Isoquinolin-1-ylidenes as Electronically Tuneable Ligands

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ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

General Experimental Procedures: Solvents were purified and dried by standard procedures. Flash chromatography was carried out on silica-gel (0.040-0.063 mm or 0.015-0.040 mm). Melting points were measured in a metal block and are uncorrected. \(^1\)H NMR spectra were recorded at 300 MHz, 400 MHz or 500 MHz. \(^13\)C NMR spectra were recorded at 75 MHz, 100 MHz or 125 MHz with the solvent peak used as the internal reference. IR were recorded in solution (CH\(_2\)Cl\(_2\)). Reactions were monitored by tlc. Standard schlenk techniques were used for air and moisture sensitive manipulations. Isoquinolines 1a and 1d are commercially available; compounds 1b, 1c, 1e, 4a, and 5a were prepared following literature procedures.

General procedure for the synthesis of isoquinolinium iodides 2a-e:
A solution of isoquinoline 1a-e (10 mmol) and 2-iodopropane (3 mL, 30 mmol) in dry toluene (10 mL) was warmed at 90 °C until consumption of the starting material. The mixture was then cooled to RT and cyclohexane (10 mL) was added. The supernatant solution was taken off with a syringe, the residue dissolved in CH\(_2\)Cl\(_2\) (20 mL), and ether (50 mL) was added.

The resulting hygroscopic precipitate was dried *in vacuo*. Starting material, reaction times, yields and characterization data for 2a-e are as follows:

**Isoquinolinium iodide 2a:**

![Image](image1)

From 1a (1.2 mL) after 1 d, 2a (2.36 g, 79%) was obtained as a pale yellow solid. M.p. 95-96 °C. \( ^1 \)H NMR (CDCl\(_3\), 500 MHz) \( \delta \) 10.80 (s, 1H), 8.89 (d, \( J = 6.8 \) Hz, 1H), 8.75 (d, \( J = 8.3 \) Hz, 1H), 8.39 (d, \( J = 6.8 \) Hz, 1H), 8.05 (d, \( J = 8.3 \) Hz, 1H), 7.99 (t, \( J = 7.8 \) Hz, 1H), 7.78 (t, \( J = 6.8 \) Hz, 1H), 5.46 (m, \( J = 6.7 \) Hz, 1H), 1.74 (d, \( J = 6.7 \) Hz, 1H). \( ^{13} \)C NMR (CDCl\(_3\), 125.7 MHz) \( \delta \) 147.2, 137.2, 136.6, 132.3, 130.7, 130.6, 127.4, 126.6, 126.4, 64.2, 23.1. HRMS (FAB) calc.: C\(_{12}\)H\(_{14}\)N 172.1126 [M-I]\(^+\); found: 172.1131. Anal. Calc. for C\(_{12}\)H\(_{14}\)IN: C 48.12, H 4.72; found: C 47.92, H 5.01.

**Isoquinolinium iodide 2b:**

![Image](image2)

From 1b (1.43 g) after 36 h, 2b (2.32 g, 74%) was obtained as a pale yellow solid. M.p. 84-85 °C. \( ^1 \)H NMR (CDCl\(_3\), 500 MHz) \( \delta \) 10.48 (s, 1H), 8.82 (d, \( J = 7.0 \) Hz, 1H), 8.75 (d, \( J = 7.0 \) Hz, 1H), 7.93-7.98 (m, 2H), 7.69 (d, \( J = 6.6 \) Hz, 1H), 5.95 (m, \( J = 6.8 \) Hz, 1H), 3.05 (s, 3H), 1.80 (d, \( J = 6.8 \) Hz, 6H). \( ^{13} \)C NMR (CDCl\(_3\), 125.7 MHz) \( \delta \) 145.9, 140.4, 138.2, 137.0, 132.0, 131.0, 127.3, 127.1, 125.1, 64.5, 23.3, 20.3. HRMS (FAB) calc.: C\(_{13}\)H\(_{16}\)N 186.1283 [M-I]\(^+\); found: 186.1291. Anal. Calc. for C\(_{13}\)H\(_{16}\)IN: C 49.86, H 5.15; found: C 49.75, H 5.31.

**Isoquinolinium iodide 2c:**

![Image](image3)

From 1c (1.59 g) after 8 h, 2c (2.27 g, 69%) was obtained as a dark yellow solid. M.p. 122-123 °C. \( ^1 \)H NMR (CDCl\(_3\), 500 MHz) \( \delta \) 10.58 (s, 1H), 8.71 (d, \( J = 8.9 \) Hz, 1H), 8.64 (dd, \( J = 7.0 \) Hz, \( J = 2.0 \) Hz, 1H), 8.32 (d, \( J = 7.0 \) Hz, 1H), 7.47 (d, \( J = 8.9 \) Hz, 1H), 7.44 (d, \( J = 2.4 \) Hz, 1H), 7.42 (d, \( J = 2.4 \) Hz), 5.41 (m, \( J = 6.7 \) Hz, 1H), 4.04 (s, 3H), 1.79 (d, \( J = 6.7 \) Hz, 1H).
13C NMR (CDCl₃, 125.7 MHz) δ 166.2, 145.9, 140.6, 132.8, 132.3, 124.8, 124.3, 123.3, 105.2, 63.6, 56.9, 23.4. HRMS (FAB) calc.: C₁₃H₁₆NO 202.1232 [M-I]⁺; found: 202.1234. Anal. Calc. for C₁₃H₁₆INO: C 47.43, H 4.90; found: C 47.21, H 5.07.

Isoquinolinium iodide 2d:

From 1d (1.74 g) after 3 d, 2d (2.58 g, 75%) was obtained as a dark pink solid. M.p. 220-222 °C. ¹H NMR (DMSO-d₆, 500 MHz) δ 10.47 (s, 1H), 9.16 (d, J = 8.0 Hz, 1H), 9.06 (d, J = 7.7 Hz, 1H), 8.96 (d, J = 8.0 Hz, 1H), 8.95 (d, J = 7.7 Hz, 1H), 8.28 (t, J = 8.0 Hz, 1H), 5.52 (m, J = 6.7 Hz, 1H), 1.74 (d, J = 6.7 Hz, 1H). 13C NMR (DMSO-d₆, 125.7 MHz) δ 149.4, 143.8, 137.4, 135.7, 133.9, 130.3, 129.2, 128.3, 121.7, 64.3, 22.1. HRMS (FAB) calc.: C₁₂H₁₃N₂O₂ 217.0996 [M-I]⁺; found: 217.0997. Anal. Calc. for C₁₂H₁₃IN₂O₂: C 41.88, H 3.81; found: C 41.74, H 3.92.

Isoquinolinium iodide 2e:

From 1e (1.89 g) after 1 d, 2e (2.11 g, 91%) was obtained as a brown pale solid. M.p. 232-234 °C. ¹H NMR (CDCl₃, 300 MHz) δ 10.51 (s, 1H), 8.42 (d, J = 6.7 Hz, 1H), 8.31 (s, 1H), 8.20 (d, J = 6.7 Hz, 1H), 7.43 (s, 1H), 5.29 (m, J = 6.8 Hz, 1H), 4.11 (s, 3H), 4.09 (s, 3H), 1.78 (s, 3H), 1.76 (s, 3H). ¹³C NMR (CDCl₃, 75.4 MHz) δ 158.6, 153.4, 143.7, 136.2, 130.7, 125.3, 124.4, 108.7, 105.4, 64.1, 57.7, 57.6, 23.9, 23.9. HRMS (FAB) calc.: C₁₄H₁₈O₂ 232.1338 [M-I]⁺; found: 232.1318.

General procedure for the synthesis of isoquinolinium chlorides 3a-e:

To a suspension of resin Dowex 22 (Cl) (1.5 g, washed with dry methanol and dried in vacuo) in dry methanol (5 mL) isoquinolinium iodide 2a-e (2.5 mmol) was added at once. The resulting suspension was stirred over 1 h and filtered over a celita pad. The filtrate was concentrated to dryness to give pure isoquinolinium chlorides 3a-e. Starting material, yields and characterization data for compounds 3a-e are as follows:
Isoquinolinium chloride 3a:

From 2a (750 mg), 3a (510 g, 98%) was obtained as a pale yellow green solid. M.p. > 200 °C (dec). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 11.02 (s, 1H), 8.90 (d, $J = 8.1$ Hz, 1H), 8.85 (dd, $J = 7.0$, $J = 1.3$ Hz, 1H), 8.43 (d, $J = 6.8$ Hz, 1H), 8.13 (t, $J = 6.8$ Hz, 1H), 7.93 (t, $J = 7.0$ Hz, 1H), 5.60 (m, $J = 6.8$ Hz, 1H), 1.85 (d, $J = 6.8$ Hz, 6H). $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 146.3, 136.5, 135.2, 132.1, 130.5, 130.4, 128.9, 126.9, 126.1, 65.1, 25.1. HRMS (FAB) calc.: C$_{12}$H$_{14}$N 172.1126 [M-Cl]$^+$; found: 172.1123.

Isoquinolinium chloride 3b:

From 2b (782 mg), 3b (532 mg, 96%) was obtained as a pale yellow solid. M.p. > 200 °C (dec.). $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 10.97 (s, 1H), 8.87 (d, $J = 6.9$ Hz, 1H), 8.41 (d, $J = 6.9$ Hz, 1H), 7.95-7.90 (m, 2H), 7.67 (d, $J = 6.1$ Hz, 1H), 6.12 (m, $J = 6.7$ Hz, 1H), 3.06 (s, 3H), 1.78 (d, $J = 6.7$ Hz, 6H). $^{13}$C NMR (CDCl$_3$, 125.7 MHz) $\delta$ 147.3, 140.8, 138.0, 136.7, 131.7, 130.7, 127.4, 127.0, 124.9, 63.9, 23.3, 19.6. HRMS (FAB) calc.: C$_{13}$H$_{16}$ClN 186.1283 [M-Cl]$^+$; found: 186.1285. Anal. Calc. for C$_{13}$H$_{16}$ClN: C 70.42, H 7.27; found: C 70.31, H 7.15.

Isoquinolinium chloride 3c:

From 2c (823 mg), 3c (570 mg, 96%) was obtained as a pale yellow solid. M.p. 195-197 °C. $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 10.89 (s, 1H), 8.73-8.71 (m, 2H), 8.25 (d, $J = 7.0$ Hz, 1H), 7.39-7.36 (m, 2H), 5.42 (m, $J = 6.7$ Hz, 1H), 3.99 (s, 3H), 1.74 (d, $J = 6.7$ Hz, 6H). $^{13}$C NMR (CDCl$_3$, 125.7 MHz) $\delta$ 166.1, 147.1, 140.4, 133.3, 132.3, 124.7, 124.0, 123.6, 105.0, 63.4, 56.4, 23.3. Anal. Calc. for C$_{13}$H$_{16}$ClNO: C 65.68, H 6.78; found: C 65.37, H 6.99.
Isoquinolinium chloride 3d:

From 2d (861 mg, 2.5 mmol), 3d (599 mg, 95%) was obtained as a dark yellow solid. M.p. > 230 °C (dec). $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 10.30 (s, 1H), 9.16 (d, $J$ = 7.3 Hz, 1H), 9.08 (d, $J$ = 8.0 Hz, 1H), 9.04 (d, $J$ = 7.3 Hz, 1H), 8.93 (d, $J$ = 8.0 Hz, 1H), 8.25 (t, $J$ = 8.0 Hz, 1H), 5.28 (m, $J$ = 6.7 Hz, 1H), 1.85 (d, $J$ = 6.7, 6H). $^{13}$C NMR (CDCl$_3$, 125.7 MHz) $\delta$ 150.5, 145.9, 138.7, 136.7, 135.6, 131.7, 130.5, 123.0, 67.0, 23.0. HRMS (FAB) calc.: C$_{12}$H$_{13}$N$_2$O$_2$ 217.0977 [M-Cl]$^+$; found: 217.0990. Anal. Calc. for C$_{12}$H$_{13}$ClN$_2$O$_2$: C 57.04, H 5.19; found: C 56.79, H 5.35.

Isoquinolinium chloride 3e:

From 2e (801 mg), 3e (667 mg, quant.) was obtained as a white off solid. M.p. 111-113 °C. $^1$H RMN (CDCl$_3$, 400 MHz) $\delta$ 10.9 (s, 1H), 8.35 (s, 1H), 8.25 (d, $J$ = 6.8 Hz, 1H), 8.03 (d, $J$ = 6.8 Hz, 1H), 7.29 (s, 1H), 5.42 (m, $J$ = 6.4 Hz, 1H), 4.12 (s, 3H), 4.11 (s, 3H), 1.78 (s, 3H), 1.76 (s, 3H). $^{13}$C RMN (CDCl$_3$, 75.4 MHz) $\delta$ 158.2, 153.0, 144.6, 135.5, 129.9, 125.1, 123.8, 108.6, 104.8, 63.5, 57.1, 57.0, 23.4, 23.4. HRMS (FAB) calc.: C$_{14}$H$_{18}$NO$_2$ 232.1338 [M-Cl]$^+$; found: 232.1325.

Isoquinolium chloride 4b:

A mixture of 1-chloro-2,4-dinitrobenzene (1.52 g, 7.5 mmol) and isoquinoline 1b (1.0 g, 7 mmol) was stirred at 90 °C for 15 min in a two neck round bottom flask equipped with a condenser and a dropping funnel. Acetone (5 mL) was then slowly added, and the resulting solution was refluxed over 30 h. After cooling to RT, the mixture was concentrated to dryness and the red-orange residue was dissolved in boiling MeOH (15 mL). Cold EtOAc (40 mL)
was added under stirring to afford 4b (1.47 g, 61%) as a pale yellow powder. M.p. 156-159 °C. \(^1\)H NMR (CD\(_3\)OD, 500 MHz) \(\delta\) 10.40 (s, 1H), 9.27 (d, \(J = 2.4\) Hz, 1H), 8.94-8.91 (m, 2H), 8.70 (d, \(J = 6.8\) Hz, 1H), 8.43 (d, \(J = 8.6\) Hz, 1H), 8.31-8.27 (m, 2H), 8.00 (d, \(J = 5.6\) Hz, 1H), 2.94 (s, 3H). \(^13\)C NMR (CD\(_3\)OD, 125.7 MHz) \(\delta\) 153.2, 148.2, 147.3, 144.6, 140.4, 139.1, 137.4, 131.2, 129.4, 127.5, 127.4, 125.2, 124.2, 117.9, 23.5. HRMS (FAB) calc.: C\(_{16}\)H\(_{12}\)N\(_3\)O\(_4\) 310.0828 [M-Cl]+; found: 310.0824. Anal. Calc. for C\(_{16}\)H\(_{12}\)ClN\(_3\)O\(_4\): C 55.58, H 3.50; found: C 55.49, H 3.71.

**Isoquinolium chloride 5b:**

\[
\text{Cl}^+ \quad \text{Ph}
\]

A solution of 4b (1.04 g, 3 mmol) and (R)-1-phenylethanamine (447 \(\mu\)L, 3.5 mmol) in dry butanol (10 mL) was refluxed over 2 d and then concentrated. Water was then added to the residue, and the red solid formed was removed by filtration and washed with water (3 x 10 mL). The resulting mother liquor was basicified with saturated aqueous NH\(_4\)Cl solution (0.5 mL), and then washed with EtOAc (3 x 30 mL). Concentration of the aqueous solution and column chromatography (99:1→95:5 CH\(_2\)Cl\(_2\)-MeOH) afforded 5b as a white off solid (602 mg, 71%). M.p. 126-128 °C. \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 11.36 (s, 1H), 8.57 (d, \(J = 6.8\) Hz, 1H), 8.36 (d, \(J = 7.0\) Hz, 1H), 7.98-7.92 (m, 1H), 7.75 (d, \(J = 6.9\) Hz, 1H), 7.71 (d, \(J = 6.9\) Hz, 1H), 7.48 (q, \(J = 7.0\) Hz, 1H), 7.49-7.31 (m, 5H), 3.13 (s, 3H), 2.16 (d, \(J = 7.0\) Hz, 3H). \(^13\)C NMR (CDCl\(_3\), 125.7 MHz) \(\delta\) 148.0, 141.2, 138.1, 137.0, 137.0, 132.0, 131.2, 129.4, 128.0, 127.5, 127.0, 125.0, 68.9, 20.8, 19.6. \([\alpha]^{20}_D\) +24.3 (c 0.2, CHCl\(_3\)). HRMS (FAB) calc.: C\(_{18}\)H\(_{18}\)N 248.1439 [M-Cl]+; found: 248.1438.

**Adduct 6b:**

Inside a dry box, a schlenk flask equipped with a magnetic stir bar was charged with isoquinolinium salt 3b (221 mg, 1 mmol) and cooled to -78 °C. A solution of KHMDS (200 mg, 1 mmol) in toluene (4 mL) was slowly added via cannula. After 10 min, the mixture was...
allowed to warm to RT, stirred for 10 min, and then salts were allowed to decant during 1 h. Concentration of the supernatant afforded 6b (345 mg, quant.) as a light yellow oil that solidifies on standing. $^1$H NMR ([D$_8$]toluene, 500 MHz) δ 7.03-6.98 (m, 2H), 6.80-6.70 (m, 4H), 6.11-6.08 (m, 4H), 5.35 (d, $J = 7.5$ Hz, 2H), 3.48 (m, $J = 6.5$ Hz, 2H), 2.19 (s, 6H), 1.09 (d, $J = 6.5$ Hz, 6H), 0.93 (d, $J = 6.5$ Hz, 6H).

$^{13}$C NMR ([D$_8$]toluene, 100 MHz) δ 142.2, 141.5, 140.5, 131.9, 126.9, 100.8, 75.9, 53.8, 26.8, 25.4, 12.3, 7.4.

**Adduct 6’b:**

![Adduct 6'b](image)

A schlenk flask equipped with a magnetic stir bar was charged with 2b (313 mg, 1 mmol) and KOTBu (112 mg, 1 mmol). Dry THF (4 mL) was added and the resulting mixture was stirred for 2 h at RT. Then the solvent was removed and dry toluene (10 mL) was added via syringe. The mixture was decanted, the supernatant separated and concentrated to afford the 6’b (218 mg, 84%) as a light yellow oil. $^1$H RMN (C$_6$D$_6$, 400 MHz) δ 7.12-7.07 (m, 1H), 6.97 (d, $J = 7.6$ Hz, 1H), 6.91 (d, $J = 7.3$ Hz, 1H), 6.20 (dd, $J = 7.3$, 1.3 Hz, 1H), 6.14 (d, $J = 1.3$ Hz, 1H), 5.86 (d, $J = 7.2$ Hz, 1H), 3.37 (m, $J = 6.6$ Hz, 1H), 2.37 (s, 3H), 1.11 (s, 9H), 1.05 (d, $J = 6.5$ Hz, 3H), 0.76 (d, $J = 6.5$ Hz, 3H).

$^{13}$C RMN (CDCl$_3$, 100 MHz) δ 134.8, 134.3, 128.4, 127.4, 127.1, 122.4, 102.9, 82.5, 53.8, 37.7, 30.1, 23.6, 20.6, 19.1. Anal. Calc. for C$_{17}$H$_{25}$NS: C 78.72, H 9.71, N 5.40; found: C 79.20, H 10.09, N 5.11.

**Selenolactam 8b:**

![Selenolactam 8b](image)

To a solution of 6b (172 mg, 0.52 mmol) in dry toluene (1.5 mL) under Ar was added Se (80 mg, 1.0 mmol) and the mixture was stirred overnight at RT. Concentration afforded a pale orange solid, which was purified by column chromatography (4:1 EtOAc-hexane) to yield 8b (121 mg, 93%) as a pale orange syrup. $^1$H RMN (CDCl$_3$, 400 MHz) δ 7.43 (m, 2H), 7.39 (m, 2H), 6.99 (d, $J = 7.2$ Hz, 1H), 6.80 (m, $J = 6.8$ Hz, 1H), 3.22 (s, 3H), 1.48 (d, $J = 6.8$ Hz, 6H).

$^{13}$C RMN (CDCl$_3$, 100 MHz) δ 184.6, 143.5, 137.6, 133.5, 133.2, 131.1, 128.1, 125.3, 115.1, 57.6, 28.8, 21.9, 21.9. HRMS (CI+) calc.: C$_{13}$H$_{15}$NSe 265.0370 [M+H]$^+$; found 265.0371.
Selenolactam 8e:

KHMDS (27 mg, 0.13 mmol) and Se (20 mg, 0.25 mmol) were added under Ar to a stirred solution of isoquinolium chloride 3e (33 mg, 0.12 mmol) in dry THF (1.5 mL) at RT. After 3 d the solution was concentrated and the residue purified by column chromatography (10:1 EtOAc-hexane) to afford 8e (17 mg, 45%) as an orange solid. M.p. 164-166 °C. ¹H RMN (CDCl₃, 400 MHz) δ 8.78 (s, 1H), 7.56 (d, J = 7.2 Hz, 1H), 7.05 (d, J = 7.2 Hz, 1H), 6.88 (m, 1H), 6.86 (s, 1H), 4.07 (s, 3H), 3.99 (s, 3H), 1.50 (s, 3H), 1.48 (s, 3H). ¹³C RMN (CDCl₃, 75.4 MHz) δ 180.3, 154.66, 151.4, 132.5, 128.2, 127.6, 116.5, 114.7, 105.5, 59.5, 56.6, 30.0, 22.3. HRMS (FAB) calc.: C₁₄H₁₈NO₂Se 312.0503 [M+H]+; found: 312.0494.

Crystals of 8e suitable for X-ray diffraction analysis were grown by slow diffusion from a CH₂Cl₂/cyclohexane mixture.

Thiolactame 8'b:

A mixture of 6'b (130 mg, 0.5 mmol) and S₈ (32 mg, 1 mmol) was charged in a schlenk flask under argon. Dry toluene (2 mL) was added and the mixture was stirred for 1 h at 80 °C. Concentration and column chromatography (5:1 EtOAc-hexane) afforded 8'b (66 mg, 61%) as a yellow oil. ¹H RMN (CDCl₃, 400 MHz) δ 7.50-7.41 (m, 1H), 7.40-7.31 (m, 3H), 6.84 (d, J = 7.3 Hz, 1H), 6.61 (m, J = 7.3 Hz, 1H), 3.21 (s, 3H), 1.43 (d, J = 6.8 Hz, 6H). ¹³C RMN (CDCl₃, 100 MHz) δ 184.0, 143.0, 133.9, 133.8, 132.6, 130.6, 127.1, 124.9, 112.6, 52.2, 28.1, 21.4, 21.4. Anal. Calc. for C₁₃H₁₅NS: C 71.84, H 6.96, N 6.44; found: C 71.80, H 7.08, N 6.31.

General procedure for the synthesis of Rhodium complexes 9a, 10a-d, 11:

A schlenk tube was charged with isoquinolinium salt 2, 3, or 5 (1 mmol) and heated in vacuo. Anhydrous, deoxygenated THF (5 mL) was added at RT and the resulting suspension was
then cooled to –30 °C. A solution of KHMDS in dry THF (1.1 eq.) was added and the mixture was stirred for 10-60 min at –20 °C. [RhCl(COD)]₂ (270 mg, 1.1 mmol) was added at once and the mixture was stirred at RT for 15 min. The solvent was removed and the residue was purified by column chromatography to afford complex 9-11. Starting material, reaction times, eluent used for the chromatographic purification, yields, and characterization data for compounds 9a, 10a-d, 11 are as follows.

**Rhodium complex 9a:**

![Rhodium complex 9a](image)

From 2a (15 min at –20 °C), column chromatography (95:5→80:20 pentane-Et₂O) afforded 9a (360 mg, 71%) as a yellow orange solid. M.p. 89-91 °C. ¹H RMN (CDCl₃, 500 MHz) δ 9.83 (d, J = 8.1 Hz, 1H), 7.76 (td, J = 1.5 Hz, J = 7.5 Hz, 1H), 7.71 (dd, J = 1.1 Hz, J = 8.1 Hz, 1H), 7.34 (d, J = 6.9 Hz, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.29 (d, J = 7.34 Hz, 1H), 7.16 (m, 1H), 5.43 (m, 1H), 5.28 (m, 1H), 3.41 (m, 2H), 2.54 (m, 1H), 2.47-2.32 (m, 3H), 2.12-1.98 (m, 2H), 1.90-1.77 (m, 2H), 1.78 (d, J = 7.0 Hz, 3H), 1.71 (d, J = 6.6 Hz, 3H). ¹³C RMN (CDCl₃, 125.7 MHz) δ 228.0 (d, J_C-Rh = 44.7 Hz), 139.5, 139.0, 132.7, 130.1, 128.9, 127.4, 126.1, 119.0, 97.0 (d, J_C-Rh = 6.6 Hz), 96.6 (d, J_C-Rh = 6.6 Hz), 75.3 (d, J_C-Rh = 16.4 Hz), 70.8 (d, J_C-Rh = 13.1 Hz), 64.9, 53.4, 32.3, 31.7, 29.6, 23.1, 22.5. Anal. Calc. for C₂₀H₂₄INRh: C 47.27, H 4.76; found: C 47.28, H 5.09.

Crystals of 9a suitable for X-ray diffraction analysis were grown by slow diffusion from a CH₂Cl₂/cyclohexane mixture.

**Rhodium complex 10a:**

![Rhodium complex 10a](image)

From 3a (15 min at –20 °C). Column chromatography (95:5→80:20 pentane-Et₂O) afforded 10a (225 mg, 54%) as a yellow solid. M.p. 68-70 °C. ¹H RMN (CDCl₃, 500 MHz) δ 10.01 (d, J = 8.0 Hz, 1H), 7.79 (td, J = 1.2 Hz, J = 6.9 Hz, 1H), 7.74 (dd, J = 1.2 Hz, J = 8.0 Hz, 1H),...
7.71 (d, J = 6.9 Hz, 1H), 7.63 (d, J = 7.5 Hz, 1H), 7.43 (m, 1H), 7.31 (d, J = 6.9 Hz, 1H), 5.25 (m, 1H), 5.08 (m, 1H), 3.24 (m, 1H), 2.65 (m, 1H), 2.55-2.45 (m, 2H), 2.38 (m, 1H), 2.15-1.87 (m, 5H), 1.80 (d, J = 6.3 Hz, 3H), 1.71 (d, J = 6.9 Hz, 3H). 13C RMN (CDCl₃, 125.7 MHz) δ 228.1 (d, J_C-Rh = 44.1 Hz), 139.5, 138.7, 132.9, 130.4, 129.0, 127.8, 126.2, 119.2, 99.3 (d, J_C-Rh = 6.6 Hz), 98.5 (d, J_C-Rh = 6.6 Hz), 71.2 (d, J_C-Rh = 14.8 Hz), 67.6 (d, J_C-Rh = 14.8 Hz), 65.6, 33.3, 32.0, 29.3, 28.3, 23.4, 23.1. Anal. Calcd. for C₂₀H₂₄ClNRh: C 57.64, H 5.80; found: C 57.28, H 6.09.

**Rhodium complex 10b:**

![Rhodium complex 10b](image)

From 3b (0.5 mmol) (30 min at –20 °C). Column chromatography (95:5→80:20 pentane-Et₂O) afforded 10b (176 mg, 82%) as a pale yellow powder. M.p. 125-129 °C. ¹H RMN (CDCl₃, 500 MHz) δ 8.17 (m, 1H), 7.72 (d, 1H, J = 6.9 Hz), 7.64-7.58 (m, 2H), 7.49 (d, 1H, J = 7.5 Hz), 7.26 (d, 1H, J = 7.5 Hz), 5.19-5.10 (m, 2H), 4.31 (s, 3H), 2.85 (m, 1H), 2.77 (m, 1H), 2.65 (m, 1H), 2.47 (m, 1H), 2.38-2.27 (m, 2H), 2.05 (m, 1H), 1.96 (m, 1H), 1.88 (d, 3H, J = 6.9 Hz), 1.84-1.68 (m, 2H), 1.75 (d, 3H, J = 6.9 Hz). ¹³C RMN (CDCl₃, 125.7 MHz) δ 227.9 (d, J_C-Rh = 42.7 Hz), 145.0, 138.5, 132.5, 131.3, 128.6, 125.2, 119.8, 97.6 (d, J_C-Rh = 6.6 Hz), 95.0 (d, J_C-Rh = 6.6 Hz), 68.7, 68.3, 68.1, 33.6, 31.6, 30.8, 29.4, 27.8, 27.1. Anal. Calc. for C₂₁H₂₆ClNRh: C 58.55, H 6.08; found: C 58.21, H 6.07.

**Rhodium complex 10c:**

![Rhodium complex 10c](image)

From 3c (1h at –20 °C). Column chromatography (95:5→80:20 pentane-Et₂O) afforded 10c (174 mg, 39%) as a pale yellow solid. M.p. 143-145 °C. ¹H RMN (CDCl₃, 500 MHz) δ 9.81 (d, J = 9.2 Hz, 1H), 7.59 (d, J = 6.9 Hz, 1H), 7.33-7.26 (m, 2H), 7.14 (d, J = 6.9 Hz, 1H), 6.86 (d, J = 2.3 Hz, 1H), 5.15 (m, 1H), 5.00 (m, 1H), 3.88 (s, 3H), 3.17 (m, 1H), 2.58 (m,
1H), 2.43 (m, 2H), 2.31 (m, 1H), 2.08-1.95 (m, 3H), 1.87 (m, 2H), 1.72 (d, J = 6.9 Hz, 3H), 1.63 (d, J = 6.9 Hz, 3H). \(^{13}\)C RMN (CDCl\(_3\), 125.7 MHz) \(\delta\) 224.6 (d, \(J_{C-Rh} = 42.7\) Hz), 163.0, 141.2, 133.8, 129.4, 119.0, 118.4, 105.2, 98.9, 98.5 (d, \(J_{C-Rh} = 6.6\) Hz), 71.1 (d, \(J_{C-Rh} = 16.4\) Hz), 67.4 (d, \(J_{C-Rh} = 16.4\) Hz), 65.1, 55.7, 33.3, 32.0, 29.3, 28.3, 23.4, 23.1. Anal. Calc. for C\(_{21}\)H\(_{26}\)ClNORh: C 56.45, H 5.87; found: C 56.01, H 6.29.

Crystals of 10c suitable for X-ray diffraction analysis were grown by slow diffusion from a CH\(_2\)Cl\(_2\)/cyclohexane mixture.

**Rhodium complex 10 d:**

![Rhodium complex 10 d](image)

From 3d (10 min at \(-20\) °C). Column chromatography (99:1→90:10 pentane/Et\(_2\)O) afforded 10d (208 mg, 45%) as an orange solid. M.p. 175-176 °C. \(^1\)H RMN (CDCl\(_3\), 500 MHz) \(\delta\) 10.48 (d, \(J = 8.0\) Hz, 1H), 8.51 (d, \(J = 7.5\) Hz, 1H), 8.15 (dd, \(J = 7.5\) Hz, 1H), 7.90 (m, 2H), 7.43 (m, 1H), 5.27 (m, 1H), 5.12 (m, 1H), 3.23 (m, 1H), 3.10 (m, 1H), 2.60 (m, 1H), 2.47 (m, 2H), 2.38 (m, 1H), 2.14-1.91 (m, 4H), 1.81 (d, \(J = 6.9\) Hz, 3H), 1.72 (d, \(J = 6.9\) Hz, 3H). \(^{13}\)C RMN (CDCl\(_3\), 125.7 MHz) \(\delta\) 230.6 (d, \(J_{C-Rh} = 42.7\) Hz), 147.0, 144.4, 139.7, 131.9, 130.0, 126.7, 124.2, 114.3, 100.6 (d, \(J_{C-Rh} = 6.6\) Hz), 99.9 (d, \(J_{C-Rh} = 6.6\) Hz), 71.8 (d, \(J_{C-Rh} = 16.4\) Hz), 68.2 (d, \(J_{C-Rh} = 13.1\) Hz), 66.2, 33.1, 32.1, 29.2, 28.4, 23.2, 23.0. Anal. Calc. for C\(_{20}\)H\(_{23}\)ClN\(_2\)O\(_2\)Rh: C 52.02, H 5.02; found: C 51.75, H 5.48.

**Rhodium complex 11:**

![Rhodium complex 11](image)

From 5b (15 min at \(-20\) °C). Column chromatography (99:1→90:10 CH\(_2\)Cl\(_2\)-Et\(_2\)O) afforded 11a (310 mg, 65 %) as a 4:1 mixture of atropoisomers. Separation of this mixture by medium pressure chromatography afforded the major isomer (215 mg, 45%) in pure form. Data for major 11a: M.p. 84-86 °C. \(^1\)H RMN (CDCl\(_3\), 500 MHz) \(\delta\) 10.09 (d, \(J = 8.0\) Hz, 1H), 8.53 (q,
J = 6.9 Hz, 1H), 7.85 (m, 1H), 7.78 (m, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 6.9 Hz, 1H), 7.43 (m, 2H), 7.38 (m, 1H), 7.32 (m, 2H), 7.27 (d, J = 6.9 Hz, 1H), 5.25 (m, 1H), 5.16 (m, 1H), 3.46 (m, 1H), 3.31 (m, 1H), 2.67 (m, 1H), 2.57 (m, 1H), 2.35 (m, 1H), 2.19 (d, J = 7.5 Hz, 3H), 2.06-1.94 (m, 4H), 1.78 (m, 1H). 13C RMN (CDCl3, 125.7 MHz) δ 230.0 (d, J_{C-Rh} = 45.9 Hz), 140.8, 139.7, 139.0, 133.2, 131.3, 130.4, 129.0, 128.0, 127.8, 126.6, 126.5, 119.0, 99.4 (d, J_{C-Rh} = 6.6 Hz), 99.3 (d, J_{C-Rh} = 6.6 Hz), 72.1 (d, J_{C-Rh} = 13.1 Hz), 67.8 (d, J_{C-Rh} = 13.1 Hz), 67.6, 33.0, 32.2, 29.0, 28.5, 21.3. [α]_{20}^{D} = –48.2 (c 0.2, CHCl3). Anal. Calc. for C25H26ClNRh: C 62.71, H 5.47; found: C 62.35, H 5.41.

Crystals of 11a suitable for X-ray diffraction analysis were grown by slow diffusion from a CH2Cl2/cyclohexane mixture.

**General procedure for the synthesis of Rhodium dicarbonyl complexes 12a,c,d:**

A CO steam (CAUTION: The operation must be done in a well ventilated hood) was bubbled through a deoxygenated solution of rhodium complexes 12a,c,d (0.1 mmol) in dry CH2Cl2 (2 mL) for 5 min. The solution was concentrated and the resulting pale yellow solid was washed with pentane (2 × 2 mL), and dried in vacuo. Starting material, yields, and characterization data for compounds 12a,c,d are as follows:

**Rhodium dicarbonyl complex 12a:**

From 10a, complex 12a (48 mg, 93%) was isolated as a white off solid. IR (CH2Cl2): ν(C=O) 2077, 1998 cm⁻¹. ¹H RMN (CDCl3, 500 MHz) 9.22 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 6.9 Hz, 1H), 7.81 (m, 1H), 7.76 (m, 2H), 7.61 (d, J = 6.9 Hz, 1H), 6.33 (m, 1H), 1.68 (d, J = 6.9 Hz, 3H), 1.63 (d, J = 6.9 Hz, 3H). ¹³C RMN (CDCl3, 125.7 MHz) δ 209.2 (d, J_{C-Rh} = 36.1 Hz), 188.2 (d, J_{C-Rh} = 52.5 Hz), 182.8 (d, J_{C-Rh} = 82.0 Hz), 139.0, 138.4, 134.0, 131.5, 129.2, 128.1, 126.2, 121.7, 66.4, 22.6, 21.1.

**Rhodium dicarbonyl complex 12c:**
From **10c**, complex **12c** (42 mg, 93%) was isolated as white off solid. IR (CH$_2$Cl$_2$): $\nu$(C=O) 2076, 1996 cm$^{-1}$. $^1$H RMN (CDCl$_3$, 500 MHz) $\delta$ 9.22 (d, $J = 9.2$ Hz, 1H), 7.80 (d, $J = 6.9$ Hz, 1H), 7.46 (d, $J = 6.9$ Hz, 1H), 7.32 (dd, $J = 6.9$, 2.3 Hz, 1H), 6.97 (d, $J = 2.3$ Hz, 1H), 6.42 (m, 1H), 3.92 (m, 3H), 1.64 (d, $J = 6.9$ Hz, 3H), 1.59 (d, $J = 6.9$ Hz, 3H). $^{13}$C RMN (CDCl$_3$, 125.7 MHz) $\delta$ 206.7 (d, $J_{C\text{-Rh}} = 36.1$ Hz), 186.5 (d, $J_{C\text{-Rh}} = 52.5$ Hz), 183.7 (d, $J_{C\text{-Rh}} = 76.8$ Hz), 164.0, 140.4, 134.5, 133.9, 128.7, 120.7, 120.2, 105.1, 66.5, 55.9, 22.7, 22.3.

**Rhodium dicarbonyl complex 12d:**

From **10d**, complex **12d** (42 mg, 91%) was isolated as a white off solid. IR (CH$_2$Cl$_2$): $\nu$(C=O) 2081, 2003 cm$^{-1}$. $^1$H RMN (CDCl$_3$, 500 MHz) $\delta$ 9.89 (d, $J = 8.0$ Hz, 1H), 8.65 (d, $J = 8.0$ Hz, 1H), 8.56 (d, $J = 7.5$ Hz, 1H), 8.13 (d, $J = 7.5$ Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 6.62 (m, 1H), 1.73 (d, $J = 6.9$ Hz, 3H), 1.69 (d, $J = 6.9$ Hz, 3H). $^{13}$C RMN (CDCl$_3$, 125.7 MHz) $\delta$ 212.6 (d, $J_{C\text{-Rh}} = 39.4$ Hz), 185.9 (d, $J_{C\text{-Rh}} = 55.8$ Hz), 183.0 (d, $J_{C\text{-Rh}} = 75.5$ Hz), 146.2, 144.3, 139.5, 132.1, 131.3, 127.4, 125.4, 117.4, 67.9, 22.6, 22.2.

**General procedure for the hydrosilylation of acetophenone**

To a solution of Rh-complex **10** (0.004 mmol) in CCl$_4$ (200 $\mu$L) were added diphenylsilane (237 $\mu$L, 1.28 mmol) and acetophenone (100 $\mu$L, 0.85 mmol) and the mixture was stirred at RT for 6 h. Methanol (1 mL) and a few crystals of $p$-TsOH were added, and after stirring 90 min at RT the solvents were evaporated and the residue analyzed by $^1$H NMR. The following peaks were used for analysis: $\delta$ = 5.07 ppm (q, PhCHOHCH$_3$, 1H), $\delta$ = 2.61 ppm (s, PhCOCH$_3$, 3H).