Supporting Information for

Oxidative Demetalation of Cyclohexadienyl Ruthenium(II) Complexes: A Net Ru-Mediated Dearomatization

F. Christopher Pigge,* John J. Coniglio, and Nigam P. Rath

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General Experimental. All commercially available reagents and solvents were used as received unless otherwise noted. Tetrahydrofuran was distilled from Na-benzophenone, CH₂Cl₂ was distilled from CaH₂. All reactions were performed in oven-dried glassware under a blanket of dry argon. Thin-layer chromatography was performed on Whatman silica gel 60 glass-backed TLC plates (250 μ m). All reactions were monitored by TLC for consumption of starting substrate. Flash column chromatography was performed using Natland International silica gel 60 (200-400 mesh). Radial chromatography was performed using a Harrison Research Chromatotron. ¹H- and ¹³C-NMR spectra were obtained on a Bruker Avance 300 or Bruker ARX 500 spectrometer. Chemical shifts (δ) are reported relative to residual solvent peaks. NMR peak assignments (when indicated) were made on the basis of 2-D experiments (HMQC, COSY, NOESY). IR spectra were recorded on a Nicolet Avatar 360 FT-IR spectrophotometer. Melting points were determined using a Thomas-Hoover melting point apparatus and are uncorrected. High-resolution mass spectra were obtained using a JEOL M-Station 700 spectrometer. Combustion analyses were obtained from Atlantic Microlabs, Norcross, GA.

Procedures for the oxidative demetalation of 4 (Table 1).

Using CuCl₂: The Ru-cyclohexadienyl substrate **4** (53 mg, 0.13 mmol) and CuCl₂ (34 mg, 0.26 mmol) were combined in 5 mL of EtOH and the resulting mixture was stirred at room temperature for 30 min. During this time a red solid precipitated from the reaction mixture. This solid was removed by filtration and the filtrate was partitioned between CH₂Cl₂ and brine. The

layers were separated and the aqueous phase was re-extracted with CH₂Cl₂ (x2). The combined organic layer was dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The residue was purified by radial chromatography (SiO₂, EtOAc) to afford **5** (30 mg, 99%) as a yellow solid. M.p. 164 °C; R_f = 0.40 (EtOAc). ¹H-NMR (300 MHz, CDCl₃) δ 2.46 (s, 3H), 2.90 (s, 3H), 3.28 (s, 2H), 3.53 (s, 3H), 6.25 (d, *J* = 9.9 Hz, 2H), 6.78 (d, *J* = 9.9 Hz, 2H). ¹³C-NMR (75 MHz, CDCl₃) δ 12.87, 30.08, 44.24, 54.35, 106.14, 127.84, 150.88, 164.38, 168.62, 186.30. IR (thin film) ν (cm⁻¹) 3030, 2952, 2913, 1660.8, 1622, 1402, 1262, 1061. HRMS (EI) calcd for C₁₃H₁₅NO₃ 233.1052 [M]⁺, found 233.1053. Anal. calcd for C₁₃H₁₅NO₃: C, 66.94; H, 6.48; N, 6.00. Found: C, 66.85; H, 6.39; N, 6.11.

Using CuCl₂ (gram scale reaction): Using the procedure described above, **4** (1.00 g, 2.4 mmol) and CuCl₂ (0.67 g, 5.0 mmol) gave **5** (0.46 g, 82%) as a crystalline yellow solid with spectroscopic properties identical to those described above.

Using DDQ: A solution of **4** (52 mg, 0.12 mmol) in CH₂Cl₂ (5 mL) was cooled to -78 °C and DDQ (85 mg, 0.37 mmol) was added. The reaction was allowed to warm to room temperature and maintained for 2 h. The reaction mixture was filtered through a short plug of Celite topped with a thin layer of silica gel and rinsed with ethyl acetate. The filtrate was concentrated *in vacuo* and the resulting residue dissolved in CH₂Cl₂, washed with brine and dried over anhydrous MgSO₄. After filtration and evaporation of the solvent, **5** (5 mg, 17%) was isolated by radial chromatography.

Using CAN: Ceric ammonium nitrate (210 mg, 0.38 mmol) was added to a solution of **4** (53 mg, 0.13 mmol) in 5 ml of acetone and the resulting mixture was stirred at room temperature. After 10 min the solvent was removed *in vacuo* to afford a brown tarry residue. The residue was partitioned between CH₂Cl₂ (10 mL) and brine (10 mL). The layers were separated and the organic phase was dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The product **5** (2 mg, 7%) was isolated and purified by radial chromatography.

General procedure for the CuCl₂-mediated oxidative demetalation of substrates shown in Table 2. The Ru-cyclohexadienyl substrates (0.12 mmol) and CuCl₂ (0.25 mmol) were combined in 5 mL of EtOH and the resulting mixtures were stirred at room temperature for 30 min. Work-up of the reactions as described above gave crude products that were then purified by radial chromatography (SiO₂, EtOAc). For the transformations shown in entries 2 and 3, the crude products mixtures were taken up in THF (~5 mL) and P(OEt)₃ (2.2 equiv based on starting Ru complex) was added. The resulting solution was stirred at room temperature for 3 h. The solvent was removed and the residue purified by radial chromatography (SiO₂, EtOAc) to afford the indicated conjugated dienones and CpRuCl[P(OEt)₃]₂. Compound characterization data is provided below.

Entry 1:

Colorless solid, m.p. 149 °C; R_f = 0.58 (EtOAc:Methanol 5:1). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 2.46 (s, 3H, H12), 2.92 (s, 3H, H8), 3.18 (d, J = 9.8 Hz, 1H, H7), 3.48 (d, J = 9.8 Hz, 1H, H7), 3.52 (s, 3H, H13), 3.57 (s, 3H, H14), 5.63 (d, J = 1.4 Hz, 1H, H3), 6.16 (dd, J = 9.7, 1.4 Hz, 1H, H5), 6.54 (d, J = 9.7 Hz, 1H, H6). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 12.52 (C12), 30.00 (C8), 46.00 (C1), 54.32 (C13), 54.84 (C7), 56.01 (C14), 102.64 (C3), 107.93 (C10), 126.25 (C6), 146.39 (C5), 163.18 (C11), 168.35 (C9), 176.22 (C2), 188.57 (C4). IR (KBr) ν (cm^{-1}) 3062, 2926, 2550, 1673, 1654, 1586, 1432, 1360, 1275, 1224. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_4$ 263.1158 $[\text{M}]^+$, found 263.1157. Anal. calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_4$: C, 63.87; H, 6.51; N, 5.32. Found: C, 63.66; H, 6.46; N, 5.28.

Entry 2:

Yellow solid, m.p. 120-123 °C; R_f = 0.50 (EtOAc). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 2.39 (s, 3H, H12), 2.89 (s, 3H, H8), 3.09 (d, J = 9.4 Hz, 1H, H7), 3.44 (d, J = 9.4 Hz, 1H, H7), 3.47 (s, 3H, H13), 6.14 (d, J = 9.8 Hz, 1H, H3), 6.18-6.27 (m, 2H, H5 & H6), 7.01 (ddd, J = 9.8, 5.1, 2.6 Hz, 1H, H4). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 12.16 (C12), 30.08 (C8), 52.99 (C1), 54.03 (C13), 56.88

(C7), 112.91 (C10), 119.28 (C5), 126.70 (C3), 140.71 (C4), 142.33 (C6), 161.21 (C11), 167.70 (C9), 202.55 (C2). IR (thin film) ν (cm^{-1}) 3039, 2937, 2865, 1663, 1629. HRMS (EI) calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_3$ 233.1052 $[\text{M}]^+$, found 233.1051. Anal. calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 66.83; H, 6.49; N, 5.95.

Entry 3:

Yellow solid, m.p. 131-134 °C; R_f = 0.43 (EtOAc). ^1H -NMR (300 MHz, acetone- d_6) δ 2.36 (s, 3H, H12), 2.83 (s, 3H, H8), 3.18 (d, J = 9.2 Hz, 1H, H7), 3.36 (d, J = 9.2 Hz, 1H, H7), 3.49 (s, 3H, H13 or H14), 3.61 (s, 3H, H13 or H14), 5.30 (d, J = 3.1 Hz, 1H, H6), 6.03 (dd, J = 10.2, 0.5 Hz, 1H, H3), 6.90 (dd, J = 10.2, 3.1 Hz, 1H, H4). ^{13}C -NMR (75 MHz, acetone- d_6) δ 11.91 (C12), 29.83 (C8), 51.81 (C1), 54.25 (C13 or C14), 55.40 (C13 or C14), 59.08 (C7), 109.56 (C3, C4, or C6), 115.98 (C10), 127.84 (C3, C4, or C6), 141.18 (C3, C4, or C6), 150.66 (C5), 160.79 (C11), 167.79 (C9), 201.91 (C2). IR (thin film) ν (cm^{-1}) 3014, 2939, 2874, 1672, 1639, 1272, 1238, 1062. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_4$ 263.1158 $[\text{M}]^+$, found 263.1157. Anal. calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_4$: C, 63.87; H, 6.51; N, 5.32. Found: C, 63.66; H, 6.63; N, 5.30.

Entry 4:

Spirocyclic dienone 9: Yellow oil, $R_f = 0.40$ (EtOAc). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 2.38 (s, 3H, H12), 2.91 (s, 3H, H8), 3.11 (d, $J = 9.2$ Hz, 1H, H7), 3.48 (s, 3H, H13), 3.54 (d, $J = 9.2$ Hz, 1H, H7), 3.74 (s, 3H, H14), 5.90 (dd, $J = 9.0, 1.7$ Hz, 1H, H6), 6.08-6.17 (m, 2H, H4/5). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 12.16 (C12), 30.16 (C8), 54.25 (C13), 54.45 (C1), 55.61 (C14), 57.22 (C7), 110.65 (C4 or C5), 113.56 (C10), 118.36 (C4 or C5), 133.48 (C6), 152.18 (C3), 160.56 (C11), 167.65 (C9), 197.41 (C2). IR (thin film) ν (cm^{-1}) 3005, 2913, 2845, 1673, 1640. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_4$ 263.1158 $[\text{M}]^+$, found 263.1159.

Tetrahydroisoquinoline 10: Yellow solid, m.p. 125-126 $^\circ\text{C}$; $R_f = 0.58$ (EtOAc). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 2.53 (s, 3H, H12), 3.10 (s, 3H, H8), 3.77 (s, 3H, H13), 3.83 (s, 3H, H14), 3.88 (s, 3H, H15), 4.39 (s, 2H, H7), 6.85 (d, $J = 8.7$ Hz, 1H, H4), 7.44 (d, $J = 8.7$ Hz, 1H, H5). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 15.13 (C12), 35.13 (C8), 46.78 (C7), 54.87 (C13), 56.09 (C15), 61.03 (C14), 109.41 (C10), 111.23 (C4), 124.27 (C5), 126.28 (C1 or C6), 126.52 (C1 or C6), 143.82 (C2 or C3), 150.13 (C2 or C3), 160.71 (C11), 168.24 (C9). IR (thin film) ν (cm^{-1}) 2966, 2938, 1725, 1677, 1589, 1496, 1457, 1280. HRMS (EI) calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_4$ 277.1314 $[\text{M}]^+$, found 277.1313. Anal. calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_4$: C, 64.97; H, 6.91; N, 5.05. Found: C, 64.59; H, 6.76; N, 4.98.

Entry 5:

Yellow solid, m.p. 152 °C; R_f = 0.58 (EtOAc). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 2.53 (s, 3H, H12), 3.09 (s, 3H, H8), 3.77 (s, 3H, H13), 3.81 (s, 3H, H14), 4.28 (s, 2H, H7), 6.67 (d, J = 2.6 Hz, 1H, H2), 6.82 (dd, J = 8.7, 2.6 Hz, 1H, H4), 7.67 (d, J = 8.7 Hz, 1H, H5). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 15.12 (C12), 34.98 (C8), 52.82 (C7), 54.87 (C13), 55.54 (C14), 109.56 (C10), 110.23 (C2), 112.55 (C4), 125.71 (C1 or C6), 129.81 (C5), 133.36 (C1 or C6), 157.60 (C3), 160.53 (C11), 168.33 (C9). IR (thin film) ν (cm^{-1}) 3071, 3014, 2966, 2939, 1674, 1598, 1499, 1457, 1311, 1279. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_3$ 247.1208 $[\text{M}]^+$, found 247.1210. Anal. calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 67.84; H, 6.99; N, 5.66.

Entry 6:

Yellow oil, R_f = 0.45 (EtOAc). $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 2.52 (s, 3H, H12), 3.08 (s, 3H, H8), 3.77 (s, 3H, H13), 3.86 (s, 6H, H14/15), 4.26 (s, 2H, H7), 6.62 (s, 1H, H2), 7.33 (s, 1H, H5). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ 15.12 (C12), 34.94 (C8), 52.40 (C7), 54.86 (C13), 56.16 (C14 or C15), 56.20 (C14 or C15), 108.08 (C2), 109.78 (C10), 112.17 (C5), 124.49 (C1 or C6), 125.71 (C1 or C6), 147.21 (C3 or C4), 147.60 (C3 or C4), 160.47 (C11), 168.05 (C9). IR (thin

film) ν (cm^{-1}) 2969, 2935, 2850, 1637, 1508, 1253, 1065. HRMS (EI) calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_4$ 277.1314 $[\text{M}]^+$, found 277.1316.

Entry 7:

Yellow oil, R_f = 0.61 (EtOAc). ^1H -NMR (500 MHz, acetone- d_6) δ 2.30 (s, 3H), 2.81 (s, 1H), 3.02 (s, 3H), 3.80 (s, 3H), 3.84 (s, 3H), 4.33 (d, J = 16.0 Hz, 1H), 4.64 (d, J = 16.0 Hz, 1H), 6.45 (d, J = 2.2 Hz, 1H), 6.49 (d, J = 2.2 Hz, 1H). ^{13}C -NMR (125 MHz, acetone- d_6) δ 30.43, 34.42, 53.26, 55.83, 56.14 (two coincident carbon signals, based on DEPT90 and HMQC spectroscopic data), 98.02, 102.54, 113.83, 134.82, 157.88, 161.40, 165.83, 203.64. IR (thin film) ν (cm^{-1}) 3482, 3001, 2938, 2837, 1719, 1647, 1609, 1500, 1201, 1152. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_4$ 263.1158 $[\text{M}]^+$, found 263.1158.

Entry 8:

Yellow solid, R_f = 0.36 (EtOAc:Hexanes 1:1). ^1H -NMR (300 MHz, CDCl_3) δ 2.50 (s, 3H, H12), 3.07 (s, 3H, H8), 3.76 (s, 3H, H13), 4.19 (s, 2H, H7), 5.94 (s, 2H, H14), 6.59 (s, 1H, H2), 7.22 (s, 1H, H5). ^{13}C -NMR (75 MHz, CDCl_3) δ 15.12 (C12), 34.89 (C8), 52.52 (C7), 54.90 (C13),

101.13 (C14), 105.30 (C2 or C5), 109.03 (C2 or C5), 109.86 (C1, 6, or 10), 125.73 (C1, 6, or 10), 126.85 (C1, 6, or 10), 145.57 (C3 or C4), 146.48 (C3 or C4), 160.55 (C11), 168.12 (C9). IR (neat solid) ν (cm⁻¹) 3034, 2947, 2909, 2843, 1636, 1594, 1479, 1225, 1026. HRMS (EI) calcd for C₁₄H₁₅NO₄ 261.1001 [M]⁺, found 261.0998.

Entry 9:

Chlorotetrahydroisoquinoline 15: Yellow oil, R_f = 0.64 (EtOAc). ¹H-NMR (500 MHz, acetone-d₆) δ 2.52 (s, 3H, H12), 3.06 (s, 3H, H8), 3.80 (s, 3H, H13), 4.43 (s, 2H, H7), 7.19-7.25 (m, 2H, H3/4), 7.67 (dd, J = 7.5, 1.3 Hz, 1H, H5). ¹³C-NMR (125 MHz, acetone-d₆) δ 15.07 (C12), 34.71 (C8), 49.76 (C7), 55.25 (C13), 109.25 (C10), 126.48 (C3 or C4), 128.16 (C5), 128.56 (C3 or C4), 130.49 (C2), 130.82 (C1 or C6), 136.61 (C1 or C6), 163.82 (C11), 167.52 (C9). IR (thin film) ν (cm⁻¹) 3063, 2944, 2841, 1645. HRMS (EI) calcd for C₁₃H₁₄ClNO₂ 251.0713 [M]⁺, found 251.0714.

Chlorotetrahydroisoquinoline 16: Yellow oil, R_f = 0.43 (EtOAc). ¹H-NMR (500 MHz, acetone-d₆) δ 2.50 (s, 3H, H12), 3.01 (s, 3H, H8), 3.81 (s, 3H, H13), 4.33 (s, 2H, H7), 7.19-7.31 (m, 2H, H2/4), 7.71 (d, J = 8.3 Hz, 1H, H5). ¹³C-NMR (125 MHz, acetone-d₆) δ 14.98 (C12), 34.49 (C8), 52.05 (C7), 55.22 (C13), 109.37 (C10), 125.52 (C2), 127.17 (C4), 130.76 (C5), 130.90 (C1,3, or 6), 133.24 (C1,3, or 6), 135.47 (C1,3, or 6), 163.42 (C11), 167.67 (C9). IR

(thin film) ν (cm^{-1}) 3000, 2941, 2845, 1643. HRMS (EI) calcd for $\text{C}_{13}\text{H}_{14}\text{ClNO}_2$ 251.0713 $[\text{M}]^+$, found 251.0713.

Chlorotetrahydroisoquinoline 17: Yellow solid, m.p. 96-98 °C; R_f = 0.72 (EtOAc). ^1H -NMR (500 MHz, acetone- d_6) δ 2.52 (s, 3H, H12), 3.01 (s, 3H, H8), 3.84 (s, 3H, H13), 4.32 (s, 2H, H7), 7.13 (dd, J = 8.1, 2.1 Hz, 1H, H3), 7.20 (d, J = 8.1 Hz, 1H, H2), 7.72 (d, J = 2.1 Hz, 1H, H5). ^{13}C -NMR (125 MHz, acetone- d_6) δ 15.06 (C12), 34.52 (C8), 51.98 (C7), 55.31 (C13), 109.14 (C10), 125.85 (C3), 127.21 (C2), 128.70 (C5), 132.13 (C1,4, or 6), 132.64 (C1,4, or 6), 136.31 (C1,4, or 6), 164.02 (C11), 167.45 (C9). IR (thin film) ν (cm^{-1}) 3014, 2941, 2847, 1640, 1596. HRMS (EI) calcd for $\text{C}_{13}\text{H}_{14}\text{ClNO}_2$ 251.0713 $[\text{M}]^+$, found 251.0713.

X-Ray Crystal Structure Determination of 5. A single crystal with dimensions 0.28 x 0.24 x 0.20 mm was mounted on glass fibers in random orientation. Preliminary examination and data collection were performed using a Bruker SMART Charge Coupled Device (CCD) Detector single crystal X-Ray diffractometer using graphite monochromated Mo $\text{K}\alpha$ radiation (λ = 0.71073 Å) equipped with a sealed tube X-Ray source. Preliminary unit cell constants were determined with a set of 45 narrow frames (0.3° in ϖ) scans. Data collection consisted of 3636 frames of intensity data collected with a frame width of 0.3° in ϖ and counting time of 15 seconds/frame at a crystal to detector distance of 4.950 cm. The double pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. SMART and SAINT software packages (Bruker Analytical X-Ray, Madison, WI, 2001) were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement of xyz centroids of thresholded reflections from the complete data set.

Collected data were corrected for systematic errors using SADABS (Blessing, R. H., Acta Cryst. (1995), A51, 33-38) based on the Laue symmetry using equivalent reflections.

Structure solution and refinement were carried out using the SHELXTL- PLUS software package (Sheldrick, G. M., Bruker Analytical X-Ray Division, Madison, WI, 2001). The structure was solved by direct methods and refined successfully in the orthorhombic space group Pbca. Full matrix least-squares refinement was carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence with final residual values: $R_1 = 6.6\%$, $wR_2 = 16.0\%$. The hydrogen atoms were treated using appropriate riding model (AFIX m3). Complete crystallographic details have been deposited with the Cambridge Crystallographic Database (CCDC 202848).

Crystal data: $C_{13}H_{15}NO_3$, $M = 233.26$, orthorhombic, space group Pbca, $a = 12.4162(3)$, $b = 7.6844(2)$, $c = 26.1667(6)$ Å, $V = 2496.59(11)$ Å³, $Z = 8$, $D_{\text{calc}} = 1.241$ g cm⁻³, $T = 223(2)$ K, $\mu(\text{Mo-K}\alpha) = 0.088$ mm⁻¹, 59698 reflections collected of which 3011 were independent ($R_{\text{int}} = 0.069$), all non-hydrogen atoms were refined anisotropically using full matrix least squares on F^2 to give $R_1 = 0.0664$ and $wR_2 = 0.1605$.

Figure S1. Molecular structure of **5** (ORTEP).

Figure S2

Figure S3

Figure S4

Figure S5

Figure S6

Figure S7

Figure S8