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Highly modular access to functionalised metal-carbenes via post-modifications of a single bromoalkyl-substituted NHC Pd(II) complex

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Experimental procedures, spectroscopic data, and crystallographic analyses

General Considerations. If not noted otherwise, all manipulations were carried out without taking precautions to exclude air and moisture. All solvents and chemicals were used as received without further purification if not mentioned otherwise. Salt **A** was synthesised according to a literature procedure.[S1] ^{1}H and ^{13}C, NMR spectra were recorded on a Bruker ACF 300 and Bruker AMX 500 spectrometer and the chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (^{1}H, ^{13}C). Mass spectra were measured using a Finnigan MAT LCQ (ESI) spectrometer. Infrared spectra were recorded as KBr pellets with a Varian 3100 FT-IR spectrometer. Elemental analyses were performed on an Elementar Vario Micro Cube elemental analyzer at the Department of Chemistry, National University of Singapore. X-Ray data were collected with a Bruker AXS SMART APEX diffractometer, using Mo-Kα radiation at 223(2)K (for **1**, **2**) or at 100(2)K (for **7**·$CHCl_3$, **9**·$CHCl_3$ and **11**·$2CHCl_3$) with a SMART suite of Programs.[S2] Data were processed and corrected for Lorentz and polarisation effects with SAINT,[S3] and for absorption effect with SADABS.[S4] Structural solution and refinement were carried out with the SHELXTL suite of pograms.[S5] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light,

non-hydrogen atoms. All hydrogen atoms were put at calculated positions. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. A summary of the most important crystallographic data is given in Table 1.

di-*μ*-bromo-bis[1-benzyl-3-(3-acetatopropyl)benzimidazolin-2-ylidene]dibromo-dipalladium(II) (1)

Salt **A** (820 mg, 2 mmol), $Pd(OAc)_2$ (449 mg, 2 mmol) and NaBr (823 mg, 8 mmol) were mixed in DMSO (10 mL) and stirred at 90 °C for 24 h. The solvent of the mixture was removed by vacuum distillation, and DCM (50 mL) was added. The suspension was filtered over Celite and the filtrate was concentrated to 2 mL, which was subjected to column chromatography using a mixture of ethyl acetate and hexane as eluent, giving the product as red brown solid (437 mg, 0.38 mmol, 38%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (ps–d, 4 H, Ar–H), 7.42–7.30 (m, 10 H, Ar–H), 7.15 (t, 2 H, Ar–H), 7.08 (ps–d, 2 H, Ar–H), 6.19 (s, 4 H, NCH_2Ph), 5.00 (t, 4 H, NCH_2), 4.26 (t, 4 H, CH_2OCOCH_3), 2.63 (m, 4 H, $CH_2CH_2CH_2$), 2.10 (s, 6 H, $COCH_3$). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$): δ 171.6 (s, CO), 160.6 (s, $C_{carbene}$), 135.4, 134.9, 134.8, 129.7, 129.1, 128.6, 124.5 (2 ×), 112.6, 110.0 (s, Ar–C), 62.2 (s, CH_2OCOCH_3), 54.4 (s, NCH_2Ph), 46.5 (s, NCH_2), 29.3 (s, CH_2OCOCH_3), 21.7 (s, $CH_2CH_2CH_2$). IR (KBr pellet) $\tilde{\nu}$ = 1738 cm^{-1} (s, C=O). Anal. Calc for $C_{38}H_{40}Br_4N_4Pd_2$: C, 39.71; H, 3.51; N, 4.88. Found: C, 40.00; H, 3.45; N, 4.89. MS (ESI): *m/z* = 682 $[M/2 + Pd + H]^+$.

di-*μ*-bromo-bis[1-benzyl-3-(3-bromopropyl)benzimidazolin-2-ylidene]dibromo-dipalladium(II) (2)

A mixture of Ag_2O (232 mg, 1 mmol) and salt **A** (820 mg, 2 mmol) was suspended in CH_2Cl_2 (30 mL) and stirred at ambient temperature for 3 h shielded from light. The resulting mixture was filtered into a solution of $[PdBr_2(CH_3CN)_2]$, which in turn was prepared in situ by heating $PdBr_2$ (533 mg, 2 mmol) in CH_3CN (50 mL) at 80 °C for 6 h. The reaction mixture was stirred for 20 h and filtered through a sintered funnel. The

solvent of the filtrate was removed under vacuum to give a red brown residue, which was suspended and stirred in Et_2O (100 mL) overnight. The resulting suspension was filtered through a sintered funnel and washed with Et_2O (10 mL × 3). Drying the residue in vacuo afforded the product as red brown powder (1.0 g, 0.86 mmol, 86%). ^{1}H NMR (500 MHz, d_6–DMSO): δ 7.77 (d, 2 H, Ar–H), 7.60 (d, 4 H, Ar–H), 7.38–7.29 (m, 8 H, Ar–H), 7.24 (m, 4 H, Ar–H), 6.07 (s, 4 H, NCH_2Ph), 4.94 (t, 4 H, NCH_2), 3.76 (t, 4 H, CH_2Br), 2.69 (m, 4 H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (125.77 MHz, d_6–DMSO): δ 135.0, 134.1, 133.3, 128.5, 128.0 (2 ×), 123.5, 123.4, 111.6, 110.9 (s, Ar–C), 52.2 (s, NCH_2Ph). 46.6 (s, NCH_2), 31.7 (s, CH_2Br), 31.5 (s, $CH_2CH_2CH_2$), the $C_{carbene}$ signal could not be detected. Anal. Calc for $C_{34}H_{34}Br_6N_4Pd_2$: C, 34.29; H, 2.88; N, 4.70. Found: C, 34.63; H, 2.87; N, 4.64. MS (ESI): *m/z* = 329 $[L + H]^+$.

***trans*-Dibromo(acetonitrile)[1-benzyl-3-(3-bromopropyl)benzimidazolin-2-ylidene]palladium(II) (3)**

A suspension of complex **2** (120 mg, 0.1 mmol) in CH_3CN (20 mL) was stirred at 80 °C overnight. The reaction mixture was filtered over Celite and removal of the solvent from the filtrate in vacuo afforded the product as a yellow powder (57 mg, 0.09 mmol, 90%). ^{1}H NMR (300 MHz, CD_3CN): δ 7.61 (d, 1 H, Ar–H), 7.54–7.51 (m, 2 H, Ar–H), 7.34–7.30 (m, 4 H, Ar–H), 7.20–7.14 (m, 2 H, Ar–H), 6.06 (s, 2 H, NCH_2Ph), 4.93 (t, 2 H, NCH_2), 3.65 (t, 2 H, CH_2Br), 2.76 (m, 2 H, $CH_2CH_2CH_2$), 1.95 (s, $NCCH_3$, correct integration was not obtained due to ligand exchange with the solvent). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_3CN): δ 161.8 (s, $C_{carbene}$), 136.0, 135.5, 134.7, 129.5, 129.05 (2 ×), 124.6, 124.5 (s, Ar–C), 118.3 (s, CN), 112.5, 111.7 (s, Ar–C), 53.8 (s, NCH_2Ph), 47.8 (s, NCH_2), 32.8 (s, CH_2Br), 31.8 (s, $CH_2CH_2CH_2$). Anal. Calc for $C_{19}H_{20}Br_3N_3Pd$: C, 35.85; H, 3.17; N, 6.60. Found: C, 35.78; H, 2.98; N, 6.63. MS (ESI): *m/z* = 558 $[M – Br]^+$.

trans-Dibromo[1-benzyl-3-(3-bromopropyl)benzimidazolin-2-ylidene](pyridine)-palladium(II) (4)

Pyridine (88.6 μL, 1.1 mmol) was added to the suspension of complex **2** (596 mg, 0.5 mmol) in DCM (25 mL) and stirred at ambient temperature for 2 h. The solvent was removed under reduced pressure, and the residue was washed with diethyl ether to give a yellow solid product (277 mg, 0.4 mmol, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.05 (d, 2 H, py–H), 7.76 (t, 1 H, py–H), 7.58 (ps–d, 2 H, py–H), 7.54 (d, 1 H, Ar–H), 7.38–7.30 (m, 5 H, Ar–H), 7.25 (t, 1 H, Ar–H), 7.11 (t, 1 H, Ar–H), 7.05 (ps–d, 1 H, Ar–H), 6.17 (s, 2 H, NCH_2Ph), 5.07 (t, 2 H, NCH_2), 3.67 (t, 2 H, CH_2Br), 2.93 (m, 2 H, $CH_2CH_2CH_2$). $^{13}C\{^{1}H\}$ NMR (125.77 MHz, $CDCl_3$): δ 164.6 (s, $C_{carbene}$), 153.3, 138.7, 135.8, 135.5, 135.0, 129.5, 128.9, 128.8, 125.3, 124.0, 123.9, 112.3, 111.0 (s, Ar–C), 54.5 (s, NCH_2Ph), 47.4 (s, NCH_2), 32.7 (s, CH_2Br), 31.8 (s, $CH_2CH_2CH_2$). Anal. Calc for $C_{22}H_{22}Br_3N_3Pd$: C, 39.17; H, 3.29; N, 6.23. Found: C, 39.60; H, 3.43; N, 6.53. MS (ESI): m/z = 594 $[M - Br]^+$.

trans-Dibromo[1-benzyl-3-(3-acetatopropyl)benzimidazolin-2-ylidene](pyridine) palladium(II) (5)

Potassium acetate (25 mg, 0.25 mmol) was added to the solution of complex **4** (67 mg, 0.1 mmol) in acetonitrile (20 mL) and refluxed overnight. After removal of the solvent, 30 mL of DCM was added. The resulting suspension was filtered over Celite and the solvent removed under reduced pressure, giving the product as red brown powder (588 mg, 0.9 mmol, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.04 (dd, 2 H, py–H), 7.76 (t, 1 H, py–H), 7.57 (ps–d, 2 H, py–H), 7.40 (d, 1 H, Ar–H), 7.38–7.31 (m, 5 H, Ar–H), 7.23 (t, 1 H, Ar–H), 7.10 (t, 1 H, Ar–H), 7.04 (ps–d, 1 H, Ar–H), 6.16 (s, 2 H, NCH_2Ph), 4.99 (t, 2 H, NCH_2), 4.31 (t, 2 H, CH_2OCOCH_3), 2.68 (m, 2 H, $CH_2CH_2CH_2$), 2.09 (s, 3 H, CH_3). $^{13}C\{^{1}H\}$ NMR (75.48 MHz, $CDCl_3$): δ 171.5 (s, C=O), 164.3 (s, $C_{carbene}$), 153.2, 138.7, 135.6, 135.4, 134.9, 129.5, 128.8, 128.7, 125.2, 123.9. 123.8, 112.3, 110.7 (s, Ar–C), 62.5 (s, CH_2OCOCH_3), 54.3 (s, NCH_2Ph). 46.3 (s, NCH_2), 29.0 (s, CH_2OCOCH_3), 21.6 (s, $CH_2CH_2CH_2$). Anal. Calc for

$C_{24}H_{25}Br_2N_3O_2Pd$: C, 44.10; H, 3.85; N, 6.43. Found: C, 44.58; H, 3.49; N, 6.30. MS (ESI): *m/z* = 573 $[M - Br]^+$.

trans-Dibromo[1-benzyl-3-(3-azidopropyl)benzimidazolin-2-ylidene](pyridine) palladium(II) (6)

Sodium azide (85 mg, 0.13 mmol) and complex **4** (67 mg, 0.1 mmol) were suspended in acetonitrile (20 mL) and stirred overnight. The solvent of the mixture was removed under vacuum, and H_2O (3 × 5 mL) was added to wash off the excess NaN_3. 30 mL of DCM, and $NaSO_4$ were added to the residue. The resulting mixture was filtered over Celite, and the solvent of the filtrate was evaporated to afford the product as yellow powder, Yield: 64 mg (0.1mmol, >99%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.04 (d, 2 H, py–H), 7.76 (t, 1 H, py–H), 7.58 (ps–d, 2 H, py–H), 7.46 (d, 1 H, Ar–H), 7.38–7.30 (m, 5 H, Ar–H), 7.25 (t, 1 H, Ar–H), 7.11 (t, 1 H, Ar–H), 7.05 (ps–d, 1 H, Ar–H), 6.17 (s, 2 H, NCH_2Ph), 4.98 (t, 2 H, NCH_2), 3.60 (t, 2 H, CH_2N_3), 2.61 (m, 2 H, $CH_2CH_2CH_2$). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$): δ 164.4 (s, $C_{carbene}$), 153.2, 138.7, 135.7, 135.4, 134.9, 129.5, 128.9, 128.7, 125.3, 124.0. 123.9, 112.3, 110.8 (s, Ar–C), 54.4 (s, NCH_2Ph), 49.3 (s, NCH_2), 46.2 (s, CH_2N_3), 29.2 (s, $CH_2CH_2CH_2$). Anal. Calc for $C_{22}H_{22}Br_2N_6Pd$: C, 41.50; H, 3.48; N, 13.20. Found: C, 41.96 ;H, 3.96; N, 13.49. MS (ESI): *m/z* = 557 $[M - Br]^+$.

***trans*-Diiodo[1-benzyl-3-(3-iodopropyl)benzimidazolin-2-ylidene](pyridine)palladium(II) (7)**

NaI (1.5 g, 10 mmol) was added into the solution of complex **4** (675 mg, 1 mmol) in acetone and stirred at ambient temperature for 4 h. The solvent of the suspension was removed in vacuo, and 50 mL of DCM was added. The resulting red orange suspension was filtered over Celite, and the solvent of the filtrate was removed under reduced pressure to give the product as an orange powder. Slow evaporation of a concentrated chloroform/hexane solution of the product yielded transparent prisms suitable for X-ray diffraction studies. Yield: 775 mg (0.95 mmol, 95%). ^{1}H NMR (500

MHz, $CDCl_3$): δ 9.07 (d, 2 H, py–H), 7.74 (t, 1 H, py–H), 7.58 (ps–d, 2 H, py–H), 7.52 (d, 1 H, Ar–H), 7.38–7.31 (m, 5 H, Ar–H), 7.23 (t, 1 H, Ar–H), 7.08 (t, 1 H, Ar–H), 6.95 (ps–d, 1 H, Ar–H), 6.05 (s, 2 H, NCH_2Ph), 4.94 (t, 2 H, NCH_2), 3.43 (t, 2 H, CH_2I), 2.86 (m, 2 H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$): δ 163.3 (s, $C_{carbene}$), 154.6, 138.4, 135.9, 135.3, 135.2, 129.4, 129.0, 128.9, 125.2, 123.8. 123.7, 112.4, 111.0 (s, Ar–C), 55.4 (s, NCH_2Ph), 50.3 (s, NCH_2), 32.3 (s, CH_2I), 4.0 (s, $CH_2CH_2CH_2$). Anal. Calc for $C_{22}H_{22}I_3N_3Pd$: C, 32.40; H, 2.72; N, 5.15. Found: C, 32.84; H, 2.98; N, 5.69. MS (ESI): m/z = 687 $[M - I]^+$.

trans-Dibromo[1-benzyl-3-(3-azidopropyl)benzimidazolin-2-ylidene](pyridine) palladium(II) (8)

Sodium azide (13 mg, 0.2 mmol) and complex **7** (159 mg, 0.195 mmol) were stirred in CH_3CN (20 mL) overnight at 90 °C. The suspension was filtered over Celite, and the solvent of the filtrate was removed under reduced pressure, affording a red-orange solid. After washing with H_2O (3 × 5 mL), 50 mL of DCM was added. The resulting suspension was filtered over Celite, and the filtrate was dried in vacuo giving the product as a red-orange solid (144 mg, 0.20 mmol, 98%). ^1H NMR (500 MHz, $CDCl_3$): δ 9.05 (d, 2 H, py–H), 7.73 (t, 1 H, py–H), 7.59 (ps–d, 2 H, py–H), 7.46 (d, 1 H, Ar–H), 7.39–7.31 (m, 5 H, Ar–H), 7.24 (t, 1 H, Ar–H), 7.08 (t, 1 H, Ar–H), 6.96 (ps–d, 1 H, Ar–H), 6.06 (s, 2 H, NCH_2Ph), 4.90 (t, 2 H, NCH_2), 3.60 (t, 2 H, CH_2N_3), 2.63 (m, 2 H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$): δ 163.0 (s, $C_{carbene}$), 154.4, 138.4, 135.8, 135.2, 135.1, 129.4, 128.9, 128.8, 125.2, 123.8. 123.7, 112.4, 110.7 (s, Ar–C), 55.3 (s, NCH_2Ph). 49.4 (s, NCH_2), 47.0 (s, CH_2N_3), 28.5 (s, $CH_2CH_2CH_2$). Anal. Calc for $C_{22}H_{22}I_2N_6Pd$: C, 36.16; H, 3.03; N, 11.50. Found: C, 36.32; H, 2.94; N 10.13. MS (ESI): m/z = 249 $[L - N_3]^+$.

trans-Diiodo[1-benzyl-3-(3-thiocyanatopropyl)benzimidazolin-2-ylidene](pyridine)palladium(II) (9)

Potassium thiocyanate (19 mg, 0.2 mmol) and complex **7** (163 mg, 0.2 mmol) were

mixed in CH_3CN (20 mL) and stirred overnight under reflux. The solvent of the suspension was removed in vacuo, and 50 mL of DCM was added. The resulting suspension was filtered over Celite, and the solvent of the filtrate was removed under reduced pressure to give the product as red powder (135 mg, 0.18 mmol, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.04 (d, 2 H, py–H), 7.76 (t, 1 H, py–H), 7.56 (ps–d, 2 H, py–H), 7.45 (d, 1 H, Ar–H), 7.38–7.34 (m, 5 H, Ar–H), 7.26 (t, 1 H, Ar–H), 7.11 (t, 1H, Ar–H), 6.98 (d, 1 H, Ar–H), 6.06 (s, 2 H, NCH_2Ph), 5.01 (t, 2 H, NCH_2), 3.28 (t, 2 H, CH_2SCN), 2.89 (m, 2 H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$): 163.9 (s, $C_{carbene}$), δ 154.6, 138.5, 135.7, 135.5, 135.1, 129.5, 129.0 (2 ×), 125.3, 124.1. 124.0, 112.7 (s, Ar–C), 112.4 (s, SCN), 110.7 (s, Ar–C), 55.6 (s, NCH_2Ph). 47.7 (s, NCH_2), 32.5 (s, CH_2SCN), 28.9 (s, $CH_2CH_2CH_2$). Anal. Calc. For $C_{23}H_{22}I_2N_4PdS$: C, 36.99; H, 2.97; N, 7.50. Found: C, 36.77; H, 3.26; N, 7.96. MS (ESI): *m/z* = 719 [M – SCN + MeOH]$^+$.

trans-Diiodo[1-benzyl-3-(3-thioacetatopropyl)benzimidazolin-2-ylidene](pyridine)palladium(II) (10)

Potassium thioacetate (24 mg, 0.21 mmol) and complex **7** (163 mg, 0.2 mmol) were mixed in CH_3CN (20 mL) and stirred under reflux overnight. The solvent of the suspension was removed in vacuo, and 50 mL of DCM was added. The resulting suspension was filtered over Celite. Drying of the filtrate under reduced pressure gave the product as a brown powder (99 mg, 0.13 mmol, 65%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.06 (d, 2 H, py–H), 7.74 (t, 1 H, py–H), 7.56 (ps–d, 2 H, py–H), 7.48 (d, 1 H, Ar–H), 7.37–7.34 (m, 5 H, Ar–H), 7.22 (t, 1 H, Ar–H), 7.06 (t, 1 H, Ar–H), 6.93 (ps–d, 1 H, Ar–H), 6.03 (s, 2 H, NCH_2Ph), 4.85 (t, 2 H, NCH_2), 3.14 (t, 2 H, CH_2SCOCH_3), 2.62 (m, 2 H, $CH_2CH_2CH_2$), 2.38 (s, 3 H, $SCOCH_3$). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$): δ 196.0 (s, C=O), 162.9 (s, $C_{carbene}$), 154.5, 138.4, 135.7, 135.2 (2 ×), 129.4, 128.9, 128.8, 125.2, 123.7. 123.6, 112.4, 110.8 (s, Ar–C), 55.2 (s, NCH_2Ph). 48.7 (s, NCH_2), 31.4 (s, SCH_2), 28.9 (s, $SCOCH_3$), 27.3 (s, $CH_2CH_2CH_2$). Anal. Calc. for $C_{24}H_{25}I_2N_3OPdS$: C, 37.74; H, 3.30; N, 5.50. Found: C, 37.49; H, 3.28;

N, 5.26. MS (ESI): *m/z* = 763 $[M - I]^+$.

Dinuclear complex 11

Sodium hydroxide (10 mg, 0.25 mmol) in methanol (6 mL) was added to the solution of complex **10** (130 mg, 0.17 mmol) in DCM (10 mL) and stirred overnight. The solvent of the mixture was removed, and DCM (20 mL) was added. The resulting suspension was filtered though Celite, and removal of the solvent of the filtrate gave the product as an orange powder (73 mg, 0.07 mmol, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (ps–d, 3 H, Ar–H), 7.39 (ps–d, 3 H, Ar–H), 7.33 (t, 4 H, Ar–H), 7.30–7.24 (m, 6 H, Ar–H), 7.18 (t, 2 H, Ar–H), 6.37 (d, ^2J(H, H) = 15.8 Hz, 2 H, NC*H*HPh), 6.25 (m, 2 H, NC*H*H), 5.32 (d, ^2J(H, H) = 15.8 Hz, 2 H, NCH*H*Ph), 4.65 (m, 2 H, NCH*H*), 3.10–3.00 (m, 4 H, SCH_2), 2.25 (m, 2 H, CH_2CHHCH_2), 1.72 (m, 2 H, CH_2CHHCH_2). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$): δ 174.8 (s, $C_{carbene}$), 136.0, 135.5, 134.0, 129.5, 128.9, 128.5, 124.3, 124.1, 112.4, 110.7 (s, Ar–C), 54.0 (s, NCH_2Ph). 43.9(s, NCH_2), 27.1 (s, SCH_2), 27.0 (s, $CH_2CH_2CH_2$). Anal. Calc. for $C_{34}H_{34}I_2N_4Pd_2S_2$: C, 39.67; H, 3.33; N, 5.44. Found: C, 40.90; H, 3.47; N, 5.07. MS (ESI): *m/z* = 903 $[M - I]^+$.

References

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S2 SMART *version* 5.628; Brucker AXS Inc., Madison, Wisconsin, USA, 2001.
S3 *SAINT + version 6.22a*; Brucker AXS Inc., Madison, Wisconsin, USA, 2001.
S4 G. W. Sheldrick, *SADABS version 2.10*; University of Göttingen, 2011.
S5 *SHELXTL version 6.14*; Bruker AXS Inc., Madison, Wisconsin, USA, 2000.

Table 1 Selected X-ray crystallographic data for complexes **1**, **3**, **7**, **9**, **11**

	1	**3**	**7**·$CHCl_3$	**9**·$CHCl_3$	**11**·$2CHCl_3$
formula	$C_{38}H_{40}Br_4N_4O_4Pd_2$	$C_{19}H_{20}Br_3N_3Pd$	$C_{22}H_{22}I_3N_3Pd{\cdot}CH_2Cl_2$	$C_{23}H_{22}I_2N_4PdS{\cdot}CHCl_3$	$C_{34}H_{34}I_2N_4Pd_2S_2{\cdot}C_2H_2Cl_6$
fw	1149.18	636.51	934.89	866.07	1268.11
color, habit	orange, plate	yellow, block	orange, block	orange, thin plate	yellow, thin plate
cryst size [mm]	0.28 × 0.14 × 0.06	0.60 × 0.24 × 0.20	0.40 × 0.16 × 0.14	0.44 × 0.20 × 0.10	0.46 × 0.24 × 0.04
temp [K]	223(2)	223(2)	100(2)	100(2)	100(2)
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	*P*2(1)/c	*P*2(1)/n	P–1	P1	*P*2(1)/n
a[Å]	9.0803(8)	7.8905(9)	8.1776(9)	8.339(5)	12.340(5)
b [Å]	21.2409(19)	12.5212(14)	9.2817(11)	8.954(5)	28.317(12)
c [Å]	10.8280(10)	21.373(2)	20.433(2)	11.504(7)	13.650(6)
α [deg]	90.00	90.00	82.449(2)	94.540(11)	90.00
β [deg]	90.902(2)	90.503(3)	88.771(2)	103.912(11)	113.731(9)
γ [deg]	90.00	90.00	66.713(2)	116.140(10)	90.00
V [$Å^3$]	2088.2(3)	2111.5(4)	1411.4(3)	731.4(7)	4366(3)
Z	2	4	2	1	4
D_c [g cm^{-3}]	1.828	2.002	2.200	1.966	1.929
radiation used	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ [mm^{-1}]	4.730	6.564	4.240	3.111	2.732
θ range [deg]	1.92–27.49	1.88–27.47	2.01–27.50	1.87–27.45	1.78–27.50
no. of unique data	14436	14614	18736	9659	29974
max., min. transmn	0.7645, 0.3509	0.4915, 0.1529	0.5883, 0.2818	0.4305, 0.3455	0.8986, 0.3663
final R indices	R_1 = 0.0541,	R_1 = 0.0369	R1 = 0.0275,	R1 = 0.0345,	R_1 = 0.0706,
[$I > 2\sigma(I)$]	wR_2 = 0.1314	wR_2 = 0.0875	wR2 = 0.0661	wR2 = 0.0856	wR_2 = 0.1479
R indices (all data)	R_1 = 0.0823,	R_1 = 0.0512,	R1 = 0.0302,	R1 = 0.0360,	R_1 = 0.1003,
	wR_2 = 0.1432	wR_2 = 0.0927	wR2 = 0.0674	wR2 = 0.0866	wR_2 = 0.1587
goodness-of-fit	1.006	1.014	1.055	1.027	1.127
peak/hole [e $Å^{-3}$]	1.774/–0.771	0.624/–1.047	1.218/–0.825	1.540/–0.931	2.625 /–1.897
Flack parameter	-	-	-	–0.008(19)	-