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Synthesis, structure and catalytic activity of xylylene-bridged dipalladium complexes with triazolylidene ligands

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Abstract A series of di-N-heterocyclic carbene (NHC) dipalladium complexes, $[PdPyBr_2]_2$(di-NHC) (**2a–h**), in which di-NHC represents a di-triazolylidene, featuring a 1,4-xylylene spacer between the carbene units, have been prepared from the reactions of the corresponding ditriazolium bromides with $PdCl_2$ and excess NaBr as an additive in the presence of K_2CO_3 in pyridine. All of the complexes were fully characterized by NMR spectra, IR and elemental analyses. The molecular structure of **2b** was determined by X-ray diffraction study, showing the intermolecular hydrogen bonding of Br···H–C. The influences of size of ligands on the catalytic activity have been investigated in the Heck reaction of styrene with bromobenzene. The complex **2g** showed the best catalytic activity, and it is active for various aryl bromides with different electronic and steric properties and styrenes with both electron-donating and electron-withdrawing groups.

Introduction

The use of *N*-heterocyclic carbenes (NHCs) as a class of C donor ligands in coordination chemistry has attracted considerable attention since the report of the first N-heterocyclic carbene (NHC) in 1991 [1]. The transition metal NHC complexes as catalysts have been successfully applied in many important reactions, such as Pd-catalyzed cross-coupling reactions [2, 3] and ruthenium-mediated olefin metathesis [4, 5]. Compared to widely used and studied imidazolylidene-based NHC ligands, less studied triazolylidene-based ligands have proved to be a class of useful NHCs as well. For example, Enders and coworkers reported a stable carbene based on a 1,2,4-triazol-5-ylidene derivative in 1995, which has since proved to be extremely useful in organocatalysis (Scheme 1) [6]. Since then, several metal complexes using Enders carbene as a monodentate ligand have been reported, e.g., ruthenium [7], palladium [8], rhodium [9], iridium [10] or platinum [11] complexes.

We have been interested in developing binuclear palladium–NHC complexes and studying their catalytic properties, as introducing multiple catalytic sites into a catalyst may induce cooperative effects resulting in improving the activities and selectivities [12–15]. However, only NHCs bearing an imidazolylidene backbone have been studied in these di-NHC dipalladium complexes so far. In this paper, we designed and prepared a series of binuclear Pd–NHC complexes bearing triazolylidene ligands linked with a xylylene spacer. In order to elucidate the influence of steric effect of the ligands, we altered the size of the triazolylidene by changing the wingtip substituent in position N(1) of the triazole ring. The steric effects of the ligands on the catalytic activity were studied in Heck reactions.

Yufeng Du and Beibei Liang have contributed equally to the work.

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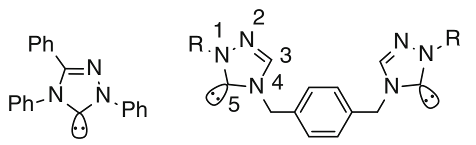


Scheme 1 Enders carbene (*left*) and triazolylidene (NHC) ligands employed in this study (*right*). R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *n*-pentyl, *n*-hexyl, cyclohexyl

Experimental

Materials and methods

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk or glovebox techniques. Solvents were purified and degassed by standard procedures. DMF and pyridine were distilled over calcium hydride under argon atmosphere prior to use. Potassium carbonate and tripotassium phosphate were 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 recorded on a Bruker AV 400-MHz spectrometer at room temperature and referenced to the residual signals of the solvent. Elemental analyses were obtained on a EuroVektor EuroEA-3000 elemental analyzer. IR spectra were recorded on KBr pellets on a FTIR Tensor 27 spectrometer. GC–MS was performed on an Agilent 6890–5973-N system with electron ionization (EI) mass spectrometry. X-ray crystallography was conducted on a BRUKER smart CCD device with Mo Kα radiation ($\lambda = 0.71073$ Å). Absorption correction was performed using the SADABS program. The structure was solved by directed methods using the SHELXS-2016 program and refined by full-matrix least square techniques on F^2. The SQUEEZE program was used to remove the contributions of disordered solvent.

Synthesis of triazolium bromides (1a–h)

In a typical run, a 10-mL thick wall pressure tube was charged with 1,4-bis(bromomethyl)benzene (0.20 g, 0.76 mmol), the corresponding 1-alkyl-1*H*-1,2,4-triazoles (1.60 mmol) and DCM (3 mL). The reaction mixture was heated at 120 °C for 12–16 h. The reaction mixture was cooled to room temperature and extracted with water (3 × 5 mL). The collected aqueous phase was dried by rotovap, and the crude product was recrystallized from methanol/acetone (1:4) to give the product as a white solid.

*4,4′-(1,4-phenylenebis(methylene))bis(1-methyl-1,2,4-triazol-4-ium) dibromide (**1a**)*

Yield: 89%. White solid. M.p.: 276–277 °C. IR (KBr): 3103($\upsilon_{\mathrm{C-H}}$), 3025($\upsilon_{\mathrm{C-H}}$), 2988($\upsilon_{\mathrm{=C-H}}$), 2813($\upsilon_{\mathrm{=C-H}}$), 1578($\upsilon_{\mathrm{C=N}}$), 1527($\upsilon_{\mathrm{C=C}}$), 1456, 1402, 1161, 1066, 981, 899, 769, 734, 673, 620, 503 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): 10.33 (s, 2H, H$_{\text{5-triazole}}$), 9.35 (s, 2H, H$_{\text{3-triazole}}$), 7.57 (s, 4H, Ph), 5.57 (s, 4H, CH$_2$), 4.07 (s, 6H, CH$_3$). ^{13}C NMR (100 MHz, DMSO-d_6): 144.9, 143.4, 135.0, 130.0, 50.4, 39.3. Anal. Calc. for $C_{14}H_{18}Br_2N_6$ (430.14 g/mol): C, 39.09; H, 4.22; N, 19.54, Found: C: 39.23; H: 4.29; N: 19.67%.

*4,4′-(1,4-phenylenebis(methylene))bis(1-ethyl-1,2,4-triazol-4-ium) dibromide (**1b**)*

Yield: 93%. White solid. M.p.: 271–272 °C. IR (KBr): 3101($\upsilon_{\mathrm{C-H}}$), 3027($\upsilon_{\mathrm{C-H}}$), 2990($\upsilon_{\mathrm{=C-H}}$), 1578($\upsilon_{\mathrm{C=N}}$), 1527($\upsilon_{\mathrm{C=C}}$), 1452, 1387, 1331, 1242, 1151, 993, 871, 779, 741, 623, 508 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): 10.44 (s, 2H, H$_{\text{5-triazole}}$), 9.39 (s, 2H, H$_{\text{3-triazole}}$), 7.60 (s, 4H, Ph), 5.57 (s, 4H, CH$_2$), 4.40 (q, $J = 7.2$ Hz, 4H, CH$_2$CH$_3$), 1.47 (t, $J = 7.2$ Hz, 6H, CH$_2$CH$_3$). ^{13}C NMR (100 MHz, DMSO-d_6): 145.0, 142.7, 134.9, 130.0, 50.4, 47.7, 14.0. Anal. Calc. for $C_{16}H_{22}Br_2N_6$ (458.19 g/mol): C, 41.94; H, 4.84; N, 18.34. Found: C: 41.71; H: 4.77; N: 18.21%.

*4,4′-(1,4-phenylenebis(methylene))bis(1-propyl-1,2,4-triazol-4-ium) dibromide(**1c**)*

Yield: 95%. White solid. M.p. >300 °C. IR (KBr): 3103($\upsilon_{\mathrm{C-H}}$), 2976($\upsilon_{\mathrm{=C-H}}$), 2877($\upsilon_{\mathrm{=C-H}}$), 1585($\upsilon_{\mathrm{C=N}}$), 1518($\upsilon_{\mathrm{C=C}}$), 1419, 1389, 1297, 1181, 1151, 998, 878, 783, 761, 621, 520 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): 10.49 (s, 2H, H$_{\text{5-triazole}}$), 9.42 (s, 2H, H$_{\text{3-triazole}}$), 7.60 (s, 4H, Ph), 5.59 (s, 4H, CH$_2$), 4.36 (t, $J = 7.0$ Hz, 4H, CH$_2$CH$_2$), 1.92–1.83 (m, 4H, CH$_2$CH$_3$), 0.89 (t, $J = 7.4$ Hz, 6H, CH$_2$CH$_3$). ^{13}C NMR (100 MHz, DMSO-d_6): 145.1, 143.1, 134.9, 130.0, 53.6, 50.4, 22.0, 10.9. Anal. Calc. for $C_{18}H_{26}Br_2N_6$ (486.25 g/mol): C, 44.46; H, 5.39; N, 17.28. Found: C: 44.31; H: 5.32; N: 17.41%.

*4,4′-(1,4-phenylenebis(methylene))bis(1-isopropyl-1,2,4-triazol-4-ium) dibromide (**1d**)*

Yield: 92%. White solid. M.p.: 289–290 °C. IR (KBr): 3099($\upsilon_{\mathrm{C-H}}$), 2976($\upsilon_{\mathrm{=C-H}}$), 2806($\upsilon_{\mathrm{=C-H}}$), 1585($\upsilon_{\mathrm{C=N}}$), 1513($\upsilon_{\mathrm{C=C}}$), 1421, 1388, 1355, 1296, 1181, 1151, 998, 878, 785, 739, 621, 530 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): 10.47 (s, 2H, H$_{\text{5-triazole}}$), 9.37 (s, 2H, H$_{\text{3-triazole}}$), 7.61 (s, 4H, Ph), 5.55 (s, 4H, CH$_2$), 4.86–4.75 (m, 2H, CH), 1.51 (d, $J = 6.8$ Hz, 12H, CH$_3$). ^{13}C NMR (100 MHz, DMSO-d_6): 145.0, 142.0, 135.0, 130.0, 55.7, 50.4, 21.6. Anal. Calc. for $C_{18}H_{26}Br_2N_6$ (486.25 g/mol): C, 44.46; H, 5.39; N, 17.28. Found: C: 44.22; H: 5.45; N: 17.36%.

*4,4′-(1,4-phenylenebis(methylene))bis(1-butyl-1,2,4-triazol-4-ium) dibromide (**1e**)*

Yield: 89%. White solid. M.p.: 278–279 °C. IR (KBr): $3102(\upsilon_{C-H})$, $3020(\upsilon_{C-H})$, $2955(\upsilon_{=C-H})$, $2871(\upsilon_{=C-H})$, $1580(\upsilon_{C=N})$, $1520(\upsilon_{C=C})$, 1417, 1391, 1332, 1303, 1245, 1197, 1151, 996, 871, 783, 759, 622, 510 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): 10.39 (s, 2H, $H_{5\text{-triazole}}$), 9.36 (s, 2H, $H_{3\text{-triazole}}$), 7.58 (s, 4H, Ph), 5.56 (s, 4H, CH_2), 4.38 (t, $J = 7.2$ Hz, 4H, $H_{1\text{-Bu}}$), 1.87–1.79 (m, 4H, $H_{2\text{-Bu}}$), 1.34–1.25 (m, 4H, $H_{3\text{-Bu}}$), 0.90 (t, $J = 7.4$ Hz, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): 145.1, 143.0, 135.0, 130.0, 51.9, 50.5, 30.4, 19.2, 13.7. Anal. Calc. for $C_{20}H_{30}Br_2N_6$ (514.30 g/mol): C, 46.71; H, 5.88; N, 16.34. Found: C: 46.48; H: 5.94; N: 16.22%.

*4,4′-(1,4-phenylenebis(methylene))bis(1-pentyl-1,2,4-triazol-4-ium) dibromide (**1f**)*

Yield: 83%. White solid. M.p.: 285–286 °C. IR (KBr): $3102(\upsilon_{C-H})$, $3030(\upsilon_{C-H})$, $2959(\upsilon_{=C-H})$, $2869(\upsilon_{=C-H})$, $2853(\upsilon_{=C-H})$, $1580(\upsilon_{C=N})$, $1518(\upsilon_{C=C})$, 1463, 1390, 1334, 1245, 1151, 1068, 998, 871, 783, 759, 623, 511 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): 10.35 (s, 2H, $H_{5\text{-triazole}}$), 9.34 (s, 2H, $H_{3\text{-triazole}}$), 7.58 (s, 4H, Ph), 5.56 (s, 4H, CH_2), 4.37 (t, $J = 7.0$ Hz, 4H, $H_{1\text{-pentyl}}$), 1.89–1.82 (m, 4H, $H_{2\text{-pentyl}}$), 1.34–1.24 (m, 8H, $H_{3\text{-pentyl}}$, $H_{4\text{-pentyl}}$), 0.87 (t, $J = 7$ Hz, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): 145.1, 143.0, 134.9, 129.9, 52.2, 50.5, 28.1, 28.0, 21.9, 14.2. Anal. Calc. for $C_{22}H_{34}Br_2N_6$ (542.35 g/mol): C, 48.72; H, 6.32; N, 15.50. Found: C: 48.58; H: 6.26; N: 15.62%.

*4,4′-(1,4-phenylenebis(methylene))bis(1-hexyl-1,2,4-triazol-4-ium) dibromide (**1g**)*

Yield: 96%. White solid. M.p. >300 °C. IR (KBr): $3101(\upsilon_{C-H})$, $3031(\upsilon_{C-H})$, $2952(\upsilon_{=C-H})$, $2867(\upsilon_{=C-H})$, $1578(\upsilon_{C=N})$, $1517(\upsilon_{C=C})$, 1464, 1389, 1332, 1245, 1151, 1068, 890, 871, 760, 726, 703, 623, 511 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): 10.30 (s, 2H, $H_{5\text{-triazole}}$), 9.32 (s, 2H, $H_{3\text{-triazole}}$), 7.60 (s, 4H, Ph), 5.55 (s, 4H, CH_2), 4.37 (t, $J = 7.0$ Hz, 4H, $H_{1\text{-hexyl}}$), 1.88–1.81 (m, 4H, $H_{2\text{-hexyl}}$), 1.33–1.78 (m, 12H, $H_{3\text{-hexyl}}$, $H_{4\text{-hexyl}}$, $H_{5\text{-hexyl}}$), 0.86 (t, $J = 6.4$ Hz, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): 145.1, 143.0, 135.0, 130.0, 52.2, 50.5, 31.0, 28.5, 25.5, 22.3, 14.3. Anal. Calc. for $C_{24}H_{38}Br_2N_6$ (570.41 g/mol): C, 50.54; H, 6.71; N, 14.73. Found: C: 50.35; H: 6.64; N: 14.84%.

*4,4′-(1,4-phenylenebis(methylene))bis(1-cyclohexyl-1,2,4-triazol-4-ium) dibromide (**1 h**)*

Yield: 83%. White solid. M.p.: 280–281 °C. IR (KBr): $3099(\upsilon_{C-H})$, $3024(\upsilon_{C-H})$, $2932(\upsilon_{=C-H})$, $2852(\upsilon_{=C-H})$, $2802(\upsilon_{=C-H})$, $1586(\upsilon_{C=N})$, $1515(\upsilon_{C=C})$, 1445, 1365, 1309, 1153, 993, 892, 759, 619, 527 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): 10.45 (s, 2H, $H_{5\text{-triazole}}$), 9.36 (s, 2H, $H_{3\text{-triazole}}$), 7.60 (s, 4H, Ph), 5.55 (s, 4H, CH_2), 4.55–4.47 (m, 2H, $H_{1\text{-cyclohexane}}$), 2.17–2.13 (m, 4H, $H_{\text{cyclohexane}}$), 1.85–1.81 (m, 4H, $H_{\text{cyclohexane}}$), 1.77–1.65 (m, 6H, $H_{\text{cyclohexane}}$), 1.47–1.37 (m, 4H, $H_{\text{cyclohexane}}$), 1.30–1.17 (m, 2H, $H_{\text{cyclohexane}}$). ^{13}C NMR (100 MHz, DMSO-d_6): 144.9, 142.0, 135.0, 130.0, 61.6, 50.4, 31.7, 24.9, 24.4. Anal. Calc. for $C_{24}H_{34}Br_2N_6$ (566.37 g/mol): C, 50.90; H, 6.05; N, 14.84. Found: C: 50.78; H: 6.10; N: 14.92%.

Synthesis of di-NHC dipalladium complexes (2a–h)

In a typical run, to a mixture of bis(triazolium) bromide (1.0 mmol), $PdCl_2$ (0.534 g, 2.0 mmol), NaBr (0.823 g, 8 mmol) and K_2CO_3 (2.764 g, 20 mmol) in a 50-mL round-bottom flask was added 15 mL of pyridine. The reaction mixture was heated at 85°C for 20 h, after which time the mixture was filtered through Celite and washed with DCM. The solvent was removed under vacuum, and the crude product was washed with diethyl ether (15 mL). The product was obtained as a yellow solid by recrystallization from ether/DCM.

*Complex **2a***

Yield: 83%. Light yellow solid. IR (KBr): $3134(\upsilon_{C-H})$, $3064(\upsilon_{C-H})$, $3002(\upsilon_{C-H})$, $2942(\upsilon_{=C-H})$, 1604 $(\upsilon_{C=N})$, $1538(\upsilon_{C=C})$, 1485, 1447, 1410, 1358, 1332, 1231, 1171, 1117, 1073, 978, 863, 791, 762, 693, 645 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 8.95 (d, $J = 4.8$ Hz, 4H, $H_{\alpha\text{-Py}}$), 7.85 (s, 2H, H_{triazole}), 7.78 (t, $J = 7.6$ Hz, 2H, $H_{\gamma\text{-Py}}$), 7.61 (s, 4H, Ph), 7.36 (t, $J = 7.0$ Hz, 4H, $H_{\beta\text{-Py}}$), 5.75 (s, 4H, CH_2), 4.27 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 155.9, 152.6, 142.5, 138.1, 134.9, 130.3, 124.8, 52.5, 40.5. Anal. Calc. for $C_{24}H_{26}Br_4N_8Pd_2$ (958.98 g/mol): C, 30.06; H, 2.73; N, 11.68. Found: C: 30.31; H: 2.71; N: 11.82%.

*Complex **2b***

Yield: 85%. Light yellow solid. IR (KBr): $3136(\upsilon_{C-H})$, $3053(\upsilon_{C-H})$, $2986(\upsilon_{=C-H})$, $1604(\upsilon_{C=N})$, $1542(\upsilon_{C=C})$, 1479, 1447, 1369, 1352, 1333, 1245, 1217, 1073, 965, 757, 737, 695, 663 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 8.96 (d, $J = 4.8$ Hz, 4H, $H_{\alpha\text{-Py}}$), 7.86 (s, 2H, H_{triazole}), 7.77 (t, $J = 7.6$ Hz, 2H, $H_{\gamma\text{-Py}}$), 7.62 (s, 4H, Ph), 7.36 (t, $J = 7.0$ Hz, 4H, $H_{\beta\text{-Py}}$), 5.75 (s, 4H, CH_2), 4.73 (q, $J = 7.4$ Hz, 4H, CH_2CH_3), 1.65 (t, $J = 7.4$ Hz, 6H, CH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 155.1, 152.7, 142.7, 138.2, 135.0, 130.5, 124.9, 52.7, 49.0, 14.9. Anal. Calc. for $C_{26}H_{30}Br_4N_8Pd_2$ (987.03 g/mol): C, 31.64; H, 3.06; N, 11.35. Found: C: 31.50; H: 3.11; N: 11.42%.

Complex ***2c***

Yield: 81%. Light yellow solid. IR (KBr): 3112($\upsilon_{\text{C–H}}$), 3043($\upsilon_{\text{C–H}}$), 2963($\upsilon_{\text{=C–H}}$), 2933($\upsilon_{\text{=C–H}}$), 2873($\upsilon_{\text{=C–H}}$), 1604($\upsilon_{\text{C=N}}$), 1536($\upsilon_{\text{C=C}}$), 1477, 1447, 1380, 1218, 1168, 1074, 1017, 993, 857, 802, 758, 693, 646 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): 8.98 (d, $J = 4.8$ Hz, 4H, H$_{\alpha\text{-Py}}$), 7.88 (s, 2H, H$_{\text{triazole}}$), 7.79 (t, $J = 7.6$ Hz, 2H, H$_{\gamma\text{-Py}}$), 7.64 (s, 4H, Ph), 7.38 (t, $J = 7.0$ Hz, 4H, H$_{\beta\text{-Py}}$), 5.79 (s, 4H, CH$_2$), 4.64 (t, $J = 7.6$ Hz, 4H, CH$_2$CH$_2$), 2.24–2.14 (m, 4H, CH$_2$CH$_3$), 1.10 (t, $J = 7.4$ Hz, 6H, CH$_2$CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): 155.1, 152.6, 142.4, 138.1, 134.9, 130.3, 124.7, 55.0, 52.6, 22.8, 11.3. Anal. Calc. for $C_{28}H_{34}Br_4N_8Pd_2$ (1015.08 g/mol): C, 33.13; H, 3.38; N, 11.04. Found: C: 33.00; H: 3.34; N: 11.11%.

Complex ***2d***

Yield: 83%. Light yellow solid. IR (KBr): 3115($\upsilon_{\text{C–H}}$), 2981($\upsilon_{\text{=C–H}}$), 2934($\upsilon_{\text{=C–H}}$), 1605($\upsilon_{\text{C=N}}$), 1538($\upsilon_{\text{C=C}}$), 1471, 1447, 1368, 1216, 1179, 1072, 1047, 992, 857, 753, 696, 659, 645 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): 8.98 (d, $J = 5.2$ Hz, 4H, H$_{\alpha\text{-Py}}$), 7.88 (s, 2H, H$_{\text{triazole}}$), 7.79 (t, $J = 7.6$ Hz, 2H, H$_{\gamma\text{-Py}}$), 7.64 (s, 4H, Ph), 7.37 (t, $J = 7.0$ Hz, 4H, H$_{\beta\text{-Py}}$), 5.79–5.72 (m, 6H, CH$_2$, CH), 1.61 (d, $J = 6.8$ Hz, 12H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): 153.7, 152.6, 142.6, 138.1, 134.8, 130.3, 124.7, 55.6, 52.5, 21.8. Anal. Calc. for $C_{28}H_{34}Br_4N_8Pd_2$ (1013.77 g/mol): C: 33.01; H: 3.32; N: 11.13%.

Complex ***2e***

Yield: 77%. Light yellow solid. IR (KBr): 3117($\upsilon_{\text{C–H}}$), 3063($\upsilon_{\text{C–H}}$), 2953($\upsilon_{\text{=C–H}}$), 2869($\upsilon_{\text{=C–H}}$), 1604($\upsilon_{\text{C=N}}$), 1541($\upsilon_{\text{C=C}}$), 1475, 1447, 1366, 1239, 1216, 1165, 1073, 1018, 1002, 951, 859, 762, 698, 646 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): 8.97 (d, $J = 4.9$ Hz, 4H, H$_{\alpha\text{-Py}}$), 7.88 (s, 2H, H$_{\text{triazole}}$), 7.79 (t, $J = 7.8$ Hz, 2H, H$_{\gamma\text{-Py}}$), 7.64 (s, 4H, Ph), 7.38 (t, $J = 7.0$ Hz, 4H, H$_{\beta\text{-Py}}$), 5.78 (s, 4H, CH$_2$), 4.67 (t, $J = 7.4$ Hz, 4H, H$_{\text{1-Bu}}$), 2.16–2.10 (m, 4H, H$_{\text{2-Bu}}$), 1.57- 1.47 (m, 4H, H$_{\text{3-Bu}}$), 1.05 (t, $J = 7.4$ Hz, 6H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): 155.1, 152.6, 142.4, 138.1, 134.9, 130.3, 124.7, 52.6, 31.2, 29.7, 19.8, 13.7. Anal. Calc. for $C_{30}H_{38}Br_4N_8Pd_2$ (1043.13 g/mol): C, 34.54; H, 3.67; N, 10.74. Found: C: 34.37; H: 3.62; N: 10.82%.

Complex ***2f***

Yield: 79%. Light yellow solid. IR (KBr): 3116($\upsilon_{\text{C–H}}$), 3064($\upsilon_{\text{C–H}}$), 2953($\upsilon_{\text{=C–H}}$), 2869($\upsilon_{\text{=C–H}}$), 1603($\upsilon_{\text{C=N}}$), 1539($\upsilon_{\text{C=C}}$), 1475, 1447, 1369, 1217, 1071, 1016, 976, 862, 758, 699, 664, 645 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): 8.98 (d, $J = 4.9$ Hz, 4H, H$_{\alpha\text{-Py}}$), 7.88 (s, 2H, H$_{\text{triazole}}$), 7.79 (t, $J = 7.6$ Hz, 2H, H$_{\gamma\text{-Py}}$), 7.64 (s, 4H, Ph), 7.38 (t, $J = 7.0$ Hz, 4H, H$_{\beta\text{-Py}}$), 5.78 (s, 4H, CH$_2$), 4.66 (t, $J = 7.6$ Hz, 4H, H$_{\text{1-pentyl}}$), 2.18–2.13 (m, 4H, H$_{\text{2-pentyl}}$), 1.50–1.46 (m, 8H, H$_{\text{3-pentyl}}$, H$_{\text{4-pentyl}}$), 0.97 (t, $J = 7.0$ Hz, 6H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): 155.1, 152.6, 142.4, 138.1, 134.9, 130.3, 124.7, 52.6, 30.9, 29.0, 28.7, 22.3, 13.9. Anal. Calc. for $C_{32}H_{42}Br_4N_8Pd_2$ (1071.20 g/mol): C, 35.88; H, 3.95; N, 10.46. Found: C: 36.01; H: 3.91; N: 10.40%.

Complex ***2g***

Yield: 88%. Light yellow solid. IR (KBr): 3114($\upsilon_{\text{C–H}}$), 3042($\upsilon_{\text{C–H}}$), 2950($\upsilon_{\text{=C–H}}$), 2857($\upsilon_{\text{=C–H}}$), 1602($\upsilon_{\text{C=N}}$), 1534($\upsilon_{\text{C=C}}$), 1473, 1447, 1389, 1215, 1198, 1068, 1016, 979, 783, 762, 701, 667, 644 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): 8.97 (d, $J = 4.9$ Hz, 4H, H$_{\alpha\text{-Py}}$), 7.87 (s, 2H, H$_{\text{triazole}}$), 7.79 (t, $J = 7.6$ Hz, 2H, H$_{\gamma\text{-Py}}$), 7.64 (s, 4H, Ph), 7.38 (t, $J = 7.2$ Hz, 4H, H$_{\beta\text{-Py}}$), 5.78 (s, 4H, CH$_2$), 4.66 (t, $J = 7.4$ Hz, 4H, H$_{\text{1-hexyl}}$), 2.19–2.12 (m, 4H, H$_{\text{2-hexyl}}$), 1.53–1.35 (m, 12H, H$_{\text{3-hexyl}}$, H$_{\text{4-hexyl}}$, H$_{\text{5-hexyl}}$), 0.92 (t, $J = 7.0$ Hz, 6H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): 155.1, 152.6, 142.4, 138.1, 134.9, 130.3, 124.7, 53.4, 52.6, 31.3, 29.2, 26.3, 22.5, 14.1. Anal. Calc. for $C_{34}H_{46}Br_4N_8Pd_2$ (1099.24 g/mol): C, 37.15; H, 4.22; N, 10.19. Found: C: 36.98; H: 4.29; N: 10.27%.

Complex ***2h***

Yield: 69%. Light yellow solid. IR (KBr): 3113($\upsilon_{\text{C–H}}$), 3041($\upsilon_{\text{C–H}}$), 2939($\upsilon_{\text{=C–H}}$), 2856($\upsilon_{\text{=C–H}}$), 1604($\upsilon_{\text{C=N}}$), 1539($\upsilon_{\text{C=C}}$), 1469, 1447, 1378, 1217, 1158, 1071, 1017, 995, 895, 821, 761, 696, 659, 644 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): 9.00 (d, $J = 4.9$ Hz, 4H, H$_{\alpha\text{-Py}}$), 7.83 (s, 2H, H$_{\text{triazole}}$), 7.77 (t, $J = 7.8$ Hz, 2H, H$_{\gamma\text{-Py}}$), 7.61 (s, 4H, Ph), 7.35 (t, $J = 7.0$ Hz, 4H, H$_{\beta\text{-Py}}$), 5.75 (s, 4H, CH$_2$), 5.32–5.25 (m, 2H, H$_{\text{1-cyclohexyl}}$), 2.28–2.25 (m, 4H, H$_{\text{cyclohexyl}}$), 1.94–1.74 (m, 10H, H$_{\text{cyclohexyl}}$), 1.60–1.49 (m, 4H, H$_{\text{cyclohexyl}}$), 1.32–1.26 (m, 2H, H$_{\text{cyclohexyl}}$). ^{13}C NMR (100 MHz, CDCl$_3$): 153.7, 152.7, 142.4, 138.1, 134.8, 130.3, 124.7, 62.5, 52.6, 31.9, 25.3, 25.1. Anal. Calc. for $C_{34}H_{42}Br_4N_8Pd_2$ (1095.22 g/mol): C, 37.29; H, 3.87; N, 10.23. Found: C: 39.05; H: 3.90; N: 10.44%.

Procedure for the catalytic Heck coupling reaction

In a typical run, a 5-mL vial equipped with a magnetic stirrer was charged with a mixture of phenyl bromide (78.5 mg, 0.5 mmol), styrene (62.5 mg, 0.6 mmol), Pd catalyst (0.0025 mmol), K_3PO_4 (212 mg, 1.0 mmol) and DMF (1 mL) under nitrogen. The mixture was heated at 100 °C for 4 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

The 1-alkyl-1*H*-1,2,4-triazoles were prepared from the nucleophilic substitution reaction of the corresponding alkyl bromide or iodide with 1*H*-1,2,4-triazole according to the literature procedure [16]. The bis(triazolium) bromides **1a–h** were prepared by direct alkylation of triazoles with 1,4-xylylene dibromide in CH_2Cl_2 in good yields. The synthesis of di-NHC dipalladium complexes (**2a–h**) was achieved by the reactions of the corresponding bis(triazolium) bromides with $PdCl_2$ in the presence of K_2CO_3 with NaBr as additive in pyridine at 85 °C for 20 h (Scheme 2). All the complexes were isolated in good yields of 69–88%.

The bis(triazolium) bromides and palladium–NHC complexes were fully characterized by ^1H and ^{13}C NMR spectra, IR spectra and elemental analyses. For example, in the ^1H NMR spectrum of imidazolium bromide **1b**, two singlets at 10.44 and 9.39 ppm correspond to two triazole protons; one singlet at 7.60 ppm corresponds to phenyl protons of xylene; one singlet at 5.57 ppm corresponds to methylene proton of xylene and a quartet at 4.40 and a triplet at 1.47 ppm correspond to ethyl protons. In the ^{13}C NMR spectrum of **1b**, four signals (145.0, 142.7, 134.9, 130.0 ppm) corresponding to triazole and phenyl moieties are observed in the aromatic region and three signals (50.4, 47.7, 14.0 ppm) corresponding to methylene and ethyl moieties are observed in the alkyl region. In the ^1H NMR spectra of palladium complexes **2a–h**, the proton signals of NCHN (ca. 10.49–10.30 ppm) in the starting ligand precursors were absent after metalation, due to the formation of Pd–$C_{carbene}$ bonds. The upfield shifts of the signals relative to the triazolidene proton are observed, and the proton signals relative to pyridine are observed. In the ^{13}C NMR

Scheme 2 Synthesis of di-NHC dipalladium complexes **2a–h**

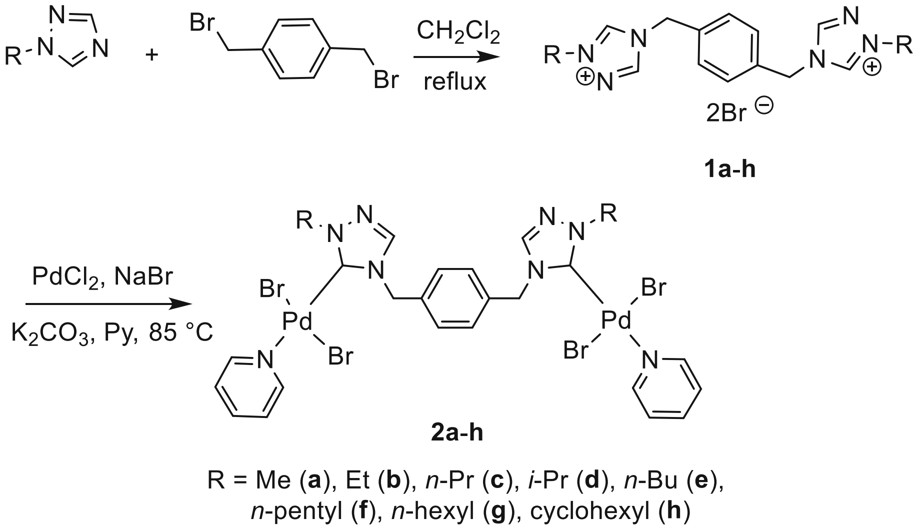


Table 1 Selected ^1H and ^{13}C NMR data of bis(triazolium) salt **1a–h**, and bis(NHC) palladium complexes **2a–h**

Bis(triazolium) bromide	^1H (triazole)[a]	^{13}C (5-triazole)	Pd complex	^1H (triazole)[b]	^1H (pyridine)[b]	^1H (methylene of xylene)[b]	^{13}C (carbene–Pd)[b]
1a	10.33, 9.35	143.4	**2a**	7.85	8.95, 7.78, 7.36	5.75	155.9
1b	10.44, 9.39	145.0	**2b**	7.86	8.96, 7.77, 7.36	5.75	155.1
1c	10.49, 9.42	145.1	**2c**	7.88	8.98, 7.79, 7.38	5.79	155.1
1d	10.47, 9.37	145.0	**2d**	7.88	8.98, 7.79, 7.37	5.74	153.7
1e	10.39, 9.36	145.1	**2e**	7.88	8.97, 7.79, 7.38	5.78	155.1
1f	10.35, 9.34	145.1	**2f**	7.88	8.98, 7.79, 7.38	5.78	155.1
1 g	10.30, 9.32	145.1	**2g**	7.87	8.97, 7.79, 7.38	5.78	155.1
1 h	10.45, 9.36	144.9	**2h**	7.83	9.00, 7.77, 7.35	5.75	153.7

[a] In ppm in DMSO-d_6

[b] In ppm in $CDCl_3$

spectra of palladium complexes **2a–h**, the signal at ca. 155 ppm which is assigned to the $C_{carbene}$–Pd resonance shifted downfield relative to that of its precursor (ca. 145 ppm) providing direct evidence of the metalation of the ligand. The selected ^1H and ^{13}C NMR data of bis(triazolium) bromides and their corresponding palladium complexes are listed in Table 1. The infrared spectra of **1a–h** and **2a–h** showed the absorption bands corresponding to the stretching vibrations of C–H of saturated alkanes and unsaturated alkenes, C=C and C=N double bonds. The absorption bands shift to higher frequencies upon metalation.

The palladium complexes **2a–h** are air- and moisture-stable in the solid state and even in common organic solvents.

Description of the structures

Suitable crystals of complex **2b** for X-ray diffraction analysis were obtained by slow diffusion of methanol into a dichloromethane-saturated solution at room temperature. The selected crystallographic data and refinement parameters are summarized in Table 2. The molecular structure of complex **2b** is unambiguously confirmed by means of X-ray diffraction studies, and Fig. 1 shows the molecular diagram of the complex. The molecule consists of two palladium centers bound by a xylylene-bridged bis(triazolylidene) ligand. Each palladium atom completes its coordination sphere with two bromides in a *trans* conformation and a pyridine. The geometry around the palladium center is slightly distorted from square planar. The bond angles around palladium are a little off from 180° or 90° [angle of Br–Pd–Br: 174.089(17)°; angle of $C_{carbene}$–Pd–

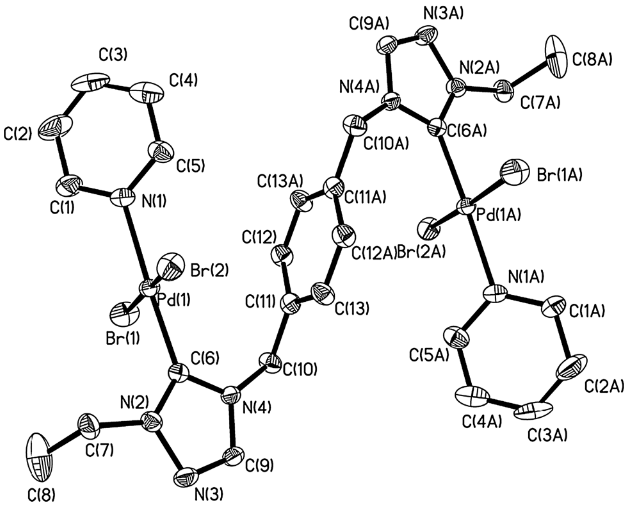


Fig. 1 Molecular structure of complex **2b**. Hydrogen atoms are omitted for clarity. Ellipsoids are at the 50% probability level

Table 2 Crystallographic parameters of **2b**

Formula	$C_{26}H_{30}Br_4N_8Pd_2$
FW	987.02
Crystal system	Monoclinic
Space group	*C2/c*
Crystal size/(mm)	0.21 × 0.20 × 0.19
Radiation	Mo Kα ($\lambda = 0.71073$)
a (Å)	12.2695(5)
b (Å)	11.4067(5)
c (Å)	26.5584(12)
α (°)	90
β (°)	103.3557(5)
γ (°)	90
V (Å^3)	3616.4(3)
Z	4
D_{calcd}.(mg cm^{-3})	1.813
Absorption coefficient (mm^{-1})	5.441
F(000)	1896
θ range (°)	2.71–28.71
Index ranges	$-16 \le h \le 16$, $-11 \le k \le 14$, $-35 \le l \le 35$
Reflections collected/unique	24252/4593
Data/restraints/parameters	4593/0/183
Goodness of fit on F_2	1.003
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0447$, $wR_2 = 0.0914$
R indices (all data)	$R_1 = 0.0548$, $wR_2 = 0.0938$

Br(1): 86.88(8) °]. The two palladium fragments are located on one side of the plane defined by the xylylene bridge showing an *anti*-orientation with respect to the bis-NHC ligand. This conformation leads to a separation of 7.454 Å between two Pd. The Pd–C$_{carbene}$ distance is 1.956(3) Å (Table 3), similar to the values for other palladium-related species [14]. The crystal packing of the molecule reveals the intermolecular hydrogen bonding of Br···H-C with Br···H distance of 2.997(5) Å (Fig. 2).

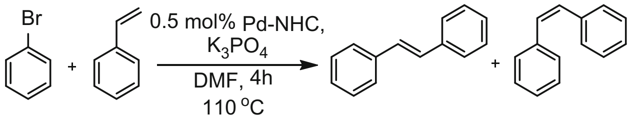
Catalytic studies

To elucidate the influence of steric effects of the ligands, the catalytic activity of complexes **2a–h** with different alkyl substitution in N(1) position of the triazole ring was investigated in the arylation of styrene with bromobenzene (Table 4). The results revealed that the complex **2e** with *n*-butyl and **2g** with *n*-hexyl substitution on 1-triazolylidene showed good performance in the coupling reaction giving good yield and regioselectivity (96% yield with 27:1 of *E*:*Z* ratio for **2e** and 98% yield of 26:1 of E:Z ratio for **2g**). Complex **2 h** with cyclohexyl substitution led to a lower yield (69%) and poor selectivity (13:1 of E:Z ratio).

Table 3 Selected bond lengths (Å) and angles (°) for **2b**

Distance (Å)		Angle (°)	
Pd(1)–C(6)	1.956(3)	C(6)–Pd(1)–N(1)	176.78(11)
Pd(1)–N(1)	2.099(3)	C(6)–Pd(1)–Br(1)	86.88(8)
Pd(1)–Br(1)	2.4296(4)	N(1)–Pd(1)–Br(1)	91.45(8)
Pd(1)–Br(2)	2.4460(4)	C(6)–Pd(1)–Br(2)	89.83(8)
N(2)–C(6)	1.325(4)	N(1)–Pd(1)–Br(2)	92.07(8)
N(2)–N(3)	1.376(3)	Br(1)–Pd(1)–Br(2)	174.089(17)
N(3)–C(9)	1.296(4)	N(2)–C(6)–N(4)	104.0(2)
N(4)–C(6)	1.355(4)		
N(4)–C(9)	1.356(4)		

Table 4 Arylation of styrene with bromobenzene catalyzed by **2a–h**



Entry[a]	Catalyst	Yield (%)[a]	*E/Z* ratio[b]
1	**2a**	83	23:1
2	**2b**	87	20:1
3	**2c**	90	23:1
4	**2d**	92	21:1
5	**2e**	96	27:1
6	**2f**	95	22:1
7	**2g**	98	26:1
8	**2h**	69	13:1

[a] Reaction conditions: phenylbromide (0.5 mmol, 52 μL), styrene (0.6 mmol, 63 μL), Pd–NHC complex (0.0025 mmol) and K_3PO_4 (1 mmol, 0.23 g) in DMF (2 mL)

[b] Determined by GC using dodecane as internal standard

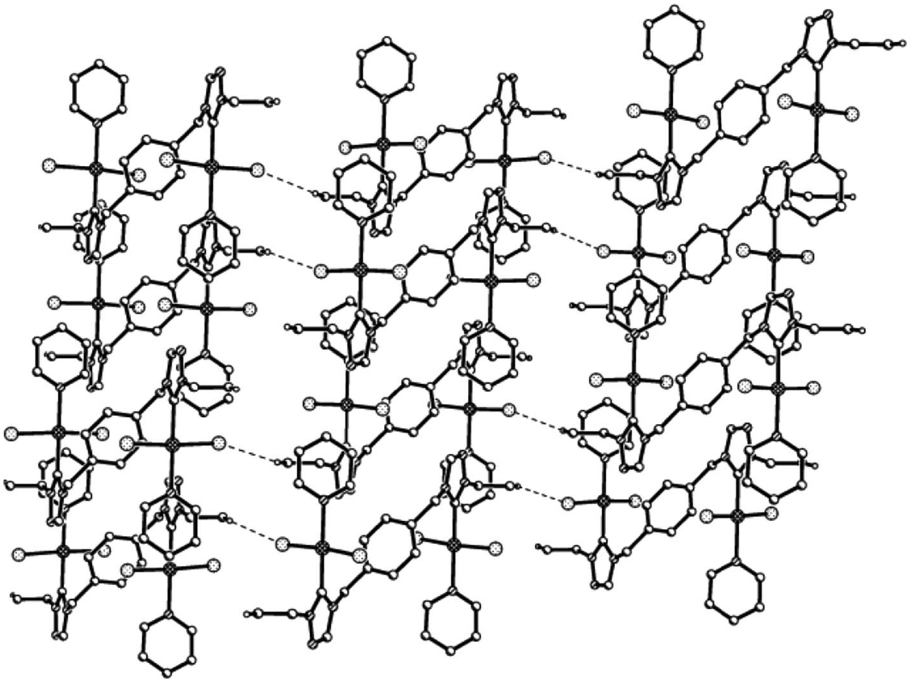
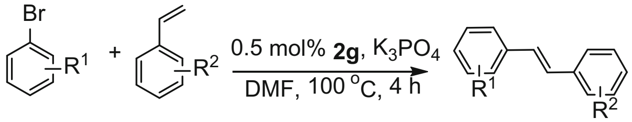


Fig. 2 One section of the crystal packing of complex **2b**, showing the hydrogen bonding of Br···H–C. Other hydrogen atoms are omitted for clarity

Table 5 Arylation of styrene with aryl bromide catalyzed by **2g**



Entry[a]	R^1	R^2	Yield (%)[b]
1	H	H	86
2	*o*-OMe	H	91
3	*p*-OMe	H	93
4	*o*-F	H	82
5	*m*-F	H	82
6	*p*-F	H	77
7	2,3-*benzo*	H	96
8	H	*p*-OMe	84
9	*o*-OMe	*p*-OMe	85
10	*p*-OMe	*p*-OMe	93
11	*o*-F	*p*-OMe	83
12	*m*-F	*p*-OMe	86
13	*p*-F	*p*-OMe	73
14	2,3-*benzo*	*p*-OMe	90
15	H	*p*-Cl	77
16	*o*-OMe	*p*-Cl	81
17	*p*-OMe	*p*-Cl	82
18	*o*-F	*p-Cl*	73
19	*m*-F	*p-Cl*	75
20	*p*-F	*p*-Cl	80
21	2,3-*benzo*	*p*-Cl	86

[a] Reaction conditions: phenylbromide (0.5 mmol, 52 μL), styrene (0.6 mmol, 63 μL), complex **2g** (0.0025 mmol) and K_3PO_4 (1 mmol, 0.23 g) in DMF (2 mL)

[b] Isolated yield

Therefore, suitable size of the substituted ligand, neither too large nor too small, appears to be necessary for good catalytic results.

A variety of aryl bromides with different electronic and steric effects were examined in the Heck reaction; meanwhile, styrenes bearing either electron-donating or electron-withdrawing group were also examined. Details of the experiment setup are given in the experimental section, and the results are given in Table 5. The reactions went well with aryl bromides bearing both electron-donating and electron-withdrawing groups; however, the better yield was generally obtained with aryl bromides bearing electron-donating groups. The yields decreased when styrenes having electron-withdrawing group were used. In addition, the steric effect of the aryl bromides does not play an important role in the reactions; for example, comparable results were obtained in the reactions of styrene with 1-bromo-2-methoxybenzene and with 1-bromo-4-methoxybenzene (Table 5, entries 2 and 3).

Conclusion

We have synthesized a series of dipalladium complexes **2a–h** having di-triazolylidene ligands linked by xylylene spacers. X-ray study showed that both palladium centers are coordinated by the triazolylidene, two bromides in a *trans* configuration and a pyridine ligand with slightly distorted square-planar geometry. Two pseudo-square-planar palladium fragments are in an *anti*-orientation. The crystal packing of the molecule reveals the intermolecular hydrogen bonding of Br···H–C. Catalytic results of complexes **2a–h** in the arylation of styrene with phenyl bromide show that suitable size of the substituted ligand is important for the good catalytic results. The catalyst **2g** is active for various aryl bromides with different electronic and steric properties and also active for styrenes with both electron-donating and electron-withdrawing groups.

Supplementary material

CCDC 1511565 (**2b**) contains 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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