Supplementary Material (ESI) for Chemical Communications

Entrapment of a Dirhodium Tetracarboxylate Unit Inside the Aromatic Bowl of a Calix[4]arene: Unique Catalysts for C–H Amination

Supplementary Material

(6 pages)

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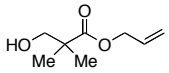
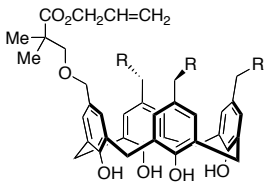
General. All reagents were obtained commercially unless otherwise noted. Reactions were performed using oven-dried glassware under an atmosphere of dry nitrogen. Air- and moisture-sensitive solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated under reduced pressure (~20 Torr) by rotary evaporation. Benzene, *N,N*-dimethylformamide (DMF), and dichloromethane (CH_2Cl_2) were passed through two columns of activated alumina prior to use. Chlorobenzene was dried over activated 3 Å molecular sieves. 1,2-Dichloroethane (DCE) was distilled from CaH_2 immediately before use. Chromatographic purification of products was accomplished using forced flow chromatography on Silicycle silica gel 60 (40-63 μm). Thin layer chromatography was performed on EM science silica gel 60 F_{254} plates (250 μm). Visualization of the developed chromatogram was accomplished by fluorescence quenching and by staining with ethanolic anisaldehyde, aqueous potassium permanganate, or aqueous ceric ammonium molybdate (CAM) solution.

Nuclear Magnetic Resonance (NMR) spectra were acquired on a Varian Mercury 400 or Varian Inova 500 operating at 400 or 500, 100 or 125, and 376 MHz for ^1H, ^{13}C, and ^{19}F, respectively. ^1H and ^{13}C spectra are referenced internally according to residual solvent signals ($CHCl_3$ δ = 7.26 ppm, $CDCl_3$ δ = 77.23 ppm). ^{19}F NMR spectra are referenced internally using α,α,α-trifluorotoluene as a standard (δ = –63.72 ppm). Data for ^1H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br broad), integration, and coupling constant (Hz). Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ, ppm). Infrared (IR) spectra were recorded as either thin films using NaCl plates or as KBr pellets on a Thermo-Nicolet 300 FT-IR spectrometer, and are reported in frequency of absorption. High resolution mass spectra were obtained from the Vincent Coates Foundation Mass Spectrometry Laboratory at Stanford University.

Experimental Procedures and Characterization Data



2-Propenyl 2,2-dimethyl-3-hydroxypropanoate: A single portion of anhydrous K_2CO_3 (2.07 g, 15.0 mmol) was added to a 0 °C solution of 2,2-dimethyl-3-hydroxypropionic acid (1.77 g, 15.0 mmol) in 15 mL of DMF. After stirring the suspension for 10 min, neat allyl bromide (1.81 g, 15.0 mmol) was added dropwise. The ice bath was removed and the reaction mixture was stirred for 18 h. Following this time, the mixture was diluted with 60 mL of Et_2O and 30 mL of H_2O and the contents transferred to a separatory funnel. The organic layer was collected and the aqueous layer was extracted with 3 x 10 mL of Et_2O. The combined organic fractions were washed with 1 x 20 mL of H_2O and 1 x 20 mL of saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure to an oily residue. Purification of this material by column chromatography on silica gel (3:1 hexanes/EtOAc) furnished the desired product as a colorless oil (2.09 g, 88%). TLC R_f = 0.38 (7:3 hexanes/EtOAc); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.96–5.86 (m, 1H), 5.34–5.29 (m, 1H), 5.26–5.22 (m, 1H), 4.62–4.59 (m, 2H), 3.57 (s, 2H), 2.27 (br s, 1H), 1.21 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.5, 132.2, 118.3, 69.9, 65.4, 44.4, 22.3 ppm; IR (thin film) ν 3444, 2976, 2878, 1729, 1475, 1303, 1210, 1146, 1052 cm^{-1}; HRMS (ES^+) calcd for $C_8H_{14}O_3$ 158.0943 found 181.0845 (MNa^+).

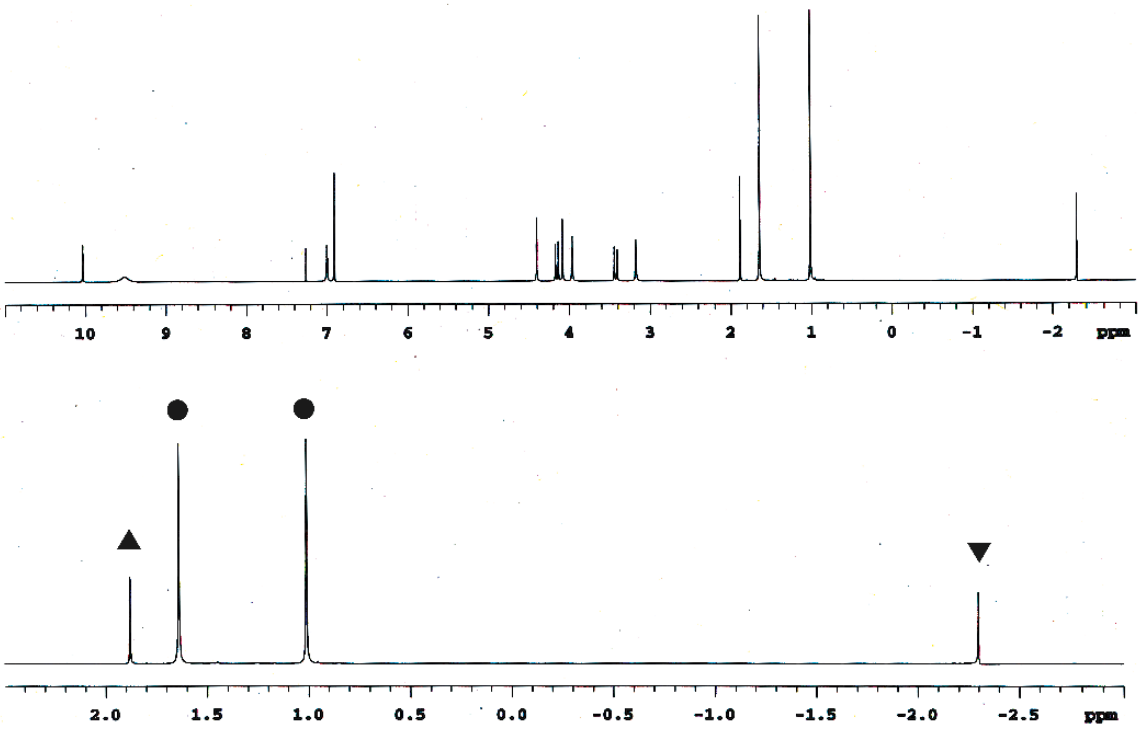


CLX-(allyl ester)$_4$: To a solution of 2-propenyl 2,2-dimethyl-3-hydroxypropanoate (2.66 g, 16.82 mmol, 8.0 equiv) in 42 mL of benzene was added successively tetrachloromethylcalix[4]arene **1**[1] (1.30 g, 2.10 mmol), anhydrous K_2CO_3 (2.32 g, 16.82 mmol, 8.0 equiv), and $^nBu_4NI$ (78 mg, 0.21 mmol, 0.1 equiv). The reaction flask was

equipped with a reflux condenser and the contents were stirred at 80 °C for 36 h. During this time, the suspension turned from pale yellow to blood red. After cooling to 23 °C, the reaction was quenched by the slow and cautious addition of 35 mL of 1 N aqueous HCl. The biphasic mixture was transferred to a separatory funnel with 50 mL of Et_2O, the organic layer was collected, and the aqueous layer was extracted with 3 x 15 mL of Et_2O. The combined organic extracts were washed with 1 x 20 mL of saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure to a viscous oil. Purification by chromatography on silica gel (9:1 toluene/Et_2O) afforded the desired product as a thick, colorless oil (1.92 g, 83%). TLC R_f = 0.26 (9:1 toluene/Et_2O); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.17 (s, 4H), 6.97 (s, 8H), 5.93–5.83 (m, 4H), 5.32–5.26 (m, 4H), 5.19–5.16 (m, 4H), 4.59–4.57 (m, 8H), 4.28 (s, 8H), 4.23 (br d, 4H, *J* = 13.6 Hz), 3.49 (br d, 4H, *J* = 13.6 Hz), 3.38 (s, 8H), 1.20 (s, 24H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.3, 148.3, 132.6, 132.3, 128.5, 128.2, 117.7, 76.9, 72.8, 65.2, 43.9, 32.0, 22.7 ppm; IR (thin film) ν 3174, 2975, 2936, 2872, 1733, 1476, 1305, 1224, 1150, 1098 cm^{-1}; HRMS (ES$^+$) calcd for $C_{64}H_{80}O_{16}$ 1104.5446 found 1127.5350 (MNa^+).

CLX–H_4:[2] Pyrollidine (831 mg, 11.68 mmol, 8.0 equiv) was added to an ice-cold solution of CLX-(allyl ester)$_4$ (1.61 g, 1.46 mmol) in 52 mL of CH_2Cl_2. Subsequent dropwise addition of a solution of $Pd(PPh_3)_4$ (33 mg, 29 μmol, 0.02 equiv) in 6 mL of CH_2Cl_2 afforded a yellow solution, which was stirred at 0 °C for 1 h. The cold mixture was then poured into a separatory funnel containing 120 mL of Et_2O and 45 mL of 5 wt.% aqueous $NaHCO_3$. The aqueous layer was collected and the organic layer was washed with 2 x 10 mL of 5 wt.% aqueous $NaHCO_3$ and then discarded. The combined aqueous fractions were stirred vigorously while ~25 mL of 2 N aqueous HCl was added slowly to adjust the pH to 1–2. The acidified solution was transferred to a separatory funnel and extracted with 3 x 50 mL of CH_2Cl_2. The combined CH_2Cl_2 fractions were washed with 1 x 25 mL of H_2O and 1 x 25 mL of saturated aqueous NaCl, dried over $MgSO_4$, and concentrated under reduced pressure to give a pale yellow solid (1.31 g, 95%). This material was determined by ^{1}H NMR to be of sufficient purity for use in the Rh complexation reactions. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.23 (s, 4H), 6.96 (s, 8H), 4.35 (s, 8H), 4.24 (d, 4H, *J* = 14.0 Hz), 3.50 (d, 4H, *J* = 14.0 Hz), 3.49 (s, 8H), 1.24 (s, 24H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.5, 147.9, 132.0, 128.2, 127.2, 77.4, 72.4, 43.9, 32.1, 22.5 ppm; IR (thin film) ν 3155, 2976, 2931, 1703, 1478, 1246, 1101, 910 cm^{-1}; HRMS (ES$^+$) calcd for $C_{52}H_{64}O_{16}$ 944.4194 found 967.4100 (MNa^+).

Rh_2(CLX-H_2)(OAc)$_2$ (2): A thick-walled sealed tube containing a magnetic stir bar was charged with CLX-H_4 (500 mg, 0.53 mmol), $Rh_2(OAc)_4$ (234 mg, 0.53 mmol), and 21 of DCE. The vessel was sealed with a Teflon screw cap and placed in an oil bath pre-heated to 125 °C. The green suspension was stirred at this temperature for 4 h then cooled to 23 °C. The mixture was filtered through a glass pipette containing a plug of glass wool to remove a small amount of particulate matter, and the flask and filter rinsed with 2 x 2 mL of CH_2Cl_2. The combined filtrates were concentrated under reduced pressure to give a blue glassy solid, which was immediately purified by chromatography on silica gel (0.6% MeOH/CH_2Cl_2). The first blue band to elute from the column was collected and the fractions were concentrated under reduced pressure to furnish the desired product as a dark green solid (448 mg, 67%). The pure product was desolvated by gentle warming (50 °C) under high vacuum (~ 1 Torr). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.03 (s, 2H), 9.51 (br s, 4H), 7.00 (s, 4H), 6.91 (s, 4H), 4.40 (s, 4H), 4.15 (d, 4H, *J* = 13.6 Hz), 4.08 (s, 4H), 3.96 (s, 4H), 3.42 (d, 4H, *J* = 13.6 Hz), 3.17 (s, 4H), 1.88 (s, 3H), 1.64 (s, 12H), 1.01 (s, 12H), –2.30 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.9, 191.9, 191.2, 186.7, 148.0, 147.0, 133.7, 132.7, 128.5, 128.4, 128.2, 125.5, 78.7, 77.8, 73.2, 71.7, 45.5, 45.1, 31.2, 23.7, 22.8, 22.5, 15.6 ppm; IR (thin film) ν 3205, 2973, 2876, 1680, 1586, 1478, 1419, 1269, 1151, 1111 cm^{-1}; HRMS (ES$^+$) calcd for $C_{56}H_{68}O_{20}Rh_2$ 1266.2414 found 1289.2341 (MNa^+).



Top spectrum: Complete ^{1}H NMR spectrum of **Rh_2(CLX-H_2)(OAc)$_2$** (400 MHz, $CDCl_3$). **Bottom spectrum:** Upfield region of ^{1}H NMR spectrum of **Rh_2(CLX-H_2)(OAc)$_2$**; ▲ = signal for non-entrapped acetate ligand; ▼ = signal for entrapped acetate ligand; ● = signals for –CH_3 groups of CLX–H_2 ligand.

General Procedure for Ligand Metathesis Reactions

To a 0.01 M solution of $Rh_2(OAc)_2$(CLX) (1 equiv) in chlorobenzene was added 5 equiv of carboxylic acid (as indicated below). The reaction flask was equipped with a reflux condenser and placed in an oil bath pre-heated to 150 °C. The mixture was stirred vigorously until no further reaction was observed, as indicated by TLC (reaction times given below). After cooling to 23 °C, the solution was filtered through a plug of glass wool to remove a small amount of particulate matter. The flask and solid residue were rinsed with 2 x 2 mL of chlorobenzene. The combined filtrates were concentrated under reduced pressure and the material obtained was purified by chromatography on silica gel (conditions given below) to furnish the desired product.

Rh_2(CLX-H_2)(OAc)(O_2CCF_3) (3): Reaction performed with CF_3CO_2H; 10 min reaction time. Purified by chromatography on silica gel (0.5% MeOH/CH_2Cl_2); blue solid (85%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.95 (s, 2H), 9.50 (br s, 4H), 6.99 (s, 4H), 6.89 (s, 4H), 4.41 (s, 4H), 4.16 (d, 4H, J = 14.0 Hz), 4.07 (s, 4H), 3.98 (s, 4H), 3.42 (d, 4H, J = 14.0 Hz), 3.22 (s, 4H), 1.66 (s, 12H), 1.01 (s, 12H), –2.30 (s, 3H) ppm; ^{19}F NMR ($CDCl_3$, 376 MHz) δ –75.25 (s) ppm; IR (thin film) ν 3205, 2974, 2876, 1678, 1635, 1478, 1420, 1199, 1162, 1112 cm^{-1}; HRMS (ES$^+$) calcd for $C_{56}H_{65}F_3O_{20}Rh_2$ 1320.2131 found 1343.2007 (MNa^+).

Rh_2(CLX-H_2)(OAc)(O_2CPh): Reaction performed with $PhCO_2H$; 30 min reaction time. Purified by chromatography on silica gel (0.5% MeOH/CH_2Cl_2); blue-green solid (84%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.10 (br s, 2H), 9.51 (br s, 4H), 7.97 (d, 2H, J = 8.0 Hz), 7.34 (t, 1H, J = 7.6 Hz), 7.22 (t, 2H, J = 7.6 Hz), 7.02 (s, 4H), 6.92 (s, 4H), 4.44 (s, 4H), 4.17 (d, 4H, J = 13.6 Hz), 4.08 (s, 4H), 4.01 (s, 4H), 3.44 (d, 4H, J = 13.6 Hz), 3.19 (s, 4H), 1.69 (s, 12H), 0.96 (s, 12H), –2.26 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.9, 192.0, 186.7, 185.1,

148.0, 147.0, 133.8, 132.8, 131.75, 131.68, 129.6, 128.5, 128.3, 127.3, 125.6, 78.6, 77.9, 73.2, 71.7, 45.6, 45.2, 31.2, 22.7, 22.6, 15.7 ppm; IR (thin film) ν 3205, 2973, 2932, 2876, 1679, 1595, 1575, 1478, 1401, 1244, 1151, 1112 cm^{-1}; HRMS (ES^+) calcd for $C_{61}H_{70}O_{20}Rh_2$ 1328.2570 found 1351.2448 (MNa^+).

Rh_2(CLX-H_2)(OAc)(O_2CCPh_3): Reaction performed with Ph_3CCO_2H; 30 min reaction time. Purified by chromatography on silica gel (0.5% MeOH/CH_2Cl_2); dark green solid (80%): ^1H NMR ($CDCl_3$, 400 MHz) δ 10.11 (br s, 2H), 9.51 (br s, 4H), 7.13–7.07 (m, 9H), 6.99 (s, 4H), 6.89–6.86 (m, 10H), 4.43 (s, 4H), 4.15 (d, 4H, *J* = 14.0 Hz), 4.06 (s, 4H), 3.92 (s, 4H), 3.41 (d, 4H, *J* = 14.0 Hz), 3.19 (s, 4H), 1.59 (s, 12H), 0.90 (s, 12H), –2.33 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.1, 191.71, 191.68, 185.6, 147.8, 147.2, 144.3, 133.8, 132.9, 130.9, 128.4, 128.2, 128.0, 127.1, 126.3, 125.6, 78.3, 77.9, 72.9, 71.8, 68.8, 45.4, 44.9, 31.2, 22.7, 22.5, 15.5 ppm; IR (thin film) ν 3201, 2973, 2932, 2875, 1680, 1588, 1478, 1393, 1371, 1268, 1244, 1151, 1111 cm^{-1}; HRMS (ES^+) calcd for $C_{74}H_{80}O_{20}Rh_2$ 1494.3353 found 1517.3253 (MNa^+).

Rh_2(CLX-H_2)(OAc)($O_2CC_6H_4$-*o*-Ph): Reaction performed with 2-phenylbenzoic acid; 40 min reaction time. Purified by chromatography on silica gel (0.5% MeOH/CH_2Cl_2); blue-green solid (81%): ^1H NMR ($CDCl_3$, 400 MHz) δ 10.08 (br s, 2H), 9.50 (br s, 4H), 7.73 (dd, 1H, *J* = 7.7, 1.0 Hz), 7.36–7.32 (m, 1H), 7.29–7.21 (m, 3H), 7.19–7.14 (m, 2H), 7.10–7.07 (m, 2H), 6.98 (s, 4H), 6.89 (s, 4H), 4.40 (s, 4H), 4.15 (d, 4H, *J* = 13.7 Hz), 4.10 (s, 4H), 3.94 (s, 4H), 3.42 (d, 4H, *J* = 13.7 Hz), 3.17 (s, 4H), 1.60 (s, 12H), 0.99 (s, 12H), –2.33 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.4, 191.7, 186.8, 186.0, 148.0, 147.0, 141.61, 141.55, 133.8, 132.8, 132.6, 130.6, 130.43, 130.41, 129.5, 128.4, 128.3, 128.1, 127.3, 126.6, 126.5, 125.6, 78.5, 77.7, 73.0, 71.7, 45.5, 45.0, 31.2, 22.63, 22.56, 15.6 ppm; IR (thin film) ν 3203, 2972, 2928, 2856, 1681, 1585, 1478, 1396, 1244, 1222, 1113 cm^{-1}; HRMS (ES^+) calcd for $C_{67}H_{74}O_{20}Rh_2$ 1404.2884 found 1427.2755 (MNa^+).

Rh_2(CLX-H_2)(OAc)($O_2CC_6H_4$-*p*-vinyl): Reaction performed with 4-vinylbenzoic acid; 75 min reaction time. Purified by chromatography on silica gel (0.5% MeOH/CH_2Cl_2); blue-green solid (91%): ^1H NMR ($CDCl_3$, 400 MHz) δ 10.11 (s, 2H), 9.52 (br s, 4H), 7.94 (d, 2H, *J* = 8.4 Hz), 7.26 (d, 2H, *J* = 8.4 Hz), 7.03 (s, 4H), 6.92 (s, 4H), 6.66 (dd, 1H, *J* = 17.6, 10.8 Hz), 5.77 (d, 1H, *J* = 17.6 Hz), 5.27 (d, 1H, *J* = 10.8 Hz), 4.44 (s, 4H), 4.17 (d, 4H, *J* = 13.6 Hz), 4.09 (s, 4H), 4.02 (s, 4H), 3.44 (d, 4H, *J* = 13.6 Hz), 3.19 (s, 4H), 1.69 (s, 12H), 0.96 (s, 12H), –2.26 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.9, 192.0, 186.7, 184.7, 148.0, 147.0, 140.6, 137.7, 136.5, 133.8, 132.8, 131.0, 129.9, 128.5, 128.2, 125.6, 125.2, 115.6, 78.6, 77.9, 73.2, 71.6, 45.6, 45.2, 31.2, 22.7, 22.6, 15.7 ppm; IR (thin film) ν 3203, 2973, 2932, 2875, 1679, 1588, 1566, 1478, 1401, 1244, 1151, 1111, 910 cm^{-1}; HRMS (ES^+) calcd for $C_{63}H_{72}O_{20}Rh_2$ 1354.2727 found 1377.2625 (MNa^+).

Rh_2(CLX-H_2)(OAc)(OAd): Reaction performed with 1-adamantanecarboxylic acid; 1 h reaction time. Purified twice by chromatography on silica gel (0.5% MeOH/CH_2Cl_2); blue-green solid (79%): ^1H NMR ($CDCl_3$, 500 MHz) δ 10.10 (br s, 2H), 9.49 (br s, 4H), 7.01 (s, 4H), 6.90 (s, 4H), 4.42 (s, 4H), 4.15 (d, 4H, *J* = 14.0 Hz), 4.07 (s, 4H), 3.97 (s, 4H), 3.42 (d, 4H, *J* = 14.0 Hz), 3.21 (s, 4H), 1.84 (br s, 3H), 1.69 (d, 6H, *J* = 2.5 Hz), 1.65 (s, 12H), 1.60–1.52 (m, 6H), 1.00 (s, 12H), –2.31 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.4, 196.3, 191.5, 186.1, 147.9, 147.0, 133.8, 132.9, 128.5, 128.4, 128.2, 125.6, 78.4, 77.9, 73.0, 71.6, 45.3, 45.0, 42.9, 39.4, 36.8, 31.2, 28.4, 22.8, 22.6, 15.6 ppm; IR (thin film) ν 3204, 2907, 2853, 1680, 1582, 1478, 1405, 1269, 1244, 1151, 1112 cm^{-1}; HRMS (ES^+) calcd for $C_{65}H_{80}O_{20}Rh_2$ 1386.3353 found 1409.3242 (MNa^+).

Rh_2(CLX-H_2)(OAc)(OC_5H_4N): Prepared using Rh_2(CLX-H_2)(OAc)(O_2CCF_3) **3** and 2-hydroxypyridine (2.0 equiv); 5 min reaction time. Purified by chromatography on silica gel (2% MeOH/CH_2Cl_2); blue solid (67%): ^1H NMR ($CDCl_3$, 400 MHz) δ 10.48 (br s, 1H), 10.17 (br s, 1H), 9.54 (br s, 4H), 8.12 (d, 1H, *J* = 5.6 Hz), 7.07–7.02 (m, 5H), 6.94 (s, 4H), 6.29–6.25 (m, 2H), 4.45 (s, 2H), 4.43 (s, 2H), 4.18 (d, 2H, *J* = 13.6 Hz), 4.17 (d, 2H, *J* = 13.6

Hz), 4.12–4.05 (m, 4H), 3.96 (s, 2H), 3.93 (s, 2H), 3.45 (d, 2H, *J* = 13.6 Hz), 3.44 (d, 2H, *J* = 13.6 Hz), 3.19–3.11 (m, 4H), 1.66 (s, 6H), 1.64 (s, 6H), 0.90 (s, 6H), 0.86 (s, 6H), –2.20 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 195.9, 189.8, 186.4, 186.3, 179.2, 148.6, 147.9, 147.2, 147.0, 136.4, 133.8, 133.5, 133.0, 128.6, 128.43, 128.41, 128.37, 128.3, 128.2, 125.67, 125.65, 116.4, 110.8, 78.8, 78.7, 77.8, 73.0, 72.0, 71.8, 45.4, 45.1, 44.8, 31.3, 31.2, 22.8, 22.6, 22.5, 22.4, 15.7 ppm; IR (thin film) ν 3204, 2971, 2929, 2856, 1680, 1611, 1573, 1476, 1393, 1352, 1276, 1151, 1112, 910 cm^{-1}; HRMS (ES$^+$) calcd for $C_{59}H_{69}NO_{19}Rh_2$ 1301.2574 found 1324.2458 (MNa^+).

Rh_2(CLX-H_2)(OAc)(NHCOPh): Prepared using Rh_2(CLX-H_2)(OAc)(O_2CCF_3) **3** and $PhCONH_2$ (5.0 equiv), 4.5 h reaction time. Purified by chromatography on silica gel (1% MeOH/CH_2Cl_2); blue solid (47%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.36 (br s, 1H), 10.22 (br s, 1H), 9.53 (s, 4H), 7.70–7.67 (m, 2H), 7.32–7.29 (m, 1H), 7.24–7.22 (m 2H), 7.05 (s, 4H), 6.94 (s, 4H), 5.61 (br s, 1H), 4.44 (s, 4H), 4.18 (d, 4H, *J* = 14.0 Hz), 4.10 (s, 4H), 3.98 (s, 2H), 3.92 (s, 2H), 3.45 (d, 4H, *J* = 14.0 Hz), 3.19–3.13 (m, 4H), 1.65 (s, 6H), 1.62 (s, 6H), 0.96 (s, 6H), 0.94 (s, 6H), –2.20 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 195.9, 189.6, 186.4, 186.3, 183.5, 148.0, 147.12, 147.08, 134.6, 133.8, 133.7, 132.9, 130.1, 128.53, 128.48, 128.4, 128.24, 128.22, 127.9, 126.4, 125.7, 78.7, 78.6, 77.9, 73.0, 71.9, 71.8, 45.4, 45.0, 44.9, 31.3, 22.74, 22.71, 22.6, 22.5, 15.7 ppm; IR (thin film) ν 3202, 2972, 2932, 2876, 1679, 1597, 1575, 1478, 1392, 1223, 1151, 1111, 910 cm^{-1}; HRMS (ES$^+$) calcd for $C_{61}H_{71}NO_{19}Rh_2$ 1327.2730 found 1350.2637 (MNa^+).

Preparation of Rh_2(CLX–H_2)(O_2CH)$_2$

A thick-walled sealed tube containing a magnetic stir bar was charged with CLX-H_4 (67 mg, 71 μmol), $Rh_2(O_2CH)_4$•$2H_2O$[3] (30 mg, 71 μmol), and 2.8 mL of DCE. The vessel was sealed with a Teflon screw cap and placed in an oil bath pre-heated to 125 °C. The green suspension was stirred at this temperature for 4 h then cooled to 23 °C. The mixture was filtered through a pipette containing a plug of glass wool to remove insoluble precipitates, and the flask and filter cake were washed with 2 x 2 mL of CH_2Cl_2. The combined filtrates were concentrated under reduced pressure to give a green glassy solid, which was immediately purified by chromatography on silica gel (2% MeOH/CH_2Cl_2). The first green band to elute from the column was collected and the fractions were concentrated under reduced pressure to afford the desired product as a dark green solid (16 mg, 18%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.11 (br s, 2H), 9.70 (br s, 4H), 6.96 (s, 4H), 6.96–6.93 (m, 1H), 6.86 (s, 4H), 4.46 (s, 4H), 4.16 (d, 4H, *J* = 13.6 Hz), 4.12 (s, 4H), 3.94 (s, 4H), 3.41 (d, 4H, *J* = 13.6 Hz), 3.27 (br t, 1H, *J* = 4.0 Hz), 3.11 (s, 4H), 1.62 (s, 12H), 1.01 (s, 12H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.4, 186.9, 181.5, 179.9, 147.6, 146.7, 133.3, 132.3, 128.6, 128.2, 128.1, 125.8, 78.2, 77.3, 73.1, 72.2, 45.8, 45.3, 31.5, 22.7, 22.6 ppm; IR (thin film) ν 3199, 2973, 2931, 2862, 1680, 1595, 1478, 1362, 1336, 1268, 1150, 1110 cm^{-1}.

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