

Olefin Metathesis Involving Ruthenium Enoic Carbene Complexes

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Supporting Material

Experimental procedures and characterization (^1H and ^{13}C NMR, HRMS) employed in the preparation of metathesis products.

General Experimental Section. NMR spectra were recorded on Varian-300 NMR. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) with reference to internal solvent. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), and multiplet (m). The reported ^1H NMR data refer to the major olefin isomer unless stated otherwise. The reported ^{13}C NMR data include all peaks observed and no peak assignments were made. High-resolution mass spectra (EI) were provided by the UCLA Mass Spectrometry Facility (University of California, Los Angeles).

Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Flash column chromatography was performed using silica gel 60 (230-400 mesh) from EM Science. All other chemicals were purchased from the Aldrich, Strem, or Nova Biochem Chemical Companies, and used as delivered unless noted otherwise. CH_2Cl_2 was purified by passage through a solvent column prior to use.¹

General Procedure: To a flask charged with catalyst **1** (0.05 equiv in 0.05 to 0.4 M CH₂Cl₂), α,β -unsaturated carbonyl compounds, or disubstituted olefins were added via syringe. The flask was fitted with a condenser and refluxed under argon for 3 to 5 hours. The reaction was monitored by TLC. After the solvent was evaporated, the product was purified directly on a silica gel column.

Compound 6. see **General Procedure.** The product was purified directly on a silica gel column, eluting with 1: 10 = ethyl acetate: hexane. 40 μ l of *n*-butyl acrylate gave 22.7 mg of the dimer in 87% yield (R_f = 0.3 in 1: 10 = EA: Hx, white solid). ¹H NMR (400 MHz, CDCl₃, ppm): δ 6.83(2H, s), 4.19(4H, t, J = 6.6 Hz), 1.65(4H, m), 1.38(4H, m), 0.93(6H, q, J = 7.4 Hz). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 165.2, 133.8, 65.5, 30.9, 19.5, 14.0. HRMS (EI) calcd for C₁₂H₂₀O₄ 228.1362, found 228.1373.

Compound 7. see **General Procedure.** The product was purified directly on a silica gel column, eluting with 1: 15 = ethyl acetate: hexane. 50.6 mg of cyclohexyl acrylate gave 34.7 mg of the dimer (R_f = 0.5 in 1: 10 = EA: Hx, white solid). Characterization by: Kansui, Hisao; Hiraoka, Shingo; Kunieda, Takehisa; J.Amer.Chem.Soc.; 118; 23; 1996; 5346.

Compound 8. see **General Procedure.** The product was purified directly on a silica gel column, eluting with 1: 20 = ethyl acetate: hexane. 30 μ l of *t*-butyl acrylate gave 21.9 mg of the dimer (R_f = 0.5 in 1: 10 = EA: Hx, clear oil). Characterization by: Charlton, James L.; Maddaford, Shawn; Can.J.Chem.; 71; 6; 1993; 827.

Compound 9. see **General Procedure.** The product was purified directly on a silica gel column, eluting with 1: 20 = ethyl acetate: hexane. 40.0 mg of adamantyl acrylate gave 37.3 mg of the dimer (R_f = 0.4 in 1: 10 = EA: Hx, white solid). Characterization by: Matsumoto, Akikazu; Otsu, Takayuki; Chem.Lett.; 8; 1991; 1361.

Compound 10. see **General Procedure.** The product was purified directly on a silica gel column, eluting with 1: 20 = ethyl acetate: hexane. 14.0 mg of hexyl vinyl ketone gave 9.7 mg of the dimer ($R_f = 0.4$ in 1: 10 = EA: Hx, white solid). $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 6.65 (2H, s) 2.62 (4H, t, $J = 8.0$ Hz), 1.59 (4H, m), 1.27(12H, m), 0.863(6H, t, $J = 7.0$ Hz). $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , ppm): δ 200.9, 136.4, 42.0, 31.9, 29.1, 24.1, 22.8, 14.4. HRMS (EI) calcd for $\text{C}_{16}\text{H}_{28}\text{O}_2$ 252.2089, found 252.2090.

Compound 11. see **General Procedure.** The product was purified directly on a silica gel column, eluting with 1: 20 = ethyl acetate: hexane. 13.8 mg of cyclohexyl vinyl ketone gave 11.8 mg of the dimer ($R_f = 0.4$ in 1: 10 = EA: Hx, white solid). Characterization by: House, H.O. et al.; *J.Org.Chem.*; 36; 22; 1971; 3429.

Compound 12. To a flask charged with catalyst **1** (0.05 equiv in 0.05 CD_2Cl_2), 20 μl of ethyl vinyl ketone was added via syringe. After 3 hours, the crude solution was put into a NMR tube. The conversion was determined by integration ratio between 6.8 ppm and 6.4 ppm. Characterization by Bach, Jordi; Berenguer, Ramon; Garcia, Jordi; Lopez, Marta; Manzanal, Judith; Vilarrasa, Jaume; *Tetrahedron*; 54; 49; 1998; 14947.

Compound 13. see **General Procedure.** The product was purified directly on a silica gel column, eluting with 1: 15 = ethyl acetate: hexane. 28.0 mg of the product was obtained ($R_f = 0.4$ in 1: 10 = EA: Hx, clear oil). $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 6.80 (2H, dt, $J = 15.6$ Hz, 6.9 Hz), 5.70 (2H, d, $J = 15.9$ Hz), 2.14 (4H, m), 1.44 (22H, m) $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , ppm): δ 166.2, 147.6, 123.4, 80.3, 32.1, 28.5, 27.9. HRMS (EI) calcd for $\text{C}_{18}\text{H}_{30}\text{O}_4$ 310.2144, found 310.2151.

Compound 14. see **General Procedure.** The product was purified directly by filtering and washed with dichloromethane. 29.1 mg of the product was obtained (white solid). $^1\text{H NMR}$ (300 MHz, THF-d_8 , ppm): δ 10.64 (2H, s), 6.80 (2H, dt, $J =$

15.6, 6.3 Hz), 5.75 (2H, d, $J = 15.6$ Hz), 2.20 (4H, m), 1.50 (4H, m). ^{13}C NMR (75 MHz, THF- d_8 , ppm): δ 168.3, 149.9, 123.9, 33.8, 29.8. HRMS (EI) calcd for $\text{C}_{10}\text{H}_{14}\text{O}_4$ 198.0893, found 198.0896.

Compound 15. see **General Procedure.** The product was purified directly on a silica gel column, eluting with 1: 4 = ethyl acetate: hexane. 15.4 mg of the product was obtained ($R_f = 0.3$ in 1: 3 = EA: Hx, clear oil). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 6.80 (2H, dt, $J = 15.6$ Hz, 6.9 Hz), 6.05 (2H, d, $J = 15.6$ Hz), 2.52 (4H, q, $J = 7.5$ Hz), 2.19 (4H, m), 1.47 (4H, m), 1.06 (6H, t, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 201.1, 146.4, 130.5, 39.7, 32.5, 28.0, 8.5. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{22}\text{O}_2$ 222.1620, found 222.1622.

Compound 16. see **General Procedure.** The product was purified directly on a silica gel column, eluting with 1: 3 = ethyl acetate: hexane. 25.0 mg of the product was obtained ($R_f = 0.3$ in 1: 3 = EA: Hx, white solid). Characterization by: Verhe, R. et al.; J.Org.Chem.; 42; 7; 1977; 1256.

Compound 17. see **General Procedure.** The product was purified directly on a silica gel column, eluting with 1: 15 = ethyl acetate: hexane. 15.0 mg of the product was obtained ($R_f = 0.4$ in 1: 10 = EA: Hx, clear oil). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 6.94 (1H, d, $J = 16.2$ Hz), 6.57 (1H, d, $J = 15.9$ Hz), 2.63 (2H, q, $J = 7.2$ Hz), 1.49 (9H, s), 1.10 (3H, t, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 200.5, 164.9, 138.6, 132.8, 82.2, 34.9, 28.3, 8.0 HRMS (EI) calcd for $\text{C}_{10}\text{H}_{16}\text{O}_3$ 184.1099, found 184.1103.

Compound 18. see **General Procedure.** The product was purified directly on a silica gel column, eluting with 1: 15 = ethyl acetate: hexane. 29.7 mg of the product was obtained ($R_f = 0.4$ in 1: 10 = EA: Hx, clear oil). *E / Z* ratio was confirmed by ^1H NOE. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 5.62 (1H, s), 4.12 (2H, m), [2.58 (2H, t, J

= 7.5 Hz), 1.84 (3H, s) for *cis*], [2.11 (3H, s), 2.00 (2H, $J = 7.5$ Hz), for *trans*] 1.50 (2H, m), 1.30 (6H, m), 0.86 (3H, $J = 6.9$ Hz). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ [167.0, 160.5, 115.6, 59.7, 41.2, 31.7, 27.4, 22.8, 19.1, 14.7, 14.4. for *trans*] [166.5, 160.9, 116.1, 59.7, 33.7, 32.3, 28.2, 25.5, 22.9, 14.7, 14.3. for *cis*] HRMS (EI) calcd for $\text{C}_{11}\text{H}_{20}\text{O}_2$ 184.1463, found 184.1460.

Compound 19. see **General Procedure.** The product was purified directly on a silica gel column, eluting with 1: 5 = ethyl acetate: hexane. 26.5 mg of the product was obtained ($R_f = 0.3$ in 1: 5 = EA: Hx, white solid). *E / Z* ratio was confirmed by ^1H NOE. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 5.67 (1H, s), [2.60 (2H, t, $J = 7.5$ Hz), 1.90 (3H, s) for *cis*], [2.14 (3H, s), 2.10 (2H, $J = 7.0$ Hz), for *trans*] 1.50 (2H, m), 1.30 (6H, m), 0.87 (3H, $J = 6.6$ Hz). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ [172.6, 163.8, 115.2, 41.5, 31.7, 27.4, 22.8, 19.4, 14.4. for *trans*] [172.6, 163.8, 115.7, 33.8, 32.2, 28.2, 25.9, 19.4, 14.4. for *cis*] HRMS (EI) calcd for $\text{C}_9\text{H}_{16}\text{O}_2$ 156.1150, found 156.1145.

Compound 20. see **General Procedure.** The product was purified directly on a silica gel column, eluting with 1: 15=ethyl acetate: hexane. 22.0 mg of the product was obtained ($R_f = 0.4$ in 1: 10 = EA: Hx, white solid). *E / Z* ratio was confirmed by ^1H NOE. ^1H NMR (300 MHz, CDCl_3 , ppm): δ 6.02 (1H, s), [2.54 (2H, t, $J = 7.5$ Hz), 1.83 (3H, s) for *cis*], [2.10 (3H, s), 2.08 (2H, $J = 7.0$ Hz), for *trans*] 2.40 (2H, $J = 5.4$ Hz), 1.50 (2H, m), 1.30 (6H, m), 1.00 (3H, $J = 6.6$ Hz), 0.87 (3H, $J = 6.6$ Hz). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ [201.8, 158.7, 123.0, 41.5, 37.7, 31.8, 27.5, 22.8, 19.6, 14.4, 8.5. for *trans*] [201.2, 159.4, 123.5, 37.7, 34.1, 32.3, 28.3, 25.8, 22.9, 14.4, 8.5. for *cis*] HRMS (EI) calcd for $\text{C}_{10}\text{H}_{20}\text{O}$ 168.1514, found 168.1513.

Compound 21. see **General Procedure.** The product was purified directly on a silica gel column, eluting with 1: 30 = ethyl acetate: hexane. 30.6 mg of the product

was obtained ($R_f = 0.35$ in 1: 30 = EA: Hx, clear oil). Characterization by: Inoue, Sumie; Sato, Yoshiro; *J.Org.Chem.*; 56; 1; 1991; 347.

Compound 22. see **General Procedure.** The product was purified directly on a silica gel column, eluting with 1: 3 = ethyl acetate: hexane. 23.8 mg of the product was obtained ($R_f = 0.35$ in 1: 3 = EA: Hx, white solid). Characterization by : Brittelli, David R.; *J.Org.Chem.*; 46; 12; 1981; 2514.

Compound 23. see **General Procedure.** The product was purified directly on a silica gel column, eluting with 1: 15 = ethyl acetate: hexane. 29.3 mg of the product was obtained ($R_f = 0.40$ in 1: 10 = EA: Hx, clear oil). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 5.94 (1H, s), 2.77 (2H, s), 2.39 (2H, t, $J = 7.2$ Hz), 2.13 (2H, t, $J = 5.1$ Hz), 1.56 (6H, m) 1.03 (3H, t, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 202.4, 161.7, 120.9, 38.4, 37.8, 30.3, 29.2, 28.3, 26.6, 8.5. HRMS (EI) calcd for $\text{C}_{10}\text{H}_{16}\text{O}$ 152.1201, found 152.1203.

(i) The solvent columns are composed of activated alumina (A-2) and supported copper redox catalyst (Q-5 reactant). See: Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.