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Note

Syntheses and characterization of palladium(II) complexes with a bidentate bis-NHC ligand having methyl and aryl substituents on terminal nitrogen atoms

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ABSTRACT

An imidazolium salt, *N*-chloromethyl-*N*′-methylimidazolium bromide was prepared as an intermediate for the syntheses of unsymmetrical bidentate bis-NHC ligands bearing methyl and aryl substituents on the terminal nitrogen atoms. Three bis-NHC ligand precursors and their corresponding palladium(II) complexes were also prepared. ^{1}H NMR spectra of the imidazolium salts of the bidentate ligands implied that the carbene on a methyl-substituted imidazolylidene ring is a stronger donor than one on an aryl-substituted ring. The crystal structures of the palladium(II) complexes showed a distorted square-planar structure. The complexes demonstrated good catalytic performance in the Heck reaction.

Introduction

Since a stable *N*-heterocyclic carbene (NHC) was isolated by Arduengo et al. [1], various types of NHC compounds such as imidazolylidene, dehydroimidazolylidene, oxazolylidene, thiazolylidene, and triazolylidene, and their corresponding complexes have been developed [2]. Transition metal complexes, including monodentate and bidentate NHC ligands, often exhibit high stability and catalytic activity towards various synthetic organic reactions. Of the bidentate imidazolylidene NHC ligands, mono-NHC ligands with a hetero-donor atom pendant or symmetrical bis-NHC ligands have usually been used as supporting ligands. On the other hand, unsymmetrical bis-NHC ligands, having different substituents on the terminal nitrogen atoms, are much less common, probably due to the difficulty of their preparation. Only a few examples of ethylene-bridged bis-imidazolylidene NHCs [3], propylene-bridged bis-NHCs [4], and NHC/MIC dicarbenes [5], have been prepared via unsymmetrical imidazolium intermediates. Recently, aryl and halo-methyl substituted imidazolium salts have been reported in the preparation of unsymmetrical methylene-bridged bis-imidazolylidene NHC ligands [6]. Syntheses of unsymmetrical NHC ligands by combining methyl and halo-methyl substituted imidazolium species with a bulky arylimidazole would readily afford a series of unsymmetrical bis-NHC ligands. In this paper, we report the preparations of an *N*-chloromethyl-*N*′-methylimidazolium salt, diimidazolium salts as precursors of unsymmetrical bis-NHC ligands, and their Pd(II) complexes. We also report the characterizations of their structures using X-ray crystallography and NMR methods.

Results and discussion

Key compounds used in the previously reported preparation of unsymmetrical bidentate bis-NHC ligand precursors were alkynyl or halo-alkyl substituted imidazolium species. The latter is a better choice for the preparation of a wide range of unsymmetrical bis-NHC ligands because a subsequent S_N2 reaction with another NHC ring is facilitated. Thus, *N*-halomethyl-*N*′-methylimidazolium salt was targeted as a key compound for the preparation of methyl- and aryl-substituted unsymmetrical bidentate bis-NHC ligand precursors with a large steric contrast. We first tried to prepare *N*-bromomethyl-*N*′-methylimidazolium bromide by the reaction of *N*-methylimidazole with an excess amount of dibromomethane. The reaction afforded only 1,1′-dimethyl-3,3′-methylenediimidazolium dibromide, probably due to the facile substitution reaction of the formed *N*-bromomethyl-*N*′-methylimidazolium with *N*-methylimidazole. Then, bromochloromethane was employed instead of

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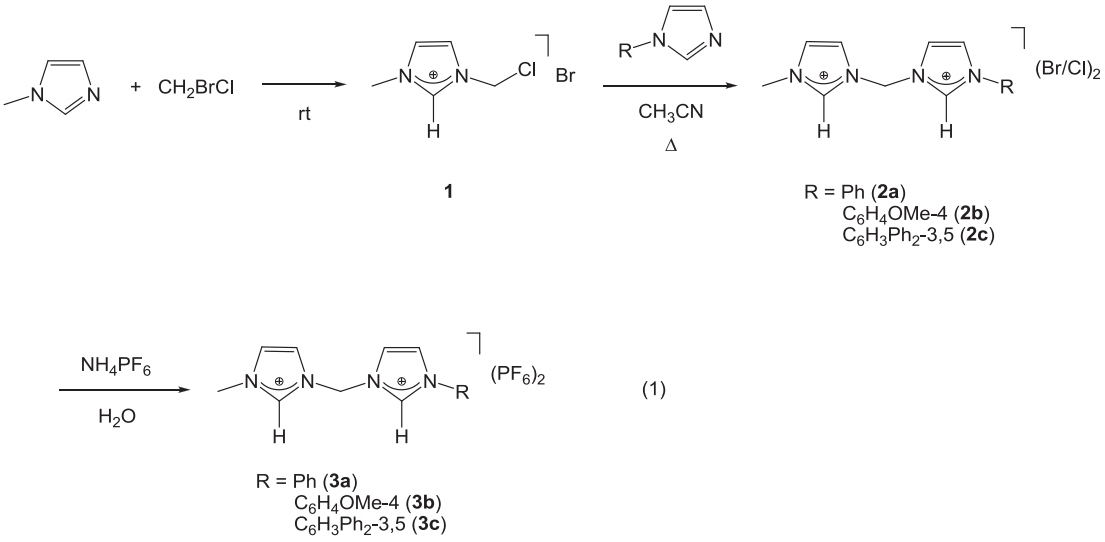
dibromomethane to lower the reactivity of the intermediate towards a second substitution. After 7 days at room temperature, the reaction afforded a mixture of the desired *N*-chloromethyl-*N*′-methylimidazolium bromide (**1**) and a byproduct, 1,1′-dimethyl-3,3′-methylenediimidazolium (Eq. (1)). Mono-imidazolium compound **1** could be extracted from the mixture with CH_2Cl_2. It was observed that elevating the reaction temperature increased the formation of undesired symmetrical diimidazolium species.



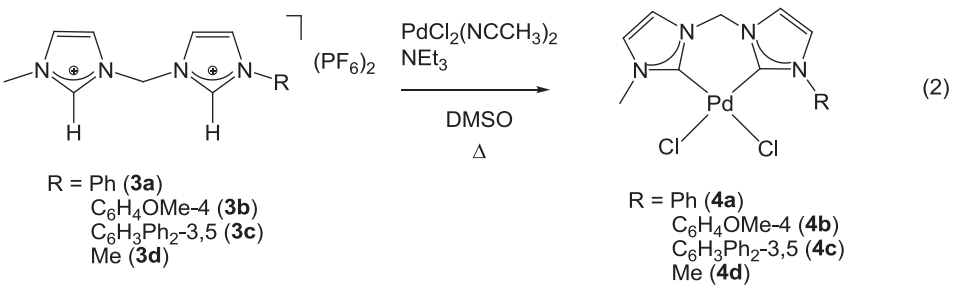
(1)

(1)

The unsymmetrical bidentate bis-NHC ligand precursors were prepared as shown in Eq. (1). A mixture of **1** and arylimidazole in CH_3CN was stirred at 90 °C in a sealed tube. The resultant white precipitate was collected and washed with acetone to give the diimidazolium dihalide salt (**2a**–**c**). Using this method, compound **1** can be used to easily introduce a small methyl and a bulky aryl substituent in various unsymmetrical diimidazolium salts. The counter anions, bromide and chloride, were changed to PF_6^- (**3a**–**c**) in order to avoid any confusion of halides in the preparation of the complex. Yields of **3a**–**c** from **1** were 62, 86, and 81%, respectively. The ^{1}H NMR spectra of **3a**–**c** in DMSO-d_6 exhibited signals of 2- and 2′-imidazolium protons at δ 9.34 and 9.97 (**3a**), 9.33 and 9.88 (**3b**), and 9.41 and 10.26 (**3c**) (Fig. 2). Observed signals at higher magnetic field were assigned to the 2-imidazolium proton of *N*-methyl imidazolium. These differences are probably due to the greater electron donating ability of the methyl substituent.

Corresponding palladium(II) complexes with an unsymmetrical bidentate bis-NHC ligand (**4a**–**c**) and with a symmetrical one (**4d**) were prepared using a modified literature method (Eq. (2)) [7]. Fig. 1 shows the crystal structures for **4a** and **4c** [8]. The complexes have distorted square-planar palladium centers that are bonded to two carbene carbon atoms and two chloride anions in a *cis* configuration. The two Pd–C bonds in **4a** have similar bond distances (1.976(3) and 1.981(3) Å), whereas the Pd–C2 bond distance (1.963(4) Å) in **4c** is slightly shorter than the Pd–C6 bond (1.973(4) Å). The bond distances are comparable to those of reported complexes with symmetric bidentate NHC moieties in a *cis* disposition (1.948(3)–2.005(7) Å) [3,6,7,9,10]. The chelate bite angles of C2–Pd–C6 (**4a**: 84.4(1)° and **4c**: 83.7(1)°) are also similar to those of various metal complexes with six-membered chelate rings consisting of two imidazolylidene rings and a bridging methylene group (81.49(9)–87.2(3)°) [6,7,10]. Similar bond distances and angles around the Pd centers in **4a** and **4c** show little steric effect of the diphenyl substituents of **4c** on the structure of the ground state.

The catalytic activities of complexes **4a**–**d** have been investigated in the Heck reaction of iodobenzene with styrene in DMA as shown in Table 1. For **4a**–**c**, the reactions proceeded quantitatively at 110 °C (entries 1–5). In all cases, the reactions afforded two products, *trans*-stilbene (A) and geminal olefin (B), in a ratios of



(2)

(2)

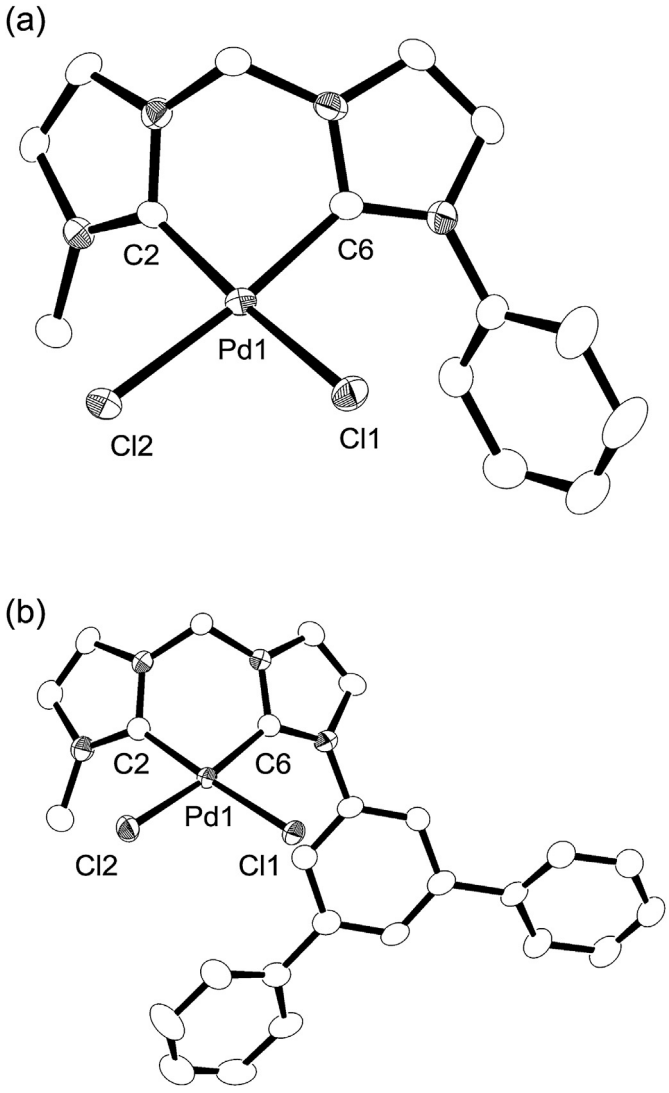
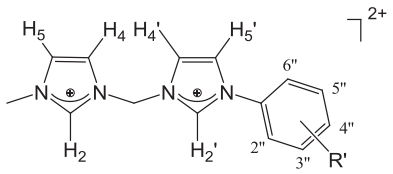


Fig. 1. ORTEP drawing of **4a** (a) and **4c** (b) (50% probability). Selected bond length (Å) and angles (°) for **4a**: Pd1–C2 1.976(3), Pd1–C6 1.981(3), Pd1–Cl1 2.3653(8), Pd1–Cl2 2.3773(8), C2–Pd1–C6 84.4(1), C2–Pd1–Cl1 174.72(9), C2–Pd1–Cl2 91.78(8), C6–Pd1–Cl1 92.95(9), C6–Pd1–Cl2 174.46(9), Cl1–Pd1–Cl2 90.55(3). Selected bond length (Å) and angles (°) for **4c**: Pd1–C2 1.963(4), Pd1–C6 1.973(4), Pd1–Cl1 2.3548(9), Pd1–Cl2 2.3626(9), C2–Pd1–C6 83.7(1), C2–Pd1–Cl1 176.7(1), C2–Pd1–Cl2 92.8(1), C6–Pd1–Cl1 93.0(1), C6–Pd1–Cl2 173.3(1), Cl1–Pd1–Cl2 90.35(3).

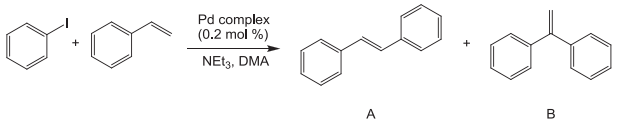
about 90:10. These results imply that aryl substituents have no effect on selectivity in this reaction. We are now investigating other reactions in order to extend the utility of these complexes to regio- and/or stereo-selective catalytic reactions.



R' = H (**3a**)
OMe-4" (**3b**)
Ph_2-3",5" (**3c**)

Fig. 2. Designation of hydrogens in the NMR spectra.

Table 1
Heck coupling reactions of iodobenzene with styrene.[a]



Entry	Complex	*T*/°C	Time/h	Yield/%[b]	Ratio of A:B
1	**4a**	110	24	92	88:12
2	**4b**	110	24	99	88:12
3	**4c**	110	24	91	88:12
4	**4d**	110	24	64	88:12
5	**4d**	140	24	92	86:14

[a] Reactions were carried out with 2.0 mmol of iodobenzene, 2.8 mmol of styrene, and 2.2 mmol of base in 5 mL of DMA.
[b] Total yields for A and B were determined by GC.

Summary

In summary, a new *N*-chloromethyl-*N*′-methylimidazolium salt, three unsymmetrical bidentate bis-NHC ligand precursors, and their corresponding Pd(II) complexes have been prepared. ^{1}H NMR spectra of the imidazolium salts showed that the electron density of a 2-imidazolium proton differs moderately between methyl- and aryl-substituted imidazolium rings. The structures of the square-planar complexes **4a** and **4c** were determined by single crystal X-ray diffraction methods. These complexes showed good catalytic activities in the Heck reaction.

Experimental section

General procedures and instrumentation

Manipulations of the complexes were carried out under air. Complexes **4a**–**d** were prepared according to a modified literature method [7]. All the chemicals used in this study were commercially available. The ^{1}H NMR spectra were recorded on a Bruker AV400N spectrometer. NMR measurements for **4a** and **4c** were performed in the presence of excess amounts of LiCl to avoid the complexity of Cl^- dissociation. Elemental analyses were carried out using a Perkin Elmer 2400 series II CHNS/O Analyzer and an Elementar Vario EL cube.

*Preparation of N-chloromethyl-N′-methylimidazolium bromide (**1**)*

A mixture of *N*-methylimidazole (8.20 g, 99.9 mmol) and bromochloromethane (13.7 g, 106 mmol) was stirred at rt for 6 d in a sealed tube. To the resulting suspension was added Et_2O, then the precipitates were filtered and washed with Et_2O under Ar. The obtained solid was treated with CH_2Cl_2 in a Soxhlet extractor. Removing the solvent from the extracted CH_2Cl_2 solution afforded a white solid, which was dried under vacuum (7.70 g, 36.4 mmol, 36%). Anal. Calcd for $C_5H_8BrClN_2$: C, 28.40; H, 3.81; N, 13.25. Found: C, 28.22; H, 4.20; N, 13.16. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.90 (s, 3H, Me), 6.22 (s, 2H, $-CH_2-$), 7.79 (dd, 1H, H_4), 7.96 (dd, 1H, H_5), 9.39 (s, 1H, H_2).

Preparation of N-(3,5-diphenylphenyl)imidazole

A mixture of 3,5-diphenylbromobenzene (1.33 g, 4.30 mmol), imidazole (0.381 g, 5.60 mmol), KOH (0.318 g, 5.67 mmol), and CuI (0.169 g, 0.887 mmol), in dry DMF (7 mL) was stirred at 115 °C for 4

d under Ar. The solvent was removed, and CH_2Cl_2 and alkaline EDTA solution were added to the residue. The reaction mixture was further extracted with CH_2Cl_2. The combined organic phases were dried over magnesium sulfate. The solvent was removed to afford the yellow residue, which was purified by column chromatography on silica gel (CH_2Cl_2) and alumina (CH_2Cl_2) (1.04 g, 3.51 mmol, 82%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.15 (dd, 1H, H_4 or H_5, 0.8 and 1.3 Hz), 7.44 (t, 2H, $H_{4''}$, 7.3 Hz), 7.53 (dd, 4H, $H_{3''}$, 7.3 and 7.6 Hz), 7.9 (m, 7H, $H_{2'}$, $H_{4'}$, and $H_{2''}$), 8.02 (dd, 1H, H_4 or H_5, 1.3 and 1.3 Hz), 8.51 (dd, 1H, H_2, 0.8 and 1.3 Hz).

*Preparation of 1-methyl-1′-phenyl-3,3′-methylenediimidazolium hexafluorophosphate (**3a**)*

A mixture of **1** (0.653 g, 3.09 mmol) and *N*-phenylimidazole (1.03 g, 7.14 mmol) in CH_3CN (3 mL) was stirred at 90 °C for 5 d in a sealed tube. The resulting precipitates were filtered, washed with acetone, and dried under vacuum to yield dihalide salt **2a** (1.03 g) as a white powder. To an aqueous solution of **2a** (1.97 g), we added an aqueous solution of NH_4PF_6 (1.83 g, 11.2 mmol). The resulting precipitates were filtered, washed with water, and dried under vacuum to result in a white powder (1.94 g, 3.66 mmol). Anal. Calcd for $C_{14}H_{16}F_{12}N_4P_2$: C, 31.71; H, 3.04; N, 10.57. Found: C, 31.77; H, 2.84; N, 10.31. ^{1}H NMR (400 MHz, DMSO-d_6): 3.92 (s, 3H, Me), 6.69 (s, 2H, $-CH_2-$), 7.65 (t, 1H, $H_{4''}$, 7.2 Hz), 7.72 (dd, 2H, $H_{3''}$, 7.2 and 8.0 Hz), 7.76 (d, 2H, $H_{2''}$, 8.0 Hz), 7.82 (dd, 1H, H_4 or H_5), 7.98 (dd, 1H, H_4 or H_5), 8.17 (dd, 1H, $H_{4'}$ or $H_{5'}$), 8.40 (dd, 1H, $H_{4'}$ or $H_{5'}$), 9.34 (s, 1H, H_2), 9.97 (s, 1H, $H_{2'}$).

*Preparation of 1-methyl-1′-(4″-methoxyphenyl)-3,3′-methylenediimidazolium hexafluorophosphate (**3b**)*

A mixture of **1** (2.62 g, 12.4 mmol) and *N*-(4-methoxyphenyl) imidazole (1.90 g, 10.9 mmol) in CH_3CN (10 mL) was stirred at 90 °C overnight in a sealed tube. The resulting precipitates were filtered and dried under vacuum to yield dihalide salt **2b** (3.70 g) as a white powder. To an aqueous solution of **2b** (2.65 g), we added an aqueous solution of NH_4PF_6 (2.57 g, 15.8 mmol). The resulting precipitates were filtered, washed with water, and dried under vacuum to yield a white powder (3.77 g, 6.73 mmol). Anal. Calcd for $C_{15}H_{18}F_{12}N_4OP_2$: C, 32.16; H, 3.24; N, 10.00. Found: C, 32.48; H, 3.63; N, 10.27. ^{1}H NMR (400 MHz, DMSO-d_6): 3.85 (s, 3H, OMe or Me), 3.92 (s, 3H, OMe or Me), 6.67 (s, 2H, $-CH_2-$), 7.24 (d, 2H, $H_{3''}$, 9.1 Hz), 7.68 (d, 2H, $H_{2''}$, 9.1 Hz), 7.82 (s, 1H, H_4, H_5, $H_{4'}$, or $H_{5'}$), 7.97 (s, 1H, H_4, H_5, $H_{4'}$, or $H_{5'}$), 8.14 (s, 1H, H_4, H_5, $H_{4'}$, or $H_{5'}$), 8.32 (s, 1H, H_4, H_5, $H_{4'}$, or $H_{5'}$), 9.33 (s, 1H, H_2), 9.88 (s, 1H, $H_{2'}$).

*Preparation of 1-methyl-1′-(3″,5″-diphenylphenyl)-3,3′-methylenediimidazolium hexafluorophosphate (**3c**)*

A mixture of **1** (0.930 g, 4.40 mmol) and *N*-(3,5-diphenylphenyl) imidazole (1.04 g, 3.51 mmol) in CH_3CN (7 mL) was stirred at 90 °C for 4 d in a sealed tube. The resulting precipitates were filtered and dried under vacuum to afford dihalide salt **2c** (1.59 g) as a white powder. An aqueous solution of NH_4PF_6 (0.287 g, 1.76 mmol) was added to an aqueous of **2c** (0.359 g). The resulting precipitates were filtered, washed with water, and dried under vacuum to give a white powder (0.439 g, 0.643 mmol). Anal. Calcd for $C_{26}H_{24}F_{12}N_4P_2$: C, 45.76; H, 3.54; N, 8.21. Found: C, 45.51; H, 3.43; N, 8.07. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.93 (s, 3H, Me), 6.75 (s, 2H, $-CH_2-$), 7.50 (t, 2H, $H_{4'''}$, 7.3 Hz), 7.58 (dd, 4H, $H_{3'''}$, 7.3 and 7.6 Hz), 7.84 (dd, 1H, H_4 or H_5), 7.92 (d, 4H, $H_{2'''}$, 7.6 Hz), 8.02 (dd, 1H, H_4 or H_5), 8.07 (d, 2H, $H_{2''}$, 1.5 Hz), 8.18 (t, 1H, $H_{4''}$, 1.5 Hz), 8.23 (dd, 1H, $H_{4'}$ or $H_{5'}$), 8.66 (dd, 1H, $H_{4'}$ or $H_{5'}$), 9.41 (s, 1H, H_2), 10.26 (s, 1H, $H_{2'}$).

*Preparation of dichloro(1-methyl-1′-phenyl-3,3′-methylenediimidazolin-2,2′-diylidene)palladium(II) (**4a**)*

A mixture of **3a** (0.514 g, 0.969 mmol), $PdCl_2(NCCH_3)_2$ (0.246 g, 0.948 mmol), and NEt_3 (0.251 g, 2.48 mmol) in DMSO (4 mL) was stirred at 60 °C for 2 h and then at 80 °C for 7 h. The resulting precipitates were filtered, washed with acetone, and dried under vacuum (0.269 g, 0.647 mmol, 68%). Anal. Calcd for $C_{14}H_{14}Cl_2N_4Pd$: C, 40.46; H, 3.40; N, 13.48. Found: C, 40.33; H, 3.31; N, 13.30. ^{1}H NMR (400 MHz, addition of LiCl, DMSO-d_6): δ = 4.01 (s, 3H, Me), 6.34 (d, 1H, $-CH_2-$, 13 Hz), 6.54 (d, 1H, $-CH_2-$, 13 Hz), 7.43 (m, 2H, H_4 or H_5, and $H_{4''}$), 7.51 (dd, 2H, $H_{3''}$), 7.69–7.76 (m, 4H, H_4 or H_5, $H_{2''}$, $H_{4'}$ or $H_{5'}$), 7.86 (s, 1H, $H_{4'}$ or $H_{5'}$).

*Preparation of dichloro(1-methyl-1′-(4″-methoxyphenyl)-3,3′-methylenediimidazolin-2,2′-diylidene)palladium(II) (**4b**)*

A mixture of **3b** (0.996 g, 1.78 mmol), $PdCl_2(NCCH_3)_2$ (0.453 g, 1.75 mmol), and NEt_3 (0.434 g, 4.29 mmol) in DMSO (7 mL) was stirred at rt for 4 h, 60 °C overnight, and 80 °C for 3 h. The resulting precipitates were filtered, washed with acetone, and dried under vacuum (0.524 g, 1.16 mmol, 66%). Anal. Calcd for $C_{15}H_{16}Cl_2N_4OPd$: C, 40.43; H, 3.62; N, 12.57. Found: C, 40.08; H, 3.89; N, 12.31. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.20 (s, 3H, OMe), 3.77 (s, 3H, Me), 6.50 (d, 1H, $-CH_2-$, 2.9 Hz), 6.66 (d, 1H, $-CH_2-$, 2.9 Hz), 6.91 (d, 2H, $H_{3''}$, 8.9 Hz), 6.96 (d, 1H, H_4 or H_5, 1.7 Hz), 7.41 (d, 1H, H_4 or H_5, 1.7 Hz), 7.65 (d, 2H, $H_{2''}$, 8.9 Hz), 7.88 (d, 1H, $H_{4'}$ or $H_{5'}$, 1.8 Hz), 7.99 (d, 1H, $H_{4'}$ or $H_{5'}$, 1.8 Hz).

*Preparation of dichloro(1-methyl-1′-(3″,5″-diphenylphenyl)-3,3′-methylenediimidazolin-2,2′-diylidene)palladium(II)·H_2O (**4c·H_2O**)*

A mixture of **3c** (1.07 g, 1.57 mmol), $PdCl_2(NCCH_3)_2$ (416 mg, 1.60 mmol), and NEt_3 (0.437 g, 4.32 mmol) in DMSO (13 mL) was stirred at 40 °C for 2 h, 60 °C overnight, and 80 °C for 4 h. The reaction was filtered and to the filtrate was added acetone and Et_2O. The resulting precipitates were filtered and washed with acetone. To a suspension of the crude product in EtOH, we added tetraethylammonium chloride (0.884 g, 5.33 mmol), and this was stirred at rt overnight. The resulting precipitates were filtered and dried under vacuum (0.401 g, 0.706 mmol, 45%). Anal. Calcd for $C_{26}H_{22}Cl_2N_4Pd\cdot H_2O$: C, 53.31; H, 4.13; N, 9.56. Found: C, 53.23; H, 3.90; N, 9.45. ^{1}H NMR (400 MHz, addition of LiCl, DMSO-d_6): δ = 4.02 (s, 3H, Me), 6.37 (m, 1H, $-CH_2-$), 6.79 (m, 1H, $-CH_2-$), 7.45 (m, 3H, H_4 or H_5, and $H_{4'''}$), 7.54 (dd, 4H, $H_{3'''}$), 7.78 (s, 1H, H_4 or H_5), 7.98 (m, 6H, $H_{4''}$ and $H_{2'''}$, $H_{4'}$ or $H_{5'}$), 8.08 (s, 1H, $H_{4'}$ or $H_{5'}$), 8.19 (s, 2H, $H_{2''}$).

General procedure for the Heck reaction

All reactions were carried out with iodobenzene (2.0 mmol), styrene (2.8 mmol), NEt_3 (2.2 mmol), and the Pd complex (4.0 μmol) in 5 mL of dry DMA under Ar. Di-*p*-tolyl ether was used as an internal standard. The yields of *trans*-stilbene and 1,1-diphenylethylene were determined by GC.

Crystal structure determination

Crystals of **4a** and **4c**, suitable for X-ray diffraction studies, were obtained from a DMSO–acetone–Et_2O solution. Crystallographic and diffraction data were obtained using a Rigaku/MSC Mercury CCD with graphite monochromated Mo *K*α radiation at −100 °C. The structures were solved using direct methods and expanded using Fourier techniques. Atomic scattering factors and anomalous dispersion terms were taken from International Tables for X-ray

Crystallography IV [11]. All non-hydrogen atoms were refined using a full-matrix least-squares method with an anisotropic displacement parameter. Hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters. All calculations were performed using a *teXsan* crystallographic software package of Molecular Structure Corporation [12].

Appendix A. Supplementary material

CCDC 999244 (**4a**) and 999245 (**4c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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