Supporting Information

Highly Selective Ruthenium Metathesis Catalysts for Ethenolysis

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General Information.

$^1$H and $^{13}$C NMR spectra were recorded on a Varian Mercury ($^1$H, 300 MHz), a Varian Inova 400 ($^1$H, 400 MHz), a Varian Inova 500 ($^1$H, 500 MHz; $^{13}$C, 125 MHz), or an automated Varian Inova 500 ($^1$H, 500 MHz; $^{13}$C, 125 MHz) spectrometer and chemical shifts are reported in ppm downfield from Me$_4$Si by using the residual solvent peak as an internal standard. High resolution mass spectrometry (FAB) was done at the California Institute of Technology Mass Spectrometry Facility. X-ray crystallographic structures were obtained at the Beckman Institute X-ray Crystallography Laboratory at the California Institute of Technology. All air-sensitive reactions were conducted either in a nitrogen atmosphere glovebox or under an argon atmosphere using standard Schlenk-line techniques.

Materials.

Toluene and benzene were dried by passage through solvent purification systems.$^1$ Ruthenium precursors RuCl$_2$(PCy$_3$)(=CH-o-O$i$Pr-C$_6$H$_4$) and RuCl$_2$(PCy$_3$)$_2$(=CHPh) were received from Materia, Inc. All other reagents and solvents were used as purchased without further purification.

SYNTHESIS OF 12.

The procedure for synthesizing S1, S2, S3, and S4 was very similar to that outlined in reference 2, with slight modifications.

Synthesis of S1. Anhydrous potassium carbonate (112.8 mmol, 15.6 grams) and acetonitrile (150 mL) were added to a 250 mL RB flask containing a stir bar. 2,6-Diisopropyl aniline (56.4 mmol, 10.0 mL) was added via syringe with stirring, and chloroacetyl chloride (56.4 mmol, 4.5 mL) was then added dropwise. The reaction was stirred at RT for 43 hours, after which the resulting mixture was filtered through a thin pad of silica gel. The filtrate was concentrated under partial
vacuum on a rotary evaporator, and hexanes were added to the obtained cream colored residue. The hexanes dissolved away the off-white color and the remaining white solids were filtered and washed with more hexanes to yield \( \text{S2} \) (11.33 g, 79% yield). \(^1\)H NMR (CDCl\(_3\), 500 MHz): \( \delta \) 7.79 (s, 1H), 7.32 (t, \( J = 8 \) Hz, 1H), 7.20 (d, \( J = 7 \) Hz, 2H), 4.27 (s, 2H), 3.02 (sept, \( J = 6.5 \) Hz, 2H), 1.21 (d, \( J = 7 \) Hz, 12H) ppm. \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \( \delta \) 165.45, 146.16, 130.12, 129.00, 123.83, 43.02, 29.08, 23.82 ppm.

Synthesis of \( \text{S2} \). Anhydrous potassium carbonate (40.9 mmol, 5.65 grams) and \( \text{S1} \) (20.4 mmol, 5.19 g) were added to a 250 mL round bottom flask containing a stir bar. Acetonitrile (100 mL) was added, followed by (S)-(−)-1-(1-Napthyl)ethylamine (20.4 mmol, 3.50 g). A reflux condenser was attached to the flask, and the reaction was heated at 85 °C for 37 hours with stirring. The crude reaction mixture was then filtered through a thin pad of silica gel, and the filtrate was concentrated in vacuo. The crude solids obtained were then dissolved in diethyl ether and loaded onto a silica gel column for purification (100% diethyl ether as the eluting solvent). Upon concentration of the fractions containing product, \( \text{S2} \) was obtained as a white solid (3.97 g, 50% yield). \(^1\)H NMR (CDCl\(_3\), 500 MHz): \( \delta \) 8.64 (s, 1H), 8.16 (d, \( J = 8.5 \) Hz, 1H), 7.92 – 7.88 (m, 1H), 7.60 (d, \( J = 6.8 \) Hz, 1H), 7.56 – 7.43 (m, 3H), 7.28 – 7.26 (m, 1H), 7.16 (d, \( J = 7.7 \) Hz, 2H), 4.78 (q, \( J = 6.7 \) Hz, 1H), 3.59 – 3.42 (m, 2H), 3.02 – 2.85 (m, 2H), 2.20 (s, 1H), 1.63 (d, \( J = 6.6 \) Hz, 3H), 1.15 (d, \( J = 6.9 \) Hz, 6H), 1.13 (d, \( J = 6.9 \) Hz, 6H) ppm. \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \( \delta \) 171.23, 146.03, 139.92, 136.64, 134.01, 131.40, 129.39, 128.34, 128.10, 126.42, 125.86, 125.68, 123.63, 122.80, 50.95, 48.85, 29.09, 23.95, 23.68, 23.54 ppm.

Synthesis of \( \text{S3} \). In a nitrogen atmosphere glovebox, \( \text{S2} \) (2.10 grams, 5.4 mmol) was added to a 100 mL round bottom flask containing a stir bar, followed by the addition of dry tetrahydrofuran (5 mL). In a separate flask, lithium aluminum hydride (0.820 grams, 21.6 mmol) was weighed out and dry THF (5 mL) was slowly added. This lithium aluminum hydride suspension was then very slowly added to the solution of \( \text{S2} \), and the round bottom flask was sealed and brought out of the glovebox. The reaction was sealed heated at 70 °C for 5 days. The reaction mixture was then removed from the oil bath and allowed to cool. Water was slowly added to quench and the THF/water mixture was stirred for 3 hours. The mixture was then extracted with methylene chloride (4 x 20 mL). The combined organic layers were dried over MgSO\(_4\) and filtered. Concentration of the filtrate afforded a clear oil. The oil (0.372 g) was a mixture of product \( \text{S3} \) and unreacted starting material \( \text{S2} \) (91% and 9%, respectively). This crude mixture was carried directly on to the next step in the synthesis. \(^1\)H NMR (CDCl\(_3\), 500 MHz): \( \delta \) 8.24 (d, \( J = 8.4 \) Hz, 1H), 7.91 – 7.87 (m, 1H), 7.78 (d, \( J = 8.1 \) Hz, 1H), 7.69 (d, \( J = 6.5 \) Hz, 1H), 7.55 – 7.46 (m, 3H), 7.11 – 7.07 (m, 2H), 7.05 (dd, \( J = 8.7, 6.4 \) Hz, 1H), 4.71 (q, \( J = 6.6 \) Hz, 1H), 3.32 (sept, \( J = 6.8 \) Hz, 2H), 3.03 – 2.94 (m, 2H), 2.91 – 2.81 (m, 2H), 1.56 (d, \( J = 6.6 \) Hz, 3H), 1.23 (d, \( J = 6.9 \) Hz, 6H), 1.21 (d, \( J = 6.9 \) Hz, 6H) ppm.

Synthesis of \( \text{S4} \). \( \text{S3} \) (0.91 mmol, 0.372 g crude) was transferred to a 50 mL Schlenk tube containing a stir bar. Under an atmosphere of argon on the Schlenk line, 4M HCl in 1,4-dioxane (0.99 mL) was added via syringe through the septum cap. The mixture was stirred at room
temperature for 2 hours. Vacuum was then applied to the Schlenk tube to remove excess HCl and 1,4-dioxane. The Schlenk tube was placed back under an argon atmosphere and anhydrous triethyl orthoformate (9.9 mmol, 1.65 mL) was added via syringe. The schlenk tube was sealed under the argon atmosphere and heated to 120 °C for 18 hours. After allowing the solution to cool, the crude mixture was added to a silica gel column to purify (solvent system 5% MeOH in CH$_2$Cl$_2$). A white powder (0.244 g, 64% yield) was obtained upon concentrating and drying the fractions containing product. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 10.00 (s, 1H), 8.55 (d, $J$ = 8.5 Hz, 1H), 7.92-7.90 (m, 1H), 7.70 (t, $J$ = 7 Hz, 1H), 7.62 (d, $J$ = 7 Hz, 1H), 7.58 (d, $J$ = 7 Hz, 1H), 7.56 (d, $J$ = 7 Hz, 1H), 7.51 (t, $J$ = 8 Hz, 1H), 7.38 (t, $J$ = 8 Hz, 1H), 7.20-7.17 (m, 1H), 6.92 (q, $J$ = 7 Hz, 1H), 4.25 (dt, $J$ = 9.5 Hz, $J$ = 12 Hz, 1H), 4.09 (dt, $J$ = 8.5 Hz, $J$ = 12 Hz, 1H), 3.94 (dt, $J$ = 9.5 Hz, $J$ = 12 Hz, 1H), 3.75 (dt, $J$ = 8.5 Hz, $J$ = 12 Hz, 1H), 2.85 (sept, $J$ = 6.5 Hz, 1H), 2.70 (sept, $J$ = 6.5 Hz, 1H), 2.05 (d, $J$ = 6 Hz, 3H), 1.91 (m, 6H), 1.64 (d, $J$ = 6 Hz, 3H), 1.19 (m, 6H), 1.02 (d, $J$ = 7 Hz, 3H), 0.88 – 0.85 (m, 3H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 159.11, 146.63, 134.38, 131.27, 130.44, 129.33, 128.09, 126.83, 125.10, 123.55, 113.28, 100.83, 94.70, 86.57, 53.81, 53.21, 46.00, 29.18, 25.34, 25.13, 24.35, 24.24, 18.54 ppm.

Synthesis of 12. In a nitrogen atmosphere glovebox, S4 (1.35 mmol, 0.570 g), sodium tert-butoxide (2.46 mmol, 0.237 g), and RuCl$_2$(PCy$_3$)(=CH-o-O$i$PrC$_6$H$_4$) (1.23 mmol, 0.740 g) were added to a 100 mL round bottom flask. Dry toluene (15 mL) was added to this mixture and the flask was sealed and brought out of the glovebox. The reaction was stirred at room temperature for 24 hours. The crude mixture was then loaded directly onto a silica gel column. The eluting solvent was 10% diethyl ether in pentane. The product was isolated from a green band that came off of the column. Concentration of fractions from this green band afforded 12 as a dark green powder (0.382 grams, 40% yield). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 16.48 (s, 1H), 8.87 (d, $J$ = 8Hz, 1H), 7.90 (d, $J$ = 7Hz, 1H), 7.85 (d, $J$ = 8Hz, 1H), 7.70 (d, $J$ = 7.5 Hz, 1H), 7.60 (t, $J$ = 7.5 Hz, 1H), 7.57 – 7.47 (m, 3H), 7.41 – 7.32 (m, 3H), 6.91 (d, $J$ = 8.5 Hz, 1H), 6.86 (d, $J$ = 4.5 Hz, 2H), 5.11 (sept, $J$ = 6 Hz, 1H), 3.86 – 3.78 (m, 4H), 3.52 – 3.46 (m, 1H), 3.33 (sept, $J$ = 7 Hz, 1H), 3.20 (sept, $J$ = 6.5 Hz, 1H), 2.48 (d, $J$ = 7 Hz, 3H), 1.81 (d, $J$ = 6 Hz, 3H), 1.64 (d, $J$ = 6 Hz, 3H), 1.19 (m, 6H), 1.02 (d, $J$ = 7 Hz, 3H), 0.88 – 0.85 (m, 3H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 211.33, 152.83, 148.72, 148.67, 144.11, 138.37, 137.42, 134.20, 131.60, 129.80, 129.65, 128.89, 128.74, 126.07, 126.01, 125.41, 125.30, 125.17, 124.97, 124.33, 122.55, 122.51, 113.23, 75.26, 55.78, 54.87, 45.95, 28.18, 28.02, 25.98, 25.75, 24.15, 24.08, 22.59, 22.28, 20.39 ppm. High resolution mass spectrometry: [C$_3$H$_4$Cl$_2$N$_2$ORu][M-H] Calc. = 704.1875. Found = 704.1899.

The same synthetic procedure was used for the synthesis of complexes 13-20, 22, and 23. Complexes 21 and 24 were made as discussed below.
SYNTHESIS OF COMPLEX 13.

**Compound S5.** The product was isolated as white crystalline needles (25.413 g, 81% yield). $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.77 (s, 1H), 6.92 (s, 2H), 4.25 (s, 2H), 2.28 (s, 3H), 2.20 (s, 6H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 164.60, 137.79, 135.20, 130.17, 129.26, 43.02, 21.20, 18.43 ppm.

**Compound S6.** The product was isolated as white solids (2.750 g, 60% yield). $^1$H NMR (CDCl$_3$, 500 MHZ): $\delta$ 8.60 (s, 1H), 8.17 (d, $J = 8.4$ Hz, 1H), 7.93 – 7.88 (m, 1H), 7.80 (d, $J = 8.2$ Hz, 1H), 7.62 (d, $J = 6.7$ Hz, 1H), 7.56 – 7.47 (m, 3H), 6.89 (s, 2H), 4.88 – 4.70 (m, 1H), 3.48 (q, $J = 17.2$ Hz, 2H), 2.27 (s, 3H), 2.13 (s, 6H), 1.63 (d, $J = 6.6$ Hz, 3H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 170.43, 139.97, 136.71, 134.85, 134.10, 131.25, 131.16, 129.16, 128.91, 127.85, 126.21, 125.65, 125.58, 122.74, 54.03, 52.23, 50.69, 23.35, 21.04, 18.49 ppm.

**Compound S7.** The reaction afforded 99% conversion to product (1.015 g of crude mixture isolated). This mixture was carried onto the next step crude without further purification. $^1$H NMR (CDCl$_3$, 500 MHZ): $\delta$ 8.23 (d, $J = 8.3$ Hz, 1H), 7.89 (m, $J = 7.7$, 1.9 Hz, 1H), 7.77 (d, $J = 8.1$ Hz, 1H), 7.65 (dd, $J = 7.1$, 0.7 Hz, 1H), 7.55 – 7.45 (m, 3H), 6.85 – 6.82 (m, 2H), 4.67 (q, $J = 6.6$ Hz, 1H), 3.08 – 3.01 (m, 2H), 2.85 – 2.77 (m, 2H), 2.27 (s, 6H), 2.25 – 2.22 (m, 3H), 1.54 (d, $J = 6.6$ Hz, 3H) ppm.
Compound **S8**. The product was purified by silica gel column chromatography (10% MeOH in CH2Cl2) and isolated as a cream powder. Yield= 23% (0.582 g). $^1$H NMR (CDCl3, 500 MHZ): $\delta$ 10.10 (s, 1H), 8.51 (d, $J$ = 8.4 Hz, 1H), 7.69 – 7.66 (m, 2H), 7.62 (d, $J$ = 6.5 Hz, 1H), 7.58 – 7.55 (m, 2H), 7.52 (dd, $J$ = 8.1, 7.2 Hz, 1H), 6.91 (s, 2H), 6.76 – 6.73 (m, 1H), 4.17 – 4.02 (m, 2H), 4.00 – 3.87 (m, 1H), 3.73 – 3.62 (m, 1H), 2.30 (s, 3H), 2.27 (s, 3H), 2.23 (s, 3H), 2.05 (d, $J$ = 6.8 Hz, 3H) ppm. $^{13}$C NMR (CDCl3, 125 MHz): $\delta$ 159.24, 140.41, 135.34, 134.26, 132.32, 131.11, 130.89, 130.26, 130.14, 129.29, 127.93, 126.71, 125.29, 124.77, 123.40, 53.84, 50.77, 45.99, 21.16, 18.73, 18.15 ppm.

Complex **13**. The product was isolated as a green solid (14.2 mg) in 11% yield after purification by silica gel column chromatography (10% ether in pentane as the eluting solvent). $^1$H NMR (CDCl3, 500 MHZ): $\delta$ 16.51 (s, 1H), 8.69 (d, $J$ = 8.1 Hz, 1H), 7.93 – 7.88 (m, 1H), 7.83 (dd, $J$ = 8.9, 4.1 Hz, 1H), 7.69 (d, $J$ = 7.2 Hz, 1H), 7.57 – 7.45 (m, 4H), 7.17 (q, $J$ = 6.7 Hz, 1H), 7.09 (d, $J$ = 3.7 Hz, 2H), 6.95 – 6.87 (m, 3H), 5.10 (sept, $J$ = 6.1 Hz, 1H), 4.00 – 3.89 (m, 2H), 3.88 – 3.82 (m, 1H), 3.79 – 3.66 (m, 1H), 2.48 (s, 3H), 2.43 (s, 3H), 2.32 (s, 3H), 2.31 (s, 3H), 1.71 (d, $J$ = 6.1 Hz, 3H), 1.62 (d, $J$ = 6.1 Hz, 3H) ppm. $^{13}$C NMR (CDCl3, 125 MHz): $\delta$ 210.97, 152.57, 144.77, 138.58, 138.33, 138.30, 137.83, 134.25, 131.20, 129.99, 129.86, 129.79, 129.03, 128.59, 126.21, 125.93, 125.52, 124.95, 124.14, 123.04, 122.65, 113.20, 75.11, 56.34, 51.78, 46.77, 22.37, 22.33, 21.43, 21.09, 18.55, 18.51, 1.24 ppm. HRMS: [C$_{34}$H$_{39}$Cl$_2$N$_2$ORu] [M+] Calc. = 663.1484. Found = 663.1499.

**SYNTHESIS OF COMPLEX 14.**

Compound **S9**. The product was isolated as white solids (21.441 g) in 71% yield. $^1$H NMR (CDCl3, 500 MHZ): $\delta$ 8.44 (s, 1H), 7.66 (dd, $J$ = 10 Hz, 3 Hz, 1H), 7.42 (dd, $J$ = 10.5 Hz, 3 Hz, 1H), 7.28 – 7.16 (m, 2 H), 4.26 (s, 2H), 1.43 (s, 9H) ppm. $^{13}$C NMR (CDCl3, 125 MHz): $\delta$ 163.96, 142.52, 134.32, 127.11, 126.98, 126.89, 126.76, 43.38, 34.79, 30.83 ppm.
Compound S10. The product was purified by running a silica gel column using diethyl ether as the eluting solvent and isolated white solids (2.965 g) in 46% yield. $^1$H NMR (CDCl$_3$, 500 MHZ): $\delta$ 9.51 (s, 1H), 8.11 (d, $J = 8.3$ Hz, 1H), 7.90 (m, 1H), 7.85 – 7.82 (m, 1H), 7.80 (d, $J = 8.1$ Hz, 1H), 7.59 (dd, $J = 8.7$, 4.0 Hz, 1H), 7.55 – 7.47 (m, 3H), 7.40 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.17 – 7.15 (m, 1H), 4.80 – 4.77 (m, 1H), 1.63 – 1.61 (m, 3H), 1.46 (s, 9H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 169.83, 140.96, 139.91, 135.33, 134.05, 131.16, 129.17, 127.86, 126.85, 126.47, 126.30, 125.74, 125.69, 125.55, 125.37, 122.57, 122.34, 53.87, 51.42, 34.62, 30.62, 23.41 ppm.

Compound S11. The reaction gave 95% conversion to product (1.703 g of crude mixture). The mixture was carried on to the next step crude without further purification. $^1$H NMR (CDCl$_3$, 500 MHZ): $\delta$ 8.22 (d, $J = 8.0$ Hz, 1H), 7.94 – 7.89 (m, 1H), 7.79 (d, $J = 8.2$ Hz, 1H), 7.71 – 7.68 (m, 1H), 7.56 – 7.49 (m, 3H), 7.30 – 7.28 (m, 1H), 7.17 – 7.12 (m, 1H), 6.74 – 6.71 (m, 1H), 6.68 (dd, $J = 8.1$, 1.2 Hz, 1H), 4.74 (q, $J = 6.5$ Hz, 1H), 3.32 – 3.20 (m, 2H), 3.01 – 2.94 (m, 2H), 1.56 (d, $J = 6.6$ Hz, 3H), 1.51 (s, 9H) ppm.

Compound S12. The product was isolated as a cream colored powder (0.476 g) in 60% yield. $^1$H NMR (CDCl$_3$, 500 MHZ): $\delta$ 9.06 (s, 1H), 8.33 (d, $J = 8.5$ Hz, 1H), 7.92 – 7.87 (m, 1H), 7.81 (d, $J = 7.5$ Hz, 1H), 7.63 (t, $J = 7.3$ Hz, 1H), 7.59 (d, $J = 7.1$ Hz, 1H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.50 (t, $J = 7.7$ Hz, 1H), 7.48 – 7.43 (m, 1H), 7.36 – 7.32 (m, 1H), 7.32 – 7.27 (m, 1H), 6.43 (m, 1H), 4.26 – 4.22 (m, 2H), 4.12 (dd, $J = 21.5$, 10.9 Hz, 1H), 3.93 (m, 1H), 2.05 (d, $J = 6.8$ Hz, 3H), 1.30 (s, 9H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 158.73, 146.97, 134.46, 134.31, 132.79, 131.01, 130.83, 130.70, 130.19, 129.42, 128.62, 128.57, 127.88, 126.68, 125.45, 124.88, 123.06, 55.21, 54.86, 35.91, 32.29, 19.32 ppm.
Complex 14. The complex was purified by silica gel chromatography (10% ether in pentane as the eluting solvent) to obtain green solids (89.7 mg) in 13% yield. This complex was very unstable, and required storage under inert atmosphere. Complex 14 decomposed in solution, yielding a mixture of unidentifiable compounds in the $^1$H and $^{13}$C NMR spectra. High resolution mass spectrometry: $[\text{C}_{35}\text{H}_{40}\text{Cl}_2\text{N}_2\text{ORu}]\text{[(M+H)-H}_2]$ Calculated = 676.1562. Found = 676.1570.

SYNTHESIS OF COMPLEX 15.

Compound S13. The product was isolated as white crystals (1.589 g) in 28% yield. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 8.68 (s, 1H), 7.39 – 7.32 (m, 4H), 7.32 – 7.26 (m, 2H), 7.18 (d, $J$ = 7.7 Hz, 2H), 3.90 (q, $J$ = 6.6 Hz, 1H), 3.51 – 3.27 (m, 2H), 3.04 – 2.94 (m, 2H), 1.47 (d, $J$ = 6.6 Hz, 3H), 1.21 (d, $J$ = 6.9 Hz, 6H), 1.19 (d, $J$ = 6.9 Hz, 6H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 171.39, 146.03, 144.43, 131.41, 128.94, 128.33, 127.72, 126.73, 123.65, 58.73, 50.65, 29.08, 24.18, 23.88, 23.78 ppm.

Compound S14. The reaction gave 89% conversion to product (0.904 g) as a pale yellow, viscous oil. The mixture was carried on crude to the next step. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.29 – 7.26 (m, 3H), 7.18 (m, 2H), 7.03 – 6.99 (m, 2H), 6.96 (dd, $J$ = 8.4, 6.6 Hz, 1H), 3.74 (q, $J$ = 6.6 Hz, 1H), 3.26 – 3.22 (m, 2H), 2.95 – 2.79 (m, 2H), 2.72 – 2.56 (m, 2H), 1.33 (d, $J$ = 6.6 Hz, 3H), 1.15 (d, $J$ = 3.6 Hz, 6H), 1.13 (d, $J$ = 3.6 Hz, 6H) ppm.
Compound **S15**. The product was isolated as a peach colored powder (0.683 g) in 74% yield. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 9.98 (s, 1H), 7.60 – 7.55 (m, 2H), 7.46 – 7.36 (m, 4H), 7.24 – 7.21 (m, 2H), 6.17 (q, $J = 7.0$ Hz, 1H), 4.24 – 4.09 (m, 2H), 4.07 – 3.95 (m, 2H), 2.91 (sept, $J = 6.8$ Hz, 1H), 2.76 (sept, $J = 6.8$ Hz, 1H), 1.82 (d, $J = 7.0$ Hz, 3H), 1.32 (d, $J = 6.8$ Hz, 3H), 1.28 (d, $J = 7.0$ Hz, 3H), 1.27 (d, $J = 7.0$ Hz, 3H), 1.21 (d, $J = 5.6$ Hz, 3H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 159.14, 146.73, 146.56, 137.57, 131.27, 130.37, 129.50, 129.29, 127.52, 125.10, 56.98, 53.28, 45.65, 29.10, 25.33, 25.21, 24.40, 24.15, 17.94 ppm.

**SYNTHESIS OF COMPLEX 16.**

Compound **S16**. The product was isolated as white solids (4.351 g) in 42% yield. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 8.67 (s, 1H), 7.39 – 7.33 (m, 2H), 7.32 – 7.26 (m, 4H), 7.18 (d, $J = 7.7$ Hz, 2H), 3.60 (dd, $J = 7.5$, 6.4 Hz, 1H), 3.35 (s, 2H), 3.07 – 2.89 (m, 1H), 1.90 – 1.80 (m, 1H), 1.79 – 1.71 (m, 1H), 1.21 (d, $J = 6.9$ Hz, 6H), 1.19 (d, $J = 6.9$ Hz, 6H), 0.88 (t, $J = 7.4$ Hz, 3H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 171.46, 146.03, 142.97, 131.44, 128.85, 128.79, 128.32, 127.74, 127.39, 126.49, 123.65, 65.50, 50.58, 31.00, 29.07, 23.87, 23.80, 11.15 ppm.
Compound S17. The reaction yielded 97% conversion to product (1.907 g). The mixture was carried on crude to the next step. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.35 – 7.30 (m, 2H), 7.29 – 7.26 (m, 2H), 7.24 – 7.21 (m, 1H), 7.08 (d, $J$ = 1.5 Hz, 1H), 7.06 (s, 1H), 7.04 – 6.99 (m, 1H), 3.53 (dd, $J$ = 7.5, 6.1 Hz, 1H), 3.29 (sept, $J$ = 6.8 Hz, 2H), 2.94 (dt, $J$ = 11.6, 5.7 Hz, 1H), 2.90 – 2.82 (m, 1H), 2.68 (t, $J$ = 5.6 Hz, 2H), 1.84 – 1.72 (m, 1H), 1.72 – 1.60 (m, 1H), 1.22 (d, $J$ = 3.6 Hz, 6H), 1.21 (d, $J$ = 3.6 Hz, 6H), 0.86 (t, $J$ = 10 Hz, 3H) ppm.

Compound S18. The product was isolated as fluffy white solids (0.530 g) in 25% yield. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 10.22 (s, 1H), 7.60 (d, $J$ = 7.1 Hz, 2H), 7.49 – 7.35 (m, 4H), 7.24 – 7.21 (m, 2H), 5.96 (t, $J$ = 7.8 Hz, 1H), 4.19 – 4.08 (m, 2H), 4.08 – 3.93 (m, 2H), 2.89 (dt, $J$ = 13.6, 6.8 Hz, 1H), 2.77 (dt, $J$ = 13.7, 6.9 Hz, 1H), 2.30 – 2.26 (m, 2H), 2.21 – 2.09 (m, 2H), 1.34 (d, $J$ = 6.8 Hz, 3H), 1.30 (d, $J$ = 4.2 Hz, 3H), 1.29 (d, $J$ = 4.3 Hz, 3H), 1.22 (d, $J$ = 6.8 Hz, 3H), 1.08 (t, $J$ = 7.3 Hz, 3H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 159.58, 146.67, 146.61, 136.33, 131.30, 130.35, 129.51, 129.31, 128.18, 125.13, 125.05, 62.77, 53.10, 45.49, 29.91, 29.23, 29.13, 25.33, 25.30, 24.20, 24.16, 10.85 ppm.

Compound 16. The complex was obtained after silica gel column chromatography as a green powder (0.420 g) in 75% yield. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 16.37 (s, 1H), 7.94 (d, $J$ = 7.4 Hz, 2H), 7.58 (t, $J$ = 7.8 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.47 (t, $J$ = 6.8 Hz, 2H), 7.40 – 7.34 (m, 3H), 6.94 (d, $J$ = 8.3 Hz, 1H), 6.87 (d, $J$ = 4.4 Hz, 2H), 6.24 (dd, $J$ = 11.8, 2.9 Hz, 1H), 5.17 (sept, $J$ = 6.1 Hz, 1H), 3.94 – 3.81 (m, 3H), 3.82 – 3.72 (m, 1H), 3.56 – 3.45 (m, 1H), 3.20 (sept, $J$ = 6.6 Hz, 1H), 3.04 (sept, $J$ = 6.8 Hz, 1H), 2.88 – 2.85 (m, 1H), 2.53 – 2.39 (m, 1H), 1.85 (d, $J$ = 6.1 Hz, 3H), 1.82 (d, $J$ = 6.1 Hz, 3H), 1.21 (d, $J$ = 6.9 Hz, 3H), 1.14 (d, $J$ = 6.9 Hz, 3H), 1.07 (t, $J$ = 7.3 Hz, 3H), 0.90 (d, $J$ = 6.7 Hz, 3H), 0.88 (d, $J$ = 6.6 Hz, 3H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 208.25, 152.81, 148.83, 148.71, 144.04, 138.09, 137.58, 129.68, 129.64, 129.61, 128.77, 128.10, 125.06, 125.00, 122.58, 122.49, 113.21, 75.23, 64.88, 54.96, 44.33, 28.14, 28.03.
25.87, 25.81, 25.32, 24.09, 24.03, 22.59, 22.45, 11.53 ppm. HRMS: [C_{34}H_{44}Cl_2N_2ORu][(M+H)-H_2] Calc. = 668.1875. Found = 668.1871.

**SYNTHESIS OF COMPLEX 17.**

[Chemical structure image]

Compound S19. The product was isolated as cream colored solids (4.716 g) in 48% yield. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 8.85 (s, 1H), 7.43 (d, $J$ = 6.6 Hz, 1H), 7.28 (dd, $J$ = 14.7, 7.1 Hz, 1H), 7.19 (d, $J$ = 7.4 Hz, 4H), 7.14 – 7.01 (m, 1H), 3.92 (broad s, 1H), 3.61 – 3.57 (m, 2H), 3.07 – 3.00 (m, 2H), 2.88 – 2.82 (m, 1H), 2.81 – 2.73 (m, 1H), 2.04 – 1.95 (m, 2H), 1.95 – 1.85 (m, 2H), 1.86 – 1.74 (m, 1H), 1.21 (d, $J$ = 6.8 Hz, 12H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 171.68, 146.07, 138.16, 137.80, 129.54, 128.86, 128.35, 127.47, 126.26, 123.70, 56.56, 50.67, 29.55, 29.13, 29.00, 23.90, 19.25 ppm.

[Chemical structure image]

Compound S20. The reaction gave 53% conversion to product (2.355 g). The mixture was carried on crude to the next step. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.51 – 7.45 (m, 1H), 7.21 – 7.14 (m, 2H), 7.10 (d, $J$ = 7.5 Hz, 3H), 7.07 – 7.01 (m, 1H), 3.88 – 3.76 (m, 1H), 3.36 (sept, $J$ = 6.8 Hz, 2H), 3.08 – 2.99 (m, 2H), 3.00 – 2.88 (m, 2H), 2.88 – 2.80 (m, 1H), 2.80 – 2.70 (m, 1H), 2.05 – 1.93 (m, 2H), 1.90 – 1.81 (m, 1H), 1.80 – 1.69 (m, 1H), 1.24 (d, $J$ = 6.8 Hz, 12H) ppm.

[Chemical structure image]

Compound S21. The product was isolated as cream colored solids (1.408 g) in 53% yield. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 9.01 (s, 1H), 7.52 – 7.46 (m, 1H), 7.42 (t, $J$ = 7.8 Hz, 1H), 7.25 – 7.21 (m, 3H), 7.19 – 7.15 (m, 2H), 5.99 (t, $J$ = 5.5 Hz, 1H), 4.69 – 4.55 (m, 1H), 4.41 – 4.28 (m, 1H), 4.23 – 4.07 (m, 2H), 3.02 (sept, $J$ = 6.8 Hz, 1H), 2.90 (sept, $J$ = 6.9 Hz, 1H), 2.82 (t, $J$ = 12.3 Hz, 2H), 2.29 – 2.31 (m, 1H), 2.20-2.22 (m, 1H), 2.07 – 1.95 (m, 1H), 1.87 – 1.76 (m, 1H), 1.32 (d, $J$ = 5.1 Hz, 3H), 1.31 (d, $J$ = 6.6 Hz, 6H), 1.24 (d, $J$ = 6.8 Hz, 3H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 159.13, 147.11, 138.56, 131.36, 131.04, 130.09, 129.12, 129.04, 127.35, 125.34, 124.96, 56.61, 53.83, 47.18, 29.28, 29.00, 27.34, 25.35, 25.26, 24.39, 24.08, 19.45 ppm.
Compound 17. The complex was purified by silica gel chromatography (eluting solvent starting at 10% ether in pentane and increased to 100% ether over 30 minutes) and isolated as a greenish-brown powder (0.910 g). Yield = 58%. \( ^1H \) NMR (CDCl\(_3\), 500 MHz): \( \delta \) 16.32 (s, 1H), 7.92 (d, \( J = 7.8 \) Hz, 1H), 7.61 (t, \( J = 7.8 \) Hz, 1H), 7.53 – 7.43 (m, 1H), 7.40 (td, \( J = 8.1, 1.4 \) Hz, 2H), 7.33 – 7.27 (m, 1H), 7.24 (d, \( J = 6.6 \) Hz, 1H), 7.18 (d, \( J = 7.5 \) Hz, 1H), 6.92 (d, \( J = 8.4 \) Hz, 1H), 6.89 – 6.83 (m, 2H), 6.52 (dd, \( J = 10.4, 5.6 \) Hz, 1H), 5.11 (sept, \( J = 6.1 \) Hz, 1H), 4.11 – 3.85 (m, 2H), 3.78 (dd, \( J = 20.9, 10.1 \) Hz, 1H), 3.63 – 3.60 (m, 1H), 3.25 – 3.22 (m, 2H), 3.16 – 3.01 (m, 1H), 3.00 – 2.80 (m, 2H), 2.24 – 2.10 (m, 1H), 2.09 – 1.92 (m, 2H), 1.79 (d, \( J = 6.1 \) Hz, 3H), 1.69 (d, \( J = 6.1 \) Hz, 3H), 1.28 (d, \( J = 6.9 \) Hz, 3H), 1.22 (d, \( J = 10.0 \) Hz, 3H), 0.98 (d, \( J = 6.7 \) Hz, 3H), 0.90 (d, \( J = 6.7 \) Hz, 3H) ppm. \( ^{13}C \) NMR (CDCl\(_3\), 125 MHz): \( \delta \) 289.81, 209.36, 152.90, 148.80, 143.95, 138.76, 137.98, 134.74, 129.71, 129.53, 129.35, 129.32, 127.67, 126.37, 125.07, 125.02, 122.54, 122.48, 113.19, 75.27, 60.01, 55.09, 43.54, 30.05, 28.46, 28.34, 28.13, 25.98, 25.70, 24.10, 22.42, 22.40, 22.28 ppm. HRMS: [C\(_{35}\)H\(_{44}\)Cl\(_2\)N\(_2\)ORu]([M+H]-H\(_2\)) Calc. = 680.1875. Found = 680.1877.

### SYNTHESIS OF COMPLEX 18.

Compound S22. The product was isolated as white solids (3.118 g) in 65% yield. \( ^1H \) NMR (CDCl\(_3\), 500 MHz): \( \delta \) 8.86 (s, 1H), 7.28 (dd, \( J = 13.6, 6.2 \) Hz, 1H), 7.18 (d, \( J = 7.7 \) Hz, 2H), 3.57 – 3.47 (m, 2H), 3.12 – 2.99 (m, 3H), 2.55 – 2.46 (m, 1H), 2.44 – 2.34 (m, 1H), 2.05 – 1.96 (m, 1H), 1.88 – 1.79 (m, 2H), 1.70 – 1.62 (m, 1H), 1.24 (s, 3H), 1.22 (d, \( J = 3.6 \) Hz, 6H), 1.20 (d, \( J = 3.6 \) Hz, 6H), 1.17 (d, \( J = 7.2 \) Hz, 3H), 0.99 (s, 3H), 0.91 (d, \( J = 9.8 \) Hz, 1H) ppm. \( ^{13}C \) NMR (CDCl\(_3\), 125 MHz): \( \delta \) 171.72, 146.04, 131.52, 128.28, 123.67, 57.37, 50.31, 48.07, 45.79, 41.94, 38.77, 36.98, 34.55, 29.13, 28.02, 23.86, 23.82, 23.45, 21.77 ppm.
Compound S23. The product (1.44 g) was isolated as a clear oil. There was 87% conversion to product. The crude mixture was carried on directly to the next step. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.12 – 7.07 (m, 2H), 7.06 – 7.01 (m, 1H), 3.36 (sept, $J = 5.0$ Hz, 2H), 3.06 – 2.99 (m, 1H), 2.98 – 2.89 (m, 3H), 2.88 – 2.78 (m, 1H), 2.43 – 2.32 (m, 2H), 2.01 – 1.89 (m, 1H), 1.84 – 1.74 (m, 2H), 1.65 – 1.60 (m, 1H), 1.25 (d, $J = 6.8$ Hz, 12H), 1.23 (s, 3H), 1.15 (d, $J = 7.2$ Hz, 3H), 0.99 (s, 3H), 0.96 (d, $J = 9.6$ Hz, 1H) ppm.

Compound S24. Crude S23 (0.724 g) was carried on directly to the reaction to synthesize S24. Product S24 (0.238 g) was isolated as a cream colored powder in 30% yield. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 10.15 (s, 1H), 7.40 – 7.35 (m, 1H), 7.19 – 7.15 (m, 2H), 5.35 (dt, $J = 10.3$, 7.3 Hz, 1H), 4.35 – 4.19 (m, 3H), 4.21 – 4.04 (m, 1H), 2.89 (sept, $J = 5.0$ Hz, 1H), 2.74 (sept, $J = 5.0$ Hz, 1H), 2.46 – 2.44 (m, 1H), 2.21 – 2.11 (m, 1H), 2.05 – 2.01 (m, 2H), 1.93 – 1.84 (m, 2H), 1.26 (d, $J = 6.8$ Hz, 6H), 1.25 – 1.22 (m, 6H), 1.21 (s, 3H), 1.16 (d, $J = 7.2$ Hz, 3H), 1.08 (s, 3H), 0.84 (d, $J = 10.3$ Hz, 1H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 160.18, 146.92, 146.39, 131.07, 130.40, 125.09, 124.84, 56.96, 53.29, 47.36, 44.00, 41.45, 40.43, 38.65, 35.28, 31.88, 29.17, 29.06, 28.20, 25.37, 25.17, 24.37, 24.10, 23.69, 20.02 ppm.

Compound 18. The complex was purified by silica gel column chromatography (5% methanol in methylene chloride as the eluting solvent) to give 1.161g of grayish-green solids in 56% yield. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 16.37 (s, 1H), 7.59 (t, $J = 7.8$ Hz, 1H), 7.53 – 7.45 (m, 1H), 7.41 – 7.33 (m, 2H), 6.92 (d, $J = 8.3$ Hz, 1H), 6.86 (d, $J = 4.3$ Hz, 2H), 5.59 (dt, $J = 10.0$, 6.3 Hz, 1H), 5.13 – 5.11 (m, 1H), 4.07 – 4.05 (m, 2H), 4.00 – 3.94 (m, 1H), 3.95 – 3.79 (m, 1H), 3.25 – 3.03 (m, 3H), 2.52 (ddt, $J = 13.9$, 6.9, 1.3 Hz, 1H), 2.49 – 2.38 (m, 1H), 2.19 – 2.06 (m, 1H), 2.00 – 1.98 (m, 2H), 1.78 (d, $J = 6.1$ Hz, 3H), 1.76 (d, $J = 6.1$ Hz, 3H), 1.57 (d, $J = 7.0$ Hz, 3H), 1.31 (s, 3H), 1.25 (s, 3H), 1.22 (d, $J = 4.1$ Hz, 3H), 1.21 (d, $J = 4.1$ Hz, 3H), 1.05 (d, $J = 9.9$ Hz, 1H), 0.90 (d, $J = 3.2$ Hz, 3H), 0.88 (d, $J = 3.2$ Hz, 3H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 209.86, 152.66, 148.88, 148.65, 144.21, 138.40, 129.60, 129.56, 125.05, 125.00, 122.53, 122.51, 113.23, 75.06, 59.98, 54.90, 48.62, 43.34, 42.09, 41.10, 38.85, 34.54, 34.13, 28.19, 28.05, 26.01, 25.79, 24.08, 24.02, 23.78, 22.53, 22.49, 21.86 ppm. HRMS: [C$_{35}$H$_{50}$Cl$_2$N$_2$ORu][(M+H)-H$_2$] Calc. = 686.2344. Found = 686.2350.
SYNTHESIS OF COMPLEX 19.

Compound S25. The product was isolated as white crystals (1.669 g) in 46% yield. \(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) 8.78 (s, 1H), 7.30 – 7.25 (m, 1H), 7.18 (d, \(J = 7.7\) Hz, 2H), 3.64 – 3.32 (m, 2H), 3.04 (sept, \(J = 6.9\) Hz, 2H), 2.96 (d, \(J = 7.8\) Hz, 2H), 2.34 – 2.28 (m, 1H), 1.81 – 1.71 (m, 1H), 1.71 – 1.63 (m, 2H), 1.58 (s, 1H), 1.41 – 1.33 (m, 1H), 1.21 (d, \(J = 1.7\) Hz, 6H), 1.20 (d, \(J = 1.7\) Hz, 6H), 1.19 – 1.14 (m, 1H), 0.90 (s, 3H), 0.88 (s, 6H) ppm. \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) 171.83, 146.05, 131.52, 128.29, 123.68, 63.96, 51.66, 49.08, 48.47, 45.04, 38.21, 29.12, 28.65, 27.57, 23.91, 19.99, 18.72, 14.43 ppm.

Compound S26. The reaction afforded 61% conversion to product (1.407 g). The mixture was carried on crude to the next step. \(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) 7.09 – 7.06 (m, 2H), 7.04 – 6.99 (m, 1H), 3.35 (sept, \(J = 6.8\) Hz, 2H), 2.95 (m, 2H), 2.21 – 2.12 (m, 1H), 1.81 – 1.77 (m, 2H), 1.76 – 1.72 (m, 2H), 1.70 – 1.66 (m, 2H), 1.67 – 1.61 (m, 2H), 1.41 – 1.25 (m, 2H), 1.23 (d, \(J = 6.9\) Hz, 12H), 0.88 (s, 6H), 0.87 (s, 3H) ppm.

Compound S27. The product was isolated as cream colored solids (0.349 g) in 36% yield. \(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) 9.19 (s, 1H), 7.41 (t, \(J = 8\) Hz, 1H), 7.24 – 7.21 (m, 2H), 4.71 (broad d, \(J = 11\) Hz, 1H), 4.44 (t, \(J = 10.5\) Hz, 2H), 4.22 (t, \(J = 11\) Hz, 2H), 3.02 (sept, \(J = 6.5\) Hz, 1H), 2.89 (sept, \(J = 6.5\) Hz, 1H), 2.50 – 2.45 (m, 1H), 1.89 – 1.86 (m, 2H), 1.84 – 1.82 (m, 1H), 1.60 – 1.55 (m, 1H), 1.46 – 1.42 (m, 1H), 1.39 – 1.37 (m, 1H), 1.32 – 1.27 (m, 12H), 1.03 (s, 3H), 0.99 (s, 3H), 0.91 (s, 3H) ppm. \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) 159.62, 147.00, 146.62, 131.25, 130.28, 125.18, 125.04, 64.51, 53.40, 51.19, 50.83, 49.17, 44.71, 32.83, 29.10, 29.03, 28.72, 28.26, 25.35, 25.31, 24.47, 24.34, 19.77, 18.90, 14.32 ppm.
Compound 19. The complex was purified by silica gel column chromatography (10% ether in pentane as the eluting solvent) to give a green powder (0.1544 g) in 34% yield. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 16.46 (s, 1H), 7.62 (t, $J = 7.8$ Hz, 1H), 7.51 (ddd, $J = 8.4, 7.1, 2.0$ Hz, 1H), 7.42 – 7.40 (m, 2H), 6.93 (d, $J = 8.4$ Hz, 1H), 6.89 – 6.82 (m, 2H), 5.39 (ddd, $J = 10.9, 5.4, 1.7$ Hz, 1H), 5.12 (sept, $J = 6.2$ Hz, 1H), 4.23 (q, $J = 9.3$ Hz, 1H), 4.07 – 4.11 (m, 1H), 3.94 – 3.98 (m, 1H), 3.94 – 3.98 (m, 2H), 3.22 (sept, $J = 7.0$ Hz, 1H), 3.09 (sept, $J = 6.6$ Hz, 1H), 2.91 – 2.75 (m, 1H), 2.17 – 2.03 (m, 1H), 2.00 – 1.92 (m, 1H), 1.90 (t, $J = 4.5$ Hz, 1H), 1.78 (d, $J = 6.1$ Hz, 3H), 1.75 (d, $J = 6.1$ Hz, 3H), 1.71 – 1.64 (m, 2H), 1.46 – 1.41 (m, 1H), 1.33 (s, 3H), 1.25 (d, $J = 5.1$ Hz, 3H), 1.23 (d, $J = 7.4$ Hz, 6H), 1.01 (s, 3H), 0.94 (d, $J = 6.6$ Hz, 3H), 0.89 (d, $J = 6.7$ Hz, 3H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 212.80, 152.60, 148.71, 148.35, 144.09, 138.54, 129.70, 129.61, 125.07, 125.07, 122.72, 122.48, 113.25, 74.93, 67.82, 55.93, 51.88, 49.09, 46.79, 44.39, 34.66, 30.49, 28.66, 28.11, 28.08, 25.95, 25.80, 24.06, 24.03, 22.82, 22.65, 21.01, 19.96, 16.18 ppm. HRMS: [C$_{35}$H$_{50}$Cl$_2$N$_2$ORu][(M+H)-H$_2$] Calc. = 686.2344. Found = 686.2316.

**SYNTHESIS OF COMPLEX 20.**

Compound S28. The product was isolated as white crystals (4.21 g) in 18% yield. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 8.82 (s, 1H), 7.44 – 7.41 (m, 1H), 7.22 – 7.16 (m, 2H), 7.14 – 7.10 (m, 1H), 6.91 (s, 2H), 3.90 (t, $J = 4.6$ Hz, 1H), 3.58 (q, $J = 17.3$ Hz, 2H), 2.89 – 2.72 (m, 2H), 2.27 (s, 3H), 2.19 (s, 6H), 2.01 – 1.93 (m, 2H), 1.93 – 1.85 (m, 1H), 1.85 – 1.73 (m, 1H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 170.79, 138.20, 148.71, 148.35, 144.09, 138.54, 129.70, 129.61, 128.84, 127.41, 126.24, 56.41, 50.58, 29.52, 28.83, 21.11, 19.23, 18.64 ppm.

Compound S29. The reaction gave 99% conversion to product (0.720 g). The mixture was carried on crude to the next step. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.40 – 7.42 (m, 1H), 7.15 – 7.17
(m, 2H), 7.09 – 7.11 (m, 1H), 6.81 (s, 2H), 3.81 (s, 1H), 3.13 – 3.02 (m, 2H), 3.03 – 2.92 (m, 1H), 2.93 – 2.85 (m, 1H), 2.85 – 2.78 (m, 1H), 2.78 – 2.69 (m, 1H), 2.27 (s, 6H), 2.23 (s, 3H), 2.03 – 1.89 (m, 2H), 1.90 – 1.79 (m, 1H), 1.79 – 1.70 (m, 1H) ppm.

Compound S30. The product was isolated as white solids (0.202 g) in 25% yield. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 9.75 (s, 1H), 7.43 – 7.38 (m, 1H), 7.27 – 7.23 (m, 2H), 7.18 – 7.13 (m, 1H), 6.94 (s, 2H), 6.04 (t, $J$ = 6.4 Hz, 1H), 4.40 – 4.30 (m, 1H), 4.29 – 4.21 (m, 1H), 4.16 – 4.05 (m, 1H), 4.00 – 3.90 (m, 1H), 2.89 – 2.74 (m, 2H), 2.34 (s, 6H), 2.29 (s, 3H), 2.15 – 2.06 (m, 2H), 2.03 – 1.91 (m, 1H), 1.91 – 1.82 (m, 1H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 160.01, 140.56, 138.64, 131.06, 130.88, 130.21, 130.06, 128.83, 128.43, 127.25, 56.64, 51.14, 46.07, 29.10, 27.92, 21.19, 20.13, 18.26 ppm. HRMS: [C$_{32}$H$_{38}$Cl$_2$N$_2$ORu][(M+H)-H$_2$] Calc. = 638.1405. Found = 638.1436.

Compound 20. The complex was purified by silica gel column chromatography (10% ether in pentane as the eluting solvent) to afford a green powder (36.6 mg) in 11% yield. $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 16.28 (s, 1H), 7.89 (d, $J$ = 7.5 Hz, 1H), 7.48 (dt, $J$ = 7 Hz, $J$ = 2 Hz, 1H), 7.26 (t, $J$ = 7 Hz, 1H), 7.21 (t, $J$ = 6.5 Hz, 1H), 7.15 (d, $J$ = 7 Hz, 1H), 7.07 (d, $J$ = 3.5 Hz, 2H), 6.93 – 6.88 (m, 3H), 6.48 – 6.45 (m, 1H), 5.11 (sept, $J$ = 6.5 Hz, 1H), 3.94 (quintet, $J$ = 9.5 Hz, 1H), 3.91 – 3.87 (m, 1H), 3.77 (quartet, $J$ = 10.5 Hz, 1H), 3.63 – 3.58 (m, 1H), 3.03 – 3.01 (m, 1H), 2.92 – 2.89 (m, 2H), 2.45 (s, 3H), 2.33 (s, 3H), 2.25 (s, 3H), 2.16 – 2.12 (m, 1H), 2.04 – 2.02 (m, 1H), 1.97 – 1.92 (m, 1H), 1.72 (d, $J$ = 6 Hz, 3H), 1.66 (d, $J$ = 5.5 Hz, 3H), 1.30 – 1.23 (m, 1H) ppm. $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 293.00, 208.95, 152.59, 144.61, 144.59, 138.95, 138.70, 138.48, 138.44, 138.17, 134.64, 129.85, 129.70, 129.38, 129.30, 127.70, 126.40, 122.97, 122.67, 113.12, 75.15, 59.85, 51.80, 43.75, 30.01, 28.35, 22.40, 22.12, 22.09, 21.43, 18.46, 18.44 ppm. HRMS: [C$_{32}$H$_{38}$Cl$_2$N$_2$ORu][(M+H)-H$_2$] Calc. = 638.1405. Found = 638.1436.
Synthesis of S31. S31 was made as outlined in reference 3.

Synthesis of S32. A Schlenk flask with a Teflon stopper was charged with S31 (0.59 g, 3.31 mmol), 1-bromobutane (0.54 g, 3.97 mmol), p-toluene sulfonic acid monohydrate (0.031 g, 0.167 mmol), CH(OEt)3 (8 mL), and toluene (8 mL). The flask was sealed under air and heated to 115 °C for 10 h. After cooling to RT, an off-white precipitate formed and ca. 30 mL of ether was added to ensure full precipitation. The suspension was stirred for several hours after which the precipitate was collected by filtration and dried in vacuo to give S32 (0.72 g, 67% yield) as an off-white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.97 (s, 1H), 6.39 (s, 2H), 3.76 (dd, J = 22.5, 8.2 Hz, 4H), 3.42 (s, 2H), 1.77 (s, 9H), 1.20 (br s, 2H), 0.89 (br s, 2H), 0.46 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 158.74, 139.93, 135.15, 130.56, 129.78, 51.00, 48.86, 48.14, 29.08, 20.92, 19.44, 18.03, 13.59.

Synthesis of 21. In a glovebox under a nitrogen atmosphere, a 100 mL RB flask was charged with S32 (0.73 g, 2.25 mmol), NaO’Bu (0.22 g, 2.25 mmol), and 1st generation Grubbs catalyst (1.23 g, 1.5 mmol). The flask was cooled to -30 °C and prechilled THF (20 mL) was added. The reaction was stirred at -30 °C for 15 min after which the flask was removed from the cold bath and allowed to stir at RT for 10 h. The flask was then exposed to air and concentrated in vacuo to give a brownish red residue. The residue was dissolved in a minimal amount of benzene and loaded onto a silica gel column (150 mL) where it was flashed with 10% ether in pentane to collect residual 1st generation Grubbs catalyst as a purple band followed by 30% ether in pentane to collect 21 as a red/pink band. The appropriate fractions were concentrated to yield 21 (0.61 g, 63%) as a dark pink residue which could be lyophilized from benzene to give a pink powder. ¹H NMR (500 MHz, C₆D₆) δ 19.51 (s, 1H), 7.17 (m, 4H), 6.99 (t, J = 7.4 Hz, 2H), 6.21 (br s, 1H), 4.29 (t, J = 7.1 Hz, 2H), 3.23 – 3.06 (m, 4H), 2.59 (q, J = 11.9 Hz, 3H), 2.35 (br s, 5H), 1.92 – 1.77 (m, 11H), 1.73 – 1.56 (m, 11H), 1.48 (q, J = 12.4 Hz, 6H), 1.33 – 1.08 (m, 10H), 1.06 – 0.96 (m, 3H) ppm. ¹³C NMR (126 MHz, C₆D₆) δ 220.22, 219.61, 151.74, 137.53, 137.48, 137.12, 129.14, 50.88, 50.66, 48.01, 47.99, 32.07, 31.95, 30.91, 29.95, 28.26, 28.19, 27.06, 21.04, 20.50, 18.82, 14.56 ppm. ³¹P NMR (121 MHz, C₆D₆) δ 32.58 ppm. HRMS: Calc. = 786.3150. Found = 786.3158.
References.


Crystallographic Data for Complex 12

Contents

Table 1. Crystal data
Figures Minimum overlap
Table 2. Atomic Coordinates
Table 3. Selected bond distances and angles

Complex 12

Note: Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 804197.
Table 1. Crystal data and structure refinement for Complex 12 (CCDC 804197).

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### Data Collection

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Special Refinement Details

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

Refinement of F^2 against ALL reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of F^2 > 2σ(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for Complex 12 (CCDC 804197). U(eq) is defined as the trace of the orthogonalized U_{ij} tensor.

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Table 3. Selected bond lengths [Å] and angles [°] for Complex 12 (CCDC 804197).

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<td>O(1)-Ru(1)-Cl(2)</td>
<td>86.079(16)</td>
</tr>
<tr>
<td>Cl(1)-Ru(1)-Cl(2)</td>
<td>156.580(8)</td>
</tr>
</tbody>
</table>
Crystallographic Data for Complex 15

Contents

Table 4. Crystal data
Figures Minimum overlap
Table 5. Atomic Coordinates
Table 6. Selected bond distances and angles

Complex 15

Note: Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 804198.
Table 4. Crystal data and structure refinement for Complex 15 (CCDC 804198).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{33}$H$</em>{42}$N$_2$OCl$_2$Ru</td>
</tr>
<tr>
<td>Formula weight</td>
<td>654.66</td>
</tr>
<tr>
<td>Crystallization Solvent</td>
<td>Ether/pentane</td>
</tr>
<tr>
<td>Crystal Habit</td>
<td>Block</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.22 x 0.18 x 0.16 mm$^3$</td>
</tr>
<tr>
<td>Crystal color</td>
<td>Green</td>
</tr>
<tr>
<td><strong>Data Collection</strong></td>
<td></td>
</tr>
<tr>
<td>Type of diffractometer</td>
<td>Bruker KAPPA APEX II</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å MoKα</td>
</tr>
<tr>
<td>Data Collection Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>θ range for 9859 reflections used in lattice determination</td>
<td>2.56 to 36.04°</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 10.5474(3) Å, b = 15.6796(5) Å, c = 19.1646(6) Å, α = 90°, β = 90°, γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>3169.42(17) Å$^3$</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 2,2,2$_1$</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.372 Mg/m$^3$</td>
</tr>
<tr>
<td>F(000)</td>
<td>1360</td>
</tr>
<tr>
<td>Data collection program</td>
<td>Bruker APEX2 v2009.7-0</td>
</tr>
<tr>
<td>θ range for data collection</td>
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<tr>
<td>Completeness to θ = 36.56°</td>
<td>99.9 %</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-17 ≤ h ≤ 17, -25 ≤ k ≤ 26, -31 ≤ l ≤ 32</td>
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<tr>
<td>Data collection scan type</td>
<td>ω scans; 8 settings</td>
</tr>
<tr>
<td>Data reduction program</td>
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<tr>
<td>Reflections collected</td>
<td>79037</td>
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<tr>
<td>Independent reflections</td>
<td>15623 [R$_{int}$ = 0.0482]</td>
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<tr>
<td>Absorption coefficient</td>
<td>0.691 mm$^{-1}$</td>
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<tr>
<td>Absorption correction</td>
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<tr>
<td>Max. and min. transmission</td>
<td>0.8975 and 0.8629</td>
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</table>
### Structure solution and Refinement

<table>
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<tr>
<th>Description</th>
<th>Details</th>
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<tr>
<td>Structure solution program</td>
<td>SHELXS-97 (Sheldrick, 2008)</td>
</tr>
<tr>
<td>Primary solution method</td>
<td>Direct methods</td>
</tr>
<tr>
<td>Secondary solution method</td>
<td>Difference Fourier map</td>
</tr>
<tr>
<td>Hydrogen placement</td>
<td>Difference Fourier map</td>
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<td>Structure refinement program</td>
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<td>Refinement method</td>
<td>Full matrix least-squares on F²</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>15623 / 0 / 520</td>
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<tr>
<td>Treatment of hydrogen atoms</td>
<td>Unrestrained</td>
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<td>Goodness-of-fit on F²</td>
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<tr>
<td>Final R indices [I&gt;2σ(I), 14090 reflections]</td>
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</tr>
<tr>
<td>R indices (all data)</td>
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<tr>
<td>Type of weighting scheme used</td>
<td>Sigma</td>
</tr>
<tr>
<td>Weighting scheme used</td>
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<td>Average shift/error</td>
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<td>Anomalous differences</td>
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<tr>
<td>Absolute structure parameter</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.685 and -0.647 e.Å⁻³</td>
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Table 5. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters (Å²x $10^3$) for Complex 15 (CCDC 804198). U(eq) is defined as the trace of the orthogonalized $U_{ij}$ tensor.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{eq}$</th>
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<td>9(1)</td>
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<td>7275(1)</td>
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Table 6. Selected bond lengths [Å] and angles [°] for Complex 15 (CCDC 804198).

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<tr>
<th>Bond</th>
<th>Length</th>
<th>Angle</th>
<th></th>
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</thead>
<tbody>
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<td>Ru(1)-C(24)</td>
<td>1.8287(12)</td>
<td>C(24)-Ru(1)-C(1)</td>
<td>101.32(5)</td>
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<td>78.95(4)</td>
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<td>Ru(1)-O(1)</td>
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<td>C(1)-Ru(1)-O(1)</td>
<td>177.03(4)</td>
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<td>Ru(1)-Cl(1)</td>
<td>2.3289(3)</td>
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<td>101.10(4)</td>
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<td>Ru(1)-Cl(2)</td>
<td>2.3336(3)</td>
<td>C(1)-Ru(1)-Cl(1)</td>
<td>89.36(3)</td>
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<td>87.70(2)</td>
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<tr>
<td></td>
<td></td>
<td>Cl(1)-Ru(1)-Cl(2)</td>
<td>153.208(12)</td>
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</table>
The Bruker KAPPA APEXII X-ray diffractometer was purchased via an NSF CRIF:MU award to the California Institute of Technology, CHE-0639094.