Imidazo[1,5-a]pyridine: A versatile architecture for stable N-heterocyclic carbenes

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SUPPORTING INFORMATION

General Experimental Procedures: Melting points were determined using a metal block and are uncorrected. Optical rotations were measured at room temperature. \(^1\)H and \(^{13}\)C-NMR spectra were obtained in CDCl\(_3\), C\(_6\)D\(_6\), or acetone-d\(_6\) as the solvent. EI-mass spectra were recorded at 70 eV, using an ionizing current of 100 mA, an accelerating voltage of 4kV, and a resolution of 1000 or 10000 (10% valley definition). The reactions were monitored by TLC. Solvents were dried using standard techniques.

2,5-Dimethylimidazo[1,5-a]pyridinium iodide (2a): To a solution of 1 (600 mg, 4.6 mmol) in dry THF (2 mL) was added MeI (3.2 g, 23 mmol) and the mixture was stirred at 40 °C for 24 h. The yellow precipitate formed was filtered, washed with dry Et\(_2\)O and dried \textit{in vacuo} to afford 1 in 97% yield as a hygroscopic powder. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.57 (s, 1H), 8.13 (d, \(J = 1.6 \) Hz, 1H), 7.62 (d, \(J = 9.3 \) Hz, 1H), 7.17 (dd, \(J = 6.9, 9.3 \) Hz, 1H), 6.88 (d, \(J = 6.9 \) Hz, 1H), 4.46 (s, 3H), 2.83 (s, 3H). \(^{13}\)C NMR (50 MHz, CDCl\(_3\)) \(\delta\) 133.6, 130.7, 126.1, 126.0, 117.1, 116.2, 115.2, 38.7, 19.7. Anal. Calcd for C\(_9\)H\(_{11}\)N\(_2\)I (%): C 39.44; H 4.04; N 10.22, found: C 39.49; H 4.12; N 10.19.

2-Benzyl-5-methylimidazo[1,5-a]pyridinium bromide (2b): To a solution of 1 (1g, 7.6 mmol) in dry THF (5 mL) was added BnBr (5.2 g, 30.3 mmol) and the mixture was heated at 60 °C overnight. The hygroscopic off-white precipitate formed was washed and dried \textit{in vacuo} to give 2b in 94% yield. \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\) 11.24 (s, 1H), 8.07 (d, \(J = 1.4 \) Hz, 1H), 7.69 (m, 2H), 7.50 (d, \(J = 9.3 \) Hz, 1H), 7.32 (m, 3H), 7.09 (dd, \(J = 6.9, 9.3 \) Hz, 1H).
= 6.8, 9.3 Hz, 1H), 6.80 (d, J = 6.8 Hz, 1H), 6.01 (s, 2H), 2.80 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 135.6, 130.4, 129.5, 129.4, 129.0, 128.4, 125.7, 125.4, 116.4, 115.8, 113.0, 54.1, 18.9. Anal. Calcd for C$_{15}$H$_{15}$N$_2$Br (%): C 59.42; H 4.99; N 9.24, found: C 59.19; H 4.68; N 8.98.

2-Isopropyl-3-phenylimidazo[1,5-a]pyridinium iodide (10a): To a solution of 3-phenylimidazo[1,5-a]pyridine (980 mg, 5 mmol) in toluene (5 mL) was added isopropyl iodide (5.1 g, 30.0 mmol) and the mixture was heated at 60 ºC for 3 days. The hygroscopic off-white precipitate formed was filtered, washed with pentane, and dried in vacuo to afford 10a in 59% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.73 (s, 1H), 7.95 (d, J = 9.6 Hz, 1H), 7.60-7.80 (m, 6H), 7.20 (dd, J = 9.2, 6.8 Hz, 1H), 7.05 (dd, J = 8.8, 6.0 Hz, 1H), 4.70 (m, J = 6.8 Hz, 1H), 1.66 (d, J = 6.8 Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 133.2, 132.5, 131.0, 130.7, 130.3, 124.7, 121.5, 120.4, 119.7, 118.9, 111.9, 53.0, 23.8. Anal. Calcd for C$_{16}$H$_{17}$N$_2$I (%): C 52.76; H 4.70; N 7.69, found: C 52.84; H 4.62; N 7.75.

General procedure for the direct synthesis of imidazo[1,5-a]pyridinium salts: To a solution of amide 5c-f or N-mesityl, N-(pyridin-2-yl)methy benzamide (4 mmol) in toluene (10 mL) was added POCl$_3$ (410 µl, 4.4 mmol) and the mixture was stirred at 80º C overnight. Solvents were then removed in vacuo and residue was purified by column chromatography (95:5→90:10 DCM:MeOH) to afford salts 2 or 10b as chlorides. Hexafluorophosphates were obtained by addition of a saturated solution of KPF$_6$ (1.1 eq.) in water to solutions of the chlorides in the minimum amount of water. The white precipitates formed were filtered, washed with Et$_2$O and crystallised from acetone- Et$_2$O.

2-Benzylimidazo[1,5-a]pyridinium chloride (2c): 50% yield. $^1$H NMR (300 MHz, CD$_3$OD) δ 9.52 (s, 1H), 8.45 (d, J = 6.6 Hz, 1H), 8.10 (s, 1H), 7.75 (d, J = 8.7 Hz, 1H), 7.45-7.55 (m, 5H), 7.22-7.28 (m, 1H), 7.15 (t, J = 6.6 Hz, 1H), 5.72 (s, 2H); $^{13}$C NMR (75 MHz, CD$_3$OD) δ 129.5, 129.4, 128.9, 125.1, 125.0, 124.0, 118.2, 118.0, 113.3, 54.1. Anal. Calcd for C$_{14}$H$_{13}$ClN$_2$: C 68.71; H 5.35; N11.45. Found C 68.45; H 5.67; N 11.67.
2-Benzylimidazo[1,5-a]quinolinium chloride [2d(Cl)]: 59% yield. $^1$H NMR (300 MHz, CD$_3$OD) $\delta$ 10.45 (s, 1H), 8.26-8.42 (m, 1H), 8.02-8.15 (m, 1H), 7.35-7.95 (m, 1H), 5.75 (br s, 2H); $^{13}$C NMR (75 MHz, CD$_3$OD) $\delta$ 134.0, 130.5, 129.8, 129.4, 129.3, 128.8, 127.1, 124.8, 116.4, 115.3, 114.7, 54.3. Anal. Calcd for C$_{18}$H$_{15}$N$_2$Cl (%): C 73.34; H 5.13; N 9.50; found: C 72.94; H 4.86; N 9.23.

2-Benzylimidazo[1,5-a]quinolinium hexafluorophosphate [2d(PF$_6$)]: 58% yield; m.p. 144-146 °C. $^1$H NMR (300 MHz, acetone-d$_6$) $\delta$ 10.45 (s, 1H), 8.46 (d, $J = 8.2$ Hz, 1H), 8.25 (s, 1H), 8.05 (d, $J = 7.1$ Hz, 1H), 7.95-7.56 (m, 6H), 7.43 (br s, 3H), 5.89 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 134.9, 131.3, 130.7, 130.4, 130.3, 130.2, 130.1, 129.7, 128.4, 127.8, 125.5, 117.3, 116.3, 115.9, 55.0. Anal. Calcd for C$_{18}$H$_{15}$N$_2$F$_6$P (%): C 53.47; H 3.74; N 6.93, found: C 59.19; H 4.68; N 8.98.

2-Mesityl-5-methylimidazo[1,5-a]pyridinium hexafluorophosphate (2e): 52% yield; m.p. 218-219 °C. $^1$H NMR (300 MHz, acetone-d$_6$) $\delta$ 9.80 (s, 1H), 8.34 (d, $J = 1.5$ Hz, 1H), 7.94 (s, 1H), 7.45 (dd, $J = 9.3$, 6.9Hz, 1H), 7.23 (d, $J = 6.9$ Hz, 1H), 7.19 (s, 2H), 2.86 (s, 3H), 2.39 (s, 3H), 2.09 (s, 6H). $^{13}$C NMR (75 MHz, acetone-d$_6$) $\delta$ 142.1, 135.5, 134.8, 132.6, 132.3, 130.3, 126.9, 126.0, 117.9, 117.1, 116.1, 21.0, 17.9, 17.2. Anal. Calcd for C$_{17}$H$_{19}$N$_2$F$_6$P (%): C 51.52; H 4.83; N 7.07 found: C 51.43; H 4.38; N 7.01.

2-t-Butylimidazo[1,5-a]pyridinium hexafluorophosphate (2f): 48% yield. $^1$H NMR (300 MHz, acetone-d$_6$) $\delta$ 9.69 (s, 1H), 8.52 (d, $J = 7.2$ Hz, 1H), 8.39 (s, 1H), 7.84 (d, $J = 9.3$ Hz, 1H), 7.33 (t, $J = 6.6$ Hz, 1H), 7.25 (t, $J = 6.9$ Hz, 1H), 1.87 (s, 9H). $^{13}$C NMR (75 MHz, acetone-d$_6$) $\delta$ 131.1, 125.7, 125.5, 124.9, 119.1, 118.6, 112.1, 62.3, 29.9. Anal. Calcd for C$_{11}$H$_{15}$N$_2$F$_6$P (%): C 41.26; H 4.72; N 8.75, found: C 41.31; H 4.28; N 8.50

2-Mesityl-3-phenylimidazo[1,5-a]pyridinium chloride (10b): This product was prepared following the general procedure but heating was prolonged for 7 days. Very hygroscopic yellow foam. 58% yield. $^1$H NMR (400 MHz, acetone-d$_6$) $\delta$ 8.51 (s, 1H), 8.47 (d, $J = 6.4$ Hz, 1H), 8.09 (d, $J = 8.4$ Hz, 1H), 7.73 (d, $J = 7.2$ Hz, 2H), 7.61 (m, 3H), 7.47 (t, $J = 6.8$ Hz, 1H), 7.33 (t, $J = 6.8$ Hz, 1H), 7.06 (s, 2H), 2.29 (s, 3H), 2.06 (s, 6H); $^{13}$C
NMR (100 MHz, acetone-\textit{d}_6) \delta 142.0, 135.7, 135.3, 133.4, 131.9, 1301.6, 131.0, 130.6, 130.5, 126.6, 124.2, 122.1, 120.0, 119.7, 116.4, 21.0, 17.8. Anal. Calcd for C_{22}H_{21}N_{2}Cl (%): C 75.74; H 6.07; N 8.03, found: C 76.01; H 6.31; N 7.87.

**General procedure for the synthesis of carbenes 4:** Inside a dry box, a schlenk flask equipped with a magnetic stir bar was charged with 2 (1 mmol), NaH (29 mg, 1.1 mmol ) and a catalytic amount of KO{\textsuperscript{t}Bu. Dry THF (5 mL) was added and the resulting pink-orange mixture was stirred for 2 hours at r.t. Then the solvent was evaporated \textit{in vacuo} and dry toluene (10 mL) was added via syringe. The mixture was then filtered through a celite plug and washed again with toluene (10 mL). Combined filtrates were evaporated \textit{in vacuo} to afford crude free carbenes 4 as syrups. These compounds were used without further purification.

2,5-Dimethylimidazo[1,5-\textit{a}]pyridine-3-ylidene (4a): \textsuperscript{1}H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}) \delta 6.87 (d, J = 9.5 Hz, 1H), 6.59 (s, 1H), 6.34 (dd, J = 6.5, 9.5 Hz, 1H), 5.86 (d, J = 6.5 Hz, 1H), 3.60 (s, 3H), 2.72 (s, 3H). \textsuperscript{13}C NMR (125MHz, C\textsubscript{6}D\textsubscript{6}) \delta 206.9, 139.6, 131.5, 121.1, 114.5, 110.1, 108.9, 38.4, 19.8.

2-Benzyl-5-methylimidazo[1,5-\textit{a}]pyridine-3-ylidene (4b): \textsuperscript{1}H NMR (300 MHz, C\textsubscript{6}D\textsubscript{6}) \delta 7.16-6.98 (m, 5H), 6.80 (d, J = 9.9 Hz, 1H), 6.64 (s, 1H), 6.31 (dd, J = 6.6, 9.0 Hz, 1H), 5.85 (d, J = 6.3 Hz, 1H), 5.28 (s, 2H), 2.77 (s, 3H). \textsuperscript{13}C NMR (75 MHz, C\textsubscript{6}D\textsubscript{6}) \delta 206.2, 139.7, 138.4, 131.8, 128.4, 127.8, 127.4, 121.2, 114.8, 109.3, 109.1, 55.9, 19.8.

2-Mesyl-5-methyl imidazo[1,5-\textit{a}]pyridine-3-ylidene (4e): \textsuperscript{1}H NMR (300 MHz, C\textsubscript{6}D\textsubscript{6}) \delta 6.90 (d, J = 9.0 Hz, 1H), 6.76 (s, 2H) 6.68 (s, 1H), 6.35 (dd, J = 6.6, 9.3 Hz, 1H), 5.89 (d, J = 6.2 Hz, 1H), 2.71 (s, 3H), 2.12 (s, 3H), 1.95 (s, 6H). \textsuperscript{13}C NMR (50 MHz, CDCl\textsubscript{3}) \delta 206.9, 140.0, 139.0, 137.2, 134.7 131.2, 128.7, 121.4, 115.0, 111.1, 109.5, 20.6, 19.7, 17.4.

2-Benzylimidazo[1,5-\textit{a}]quinoline-3-ylidene (4d): \textsuperscript{1}H NMR (500 MHz, C\textsubscript{6} D\textsubscript{6}) \delta 9.44 (d, J = 8.5 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.15 (d, J =6.5 Hz, 2H), 7.09 (d, J = 7.0 Hz, 2H),
7.05-6.98 (m, 4H), 6.61 (d, J = 9.5 Hz, 1H), 5.56 (d, J = 9.5 Hz, 1H), 6.48 (s, 1H), 5.25 (s, 2H). $^{13}$C NMR (75 MHz, CD$_6$D$_6$) δ 208.7, 138.3, 137.3, 136.5, 129.7, 128.8, 128.5, 127.5, 124.7, 123.8, 122.9, 117.6, 115.7, 111.7, 55.8.

General procedure for the synthesis of complexes 5 and 11: To a solution of 2a-c, 2d(Cl), or 10a (3 mmol) in CH$_2$Cl$_2$ (50 mL) was added solid Ag$_2$O (370.7 mg, 1.6 mmol) and the mixture was stirred in darkness at r.t. during two hours. The solution was then filtered through a celite plug and the filtrate was evaporated in vacuo.

Iodo(2,5-dimethylimidazo[1,5-a]pyridine-3-ylidene)silver (I) (5a): Following the general procedure but using 300 ml of DCM. White solid, 63% yield. $^1$H NMR (200 MHz, CDCl$_3$) δ 7.51 (s, 1H), 7.31 (d, J = 9.2 Hz, 1H), 6.83 (dd, J = 5.8, 9.3 Hz, 1H), 6.47 (d, J = 5.8 Hz, 1H), 4.30 (s, 3H), 3.01 (s, 3H). Anal. Calcd for C$_9$H$_{10}$N$_2$AgI (%): C 28.30; H 2.90; N 7.33, found: C 27.94; H 2.65; N 6.98. No further characterization was done due to the poor solubility of 5a in all common organic solvents.

Bromo(2-benzyl-5-methylimidazo[1,5-a]pyridine-3-ylidene)silver (I) (5b): Off white solid, 92% yield. $^1$H NMR (200 MHz, CDCl$_3$) δ 7.45-7.25 (m, 7H), 6.78 (dd, J = 6.7, 9.3 Hz, 1H), 6.53 (dt, J = 1.1, 6.7 Hz, 1H), 5.64 (s, 2H), 3.00 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 136.1, 135.2, 132.9, 129.2, 128.9, 128.1, 123.1, 115.9, 114.3, 111.7, 58.0, 21.7, Carbene carbon signal not found. Anal. Calcd for C$_{15}$H$_{14}$N$_2$AgBr (%): C 43.83; H 3.68; N 6.81, found: C 44.09; H 3.84; N 6.97.

Chloro(2-benzylimidazo[1,5-a]quinoline-3-ylidene)silver (I) (5d): White foam, 96% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.24 (d, J = 8.4 Hz, 1H), 7.54 (dd, J = 7.6, 1.6 Hz, 1H), 7.48 (dt, J = 7.6, 1.6 Hz, 1H), 7.41 (dt, J = 7.6, 1.2 Hz, 1H), 7.32-7.28 (m, 6H), 7.10 (s, 2H), 5.57 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.9, 135.1, 133.2, 131.0, 129.6, 129.3, 129.0, 128.1, 127.1, 125.3, 124.6, 116.1, 115.1, 113.7, 58.2. Anal. Calcd for C$_{18}$H$_{14}$N$_2$AgCl (%): C 53.83; H 3.51; N 6.97, found: C 54.15; H 3.76; N 7.12.
(2-Benzylimidazo[1,5-a]pyridine-3-ylidene) chloro silver (I) (5c): White foam, 98% yield. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.26 (dd, $J = 7.2$, 0.9 Hz, 1H), 7.40-7.20 (m, 6H), 6.86 (dd, $J = 8.7$, 2.4 Hz, 1H), 6.64 (t, $J = 7.5$ Hz, 1H), 5.50 (s, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 171.7, 135.4, 131.9, 129.5, 129.2, 128.7, 128.3, 123.7, 117.7, 114.5, 111.2, 57.3. Anal. Calcd for C$_{14}$H$_{12}$N$_2$AgCl (%): C 47.83; H 3.44; N 7.97, found: C 47.98; H 3.77; N 7.66.

Iodo(2-Isopropyl-3-phenylimidazo[1,5-a]pyridine-1-ylidene)silver (I) (11): White foam, 89% yield. $^1$H NMR (500 MHz, CD$_2$Cl$_2$) δ 7.79 (d, $J = 9.5$ Hz, 1H), 7.73 (m, 3H), 7.68 (d, $J = 7.0$ Hz, 1H), 7.50 (m, 2H), 6.88 (dd, $J = 9.0$, 6.5 Hz, 1H), 6.80 (t, $J = 6.0$ Hz, 1H), 4.76 (sep, $J = 6.5$ Hz, 1H), 1.76 (d, $J = 6.5$ Hz, 6H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 150.8, 137.5, 133.5, 132.1, 130.7, 130.5, 125.5, 123.9, 121.1, 119.9, 117.9, 52.0, 24.7. Anal. Calcd for C$_{16}$H$_{16}$N$_2$AgI (%): C 40.79; H 3.42; N 5.95, found: C 41.04; H 3.34; N 5.69.

**General procedure for the synthesis of complexes 6 and 12 by transmetallation from silver carbenes:** To a solution of 5 or 11 (1 mmol) in CH$_2$Cl$_2$ (20 mL) was added [RhCl(COD)]$_2$ (246 mg, 0.5 mmol) and the mixture was stirred during three hours. The reaction mixture was then filtered through a celite plug and concentrated to afford 6 as a yellow solid that was purified by crystallization from CH$_2$Cl$_2$-Et$_2$O (6a, 6b, and 6e) or by column chromatography (1:2 AcOEt-Hexane) (6f and 12).

Chloro(1,5-cyclooctadiene)(2,5-dimethylimidazo[1,5-a]pyridine-3-ylidene)rhodium (I) (6a) 91% yield. m.p. 156-157 °C (dec). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.22 (s, 1H), 7.04 (d, $J = 9.2$ Hz, 1H), 6.63 (dd, $J = 6.5$, 9.2 Hz, 1H), 6.30 (dt, $J = 1.0$, 6.5 Hz, 1H), 5.07 (m, 2H), 4.58 (s, 3H), 3.78 (s, 3H), 3.18 (m, 2H), 2.60-2.30 (m, 4H), 2.07-1.73 (m, 4H). $^{13}$C NMR (50 MHz, CDCl$_3$) δ 172.3 (d, $J_{C-Rh} = 51$ Hz), 137.8, 133.9, 122.2, 115.7, 113.0, 112.9, 97.6 (d, $J_{C-Rh} = 7.5$ Hz), 95.9 (d, $J_{C-Rh} = 7.5$ Hz), 69.9 (d, $J_{C-Rh} = 15$ Hz), 68.0 (d, $J_{C-Rh} = 15$ Hz), 40.8, 33.7, 32.7, 29.7, 29.1, 24.0. Anal. Calcd for C$_{17}$H$_{22}$N$_2$RhCl (%): C 51.99; H 5.65; N 7.13, found: C 51.87; H 5.83; N 7.21.
(2-Benzyl-5-methylimidazo[1,5-a]pyridine-3-ylidene)chloro(1,5-cyclooctadiene)rhodium (I) (6b) 96% yield. m.p. 177-178 °C (dec). This procedure invariably affords complex 6b contaminated with a 15% of the bromide analogue (6bBr): The mixture was transformed in 6bBr by addition of NaBr to a solution of 6b in CHCl₃.

6b ¹H NMR (400 MHz, CDCl₃) δ 7.49 (m, 2H), 7.38 (m, 3H), 7.00 (s, 1H), 6.98 (d, J = 9.2 Hz, 1H), 6.75 (d, J = 14.6 Hz, 1H), 6.61 (dd, J = 6.5, 9.2 Hz, 1H), 6.31 (d, J = 6.5 Hz, 1H), 6.11 (d, J = 14.6 Hz, 1H). 5.11 (br s, 2H), 3.84 (s, 3H), 3.28 (br s, 2H), 2.50-2.25 (m, 4H), 2.07-1.70 (m, 4H). ¹³C NMR (50 MHz, CDCl₃) δ 172.7 (d, J_C-Rh = 50.2 Hz), 138.0, 136.6, 134.2, 129.4, 129.1, 128.8, 116.0, 113.1, 111.4, 97.9 (d, J_C-Rh = 7.5 Hz), 96.0 (d, J_C-Rh = 7.5 Hz), 70.2 (d, J_C-Rh = 15 Hz), 68.3 (d, J_C-Rh = 15 Hz), 57.8, 33.5, 32.8, 29.7, 29.2, 23.9; 6bBr ¹H NMR (400 MHz, CDCl₃) δ 7.47 (m, 2H), 7.36 (m, 3H), 6.98 (s, 1H), 6.95 (d, J = 9.2 Hz, 1H), 6.66 (d, J = 14.6 Hz, 1H), 6.61 (dd, J = 6.5, 9.2 Hz, 1H), 6.30 (d, J = 6.5 Hz, 1H), 6.07 (d, J = 14.6 Hz, 1H), 5.19 (br s, 2H), 3.81 (s, 3H), 3.37 (m, 2H), 2.60-2.28 (m, 4H), 2.09-1.94 (m, 1H), 1.90-1.73 (m, 3H). ¹³C NMR (50 MHz, CDCl₃) δ 172.4 (d, J_C-Rh = 50.0 Hz), 137.9, 136.5, 134.3, 129.4, 129.2, 128.8, 122.3, 116.0, 113.1, 111.6, 97.2 (d, J_C-Rh = 7.0 Hz), 95.6 (d, J_C-Rh = 7.0 Hz), 70.2 (d, J_C-Rh = 15 Hz), 69.2 (d, J_C-Rh = 15 Hz), 57.7, 33.6, 32.4, 30.1, 29.2, 23.8. Anal. Calcd for C₂₃H₂₂N₂RhBr (%): C 53.82; H 5.11; N 5.46, found: C 53.80; H 5.42; N 5.32.

(2-Benzylimidazo[1,5-a]quinoline-3-ylidene)chloro(1,5-cyclooctadiene)rhodium (I) (6d): 92% yield. m.p. 243-245 °C (dec). ¹H NMR (300 MHz, CDCl₃) δ 11.56 (d, J = 8.4 Hz, 1H), 7.78 (t, J = 8.4 Hz, 1H), 7.62-7.30 (m, 5H), 6.98 (d, J = 8.1 Hz, 1H), 6.92 (s, 1H), 6.56 (d, J = 14.7 Hz, 1H), 6.17 (d, J = 14.7 Hz, 1H), 5.30 (m, 1H), 5.18 (m, 1H), 3.29 (m, 1H), 3.18 (m, 1H), 2.55 (m, 1H), 2.50-2.20 (m, 3H), 2.10-1.75 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 177.4 (d, J_C-Rh = 63.7 Hz), 136.3, 134.6, 131.8, 129.3, 129.0, 128.8, 128.7, 128.4, 126.4, 125.1, 124.5, 121.1, 115.6, 113.3, 98.8 (d, J_C-Rh = 7.3 Hz), 97.2 (d, J_C-Rh = 7.2 Hz), 70.7 (d, J_C-Rh = 14.5 Hz), 69.4 (d, J_C-Rh = 14.7 Hz), 57.9, 33.0, 32.9, 29.5, 29.3. Anal. Calcd for C₂₆H₂₆N₂RhCl (%): C 61.85; H 5.19; N 5.55, found: C 61.76; H 5.23; N 5.43.
(2-Benzylimidazo[1,5-a]pyridine-3-ylidene)chloro(1,5-cyclooctadiene)rhodium (I) (6c): 96% yield. m.p. 178-179 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.93 (dd, J = 7.2, 0.6 Hz, 1H), 7.40-7.26 (m, 5H), 7.04 (d, J = 9.6 Hz, 1H), 6.95 (s, 1H), 6.70 (dd, J = 6.4, 0.8 Hz, 1H), 6.52 (dt, J = 6.4, 0.8 Hz, 1H), 6.02 (d, J = 14.8 Hz, 1H), 5.94 (d, J = 14.8 Hz, 1H), 5.13 (m, 1H) 3.35 (m, 1H), 3.25 (m, 1H), 2.60-2.33 (m, 3H), 2.25 (m, 1H), 1.97 (m, 1H), 1.86 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 173.7 (d, J_C-Rh = 52.7 Hz), 136.2, 131.7, 129.0, 128.6, 128.5, 128.4, 122.3, 117.4, 112.4, 110.7, 99.94 (d, J_C-Rh = 4.8 Hz), 68.8 (d, J_C-Rh = 14.2 Hz), 68.6 (d, J_C-Rh = 14.4 Hz), 55.9, 33.2, 32.9, 29.0, 28.9. Anal. Calcd for C₂₂H₂₄N₂RhCl (%): C 58.10; H 5.32; N 6.16, found: C 57.98; H 5.45; N 6.40.

Chloro(1,5-cyclooctadiene)(2-Isopropyl-3-phenylimidazo[1,5-a]pyridine-1-ylidene)iridium (I) (12): 38% yield, yellow foam. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 7.4 Hz, 1H), 7.70-7.55 (m, 3H), 7.42 (d, J = 6.0 Hz, 1H), 7.38 (d, J = 6.4 Hz, 1H), 7.20 (d, J = 5.2 Hz, 1H), 6.63-6.54 (m, 2H), 5.90 (sep, J = 6.8 Hz, 1H), 4.56 (m, 1H), 4.42 (m, 1H), 3.12 (m, 1H), 3.04 (m, 1H), 2.33 (m, 2H), 2.18 (m, 2H), 1.77 (m, 1H), 1.61 (m, 3H), 1.53 (d, J = 6.8 Hz, 3H), 1.49 (d, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.8, 131.8, 131.6, 131.5, 130.6, 129.9, 129.7, 125.9, 125.8, 119.7, 117.6, 116.3, 81.4, 81.0, 57.9, 53.3, 50.7, 34.5, 33.3, 30.3, 29.6, 23.9, 23.2. Anal. Calcd for C₂₄H₂₈N₂RhCl (%): C 50.38; H 4.93; N 4.90, found: C 50.29; H 4.86; N 4.78.

General procedure for the direct synthesis of complexes (6): To a solution of carbene 4 (0.4 mL) in toluene (5 mL) was added [Rh(cod)Cl]₂ (93 mg, 0.19 mmol) and the mixture was stirred at room temperature for 2 h. Products 6 were isolated and purified as described above to afford 6a (93%), 6b (94%), or 6d (91%).

General procedure for the synthesis of complexes 7: To a slurry of [Rh(COD)Cl]₂ (74 mg, 0.15 mmol) in THF (4 mL) was added solid KO'Bu (68 mg, 0.6 mmol). The mixture was stirred for 5 min, and salt 2d(PF₆), 2e, or 2f was then added in one portion (0.6 mmol). The reaction mixture was stirred under argon overnight and the yellow-orange solid formed was filtered and washed with Et₂O (2 × 2 mL). Crystallization was performed by slow diffusion of Et₂O in a DCM solution of the complex.
Bis(2-benzylimidazo[1,5-a]quinoline-3-ylidene)(1,5-cyclooctadiene)rhodium (I) hexafluorophosphate (7d): 71% yield. m.p. 220-221 °C (dec). $^1$H NMR (400 MHz, acetone-$d_6$) δ 12.00 (d, $J = 8.4$ Hz, 2H), 7.92 (t, $J = 6.8$ Hz, 2H), 7.71 (d, $J = 6.4$ Hz, 2H), 7.64 (t, $J = 6.8$ Hz, 2H), 7.51 (s, 2H), 7.17 (d, $J = 9.6$ Hz, 2H), 7.11 (d, $J = 9.6$ Hz, 2H), 7.00 (t, $J = 7.2$ Hz, 2H), 6.91 (t, $J = 7.6$ Hz, 4H), 6.25 (d, $J = 7.2$ Hz, 4H), 6.12 (d, $J = 16$ Hz, 2H), 5.68 (d, $J = 16$ Hz, 2H), 5.33 (t, $J = 7.2$ Hz, 2H), 3.88 (dd, $J = 14.8$, 6.8 Hz, 2H), 3.22 (m, 2H), 2.55 (dd, $J = 15.6$, 6.4 Hz, 2H), 2.20 (m, 2H), 1.85 (m, 2H). $^{13}$C NMR (100 MHz, acetone-$d_6$) δ 173.5 (d, $J = 54.4$ Hz), 136.4, 134.6, 133.7, 130.0, 128.8, 128.1, 128.0, 127.6, 126.7, 125.9, 124.9, 121.8, 117.1, 116.8, 94.3 (d, $J = 8.7$ Hz), 87.1 (d, $J = 7.6$ Hz), 56.8, 35.6, 27.7. Anal. Calcd for C$_{44}$H$_{40}$N$_4$RhF$_6$P (%): C 60.56; H 4.62; N 6.42, found C 60.41; H 4.48; N 6.26.

Bis(2-mesityl-5-methylimidazo[1,5-a]pyridine-3-ylidene)(1,5-cyclooctadiene)rhodium (I) hexafluorophosphate (7e): 72% yield. m.p. 152-153 °C (dec). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.25 (d, $J = 8.8$ Hz, 2H), 7.10 (s, 2H), 7.07 (s, 2H), 6.87 (dd, $J = 8.8$, 6.4 Hz, 2H), 6.38 (d, $J = 6.4$ Hz, 2H), 5.10 (t, $J = 7.2$ Hz, 2H), 3.60 (q, $J = 7.9$ Hz, 2H), 3.25 (s, 6H), 2.26 (s, 6H), 2.30 (m, 2H), 1.97 (m, 4H), 1.73 (s, 6H), 1.45 (m, 2H), 0.76 (m, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 168.7 (d, $J = 53.9$ Hz), 140.2, 138.6, 136.8, 135.2, 134.8, 134.9, 139.3, 129.7, 122.9, 116.6, 116.2, 115.2, 90.1 (d, $J = 9.8$ Hz), 82.9 (d, $J = 7.8$ Hz), 34.8, 27.0, 22.1, 21.4, 18.2, 17.2. Anal. Calcd for C$_{42}$H$_{48}$N$_4$RhF$_6$P (%): C 58.88; H 5.65; N 6.54, found: C 58.96; H 5.72; N 6.35.

Bis(2-t-butylimidazo[1,5-a]pyridine-3-ylidene)(1,5-cyclooctadiene)rhodium (I) hexafluorophosphate (7f): 84 % yield. m.p. 201-202 °C. $^1$H NMR (400 MHz, acetone-$d_6$) δ 9.62 (dd, $J = 7.2$, 0.8 Hz, 2H), 7.88 (s, 2H), 7.47 (d, $J = 8.8$ Hz, 2H), 7.03-6.96 (m, 6H), 4.82 (t, $J = 7.2$ Hz, 2H), 3.80 (q, $J = 7.2$ Hz, 2H), 2.98 (m, 2H), 2.48 (m, 2H), 2.28 (m, 2H), 1.87 (m, 2H), 1.57 (s, 18H). $^{13}$C NMR (100 MHz, acetone-$d_6$) δ 167.2 (d, $J = 54.9$ Hz), 132.3, 131.4, 122.7, 119.3 114.3, 93.6 (d, $J = 8.8$ Hz), 87.6 (d, $J = 8.1$ Hz), 60.2, 35.5, 31.2, 26.8. Anal. Calcd for C$_{30}$H$_{40}$N$_4$RhF$_6$P (%): C 51.14; H 5.72; N 7.95, found: C 50.96; H 5.72; N 7.55.
Chloro(1,5-cyclooctadiene)(2-mesityl-3-phenylimidazo[1,5-a]pyridine-1-ylidene)rhodium (I) (13): To a slurry of [Rh(COD)Cl]_2 (74 mg, 0.15 mmol) in dry THF (4 mL) was added solid KN(SiMe_3)_2 (60 mg, 0.3 mmol). The resulting solution was stirred for 5 min, and salt 10b (0.3 mmol) was then added in one portion. The reaction mixture was stirred under argon overnight, concentrated, and the yellow residue was purified by column chromatography (1:2 AcOEt-hexane) to afford 13 in 39% yield. Crystals suitable for X-ray diffraction may be grown by slow diffusion of pentane in a CH_2Cl_2 solution of the complex. ^1H NMR (500 MHz, CDCl_3) δ 8.46 (m, 1H), 7.89 (m, 1H), 7.34 (m, 3H), 7.16 (m, 2H), 7.11 (br s, 1H), 6.76 (m, 2H), 6.67 (br s, 1H), 4.18 (br s, 2H), 3.58 (br s, 1H), 2.80 (br s, 1H), 2.60 (br s, 3H), 2.46 (br s, 1H), 2.31 (s, 3H), 2.18 (br s, 1H), 2.02 (br s, 1H), 1.87 (br s, 1H), 1.76 (br s, 1H), 1.67 (br s, 1H), 1.42 (br s, 3H). ^13C NMR (125 MHz, CDCl_3) δ 162.4 (d, J_C-Rh = 47.5 Hz), 138.8, 135.8, 134.1, 132.8, 130.1, 129.3, 128.7, 128.6, 128.1, 124.1, 119.7, 118.8, 117.2, 95.2 (br s), 69.4 (br s), 65.9 (br s), 34.5 (br s), 31.5 (br s), 29.7 (br s), 28.0, 21.1, 20.9 (br s), 17.8 (br s). Anal. Calcd for C_{30}H_{32}N_2RhCl (%): C 64.46; H 5.77; N 5.01, found C 64.32; H 5.89; N 4.93.

Seleno lactame (15): KHMDS (100 mg, 0.5 mmol) and Se powder (80 mg, 1mmol) were added in one portion to a suspension of 10b (174 mg, 0.5 mmol) in THF (4 mL). After stirring for two days, the mixture was concentrated and the residue was purified by column chromatography (3:1 AcOEt-hexane) to afford 15 in 61% yield. ^1H NMR (300 MHz, CDCl_3) δ 8.08 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 5.7 Hz, 1H), 7.52 (m, 3H), 7.39 (m, 2H), 6.93 (s, 2H), 6.70 (m, 2H), 2.30 (s, 3H), 1.99 (s, 6H). ^13C NMR (100 MHz, CDCl_3) δ 148.4, 139.8, 135.7, 132.1, 131.8, 131.1, 130.9, 129.6, 129.0, 128.8, 124.3, 123.3, 119.9, 119.8, 118.1, 21.3, 18.6. HRMS: m/z calculated for C_{22}H_{20}N_2Se 392.0792, found 392.0781.

Chlorodicarbonyl(2,5-dimethylimidazo[1,5-a]pyridine-3-ylidene)rhodium (I) (16): A schlenk flask was charged with 6a (197 mg, 0.5 mmol) and dry THF (6 mL). CO was bubbled for 10 min and the solvent was evaporated in vacuo. The remaining oil was washed with hexane and dried to afford 16 in quantitative yield. ^1H NMR (500 MHz,
CDCl₃ δ 7.37 (s, 1H), 7.19 (d, J = 9.0 Hz, 1H), 6.77 (dd, J = 6.6, 9.0 Hz, 1H), 6.41 (dt, J = 0.9, 6.2 Hz, 1H), 4.30 (d, J = 0.6 Hz, 3H), 3.23 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 185.6 (d, J_CO-Rh = 33.0 Hz), 182.4 (d, J_CO-Rh = 44.7 Hz), 136.7, 133.6, 128.7, 122.8, 115.5, 113.9, 113.6, 41.1, 24.5; FTIR (CH₂Cl₂), ν_CO = 2079, 2000 cm⁻¹. HRMS: m/z calculated for C₁₁H₁₀N₂O₂Rh 339.9486, found 339.9483.

Chlorodicarbonyl(2-mesityl-3-phenylimidazo[1,5-a]pyridine-1-ylidene)rhodium (I) (17): Starting from 13, reaction with CO as above yielded 17 in quantitative yield as a light yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 8.18 (m, 1H), 7.94 (m, 1H), 7.42 (m, 3H), 7.24 (m, 3H), 6.88 (s, 2H), 6.84 (d, J = 1.2 Hz, 1H), 2.28 (s, 3H), 1.98 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 186.2 (d, J_CO-Rh = 52.6 Hz), 184.1 (br. s), 154.9 (d, J_C-Rh = 40.05), 139.8, 135.8, 134.9, 133.3, 131.2, 129.8, 129.6, 127.0, 123.8, 120.5, 119.3, 119.1, 21.4, 19.1 FTIR (CH₂Cl₂), ν_CO = 2072, 1992 cm⁻¹. Anal. Calcd for C₂₄H₂₀N₂O₂RhCl (%): C 56.88; H 3.98; N 5.53, found C: 56.70; H: 4.08; N: 5.76.