidazolium dichloride

Yield: (62 %). ^{1}H NMR (400 MHz, D_2O): 9.39 (s, 2H, NC*H*N), 7.95 (s, 2H, NC*H*), 7.88 (s, 4H, Ar), 7.72 (s, 2H, NC*H*), 4.31 (t, J = 7.0 Hz, 4H, CH_2), 1.92 (m, 4H, CH_2), 1.37 (m, 4H, CH_2), 0.92 (t, J = 7.3 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, D_2O-DMSO): 137.2, 136.3, 125.6, 124.9, 123.2, 51.5, 32.7, 20.4, 14.3. Anal. Calc. for $C_{20}H_{28}Cl_2N_4$ (395.4 g/mol): C, 60.8; H, 7.1; N, 14.2. Found: C, 60.9; H, 7.2; N, 14.0 %.

1,1′-Diisopropyl-3,3′-(1,4-phenylene)bisimidazolium dibromide

Yield: 78 %. ^{1}HNMR (D_2O, 400 MHz): 9.41 (s, 2H, NC*H*N), 7.95 (d, J = 2.0 Hz, 2H, NC*H*), 7.89 (s, 4H, Ar), 7.80 (d, J = 2.0 Hz, 2H, NC*H*), 4.76 (octet, J = 6.8 Hz, 2H, C*H*), 1.62 (d, J = 6.4 Hz, 12H,CH_3). ^{13}C NMR (100 MHz, D_2O-DMSO): 137.5, 135.2, 126.1, 125.8, 123.4, 123.2, 55.6, 23.6. Anal. Calc. for $C_{18}H_{24}Br_2N_4$ (456.22 g/mol): C, 47.4; H, 5.3; N, 12.3. Found: C, 47.9; H, 5.0; N, 12.6 %.

Synthesis of palladium bromide complexes (**1**, **3**, **5**)

To a mixture of the required bisimidazolium dibromide (1 mmol), $PdCl_2$ (0.351 g, 1.98 mmol), NaBr (1.029 g, 10 mmol), and K_2CO_3 (1.382 g, 10 mmol) was added pyridine (10 mL). The reaction mixture was stirred and heated at 80–95 °C for 8–10 h, then filtered through Celite

and washed with CH_2Cl_2. The solvent was removed under vacuum, and the crude product was washed with diethyl ether (3 × 5 mL). The pure compounds were obtained as yellow solids by recrystallization from CH_2Cl_2/ether.

Synthesis of palladium chloride complexes (**2**, **4**)

To a mixture of the required bisimidazolium dichloride (1 mmol), $PdCl_2$ (0.351 g, 1.98 mmol), and K_2CO_3 (1.382 g, 10 mmol) was added pyridine (10 mL). The reaction mixture was stirred and heated at 80–95 °C for 8–10 h, then filtered through Celite and washed with CH_2Cl_2. The solvent was removed under vacuum, and the crude product was washed with diethyl ether (3 × 5 mL). The pure compounds were obtained as yellow solids by recrystallization from CH_2Cl_2/ether.

Complex 1

Yield: 0.86 g (80 %). ^{1}H NMR (400 MHz, d_6-DMSO): 8.71 (d, $J = 4.8$ Hz, 4H, Py), 8.46 (s, 4H, Ar), 7.94 (d, $J = 2.0$ Hz, 2H, NC*H*C), 7.81 (t, $J = 7.6$ Hz, 2H, Ar), 7.69 (m, 4H, Py), 7.52 (d, $J = 2.0$ Hz, 2H, NC*H*), 7.45–7.36 (m, 10H, Ar, Py), 5.89 (s, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): 154.3, 152.6, 138.4, 137.5, 134.8, 129.4, 129.0, 128.7, 127.4, 125.0, 124.8, 124.5, 53.4. Anal. Calc. for $C_{36}H_{32}Br_4N_6Pd_2$ (1,081.1 g/mol): C, 40.0; H, 3.0; N, 7.8. Found: C, 40.3; H, 3.2; N, 7.6 %.

Complex 2

Yield: 0.74 g (82 %). ^{1}H NMR (400 MHz, $CDCl_3$): 8.85 (d, $J = 4.8$ Hz, 4H, Py), 8.29 (s, 4H, Ar), 7.68 (t, $J = 7.6$ Hz, 2H, Ar), 7.60 (m, 4H, Py), 7.45–7.37 (m, 6H, Ar, Py), 7.26 (m, 6H, Ar, NC*H*), 6.91 (d, $J = 2.0$ Hz, 2H, NC*H*), 6.00 (s, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): 151.7, 151.4, 139.6, 137.9, 134.8, 129.2, 129.0, 128.7, 127.0, 124.5, 123.4, 121.8, 55.1. Anal. Calc. for $C_{36}H_{32}Cl_4N_6Pd_2$ (903.3 g/mol): C, 47.9; H, 3.6; N, 9.3. Found: C, 47.6; H, 3.8; N, 9.6 %.

Complex 3

Yield: 0.84 g (83 %). ^{1}H NMR (400 MHz, d_6-DMSO): 8.68 (d, $J = 4.8$ Hz, 4H, Py), 8.42 (s, 4H, Ar), 7.91 (d, $J = 2.0$ Hz, 2H, NC*H*C), 7.81 (t, $J = 7.6$ Hz, 2H, Py), 7.75 (d, $J = 2.0$ Hz, 2H, NC*H*C), 7.32 (t, $J = 6.4$ Hz, 4H, Py), 4.58 (t, $J = 7.6$ Hz, 4H, CH_2), 2.14 (sextet, $J = 7.2$ Hz, 4H, CH_2), 1.47 (septet, $J = 7.6$ Hz, 4H, CH_2), 1.03 (t, $J = 7.2$ Hz, 6H, CH_3). ^{13}C NMR (100 MHz, d_6-DMSO): 151.8, 148.1, 138.9, 138.3, 125.8, 124.6, 123.6, 123.3, 50.4, 31.3, 19.2, 13.5. Anal. Calc. for $C_{30}H_{36}Br_4N_6Pd_2$ (1,013.10 g/mol): C, 35.6; H, 3.6; N, 8.3. Found: C, 35.8; H, 3.2; N, 8.6 %.

Complex 4

Yield: 0.72 g (87 %). ^{1}H NMR (400 MHz, $CDCl_3$): 8.82 (d, $J = 4.8$ Hz, 4H, Py), 8.24 (s, 4H, Ar), 7.58 (t, $J = 7.6$ Hz, 2H, Py), 7.28 (d, $J = 2.0$ Hz, 2H, NC*H*C), 7.24 (t, $J = 6.4$ Hz, 4H, Py), 7.13 (d, $J = 2.0$ Hz, 2H, NC*H*C), 4.67 (m, 4H, CH_2), 2.17 (sextet, $J = 7.2$ Hz, 4H, CH_2), 1.58 (septet, $J = 6.8$ Hz, 4H, CH_2), 1.08 (t, $J = 7.2$ Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 152.0, 151.4, 129.0, 128.2, 127.3, 127.0, 124.4, 122.2, 51.2, 32.4, 20.0, 13.8. Anal. Calc. for $C_{30}H_{36}Cl_4N_6Pd_2$ (835.3 g/mol): C, 43.1; H, 4.3; N, 10.1. Found: C, 43.7; H, 4.1; N, 9.6 %.

Complex 5

Yield: 0.61 g (76 %). ^{1}H NMR (400 MHz, $CDCl_3$): 8.84 (d, $J = 4.8$ Hz, 4H, Py), 8.24 (s, 4H, Ar), 7.61 (t, $J = 7.6$ Hz, 2H, Py), 7.33 (d, $J = 2.0$ Hz, 2H, NC*H*C), 7.27–7.16 (m, 6H, Py, NCHC) 5.96 (m, 2H, CH), 1.67 (m, 12H, CH_3). ^{13}C NMR (100 MHz, d_6-DMSO): 151.6, 143.1, 138.5, 130.6, 125.0, 124.9, 124.2, 119.8, 50.0, 22.2. Anal. Calc. for $C_{28}H_{32}Br_4N_6Pd_2$ (985.0 g/mol): C, 34.1; H, 3.3; N, 8.5. Found: C, 34.4; H, 2.9; N, 8.9 %.

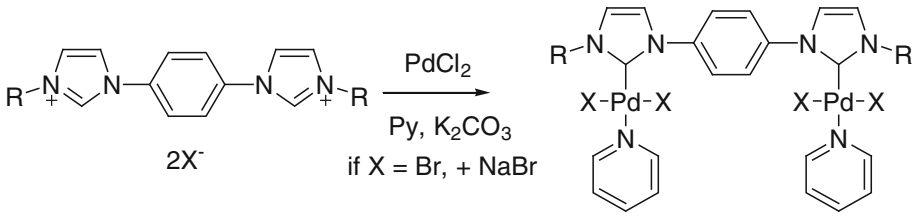
Procedure for the Mono–Heck coupling reaction

In a typical run, a 5 mL vial equipped with a magnetic stirrer was charged with a mixture of phenyl bromide (0.5 mmol), styrene (62.5 mg, 0.6 mmol), Pd catalyst (0.005 mmol), K_3PO_4 (207 mg, 1.5 mmol), and DMAC (1 mL) under argon. The mixture was heated at 100 °C for 5 h and then cooled to room temperature. Brine was added, and the resulting mixture was extracted with ethyl acetate (3 × 5 mL). The GC–MS samples were prepared by diluting 10 μL of ethyl acetate solution to 1 mL.

Results and discussion

Synthesis

1,4-Bis(1-imidazolyl)benzene was synthesized by the CuI-catalyzed C–N coupling reaction of 1,4-dibromobenzene with 1*H*-imidazole, using cheap hexamethylenetetramine (HMTA) as additive and dimethylacetamide (DMAC) as solvent [22]. The bisimidazolium dihalides were prepared by the reaction of bisimidazolylbenzene and the corresponding dihaloalkanes at elevated temperature. *n*-Butyl [14] and benzyl [23] substituted bisimidazolium bromides



Scheme 2 Synthesis of complexes **1**–**5**. X = Br, Cl, R = CH_2Ph (**1′**); X = Br, R = CH_2Ph (**1**); X = Cl, R = CH_2Ph (**2**); X = Br, R = *n*-Bu (**3**); X = Cl, R = *n*-Bu (**4**); X = Br, R = *i*-Pr (**5**)

have been reported previously, whereas the other imidazolium halides are unknown. Unfortunately, an attempt to prepare *i*-propyl substituted imidazolium chloride failed, most likely due to the steric hindrance of *i*-propyl chloride. The identities of the new compounds were confirmed by ^{1}H NMR, ^{13}C NMR, and elemental analysis.

The bimetallic palladium complexes **1**–**5** were prepared by the procedure shown in Scheme 2. Reaction of the corresponding imidazolium chloride with one equivalent of $PdCl_2$ in pyridine in the presence of K_2CO_3 as a base afforded palladium complexes with chloro co-ligands (**2** and **4**) in good yield. The synthesis of di-NHC di-Pd complexes bearing bromo ligands (**1**, **3**, and **5**) was similar to that of **2** and **4**, except that NaBr was also added to the reaction (Scheme 2). The exchange of chloride to bromide was tested by adding different amounts of NaBr into the reaction. It was found that the exchange of chloride to bromide was incomplete with only 3 equivalents of NaBr, and complex **1′** with mixed halo ligands was observed. The complete exchange of chloride to bromide was detected with 10 equivalents of NaBr. These complexes were fully characterized by NMR spectroscopy and gave satisfactory elemental analyses. The formation of the metal complexes **1**–**5** was indicated by the expected 1:1 pyridine/imidazolylidene ratio in the ^{1}H NMR spectra. The proton signal of NC*H*N from the imidazolium salts (9.35–10.37 ppm) was absent from the ^{1}H NMR spectra of the palladium complexes, confirming the carbene generation. The complexes are air and moisture stable and can be stored at air in the solid state for many months without any noticeable decomposition.

Description of the structures

Suitable crystals of complexes **1′**, **3**, and **4** for X-ray diffraction analysis were obtained by slow evaporation of a dichloromethane or chloroform-saturated solution at room temperature. The selected crystallographic data and refinement parameters are summarized in Table 1. The molecular diagrams of **1′**, **3**, and **4** are shown in Figs. 1, 2, 3, respectively, and selected bond lengths and angles are given below the figures. The molecular structures of these complexes confirm the bridging coordination mode of the ditopic carbene ligand and the halide exchange under the reaction conditions.

All the complexes show slightly distorted square-planar geometries around both palladium centers, which are coordinated by the imidazolylidene, two halide ligands in a *trans* configuration, and a pyridine ligand. The solid-state structures of these complexes are largely dependent on the different substituents and halide ligands. For complex **1′** with benzyl substitution and bromo/chloro ligands, two pseudo-square-planar subunits are in a *trans* configuration with torsion angle of 180° involving the backbone atoms N3–C13–C13A–N3A, and the angle between the planes of the imidazole and phenylene rings is 34.30°. For complex **3** with n-butyl substitution and bromo ligands, the two subunits are in an *X* configuration with torsion angle of −72.68° involving the backbone atoms N1–C7–C7A–N1A, and the angle between the planes of the imidazole and phenylene rings is 51.44°. For complex **4** with n-butyl substitution and chloride ligands, the two subunits are in a *trans* configuration with torsion angle of 180° involving the backbone atoms N1–C7–C7A–N1A, and the angle between the planes is 41.72°. Hence, the two NHC–Pd–Py subunits in **3** are mutually staggered, whereas the subunits in **1′** and **4** are parallel. It is worth noting that the observed geometries of these complexes are the result of symmetry. Although the spacer between two NHCs is the same in these complexes, the Pd to Pd distance is very different, due to the different geometries. The Pd–Pd distances are 8.630 Å for **1′**, 6.493 Å for **3**, and 8.556 Å for **4**. In addition, from the point of view of structure, the two Pd centers most likely have weak or no communication because the NHC fragment and benzene ring are noncoplanar, resulting in a lack of significant conjugation between them. The Pd–C bond lengths are comparable within the margin of error. The same applies to the Pd–N, Pd–Cl, and Pd–Br bonds. The Pd–$C_{carbene}$ distance is 1.975(3) Å for **1′**, 1.953(4) Å for **3**, and 1.943(7) Å for **4**, similar to the values for other palladium-related species [18]. The Pd–$N_{pyridine}$ distances in complex **1′** [2.086(2) Å],

Table 1 Selected crystallographic data for complexes **1′**, **3**, and **4**

Compound	**1′**	**3**	**4**
Empirical formula	$C_{38}H_{36}Br_{2.53}Cl_{5.47}N_6Pd_2$	$C_{30}H_{36}Br_4N_6Pd_2$	$C_{34}H_{40}Cl_{16}N_6Pd_2$
Formula weight	1,184.28	1,013.09	1,312.76
Temperature/K	298(2)	293(2)	298(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P 21/c	C2/c	P-1
Crystal size/mm	0.30 × 0.20 × 0.10	0.3 × 0.25 × 0.2	0.30 × 0.20 × 0.10
a/Å	10.3247(2)	26.4139(11)	9.2177(18)
b/Å	8.26410(10)	8.8683(5)	12.368(3)
c/Å	25.5408(4)	15.2547(6)	13.079(3)
α/°	90	90	75.06(3)
β/°	93.339(3)	93.049(3)	69.91(3)
γ/°	90	90	70.68(3)
V/Å^3	2175.55(6)	3,568.3(3)	1,303.9(4)
Z	2	4	1
$D_{calcd.}$/mg cm^{-3}	1.808	1.886	1.672
Absorption coefficient/mm^{-1}	3.496	5.516	1.542
F(000)	1,158	1,960	650
θ range/°	3.16 to 25.02°	2.42 to 25.01°	3.33 to 25.01°
Reflections collected/unique	15,882/3,834	9,806/3,150	10,285/4,572
Goodness-of-fit on F_2	1.055	0.972	1.081
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0264$	$R_1 = 0.0335$	$R_1 = 0.0714$
	$wR_2 = 0.0622$	$wR_2 = 0.0638$	$wR_2 = 0.2244$
R indices (all data)	$R_1 = 0.0293$	$R_1 = 0.0491$	$R_1 = 0.0753$
	$wR_2 = 0.0608$	$wR_2 = 0.069$	$wR_2 = 0.2297$

3 [2.113(3) Å], and **4** [2.109(6) Å] are comparable to those of related palladium carbene analogues [18]. All other distances and angles lie in the expected ranges.

Catalytic studies

The palladium-catalyzed arylation of olefins has wide application in organic synthesis. The activity of complexes **1**–**5** in the catalytic Heck reaction was tested in order to elucidate the influence of substituents and halide ligands (Scheme 3). Table 2 shows their relative reactivities for a model system (styrene with bromobenzene) at 0.5 M substrate concentration in DMAC solvent at 100 °C for a reaction period of 5 h. Details of the experimental setup are given in the Experimental section. Complex **4** gave the highest yield with good selectivity, while complex **1** showed lowest activity, albeit still with good selectivity under identical conditions (Table 2). The different substituents and halide ligands do indeed affect the catalytic activities of these palladium complexes. Thus, the activity increased as benzyl < *i*-Pr < *n*-Bu and Br < Cl.

In order to elucidate the influence of the reaction conditions, we studied the arylation with catalyst **4** (Scheme 4), with the results shown in Table 3. Of the various bases used, K_3PO_4 gave the best yield and good regioselectivity, while almost no product was obtained with pyridine (Table 3, entries 1–4). The choice of solvents also has a great effect on the reaction. When the reaction was conducted in DMSO, only trace amount of product was detected by GC. With DMAC as solvent, the yield and regioselectivity were both good. Although all the reactions were tested with 1 mol% catalyst loadings, comparable yields can be obtained with 0.5 % mol catalyst loading and longer reaction times (Table 3, entry 9). The arylation of styrene with different substituted bromobenzenes catalyzed by **4** was also tested (Table 3, entries 10–12). The results show that the reactions with *para*-methoxybromobenzene (electron donating substituent) and *para*-bromoflourobenzene (electron withdrawing substituent) gave high yields and good selectivity, whereas the reaction with the sterically hindered *ortho*-methoxybromobenzene gave moderate yield.

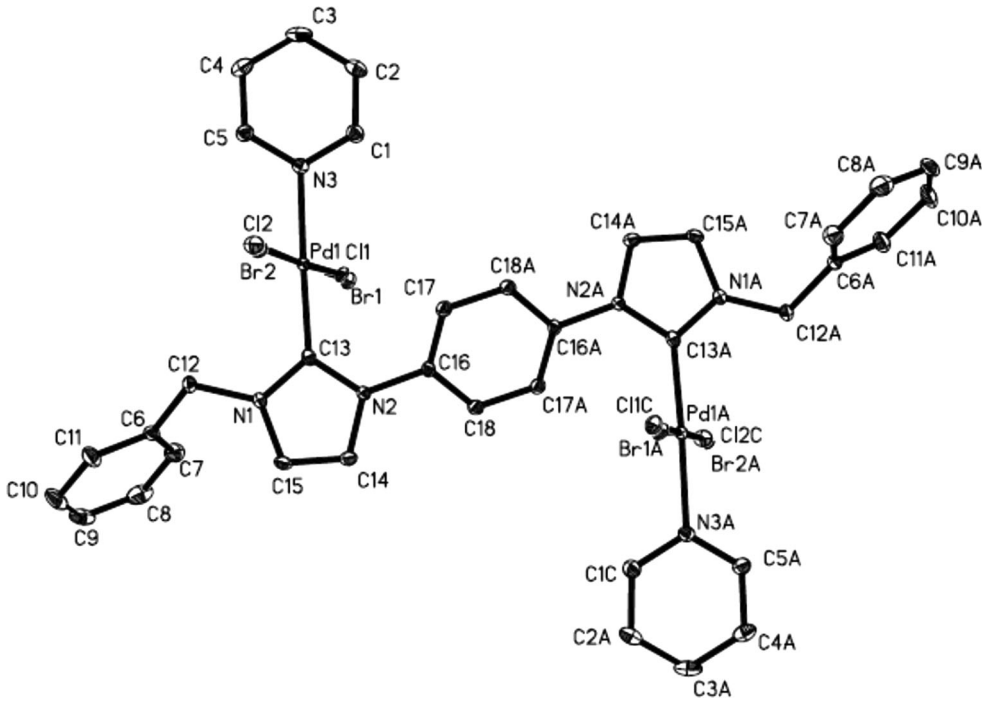


Fig. 1 ORTEP structure of complex **1′** with the probability ellipsoids drawn at the 50 % level. Hydrogen atoms and solvents have been omitted for clarity. Selected bond distances (Å) and angles (°): C1–N3 1.348(4), C5–N3 1.343(4), C12–N1 1.471(3), C13–N1 1.349(3), C13–N2 1.361(4), C13–Pd1 1.975(3), C16–N2 1.435(3), N3–Pd1 2.086(2), Br1–Pd1 2.439(9), Br2–Pd1 2.423(15), Pd1–Cl1 2.30(4), Pd1–Cl2 2.29(6), N1–C13–N2 104.6(2), N1–C13–Pd1 128.1(2), N2–C13–Pd1 127.28(19), C13–N1–C12 125.5(2), C13–N2–C16 126.2(2), C5–N3–C1 118.2(3), C5–N3–Pd1 121.77(19), C1–N3–Pd1 119.9(2), C13–Pd1–N3 176.96(10), C13–Pd1–Br2 90.1(4), N3–Pd1–Br2 88.4(4), C13–Pd1–Br1 90.2(2), N3–Pd1–Br1 91.3(2), Br2–Pd1–Br1 179.3(4)

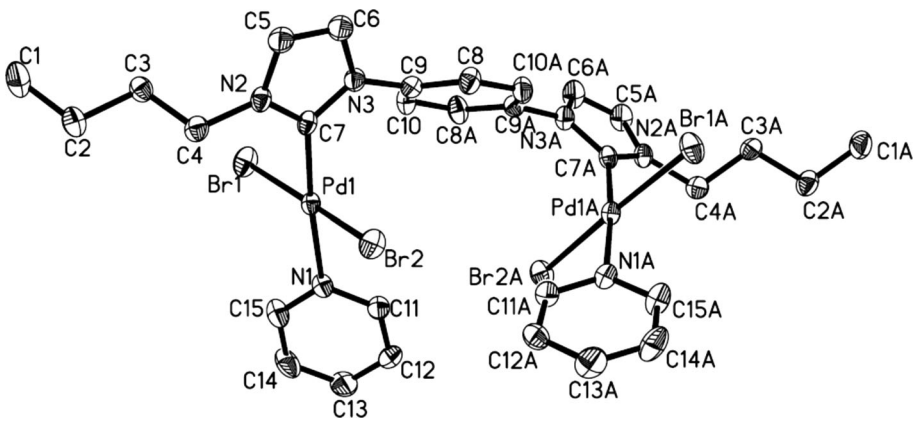


Fig. 2 ORTEP structure of complex **3** with the probability ellipsoids drawn at the 50 % level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–C7 1.953(4), Pd1–N1 2.113(3), Pd1–Br1 2.4392(5), Pd1–Br2 2.4435(5), N1–C15 1.333(5), N1–C11 1.336(5), N2–C7 1.349(5), N2–C4 1.456(5), N3–C7 1.350(5), N3–C9 1.435(5), C7–Pd1–N1 175.07(15), C7–Pd1–Br1 89.31(11), N1–Pd1–Br1 92.88(9), C7–Pd1–Br2 86.10(11), N1–Pd1–Br2 92.11(9), Br1–Pd1–Br2 173.034(19), C15–N1–C11 118.3(4), C15–N1–Pd1 123.8(3), C11–N1–Pd1 117.8(3), C7–N2–C4 125.3(3), C7–N3–C9 124.5(3), N2–C7–N3 105.7(3), N2–C7–Pd1 128.7(3), N3–C7–Pd1 125.2(3)

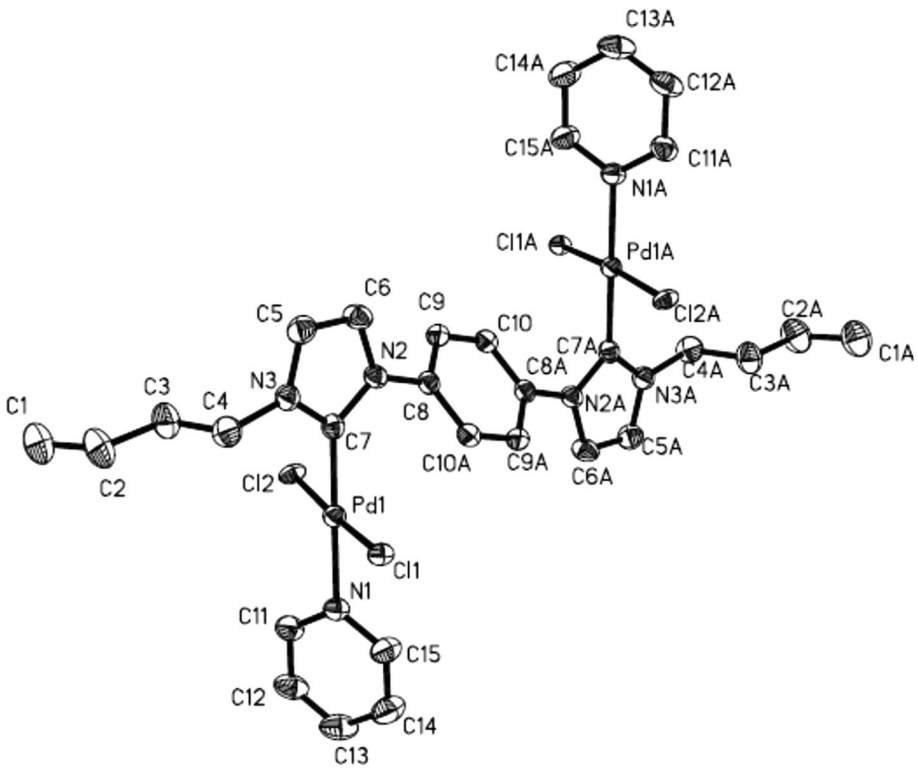
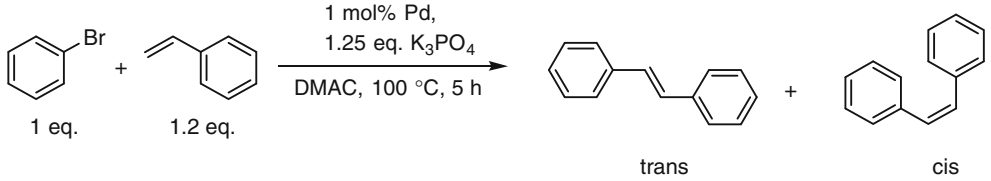


Fig. 3 ORTEP structure of complex **4** with the probability ellipsoids drawn at the 50 % level. Hydrogen atoms and solvents have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–C7 1.943(7), Pd1–N1 2.109(6), Pd1–Cl2 2.3348(17), Pd1–Cl1 2.3950(16), N1–C11 1.339(10), N1–C15 1.340(10), N2–C7 1.365(9), N2–C8 1.437(9), N3–C7 1.363(9), N3–C4 1.462(10), C7–Pd1–N1 177.9(3), C7–Pd1–Cl2 86.5(2), N1–Pd1–Cl2 91.68(18), C7–Pd1–Cl1 88.7(2), N1–Pd1–Cl1 93.15(18), Cl2–Pd1–Cl1 175.15(5), C11–N1–C15 117.6(7), C11–N1–Pd1 121.2(5), C15–N1–Pd1 121.2(5), C7–N2–C8 125.3(6), C7–N3–C4 125.5(7), N3–C7–N2 104.4(6), N3–C7–Pd1 127.9(5), N2–C7–Pd1 127.7(5)



Scheme 3 Arylation of styrene catalyzed by complexes **1–5**

Table 2 Arylation of styrene catalyzed by Pd complexes **1–5**

Entry[a]	Catalyst	GC yield[b] (%)	*Trans*:*cis* ratio
1	**1**	63	53:1
2	**2**	67	49:1
3	**3**	82	78:1
4	**4**	92	85:1
5	**5**	79	72:1

[a] Reaction conditions: bromobenzene (0.5 mmol), styrene (0.6 mmol), catalyst (0.005 mmol), K_3PO_4 (1.25 mmol), DMAC (1 mL), 100 °C, 5 h

[b] Yield was determined by GC with dodecane as an internal standard

Conclusion

We have synthesized five dicarbene palladium complexes with a rigid phenylene linker. X-ray studies showed that the molecular geometry of the solid Pd–NHC complexes is influenced significantly by the substituents and halide ligands. The Pd to Pd distances of these complexes having the same spacer vary considerably, and the two Pd centers most likely have weak or no communication. These new binuclear complexes were successfully tested as catalysts for the Heck reaction of styrene with bromobenzene, and complex **4** gave the best yield of the product with good

Scheme 4 Arylation of styrene catalyzed by **4**

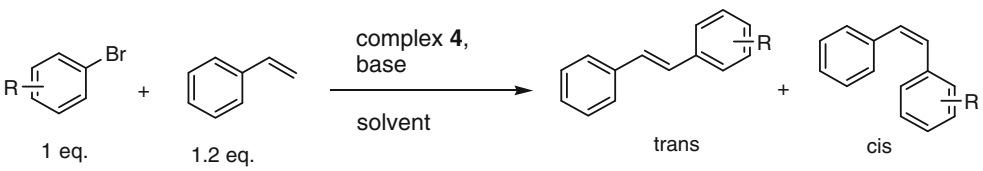


Table 3 Arylation of styrene catalyzed by **4** under different reaction conditions

Entry[a]	R	Cat. (mol%)	Solvent	Base	Temp (°C)	Time (h)	GC yield[b] (%)	A:B ratio
1	H	1	Toluene	Et_3N	110	12	62	77:1
2	H	1	Toluene	K_2CO_3	110	12	20	39:1
3	H	1	Toluene	Pyridine	110	12	Trace	–
4	H	1	Toluene	K_3PO_4	110	12	99	76:1
5	H	1	DMAC	K_3PO_4	100	8	98	84:1
6	H	1	Dioxane	K_3PO_4	100	8	75	77:1
7	H	1	DMSO	K_3PO_4	100	8	Trace	–
8	H	1	Toluene	K_3PO_4	100	8	73	62:1
9	H	0.5	DMAC	K_3PO_4	100	8	89	81:1
10	*p*-OMe	1	DMAC	K_3PO_4	100	8	87	72:1
11	*o*-OMe	1	DMAC	K_3PO_4	100	8	65	65:1
12	*p*-F	1	DMAC	K_3PO_4	100	8	99	80:1

[a] Reaction conditions: bromobenzene (0.5 mmol), styrene (0.6 mmol), complex **4** (0.0025–0.005 mmol), base (1.25 mmol), solvent, 100–110 °C, 8–12 h

[b] Yield was determined by GC with dodecane as an internal standard

selectivity. The catalytic activity of these complexes increased in the order of benzyl < *iso*-propyl < *n*-butyl and Br < Cl.

Acknowledgments We are grateful to the National and Provincial Innovative Entrepreneurial Training Programs for Undergraduate Project (HXKYZD201203, 201310320047, and 201310320047Z) and PAPD for financial support.

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