# Synthesis of xylylene-bridged dipalladium complexes with imidazole and triazole-based di-*N*-heterocyclic carbene (NHC) ligands

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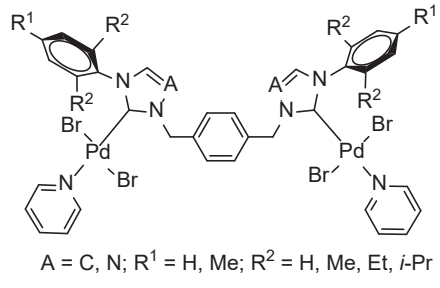
The di-*N*-heterocyclic carbene (NHC) dipalladium complexes, $[(PdPyBr_2)_2(di\text{-}NHC_{imi})]$ and $[(PdPyBr_2)_2(di\text{-}NHC_{tri})]$, $di\text{-}NHC_{imi}$ and $di\text{-}NHC_{tri}$ represent an imidazolylidene and a triazolylidene, respectively, featuring a 1,4-xylylene spacer between the carbene units, have been prepared. The influences of the imidazolylidene and triazolidene backbone and different substituents on the catalytic activity have been investigated in the Mizoroki–Heck reaction of styrene with bromobenzene.

**Keywords:** dinuclear, palladium, *N*-heterocyclic carbene, Heck reaction

In the last two decades, *N*-heterocyclic carbenes (NHCs) as a class of C donor ligands, have become alternative or complementary to the classical P or N donor ligands. Metal-NHC complexes have been successfully applied in catalysis,[1–3] material synthesis[4] and biochemistry.[5–7] In catalysis, several NHC–Ru complexes have been effectively employed as catalysts in olefin metathesis,[8,9] whilst many NHC–Pd complexes show good activity in C–C coupling reactions.[10,11]

We have been interested recently in developing NHC-based palladium systems and studying their catalytic properties. For the design of homogeneous catalysts, it is interesting to introduce multiple catalytic sites into a catalyst, as it may induce cooperative effects resulting in improving the activities and selectivities. We have designed a series of di-NHC dipalladium complexes with the flexible alkyl or rigid phenylene linker, in which the di-NHCs are geometrically isolated.[12–15] The influences of the linkers, substituents and halide ligand on the catalytic reactivity of these Pd complexes have been investigated in the Mizoroki–Heck reaction of styrene with bromobenzene. The results show that the substitution, halide ligand and spacer have some effects on the regioselectivity and yield of the product.[12–15] However, only NHCs bearing imidazolylidene backbones have been employed in these Pd–NHC complexes, and the spacer used is either too flexible or too rigid. In this paper we have designed and prepared a series of di-NHC dipalladium complexes bearing triazolylidene ligands linked with a semi-rigid xylylene spacer. For comparison, their imidazolylidene analogues were synthesised as well (Scheme 1). In order to elucidate the influence of steric and electronic effect of the ligands, the effects of different substituents and introduction of nitrogen into the imidazolylidene backbone on the catalytic activity have been studied in Heck reactions.

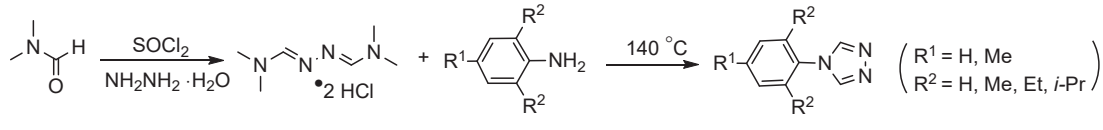



**Scheme 1** The di-NHC dipalladium complexes in this work.

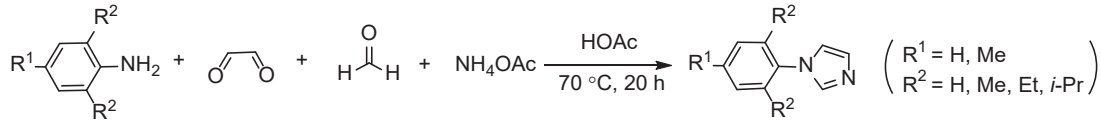
## Results and discussion

The *N*-aryl imidazoles[16] (Scheme 2) and triazoles[17] (Scheme 3) were prepared from the corresponding anilines according to literature procedures. The imidazolium and triazolium bromides (**1a**–**d** and **2a**–**d**) were prepared by direct reaction of the corresponding imidazoles and triazoles with 1,4-xylyene dibromide in $CH_2Cl_2$ under reflux (Scheme 4) in good yield. The synthesis of the di-NHC dipalladium complexes (**3a**–**d** and **4a**–**d**) was achieved by the reaction of the corresponding bis(imidazolium) bromide or bis(triazolium) bromide with $PdCl_2$ in the presence of $K_2CO_3$ with NaBr as additive in pyridine at 85 °C for 18 h (Scheme 4). All complexes were isolated in good yields of 70–82%.

The imidazolium and triazolium bromides and their palladium NHC complexes were fully characterised by $^1$H NMR, $^{13}$C NMR and elemental analysis. For example, in the $^1$H NMR spectrum of




**Scheme 2** Synthesis of *N*-aryl imidazoles.




**Scheme 3** Synthesis of *N*-aryl triazoles.

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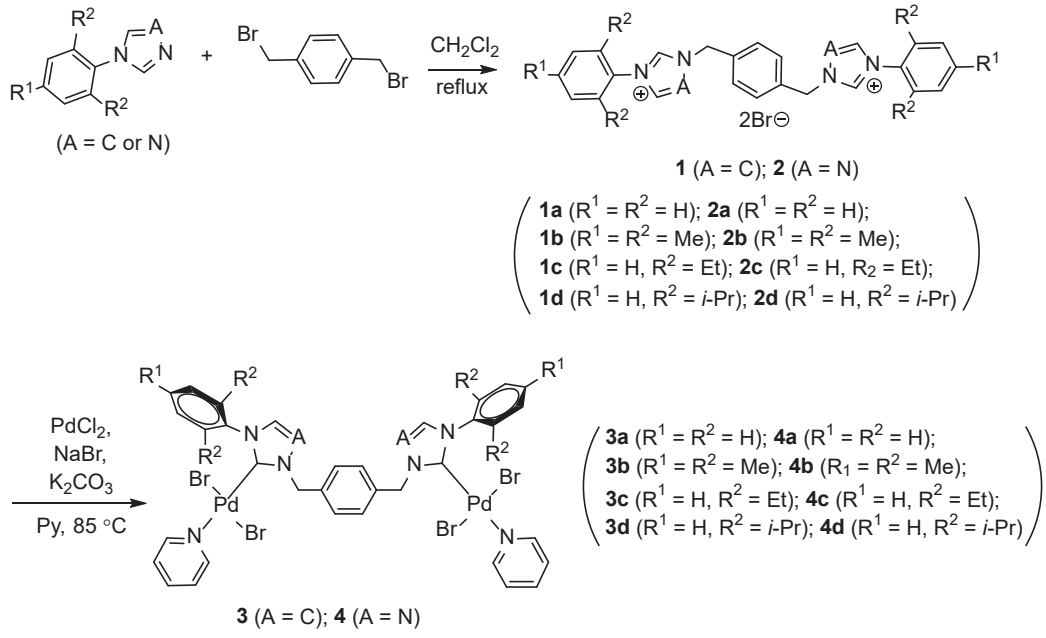



**Scheme 4** Synthesis of di-NHC dipalladium complexes **3** and **4**.

**Table 1** Selected $^{1}$H and $^{13}$C NMR data of bis(imidazolium) salt **3a–d**, bis(triazolium) salt **4a–d**, and bis(NHC) palladium complexes **3a–d** and **4a–d**

| Bis(imidazolium) bromide or bis(triazolium) bromide | $^{1}$H (NC*H*N)[a] | $^{1}$H (imidazole or triazole)[a] | Pd complex | $^{1}$H (imidazole or triazole)[b] | $^{1}$H (methylene of xylene)[b] | $^{13}$C (carbene–Pd)[b] |
|---|---|---|---|---|---|---|
| **1a** | 10.28 | 8.37, 8.09 | **3a** | 7.15, 6.93 | 5.92 | 152.5 |
| **1b** | 9.85 | 8.14, 7.97 | **3b** | 6.93, 6.86 | 6.03 | 152.6 |
| **1c** | 9.84 | 8.16, 8.08 | **3c** | 6.94, 6.93 | 6.04 | 152.5 |
| **1d** | 9.91 | 8.18, 8.13 | **3d** | 6.94, 6.92 | 6.10 | 152.5 |
| **2a** | 11.06 | 9.79 | **4a** | 8.16 | 6.03 | 157.2 |
| **2b** | 10.99 | 9.55 | **4b** | 7.90 | 6.15 | 157.9 |
| **2c** | 11.13 | 9.68 | **4c** | 7.95 | 6.14 | 158.3 |
| **2d** | 11.37 | 9.79 | **4d** | 7.95 | 6.18 | 158.7 |

[a]Chemical shifts in ppm (400 MHz) in DMSO-$d_6$; [b]Chemical shifts in ppm (400 MHz) in $CDCl_3$

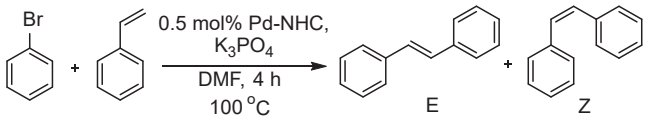
imidazolium bromide **1a**, a singlet at 10.28 ppm and two doublets at 8.37 and 8.09 ppm correspond to the imidazole protons; two multiplets around 7.84–7.81 ppm and 7.68–7.56 ppm correspond to the phenyl protons; and a singlet at 5.57 corresponds to the methylene protons of xylene. The $^{1}$H NMR spectrum of triazolium bromide **2b** shows two singlets at 11.06 and 9.79 ppm corresponding to the protons of triazole, two multiplets around 7.86–7.83 and 7.73–7.60 ppm corresponding to the protons of benzene, and one singlet at 5.74 corresponding to the methylene protons of xylene. In the $^{13}$C NMR spectrum of **1a** and **2b**, all signals corresponding to imidazole (triazole), phenyl and methylene moieties are observed in their expected regions. After metalation, the proton signals of NC*H*N (*ca.* 10 ppm for $H_{2\text{-imidazole}}$ and 11 ppm for $H_{5\text{-triazole}}$) in the starting ligand precursors were absent in the $^{1}$H NMR of palladium complexes due to the formation of Pd–$C_{carbene}$ bonds. Upfield shifts of the signals relative to the imidazolidene or triazolidene protons upon metalation are observed, whilst the proton signals relative to pyridine are observed as well. In addition, $^{13}$C NMR provides direct evidence of the metalation of the ligand, as seen by the signal at *ca.* 152–158 ppm, which is assigned to the $C_{carbene}$–Pd resonance shifted downfield relative to that of its precursor, *i.e.* imidazolium or triazolium bromide (*ca.* 140–146 ppm). Moreover, the NMR spectra of **3** and **4** indicate that the two metal centres are in geometrically equivalent environments as only one resonance for the protons of the methylene of xylylene linkers between the imidazolidenes (or triazolidenes) was observed. In addition, only one characteristic signal of the metalated carbene carbons was observed. Selected $^{1}$H and $^{13}$C NMR data of bis(imidazolium) and bis(triazolium) salts, and their corresponding palladium complexes are listed in Table 1.

Unfortunately, attempts to grow single crystals of these palladium complexes for X-ray diffraction analysis were not successful. The palladium complexes **3** and **4** are air- and moisture-stable in the solid state and even in common organic solvents. They can be stored under air atmosphere for more than 6 months without any noticeable decomposition.

In order to elucidate the influence of different substitution and replacement of C by N in the NHC backbone, the catalytic activity of complexes **3a–d** and **4a–d** in the catalytic arylation of styrene with bromobenzene was tested (Table 2). The results revealed that complex **4d**, with a triazolylidene type of NHC and isopropyl substitution on α-phenyl, performed best in the coupling reaction giving the highest yield of 92% with the best regioselectivity of 22:1 (*E/Z* ratio). Overall, all the complexes have shown good catalytic activity for the arylation of olefins with good regioselectivity. However, there is no clear trend for the activity of these Pd complexes related to their structure. The reason for the good yield and regioselectivity of complex **4d** is not very clear on the current stage, but is most likely due to a combination of electronic and steric effects.

In order to elucidate the influence of the reaction conditions, the arylation catalysed by complex **3a** was studied (Table 3). Of the various bases used, $K_3PO_4$ gave the best yield (77%) with an *E/Z* ratio 20:1, whereas $Cs_2CO_3$ and NaOH gave the highest

**Table 2** Results of the arylation of styrene with bromobenzene




| Entry[a] | Pd–NHC | Yield /%[a] | *E/Z* ratio[b] |
|---|---|---|---|
| 1 | **3a** | 77 | 20:1 |
| 2 | **3b** | 78 | 18:1 |
| 3 | **3c** | 87 | 22:1 |
| 4 | **3d** | 65 | 19:1 |
| 5 | **4a** | 81 | 19:1 |
| 6 | **4b** | 68 | 17:1 |
| 7 | **4c** | 78 | 19:1 |
| 8 | **4d** | 92 | 22:1 |

[a]Reaction conditions: phenylbromide (52 µL, 0.5 mmol), styrene (63 µL, 0.6 mmol), Pd-NHC complex (0.0025 mmol) and $K_3PO_4$ (212 mg, 1 mmol) in DMF (2 mL); [b]Determined by GC using dodecane as the internal standard.

regioselectivity (99:1 for *E/Z* ratio) with the low yield of 18%. Only a trace amount of product was observed with KOH as base (Table 3, entries 1–6). The choice of solvents also has a great effect on the reaction. When the reaction was conducted in THF, dioxane, DMAC and toluene, the product was obtained with an *E/Z* ratio of 99:1, with low yields between 5 and 28% (Table 3, entries 7–10). With DMF as solvent, the yield increased to 77%, however, the regioselectivity decreased to an *E/Z* ratio of 20:1. Upon increasing the reaction temperature from 80 to 100 °C, the yield increased, whereas the regioselectivity decreased dramatically (Table 3, entries 6, 11 and 12). However, no obvious change has been observed when the temperature was higher than 100 °C (Table 3, entries 6 and 13). In addition, the yield increased on extending the reaction time to 4 h without affecting the regioselectivity very much, and the reaction was complete after 4 h (Table 3, entries 6 and 14–16).

In conclusion, we have synthesised a series of different substituted dipalladium di-NHC complexes **3a**–**d**, (based on imidazolylidene), and **4a**–**d**, (based on triazolylidene) with xylylene linkers. Catalytic results for arylation of styrene show that the different substitution and NHC backbone has some effect on the yield and regioselectivity of the product. The complex **4d** with a triazolylidene type of NHC and isopropyl substitution on α-phenyl performed best in the coupling reaction.

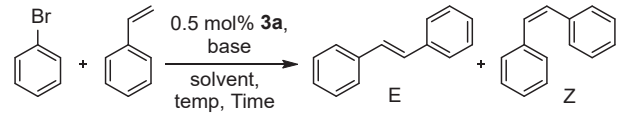
## Experimental

All manipulations were carried out using standard Schlenk techniques. DMF, DMAC and pyridine were distilled over calcium hydride under an argon atmosphere prior to use. THF, dioxane, and toluene were distilled from sodium benzophenone ketyl under an argon atmosphere. Potassium carbonate and tripotassium phosphate were ground to a fine powder prior to use. The corresponding *N*-aryl imidazoles and triazoles were prepared according to the previous method.[16,17] All other chemicals were obtained from common suppliers and used without further purification. IR spectra were recorded on KBr pellets on a FTIR-Tensor 27 spectrometer. Melting points were detected by microscope melting point apparatus. $^1$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. GC-MS was performed on an Agilent 6890-5973N system with electron ionisation (EI) mass spectrometry. Elemental analyses were performed on a EuroVektor Euro EA-300 elemental analyser.

*Synthesis of bisimidazolium bromides and triazolium bromides* (**1** and **2**); *general procedure*

1,4-bis(Bromomethyl)benzene (0.20 g, 0.76 mmol) and the appropriate imidazole or triazole (1.60 mmol) in DCM (3 mL) were refluxed for 12–16 h in a 10 mL Ace pressure tube. The reaction mixture was cooled to room temperature and extracted with water (3 × 5 mL). The aqueous phase was dried *in vacuo* and the crude product crystallised from methanol/acetone (1:4) to give pure product as a white solid.

**Table 3** The survey of reaction conditions




| Entry[a] | Base | Solvent | Temp. / °C | Time / h | Yield /%[a] | *E/Z* ratio[b] |
|---|---|---|---|---|---|---|
| 1 | $K_2CO_3$ | DMF | 100 | 4 | 11 | 99:1 |
| 2 | $Cs_2CO_3$ | DMF | 100 | 4 | 18 | 99:1 |
| 3 | KOH | DMF | 100 | 4 | Trace | - |
| 4 | NaOH | DMF | 100 | 4 | 18 | 99:1 |
| 5 | NaOAc | DMF | 100 | 4 | Trace | - |
| 6 | $K_3PO_4$ | DMF | 100 | 4 | 77 | 20:1 |
| 7 | $K_3PO_4$ | THF | 100 | 4 | 28 | 99:1 |
| 8 | $K_3PO_4$ | Dioxane | 100 | 4 | 5 | 99:1 |
| 9 | $K_3PO_4$ | DMAC | 100 | 4 | 18 | 99:1 |
| 10 | $K_3PO_4$ | Toluene | 100 | 4 | 15 | 99:1 |
| 11 | $K_3PO_4$ | DMF | 80 | 4 | 43 | 51:1 |
| 12 | $K_3PO_4$ | DMF | 90 | 4 | 60 | 34:1 |
| 13 | $K_3PO_4$ | DMF | 110 | 4 | 77 | 20:1 |
| 14 | $K_3PO_4$ | DMF | 100 | 2 | 53 | 21:1 |
| 15 | $K_3PO_4$ | DMF | 100 | 6 | 77 | 20:1 |
| 16 | $K_3PO_4$ | DMF | 100 | 8 | 77 | 20:1 |

[a]Reaction conditions: phenylbromide (52 µL, 0.5 mmol), styrene (63 µL, 0.6 mmol), complex **3** (2.7 mg, 0.0025 mmol) and $K_3PO_4$ (212 mg, 1 mmol) in solvent (2 mL); [b]Determined by GC using dodecane as internal standard.

*3,3'-[1,4-Phenylenebis(methylene)]bis(1-phenyl-1*H*-imidazol-3-ium) dibromide* (**1a**):[18] White solid; yield 91%; m.p. > 300 °C; IR ($\nu_{max}$, cm$^{-1}$) KBr: 3087, 3047, 2947, 1595, 1493, 1373, 1215, 1202, 1087, 1077, 765, 720, 623, 536; $^1$H NMR (400 MHz, DMSO-$d_6$): 10.28 (s, 2H, $H_{2\text{-imidazole}}$), 8.37 (d, $J$ = 1.8 Hz, 2H, $H_{5\text{-imidazole}}$), 8.09 (d, $J$ = 1.8 Hz, 2H, $H_{4\text{-imidazole}}$), 7.84–7.81 (m, 4H, Ph), 7.68–7.56 (m, 10H, Ph), 5.57 (s, 4H, C$H_2$); $^{13}$C NMR (100 MHz, DMSO-$d_6$): 136.1, 135.6, 135.2, 130.6, 130.3, 129.7, 123.7, 122.3, 122.1, 52.3; Anal. calcd for $C_{26}H_{24}Br_2N_4$: C, 56.54; H, 4.38; N, 10.14; found: C, 56.32; H, 4.31; N, 10.25%.

*3,3'-[1,4-Phenylenebis(methylene)]bis(1-mesityl-1*H*-imidazol-3-ium) dibromide* (**1b**): White solid; yield 95%; m.p. > 300 °C; IR ($\nu_{max}$, cm$^{-1}$) KBr: 3155, 3012, 2920, 1608, 1563, 1549, 1493, 1373, 1203, 1069, 1041, 1026, 877, 763, 716, 630, 583, 516; $^1$H NMR (400 MHz, DMSO-$d_6$): 9.85 (s, 2H, $H_{2\text{-imidazole}}$), 8.14 (d, $J$ = 1.8 Hz, 2H, $H_{5\text{-imidazole}}$), 7.97 (d, $J$ = 1.8 Hz, 2H, $H_{4\text{-imidazole}}$), 7.59 (s, 4H, Ph), 7.15 (s, 4H, Ph), 5.62 (s, 4H, C$H_2$), 2.33 (s, 6H, C$H_3$), 2.00 (s, 12H, C$H_3$); $^{13}$C NMR (100 MHz, DMSO-$d_6$): 140.8, 138.3, 135.9, 134.7, 131.6, 129.7, 129.4, 124.8, 123.7, 52.3, 21.1, 17.4; Anal. calcd for $C_{32}H_{36}Br_2N_4$: C, 60.39; H, 5.70; N, 8.80; found: C, 60.16; H, 5.62; N, 8.89%.

*3,3'-[1,4-Phenylenebis(methylene)]bis(1-(2,6-diethylphenyl)-1*H*-imidazol-3-ium) dibromide* (**1c**): White solid; yield 92%; m.p. > 300 °C; IR ($\nu_{max}$, cm$^{-1}$) KBr: 3109, 3023, 2963, 2873, 1617, 1590, 1545, 1463, 1379, 1213, 1177, 1111, 1069, 1057, 861, 811, 757, 709, 669; $^1$H NMR (400 MHz, DMSO-$d_6$): 9.84 (s, 2H, $H_{2\text{-imidazole}}$), 8.16 (d, $J$ = 1.8 Hz, 2H, $H_{5\text{-imidazole}}$), 8.08 (d, $J$ = 1.8 Hz, 2H, $H_{4\text{-imidazole}}$), 7.57–7.37 (m, 10H, Ph), 5.62 (s, 4H, C$H_2$), 2.26 (m, 8H, C$H_2$CH$_3$), 1.03 (t, $J$ = 7.6 Hz, 12H, C$H_3$); $^{13}$C NMR (100 MHz, DMSO-$d_6$): 140.8, 138.4, 136.0, 132.7, 131.6, 129.3, 127.7, 125.5, 123.8, 52.3, 24.0, 15.3; Anal. calcd for $C_{34}H_{40}Br_2N_4$: C, 61.45; H, 6.07; N, 8.43; found: C, 61.68; H, 6.01; N, 8.50%.

*3,3'-[1,4-Phenylenebis(methylene)]bis[1-(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium] dibromide* (**1d**): White solid; yield 89%; m.p. > 300 °C; IR ($\nu_{max}$, cm$^{-1}$) KBr: 3401, 2966, 2871, 1618, 1595, 1560, 1543, 1457, 1378, 1353, 1313, 1179, 1110, 1070, 1025, 877, 765, 714,

699, 629; $^1$H NMR (400 MHz, DMSO-$d_6$): 9.91 (s, 2H, $H_{2\text{-imidazole}}$), 8.18 (d, $J$ = 1.8 Hz, 2H, $H_{5\text{-imidazole}}$), 8.13 (d, $J$ = 1.8 Hz, 2H, $H_{4\text{-imidazole}}$), 7.63–7.45 (m, 10H, Ph), 5.63 (s, 4H, C$H_2$), 2.20 [m, 4H, C$H$(C$H_3$)$_3$], 1.12 (d, $J$ = 3.2 Hz, 12H, C$H_3$), 1.11 (d, $J$ = 3.2 Hz, 12H, C$H_3$); $^{13}$C NMR (100 MHz, DMSO-$d_6$): 145.4, 138.6, 136.0, 132.0, 130.9, 129.2, 125.9, 124.9, 123.9, 52.4, 28.6, 24.3, 24.0; Anal. calcd for $C_{38}H_{48}Br_2N_4$: C, 63.34; H, 6.71; N, 7.77; found: C, 63.55; H, 6.64; N, 7.84%.

*1,1'-[1,4-Phenylenebis(methylene)]bis(4-phenyl-4*H*-1,2,4-triazol-1-ium) dibromide* (**2a**): White solid; yield 87%; m.p. > 300 °C; IR ($\nu_{max}$, cm$^{-1}$) KBr: 3003, 2973, 1593, 1495, 1593, 1373, 1226, 1209, 1185, 1023, 843, 766, 752, 688, 634, 518; $^1$H NMR (400 MHz, DMSO-$d_6$): 11.06 (s, 2H, $H_{5\text{-triazole}}$), 9.79 (s, 2H, $H_{3\text{-triazole}}$), 7.86–7.83 (m, 4H, Ph), 7.73–7.60 (m, 10H, Ph), 5.74 (s, 4H, C$H_2$); $^{13}$C NMR (100 MHz, DMSO-$d_6$): 143.8, 142.5, 134.2, 132.6, 131.0, 130.7, 129.9, 123.0, 55.0; Anal. calcd for $C_{24}H_{22}Br_2N_6$: C, 52.01; H, 4.00; N, 15.16; found: C, 51.86; H, 4.05; N, 15.27%.

*1,1'-[1,4-Phenylenebis(methylene)]bis(4-mesityl-4*H*-1,2,4-triazol-1-ium) dibromide* (**2b**): White solid; yield 88%; m.p. 256–257 °C; IR ($\nu_{max}$, cm$^{-1}$) KBr: 2997, 2751, 1607, 1558, 1522, 1437, 1376, 1193, 1153, 1091, 1036, 983, 860, 733, 680, 581; $^1$H NMR (400 MHz, DMSO-$d_6$): 10.99 (s, 2H, $H_{5\text{-triazole}}$), 9.55 (s, 2H, $H_{3\text{-triazole}}$), 7.62 (s, 4H, Ph), 7.18 (s, 4H, Ph), 5.81 (s, 4H, C$H_2$), 2.34 (s, 6H, C$H_3$), 2.09 (s, 12H, C$H_3$); $^{13}$C NMR (100 MHz, DMSO-$d_6$): 146.2, 144.5, 141.5, 134.8, 134.3, 130.0, 129.9, 128.4, 55.2, 21.1, 17.7; Anal. calcd for $C_{30}H_{34}Br_2N_6$: C, 56.44; H, 5.37; N, 13.16; found: C, 56.61; H, 5.44; N, 13.21%.

*1,1'-[1,4-Phenylenebis(methylene)]bis[4-(2,6-diethylphenyl)-4*H*-1,2,4-triazol-1-ium] dibromide* (**2c**): White solid; yield 85%; m.p. 285–286 °C; IR ($\nu_{max}$, cm$^{-1}$) KBr: 3067, 2971, 2876, 2779, 1589, 1557, 1462, 1379, 1197, 1162, 1110, 1060, 820, 777, 753, 727, 680; $^1$H NMR (400 MHz, DMSO-$d_6$): 11.13 (s, 2H, $H_{5\text{-triazole}}$), 9.68 (s, 2H, $H_{3\text{-triazole}}$), 7.65–7.42 (m, 10H, Ph), 5.86 (s, 4H, C$H_2$), 2.33 (q, $J$ = 7.6 Hz, 8H, C$H_2$CH$_3$), 1.06 (t, $J$ = 7.6 Hz, 12H, C$H_3$); $^{13}$C NMR (100 MHz, DMSO-$d_6$): 146.4, 144.7, 140.9, 134.4, 132.3, 129.9, 129.5, 127.7, 55.3, 23.8, 14.8; Anal. calcd for $C_{32}H_{38}Br_2N_6$: C, 57.67; H, 5.75; N, 12.61; found: C, 57.43; H, 5.81; N, 12.56%.

*1,1'-[1,4-Phenylenebis(methylene)]bis[4-(2,6-diisopropylphenyl)-4*H*-1,2,4-triazol-1-ium] dibromide* (**2d**): White solid; yield 83%; m.p. 265–266 °C; IR ($\nu_{max}$, cm$^{-1}$) KBr: 3067, 2965, 2739, 1554, 1460, 1369, 1358, 1300, 1191, 1088, 1001, 938, 813, 762, 718, 685, 554; $^1$H NMR (400 MHz, DMSO-$d_6$): 11.37 (s, 2H, $H_{5\text{-triazole}}$), 9.79 (s, 2H, $H_{3\text{-triazole}}$), 7.70–7.49 (m, 10H, Ph), 5.90 (s, 4H, C$H_2$), 2.29 [m, 4H, C$H$(C$H_3$)$_3$], 1.15 (d, $J$ = 6.8 Hz, 12H, C$H_3$), 1.11 (d, $J$ = 6.8 Hz, 12H, C$H_3$); $^{13}$C NMR (100 MHz, DMSO-$d_6$): 146.7, 145.6, 144.9, 134.5, 132.7, 129.9, 127.7, 125.2, 55.3, 28.5, 24.08, 24.05; Anal. calcd for $C_{36}H_{46}Br_2N_6$: C, 59.84; H, 6.42; N, 11.63; found: C, 59.61; H, 6.49; N, 11.72%.

*Synthesis of di-NHC dipalladium complexes* (**3** and **4**); *general procedure*

A mixture of bis(imidazolium) bromides or bis(triazolium) bromides (2.0 mmol), $PdCl_2$ (1.069 g, 4.0 mmol), NaBr (1.646 g, 16 mmol) and $K_2CO_3$ (5.528 g, 40 mmol) was added to pyridine (30 mL) in a 50 mL round bottom flask. The reaction mixture was heated at 85 °C for 18 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 pure compound was obtained as yellow solid by recrystallisation from DCM/$Et_2O$.

*Complex* **3a**: Pale yellow solid; yield 70%; IR ($\nu_{max}$, cm$^{-1}$) KBr: 3174, 3142, 3064, 2927, 1602, 1519, 1498, 1445, 1421, 1404, 1352, 1281, 1245, 1069, 958, 762, 719, 690, 644, 551; $^1$H NMR (400 MHz, $CDCl_3$): 8.84 (m, 4H, $H_{\alpha\text{-Py}}$), 8.06 (m, 4H, $H_{\gamma\text{-Py}}$, Ph), 7.72–7.47 (m, 12H, Py, Ph), 7.28–7.25 (m, 4H, Ph), 7.15 (d, $J$ = 2.0 Hz, 2H, $H_{5\text{-imidazole}}$), 6.93 (d, $J$ = 2.0 Hz, 2H, $H_{4\text{-imidazole}}$), 5.92 (s, 4H, C$H_2$); $^{13}$C NMR (100 MHz, $CDCl_3$): 152.5, 137.7, 135.6, 135.2, 130.0, 129.2, 128.8, 126.1, 124.5, 123.5, 122.1, 118.2, 55.1; Anal. calcd for $C_{36}H_{32}Br_4N_6Pd_2$: C, 39.99; H, 2.98; N, 7.77; found: C, 40.23; H, 3.02; N, 7.82%.

*Complex* **3b**: Pale yellow solid; yield 78%; IR ($\nu_{max}$, cm$^{-1}$) KBr: 3174, 3144, 3072, 2919, 1602, 1559, 1518, 1485, 1447, 1419, 1362, 1232, 1214, 1070, 1033, 853, 758, 749, 696, 643, 588, 512; $^1$H NMR (400 MHz, $CDCl_3$): 8.79 (m, 4H, $H_{\alpha\text{-Py}}$), 7.68–7.61 (m, 6H, $H_{\gamma\text{-Py}}$, Ar), 7.21 (m, 4H, $H_{\beta\text{-Py}}$), 7.02 (s, 4H, Ph), 6.93 (d, $J$ = 2.0 Hz, 2H, $H_{5\text{-imidazole}}$), 6.86 (d, $J$ = 2.0 Hz, 2H, $H_{4\text{-imidazole}}$), 6.03 (s, 4H, C$H_2$), 2.37 (s, 6H, C$H_3$), 2.32 (s, 12 H, C$H_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): 152.6, 150.5, 139.2, 137.5, 136.3, 135.8, 134.8, 129.8, 129.3, 125.0, 124.3, 121.5, 55.4, 21.2, 19.9; Anal. calcd for $C_{42}H_{46}Br_4N_6Pd_2$: C, 43.21; H, 3.97; N, 7.20; found: C, 43.06; H, 3.89; N, 7.27%.

*Complex* **3c**: Pale yellow solid; yield 75%; IR ($\nu_{max}$, cm$^{-1}$) KBr: 3149, 3114, 3093, 2963, 2932, 1603, 1466, 1406, 1355, 1287, 1250, 1216, 1180, 1069, 958, 815, 755, 727, 693, 643; $^1$H NMR (400 MHz, $CDCl_3$): 8.74 (m, 4H, $H_{\alpha\text{-Py}}$), 7.67–7.44 (m, 8H, $H_{\gamma\text{-Py}}$, $H_{\beta\text{-Py}}$, Ph), 7.30–7.18 (m, 8H, Ph), 6.94 (m, 4H, $H_{5\text{-imidazole}}$, $H_{4\text{-imidazole}}$), 6.04 (s, 4H, C$H_2$), 2.87 (m, 4H, C$H_2$CH$_3$), 2.51 (m, 4H, C$H_2$CH$_3$), 1.18 (t, $J$ = 7.6 Hz, 12H, C$H_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): 152.5, 151.2, 142.3, 137.5, 135.80, 135.75, 129.92, 129.88, 126.4, 125.5, 124.3, 121.2, 55.4, 25.5, 15.0; Anal. calcd for $C_{44}H_{48}Br_4N_6Pd_2$: C, 44.28; H, 4.05; N, 7.04; found: C, 44.06; H, 4.12; N, 7.12%.

*Complex* **3d**: Pale yellow solid; yield 73%; IR ($\nu_{max}$, cm$^{-1}$) KBr: 3160, 3125, 2967, 2928, 2866, 1518, 1447, 1417, 1363, 1304, 1229, 1218, 1075, 959, 803, 758, 694, 641 cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$): 8.79 (m, 4H, $H_{\alpha\text{-Py}}$), 7.69-7.62 (m, 6H, $H_{\gamma\text{-Py}}$, $H_{\beta\text{-Py}}$, Ph), 7.52-7.20 (m, 10H), 6.94 (d, $J$ = 2.0 Hz, 2H, $H_{5\text{-imidazole}}$), 6.92 (d, $J$ = 2.0 Hz, 2H, $H_{4\text{-imidazole}}$), 6.10 (s, 4H, C$H_2$), 3.05 (m, 4H, C$H_2$CH$_3$), 1.43 (d, $J$ = 6.8 Hz, 12H, C$H_3$), 1.04 (d, $J$ = 6.8 Hz, 12H, C$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): 152.5, 151.4, 147.1, 137.6, 135.7, 134.4, 130.3, 130.0, 126.5, 124.3, 124.1, 120.7, 55.7, 28.6, 26.6, 23.4. Anal. calc. for $C_{48}H_{56}Br_4N_6Pd_2$ (1249.45 g mol$^{-1}$): C, 46.14; H, 4.52; N, 6.73; found: C, 45.06; H, 4.45; N, 6.81%.

*Complex* **4a**: : Light yellow solid; yield 76%; IR ($\nu_{max}$, cm$^{-1}$) KBr: 3137, 3051, 1605, 1531, 1498, 1472, 1445, 1351, 1324, 1259, 1225, 1212, 1174, 1070, 1017, 986, 851, 758, 692, 652, 559; $^1$H NMR (400 MHz, $CDCl_3$): 8.86 (m, 4H, $H_{\alpha\text{-Py}}$), 8.16 (s, 2H, $H_{3\text{-triazole}}$), 7.99–7.55 (m, 16H, $H_{\gamma\text{-Py}}$, $H_{\beta\text{-Py}}$, Ph), 7.29 (m, 4H, Ph), 6.03 (s, 4H, C$H_2$); $^{13}$C NMR (100 MHz, $CDCl_3$): 157.2, 152.6, 143.0, 138.0, 135.9, 134.5, 130.1, 129.9, 129.6, 126.1, 124.6, 56.8; Anal. calcd for $C_{34}H_{30}Br_4N_8Pd_2$: C, 37.70; H, 2.79; N, 10.35; found: C, 37.56; H, 2.82; N, 10.40%.

*Complex* **4b**: : Light yellow solid; yield 82%; IR ($\nu_{max}$, cm$^{-1}$) KBr: 3125, 3026, 2917, 2858, 1603, 1530, 1519, 1466, 1447, 1365, 1312, 1215, 1164, 1066, 1038, 1017, 985, 945, 855, 782, 757, 697, 645, 585; $^1$H NMR (400 MHz, $CDCl_3$): 8.81 (m, 4H, $H_{\alpha\text{-Py}}$), 7.90 (s, 2H, $H_{3\text{-triazole}}$), 7.74 (s, 4H, Ph), 7.68 (m, 2H, $H_{\gamma\text{-Py}}$), 7.28 (m, 4H, $H_{\beta\text{-Py}}$), 7.06 (s, 4H, Ph), 6.15 (s, 4H, C$H_2$), 2.40 (s, 6H, C$H_3$), 2.33 (s, 12H, C$H_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): 157.9, 152.7, 144.9, 140.2, 137.8, 136.1, 134.9, 131.1, 129.8, 129.6, 124.4, 57.3, 21.2, 19.9; Anal. calcd for $C_{40}H_{42}Br_4N_8Pd_2$: C, 41.16; H, 3.63; N, 9.60; found: C, 40.98; H, 3.57; N, 9.68%.

*Complex* **4c**: Light yellow solid; yield 80%; IR ($\nu_{max}$, cm$^{-1}$) KBr: 2970, 2933, 2875, 1602, 1533, 1459, 1447, 1356, 1308, 1216, 1070, 1017, 983, 864, 812, 787, 758, 700; $^1$H NMR (400 MHz, $CDCl_3$): 8.77 (m, 4H, $H_{\alpha\text{-Py}}$), 7.95 (s, 2H, $H_{3\text{-triazole}}$), 7.76 (s, 4H, Ar), 7.66 (m, 2H, $H_{\gamma\text{-Py}}$), 7.52–7.22 (m, 10H, Ph, $H_{\beta\text{-Py}}$), 6.14 (s, 4H, C$H_2$), 2.85 (m, 4H, C$H_2$CH$_3$), 2.46 (m, 4H, C$H_2$CH$_3$), 1.29 (t, $J$ = 7.6 Hz, 12H, C$H_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): 158.3, 152.7, 145.0, 142.1, 137.8, 134.9, 132.2, 130.7, 129.9, 126.6, 124.4, 57.3, 25.3, 14.8; Anal. calcd for $C_{42}H_{46}Br_4N_8Pd_2$: C, 42.20; H, 3.88; N, 9.37; found: C, 42.09; H, 3.92; N, 9.43%.

*Complex* **4d**: : Light yellow solid; yield 72%; IR ($\nu_{max}$, cm$^{-1}$) KBr: 3130, 2965, 2928, 2867, 1605, 1534, 1447, 1383, 1363, 1302, 1216, 1155, 1071, 1016, 983, 803, 785, 757, 694; $^1$H NMR (400 MHz, $CDCl_3$): 8.80 (m, 4H, $H_{\alpha\text{-Py}}$), 7.95 (s, 2H, $H_{3\text{-triazole}}$), 7.78 (s, 4H, Ar), 7.68 (m, 2H, $H_{\gamma\text{-Py}}$), 7.55–7.35 (m, 6H, Ph), 7.26 (m, 4H, $H_{\beta\text{-Py}}$), 6.18 (s, 4H, C$H_2$), 2.96 (m, 4H, C$H$), 1.43 (d, $J$ = 6.4 Hz, 12H, C$H_3$), 1.06 (d, $J$ = 6.8 Hz, 12H, C$H_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): 158.7, 152.7, 147.0, 145.5, 137.8, 134.8, 131.1, 130.7, 130.0, 124.5, 124.5, 57.5, 28.6, 26.4, 23.3; Anal. calcd for $C_{46}H_{54}Br_4N_8Pd_2$: C, 44.15; H, 4.35; N, 8.95; found: C, 44.32; H, 4.39; N, 9.00%.

*Catalytic Heck coupling reaction; general procedure*

A mixture of phenylbromide (52 µL, 0.5 mmol), styrene (63 µL, 0.6 mmol), Pd catalyst (0.0025 mmol), $K_3PO_4$ (212 mg, 1.0 mmol) and DMF (2 mL) were added to a 5 mL vial equipped with a magnetic

stirrer under argon. 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.

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