Isotopic Labelling in Ethylene Oligomerization: Addressing the Issue of 1-Octene vs. 1-Hexene Selectivity

Nathanael A. Hirscher, Jay A. Labinger, and Theodor Agapie*

Division of Chemistry and Chemical Engineering, California Institute of Technology,

 1200 East California Boulevard MC 127-72, Pasadena, California 91125, United States

Supporting Information

Contents

General Considerations

All glassware was oven-dried and kept under active vacuum prior to use. Chlorobenzene was distilled from CaH_2, stored over activated molecular sieves for at least 24 hours, and filtered through activated alumina directly before use. M-MAO 3A was purchased from AkzoNobel as a 7% w/w Al solution in heptane. Ethylene-H_4 gas was purchased from Sigma-Aldrich (99.99%) in a lecture bottle and immediately before use in catalysis was thawed under static vacuum from its condensed state in a cooled trap using high vacuum line techniques. Ethylene-D_4 gas was purchased from Cambridge Isotope Laboratories (98%-D) in a lecture bottle, and stored in a glass storage bulb under partial vacuum over dried, methylaluminoxane-treated silica (prepared using a similar procedure to that described by Bercaw and coworkers[1]) to remove traces of moisture. Immediately before use in catalysis, the ethylene-D_4 was thawed under static vacuum from its condensed state using high vacuum line techniques. $CrCl_3(THF)_3$ was synthesized according to the literature procedure, using $CrCl_3$ (anhydrous) purchased from Strem.[2] The synthesis of ^{iPr}PNP, $PNP^{(OMe)4}$, $[H(Et_2O)_2][BAr'_4]$, and $(^{tol}PNP)Cr((o\text{-}C_6H_4CH_2)_2O)(Me)$ have been previously reported.[3] Gas chromatography (GC) was performed on an Agilent 6890A instrument using a DB-1 capillary column (10 m length, 0.10 mm diameter, 0.40 μm film) and a flame ionization detector. Gas chromatography/mass spectrometry (GC-MS) was performed on an Agilent 6890A instrument using a HP-5MS column (30 m length, 0.25 mm diameter, 0.50 μm film) and an Agilent 5973N mass-selective EI detector.
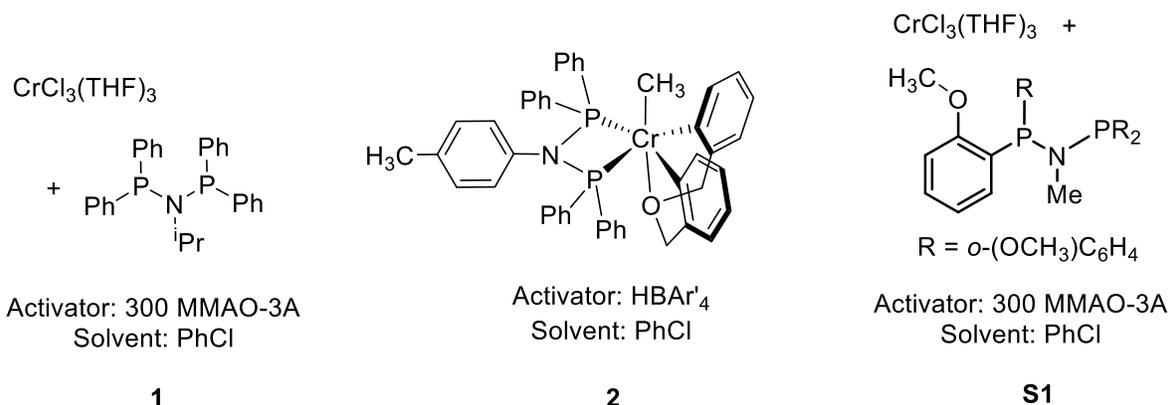
Oligomerization Catalysis Using 1:1 C_2H_4:C_2D_4

Figure S1.

For catalyst **1**, a 1.2 mL mixture of $CrCl_3(THF)_3$ (1.6 mM concentration) and ^{iPr}PNP (1.7 mM concentration) in PhCl was added to a thick-walled 8 mL glass Schlenk tube equipped with a stirbar in a nitrogen-filled glovebox. The solution was frozen in the cold well, then a 0.32 mL solution of MMAO-3A (300 equiv. Al relative to Cr) was layered on top. The Schlenk tube was sealed with a Kontes pin, then taken to the high-vacuum line and degassed using three freeze-pump-thaw cycles, resulting in an activated Cr solution with [Cr] = 1.3 mM.

For catalyst **2**, a 1.0 mL solution of $(^{tol}PNP)Cr((o\text{-}C_6H_4CH_2)_2O)(Me)$ (1.9 mM concentration) was prepared in a vial equipped with a stirbar in a nitrogen-filled glovebox. This solution was frozen in the cold well, then a 0.5 mL solution of $[H(Et_2O)_2][BAr'_4]$ (1 equiv., 3.8 mM concentration) was added to the thawing solution. Upon warming to room temperature, the mixture was transferred to a thick-walled 8 mL glass Schlenk tube, along with the stirbar. The Schlenk tube was sealed with a Kontes pin, then taken to the high-vacuum line and degassed using three freeze-pump-thaw cycles, resulting in an activated Cr solution with [Cr] = 1.3 mM.

For catalyst **S1** (known to be selective for trimerization only), a 1.2 mL mixture of $CrCl_3(THF)_3$ (1.6 mM concentration) and $PNP^{(OMe)4}$ (1.7 mM concentration) in PhCl was added to a thick-walled 8 mL glass Schlenk tube equipped with a stirbar in a nitrogen-filled glovebox. The solution was frozen in the cold well, then a 0.32 mL solution of MMAO-3A (300 equiv. Al/Cr) was layered on top. The Schlenk tube was sealed with a Kontes pin, then taken to the high-vacuum line and degassed using three freeze-pump-thaw cycles, resulting in an activated Cr solution with [Cr] = 1.3 mM.

For catalysis using **1**, **2**, or **S1**, C_2H_4 and C_2D_4 gas were independently measured in a calibrated glass bulb under partial vacuum, using high-vacuum line techniques. The gases were then mixed in a separate bulb, then condensed into the glass Schlenk tube containing a solution of the activated Cr species ([Cr] = 1.3 mM), and the tube was sealed with a Kontes pin. Approximately 1100 total equivalents of ethylene were added to the tube in this manner. After thawing the tube in a room temperature water bath, and allowing the solution to stir for 5 minutes, the reaction was cooled to -78°C, to freeze the chlorobenzene solvent. The tube was degassed using two freeze-pump-thaw cycles, then back-filled with argon. Next, the solution was quenched using 0.1 mL methanol (for the reactions using MMAO activation, acetone was used to dilute the suspension that formed upon quenching).

A weighed amount of adamantane dissolved in acetone was added to the resulting quenched solution (or suspension, for catalysis with MMAO), which was filtered and analyzed by GC/FID to quantify the oligomers vs. adamantane. An appropriately diluted solution was analyzed by GC/MS to quantify the isotopologues of 1-hexene and 1-octene which were produced. Isotopologues of each oligomer co-eluted on the GC with only

slightly shifted retention times. Therefore, quantitation of each isotopologue was achieved by recording the abundance of the parent ions detected by the MS analyzer across the full breadth of the signal in the GC trace. Figure S2 shows the isotopologue distributions for 1-hexene and 1-octene from catalysis using **1**, **2**, and **S1**.

MS Experimental and Modelled Data from the Mixed Gas Experiments

The experimental isotopologue abundances for each fraction (1-hexene or 1-octene) are modelled according to the procedure outlined by Overett and coworkers.[4] The ratios of C_2H_4:C_2D_4 (or simply H:D) incorporated into each fraction, "X", can be determined thereby, and are given in Table S1. Figure S2 shows the experimental data, the best-fit model, and the $X = 1$ model (for comparison) for fractions of products obtained from catalysts **1**, **2**, and **S1**. It is notable that $X_{1\text{-hexene}}$ from **S1** is not 1.0, but 0.92. This could be a result of error in the individual measurement of C_2H_4 & C_2D_4 gases or due to a secondary isotope effect on ethylene binding, oxidative coupling, or migratory insertion, whereby deuterated olefins react faster than non-deuterated olefins. If such a secondary isotope effect is operating, it could affect our calculated results, but the qualitative conclusions would remain valid, as both fractions (1-hexene and 1-octene) should be influenced similarly by such a KIE regardless of which class of mechanisms is considered.

Table S1. H:D isotope ratios in the products from catalysts **1**, **2**, and **S1**

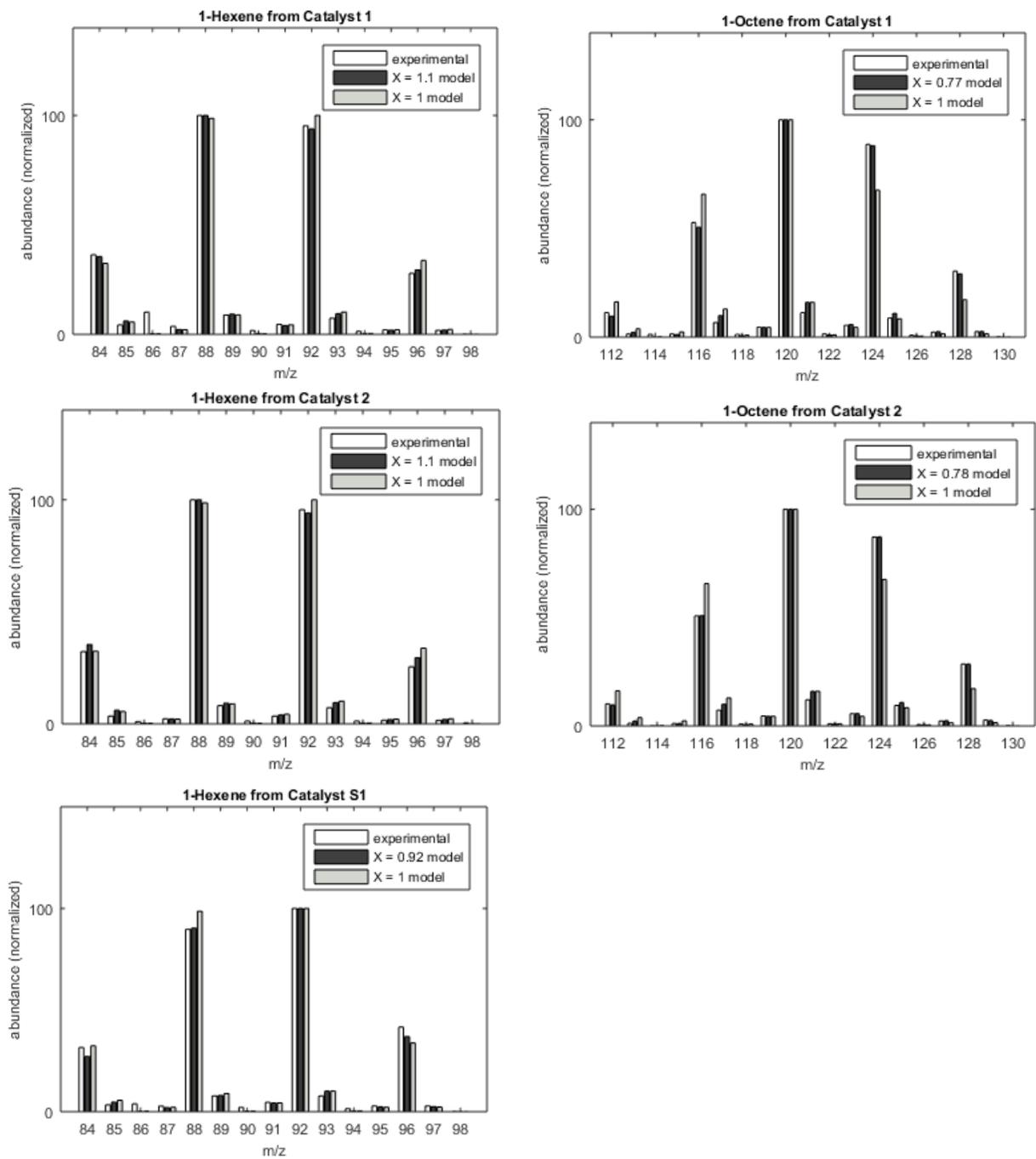| Catalyst	X_{hexene}	X_{octene}
1	1.1	0.77
2	1.1	0.78
S1	0.92	--

Figure S2. Isotopologue distributions of 1-hexene and 1-octene from catalyst **1** (top), and catalyst **2** (middle), as well as the isotopologue distribution from trimerization-selective **S1** (bottom).

Oligomerization Catalysis Using Pure C_2H_4 or Pure C_2D_4

A solution of catalyst **2** ([Cr] = 1.3 mM) was prepared and degassed in the Schlenk tube as described in the sections above. The same batch of activated Cr solution was divided for use in separate experiments using C_2H_4 and C_2D_4, to control for variability in the precatalyst activation process. Ethylene gas (approximately 1100 equivalents relative to Cr) was condensed into each Schlenk tube using high vacuum line techniques. The Schlenk tubes were sealed, and the frozen mixtures were thawed in a room temperature water bath for one minute. Then, the solutions were cooled to -78°C, to freeze the chlorobenzene solvent. The tubes were degassed using two freeze-pump-thaw cycles, then back-filled with argon. Next, the solutions were quenched using 0.1 mL methanol. Weighed amounts of adamantane were dissolved in acetone and were added to the resulting quenched solutions, which were filtered and analyzed by GC/FID to quantify the oligomers vs. adamantane. Results are shown in Table S2; it can be seen that reproducibility in terms of overall activity (as measured by the total weight of products per weight of Cr) and product distribution is quite good.

Table S2. Oligomeric products from C_2H_4 and C_2D_4 using catalyst **2**

| Entry	Gas	Yield (g)	g/g Cr	equiv. C_2H_4 in products	mol % 1-hexene	mol % 1-octene	mol % cyclic C_6	1-octene: 1-hexene
1	C_2H_4	0.017	160	290	41%	44%	15%	1.07
2	C_2H_4	0.020	190	350	40%	45%	15%	1.13
3	C_2H_4	0.018	180	340	46%	39%	15%	0.85
Average		0.018	180	330	42%	43%	15%	1.02
Std Dev		0.001	10	30	3%	3%	0%	0.12
4	C_2D_4	0.018	170	320	30%	67%	2.5%	2.23
5	C_2D_4	0.015	160	290	27%	70%	2.9%	2.59
6	C_2D_4	0.014	140	260	28%	69%	2.3%	2.46
Average		0.016	160	290	28%	69%	2.6%	2.43
Std Dev		0.002	10	30	1%	1%	0.2%	0.15
Ratio								2.39
Error								0.32

## Mechanism A1 and its Variants (A2, A3, and D):
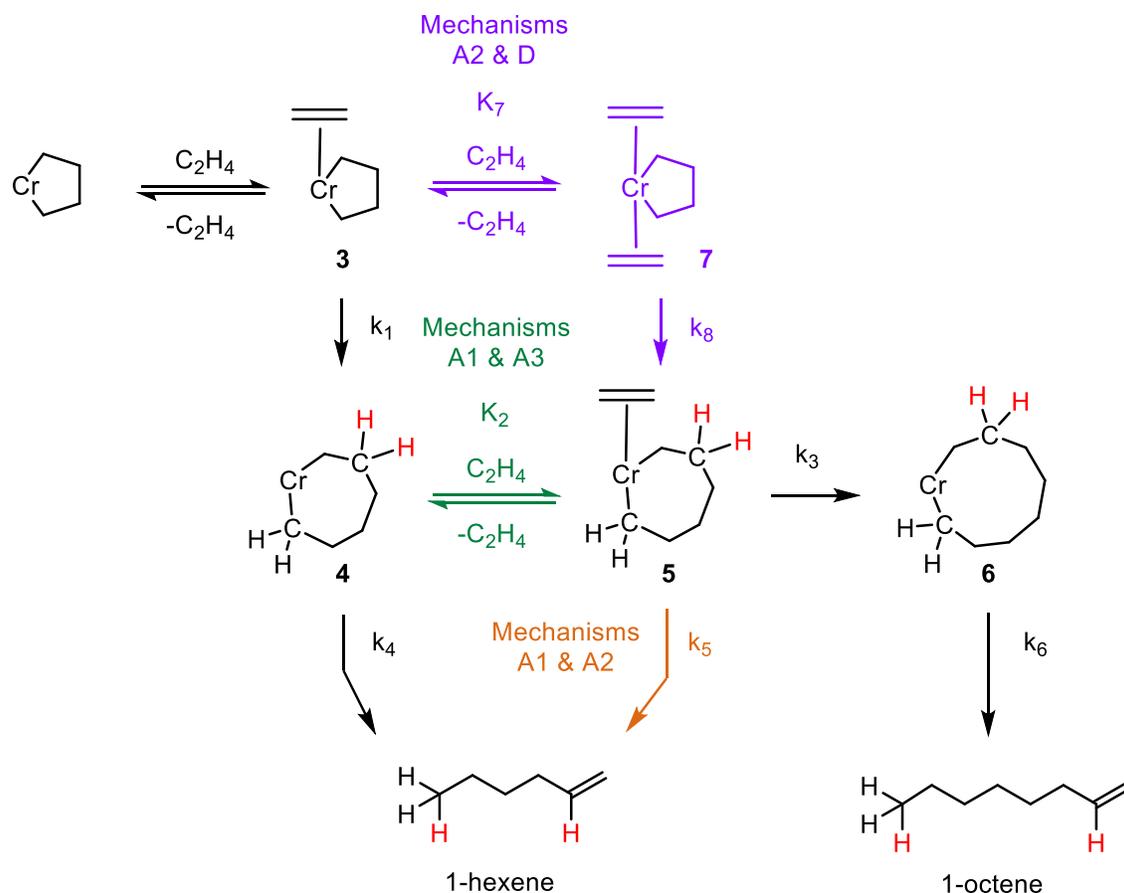
Scheme S1. Mechanism A1 and its variations (A2, A3, and D).

Variants of mechanism A1 (A2, A3, and D) are discussed here with regard to their consistency with both a primary H/D KIE and the typical 1-octene selectivity limits. Two of these are based on an alternative scenario proposed by McGuinness, Britovsek, and coworkers[5], wherein a second ethylene binds reversibly to **3** forming species **7**, as shown in Scheme S1. Subsequent migratory insertion of the ethylene ligand in **7** leads to **5**; **4** and **5** do not interconvert in those cases.

In mechanisms A1 and A3, ethylene insertion in **3** is very rapid relative to additional binding of ethylene ($k_1 \gg k_7$). So, K_2 governs a fast pre-equilibrium between **4** and **5**, such that $k_2, k_{-2} \gg k_3, k_4, k_5$. In mechanisms A2 and D, ethylene insertion in **3** and **7** is slow relative to ethylene coordination/dissociation ($k_1, k_8 \ll k_7, k_{-7}$) and reactions from **4** and **5** are fast ($k_3, k_4, k_5 \gg k_2, k_{-2}$). In mechanisms A1 and A2, the step leading to 1-hexene from **5** is included, whereas mechanisms A3 and D exclude that step. Mechanism D is not technically a class A mechanism (hence its label) as we have defined it, since 1-hexene and 1-octene are not both formed via a common chromacycloheptane intermediate; hence selectivity in mechanism D is not expected to depend on a primary H/D KIE. Selectivities in mechanisms A1, A2, and A3 all do rely on a primary H/D KIE. However, the value of this KIE cannot be determined from our experiments if mechanism A2 is operable, and saturation kinetics are not (the derivation is shown in the next section). Therefore, mechanisms A1, A2, and A3 are consistent with all our experimental data. Only for mechanisms A1 and A3 is equation (2) in the main text valid for all ethylene concentrations.
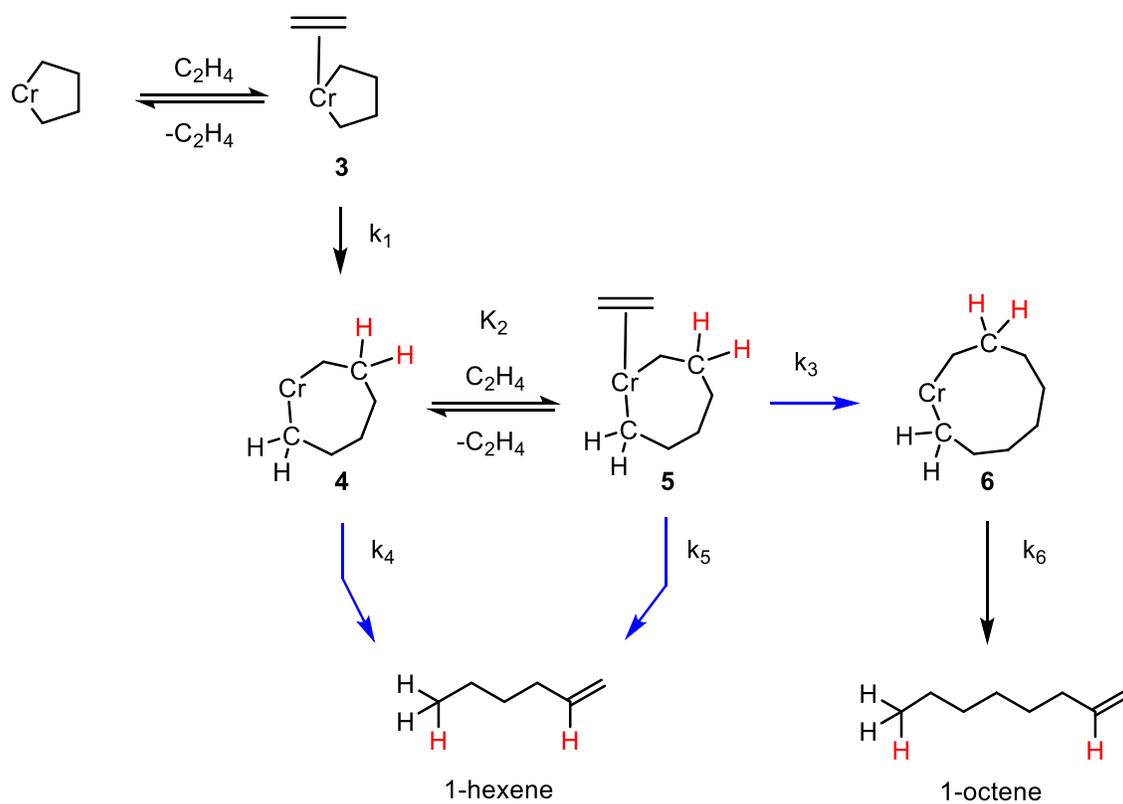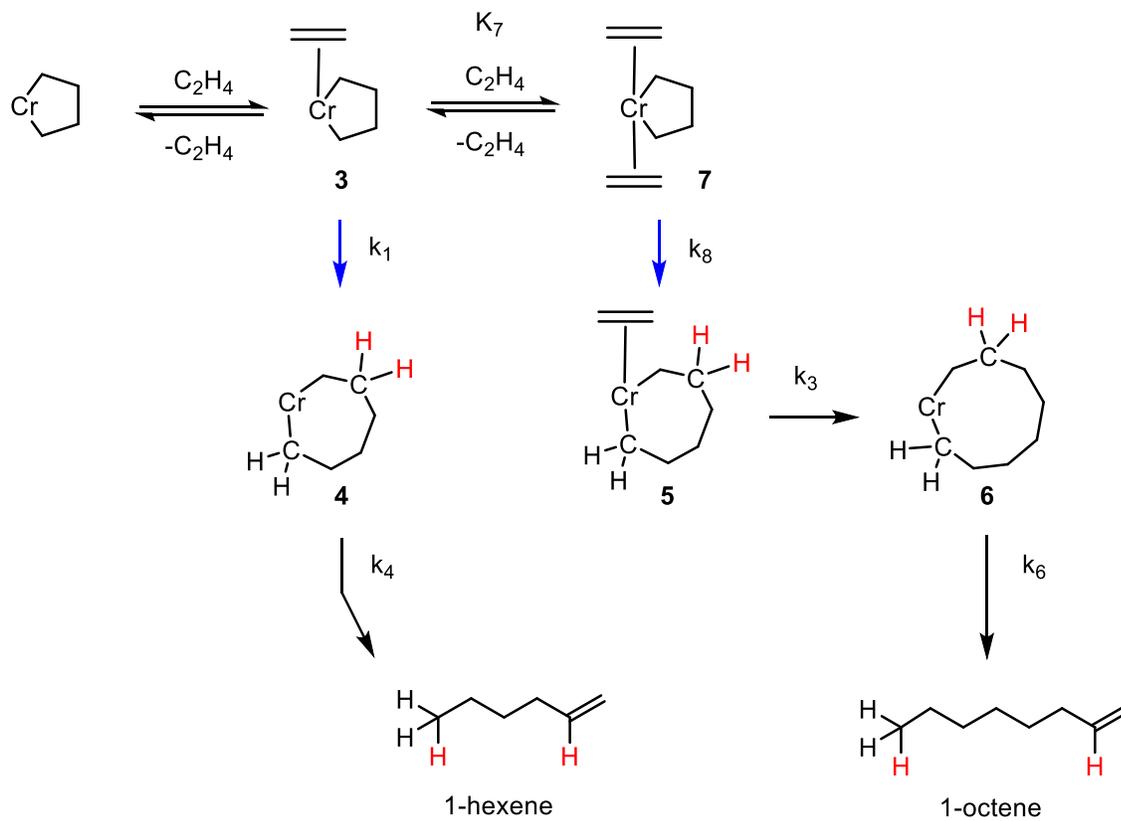
Scheme S2. Mechanism A1, which is operable when metallacycle expansion from **3** is rapid relative to further ethylene binding (distinguishing this from Mechanisms A2 or D). Also, 1-hexene is formed from both **4** and **5** (distinguishing this from Mechanism A3).
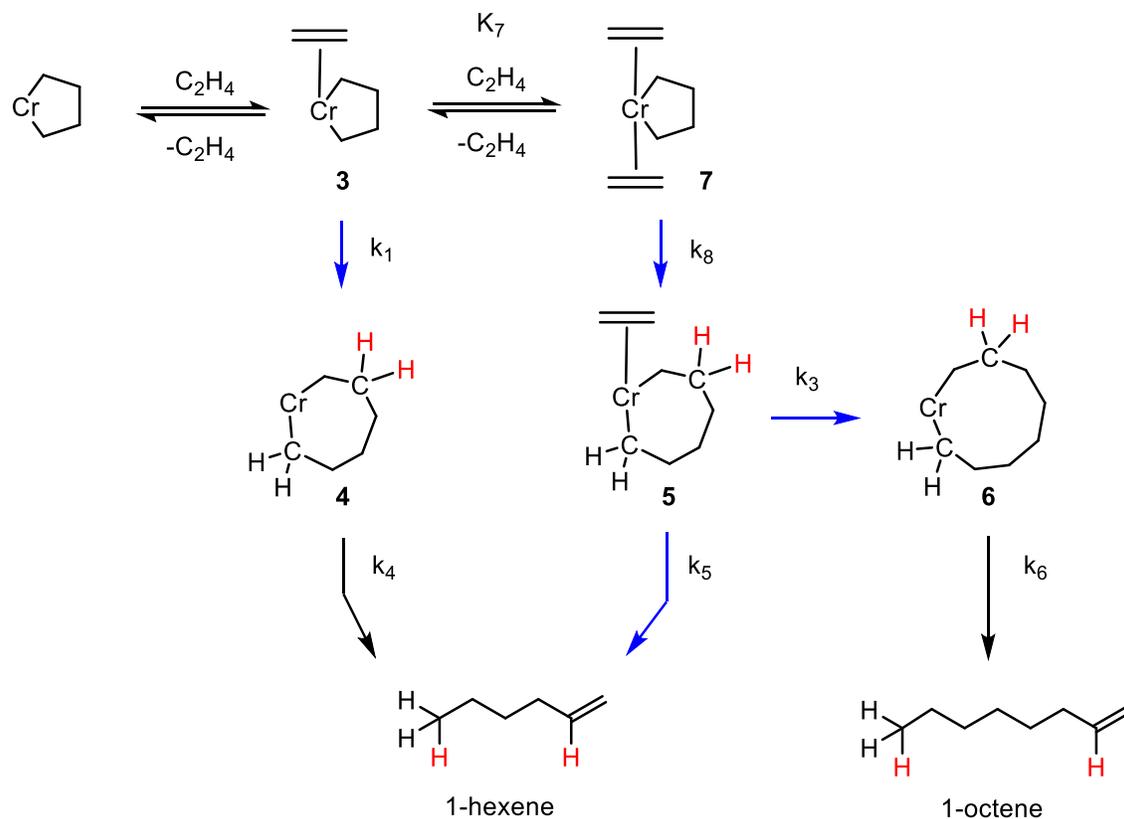
Scheme S3. Mechanism A2, which is operable when metallacycle expansion from **3** or **7** is slow relative to further ethylene binding/dissociation. Reactivity from **4** or **5** (via 1-hexene elimination or metallacycle expansion) is rapid relative to ethylene binding or dissociation (distinguishing this from mechanisms A1 or A3). Also, 1-hexene is formed from both **4** and **5** (distinguishing this from Mechanism D).
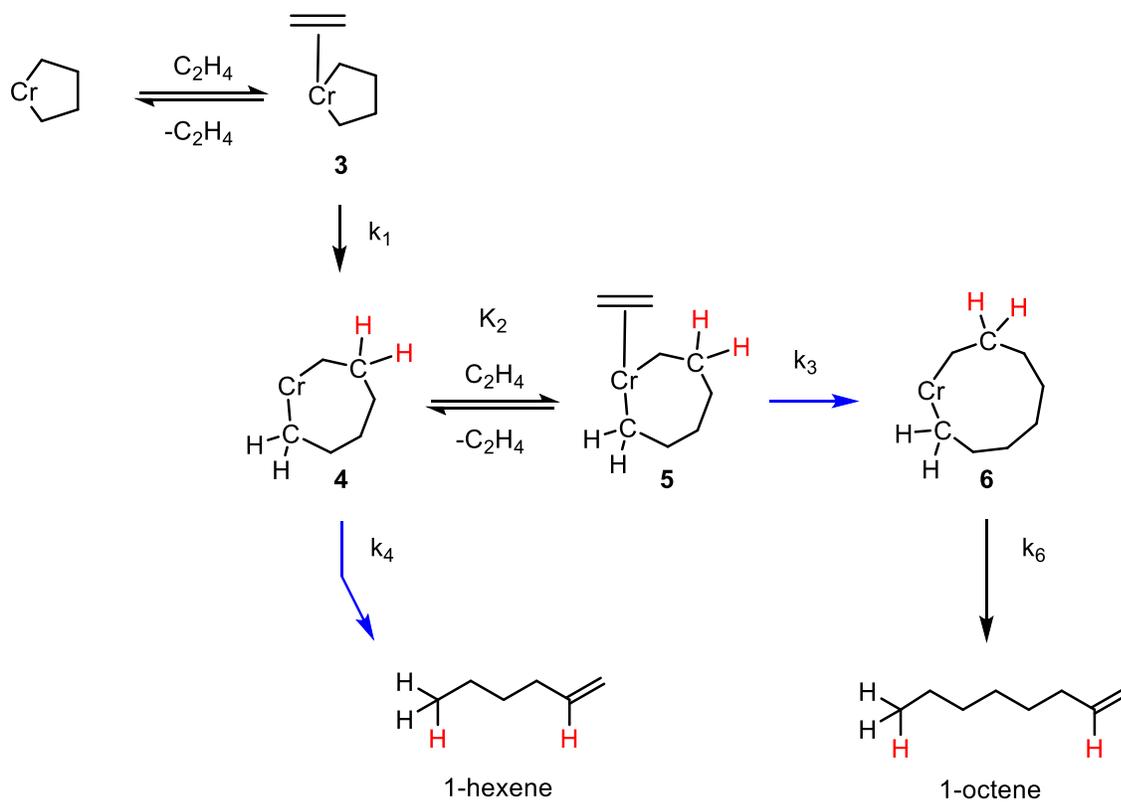
Scheme S4. Mechanism A3, which is operable when metallacycle expansion from **3** is rapid relative to further ethylene binding (distinguishing this from Mechanisms A2 or D). Also, 1-hexene is not formed from **5** (distinguishing this from Mechanism A1).

Scheme S5. Mechanism D, which is operable when metallacycle expansion from **3** or **7** is slow relative to further ethylene binding/dissociation. Reactivity from **4** or **5** (via 1-hexene elimination or metallacycle expansion) is rapid relative to ethylene binding or dissociation (distinguishing this from mechanisms A1 or A3). Also, 1-hexene is not formed from **5** (distinguishing this from Mechanism A2).

Analysis of Mechanisms A1, A2, A3, and D

For Mechanism A1, the selectivity for 1-octene (relative to 1-hexene) is given according to:

$$\text{rate (1-octene)} = \frac{k_2 k_3 [\mathbf{4}][C_2H_4]}{k_{-2}} \tag{1}$$

$$\text{rate (1-hexene)} = k_4 [\mathbf{4}] + \frac{k_2 k_5 [\mathbf{4}][C_2H_4]}{k_{-2}} \tag{2}$$

$$\frac{\text{rate (1-octene)}}{\text{rate (1-hexene)}} = \frac{\frac{k_2 k_3 [C_2H_4]}{k_{-2}}}{k_4 + \frac{k_2 k_5 [C_2H_4]}{k_{-2}}} \tag{3}$$

If under saturation kinetics, $\dfrac{k_2 k_5 [C_2H_4]}{k_{-2}} \gg k_4$, then:

$$\frac{\text{rate (1-octene)}}{\text{rate (1-hexene)}} = \frac{\frac{k_2 k_3 [C_2H_4]}{k_{-2}}}{\frac{k_2 k_5 [C_2H_4]}{k_{-2}}} = \frac{k_3}{k_5} \tag{4}$$

Using equation 4 (under the saturation kinetics approximation), and assuming no isotope effect on metallacycle expansion (k_3) it can easily be seen that:

$$\frac{\frac{1-\text{octene(D)}}{1-\text{hexene(D)}}}{\frac{1-\text{octene(H)}}{1-\text{hexene(H)}}} = \frac{\frac{\text{rate 1-octene (D)}}{\text{rate 1-hexene (D)}}}{\frac{\text{rate 1-octene (H)}}{\text{rate 1-hexene (H)}}} = \frac{\frac{k_{3D}}{k_{5D}}}{\frac{k_{3H}}{k_{5H}}} = \frac{k_5 H}{k_5 D} \tag{5}$$

If saturation kinetics are not operable, the derivation is as follows. Assuming no isotope effect on metallacycle expansion ($k_{3H} = k_{3D}$), ethylene binding or dissociation ($K_{2H} = K_{2D}$), or ethylene concentration ($[C_2D_4] = [C_2H_4]$), the relative ratios of 1-octene to 1-hexene from C_2D_4 and C_2H_4 give the following relation, using equation 3:

$$\frac{\frac{1-\text{octene(D)}}{1-\text{hexene(D)}}}{\frac{1-\text{octene(H)}}{1-\text{hexene(H)}}} = \frac{k_{4H} + \frac{k_{2H} k_{5H} [C_2H_4]}{k_{-2H}}}{k_{4D} + \frac{k_{2D} k_{5D} [C_2D_4]}{k_{-2D}}} \tag{6}$$

Which, when KIE-4 = KIE-5:

$$\frac{k_{4H}}{k_{4D}} = \frac{k_{5H}}{k_{5D}} \tag{7}$$

and because $[C_2D_4] = [C_2H_4]$, $K_{2H} = K_{2D}$, by expanding equation 6 and inserting rearranged equation 7:

$$\frac{\frac{1-octene(D)}{1-hexene(D)}}{\frac{1-octene(H)}{1-hexene(H)}} = \frac{k_{5H}(\frac{k_{4H}}{k_{5H}} + \frac{k_{2H}[C_2H_4]}{k_{-2H}})}{k_{5D}(\frac{k_{4D}}{k_{5D}} + \frac{k_{2D}[C_2D_4]}{k_{-2D}})} = \frac{k_{5H}}{k_{5D}} \tag{8}$$

For Mechanism A2, the selectivity for 1-octene (relative to 1-hexene) is given according to:

$$\text{rate (1-octene)} = \frac{k_7 k_8 k_3 [3][C_2H_4]}{k_{-7}(k_3 + k_5)} \tag{9}$$

$$\text{rate (1-hexene)} = k_1[3] + \frac{k_7 k_8 k_5 [3][C_2H_4]}{k_{-7}(k_3 + k_5)} \tag{10}$$

$$\frac{\text{rate (1-octene)}}{\text{rate (1-hexene)}} = \frac{\frac{k_7 k_8 k_3 [C_2H_4]}{k_{-7}(k_3 + k_5)}}{k_1 + \frac{k_7 k_8 k_5 [C_2H_4]}{k_{-7}(k_3 + k_5)}} \tag{11}$$

If under saturation kinetics, $\dfrac{k_7 k_8 k_5 [C_2H_4]}{k_{-7}(k_3 + k_5)} \gg k_1$, then:

$$\frac{\text{rate (1-octene)}}{\text{rate (1-hexene)}} = \frac{\frac{k_7 k_8 k_3 [C_2H_4]}{k_{-7}(k_3 + k_5)}}{\frac{k_7 k_8 k_5 [C_2H_4]}{k_{-7}(k_3 + k_5)}} = \frac{k_3}{k_5} \tag{12}$$

So, under the saturation kinetics approximation, equation 12 can be used to derive equation 5, as was done for the analysis of mechanism A1.

If saturation kinetics are not operable, and assuming no isotope effect on metallacycle expansion ($k_{3H} = k_{3D}$, $k_{8H} = k_{8D}$), ethylene binding or dissociation ($K_{7H} = K_{7D}$), or ethylene concentration ($[C_2D_4] = [C_2H_4]$), the relative ratios of 1-octene to 1-hexene from C_2D_4 and C_2H_4 give the following relation, using equation 11:

$$\frac{\frac{1-\text{octene(D)}}{1-\text{hexene(D)}}}{\frac{1-\text{octene(H)}}{1-\text{hexene(H)}}} = \frac{\frac{\text{rate 1-octene (D)}}{\text{rate 1-hexene (D)}}}{\frac{\text{rate 1-octene (H)}}{\text{rate 1-hexene (H)}}} = \frac{k_{1H}k_{3H} + k_{1H}k_{5H} + \frac{k_{8H}k_{7H}k_{5H}[C_2H_4]}{k_{-7H}}}{k_{1D}k_{3D} + k_{1D}k_{5D} + \frac{k_{8D}k_{7D}k_{5D}[C_2D_4]}{k_{-7D}}} \qquad (13)$$

So, in mechanism A2, the H/D KIE of the step leading to elimination of 1-hexene can only be obtained *if* [**7**] >> [**3**] that is, in the case of saturation kinetics.

For Mechanism A3, the selectivity for 1-octene (relative to 1-hexene) is given according to:

$$\text{rate (1-octene)} = \frac{k_2 k_3 [\mathbf{4}][C_2H_4]}{k_{-2}} \qquad (14)$$

$$\text{rate (1-hexene)} = k_4 [\mathbf{4}] \qquad (15)$$

$$\frac{\text{rate (1-octene)}}{\text{rate (1-hexene)}} = \frac{\frac{k_2 k_3 [C_2H_4]}{k_{-2}}}{k_4} \qquad (16)$$

So,

$$\frac{\text{rate (1-octene)}}{\text{rate (1-hexene)}} = \frac{k_2 k_3 [C_2H_4]}{k_{-2} k_4} \qquad (17)$$

And, the relative ratios of 1-octene to 1-hexene from C_2D_4 and C_2H_4 give the following relation:

$$\frac{\frac{1-\text{octene(D)}}{1-\text{hexene(D)}}}{\frac{1-\text{octene(H)}}{1-\text{hexene(H)}}} = \frac{\frac{\text{rate 1-octene (D)}}{\text{rate 1-hexene (D)}}}{\frac{\text{rate 1-octene (H)}}{\text{rate 1-hexene (H)}}} = \frac{k_{4H}\frac{k_{2D}k_{3D}[C_2D_4]}{k_{-2D}}}{k_{4D}\frac{k_{2H}k_{3H}[C_2H_4]}{k_{-2H}}} \qquad (18)$$

And, if there is no isotope effect on ethylene binding or dissociation, metallacycle expansion, or on ethylene concentration $K_{2H} = K_{2D}$, $k_{3H} = k_{3D}$, and $[C_2D_4] = [C_2H_4]$:

$$\frac{\frac{1-octene(D)}{1-hexene(D)}}{\frac{1-octene(H)}{1-hexene(H)}} = \frac{k_{4H}}{k_{4D}} \tag{19}$$

For Mechanism D, the selectivity for 1-octene (relative to 1-hexene) is given according to:

$$\text{rate (1-octene)} = \frac{k_7 k_8 [\mathbf{3}][C_2H_4]}{k_{-7}} \tag{20}$$

$$\text{rate (1-hexene)} = k_1[\mathbf{3}] \tag{21}$$

$$\frac{\text{rate (1-octene)}}{\text{rate (1-hexene)}} = \frac{\frac{k_7 k_8 [C_2H_4]}{k_{-7}}}{k_1} \tag{22}$$

The selectivity in mechanism D is not governed by any step exhibiting a primary H/D KIE.

Considering 1-Hexene Formation From β-H Elimination v. Hydride Shift (Or Both).

Heretofore we have simplified the analysis by not considering the formation of cyclic C6's. However, it can be seen from Table S2 that there is a significant isotope effect on the production of these two species (methylcyclopentane and methylenecyclopentane). Previous proposals have invoked β-H elimination from chromacycloheptanes (like **5**) as leading to these products (see Scheme S6). Of course, 1-hexene may be derived from this pathway, instead of from hydride shift. Or, 1-hexene may be derived from both. To account for cyclic C_6 production, both k_9 and k_{10} must be appreciable. The pertinent scenarios, and their effect on the KIE measurement, are outlined below:

Case 1: k_5 is negligible but k_{11} is appreciable (1-hexene is only derived from a β-H elimination):

$$\frac{\frac{1-\text{octene(D)}}{1-\text{hexene(D)}+\text{cyclics(D)}}}{\frac{1-\text{octene(H)}}{1-\text{hexene(H)}+\text{cyclics(H)}}} = \frac{k_{9H}}{k_{9D}} = 3.0 \pm 0.3$$
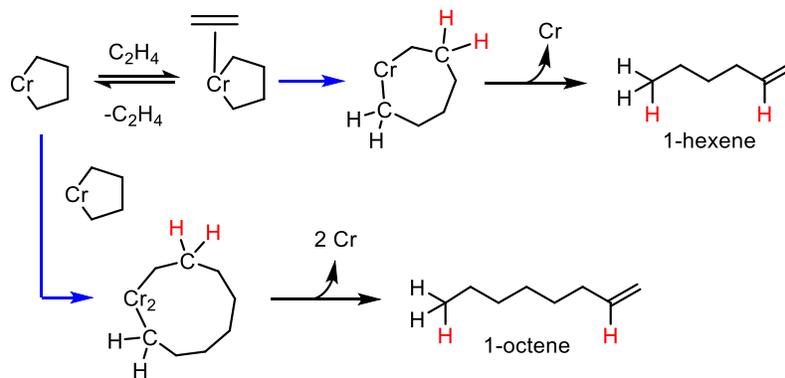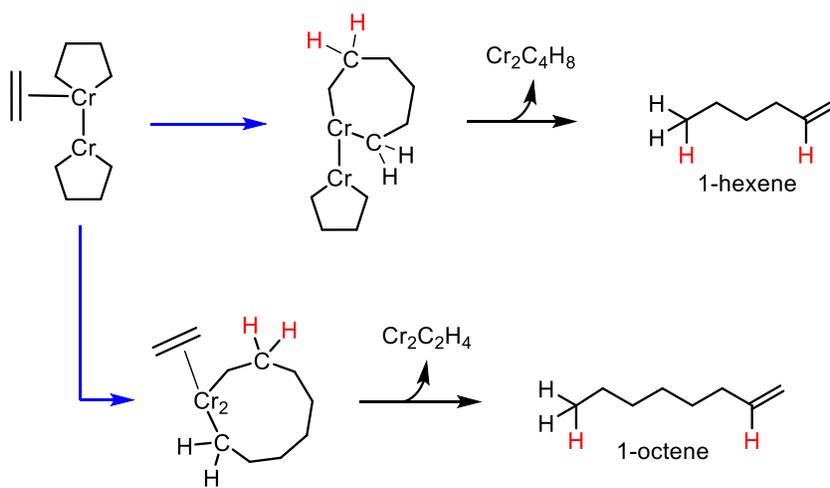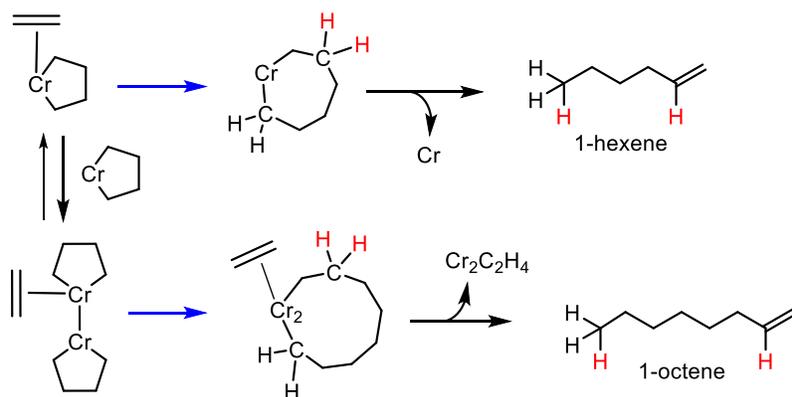
Case 2: k_{11} is negligible but k_5 is appreciable (1-hexene is only derived from a hydride shift; this is the simplification used in the preceding sections):

$$\frac{\frac{1-\text{octene(D)}}{1-\text{hexene(D)}}}{\frac{1-\text{octene(H)}}{1-\text{hexene(H)}}} = \frac{k_{5H}}{k_{5D}} = 2.4 \pm 0.3$$

Case 3: neither k_5 nor k_{11} is negligible (1-hexene is derived from both pathways):

$$\frac{\frac{1-\text{octene(D)}}{1-\text{hexene(D)}+\text{cyclics(D)}}}{\frac{1-\text{octene(H)}}{1-\text{hexene(H)}+\text{cyclics(H)}}} = \frac{k_{5H}+k_{9H}}{k_{5D}+k_{9D}} = 3.0 \pm 0.3$$

Scheme S6. Pathways to form the cyclic C6 products should start with β-H elimination (governed by k_9). 1-Hexene may or may not be derived from this pathway.

Mechanisms in Class B

Scheme S7. Example mechanisms in class B, wherein 1-octene selectivity (relative to 1-hexene) is determined by the relative rate of C-C coupling versus ethylene insertion.

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