Supporting Information

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Versatile coordination chemistry of indazole-derived carbenes

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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. Salt **1c** was synthesized as previously reported.[S1] All solvents and chemicals were used as received without further purification if not mentioned otherwise. ^{1}H, ^{13}C, ^{31}P and ^{19}F 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) or externally to 85% H_3PO_4 (^{31}P), and CF_3CO_2H (^{19}F). Mass spectra were measured using a Finnigan MAT LCQ (ESI) spectrometer. Infrared spectra were recorded in CH_2Cl_2 solutions with a Varian 3100 FT-IR spectrometer using a NaCl cell. Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

1,2-Dimethylindazolium iodide (1a)

Indazole (0.59 g, 5 mmol) was reacted with NaOH (0.32 g, 8 mmol) in CH_3CN (20 mL) for 2 h at ambient temperature. To the reaction mixture methyl iodide (0.88 mL, 14 mmol) was added and the resulting suspension was further stirred for 24 h at 75 °C. The solvent of the reaction mixture was removed under reduced pressure, and the residue was washed with water to remove NaI and excess NaOH. The resulting off-white solid was washed with ethyl acetate and dried under vacuum to yield salt **1a** (1.2 g, 4.4 mmol, 85%) as a white powder. ^{1}H NMR (500 MHz, DMSO): δ 9.22 (s, 1 H, NCH), 8.11 (d, 1 H, Ar-H), 8.02 (d, 1 H, Ar-H), 7.88 (t, 1 H, Ar-H), 7.51 (t, 1 H, Ar-H), 4.41 (s, 3 H, NCH_3), 4.28 (s, 3 H, NCH_3). $^{13}C\{^1H\}$ NMR (125.8 MHz, DMSO): 139.8 (s, NC), 132.7, 132.6, 124.8, 122.8, 118.7, 111.1 (s, Ar-C), 37.8 (s, NCH_3), 33.2 (s, NCH_3). Anal. Calcd. for $C_9H_{11}N_2I$: C, 39.44; H, 4.04; N, 10.22. Found: C, 39.32; H, 4.05; N, 10.21. ESI (MS): $m/z = 147$ $[M - I]^+$.

1,2-Diethylindazolium iodide (**1b**)

NaOH (0.32 g, 8 mmol) was added to a solution of indazole (0.590 g, 5 mmol) in CH_3CN (20 mL) and stirred for 2 h at ambient temperature. To the reaction mixture ethyl iodide (1.6 mL, 20 mmol) was added and the resulting suspension was further stirred for 36 h at 75 °C. The solvent of the filtrate was removed under vacuum. The residue was dissolved in CH_2Cl_2 and filtered. Subsequently, the solvent of the filtrate was removed under reduced pressure and the residue washed with ethyl acetate. Upon drying under vacuum salt **1b** (0.498 g, 1.65 mmol, 33%) was obtained as a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ 9.65 (s, 1 H, NCH), 8.06 (d, 1 H, Ar-H), 7.80 (t, 1 H, Ar-H), 7.73 (d, 1 H, Ar-H), 7.45 (t, 1 H, Ar-H), 5.14 (q, 2 H, ^3J(H,H) = 7.6 Hz, NCH_2), 4.96 (q, 2 H, ^3J(H,H) = 7.6 Hz, NCH_2), 1.77 (t, 3 H, ^3J(H,H) = 7.6 Hz, CH_3), 1.53 (t, 3 H, ^3J(H,H) = 7.6 Hz, CH_3). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): 140.8 (s, NC), 134.6, 133.8, 126.3, 124.3, 120.4, 111.2 (s, Ar-C), 48.5 (s, NCH_2), 44.2 (s, NCH_2), 16.1 (s, CH_3), 15.6 (s, CH_3). Anal. Calcd. for $C_{11}H_{15}N_2I$: C, 43.73; H, 5.00; N, 9.27. Found: C, 43.38; H, 5.09; N, 9.18. ESI (MS): $m/z = 175$ $[M - I]^+$.

Di-μ-iodo-bis(1,2-dimethylindazolin-3-ylidene)diiododipalladium(II) (**2a**).

Salt **1a** (0.329 g, 1.2 mmol), $Pd(OAc)_2$ (0.224 g, 1 mmol) and NaI (0.6 g, 4 mmol) were suspended in DMSO (10 mL) and the mixture was stirred at 70 °C for 24 h. The reaction mixture was filtered through Celite, and the solvent of the filtrate was removed by vacuum distillation. The residue was suspended in deionized water, filtered through a sintered funnel and washed several times with water. The remainder on the sintered funnel was redissolved in CH_3CN and the filtrate was evaporated to dryness under reduced pressure. The remaining powder was dissolved in CH_2Cl_2 and passed through silica gel. Upon removing the solvent under vacuum, an orange solid was obtained (0.3 g, 0.29 mmol, 59%). ^{1}H NMR (500 MHz, CD$_3$CN): δ 8.02 (d, 2 H, Ar-H), 7.63 (m, 2 H, Ar-H), 7.37 (d, 2 H, Ar-H), 7.28 (t, 2 H, Ar-H), 4.30 (s, 6 H, NCH$_3$), 3.99 (s, 6 H, NCH$_3$). ^{13}C{^{1}H} NMR (125.8 MHz, CD$_3$CN): 148.8 (s, C$_{\text{carbene}}$), 140.5, 132.3, 130.7, 128.8, 122.6, 110.5 (s, Ar-C), 41.5 (s, NCH$_3$), 34.2 (s, NCH$_3$). Anal. Calcd. for $C_{18}H_{20}N_4I_4Pd_2$: C, 21.35; H, 1.99; N, 5.53. Found: C, 21.34; H, 2.09; N, 5.25. ESI (MS): *m/z* = 1036 [M + Na]$^+$.

Di-*μ*-iodo-bis(1,2-diethylindazolin-3-ylidene)diiododipalladium(II) (2b)

2b was synthesized in analogy to **2a** by reacting salt **1b** (0.362 g, 1.2 mmol), Pd(OAc)$_2$ (0.224 g, 1 mmol) and NaI (0.6 g, 4 mmol) in DMSO to yield a red-orange powder (0.29 g, 0.27 mmol, 54%). ^{1}H NMR (300 MHz, CD$_3$CN): δ 8.06 (d, 2 H, Ar-H), 7.64 (m, 2 H, Ar-H), 7.43 (d, 2 H, Ar-H), 7.32 (t, 2 H, Ar-H), 4.88 (q, 4 H, ^{3}J(H,H) = 7.2 Hz, NCH$_2$), 4.43 (q, 4 H, ^{3}J(H,H) = 7.1 Hz, NCH$_2$), 1.59 (t, 6 H, ^{3}J(H,H) = 7.2 Hz, CH$_3$), 1.03 (t, 6 H, ^{3}J(H,H) = 7.1 Hz, CH$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, CD$_3$CN): 153.5 (s, C$_{\text{carbene}}$), 141.4, 132.7, 132.0, 129.5, 123.3, 111.4 (s, Ar-C), 49.2 (s, NCH$_2$), 43.9 (s, NCH$_2$), 14.1 (s, CH$_3$), 13.7 (s, CH$_3$). Anal. Calcd. for $C_{22}H_{28}N_4I_4Pd_2$: C, 24.72; H, 2.64; N, 5.24. Found: C, 24.22; H, 2.58; N, 5.00. ESI (MS): *m/z* = 983 [M – I + CH$_3$CN]$^+$.

***cis*-Diiodo(1,2-dimethylindazolin-3-ylidene)(triphenylphosphine)palladium(II) (3a).**

A mixture of complex **2a** (0.506 g, 0.5 mmol) and triphenylphosphine (0.29 g, 1.1 mmol) in CH$_2$Cl$_2$ (15 mL) was stirred under reflux conditions overnight. The solvent was removed under vacuum, and the residue was washed with ethyl acetate. Upon drying the residue under vacuum a greenish yellow powder (0.692 g, 0.9 mmol, 90%) was obtained. ^{1}H NMR (500 MHz, DMSO): δ 7.79 (d, 1 H, Ar-H), 7.62-7.51 (br m, 8 H, Ar-H), 7.38 (m, 3 H, Ar-H), 7.28 (m, 6 H, Ar-H), 7.07 (m, 1 H, Ar-H), 4.09 (s, 3 H, NCH$_3$), 3.73 (s, 3 H, NCH$_3$). ^{31}P{^{1}H} NMR (121.5 MHz, DMSO): 26.4 (s, 1 P, PPh$_3$). ^{13}C{^{1}H} NMR spectra could not be obtained due to insufficient solubility of the compound. Anal. Calcd. for $C_{27}H_{25}N_2I_2PPd$: C, 42.19; H, 3.28; N, 3.64. Found: C, 42.50; H, 3.21; N, 3.67. ESI (MS): *m/z* = 811 [M + H + CH$_3$CN]$^+$.

***cis*-Diiodo(1,2-diethylindazolin-3-ylidene)(triphenylphosphine)palladium(II) (3b).**

3b was synthesized in analogy to **3a** by reacting **2b** (0.428 g, 0.4 mmol) and triphenylphosphine (0.237 g, 0.5 mmol) yielding **3b** (0.638 g, 0.8 mmol, 94%) as greenish yellow powder. ^{1}H NMR (300 MHz, DMSO): δ 7.85 (d, 1 H, Ar-H), 7.58 (d, 2 H, Ar-H), 7.50-7.36 (br m, 12 H, Ar-H), 7.28 (d, 3 H, Ar-H), 7.13 (t, 1 H, Ar-H), 4.73 (m, 1 H, NCH_2), 4.34 (m, 2 H, NCH_2), 4.12 (m, 1 H, NCH_2), 1.48 (t, 3 H, CH_3), 0.97 (t, 3 H, CH_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, DMSO): 27.0 (s, 1 P, PPh_3). $^{13}C\{^1H\}$ NMR spectra could not be obtained due to insufficient solubility of the compound. Anal. Calcd. for $C_{29}H_{29}N_2I_2PPd$: C, 43.72; H, 3.67; N, 3.52. Found: C, 44.00; H, 3.72; N, 3.30. ESI (MS): *m/z* = 700 $[M - I + CH_3OH]^+$.

cis-Di(trifluoroacetato)(1,2-dimethylindazolin-3-ylidene)(triphenylphosphine) palladium(II) (4a).

A mixture of complex **3a** (0.054 g, 0.07 mmol) and AgO_2CCF_3 (0.034 g, 0.154 mmol) was suspended in CH_3CN (10 mL) and stirred at ambient temperature for 12 h shielded from light. The suspension was filtered over Celite and the solvent of the filtrate was removed under reduced pressure to afford an off-white powder (0.045 g, 0.06 mmol, 87%). ^{1}H NMR (300 MHz, DMSO): δ 8.05 (d, 1 H, Ar-H), 7.57-7.50 (m, 11 H, Ar-H), 7.44-7.39 (m, 6 H, Ar-H), 7.16 (t, 1 H, Ar-H), 4.27 (s, 3 H, NCH_3), 3.87 (s, 3 H, NCH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, DMSO): 159.0 (q, ^2J(F,C) = 33.5 Hz, CO), 152.3 (d, ^2J(P,C) = 7.7 Hz, $C_{carbene}$), 139.3 (s, Ar-C), 133.5 (d, Ar-C), 131.7(d, Ar-C), 131.5 (d, Ar-C), 128.8 (d, Ar-C), 127.2, 126.4 (s, Ar-C), 126.0 (d, Ar-C), 125.2 (s, Ar-C), 116.7 (q, ^1J(C,F) = 297.5 Hz, CF_3), 110.3 (s, Ar-C), 33.4 (s, CH_3), one CH_3 resonance overlaps with the DMSO solvent signal. $^{31}P\{^1H\}$ NMR (121.5 MHz, DMSO): 28.0 (s, 1 P, PPh_3), ^{19}F NMR (282.4 MHz, DMSO): 2.55 (s, CF_3). Anal. Calcd. for $C_{31}H_{25}F_6O_4N_2PPd$: C, 50.25; H, 3.40; N, 3.78. Found: C, 50.15; H, 3.35; N, 3.81. ESI (MS): *m/z* = 627 $[M - O_2CCF_3]^+$.

cis-Di(trifluoroacetato)(1,2-diethylindazolin-3-ylidene)(triphenylphosphine) palladium(II) (4b).

Complex **4b** was prepared in analogy to the **4a** by stirring **3b** (0.052 g, 0.065 mmol) and AgO_2CCF_3 (0.032 g, 0.143 mmol) in CH_3CN at ambient temperature yielding **4b**

(0.041 g, 0.054 mmol, 83%) as an off-white powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (d, 1 H, Ar-H), 7.51-7.43 (br m, 10 H, Ar-H), 7.36-7.30 (br m, 6 H, Ar-H), 7.17 (d, 1 H, Ar-H), 7.06 (t, 1 H, Ar-H), 4.85 (m, 2 H, NCH_2)., 4.30 (q, 2 H, ^3J(H,H) = 7.2 Hz, NCH_2), 1.28 (t, 3 H, ^3J(H,H) = 7.1 Hz, CH_3), 1.11 (t, 3 H, ^3J(H,H) = 7.1 Hz, CH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): 163.0 (q, ^2J(F,C) = 35.1 Hz, CO), 159.8 (d, ^2J(P,C) = 8.2 Hz, $C_{carbene}$), 140.9 (s, Ar-C), 134.5 (d, Ar-C), 133.4, 132.8 (s, Ar-C), 129.7 (d, Ar-C), 128.7 (d, Ar-C), 127.8, 127.4, 127.0, 124.3, 110.5 (s, Ar-C), 49.0 (s, NCH_2), 43.4 (s, NCH_2), 15.7 (s, CH_3), 14.3 (s, CH_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): 27.6 (s, 1 P, PPh_3), ^{19}F NMR (282.4 MHz, $CDCl_3$): 2.21 (s, CF_3). Anal. Calcd. for $C_{33}H_{29}F_6O_4N_2PPd$: C, 51.54; H, 3.80; N, 3.64. Found: C, 51.36; H, 3.79; N, 3.57. ESI (MS): *m/z* = 655 $[M - O_2CCF_3]^+$.

Di-μ-bromo-bis(1,2-diethylindazolin-3-ylidene)dibromodipalladium(II) (5)

Ag_2O (0.028 g, 0.12 mmol) was added into a CH_2Cl_2 solution of salt **1c** (0.051 g, 0.2 mmol) and the mixture stirred for 6 h at ambient temperature shielded from light. The reaction mixture was then filtered through Celite into a solution of $[PdBr_2(CH_3CN)_2]$ (0.035 g, 0.1 mmol) in CH_3CN and subsequently stirred for 6 h at ambient temperature. The resulting suspension was passed through Celite and filtrate evaporated to dryness under vacuum. The residue was washed with methanol and dried to yield **5** as an orange-red powder (0.063 g, 0.071 mmol, 71%). ^{1}H NMR (300 MHz, CD_3CN): δ 8.21 (d, 2 H, Ar-H), 7.64 (t, 2 H, Ar-H), 7.39 (d, 2 H, Ar-H), 7.31 (t, 2 H, Ar-H), 5.01 (q, 4 H, ^3J(H,H) = 7.2 Hz, NCH_2), 4.43 (q, 4 H, ^3J(H,H) = 7.1 Hz, NCH_2), 1.65 (t, 6 H, ^3J(H,H) = 7.2 Hz, CH_3), 1.10 (t, 6 H, ^3J(H,H) = 7.1 Hz, CH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3CN): 155.7 (s, $C_{carbene}$), 141.4, 132.9, 130.6, 129.1, 123.6, 111.3 (s, Ar-C), 48.6 (s, NCH_2), 43.6 (s, NCH_2), 15.5 (s, CH_3), 13.8 (s, CH_3). Anal. Calcd. for $C_{22}H_{28}N_4Br_4Pd_2$: C, 29.99; H, 3.20; N, 6.36. Found: C, 30.20; H, 3.18; N, 6.35. ESI (MS): *m/z* = 947 $[M + CH_3O + 2NH_4]^+$.

Chloro(1,2-diethlyindazolin-3-ylidene)gold(I) (6)

Ag_2O (0.03 g, 0.13 mmol) was added to a CH_2Cl_2 solution of salt **1b** (0.069 g, 0.23 mmol), and the mixture was further stirred for 6 h shielded from light at ambient temperature. The reaction mixture was then filtered through Celite into a CH_2Cl_2 solution of [AuCl(SMe$_2$)] (0.062 g, 0.21 mmol) and subsequently stirred for another 6 h. The reaction mixture was passed through a plug of Celite to remove AgI. The solvent of the filtrate was removed under reduced pressure and the residue was washed with diethyl ether and dried under vacuum to afford a white powder (0.075 g, 0.18 mmol, 88%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.00 (d, 1 H, Ar-H), 7.63 (t, 1 H, Ar-H), 7.35 (d, 1 H, Ar-H), 7.25 (t, 1 H, Ar-H), 4.72 (q, 2 H, ^3J(H,H) = 7.6 Hz, NCH$_2$), 4.47 (q, 2 H, ^3J(H,H) = 6.9 Hz, NCH$_2$), 1.58 (t, 3 H, ^3J(H,H) = 7.6 Hz, CH$_3$), 1.30 (t, 3 H, ^3J(H,H) = 6.9 Hz, CH$_3$). ^{13}C{^{1}H} NMR (125.8 MHz, CDCl$_3$): 172.6 (s, C$_{carbene}$), 141.5, 133.1, 131.5, 129.0, 123.6, 109.9 (s, Ar-C), 48.7 (s, NCH$_2$), 43.1 (s, NCH$_2$), 16.9 (s, NCH$_3$), 14.5 (s, NCH$_3$). Anal. Calcd. for $C_{11}H_{14}N_2ClAu$: C, 32.49; H, 3.47; N, 6.89. Found: C, 32.65; H, 3.40; N, 6.94. ESI (MS): *m/z* = 777 [2M – Cl]$^+$.

Chloro(η^4-1,5-cyclooctadiene)(1,2-dimethlyindazolin-3-ylidene)rhodium(I) (7)

Salt **1a** (0.137 g, 0.5 mmol) was dissolved in CH$_2$Cl$_2$-methanol (10:2) solvent mixture and Ag$_2$O (0.07 g, 0.3 mmol) was added. The mixture was further stirred for 6 h shielded from light at ambient temperature followed by addition of a solution of [RhCl(cod)]$_2$ (0.124 g, 0.25 mmol) in CH$_2$Cl$_2$ and further stirred for 6 h. The reaction mixture was filtered through Celite to remove AgI and the solvent of the filtrate was removed under reduced pressure. The residue was washed with hexane and dried under vacuum to yield the product as a yellow powder (0.171 g, 0.44 mmol, 87%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.40 (d, 2 H, Ar-H), 7.53 (t, 2 H, Ar-H), 7.23 (t, 2 H, Ar-H), 7.15 (d, 2 H, Ar-H), 5.13 (br s, 1 H, COD$_{vinyl}$), 5.04 (br s, 1 H, COD$_{vinyl}$), 4.59 (s, 3 H, NCH$_3$), 3.81 (s, 3 H, NCH$_3$), 3.53 (br s, 1 H, COD$_{vinyl}$), 3.33 (br s, 1 H, COD$_{vinyl}$), 2.55-2.36 (br m, 4 H, COD$_{allyl}$), 2.07-1.97 (br m, 4 H, COD$_{allyl}$). ^{13}C{^{1}H} NMR (125.8 MHz, CDCl$_3$): 194.2 (d, ^1J(Rh,C) = 44.9 Hz, C$_{carbene}$), 141.7, 131.8, 131.1, 130.1, 122.3, 109.4 (s, Ar-C), 99.4 (d, ^1J(Rh,C) = 6.4 Hz, COD$_{vinyl}$), 99.2 (d, ^1J(Rh,C) = 6.4 Hz, COD$_{vinyl}$), 69.8 (d, ^1J(Rh,C) = 13.6 Hz, COD$_{vinyl}$), 68.7 (d, ^1J(Rh,C) = 14.6 Hz, COD$_{vinyl}$), 40.2 (s, NCH$_3$), 34.4 (s, COD$_{allyl}$), 34.1 (s, NCH$_3$), 33.2, 30.1, 29.3 (s, COD$_{allyl}$). Anal. Calcd. for $C_{17}H_{22}N_2ClRh$: C, 51.99; H, 5.65; N, 7.13. Found: C, 51.85; H, 5.57; N, 7.35. ESI (MS): *m/z* = 357 [M – Cl]$^+$, 749 [2M – Cl]$^+$.

η^4-1,5-Cyclooctadiene(Iodo)(1,2-dimethlyindazolin-3-ylidene)rhodium(I) (8)

NaI (0.018 g, 0.012 mmol) was added to an acetone solution of **7** (0.039 g, 0.1 mmol) and the resulting mixture was further stirred for 4 h at ambient temperature. The solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 and subsequently filtered. The solvent of the filtrate was removed under vacuum to afford a yellow solid (0.035 g, 0.072 mmol, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.29 (d, 1 H, Ar-H), 7.50 (t, 1 H, Ar-H), 7.18 (m, 2 H, Ar-H), 5.23 (m, 2 H, COD_{vinyl}), 4.41 (s, 3 H, NCH_3), 3.72 (s, 3 H, NCH_3), 3.60 (m, 1 H, COD_{vinyl}), 3.46 (m, 1 H, COD_{vinyl}), 2.44-2.25 (br m, 4 H, COD_{allyl}), 2.06-1.82 (br m, 4 H, COD_{allyl}). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): 195.0 (d, ^1J(Rh-C) = 43.3 Hz, $C_{carbene}$), 141.7, 131.7, 131.3, 130.0, 122.3, 109.6, 97.2 (d, ^1J(Rh,C) = 6.6 Hz, COD_{vinyl}), 97.0 (d, ^1J(Rh,C) = 6.6 Hz, COD_{vinyl}), 73.7 (d, ^1J(Rh,C) = 14.3 Hz, COD_{vinyl}), 72.0 (d, ^1J(Rh,C) = 14.8 Hz, COD_{vinyl}), 40.7 (s, NCH_3), 34.3 (s, COD_{allyl}), 33.7 (s, NCH_3), 32.5, 30.6, 30.0 (s, COD_{allyl}). Anal. Calcd. for $C_{17}H_{22}N_2IRh \cdot H_2O$: C, 40.66; H, 4.82; N, 5.58. Found: C, 40.77; H, 4.87; N, 5.57. ESI (MS): $m/z = 357$ $[M-I]^+$, 841 $[2M-I]^+$.

cis-Chloro-dicarbonyl(1,2-dimethylindazolin-3-ylidene)rhodium(I) (9)

Complex **7** (0.028 g, 0.07 mmol) was dissolved in CH_2Cl_2 (10 mL) and carbon monoxide was bubbled for 5 min through the solution. The solvent was removed under reduced pressure and the resulting residue was subsequently washed with hexane. Upon drying the residue under vacuum a yellow solid was obtained (0.023 g, 0.066 mmol, 95%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, 1 H, Ar-H), 7.62 (t, 1 H, Ar-H), 7.28 (m, 2 H, Ar-H), 4.43 (s, 3 H, NCH_3), 3.95 (s, 3 H, NCH_3). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): 186.5 (d, ^1J(Rh,C_{co}) = 53.2 Hz, CO), 183.5 (d, ^1J(Rh,C_{co}) = 76.1 Hz, CO), 179.7 (d, ^1J(Rh,C) = 37.6 Hz, $C_{carbene}$), 141.0, 132.7, 131.2, 129.5, 123.1, 109.3 (s, Ar-C), 40.9 (s, NCH_3), 33.9 (s, NCH_3). Anal. Calcd. for $C_{11}H_{10}N_2O_2ClRh \cdot 2H_2O$: C, 34.71; H, 4.77; N, 7.36. Found: C, 34.02; H, 4.22; N, 6.87. ESI (MS): $m/z = 636$ $[2M-Cl-CO+H_2O]^+$, 644 $[2M-Cl]^+$. FT-IR (CH_2Cl_2): $\tilde{\nu}$ (CO_{sym}) 2069 cm^{-1} (s) and $\tilde{\nu}$ (CO_{asym}) 1991 cm^{-1} (s).

cis-dicarbonyl-iodo(1,2-dimethylindazolin-3-ylidene)rhodium(I) (10)

Complex **10** was prepared in analogy to **9** by reacting **c**omplex **8** (0.029 g, 0.06 mmol) with carbon monoxide. **10** was isolated as a dark yellow powder (0.024 g, 0.06 mmol, 92%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, 1 H, Ar-H), 7.62 (m, 1 H, Ar-H), 7.28 (m, 2 H, Ar-H), 4.34 (s, 3 H, NCH_3), 3.99 (s, 3 H, NCH_3). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): 188.4 (d, $^1J(Rh,C_{co})$ = 52.2 Hz, CO), 183.1 (d, $^1J(Rh,C_{co})$ = 77.9 Hz, CO), 179.2 (d, $^1J(Rh,C)$ = 34.8 Hz, $C_{carbene}$), 141.1, 132.7, 131.4, 129.7, 123.0, 109.3 (s, Ar-C), 41.6 (s, NCH_3), 34.1 (s, NCH_3). Anal. Calcd. for $C_{11}H_{10}N_2O_2IRh$: C, 30.58; H, 2.33; N, 6.48. Found: C, 30.65; H, 2.71; N, 6.94. ESI (MS): *m/z* = 503 $[M + K + CH_3OH]^+$. FT-IR (CH_2Cl_2): $\tilde{\nu}$ (CO_{sym}) 2061 cm^{-1} (s) and $\tilde{\nu}$ (CO_{asym}) 1991 cm^{-1} (s).

X-ray Diffraction Studies. X-ray data were collected with a Bruker AXS SMART APEX diffractometer, using Mo K_α radiation at 223 K (**3b, 4a, 5 and 7**) or 100 K (**6**), with the 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 programs.[S5] The structure was 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 of **3a, 4b, 5-7** is given in Table S1.

References

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S4 G. W. Sheldrick, *SADABS* version 2.10; University of Göttingen, 2001.

S5 *SHELXTL* version 6.14; Bruker AXS Inc.: Madison, Wisconsin, USA, 2000.

Table S1. Selected Crystallographic Data for **3a, 4b, 5-7**.

	3b	**4a**	**5**	**6**	**7**
formula	$C_{29}H_{29}I_2N_2PPd$	$C_{31}H_{25}F_6O_4N_2PPd$	$C_{22}H_{28}N_4Br_4Pd_2$	$C_{11}H_{14}N_2ClAu$	$C_{17}H_{22}N_2ClRh$
fw	796.71	740.9	880.92	406.66	392.73
color, habit	yellow, block	colorless, block	orange, block	yellow, block	yellow, block
cryst size [mm]	0.24 x 0.08 x 0.06	0.56 x 0.36 x 0.20	0.30 x 0.23 x 0.16	0.30 x 0.20 x 0.12	0.30 x 0.20 x 0.06
temp [K]	223(2)	223(2)	223(2)	100(2)	223(2)
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	*P*2(1)/*n*	*P*-1	*P*2(1)/*n*	*P*2(1)/*c*	*P*-1
a[Å]	11.4399(10)	9.4768(5)	9.5153(16)	8.5290(6)	7.0142(4)
b [Å]	15.6813(14)	11.0752(6)	11.2069(18)	8.5217(6)	9.5187(6)
c [Å]	16.1726(14)	15.6695(9)	12.916(2)	17.3001(11)	12.8813(8)
α [deg]	90	107.8900(10)	90	90	75.2460(10)
β [deg]	99.776(2)	100.5030(10)	95.929(4)	103.8820(10)	82.9050(10)
γ [deg]	90	96.7700(10)	90	90	74.5310(10)
V [Å^3]	2859.1(4)	1512.08(14)	1369.9(4)	1220.67(14)	800.12(8)
Z	4	2	2	4	2
D_c [g cm^{-3}]	1.851	1.627	2.136	2.213	1.630
radiation used	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ [mm^{-1}]	2.885	0.743	7.164	12.240	1.229
θ range [deg]	1.82–27.50	1.40–27.50	2.41–27.50	2.43–27.50	1.64–27.50
no. of unique data	19912	18022	9280	8394	5717
max., min. transmn	0.8459, 0.5443	0.8656, 0.6809	0.3936, 0.2224	0.3213, 0.1204	0.9299, 0.7094
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0521$, $wR_2 = 0.1156$	$R_1 = 0.0287$, $wR_2 = 0.0734$	$R_1 = 0.0645$, $wR_2 = 0.1771$	$R_1 = 0.0191$, $wR_2 = 0.0461$	$R_1 = 0.0336$, $wR_2 = 0.0829$
R indices (all data)	$R_1 = 0.0652$, $wR_2 = 0.1216$	$R_1 = 0.0302$, $wR_2 = 0.0744$	$R_1 = 0.1019$, $wR_2 = 0.1968$	$R_1 = 0.0206$, $wR_2 = 0.0467$	$R_1 = 0.0358$, $wR_2 = 0.0842$
goodness-of-fit on F^2	1.075	1.053	1.052	1.065	1.065
peak/hole [e Å^{-3}]	1.391/–1.437	0.792/–0.723	2.959/–0.993	1.301/–0.791	1.025/–0.466