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Ring Opening Metathesis. A Ruthenium Catalyst Caught in the Act

John A. Tallarico, Peter J. Bonitatebus, Jr. and Marc L. Snapper*

Eugene F. Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02167-3800

Supporting Information

General Methods:

Starting materials and reagents were purchased from commercial suppliers and used without further purification except the following: CH_2Cl_2 and pentane were distilled from CaH_2 under Ar atmosphere. Similarly, acetone (HPLC grade) was distilled from $CaSO_4$ (fresh) and $CDCl_3$ was distilled from P_2O_5, both under N_2 atmosphere. Hexanes, 2-methylbutane, and ethyl acetate were distilled prior to use.

All oxygen- or moisture-sensitive reactions were transferred by syringe or cannula and were introduced into the reaction vessel through rubber septa or through a stopcock under N_2 or Ar positive pressure. Air and/or moisture-sensitive solids were transferred in a glove box. Unless otherwise stated, reactions were stirred with a Teflon covered stirbar and carried out at rt. Concentration refers to the removal of solvent using a Büchi rotary evaporator followed by use of a vacuum pump at approximately 1 torr. Silica gel column chromatography was performed using Baxter brand silica gel 60Å (230-400 mesh ASTM). Silver impregnated silica gel was prepared and used according to the method suggested by EM Separation Technology.[1] The use of brine refers to saturated (sat.) $NaCl_{(aq.)}$.

Proton nuclear magnetic resonance (**^{1}H NMR**) were measured on either a Varian Unity-300 spectrometer (300 MHz), a Varian Gemini-400 spectrometer (400 MHz), or a Varian Unity-500 spectrometer (500 MHz). Carbon nuclear magnetic resonance (**^{13}C NMR**) spectra were recorded on either a Varian Unity-300 spectrometer (75 MHz) or a Varian Gemini-400 (100 MHz). Phosphorous nuclear magnetic resonance (**^{31}P NMR**) spectra were recorded on a Varian Unity-300 spectrometer (121 MHz) and referenced to an H_3PO_4 external standard with complete proton decoupling. All other NMR chemical shifts are reported in ppm downfield from tetramethyl silane. Infrared spectra (**IR**) were measured on a Perkin-Elmer 1310 Infrared Spectrometer, ν_{max} in cm^{-1}.

Elemental analysis (**Anal**) were performed by Robertson Microlit Laboratories, Inc., Madison, NJ and were reported in percent atomic abundance. High resolution mass spectral analysis (**HRMS**) were performed by the Mass Spectrometry Laboratory, University of Illinois at Urbana-Champaign.

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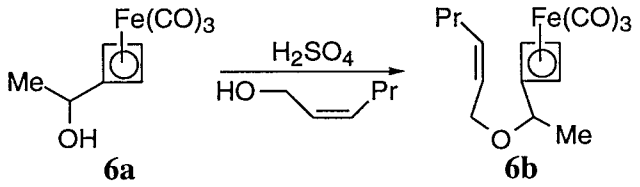
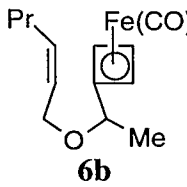
[1] Rabel, F. *Chromatogragraphy News* Vol. 4 No. 1, 1995; EM Separations Technology, Gibbstown, NJ.



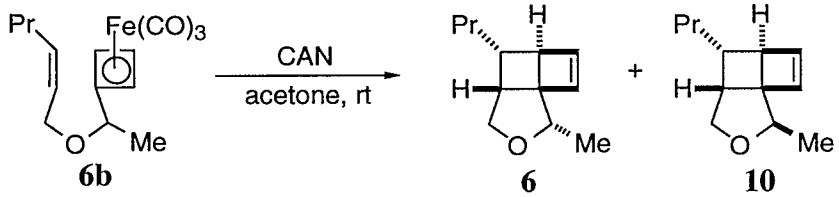
6a **6b**

Sulfuric acid (7.5 μL, 0.14 mmol) was added to a 0°C solution of alcohol **6a** (651 mg, 2.76 mmol) in *cis*-2-hexen-1-ol (4.6 mL, 12 equiv) under N_2 atmosphere. The reaction was judged complete by TLC (10:1 hexanes:Et_2O) after 155 min at rt. CH_2Cl_2 (7 mL) was added with H_2O and $NaHCO_3$ (sat., 3 mL). The organic layer was separated and the aqueous portion was backwashed with CH_2Cl_2 (5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The resulting yellow oil was purified by silica gel chromatography (20:1 hexanes:Et_2O; R_f = 0.18) to give **6b** (833 mg, 2.62 mmol, 95% yield).



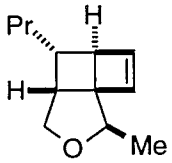
6b

(±)-Tricarbonyl[(1,2,3,4-η-hydroxymethyl-1-*cis*-4a-hexene-ether)-1,3-cyclobutadiene]-iron (6b): **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.58 (1H, dt, J = 10.8, 6.8 Hz), 5.52 (1H, dt, J = 11.2, 6.0 Hz), 4.16 (1H, d, J = 9.2 Hz), 4.13 (1H, s), 4.11 (1H, m), 4.03 (1H, d, J = 8.8 Hz), 4.01 (1H, dd, J = 6.4, 5.2 Hz), 3.88 (1H, q, J = 6.4 Hz), 2.04 (2H, q, J = 7.2 Hz), 1.40 (2H, qi, J = 7.2 Hz), 1.19 (3H, d, J = 6.4 Hz), 0.91 (3H, t, J = 7.2 Hz). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 215.2, 134.4, 126.8, 70.9, 65.0, 63.8, 63.5, 63.3, 61.3, 30.4, 23.4, 20.2, 14.4. **IR** (NaCl, thin film): 2980, 2960, 2955, 2932, 2872, 2039, 1456, 1377, 1121, 1084 cm^{-1}. **MS** (70eV) *m/z* (rel int): 318 (3, M^+), 290 (4), 262 (25), 234 (60), 204 (5), 178 (14), 152 (85), 134 (57), 110 (35), 81 (40), 56 (100). **Anal** Calcd. for $C_{15}H_{18}O_4Fe$: C, 56.63; H, 5.71. Found: C, 56.98; H, 5.61.



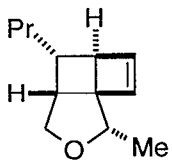
6b **6** **10**

CAN (7.5 g, 13.7 mmol) was added to a solution of iron complex **6b** (792 mg, 2.49 mmol) in acetone (2000 mL) at rt under Ar atmosphere. After 20 min, pentane (100 mL) was added to the orange solution along with $NaHCO_3$ (sat., 10 mL). The mixture was transferred to a separatory funnel and washed with H_2O (2 x 300 mL). The first aqueous layer was backwashed with pentane (50 mL) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The crude yellow oil was purified by Ag-impregnated silica gel chromatography (7.5% wt/wt, 12:1 pentane:Et_2O, R_f = 0.18 and R_f = 0.13) to diastereomers **6** (194.0 mg) and **10** (189.0 mg) in 86% combined yield as colorless oils.



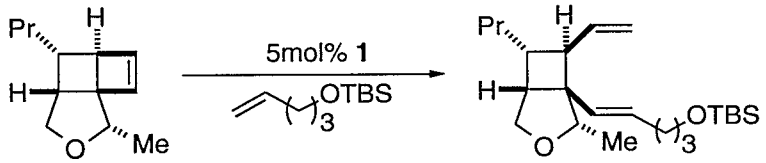
10

(±)-9β-methyl-5α-propyl-8-oxa-tricyclo[4.3.0.0^{1,4}]non-2-ene (10): **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 6.37 (1H, d, J = 2.4 Hz), 6.28 (1H, dd, J = 2.4, 1.6 Hz), 3.97 (1H, q, J = 6.4 Hz), 3.93 (1H, dd, J = 10.0, 2.0 Hz), 3.84 (1H, dd, J = 10.4, 6.8 Hz), 2.57 (1H, app t, J = 2.4 Hz), 2.42 (1H, td, J = 7.2, 2.0 Hz), 1.81 (1H, dtd, J = 6.8, 6.2, 2.4 Hz), 1.48 - 1.20 (4H, m), 1.10 (3H, d, J = 6.4 Hz), 0.91 (3H, t, J = 7.2 Hz). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 142.2, 137.9, 76.7, 65.8, 62.6, 52.3, 39.1, 35.4, 32.3, 20.9, 17.2, 14.8. **IR** (NaCl, thin film): 3087, 3025, 2958, 2923, 2858, 2466, 1456, 1367, 1100 cm^{-1}. **MS** (70eV) *m/z* (rel int): 178 (36, M^+), 163 (8), 149 (8), 135 (23), 119 (24), 105 (98), 91 (100), 77 (36), 65 (18), 51 (15). **Anal** Calcd. for $C_{12}H_{18}O$: C, 80.90; H, 10.11. Found: C, 80.87 H, 10.31.



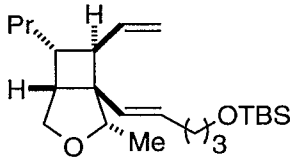
6

(±)-9α-methyl-5α-propyl-8-oxa-tricyclo[4.3.0.0^{1,4}]non-2-ene (6): **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 6.36 (1H, d, J = 2.4 Hz), 6.26 (1H, dd, J = 2.4, 1.6 Hz), 4.01 (1H, d, J = 10.0 Hz), 3.82 (1H, q, J = 6.0 Hz), 3.68 (1H, dd, J = 10.0, 7.2 Hz), 2.66 (1H, app s), 2.38 (1H, dt, J = 7.2, 1.2 Hz), 1.80 (1H, dtd, J = 8.8, 7.2, 2.4 Hz), 1.46 - 1.20 (4H, m), 1.08 (3H, d, J = 6.0 Hz), 0.91 (3H, t, J = 7.2 Hz). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 142.4, 138.0, 75.6, 68.1, 63.1, 47.5, 40.2, 35.2, 32.0, 21.0, 14.8, 14.5. **IR** (NaCl, thin film): 3026, 2956, 2930, 2871, 2850, 1465, 1379, 1289, 1125, 1100 cm^{-1}. **MS** (70eV) *m/z* (rel int): 178 (25, M^+), 163 (8), 149 (8), 135 (23), 119 (24), 105 (98), 91 (100), 77 (36), 65 (18), 51 (15). **Anal** Calcd. for $C_{12}H_{18}O$: C, 80.90; H, 10.11. Found: C, 80.66 H, 10.23.



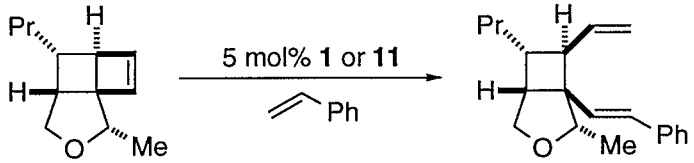
6 **8**

To a stirring solution of catalyst **1** (10.0 mg, 0.012 mmol) in CH_2Cl_2 (0.53 mL), cyclobutene **6** (43.0 mg, 0.24 mmol) and 1-*t*-butyldimethylsiloxy-pent-4-ene (240 mg, 1.2 mmol) were added by syringe over 4 h. The reaction was monitored by GC. After the addition was complete, the stirring solution was quenched with ethyl vinyl ether (2 mL), concentrated in vacuo and the crude dark oil was purified by Ag-impregnated silica gel chromatography (7.5% Ag wt/wt, 25:1 hexanes:Et_2O) to give **8** as the major regioisomer of a 7:1 mixture of regioisomers in 72% overall yield. Compound **8** was isolated as the *trans*-isomer only. The minor regioisomer was isolated as a mixture of stereoisomers (1.7:1 Z:E).



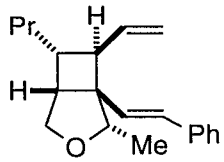
8

(±)-1α-[(E)-5'-*t*-butyldimethylsiloxy-pent-1'-enyl]-7α-ethenyl-2β-methyl-3-oxa-6β-propyl-bicyclo[6.3.0]heptane (8): **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.72 (1H, ddd, J = 17.2, 10.4, 8.4 Hz), 5.56 (1H, dt, J = 16.6, 6.4 Hz), 5.74 (1H, d, J = 16.0 Hz), 4.95 (1H, ddd, J = 17.2, 10.4, 8.4 Hz), 5.56 (1H, dt, J = 16.6, 6.4 Hz), 5.74 (1H, d, J = 16.0 Hz), 4.95 (1H, ddd, J = 17.2, 2.0, 0.8 Hz), 4.92 (1H, dd, J = 10.0, 2.0 Hz), 4.01 (1H, d, J = 10.0 Hz), 3.62 (2H, t, J = 6.4 Hz), 3.58 (1H, dd, J = 12.8, 7.2 Hz), 3.36 (1H, q, J = 6.4 Hz), 2.65 (1H, t, J = 8.0 Hz), 2.56 (1H, dd, J = 8.8, 8.4 Hz), 2.18 (1H, dd, J = 8.4, 7.6 Hz), 2.12 (2H, td, J = 7.2, 6.4 Hz), 1.61 (2H, qi, J = 6.4 Hz), 1.40 - 1.13 (4H, m), 1.15 (3H, d, J = 6.0 Hz), 0.89 (9H, s), 0.86 (3H, t, J = 7.2 Hz). 0.05 (6H, s). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 140.9, 130.7, 129.1, 115.0, 82.0, 68.0, 63.2, 56.1, 47.0, 44.0, 37.1, 33.3, 32.5, 29.7, 26.6, 20.9, 19.0, 14.9, 12.9, 4.6. **IR** (NaCl, thin film): 2954, 2929, 2856, 1472, 1463, 1382, 1256, 1100, 1046 cm^{-1}. **MS** (70eV) *m/z* (rel int): 378 (3, M^+), 363 (1), 321 (21), 303 (3), 277 (6), 225 (24), 187 (8), 159 (13), 145 (16), 121 (33), 105 (41), 75 (100), 55 (36). **Anal** Calcd. for $C_{23}H_{42}O_2Si$: C, 72.92; H, 11.10. Found: C, 73.17; H, 11.36.



6 **12**

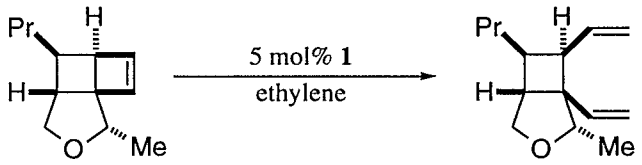
To a stirring solution of **1** (9.0 mg, 0.011 mmol) or **11** in CH_2Cl_2 (0.5 mL), cyclobutene **6** (38.5 mg, 0.22 mmol), styrene (114 mg, 1.1 mmol) and dodecane (5μL) dissolved in CH_2Cl_2 (1.0 mL), were added by syringe over 195 min. The reaction was monitored by GC. When complete, the crude reaction mixture was purified by silica gel chromatography (20:1 hexanes:Et_2O) to give a colorless oil (47.3 mg, 0.17 mmol, 76% yield). The regioisomers were separated by Ag-impregnated silica gel chromatography (7.5% Ag wt/wt, 10:1 hexanes:Et_2O, R_f = 0.18) to give **12** as the major regioisomer (43.7 mg, 0.12 mmol, 12:1 major:minor).



12

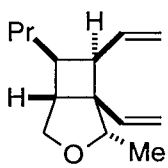
(±)-1α-[(E)-styrenyl]-7α-ethenyl-2β-methyl-3-oxa-6β-propyl-bicyclo[6.3.0]heptane (12): **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.40 (2H, dd, J = 7.2, 1.2 Hz), 7.32 (2H, td, J = 7.2, 2.0 Hz), 7.23 (1H, tt, J = 7.2, 1.2 Hz), 6.51 (1H, d, J = 16.0 Hz), 6.30 (1H, d, J = 16.4 Hz), 5.79 (1H, ddd, J = 17.2, 10.4, 8.4 Hz), 5.02 (1H, ddd, J = 17.2, 2.0, 1.2 Hz), 4.98 (1H, ddd, J = 10.4, 2.0, 0.8 Hz), 4.09 (1H, d, J = 10.0 Hz), 3.70 (1H, dd, J = 10.4, 7.2 Hz), 3.51 (1H, q, J = 6.4 Hz), 2.84 (1H, app t, J = 8.0 Hz), 2.71 (1H, app t, J = 8.8 Hz), 2.28 (1H, qi, J = 7.6 Hz), 1.46 - 1.20 (4H, m), 1.25 (3H, d, J = 6.4 Hz), 0.89 (3H, t, J = 7.6 Hz). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 140.6, 138.0, 130.2, 129.3, 129.2, 128.0, 126.8, 115.6, 81.9, 68.1, 56.7, 47.6, 44.4, 37.3, 32.5, 21.0, 14.9, 13.1. **IR** (NaCl, thin film): 3081, 3062, 3027, 2957,

2929, 2857, 1382, 1083 cm^{-1}. **MS** (70eV) *m/z* (rel int): 282 (1, M^+), 267 (1), 251 (1), 238 (14), 223 (2), 195 (4), 186 (28), 168 (14), 143 (100), 129 (36), 115 (25), 104 (9), 91 (34), 65 (10), 55 (11). **Anal** Calcd. for $C_{20}H_{26}O$: C, 85.11; H, 9.27. Found: C, 84.89; H, 9.10.



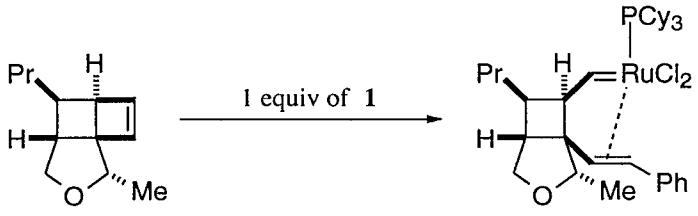
5 **18**

Cyclobutene **5** (95.1 mg, 0.53 mmol) in CH_2Cl_2 (16.7 mL) was added by syringe over 4 h to a solution of **1** (22.0 mg, 0.027 mmol) in CH_2Cl_2 (10 mL) under ethylene atmosphere. The reaction was judged complete by GC after 19 h. Ethyl vinyl ether (4 mL) was added and the reaction was stirred for 25 min. The crude product was filtered through a plug (2 cm x 2 cm) of silica gel (20:1 pentane:Et_2O), concentrated, then purified by silica gel chromatography (27:1 pentane:Et_2O) to give **18** (90.2 mg, 0.44 mmol, 83% yield).



5

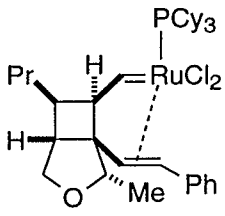
(±)-1α,7α-diethenyl-2β-methyl-3-oxa-6β-propyl-bicyclo[6.3.0]heptane (18): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.89 (1H, ddd, J = 17.6, 10.4, 9.6 Hz), 5.87 (1H, dd, J = 17.2, 10.8 Hz), 5.16 (1H, dd, J = 10.8, 1.6 Hz), 5.13 (1H, dd, J = 17.2, 1.6 Hz), 4.99 (1H, dd, J = 17.6, 2.4 Hz), 4.98 (1H, dd, J = 9.2, 2.4 Hz), 3.85 (1H, d, J = 9.2 Hz), 3.72 (1H, dd, J = 9.2, 5.6 Hz), 3.38 (1H, q, J = 6.4 Hz), 3.13 (1H, app t, J = 10.0 Hz), 2.44 (1H, dd, J = 4.8, 4.4 Hz), 1.95 (1H, dtd, J = 11.6, 6.0, 3.6 Hz), 1.44 - 1.24 (4H, m), 1.22 (3H, d, J = 6.4 hz), 0.86 (3H, t, J = 7.2 Hz). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.0, 137.7, 117.7, 114.8, 83.7, 74.2, 57.0, 47.1, 42.7, 41.0, 34.6, 21.1, 14.8, 13.3. **IR** (NaCl, thin film): 3076, 2955, 2958, 2850, 1634, 1465, 1456, 1382, 1091, 1010 cm^{-1}. **MS** (70eV) *m/z* (rel int): 206 (65, M^+), 191 (100), 177 (24), 163 (32), 146 (16), 133 (16), 109 (33), 91 (36), 67 (29), 55 (12). **Anal** Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.46; H, 10.84.



5 **11**

In a glove box, **1** (63.2 mg, 0.077 mmol) was added to flask containing a stir bar and sealed under Ar atmosphere with a septa. Cyclobutene **5** (15.0 mg, 0.085 mmol) dissolved in CH_2Cl_2 (2.6 mL) was added by syringe to the flask. Reaction progress was determined by TLC (14:1 hexanes:Et_2O, R_f = 0.15). When complete, the crude reaction mixture was concentrated and purified by silica gel

chromatography to give **11** as a yellow microcrystalline solid (37.5 mg, 0.052 mmol, 68% yield). **Recrystallized by layering**: **11** (20.9 mg, 0.03 mmol) was dissolved in CH_2Cl_2 (0.1 mL) under Ar atmosphere and chilled to 4 °C. Pentane (0.12 mL) was then slowly layered onto the CH_2Cl_2 by syringe. Golden colored crystals suitable for diffraction studies appeared over 48 h.



11

Ru complex 11: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 18.43 (1H, dd, J = 9.2, 2.8 Hz), 7.75 (2H, dd, J = 7.2, 2.0 Hz), 7.31 (3H, m), 6.83 (1H, d, J = 14.8 Hz), 6.42 (1H, dd, J = 14.8, 2.0 Hz), 4.03 (1H, q, J = 6.4 Hz), 3.79 (1H, d, J = 9.2 Hz), 3.65 (1H, dd, J = 9.6, 3.6 Hz), 2.74 (1h, dd, J = 6.0, 4.0 Hz), 2.62 (1H, tt, J = 8.4, 6.4 Hz), 2.40 (3H, app q, J = 12.0 Hz), 1.85 - 1.12 (35 H, m), 1.53 (3H, d, J = 6.4 Hz), 0.87 (3H, t, J = 6.8 Hz). **^{31}P NMR** ($CDCl_3$, 121 MHz): δ 36.06. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 321.9 (br s, Ru=CHR), 132.8, 130.3, 129.7, 128.8, 115.9, 115.8, 86.6, 80.4, 72.5, 44.5, 33.9 (*o*-C of $P(Cy)_3$), 30.8, 30.4, 28.4 (dd, J = 14.6, 10.0 Hz, *ipso*-C of $P(Cy)_3$), 26.8, 23.2, 22.0, 16.2, 14.8, 14.7. **IR** (NaCl, thin film): 3043, 2930, 2853, 1447, 1265, 1149, 1129, 1109 cm^{-1}.

Single crystal X-ray diffraction structural determination.

Table 1. Crystal data and structure refinement for complex **11**.

Empirical formula	$C_{37}H_{57}Cl_2O_1P_1Ru_1$
Formula weight	411.87
Temperature	163(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 12.399(2) A α = 90 deg. b = 13.067(3) A β = 100.837(11) deg. c = 22.177(3) A γ = 90 deg.
Volume, Z	3529.0(11) $Å^3$, 4
Density (calculated)	1.357 Mg/m^3
Absorption coefficient	0.669 mm^{-1}
F(000)	1520
Crystal size	0.20 x 0.20 x 0.15 mm
Theta range for data collection	1.76 to 28.28 deg.

Table 1. continued

Limiting indices	$-15 \le h \le 15, -17 \le k \le 2, -28 \le l \le 28$
Reflections collected	9632
Independent reflections	5629 [R(int) = 0.0464]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5629 / 0 / 379
Goodness-of-fit on F^2	1.192
Final R indices [$I>2\sigma(I)$]	R1 = 0.0567, wR2 = 0.0934
R indices (all data)	R1 = 0.0798, wR2 = 0.1031
Largest diff. peak and hole	0.397 and -0.417 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **11**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ru(1)	8120(1)	3862(1)	1578(1)	22(1)
P(1)	9956(1)	4440(1)	1822(1)	21(1)
Cl(1)	8207(1)	4345(1)	558(1)	30(1)
Cl(2)	8345(1)	2946(1)	2515(1)	33(1)
C(3)	7479(4)	5008(3)	1826(2)	23(1)
O(1)	3710(3)	4575(3)	1443(2)	42(1)
C(5)	10851(4)	3422(3)	1581(2)	25(1)
C(6)	10404(5)	2358(4)	1678(3)	33(2)
C(8)	4537(5)	3924(5)	1763(3)	40(2)
C(9)	9482(5)	6478(4)	1357(2)	31(2)
C(10)	10288(4)	5583(3)	1397(2)	22(1)
C(11)	10610(4)	4714(3)	2627(2)	23(1)
C(12)	10995(4)	3802(4)	3052(2)	28(1)
C(13)	11462(4)	5972(4)	1581(2)	31(2)
C(14)	5393(5)	7218(4)	534(3)	37(2)
C(16)	5617(4)	4194(4)	1537(2)	29(1)
C(18)	7385(5)	1142(4)	1414(3)	37(2)
C(19)	8066(5)	790(4)	322(3)	43(2)
C(20)	10509(5)	5795(4)	3557(2)	34(2)
C(21)	9906(4)	5433(4)	2938(2)	27(1)
C(22)	6295(4)	5125(4)	1835(2)	24(1)
C(24)	11042(5)	3524(4)	916(2)	29(1)
C(26)	7212(4)	1891(4)	965(3)	28(1)
C(28)	6214(5)	6625(4)	995(2)	32(2)
C(29)	11334(5)	1620(4)	860(3)	42(2)

Table 2. continued

C(30)	6673(4)	2898(4)	1026(3)	29(1)
C(31)	9740(5)	7244(4)	880(3)	44(2)
C(32)	5637(5)	5827(4)	1323(2)	31(2)
C(34)	11145(5)	1506(4)	1512(3)	42(2)
C(35)	3966(5)	4732(4)	837(3)	42(2)
C(36)	7557(5)	1695(4)	414(3)	35(2)
C(38)	6310(4)	3254(4)	1522(3)	29(1)
C(39)	10925(5)	7617(4)	1028(3)	42(2)
C(40)	11586(5)	4177(4)	3676(2)	33(2)
C(42)	11800(5)	2669(4)	769(3)	34(2)
C(43)	8239(5)	57(4)	771(3)	44(2)
C(44)	5886(5)	8038(4)	194(3)	51(2)
C(45)	10878(5)	4899(4)	3978(2)	35(2)
C(46)	7881(5)	227(4)	1322(3)	48(2)
C(47)	11718(5)	6732(4)	1102(3)	40(2)
C(48)	5184(5)	4865(4)	957(2)	29(1)
C(1)	4553(5)	4032(6)	2437(3)	60(2)

Table 3. Bond lengths [Å] and angles [deg] for **11**.

Ru(1)-C(3)	1.827(4)	C(19)-C(36)	1.374(7)
Ru(1)-C(30)	2.339(5)	C(20)-C(21)	1.511(7)
Ru(1)-C(38)	2.362(5)	C(20)-C(45)	1.513(7)
Ru(1)-P(1)	2.363(2)	C(22)-C(32)	1.564(7)
Ru(1)-Cl(2)	2.3682(14)	C(24)-C(42)	1.534(6)
Ru(1)-Cl(1)	2.3715(13)	C(26)-C(36)	1.393(7)
P(1)-C(10)	1.853(5)	C(26)-C(30)	1.494(7)
P(1)-C(11)	1.853(5)	C(28)-C(32)	1.525(7)
P(1)-C(5)	1.873(4)	C(29)-C(34)	1.514(8)
C(3)-C(22)	1.481(7)	C(29)-C(42)	1.515(7)
O(1)-C(8)	1.416(7)	C(30)-C(38)	1.347(7)
O(1)-C(35)	1.452(6)	C(31)-C(39)	1.525(8)
C(5)-C(6)	1.526(6)	C(32)-C(48)	1.545(7)
C(5)-C(24)	1.544(6)	C(35)-C(48)	1.494(7)
C(6)-C(34)	1.533(7)	C(39)-C(47)	1.505(8)
C(8)-C(1)	1.498(8)	C(40)-C(45)	1.526(7)
C(8)-C(16)	1.555(7)	C(43)-C(46)	1.393(8)
C(9)-C(10)	1.530(6)	C(3)-Ru(1)-C(30)	105.3(2)
C(9)-C(31)	1.532(7)	C(3)-Ru(1)-C(38)	80.2(2)
C(10)-C(13)	1.523(7)	C(30)-Ru(1)-C(38)	33.3(2)
C(11)-C(21)	1.530(6)	C(3)-Ru(1)-P(1)	97.1(2)
C(11)-C(12)	1.540(6)	C(30)-Ru(1)-P(1)	154.47(13)
C(12)-C(40)	1.519(7)	C(38)-Ru(1)-P(1)	169.98(14)
C(13)-C(47)	1.530(7)	C(3)-Ru(1)-Cl(2)	97.89(14)
C(14)-C(44)	1.505(7)	C(30)-Ru(1)-Cl(2)	98.03(14)
C(14)-C(28)	1.514(7)	C(38)-Ru(1)-Cl(2)	80.25(14)
C(16)-C(38)	1.503(7)	P(1)-Ru(1)-Cl(2)	90.64(5)
C(16)-C(22)	1.554(7)	C(3)-Ru(1)-Cl(1)	99.71(14)
C(16)-C(48)	1.566(7)	C(30)-Ru(1)-Cl(1)	79.16(13)
C(18)-C(46)	1.378(8)	C(38)-Ru(1)-Cl(1)	104.65(14)
C(18)-C(26)	1.383(7)	P(1)-Ru(1)-Cl(1)	85.29(5)
C(19)-C(43)	1.369(8)		

Table 3. continued

Cl(2)-Ru(1)-Cl(1)	162.29(5)	C(20)-C(21)-C(11)	112.0(4)
C(10)-P(1)-C(11)	103.6(2)	C(3)-C(22)-C(16)	111.8(4)
C(10)-P(1)-C(5)	103.1(2)	C(3)-C(22)-C(32)	115.7(4)
C(11)-P(1)-C(5)	103.7(2)	C(16)-C(22)-C(32)	89.1(4)
C(10)-P(1)-Ru(1)	116.0(2)	C(42)-C(24)-C(5)	110.5(4)
C(11)-P(1)-Ru(1)	120.7(2)	C(18)-C(26)-C(36)	118.0(5)
C(5)-P(1)-Ru(1)	107.8(2)	C(18)-C(26)-C(30)	124.8(5)
C(22)-C(3)-Ru(1)	125.3(4)	C(36)-C(26)-C(30)	117.2(5)
C(8)-O(1)-C(35)	106.6(4)	C(14)-C(28)-C(32)	110.8(5)
C(6)-C(5)-C(24)	109.8(4)	C(34)-C(29)-C(42)	110.3(5)
C(6)-C(5)-P(1)	110.9(3)	C(38)-C(30)-C(26)	127.0(5)
C(24)-C(5)-P(1)	114.6(3)	C(38)-C(30)-Ru(1)	74.2(3)
C(5)-C(6)-C(34)	112.2(4)	C(26)-C(30)-Ru(1)	102.1(3)
O(1)-C(8)-C(1)	108.4(5)	C(39)-C(31)-C(9)	112.2(5)
O(1)-C(8)-C(16)	106.8(4)	C(28)-C(32)-C(48)	117.5(4)
C(1)-C(8)-C(16)	116.7(5)	C(28)-C(32)-C(22)	121.3(5)
C(10)-C(9)-C(31)	108.7(4)	C(48)-C(32)-C(22)	89.6(4)
C(13)-C(10)-C(9)	109.9(4)	C(29)-C(34)-C(6)	111.4(5)
C(13)-C(10)-P(1)	115.2(4)	O(1)-C(35)-C(48)	103.9(5)
C(9)-C(10)-P(1)	116.1(3)	C(19)-C(36)-C(26)	120.9(5)
C(21)-C(11)-C(12)	109.7(4)	C(30)-C(38)-C(16)	125.5(5)
C(21)-C(11)-P(1)	111.7(4)	C(30)-C(38)-Ru(1)	72.4(3)
C(12)-C(11)-P(1)	118.0(3)	C(16)-C(38)-Ru(1)	105.4(3)
C(40)-C(12)-C(11)	110.4(4)	C(47)-C(39)-C(31)	111.2(5)
C(10)-C(13)-C(47)	110.1(5)	C(12)-C(40)-C(45)	112.4(5)
C(44)-C(14)-C(28)	114.7(5)	C(29)-C(42)-C(24)	111.6(4)
C(38)-C(16)-C(22)	112.6(4)	C(19)-C(43)-C(46)	119.6(5)
C(38)-C(16)-C(8)	110.6(4)	C(20)-C(45)-C(40)	109.9(4)
C(22)-C(16)-C(8)	118.1(4)	C(18)-C(46)-C(43)	119.5(6)
C(38)-C(16)-C(48)	123.2(4)	C(39)-C(47)-C(13)	111.0(4)
C(22)-C(16)-C(48)	89.2(4)	C(35)-C(48)-C(32)	116.3(4)
C(8)-C(16)-C(48)	102.1(4)	C(35)-C(48)-C(16)	105.1(4)
C(46)-C(18)-C(26)	121.4(5)	C(32)-C(48)-C(16)	89.3(4)
C(43)-C(19)-C(36)	120.5(5)		
C(21)-C(20)-C(45)	111.1(4)		

Table 4. Anisotropic displacement parameters ($A^2 \times 10^3$) for 1. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
Ru(1)	20(1)	22(1)	24(1)	0(1)	5(1)	1(1)
P(1)	20(1)	20(1)	24(1)	-1(1)	6(1)	2(1)
Cl(1)	28(1)	38(1)	22(1)	1(1)	2(1)	-5(1)
Cl(2)	29(1)	36(1)	33(1)	9(1)	4(1)	-4(1)
C(3)	26(4)	22(2)	21(3)	0(2)	5(3)	0(2)
O(1)	22(3)	49(2)	56(3)	2(2)	9(3)	9(2)
C(5)	21(3)	23(2)	31(3)	-2(2)	7(3)	5(2)
C(6)	34(4)	28(3)	41(4)	-1(2)	13(4)	4(2)

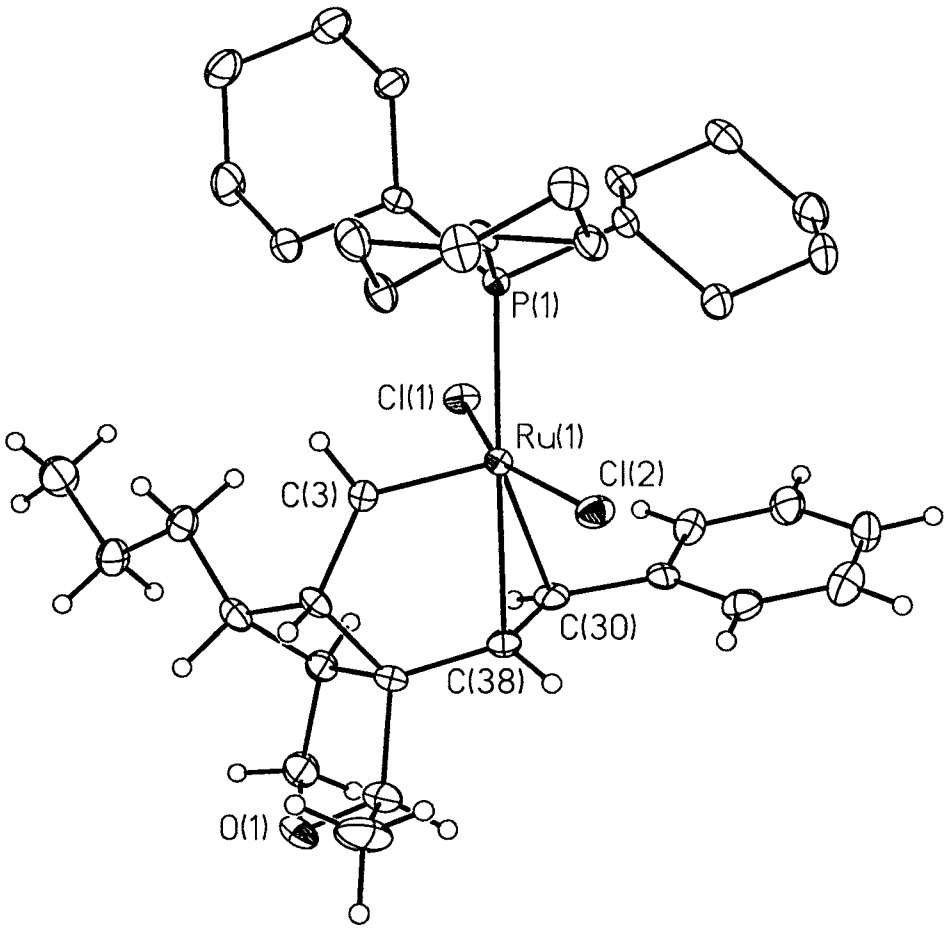
C(8)	26(4)	43(3)	52(4)	4(3)	12(4)	0(3)
C(9)	28(4)	29(3)	35(4)	5(2)	4(3)	4(2)
C(10)	18(4)	27(2)	21(3)	1(2)	2(3)	1(2)
C(11)	17(3)	25(2)	24(3)	4(2)	0(3)	7(2)
C(12)	23(4)	30(3)	30(3)	3(2)	-1(3)	6(2)
C(13)	30(4)	27(3)	35(4)	1(2)	4(3)	-6(2)
C(14)	44(4)	31(3)	34(4)	7(2)	6(4)	4(3)
C(16)	19(4)	32(3)	36(4)	0(2)	10(3)	-1(2)
C(18)	34(4)	38(3)	38(4)	-8(3)	9(3)	-11(3)
C(19)	49(5)	34(3)	46(4)	-10(3)	14(4)	-1(3)
C(20)	33(4)	34(3)	34(4)	-9(2)	4(4)	7(2)
C(21)	28(4)	30(3)	22(3)	-2(2)	0(3)	9(2)
C(22)	18(4)	32(3)	19(3)	-2(2)	1(3)	6(2)
C(24)	26(4)	32(3)	28(3)	-4(2)	2(3)	8(2)
C(26)	14(4)	31(3)	35(4)	-5(2)	-4(3)	-4(2)
C(28)	41(4)	28(3)	29(3)	-4(2)	7(4)	-2(2)
C(29)	43(4)	37(3)	46(4)	-13(3)	13(4)	6(3)
C(30)	16(4)	34(3)	33(4)	-1(2)	-6(3)	-8(2)
C(31)	54(5)	33(3)	47(4)	17(3)	13(4)	12(3)
C(32)	27(4)	35(3)	33(3)	-7(2)	9(3)	7(2)
C(34)	43(4)	25(3)	60(4)	2(3)	16(4)	10(3)
C(35)	31(5)	39(3)	51(4)	3(3)	0(4)	2(3)
C(36)	41(4)	29(3)	34(4)	0(2)	1(4)	-2(3)
C(38)	18(4)	29(3)	39(4)	-3(2)	0(3)	-6(2)
C(39)	54(5)	30(3)	47(4)	5(3)	19(4)	-9(3)
C(40)	34(4)	37(3)	24(3)	1(2)	-7(4)	4(3)
C(42)	27(4)	44(3)	31(4)	-10(3)	3(3)	8(3)
C(43)	47(5)	25(3)	59(4)	-1(3)	8(4)	5(3)
C(44)	56(5)	47(4)	55(4)	12(3)	22(4)	6(3)
C(45)	42(4)	36(3)	27(3)	-2(2)	3(3)	6(3)
C(46)	60(5)	35(3)	48(4)	7(3)	6(4)	-3(3)
C(47)	44(4)	37(3)	42(4)	-3(3)	15(4)	-10(3)
C(48)	27(4)	32(3)	28(3)	1(2)	4(3)	1(2)
C(1)	43(5)	89(5)	54(5)	19(4)	26(4)	-3(4)

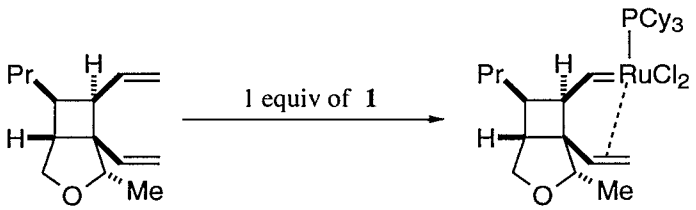
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2x 10^3) for **11**.

	x	y	z	U(eq)
H(3A)	7934(4)	5563(3)	1956(2)	28
H(5A)	11571(4)	3477(3)	1852(2)	30
H(6A)	9677(5)	2288(4)	1428(3)	40
H(6B)	10337(5)	2284(4)	2105(3)	40
H(8A)	4341(5)	3216(5)	1644(3)	48
H(9A)	9552(5)	6809(4)	1754(2)	37
H(9B)	8735(5)	6231(4)	1237(2)	37
H(10A)	10231(4)	5349(3)	972(2)	27
H(11A)	11277(4)	5102(3)	2602(2)	27
H(12A)	10367(4)	3391(4)	3102(2)	34

H(12B)	11486(4)	3375(4)	2869(2)	34
H(13A)	11969(4)	5401(4)	1614(2)	37
H(13B)	11554(4)	6304(4)	1979(2)	37
H(14A)	4997(5)	6741(4)	238(3)	44
H(14B)	4864(5)	7533(4)	748(3)	44
H(18A)	7163(5)	1259(4)	1786(3)	44
H(19A)	8294(5)	674(4)	-48(3)	51
H(20A)	10030(5)	6232(4)	3743(2)	41
H(20B)	11144(5)	6195(4)	3504(2)	41
H(21A)	9695(4)	6021(4)	2675(2)	33
H(21B)	9241(4)	5079(4)	2989(2)	33
H(22A)	6153(4)	5287(4)	2245(2)	28
H(24A)	10344(5)	3487(4)	633(2)	35
H(24B)	11371(5)	4184(4)	863(2)	35
H(28A)	6618(5)	7094(4)	1294(2)	39
H(28B)	6736(5)	6288(4)	786(2)	39
H(29A)	10645(5)	1529(4)	575(3)	50
H(29B)	11841(5)	1097(4)	776(3)	50
H(30A)	6317(4)	3205(4)	636(3)	35
H(31A)	9606(5)	6922(4)	478(3)	53
H(31B)	9250(5)	7826(4)	863(3)	53
H(32A)	5039(5)	6158(4)	1483(2)	37
H(34A)	11846(5)	1525(4)	1793(3)	50
H(34B)	10808(5)	847(4)	1556(3)	50
H(35A)	3599(5)	5337(4)	644(3)	50
H(35B)	3747(5)	4145(4)	575(3)	50
H(36A)	7442(5)	2184(4)	104(3)	42
H(38A)	6228(4)	2732(4)	1828(3)	35
H(39A)	11068(5)	8059(4)	701(3)	51
H(39B)	11037(5)	8013(4)	1405(3)	51
H(40A)	12253(5)	4529(4)	3628(2)	40
H(40B)	11793(5)	3593(4)	3942(2)	40
H(42A)	11898(5)	2736(4)	347(3)	41
H(42B)	12514(5)	2737(4)	1034(3)	41
H(43A)	8593(5)	-550(4)	709(3)	53
H(44A)	5314(5)	8375(4)	-88(3)	77
H(44B)	6397(5)	7733(4)	-29(3)	77
H(44C)	6262(5)	8527(4)	482(3)	77
H(45A)	10242(5)	4535(4)	4063(2)	42
H(45B)	11297(5)	5147(4)	4364(2)	42
H(46A)	7977(5)	-274(4)	1625(3)	58
H(47A)	12461(5)	6987(4)	1228(3)	48
H(47B)	11672(5)	6386(4)	711(3)	48
H(48A)	5528(5)	4715(4)	604(2)	35
H(1A)	3848(5)	3846(6)	2523(3)	89
H(1B)	4714(5)	4728(6)	2559(3)	89
H(1C)	5106(5)	3590(6)	2661(3)	89

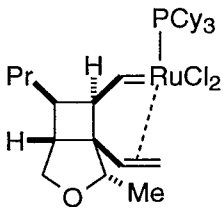
ORTEP of 11:





18 **19**

In a glove box, **1** (112.0 mg, 0.136 mmol) was added to flask containing a stir bar and sealed under Ar atmosphere with a septa. Compound **18** (28.0 mg, 0.136 mmol) dissolved in CH_2Cl_2 (4.5 mL) was added by syringe to the flask. Reaction progress was determined by TLC (9:1 hexanes:Et_2O, R_f = 0.2). When complete, the crude reaction mixture was concentrated and purified by silica gel chromatography to give **19** as a dark yellow oil (18.0 mg, 0.028 mmol, 21% yield).

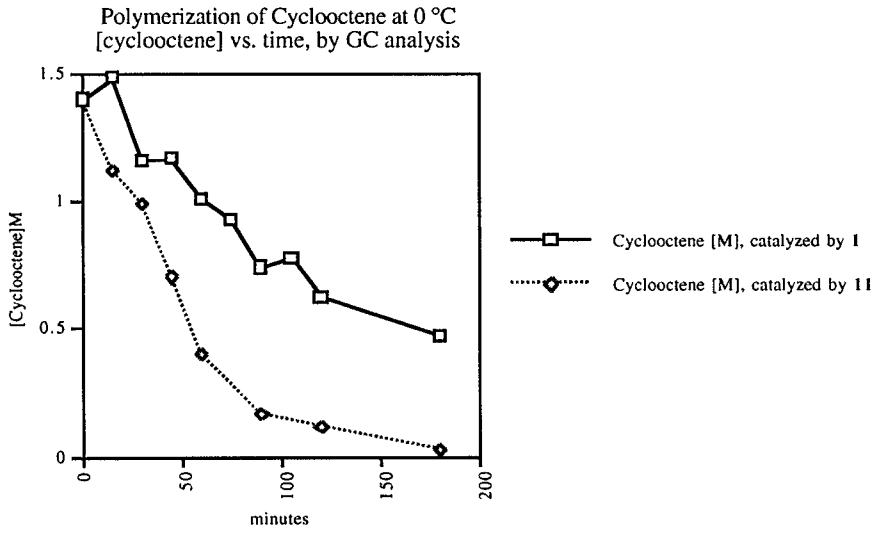


19

Ru complex 19: **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 17.86 (1H, app d, J = 10.8 Hz), 6.31 (1H, dd, J = 13.2, 9.6 Hz), 5.04 (1h, d, J = 8.0 Hz), 4.96 (1H, d, J = 15.2 Hz), 3.98 (1H, q, J = 6.0 Hz), 3.72 (1H, d, J = 9.2 Hz), 3.61 (1h, dd, J = 9.2, 3.6 Hz), 2.62 (1H, dd, J = 6.2, 3.6 Hz), 2.51 (4H, app q, J = 12.0 Hz), 2.00 - 1.00 (35 H, complex), 1.43 (3H, d, J = 5.2 Hz), 0.78 (3H, t, J = 7.2 Hz). **^{31}P NMR** ($CDCl_3$, 121 MHz): δ 33.96. **^{13}C NMR** ($CDCl_3$, 100 MHz): 315.3 (br s, Ru=CHR), 99.6, 99.4, 85.3, 79.4, 72.5, 44.5, 35.5, 30.6, 30.4, 28.5 (pseudo t, J = 6.0 Hz, *ipso*-C of P(Cy)3), 26.9, 23.0, 21.8, 16.2, 14.9, 14.7. **IR** (NaCl, thin film): 2927, 2852, 2358, 2340, 1447, 1382, 1262, 1092 cm^{-1}. **Anal** Calcd. for $C_{32}H_{53}Cl_2OPRu$: C, 57.83; H, 8.30. Found: C, 58.10; H, 8.05.

Representative experiment followed for determining rate of polymerization of cyclooctene.

Catalyst **1** (10.7 mg, 0.013 mmol) was placed in a flask and sealed under Ar atmosphere with a septa. CH_2Cl_2 (1.0 mL) was added by syringe. After ice bath cooling (0°C), cyclooctene (215 mg, 1.95 mmol) and dodecane (50 μL), both in CH_2Cl_2 (0.44 mL), were introduced to the flask by syringe.



Relative rates of cyclooctene consumption

catalyzed by 1
$t_{1/2}$ = 110 min

catalyzed by 11
$t_{1/2}$ = 45 min

The concentration of cyclooctene was measured by GC analysis relative to dodecane internal standard. Relative rates of polymerization are described as the time necessary for one half of total cyclooctene consumption ($t_{1/2}$) by the respective catalysts.

Determination of rate constant by ^{1}H NMR. Pseudo-first-order initiation rate constants were measured by integration of the H_α resonances vs. ferrocene internal standard. Catalysts **1** and **11** were weighed into NMR tubes and dissolved in $CDCl_3$ (0.25 mL) along with ferrocene internal standard. This mixture was treated with a solution of cyclooctene (20.6 mg, 0.188 mmol, 15 equiv) in $CDCl_3$ (0.06 mL). A ^{1}H NMR spectra was recorded every 60 sec for 30 min. For catalyst **1**, k_i = 0.0124 L/mol•S and for catalyst **11**, k_i = 0.0035 L/mol•S for cyclooctene polymerization. See graphs below.