Tandem Catalysis: Three Mechanistically Distinct Reactions From A Single Ruthenium Complex

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Supporting Information

General Information. All manipulations were performed in a N_2 filled drybox or using standard Schlenk techniques. Tetrahydrofuran and toluene were purified by passage through a solvent column prior to use.[1] Benzene, allyl 3-bromo-3-methyl propionate, methanol, methyl methacrylate, and cyclooctadiene were obtained from Aldrich and degassed by purging with Ar prior to use. $Cl_2(PCy_3)_2Ru{=}CHPh$ (**1**) was prepared as previously reported.[2] ^1H and ^{13}C NMR spectra were recorded on a GE-300 NMR spectrometer and are internally referenced to residual protio solvent. ^{31}P NMR spectra were recorded on a JEOL GX-400 NMR spectrometer and referenced to H_3PO_4 (external standard). IR spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Elemental analyses were performed at Midwest Microlab LLC., Indianapolis, IN. Gel permeation chromatographs were obtained on HPLC system

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

(2) Schwab, P. E.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

using a Waters model 515 pump, a Rheodyne model 7125 injector with a 100 μL loop, two 10 μm mixed bed columns and one 500 Å column connnected in series (American Polymer Standards, Inc), and a Knauer differential refractometer. The eluent (CH_2Cl_2) flow rate was set to 1.0 mL/min and molecular weights and polydispersities were reported relative to monodispersed poly(methyl methacrylate) standards (Polysciences, Inc.). Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Pyris-7 calorimeter using a scan rate of 10 °C/min under an atmosphere of nitrogen.

$Cl_2(PCy_3)_2Ru{=}CHCH_2OC(=O)C(CH_3)_2Br$ (2). A solution of $Cl_2(PCy_3)_2Ru{=}CHPh$ (**1**) (550 mg, 0.67 mmol) in 15 mL benzene was treated with allyl 2-bromo-2-methyl propionate (740 mg, 3.5 mmol) at room temperature. A color change from purple to maroon was observed after 1 hour. The solvent was removed under vacuum, and the residue was repeatedly washed with ice-cold methanol (15 mL portions) until the filtrate was colorless and then dried under vacuum. A maroon microcrystalline solid was obtained. Yield = 470 mg (75%). ^{1}H NMR (300 MHz, C_6D_6): δ 19.53 (t, *J*=3.7 Hz, 1H), 5.41 (d, *J*=4.4 Hz, 2H), 2.73 (bm, 6H), 2.03-2.00 (bm, 14H), 1.80 (s, 6H), 1.80-1.24 (bm, 46H). ^{13}C NMR (75 MHz, C_6D_6): δ 303.55 (s), 84.83 (s), 56.19 (s), 32.79 (t, *J*=9.2 Hz, *J*=9.7 Hz), 30.40 (s), 28.47 (t, *J*=5.1 Hz), 27.23 (s). ^{31}P NMR (122 MHz, C_6D_6): δ 37.3 (s). IR (KBr) 2929 (vs), 2852 (s), 1731 (vs, C=O), 1496 (w), 1445 (s), 1386 (w), 1346 (w), 1329 (w), 1265 (s), 1198 (w), 1152 (s), 1130 (w), 1109 (m), 1005 (m), 959 (w), 917 (w), 898 (w), 846 (m), 817 (w), 736 (m), 696 (w), 642 (w), 519 (w), 508 (w), 487 (w), 466 (w). Anal. Calcd for $RuCl_2P_2C_{43}H_{75}BrO_2$: C, 55.07; H, 8.06. Found: C, 55.35; H, 8.26. The crystal structure for this compound has been determined and will be disclosed at a future date.

Representative polymerization procedure. In a N_2 filled drybox, a 4 dram vial was charged with catalyst (30 mg, 32 μmol), toluene (0.6 mL), and a stir bar. After the catalyst dissolved (<5 min), methyl methacrylate (136 μL, 1.40 mmol) and cyclooctadiene (156 μL, 1.29 mmol) were added. The vial was sealed with a Teflon lined cap, removed from the drybox, and placed in an oil bath thermostatted at 65 °C. After 18 h, the reaction was poured into 100 mL of rapidly stirring methanol which caused a white solid to precipitate. The solid was collected by filtration and dried under vaccuum to afford polymer **3** in 65% yield. ^{1}H NMR (300 MHz, $CDCl_3$). δ 5.40 (br s), 3.60 (br s), 2.03 (br s), 1.81 (br s), 1.57 (br s), 1.02 (br s), 0.84 (br s). GPC: M_n = 9700, PDI = 1.5. DSC: T_g = -103 °C, 104 °C.