Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Facile base-free *in situ* generation and palladation of mesoionic and normal *N*-heterocyclic carbenes at ambient conditions

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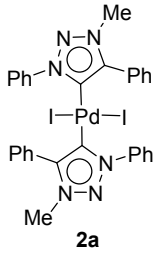
1. **General Experimental details:**

All reactions were performed under nitrogen atmosphere and distilled dichloromethane. $Pd(OAc)_2$ (Aldrich) was used as received. 1,2,3-Triazoliums salts **1a**,[1] **1b**,[2] **1c**,[3] **1d**,[4] **3**[5] and imidazolium bromide **5**[6] were prepared according to published procedures. Infrared (IR) spectra were recorded on a JASCO 4100 FT-IR spectrometer. ^{1}H NMR spectra were measured on Bruker AVANCE 400 MHz and 500 MHz spectrometers. Chemical shifts were reported in ppm from tetramethylsilane as internal standard. ^{13}C NMR spectra were recorded on Bruker 100 MHz and 125 MHz spectrometers with complete proton decoupling. Chemical shifts were reported in ppm using residual solvent peaks as internal standard. High-resolution mass spectra (HRMS) were performed on Micromass ESI Q-TOF micro mass spectrometer equipped with a Harvard apparatus syringe pump. X-ray crystallographic data were collected on a Bruker-AXS Kappa CCD-Diffractometer with graphite-monochromator Mo K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least squares techniques against F2 (SHELXL-97). Hydrogen atoms were inserted from geometry consideration using the HFIX option of the program. For thin layer chromatography (TLC) analysis, E-Merck precoated TLC plates (silica gel 60 F254 grade, 0.25 mm) were used.

2. General procedure for the preparation of $(NHC)_2PdX_2$ (X = I, Br) Complexes:

To a solution of 1,2,3-triazolium iodide (**1a-d, 3**) or imidazolium bromide (**5**) (100-200 mg scale, 1 equivalent) in dichloromethane (20 mL) under N_2 atmosphere was added solid $Pd(OAc)_2$ (0.6 equivalent in case of **1a-d** and **5** and 1.2 equivalent in case of **3**) to give a dark brown to black color solution instantaneously (See Figure below). The reaction mixture was stirred at room temperature for 18 to 72 h depending upon the substrate . The reaction was easily monitored by observing the change of color from the dark brown/black to dark orange/yellow. The reaction mixture was filtered through a cotton plug and solvent was evaporated under reduced pressure in a rotary evaporator. The crude product obtained was further purified by crystallization.

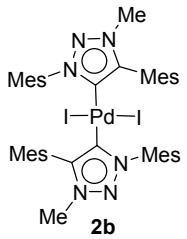
Figure 1. Color of the reaction mixture at the start of the reaction (left) and at the end of the reaction (right).



2a

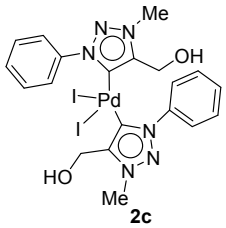
Synthesis of complex 2a: From salt **1a** (100 mg, 0.28 mmol) and $Pd(OAc)_2$ (36 mg, 0.165 mmol) complex **2a** (113 mg, 99%) was obtained as a mixture of *syn* and *anti* isomers (2:3 ratio, by ^1H NMR) after 36 h. Recrystallization from a mixture of CH_2Cl_2 and methanol gave dark yellow crystals, mp 260 ^oC, ^1H NMR (400 MHz, $CDCl_3$) δ 8.12-8.14 (m, 2H), 8.06-8.08 (m,

2H), 7.70-7.72 (m, 2H), 7.66-7.68 (m, 2H), 7.53-7.57 (m, 1H), 7.40-7.50 (m, 5H), 7.33-7.37 (m, 2H), 7.24-7.28 (m, 1H), 7.12-7.16 (m, 3H), 3.88 (s, 3H, Me), 3.86 (s,3H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.0, 37.1, 125.0, 125.6, 128.0, 128.3, 128.6, 128.8, 128.9, 129.0, 129.0, 129.1, 129.3, 130.6, 130.9, 139.9, 140.1, 145.3, 155.3, 155.6; IR (KBr, cm^{-1}): 3438, 2924, 2850, 2368, 2340, 1494, 1323, 1263, 1075, 1019, 764, 683. ESI-MS: m/z 703(M^+-127, loss of I) with isotope peaks in the expected ratios; HRMS: *m/z* calcd for $C_{30}H_{26}N_6IPd$ 703.0298, found 703.0291.



2b

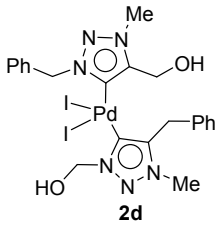
Synthesis of complex 2b: From salt **1b** (100 mg, 0.22mmol) and $Pd(OAc)_2$ (30 mg, 0.133 mmol) complex 2b (101 mg, 90%) was obtained as a mixture of *syn* and *anti* isomers (1:1 by ^{1}H NMR) after stirring for 3d. Mp 155-160 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 4H), 7.09 (s, 4H), 4.87 (s, 3H), 4.46 (s, 3H), 2.40 (s, 6H), 2.38 (s, 6H), 2.19 (s, 12H), 2.17 (s, 12H,); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 19.6, 20.8, 21.4, 21.5, 40.9, 53.3, 116.6, 129.1, 129.7, 130.2, 135.0, 137.2, 138.5, 142.1, 143.3, 143.5, 169.1; IR (KBr, cm^{-1}): 3441, 2924, 2361, 2340, 1620, 1456, 1382, 1218, 1036.



2c

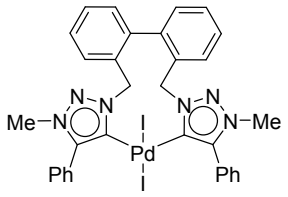
Synthesis of complex 2c: From salt **1c** (200 mg, 0.63 mmol) and $Pd(OAc)_2$ (84 mg, 0.38 mmol) complex **2c** (225 mg, 97%) was obtained as a yellow solid after stirring for 48 h. Recrystallization from a mixture of CH_2Cl_2 and methanol gave orange crystals, mp 230-235 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, 2H, J = 8 Hz), 8.06 (d, 2H, J = 8 Hz), 7.72 (d, 1H, J = 8 Hz), 7.42-7.61 (m, 10H), 5.1 (s, 2H), 4.9 (s, 2H), 4.178 (s, 3H), 4.17 (s, 3H), 2.40 (s, broad, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.5, 55.3, 55.7, 124.4, 124.8, 125.0, 128.8, 129.1, 129.3, 129.6, 130.0, 130.2, 139.6, 140.0, 144.3, 144.5, 144.5, 156.4. IR (KBr, cm^{-1}): 3438, 2920, 2850, 2361,

1655, 1592, 1498, 1340, 1162, 1008; ESI-MS: m/z 611 (M^+-127, loss of I) with isotope peaks in the expected ratios; HRMS: *m/z* calcd for $C_{20}H_{22}N_6O_2IPd$ 610.9884, found 610.9870.



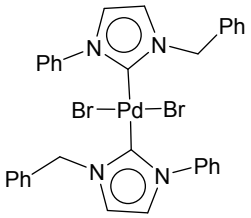
2d

Synthesis of complex 2d: From salt **1d** (100 mg, 0.3 mmol) and $Pd(OAc)_2$ (40 mg, 0.181 mmol) complex **2d** (113 mg, 98%) was obtained after stirring for 48 h as a light brown solid, mp 240 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37-7.57 (m, 10H), 5.9 and 5.7 (s, 4H), 4.96 and 4.78 (s, 4H), 4.01 (s, 6H); ^{13}C NMR (100 MHz, CDCl3) δ 36.3, 36.4, 55.1, 55.3, 58.6, 58.8, 128.4, 128.5, 128.6, 128.7, 129.0, 129.3,134.3, 144.2, 144.3, 156.2, 156.3; IR (KBr, cm^{-1}): 3419, 2954, 2851, 2360, 1653, 1559, 1452, 1329, 1076, 837; ESI-MS: m/z 639 (M^+-127, loss of I) with isotope peaks in the expected ratios; HRMS: *m/z* calcd for $C_{22}H_{26}N_6O_2IPd$ 639.0197, found 639.0198.



4

Synthesis of complex 4: From salt **3** (100 mg, 0.132 mmol) and $Pd(OAc)_2$ (32 mg, 0.145 mmol) complex **5** (111 mg, 99%) as yellow solid after stirring for 14 h, 99%. Crystallization from a mixture of CH_2Cl_2 and acetonitrile gave yellow crystals, mp: 240-245 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, 4H, J = 8 Hz), 7.33-7.44 (m, 12H), 7.24-7.26 (m, 2H), 6.39 (d, 2H, J = 12 Hz), 5.54 (d, 2H, J = 12 Hz), 4.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.2, 55.7, 127.8, 128.1, 128.4, 128.5, 129.0, 129.9, 130.1, 131.4, 133.0, 139.6, 145.9, 157.3; IR (KBr, cm^{-1}): 3057, 2924, 2853, 1473, 1442, 1316, 1155, 1071, 1015, 841, 770; ESI-MS: m/z 729 (M^+) with isotope peaks in the expected ratios, HRMS: *m/z* calcd for $C_{32}H_{28}N_6IPd$ 729.0455, found 729.0425.



6

Synthesis of complex 6: From dibromide salt **5** (140 mg, 0.44 mmol) and $Pd(OAc)_2$ (59 mg, 0.26 mmol) complex 6 (155 mg, 96%) was obtained as a dark yellow solid after 18h. Crystallization in acetonitrile gave rod shaped yellow crystals; mp 250-255 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.99-8.01 (m, 4H), 7.49-7.52 (m, 4H), 7.37-7.42 (m, 6H), 7.18-7.20 (m, 6H), 7.09 (d, 2H, J = 2 Hz), 6.76 (d, 2H, J = 2 Hz), 5.55 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.8, 120.9, 122.4, 125.5, 125.8, 128.1, 128.4, 128.9, 129.0, 129.0, 129.1, 129.4, 136.0, 140.2, 170.0. IR (KBr, cm^{-1}): 3455, 2962, 2930, 2354, 1599, 1456, 1103, 760; ESI-MS: m/z 655 (M^+-Br) with isotope peaks in the expected ratios; HRMS: *m/z* calcd for $C_{32}H_{28}N_4Br^{81}Pd$ 655.0689, found 655.0672.

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