

Supporting Information for

Mechanistic Studies of Ethylene and α -Olefin Co-oligomerization

Catalyzed by Chromium-PNP Complexes

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General Materials and Methods. Commercial reagents were used without further purification. All air- and moisture-sensitive manipulations were performed using standard Schlenk techniques or inside a nitrogen-filled glovebox. NMR spectra were recorded on either a 300 or 500 MHz Varian Mercury spectrometer, and chemical shifts for ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to residual solvent peaks.

Syntheses.

3-propyl-1-heptene. 1-Bromobutane (2.00 g, 14.6 mmol) and freshly crushed magnesium turnings (467 mg, 19.5 mmol) were combined with 10 mL of anhydrous diethyl ether in a 25 mL Schlenk flask. The reaction was stirred for ~19 h, giving a clear reddish-brown solution. This Grignard reagent was added slowly via syringe over the course of 30 min to another Schlenk flask charged with 2-hexenyl-1-acetate (1.38 g, 9.73 mmol) and copper(I) chloride (96 mg, 0.97 mmol) in 10 mL of diethyl ether. The reaction was stirred at room temperature for ~12 h, during which time the mixture became a dark red color and GC analysis showed that all of the 2-hexenyl-1-acetate starting material was consumed. The reaction was quenched with aqueous HCl, and the organic phase was isolated by distillation under atmosphere pressure. GC and GC-MS analyses indicated that the mixture contained 3-propyl-1-heptene and trans-4-decene (resulting from reaction at the γ - and α -positions respectively) in a ratio of approximately 1:1. Attempts to separate the two products by fractional distillation were unsuccessful but this sample was used as the GC standard for 3-propyl-1-heptene nevertheless. GC-MS = 140.3 [M]⁺.

5-Methyl-1-nonene. This procedure was adapted from a literature report for cross-coupling of secondary alkyl bromides.¹ 4-Bromo-1-butene (2.05 g, 15.2 mmol) and freshly crushed magnesium

turnings (436 mg, 18.2 mmol) were combined with 10 mL of anhydrous diethyl ether in a 25 mL Schlenk flask and stirred at room temperature for ~12 h. In a separate reaction flask, silver bromide (114 mg, 606 μmol), potassium fluoride (35 mg, 606 μmol), and 2-bromohexane (1.00 g, 6.06 mmol) were combined with 10 mL of anhydrous dichloromethane and cooled to -10°C . This mixture was treated with the Grignard reagent and the resulting darkly-colored solution was stirred cold for 7 h. After this time, the reaction was allowed to warm up to room temperature and stirring continued for an additional 12 h. Aqueous HCl was added and the organic layer was separated. Fractional distillation of the organic layer afforded the desired compound in ~80% purity. GC-MS = 140.0 $[\text{M}]^+$. ^{13}C NMR (CDCl_3 , 125 MHz): δ = 14.46, 19.85, 23.33, 29.57, 31.70, 32.57, 36.55, 36.94, 114.21, 139.81 ppm.

cis-4-Decene. 4-Decyne (1.00 g, 7.23 mmol), Lindlar's catalyst (5% Pd, 760 mg), and quinoline (9 mg, 72.3 μmol) were combined in 15 mL of petroleum ether and stirred under an atmosphere of hydrogen that was supplied using an H_2 -filled balloon.² The reaction was stirred for ~17 h and then filtered through a plug of silica gel to remove the catalyst and quinoline. The petroleum ether was removed by distillation under atmosphere pressure, affording *cis-4-decene* as a colorless liquid (776 mg, 77%). GC-MS = 140.3 $[\text{M}]^+$. ^1H NMR (CDCl_3 , 500 MHz): δ = 0.94 (m, 6H), 1.34-1.41 (m, 8H), 2.06 (m, 4H), 5.40 (m, 2H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz): δ = 14.08, 14.35, 23.01, 23.31, 27.60, 29.70, 29.90, 31.97, 129.92, 130.42 ppm.

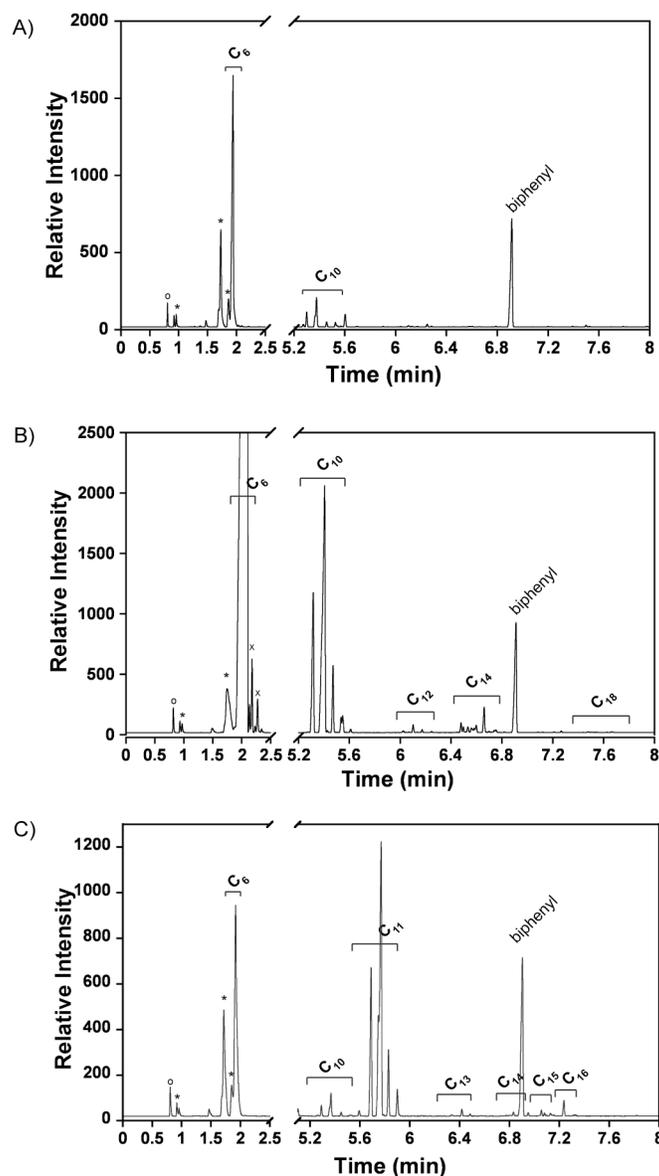


Figure S1. Gas chromatograms of the organic phase from the reaction of **1** (12 μmol)/MMAO (~660 μmol) in the presence of A) ethylene (1 atm); B) ethylene (1 atm) and 1-hexene (35 mmol); and C) ethylene (1 atm) and 1-heptene (24 mmol). The chlorobenzene and 1-heptene peaks appear in the region between 2.5-5.2 min and have been omitted for clarity. The peaks marked with an asterisk (*) and “x” indicate impurities that arise from the MMAO solution and other C_6 isomers, respectively. The peak at ~0.8 min, marked with an “o,” is present in the MMAO solution (see Figure S3) but may also be due to trace amounts of butene that is perhaps produced in the reactions. Biphenyl was added as an internal standard for GC analysis.

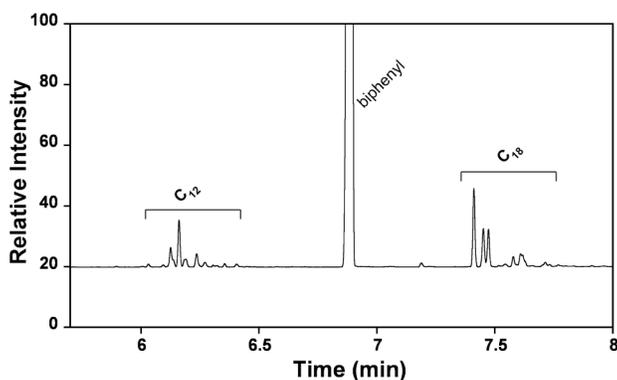


Figure S2. Gas chromatogram of the organic phase from the reaction of **1** (12 μmol) /MMAO (~ 660 μmol) in the presence of 1-hexene (35 mmol). Biphenyl was added as an internal standard for GC analysis.

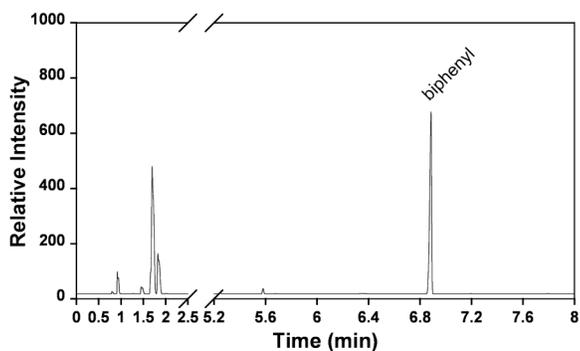


Figure S3. Gas chromatogram of the MMAO (~ 660 μmol) solution in 10 mL of chlorobenzene that was quenched with aqueous HCl. Biphenyl was added as an internal standard for GC analysis.

REFERENCES

- (1) Someya, H.; Yorimitsu, H.; Oshima, K. *Tetrahedron Lett.* **2009**, *50*, 3270-3272.
- (2) Lindlar, H.; Dubuis, R. *Org. Synth.* **1973**, *5*, 880.