

Synthesis and structure of Ag(I), Pd(II), Rh(I), Ru(II) and Au(I) NHC-complexes with pendant Lewis acidic boronic ester moiety

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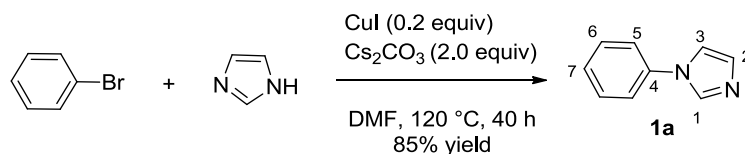
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1. General

All reactions were performed using standard Schlenk techniques under inert atmosphere of dry argon. ^1H NMR spectra were measured on a *Bruker AC 400* (400 MHz) or a *Bruker AC 300* (300 MHz) spectrometer at 298 K (24.95 °C). Data were reported as follows: chemical shifts in ppm referenced to the internal solvent signal (peak at 7.27 ppm in the case of CDCl_3 ; peak at 5.32 in the case of CH_2Cl_2), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qt = quintuplet, dd = double-doublet, m = multiplet, bs = broad), coupling constants (Hz), and assignment. ^{13}C NMR spectra were measured on a *Bruker AC 400* (100 MHz) or a *Bruker AC 300* (75 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the internal solvent signal (peak at 77.2 ppm in the case of CDCl_3 , peak at 53.8 in the case of CH_2Cl_2). High-resolution mass spectra (HRMS) were performed on a *QStar Elite* (Applied Biosystems SCIEX) spectrometer equipped with atmospheric pressure ionization source (API) pneumatically assisted. Samples were ionized by positive electrospray mode as follows: electrospray tension (ISV): 5500 V; opening tension (OR): 50 V; nebulization gas pressure (air): 20 psi. Low resolution mass spectra were recorded on ion trap *Bruker Esquire 6000*, equipped with an electrospray source (methanolic sodium chloride solution). Infrared spectra were recorded on a Vertex 70 FT-IR spectrometer from Bruker on attenuated total reflection mode, wavenumbers are reported in cm^{-1} with the corresponding intensities s (strong), m (medium), w (weak). Melting points (mp) were determined with a Buchi Melting-point B-450 apparatus and were not corrected. Thin layer chromatography (TLCs) were developed on silica *Merck 60F254*. Visualization was achieved under a UVP mineralight UVGL-58 lamp, and by developing the plates with *p*-anisaldehyde reagent or phosphomolybdic acid reagent. The products were purified by flash column chromatography on silica gel 60 (Geduran® Si 60, 0.040-0.063 mm). All reagents were obtained from commercial suppliers unless otherwise stated.

2. Synthesis of compounds

1-phenyl-1*H*-imidazole: 1a



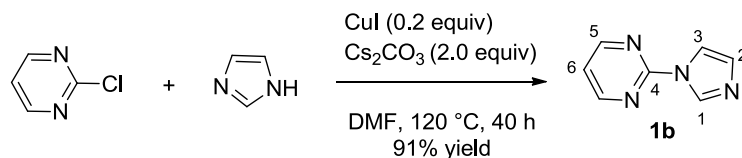
Bromobenzene (3.4 mL, 31.9 mmol, 1.0 equiv), imidazole (3.0 g, 44.6 mmol, 1.4 equiv), Cs₂CO₃ (20.80 g, 63.8.0 mmol, 2.0 equiv) and CuI (1.21 g, 6.4 mmol, 0.2 equiv) in DMF (60 mL) under argon were heated at 120 °C for 40 hours. Afterwards, the suspension was filtered through a plug of Celite[®] twice, then the filtrate concentrated in vacuum. The residue was dissolved in dichloromethane (2 mL) and then purified on a CHROMABOND Flash RS 40 SiOH (40 g) in a Combiflash Companion, eluting at 20 mL/minute (gradient; EP 100% to EP:AcOEt, 10:90 over 30 minutes). The desired fractions were combined and concentrated to give the product (3.90 g, 27.1 mmol, 85%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.23 (bs, 1H, H₂), 7.30 (bs, 1H, H₃), 7.35-7.45 (m, 3H, H₅ and H₇), 7.47-7.52 (m, 2H, H₆), 7.90 (s, 1H, H₁)

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 118.1 (C₃), 121.4 (C₅), 127.3 (C₇), 129.8 (C₆), 130.3 (C₂), 135.5 (C₁), 137.3 (C₄).

ESI MS (MeOH) m/z [M+Na]⁺ calcd for [C₉H₈N₂Na]⁺: 167.0; found: 167.0

2-(1*H*-imidazol-1-yl)pyrimidine: 1b



2-chloropyrimidine (2.28 g, 20.0 mmol, 1.0 equiv), imidazole (1.90 g, 28.0 mmol, 1.4 equiv), Cs₂CO₃ (13.0 g, 40.0 mmol, 2.0 equiv) and CuI (0.76 g, 4.0 mmol, 0.2 equiv) in DMF (40 mL) under argon were heated at 120 °C for 40 hours. Afterwards, the suspension was filtered through a plug of Celite[®] twice, then the filtrate concentrated in vacuum. The residue was dissolved in dichloromethane (2 mL) and then purified on a CHROMABOND Flash RS 40

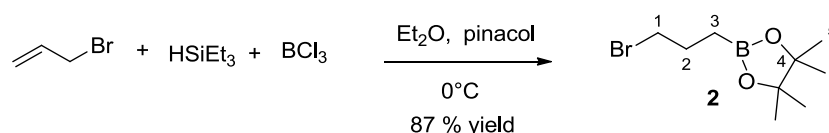
SiOH (40 g) in a Combiflash Companion, eluting at 20 mL/minute (gradient; EP 100% to EP:AcOEt, 10:90 over 30 minutes). The desired fractions were combined and concentrated to give the product (2.67 g, 18.2 mmol, 91%) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.18 (s, 1H, H₂), 7.21 (t, 1H, ³J=4.9 Hz, H₆), 7.91 (s, 1H, H₃), 8.63 (s, 1H, H₁), 8.70 (d, 2H, ³J=4.8 Hz, H₅)

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 116.5 (C₃), 118.8 (C₆), 130.7 (C₂), 136.2 (C₁), 154.8 (C₅), 158.7 (C₄).

ESI MS (MeOH) m/z [M+Na]⁺ calcd for [C₇H₆N₄Na]⁺: 169.1; found: 168.7

2-(3-bromopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: 2



To a mixture of allylbromide (3.87 g, 32.0 mmol, 1.0 equiv) and HSiEt₃ (5.4 mL, 33.92 mmol, 1.06 equiv) under argon at -78 °C was added a solution of BCl₃ (1M in hexane, 36 mL, 35.8 mmol, 1.12 equiv). The mixture was stirred at -78°C over 30 minutes after which it was allowed to warm to room temperature for 1 hour. The reaction was then cooled at 0 °C and pinacol (3.78 g, 32.0 mmol, 1.0 equiv) was added. The resulting mixture was stirred at room temperature for 3 hours. The reaction was quenched with H₂O (40 mL) and extracted twice with Et₂O (20 mL). The organic layers were combined, washed with brine and dried (MgSO₄). The solvent was evaporated and the residue was purified by column chromatography on silica gel using ethyl acetate / petroleum ether (5:95) as eluent to give 6.97 g (28.1 mmol, 87%) of pure product as colourless oil.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 0.92 (t, 2H, ³J=7.7 Hz, H₃), 1.25 (s, 12H, H₅), 1.92-2.07 (m, 2H, H₂), 3.42 (t, 2H, ³J=7.0 Hz, H₁)

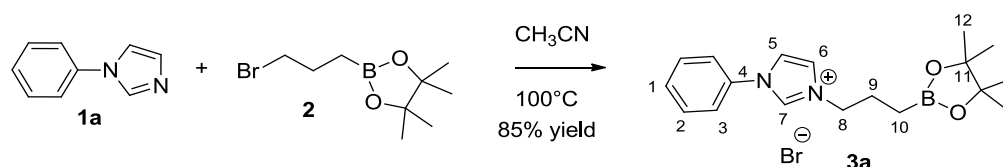
¹³C NMR (100 MHz, CDCl₃) δ (ppm) 7.8 (C_{3(HMQC)}), 24.8 (C₅), 27.5 (C₂), 36.2 (C₁), 83.2 (C₄).

¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 33.7

HRMS (ES, [M+NH₄]⁺) calcd for [C₉H₂₂BBrNO₂]⁺: 266.0924; found: 266.0920

ESI MS (MeOH) m/z $[M+Na]^+$ calcd for $[C_9H_{18}BBrNaO_2]^+$: 273.0; found: 272.8

1-phenyl-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-1*H*-imidazol-3-ium bromide: 3a



To a mixture 1-phenyl-1*H*-imidazole (1.00 g, 6.9 mmol, 1.0 equiv) and 2-(3-bromopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.73 g, 6.9 mmol, 1.0 equiv) under argon was added acetonitrile (5 mL). The resulting solution was stirred at 100 °C under pressure for 24 hours, after which the solvent was evaporated. The residue was washed with diethyl ether (5 mL), then dried under vacuo to give the desired product (2.31 g, 5.9 mmol, 85% yield) as a white solid.

Mp. 182.5°C

¹H NMR (400 MHz, CDCl₃) δ (ppm) 0.84 (t, 2H, ³*J* = 7.7 Hz, H₁₀), 1.22 (s, 12H, H₁₂), 2.03-2.11 (m, 2H, H₉), 4.57 (t, 2H, ³*J* = 7.3 Hz, H₈), 7.46-7.57 (m, 4H, H₁, H₃ and H₅), 7.73-7.81 (m, 3H, H₂ and H₆), 11.00 (s, 1H, H₇).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 7.7 (C₁₀ (HMOC)), 24.8 (C₁₂), 25.1 (C₉), 51.9 (C₈), 83.4 (C₁₁), 120.4 (C₆), 121.8 (C₂), 122.8 (C₅), 130.2 (C₁), 130.5 (C₃), 134.4 (C₄), 136.1 (C₇).

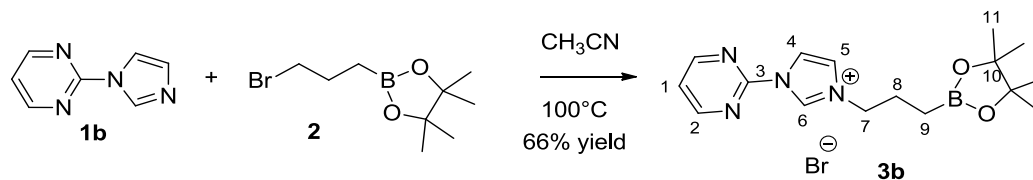
¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 34.0

HRMS (ES, $[M-Br]^+$) calcd for $[C_{18}H_{26}BN_2O_2]^+$: 313.2081; found: 313.2081

ESI MS (MeOH) m/z $[M-Br]^+$ calcd for $[C_{18}H_{26}BN_2O_2]^+$: 313.2 ; found: 313.0

FT-IR (ATR) ν (cm⁻¹) 3322 (w), 3090 (w), 2979 (w), 2948 (w), 2882 (w), 1599 (w), 1569 (w), 1549 (m), 1497 (w), 1454 (w), 1409 (w), 1382 (s), 1361 (s), 1325 (s), 1297 (m), 1278 (m), 1252 (w), 1214 (m), 1184 (w), 1169 (w), 1146 (s), 1110 (w), 1071 (m), 1033 (w), 1004 (w), 970 (m), 958 (w), 917 (w), 886 (w), 849 (m), 760 (m), 745 (s), 732 (m), 688 (s), 637 (m), 613 (w), 582 (w), 550 (w), 522 (m), 463 (w), 392 (w)

1-(pyrimidin-2-yl)-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-1*H*-imidazol-3-ium bromide: 3b



To a mixture of 2-(1*H*-imidazol-1-yl)pyrimidine (1.02 g, 6.9 mmol, 1.0 equiv) and 2-(3-bromopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.74 g, 6.9 mmol, 1.0 equiv) under argon was added acetonitrile (5 mL). The resulting solution was stirred at 100°C under pressure for 24 hours, after which the product precipitate. The solid material was filtered and washed with dry pentane (5 mL), then collected and dried under vacuo to give the desired product (2.5 g, 6.3 mmol, 66% yield) as a white solid.

Mp. 236.4°C

¹H NMR (400 MHz, CDCl₃) δ (ppm) 0.71 (t, 2H, ³*J* = 7.8 Hz, H₉), 1.03 (s, 12H, H₁₁), 2.06-2.14 (m, 2H, H₈), 4.62 (t, 2H, ³*J* = 7.0 Hz, H₇), 7.56 (t, 1H, ³*J* = 4.8 Hz, H₁), 7.97 (dd, 1H, ³*J* = 1.8 Hz, ⁴*J* = 1.8 Hz, H₄), 8.11 (dd, 1H, ³*J* = 1.8 Hz, ⁴*J* = 1.8 Hz, H₅), 8.77 (d, 2H, ³*J* = 5.0 Hz, H₂), 10.72 (bs, 1H, H₆).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 7.7 (C₉ (HMQC)), 24.4 (C₁₁), 24.6 (C₈), 52.0 (C₇), 82.9 (C₁₀), 118.3 (C₅), 122.2 (C₁), 124.1 (C₄), 134.9 (C₆), 151.6 (C₃), 159.5 (C₂).

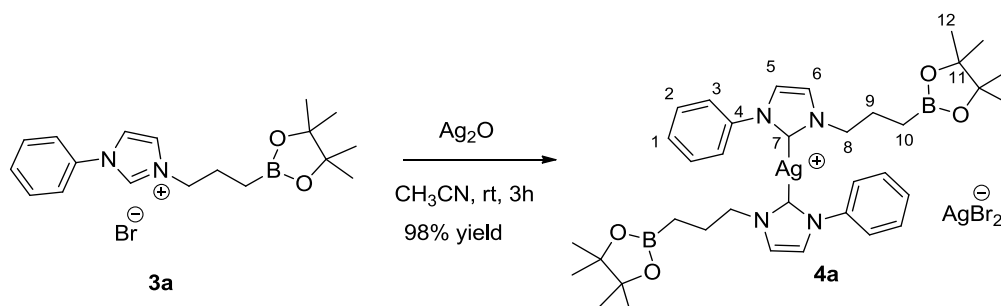
¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 33.3

HRMS (ES, [M-Br]⁺) calcd for [C₁₆H₂₄BN₄O₂]⁺: 315.1986; found: 315.1986

ESI MS (MeOH) *m/z* [M-Br]⁺ calcd for [C₁₆H₂₄BN₄O₂]⁺: 315.2; found: 315.0

FT-IR (ATR) ν (cm⁻¹) 3134 (w), 3100 (w), 3071 (w), 3044 (w), 2982 (w), 2974 (w), 2940 (w), 2899 (w), 1586 (m), 1569 (m), 1533 (w), 1454 (m), 1435 (m), 1404 (m), 1381 (m), 1361 (w), 1357 (w), 1295 (m), 1274 (m), 1243 (w), 1224 (w), 1181 (w), 1167 (w), 1146 (w), 1106 (w), 1097 (w), 1067 (w), 1041 (w), 1028 (w), 1007 (w), 997 (w), 969 (w), 953 (w), 929 (w), 886 (w), 861 (m), 848 (w), 814 (w), 790 (w), 776 (w), 746 (w), 731 (w), 718 (w), 676 (w), 638 (w), 627 (w), 581 (m), 548 (w), 509 (w), 491 (w), 443 (w).

bis(1-phenyl-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-1*H*-imidazol-2(3*H*)-ylidene)silver(I) dibromoargentate: 4a



The imidazolium salt **3a** (400 mg, 1.0 mmol, 1.0 equiv) and Ag_2O (117.8 mg, 0.5 mmol, 0.5 equiv) in dichloromethane (1 mL) were stirred under argon at room temperature for 3 hours, then the solution was filtered through a plug of celite. The solvent was evaporated in vacuo to give 489 mg (0.49 mmol, 98% yield) as a white solid.

Mp. 75.3°C

^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.77 (t, 4H, $^3J = 7.8$ Hz, H_{10}), 1.22 (s, 24H, H_{12}), 1.90-1.98 (m, 4H, H_9), 4.13 (t, 4H, $^3J = 7.3$ Hz, H_8), 7.19 (d, 2H, $^3J = 1.7$ Hz, H_6), 7.27 (d, 2H, 1H, $^3J = 1.7$ Hz, H_5), 7.38-7.51 (m, 10H, H_1 , H_2 and H_3).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 8.8 (C_{10} (HMOC)), 24.7 (C_{12}), 26.0 (C_9), 54.0 (C_8), 83.3 (C_{11}), 121.6 (C_5), 121.7 (C_6), 123.8 (C_2), 128.8 (C_1), 129.7 (C_3), 139.7 (C_4), 179.7 (C_7).

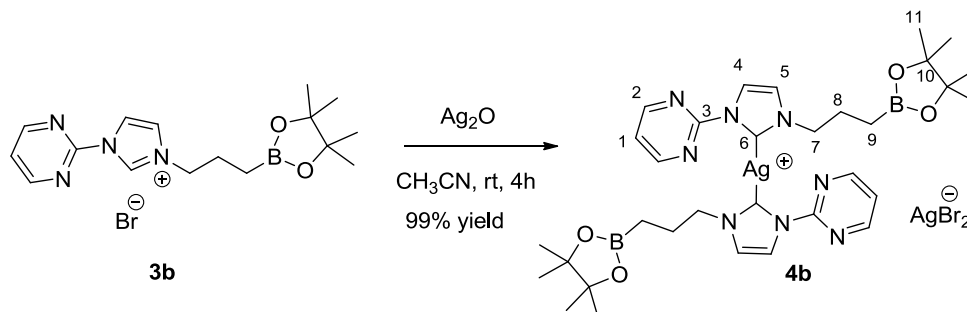
^{11}B NMR (128 MHz, CDCl_3) δ (ppm) 33.2

HRMS (ES, $[\text{M}-\text{AgBr}_2]^+$) calcd for $[\text{C}_{36}\text{H}_{50}\text{AgB}_2\text{N}_4\text{O}_4]^+$: 731.3063; found: 731.3083.

ESI MS (MeOH) m/z for $[\text{M}-\text{AgBr}_2]^+$ calcd for $[\text{C}_{36}\text{H}_{50}\text{AgB}_2\text{N}_4\text{O}_4]^+$: 731.3; found: 731.4

FT-IR (ATR) ν (cm^{-1}) 3090 (w), 2974 (w), 2931 (w), 1596 (w), 1498 (m), 1458 (w), 1414 (w), 1370 (m), 1322 (m), 1272 (w), 1243 (w), 1216 (w), 1165 (w), 1141 (s), 1108 (w), 1073 (w), 1002 (w), 967 (w), 910 (w), 844 (w), 761 (m), 735 (m), 693 (s), 631 (w), 577 (w), 542 (w), 468 (w).

bis(1-(pyrimidin-2-yl)-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-1H-imidazol-2(3H)-ylidene)silver(I) dibromoargentate: 4b



The imidazolium salt **3b** (39.5 mg, 0.1 mmol, 1.0 equiv) and Ag_2O (11.6 mg, 0.05 mmol, 0.5 equiv) in acetonitrile (1 mL) were stirred under argon at room temperature for 3 hours. Et_2O (2 mL) was added, then the precipitate filtered and washed with Et_2O (1 mL). The white solid was collected and dried in vacuo (49.7 mg, 0.49 mmol, 99% yield).

Mp. 189°C

^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.78 (t, 4H, $^3J = 7.8$ Hz, H_9), 1.19 (s, 24H, H_{11}), 1.92-2.04 (m, 4H, H_8), 4.21 (t, 4H, $^3J = 7.3$ Hz, H_7), 7.18 (d, 2H, $^3J = 2.0$ Hz, H_4), 7.38 (t, 2H, $^3J = 4.8$ Hz, H_1), 8.09 (d, 2H, $^3J = 2.0$ Hz, H_5), 8.74 (d, 4H, $^3J = 4.8$ Hz, H_2).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 8.3 (C_9 (HMQC)), 24.7 (C_{11}), 25.7 (C_8), 54.7 (C_7), 83.2 (C_{10}), 119.1 (C_5), 120.5 (C_1), 121.9 (C_4), 155.2 (C_3), 158.6 (C_2), 183.5 (C_6).

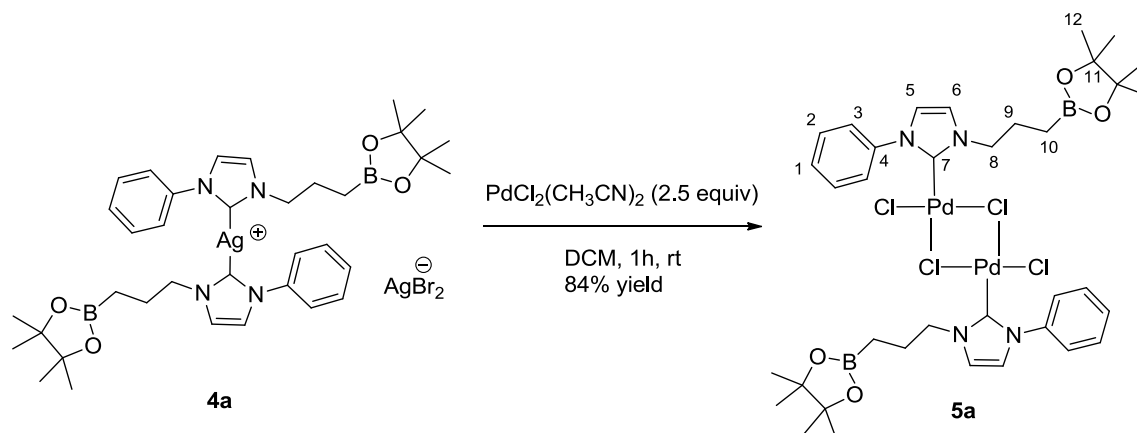
^{11}B NMR (128 MHz, CDCl_3) δ (ppm) 33.7

HRMS (ES, $[\text{M}-\text{AgBr}_2]^+$) calcd for $[\text{C}_{32}\text{H}_{46}\text{AgB}_2\text{N}_8\text{O}_4]^+$: 735.2873; found: 735.2887

ESI MS (MeOH) m/z for $[\text{M}-\text{AgBr}_2]^+$ calcd for $[\text{C}_{32}\text{H}_{46}\text{AgB}_2\text{N}_8\text{O}_4]^+$: 735.2; found: 735.1

FT-IR (ATR) ν (cm^{-1}) 3158 (w), 3074 (w), 2975 (w), 1582 (s), 1571 (s), 1417 (s), 1392 (m), 1375 (s), 1340 (m), 1319 (s), 1266 (m), 1222 (m), 1144 (s), 1112 (w), 1001 (w), 968 (m), 861 (w), 845 (w), 823 (w), 793 (w), 763 (w), 742 (w), 670 (w), 634 (w), 578 (w), 53 (w), 463 (w).

(1-phenyl-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-1H-imidazol-2(3H)-ylidene)palladium(II) chloride: 5a



$\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (130 mg, 0.50 mmol, 2.5 equiv) and **4a** (200 mg, 0.20 mmol, 1.0 equiv) were dissolved in dichloromethane (5 mL) and stirred at room temperature under argon. After 1 h, the reaction mixture was filtered through a plug of celite, then concentrated at reduced pressure and purified on a CHROMABOND Flash RS 40 SiOH (12 g) in a Combiflash Companion, eluting at 20 mL/minute (gradient; EP 100% to EP:AcOEt, 50:50 over 25 minutes). The desired fractions were combined and concentrated to give 166 mg (0.34 mmol, 84 % yield) as a yellow solid.

Mp. 133.1 °C

^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.80-0.98 (m, 4H, H_{10}), 1.27 (s, 24H, H_{12}), 2.00-2.25 (m, 4H, H_9), 4.35-4.83 (m, 4H, H_8), 7.14 (d, 2H, $^3J = 2.0$ Hz, H_5), 7.17 (d, 2H, $^3J = 2.0$ Hz, H_6), 7.55-7.73 (m, 6H, H_1 and H_3), 7.92 (d, 4H, $^3J = 7.4$ Hz, H_2).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 9.1 (C_{10} (HMOC)), 24.9 (C_{12}), 25.0 (C_9), 53.0 (C_8), 83.3 (C_{11}), 122.5 (C_6), 123.3 (C_5), 126.0 (C_2), 129.0 (C_1), 129.5 (C_3), 138.5 (C_4), 141.5 (C_7).

^{11}B NMR (128 MHz, CDCl_3) δ (ppm) 33.5

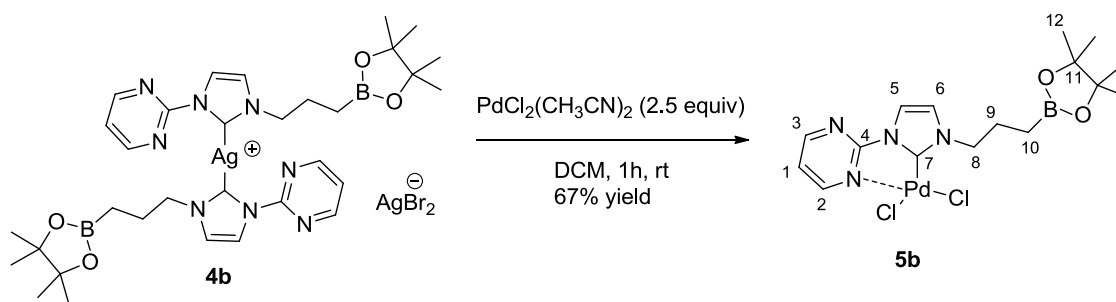
HRMS (ES, $[\text{M}+\text{Na}]^+$) calcd for $[\text{C}_{18}\text{H}_{25}\text{BCl}_2\text{N}_2\text{NaO}_2\text{Pd}]^+$: 513.0318; found: 513.0303.

ESI MS (MeOH) m/z for $[\text{M}+\text{Na}]^+$ calcd for $[\text{C}_{18}\text{H}_{25}\text{BCl}_2\text{N}_2\text{NaO}_2\text{Pd}]^+$: 513.0; found: 513.0

FT-IR (ATR) ν (cm^{-1}) 3102 (w), 2975 (w), 2930 (w), 1732 (w), 1597 (m), 1498 (w), 1461 (w), 1428 (w), 1408 (m), 1370 (m), 1323 (w), 1279 (w), 1244 (w), 1216 (w), 1165 (w), 1141

(s), 1108 (w), 1074 (w), 1027 (w), 1003 (w), 965 (w), 844 (w), 763 (m), 732 (m), 691 (s), 631 (w), 577 (w), 545 (w).

(1-(pyrimidin-2-yl)-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-1H-imidazol-2(3H)-ylidene)palladium(II) chloride: 5b



$\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (130 mg, 0.5 mmol, 2.5 equiv) and **4b** (200 mg, 0.2 mmol, 1.0 equiv) were dissolved in dichloromethane (5 mL) and stirred at room temperature under argon. After 1 h, the reaction mixture was filtered through a plug of celite, then concentrated at reduced pressure and purified on a CHROMABOND Flash RS 40 SiOH (12 g) in a Combiflash Companion, eluting at 20 mL/minute (gradient; EP 100% to EP:AcOEt, 0:100 over 25 minutes). The desired fractions were combined and concentrated to give 132 mg (0.26 mmol, 67% yield) as a yellow solid.

Mp. 283.6°C

^1H NMR (400 MHz, CDCl_3) δ (ppm) 0.86 (t, 2H, $^3J = 8.0$ Hz, H_{10}), 1.25 (s, 12H, H_{12}), 1.96-2.04 (m, 2H, H_9), 4.70 (t, 2H, $^3J = 7.5$ Hz, H_8), 7.05 (d, 1H, $^3J = 2.0$ Hz, H_5), 7.49 (t, 1H, $^3J = 5.5$ Hz, H_1), 7.78 (d, 1H, $^3J = 2.0$ Hz, H_6), 8.85 (dd, 1H, $^3J = 5.5$ Hz, $^4J = 2.2$ Hz, H_3), 9.75 (dd, 1H, $^3J = 5.5$ Hz, $^4J = 2.2$ Hz, H_2).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 8.1 (C_{10} (HMOC)), 24.9 (C_{12}), 25.9 (C_9), 52.2 (C_8), 83.3 (C_{11}), 116.5 (C_6), 119.6 (C_1), 124.1 (C_5), 153.2 (C_4), 156.7 (C_7), 159.0 (C_3), 160.4 (C_2).

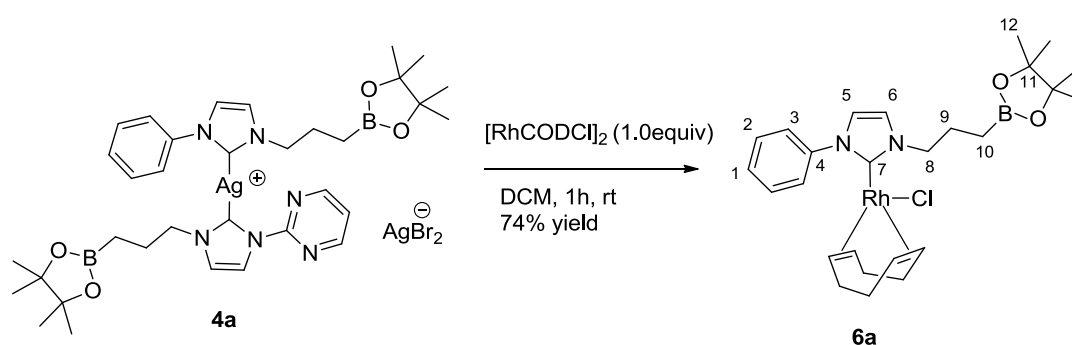
^{11}B NMR (128 MHz, CDCl_3) δ (ppm) 34.0

HRMS (ES, $[\text{M}-\text{Cl}]^+$) calcd for $[\text{C}_{16}\text{H}_{23}\text{BClN}_4\text{O}_2\text{Pd}]^+$: 455.0632; found: 455.0632.

ESI MS (MeOH) m/z $[\text{M}+\text{Na}]^+$ calcd for $[\text{C}_{16}\text{H}_{23}\text{BCl}_2\text{NaN}_4\text{O}_2\text{Pd}]^+$: 515.5; found: 514.9

FT-IR (ATR) ν (cm⁻¹) 3143 (w), 3061 (w), 2975 (w), 2927 (w), 1670 (w), 1597 (m), 1556 (w), 1481 (m), 1453 (w), 1408 (w), 1377 (w), 1359 (s), 1319 (w), 1295 (m), 1269 (w), 1191 (w), 1165 (w), 1139 (s), 1108 (w), 1073 (w), 1026 (w), 999 (w), 965 (m), 881 (w), 847 (m), 827 (w), 780 (m), 763 (w), 736 (w), 724 (m), 659 (m), 620 (w), 568 (w), 540 (w), 513 (w), 443 (w), 391 (w).

Chloro[(1,2,5,6- η)-1,5-cyclooctadiene](1-phenyl-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-1*H*-imidazol-2(3*H*)-ylidene)rhodium(I): 6a



[RhCl(COD)]₂ (157.6 mg, 0.48 mmol, 1.0 equiv) and **4a** (320 mg, 0.48 mmol, 1.0 equiv) were dissolved in dichloromethane (5 mL) and stirred at room temperature under argon. After 1 h, the reaction mixture was filtered through a plug of celite, then concentrated at reduced pressure and purified on a CHROMABOND Flash RS 40 SiOH (12 g) in a Combiflash Companion, eluting at 20 mL/minute (gradient; EP 100% to EP:AcOEt, 60:40 over 25 minutes), to give a yellow solid (401 mg, 0.72 mmol, 74% yield).

Mp. 168.4°C

¹H NMR (400 MHz, CDCl₃) δ (ppm) 0.96 (t, 2H, ³*J* = 8.0 Hz, H₁₀), 1.26 (s, 12H, H₁₂), 1.41-1.55 (m, 2H, H₉), 1.68-1.87 (m, 3H, CH_{2(COD)}), 2.01-2.41 (m, 5H, CH_{2(COD)}), 2.54-2.56 (m, 1H, CH_(COD)), 3.21-3.23 (m, 1H, CH_(COD)), 4.33 (ddd, 1H, ²*J* = 13.0 Hz, ³*J* = 9.0 Hz, ³*J* = 6.0 Hz, H_{8a}), 4.85-4.96 (m, 2H, H_{8b} and CH_(COD)), 5.00-5.07 (m, 1H, CH_(COD)), 7.01 (d, 1H, ³*J* = 2.0 Hz, H₆), 7.10 (d, 1H, ³*J* = 2.0 Hz, H₅), 7.42 (t, 1H, ³*J* = 7.5 Hz, H₁), 7.52 (t, 2H, ³*J* = 7.5 Hz, H₂), 8.15 (d, 2H, ³*J* = 8.3 Hz, H₃).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 8.4 (C₁₀ (HMQC)), 24.8 (C₁₂), 25.2 (C₉), 28.4 (CH_{2(COD)}), 28.7 (CH_{2(COD)}), 31.7 (CH_{2(COD)}), 33.1 (CH_{2(COD)}), 53.2 (C₈), 67.9 (d, CH_(COD), *J*_{Rh-C} = 14.6 Hz), 68.7 (d, CH_(COD), *J*_{Rh-C} = 14.6 Hz), 83.2 (C₁₁), 97.3 (d, CH_(COD), *J*_{Rh-C} = 7.3 Hz), 97.4 (d,

$J_{Rh-C} = 7.3$ Hz) 121.0 (C₆), 121.2 (C₅), 124.7 (C₂), 127.7 (C₁), 128.7 (C₃), 140.4 (C₄), 182.2 (d, C₇, $J_{Rh-C} = 51.3$ Hz).

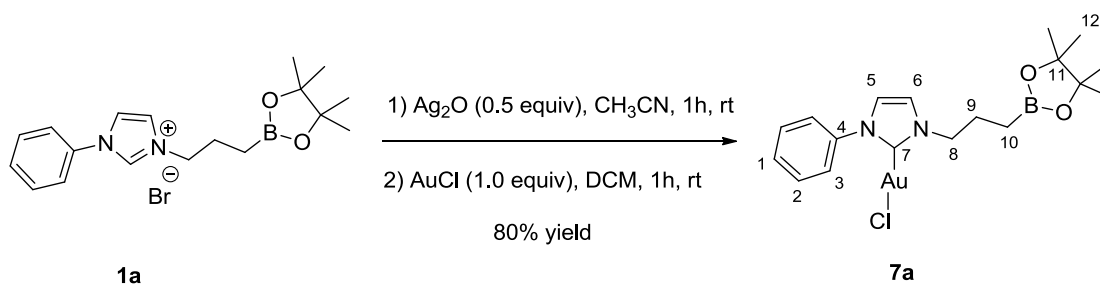
¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 33.4

HRMS (ES, [M-Cl]⁺) calcd for [C₂₆H₃₇BN₂O₂Rh]⁺: 523.1997; found: 523.2000.

ESI MS (MeOH) m/z for [M-Cl]⁺ calcd for [C₂₆H₃₇BN₂O₂Rh]⁺: 523.1; found: 523.1

FT-IR (ATR) ν (cm⁻¹) 2987 (w), 2874 (w), 2827 (w), 1596 (w), 1498 (w), 1444 (w), 1412 (w), 1368 (w), 1324 (w), 1304 (w), 1268 (w), 1239 (m), 1139 (m), 1073 (w), 962 (w), 874 (w), 843 (w), 817 (w), 764 (m), 737 (m), 694 (m), 551 (w), 478 (w), 447 (w).

(1-phenyl-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-1H-imidazol-2(3H)-ylidene)gold(I) chloride: 7a



Imidazolium salt **1a** (40 mg, 0.1 mmol, 1.0 equiv) and Ag₂O (12 mg, 0.05 mmol, 0.5 equiv) in acetonitrile (1 mL) were stirred at room temperature for 1 hour after which the solvent was evaporated. To the solid residue was added AuCl (23 mg, 0.1 mmol, 1.0 equiv) and dichloromethane (1 mL). The reaction was stirred at room temperature. After 1 h, the reaction mixture was filtered through a plug of celite and concentrated at reduced pressure, then purified on a CHROMABOND Flash RS 40 SiOH (4 g) in a Combiflash Companion, eluting at 20 mL/minute (gradient; EP 100% to EP:AcOEt, 50:50 over 25 minutes), to give a white solid (44 mg, 0.08 mmol, 80 % yield).

Mp. 158.6 °C

¹H NMR (400 MHz, CD₂Cl₂) δ (ppm) 0.83 (t, 2H, ³J = 7.5 Hz, H₁₀), 1.24 (s, 12H, H₁₂), 2.01 (qt, 2H, ³J = 7.5 Hz, H₉), 4.26 (t, 2H, ³J = 7.5 Hz, H₈), 7.16 (d, 1H, ³J = 1.6 Hz, H₆), 7.22 (d, 1H, ³J = 1.6 Hz, H₅), 7.50-7.58 (m, 3H, H₁ and H₂), 7.65 (d, 2H, ³J = 7.5 Hz, H₃).

^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm) 8.77 (C_{10} (HMQC)), 25.2 (C_{12}), 26.3 (C_9), 53.0 (C_8 overlap with the residual signal from CD_2Cl_2), 83.9 (C_{11}), 121.57 (C_6), 122.1 (C_5), 125.5 (C_2), 129.5 (C_1), 130.1 (C_3), 139.9 (C_4), 170.7 (C_7).

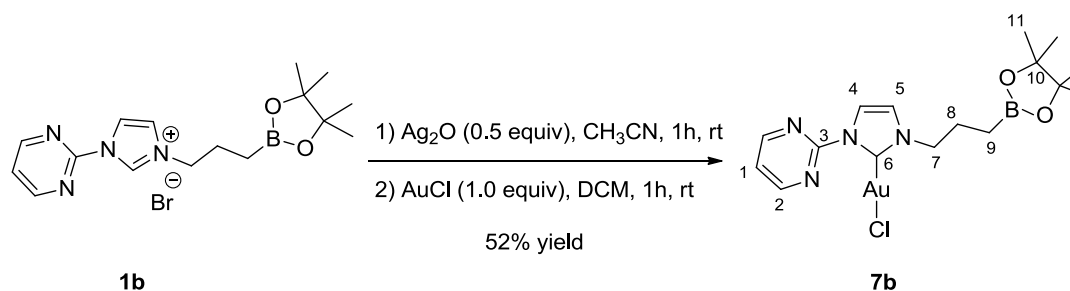
^{11}B NMR (128 MHz, CD_2Cl_2) δ (ppm) 33.7

HRMS (ES, $[\text{M}-\text{Cl}]^+$) calcd for $[\text{C}_{18}\text{H}_{25}\text{AuBN}_2\text{O}_2]^+$: 509.1669; found: 509.1667.

ESI MS (MeOH) m/z for $[\text{M}+\text{Na}]^+$ calcd for $[\text{C}_{18}\text{H}_{25}\text{AuBClN}_2\text{NaO}_2]^+$: 567.1; found: 567.0

FT-IR (ATR) ν (cm^{-1}) 3115.51 (w), 2976.56 (w), 2975.50 (w), 1595.27 (w), 1496.45 (w), 1456.69 (w), 1408.29 (w), 1365.01 (m), 1329.17 (m), 1297.75 (w), 1264.04 (w), 1227.48 (w), 1185.62 (w), 1152.08 (w), 1071.75 (m), 971.02 (w), 887.07 (w), 848.20 (w), 747.84 (m), 690.77 (m), 640.49 (m), 546.79 (w), 459.54 (w).

(1-(pyrimidin-2-yl)-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-1H-imidazol-2(3H)-ylidene)gold(I) chloride: 7b



Imidazolium salt **1b** (39.5 mg, 0.1 mmol, 1.0 eq) and Ag_2O (11.6 mg, 0.05 mmol, 0.5 equiv) in acetonitrile (2 mL) were stirred at room temperature for 1 h, after which the solvent was evaporated. To the solid residue was added AuCl (23.2 mg, 0.1 mmol, 1.0 equiv) and dichloromethane (2 mL) and the reaction was stirred at room temperature. After 1 h, the reaction mixture was filtered through a plug of celite and the solution was concentrated at reduced pressure, then purified on a CHROMABOND Flash RS 40 SiOH (4 g) in a Combiflash Companion, eluting at 20 mL/minute (gradient; EP 100% to EP:AcOEt, 30:70 over 25 minutes), to give a white solid (28.5 mg, 0.52 mmol, 52 % yield).

Mp. 198.2 °C

^1H NMR (400 MHz, CD_2Cl_2) δ (ppm) 0.83 (t, 2H, $^3J = 7.8$ Hz, H_9), 1.23 (s, 12H, H_{11}), 2.02 (qt, 2H, $^3J = 7.8$ Hz, H_8), 4.32 (t, 2H, $^3J = 7.8$ Hz, H_7), 7.15 (d, 1H, $^3J = 2.1$ Hz, H_4), 7.43 (t, 1H, $^3J = 4.8$ Hz, H_1), 8.02 (d, 1H, $^3J = 2.1$ Hz, H_5), 8.83 (d, 2H, $^3J = 4.8$ Hz, H_2).

^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm) 8.16 (C_9 (HMQC)), 25.1 (C_{11}), 25.9 (C_8), 55.1 (C_7), 83.7 (C_{10}), 120.0 (C_5), 121.2 (C_1), 121.7 (C_4), 156.1 (C_3), 159.1 (C_2), 172.2 (C_6).

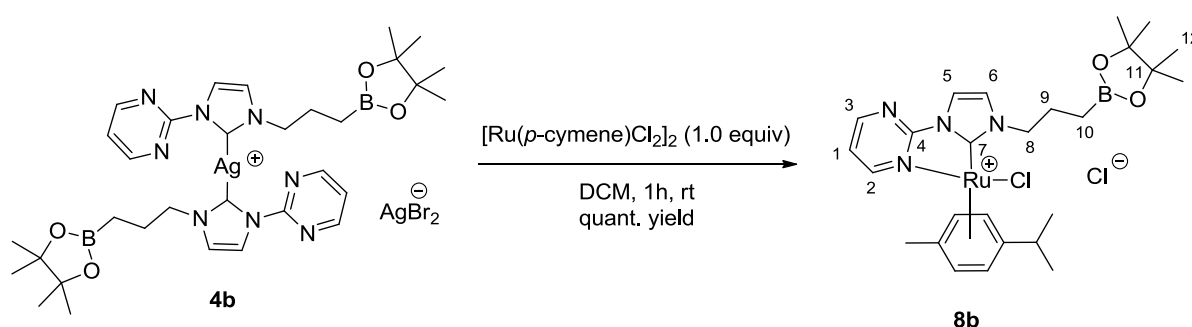
^{11}B NMR (128 MHz, CD_2Cl_2) δ (ppm) 33.9

HRMS (ES, $[\text{M}-\text{Cl}]^+$) calcd for $[\text{C}_{16}\text{H}_{23}\text{AuBN}_4\text{O}_2]^+$: 511.1574; found: 511.1569.

ESI MS (MeOH) m/z for $[\text{M}+\text{Na}]^+$ calcd for $[\text{C}_{16}\text{H}_{23}\text{AuBCIN}_4\text{NaO}_2]^+$: 569.1; found: 569.0

FT-IR (ATR) ν (cm^{-1}) 3130.29 (w), 3101.96 (w), 2923.26 (w), 1581.07 (w), 1564.56 (w), 1461.34 (m), 1417.30 (w), 1362.89 (w), 1324.51 (w), 1298.97 (w), 1266.05 (w), 1234.14 (w), 1186.65 (w), 1164.07 (w), 1144.13 (w), 1105.09 (m), 1072.52 (w), 998.53 (w), 968.49 (w), 887.31 (w), 846.21 (w), 814.49 (w), 791.60 (w), 747.71 (w), 731.26 (m), 681.12 (w), 626.21 (w), 577.27 (w), 551.58 (w), 443.69 (w).

(1-(pyrimidin-2-yl)-3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-1H-imidazol-2(3H)-ylidene) chloro[(1,2,3,4,5,6- η)-1-methyl-4-(1-methylethyl)benzene]-ruthenium chloride: **8b**



$[\text{Ru}(\text{p-cymene})\text{Cl}_2]_2$ (330 mg, 0.33 mmol, 1.0 equiv) and **4b** (201 mg, 0.33 mmol, 1.0 equiv) were dissolved in dichloromethane (5 mL) and stirred at room temperature under argon. After 1 h, the solution was filtered through a plug of celite. The solvent was evaporated in vacuo to give 396 mg (0.66 mmol, 100% yield) as a brown solid.

Mp. 94.2°C

^1H NMR (400 MHz, CD_2Cl_2) δ (ppm) 0.96 (t, 2H, $^3J = 7.5$ Hz, H_{10}), 1.02 (d, 3H, $^3J = 6.8$ Hz, CH_3 (cymene)), 1.03 (d, 3H, $^3J = 7.0$ Hz, CH_3 (cymene)), 1.26 (s, 12H, H_{12}), 1.94-2.07 (m, 1H, CH (cymene)), 2.10-2.19 (m, 1H, H_{9a}), 2.24 (s, 3H, CH_3 (cymene)), 2.55 (qt, 1H, $^3J = 7.0$ Hz, H_{9b}), 4.31-4.45 (m, 2H, H_8), 5.63 (d, 1H, $^3J = 5.6$ Hz, CH (cymene)), 6.24 (d, 1H, $^3J = 6.0$ Hz, CH (cymene)), 6.27 (d, 1H, $^3J = 6.0$ Hz, CH (cymene)), 6.48 (d, 1H, $^3J = 5.5$ Hz, CH (cymene)), 7.32 (d, 1H, $^3J = 2.3$ Hz, H_5), 7.61-7.69 (m, 1H, H_1), 7.87 (d, 1H, $^3J = 2.3$ Hz, H_6), 8.80 (d, 1H, $^3J = 3.8$ Hz, H_3), 10.04-10.15 (m, 1H, H_2).

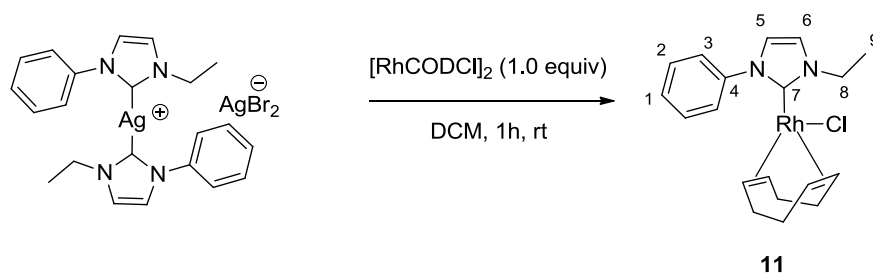
^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm) 8.0 (C_{10} (HMQC)), 19.7 (CH_3 (cymene)), 22.6 (CH_3 (cymene)), 23.3 (CH_3 (cymene)), 25.3 (C_{12}), 25.9 (C_9), 31.9 (CH (cymene)), 53.7 (C_8), 83.0 (C_{11}), 84.2 (CH (cymene)), 87.6 (CH (cymene)), 90.3 (CH (cymene)), 91.8 (CH (cymene)), 107.9 (C_6), 117.8 (C_1), 121.2 (C_5), 125.0 (C_3), 160.6 (C_4), 166.6 (C_2), 183.9 (C_7).

^{11}B NMR (128 MHz, CD_2Cl_2) δ (ppm) 33.9

HRMS (ES, $[\text{M}-\text{Cl}]^+$) calcd for $[\text{C}_{26}\text{H}_{37}\text{BClN}_4\text{O}_2\text{Ru}]^+$: 585.1736; found: 585.1742

FT-IR (ATR) ν (cm^{-1}) 3381 (w), 2977 (w), 3051 (w), 2972 (m), 2926 (w), 2866 (w), 1594 (m), 1575 (w), 1359 (w), 1489 (s), 1423 (w), 1370 (w), 1320 (m), 1271 (w), 1225 (w), 1139 (m), 964 (w), 871 (w), 845 (w), 812 (w), 779 (w), 739 (m), 676 (m).

Chloro[(1,2,5,6- η)-1,5-cyclooctadiene](1-phenyl-3-ethyl)-1*H*-imidazol-2(3*H*)-ylidene rhodium (I): 11



For procedure see **6a**

^1H NMR (400 MHz, CD_2Cl_2) δ (ppm) 1.48-1.55 (m, 2H, $\text{CH}_2(\text{COD})$), 1.57 (t, 3H, $^3J = 7.5$ Hz, H_9), 1.68-1.87 (m, 3H, $\text{CH}_2(\text{COD})$), 2.01-2.16 (m, 1H, $\text{CH}_2(\text{COD})$), 2.23-2.42 (m, 2H, $\text{CH}_2(\text{COD})$), 2.52-2.56 (m, 1H, $\text{CH}(\text{COD})$), 3.21-3.23 (m, 1H, $\text{CH}(\text{COD})$), 4.71 (m, 2H, H_8), 4.80-4.85 (m, 1H, $\text{CH}(\text{COD})$), 4.98-5.04 (m, 1H, $\text{CH}(\text{COD})$), 7.07 (d, 1H, $^3J = 2.0$ Hz, H_6), 7.22 (d, 1H, $^3J = 2.0$ Hz, H_5), 7.46 (tt, 1H, $^3J = 7.5$ Hz, $^4J = 1.2$ Hz, H_1), 7.54-7.59 (m, 2H, H_2), 8.19-8.22 (m, 2H, H_3).

^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm) 16.4 (C_9), 28.9 ($\text{CH}_2(\text{COD})$), 29.4 ($\text{CH}_2(\text{COD})$), 32.2 ($\text{CH}_2(\text{COD})$), 33.8 ($\text{CH}_2(\text{COD})$), 46.9 (C_8), 68.8 (d, $\text{CH}(\text{COD})$, $J_{\text{Rh}-\text{C}} = 14.6$ Hz), 68.9 (d, $\text{CH}(\text{COD})$, $J_{\text{Rh}-\text{C}} = 14.6$ Hz), 97.4 (d, $\text{CH}(\text{COD})$, $J_{\text{Rh}-\text{C}} = 7.3$ Hz), 97.5 (d, $J_{\text{Rh}-\text{C}} = 7.3$ Hz), 121.0 (C_6), 122.0 (C_5), 125.1 (C_2), 128.3 (C_1), 129.3 (C_3), 141.1 (C_4), 182.9 (d, C_7 , $J_{\text{Rh}-\text{C}} = 51.3$ Hz).

NMR data are in accord with those reported in the literature¹

¹ C. Mejuto, G. Guisado-Barrios, and E. Peris, *Organometallics*, **2014**, *33*, 3205–3211

3. NMR spectra of 5a and 6a and 11

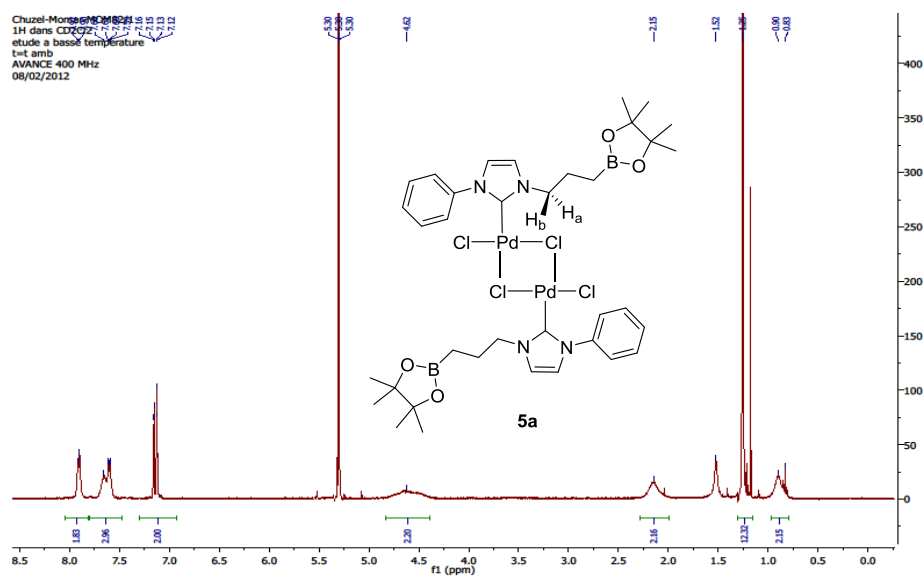


Figure S1. ^1H NMR (400 MHz, CD_2Cl_2) of **5a**.

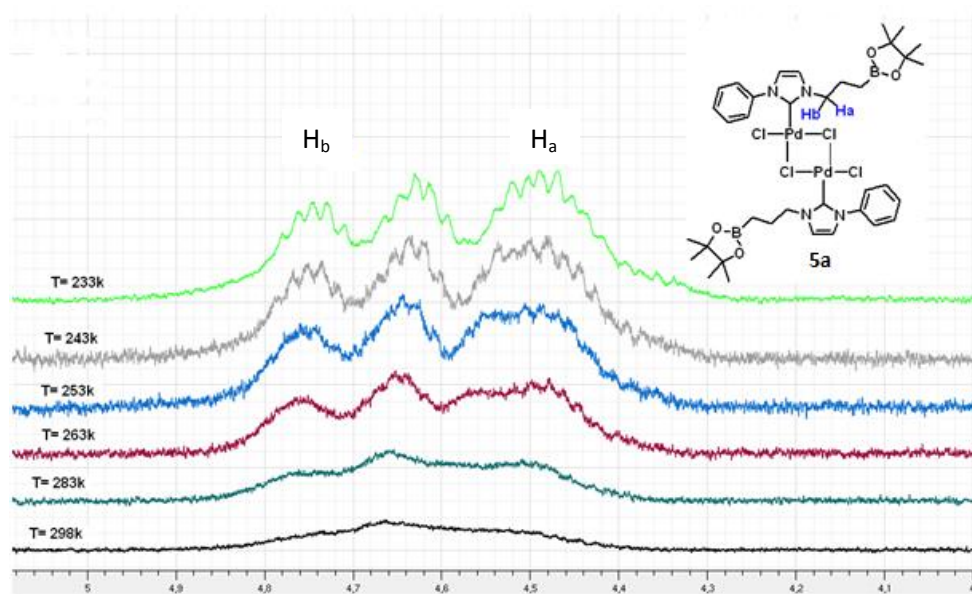


Figure S2. Temperature study for compound **5a** showing the weak anagostic interaction by ^1H NMR (400 MHz, CD_2Cl_2) (See Ha and Hb).

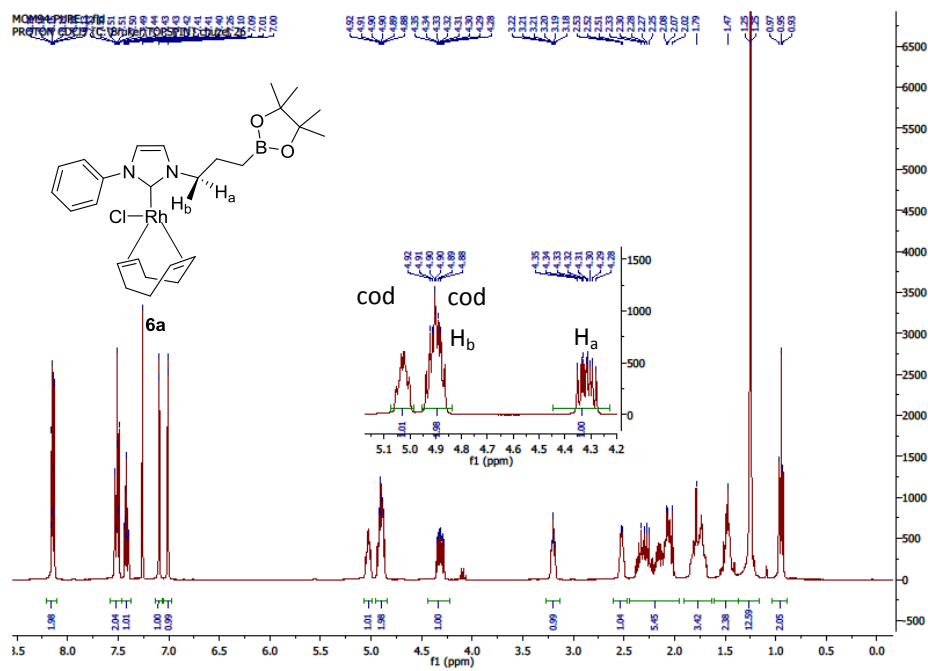


Figure S3. ^1H NMR (400 MHz, CDCl_3) of **6a**.

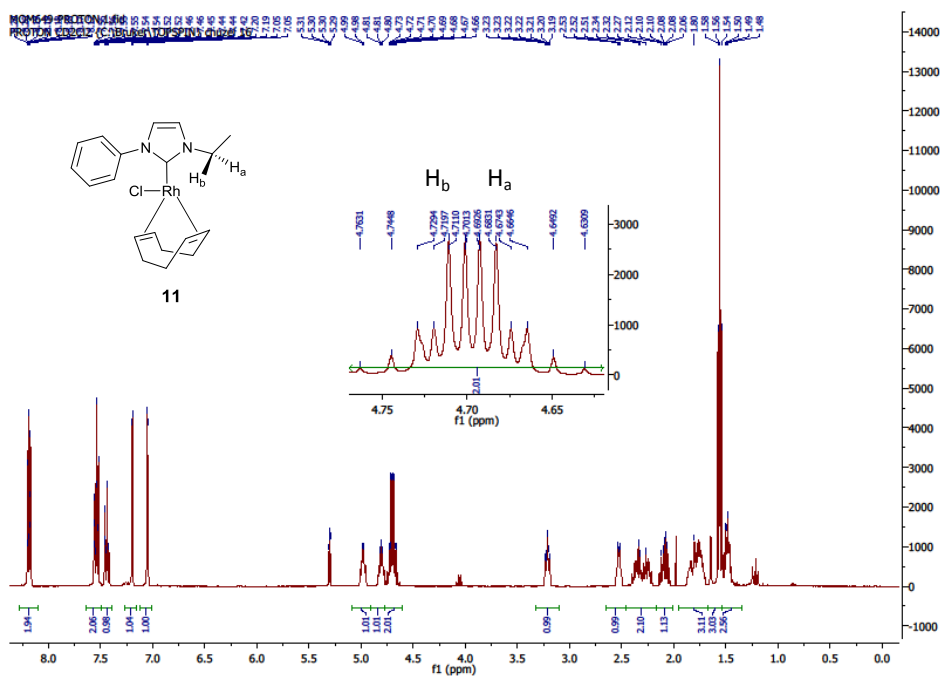


Figure S4. ^1H NMR (400 MHz, CD_2Cl_2) of **11**.

4. Hydrosilylation reaction of 9 by complexes 6a and 11.

The reaction was performed following the established literature procedure.² To a solution of the rhodium complex (1% mol) in CH₂Cl₂ (1 mL) under argon was added 1-(4-methoxyphenyl)ethanone (150 mg, 1.00 mmol, 1.0 equiv), the reaction mixture was cooled to 0°C and diphenylsilane (370 μL, 2.00 mmol, 2.0 equiv) was added dropwise over a period of 2 minutes. The reaction mixture was allowed to warm up to room temperature, and the resulting solution was stirred for 2 hours. The rate of conversion of 1-(4-methoxyphenyl)ethanone into 1-(4-methoxyphenyl)ethanol was monitored using in situ IR spectroscopy by following the C=O band at 1688 cm⁻¹ (figure S5).

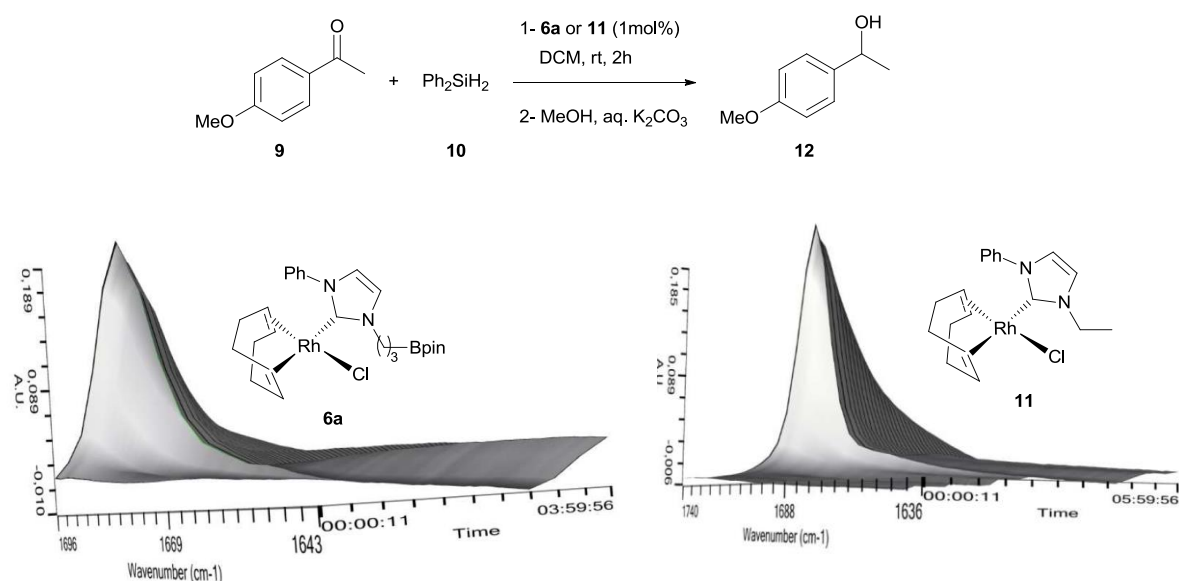
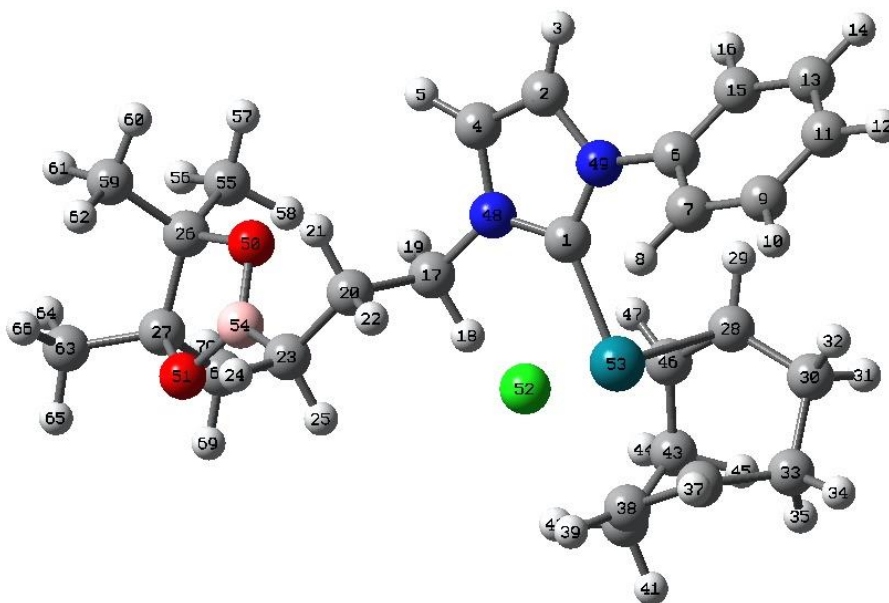


Figure S5. Hydrosilylation reaction of 9 by complexes 6a and 11 monitored by in Situ IR.

5. Computational details

² J. W. Faller, P. P. Fontaine, *Organometallics*. **2006**, 25, 5887.

All the calculations were carried out with the Gaussian 09 package.³ Structures of rhodium complex **6a** were optimized at the B3LYP level⁴ (as implemented in Gaussian09), and the def2-SV(P) basis set.⁵ ECP was used for Rh. Reported energies and natural bond orbital (NBO)⁶ are computed as single point energy calculations with the def2-TZVP basis set.⁷ NBO calculation was carried out for the electron population analysis and second order perturbation theory analysis.



Cartesian Coord. for optimized geometry of Rh complex

³ Gaussian 09, Revision A.2, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

⁴ Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648

⁵ a) J. C. Slater, *Phys. Rev.* **1951**, *81*, 385-390; b) S. H. Vosko, L. Wilk, M. Nussair, *Can. J. Phys.* **1980**, *58*, 1200-1211; c) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098-3100; d) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789; e) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.

⁶ NBO analysis was performed using the NBO Version 6.0, as implemented in the Gaussian 09 package by E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, and F. Weinhold (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2013); <http://nbo6.chem.wisc.edu/>

⁷ a) A. Schafer, C. Huber, R. Ahlrichs, *J. Chem. Phys.*, **1994**, *100*, 5829. b) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

C	-3.15831998	0.79967689	0.00000000	C	-5.11236598	4.54405889	0.62335600
C	-2.99897598	-1.43701811	-0.35961400	H	-5.59626098	4.31443489	1.56553500
H	-3.35842398	-2.44100011	-0.48969300	C	-3.78375198	4.90149089	0.67564400
C	-1.74660998	-0.94438911	-0.29600300	H	-3.32549098	4.94945589	1.65678800
H	-0.79396098	-1.43607911	-0.37745300	C	-2.98279098	5.51830289	-0.44686300
C	-5.28180398	-0.49896611	-0.13313300	H	-3.19080398	6.59396689	-0.51900900
C	-6.00413798	0.02430089	0.93477400	H	-1.92710798	5.43579589	-0.17932700
H	-5.48609498	0.55254689	1.72469400	C	-3.20749998	4.83997089	-1.81385100
C	-7.38357898	-0.14310611	0.96536600	H	-2.31876498	4.98959689	-2.43092000
H	-7.94672298	0.26274389	1.79602900	H	-4.02394398	5.32853789	-2.34952000
C	-8.03670098	-0.83498611	-0.04913200	C	-3.48839098	3.34559089	-1.70172300
H	-9.11085998	-0.96512811	-0.01445300	H	-2.72538698	2.71172489	-2.14264700
C	-7.30515598	-1.36098211	-1.10772100	N	-1.86048198	0.41837989	-0.07987600
H	-7.80584698	-1.89616711	-1.90443700	N	-3.85968798	-0.36048511	-0.17342500
C	-5.92665298	-1.19102411	-1.15452900	O	2.53575702	0.83924589	-0.09484800
H	-5.35464098	-1.57988911	-1.98740600	O	3.52144502	2.61272189	0.94715500
C	-0.71182398	1.30234989	0.12327500	Cl	-3.61320098	2.30727289	2.67477300
H	-1.08500698	2.32032089	0.01422000	Rh	-3.84010998	2.70048289	0.31720600
H	0.00993802	1.10671689	-0.67153300	B	2.39516602	1.83563889	0.84314000
C	-0.07176298	1.11691389	1.49847000	C	3.97656102	0.48577389	-2.00728600
H	0.26009002	0.08001589	1.60349700	H	5.00346202	0.51519689	-2.37695400
H	-0.84203198	1.29021689	2.25265800	H	3.58825002	-0.51968911	-2.17479100
C	1.11361602	2.06594289	1.72016800	H	3.37767802	1.18092889	-2.59220600
H	1.42866202	2.00246289	2.76833300	C	4.60806802	-0.30311711	0.27914300
H	0.78628902	3.10611889	1.60535000	H	4.08066202	-1.24028211	0.09847500
C	3.92943202	0.80942989	-0.52087800	H	5.64914402	-0.43384211	-0.01902600
C	4.42663302	2.25514189	-0.13262600	H	4.57795402	-0.09952311	1.34985900
C	-4.77516598	2.78533089	-1.59248400	C	5.85518702	2.33019289	0.38783500
H	-4.89924198	1.77496189	-1.97021800	H	6.56625802	2.01301289	-0.37778200
C	-6.07805098	3.54903789	-1.50995800	H	6.08855602	3.36056389	0.65815700
H	-6.40555898	3.86060689	-2.51141300	H	5.99533102	1.71111389	1.27147100
H	-6.83856398	2.85400689	-1.14709900	C	4.21973702	3.28871589	-1.24135900
C	-6.02314898	4.76769689	-0.56741800	H	3.19951402	3.26353989	-1.62555900
H	-7.03092098	4.98408989	-0.20665500	H	4.40094902	4.28288889	-0.83218700
H	-5.70402998	5.65566989	-1.11518100	H	4.90708702	3.13005489	-2.07347900

Selected bond distances and angles of Rh complex **6a**

	X-ray	Computed B3LYP/def2-svp
Rh-C1(NHC) (Å)	2.030	2.044
Rh-H18 (Å)	2.93	2.79
Rh-C17 (Å)	3.449	3.43
C17-H18 (Å)	0.970	1.089
C17-H19 (Å)	0.969	1.091
Rh-H18-C17 (°)	114.65	117.0

Part of the NBO listing

SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS

Threshold for printing: 0.50 kcal/mol
(Intermolecular threshold: 0.05 kcal/mol)

E(NL)-E(L)	F(L,NL)	Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol
a.u.	a.u.			

2.34	0.037			
50.	LP (1)Rh 53	132.	LV (1)Rh 53	29.52
0.72	0.130			
50.	LP (1)Rh 53	137.	BD*(1) C 1-Rh 53	2.64
0.25	0.023			
50.	LP (1)Rh 53	159.	BD*(1) C 17- H 18	0.70
0.56	0.018			
50.	LP (1)Rh 53	212.	RY (1) C 1	24.70
4.46	0.296			
50.	LP (1)Rh 53	213.	RY (2) C 1	1.78
1.35	0.044			
50.	LP (1)Rh 53	214.	RY (3) C 1	2.60
1.21	0.050			

78.	BD (1) C 15- H 16	300.	RY (1) C 6	1.85
1.83	0.052			
78.	BD (1) C 15- H 16	419.	RY (1) C 13	1.50
2.06	0.050			
79.	BD (1) C 17- H 18	132.	LV (1)Rh 53	0.58
1.04	0.022			

6. Crystal data and structure refinement

compounds	5a	5b	6a	7a	7b
Identification code	mom82	mom48	mom94	Mom100	mom102
CCDC	864270	880506	880508	1023303	1023304
Empirical formula	C ₃₆ H ₅₀ B ₂ Cl ₄ N ₄ O ₄ Pd ₂	C ₁₆ H ₂₃ BCl ₂ N ₄ O ₂ Pd	C ₂₆ H ₃₇ BCIN ₂ ORh	C ₁₈ H ₂₅ AuBCIN ₂ O ₂	C ₁₆ H ₂₃ AuBCIN ₄ O ₂
Formula weight	979.02	491.49	558.75	544.63	546.61
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	P 2 ₁ /c	P 2 ₁ /c	P -1	C 2/c	C 2
<i>a</i> (Å)	12.4975(2)	12.9882(2)	9.9764(2)	32.5490(6)	24.2473(7)
<i>b</i> (Å)	29.8395(6)	12.9376(2)	12.3976(3)	9.5091(2)	8.6331(3)
<i>c</i> (Å)	13.2162(2)	12.4940(2)	12.8407(3)	13.6925(2)	9.8278(4)
α (°)	90	90	62.448(1)	90	90
β (°)	101.059(2)	75.801(1)	76.060(1)	99.475(2)	100.011(1)
γ (°)	90	90	71.989(1)	90	90
<i>V</i> (Å ³)	4837.05	2035.3	1330.01	4180.17	2025.92
<i>Z</i>	4	4	2	8	4
<i>T</i> (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Density	1.344	1.604	1.395	1.731	1.792
Absorption coefficient	1.001	1.192	0.767	7.179	7.409
<i>F</i> (000)	1984	992	580	2112	1056
Crystal size	0.3x 0.2x 0.04	0.4x 0.3x 0.2	0.26x 0.24x 0.16	0.09x 0.05x 0.02	0.2x0.18x0.04
Theta range for data collection	1.36 to 28.7	2.26 to 28.71	2.16 to 28.69	2.64 to 28.68	2.93 to 28.62
Index ranges	-16<= <i>h</i> <=15 -37<= <i>k</i> <=40 -17<= <i>l</i> <=13	-15<= <i>h</i> <=17 -16<= <i>k</i> <=15 -15<= <i>l</i> <=16	-23<= <i>h</i> <=12 -16<= <i>k</i> <=15 -16<= <i>l</i> <=16	-43<= <i>h</i> <=42 0<= <i>k</i> <=12 0<= <i>l</i> <=17	-32<= <i>h</i> <=31 -10<= <i>k</i> <=11 0<= <i>l</i> <=13
Reflections collected	44952	18035	17867	20114	9034

Independent reflections	11983	5170	6553	5215	4793
Completeness to theta = 28.7°	0.959	0.982	0.953	0.966	0.974
Absorption correction	none	multi-scan	multi-scan	multi-scan	refdelf
Max. and min. transmission	-	0.705 and 0.699	0.848 and 0.845	0.5186 and 0.4469	0.9396 and 0.4762
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	11983/0/469	5170/0/235	6553/0/352	5215/0/226	4793/1/ 227
Goodness-of-fit on F2	1.01	1.042	1.024	0.998	1.076
Final R indices [I>2sigma(I)]	R1 = 0.0683 wR2 = 0.1939	R1 = 0.041 wR2 = 0.1097	R1 = 0.0384 wR2 = 0.0923	R1 = 0.0453 wR2 = 0.1101	R1 = 0.0562 wR2 = 0.1395
R indices (all data)	R1 = 0.1221 wR2 = 0.2203	R1 = 0.0606 wR2 = 0.1172	R1 = 0.0604 wR2 = 0.1003	R1 = 0.078 wR2 = 0.1205	R1 = 0.0642 wR2 = 0.1474
Largest diff. peak and hole	1.152 / -0.933e.Å ⁻³	0.948 /-0.8 e.Å ⁻³	0.736/ -0.636e.Å ⁻³	1.369/ -1.211e.Å ⁻³	3.672/-1.997 e.Å ⁻³