

Mechanistic Studies of Olefin and Alkyne Trimerization with Chromium Catalysts: Deuterium Labeling and Studies of Regiochemistry Using a Model Chromacyclopentane Complex

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Abstract: A system for catalytic trimerization of ethylene utilizing chromium(III) precursors supported by diphosphine ligand $\text{PNP}^{\text{O}4} = (o\text{-MeO-C}_6\text{H}_4)_2\text{PN}(\text{Me})\text{P}(o\text{-MeO-C}_6\text{H}_4)_2$ has been investigated. The mechanism of the olefin trimerization reaction was examined using deuterium labeling and studies of reactions with α -olefins and internal olefins. A well-defined chromium precursor utilized in this studies is $\text{Cr}(\text{PNP}^{\text{O}4})-(o,o'\text{-biphenyldiyl})\text{Br}$. A cationic species, obtained by halide abstraction with $\text{NaB}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4$, is required for catalytic turnover to generate 1-hexene from ethylene. The initiation byproduct is vinylbiphenyl; this is formed even without activation by halide abstraction. Trimerization of 2-butyne is accomplished by the same cationic system but not by the neutral species. Catalytic trimerization, with various $(\text{PNP}^{\text{O}4})\text{Cr}$ precursors, of a 1:1 mixture of C_2D_4 and C_2H_4 gives isotopologs of 1-hexene without H/D scrambling (C_6D_{12} , $\text{C}_6\text{D}_8\text{H}_4$, $\text{C}_6\text{D}_4\text{H}_8$, and C_6H_{12} in a 1:3:3:1 ratio). The lack of crossover supports a mechanism involving metallacyclic intermediates. Using a SHOP catalyst to perform the oligomerization of a 1:1 mixture of C_2D_4 and C_2H_4 leads to the generation of a broader distribution of 1-hexene isotopologs, consistent with a Cossee-type mechanism for 1-hexene formation. The ethylene trimerization reaction was further studied by the reaction of *trans*-, *cis*-, and *gem*-ethylene- d_2 upon activation of $\text{Cr}(\text{PNP}^{\text{O}4})(o,o'\text{-biphenyldiyl})\text{Br}$ with $\text{NaB}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4$. The trimerization of *cis*- and *trans*-ethylene- d_2 generates 1-hexene isotopomers having terminal CDH groups, with an isotope effect of 3.1(1) and 4.1(1), respectively. These results are consistent with reductive elimination of 1-hexene from a putative $\text{Cr}(\text{H})[(\text{CH}_2)_4\text{CH}=\text{CH}_2]$ occurring much faster than a hydride 2,1-insertion or with concerted 1-hexene formation from a chromacycloheptane via a 3,7-H shift. The trimerization of *gem*-ethylene- d_2 has an isotope effect of 1.3(1), consistent with irreversible formation of a chromacycloheptane intermediate on route to 1-hexene formation. Reactions of olefins with a model of a chromacyclopentane were investigated starting from $\text{Cr}(\text{PNP}^{\text{O}4})(o,o'\text{-biphenyldiyl})\text{Br}$. α -Olefins react with cationic biphenyldiyl chromium species to generate products from 1,2-insertion. A study of the reaction of 2-butenes indicated that β -H elimination occurs preferentially from the ring CH rather than exo-CH bond in the metallacycloheptane intermediates. A study of cotrimerization of ethylene with propylene correlates with these findings of regioselectivity. Competition experiments with mixtures of two olefins indicate that the relative insertion rates generally decrease with increasing size of the olefins.

Introduction

α -Olefins are important commodity chemicals with uses in a variety of applications including the copolymerization with ethylene and the generation of plasticizers, detergents, surfactants, and lubricants.¹ A significant part of the light fraction ($\text{C}_4\text{--C}_8$) is utilized as comonomer for the copolymerization with ethylene to generate linear low-density polyethylene (LLDPE). In this context, 1-hexene and 1-octene are particularly valuable, imparting to polymers good tear resistance and other desirable properties.² For this application, very good purity of α -olefin is essential, because internal olefins are unreactive and thus build up in copolymerizations. Currently, even carbon number α -ole-

fins are generated industrially mostly via nonselective oligomerization of ethylene.¹ Several recent reports describe the non-statistical oligomerization of ethylene to 1-hexene or mixtures of 1-hexene and 1-octene with good selectivities for the α -olefin.^{3–30} Ethylene trimerization has been reported for

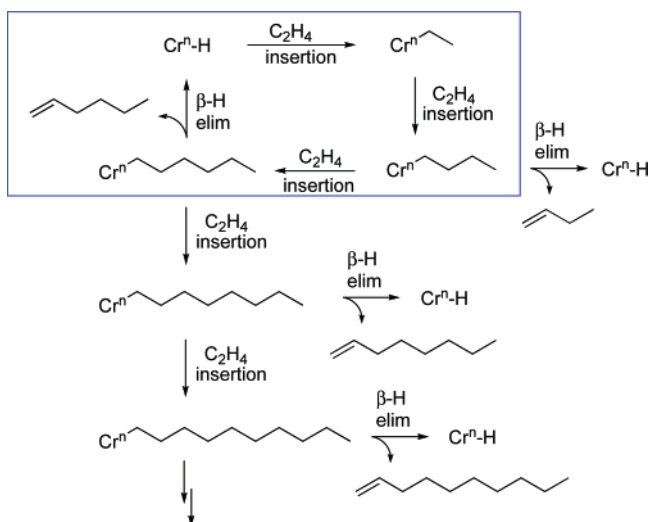
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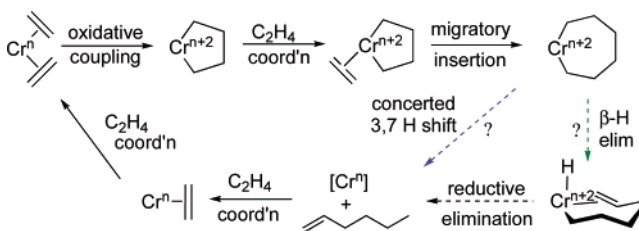
titanium,^{24,26,27} tantalum,³⁰ and chromium systems, the last being the most selective and productive. In fact, a chromium system is currently used for the commercial production of 1-hexene by Chevron–Phillips Chemical Company.^{14,31}

The chromium systems for the trimerization or tetramerization of ethylene are generally based on multidentate supporting ligands with phosphine, amine, ether, and thioether donors. Systems capable of trimerizing α -olefins, based on 1,3,5-triazacyclohexane ligands, have been reported as well; with ethylene, these systems lead to the formation of polyethylene, albeit with some trimerization activity.^{32–34} Typically, multidentate ligands are allowed to react in situ with chromium salts, followed by activation with an aluminum reagent to produce systems competent for the selective oligomerization of ethylene. Well-defined chromium complexes have been characterized and utilized as precursors to catalytic ethylene oligomerization systems upon activation with excess aluminum reagents. Only a few examples of well-defined precursors, reported by our research group, have allowed for stoichiometric activation of chromium precursors to lead to catalytically active species.^{20,21} Direct characterization of the catalytically active species nonetheless remains a challenge, mainly stemming from the fact that the initial catalytic activity of the reported systems decreases quickly indicating catalyst decomposition, as well as from the paramagnetic nature of the chromium complexes.^{20–22,32} The large majority of the reported systems involve chromium(III) precursors, but catalytic activity can be attained with chromium(II) starting materials as well. Solution measurement of the

Scheme 1



Scheme 2



magnetic susceptibility under catalytic conditions has been used to indicate the presence of chromium(III) species.³² Notably, it has been reported that alkyl aluminum species have the ability to induce oxidation state changes in the chromium complexes, possibly by disproportionation.^{35–37}

Many of the details of the mechanism of selective ethylene oligomerization (trimerization or tetramerization) of ethylene are not clear. The formation of 1-hexene in a nonselective fashion is proposed to occur via a Cossee-type mechanism involving intermediate linear alkyl chains which, upon β -H elimination, lead to the formation of α -olefins (Scheme 1). On the basis of this mechanism it is difficult to reconcile selective 1-hexene formation, rather than a Shultz–Flory distribution with formation of higher homologs. However, only recently was this mechanism shown experimentally, by our group, to be inconsistent with the selective formation of 1-hexene, under catalytic conditions.¹⁹ The most popular proposed mechanism to account for the high selectivity involves metallacyclic intermediates (Scheme 2). Initial coordination of 2 equiv of ethylene to a ligated Cr^n species followed by oxidative coupling forms a chromacyclopentane of oxidation state Cr^{n+2} . The transition state for β -hydrogen elimination from the chromacyclopentane leading to 1-butene is expected to be rather strained; hence, ring expansion by ethylene insertion dominates. The resulting chromacycloheptane is flexible enough to undergo rapid β -hydrogen elimination, giving a chromium-alkenyl-hydride species that reductively eliminates 1-hexene to regenerate Cr^n and closes

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the catalytic cycle (green dashed arrow). In agreement, Emrich et al. have reported well-characterized chromacyclopentane and chromacycloheptane complexes; the latter decomposes more readily and yields 1-hexene.³⁸ More recently, it has been suggested that the release of 1-hexene from the metallacycloheptane intermediate proceeds via a concerted 3,7-hydrogen shift with formal two-electron reduction of the metal (purple dashed arrow).^{39–46}

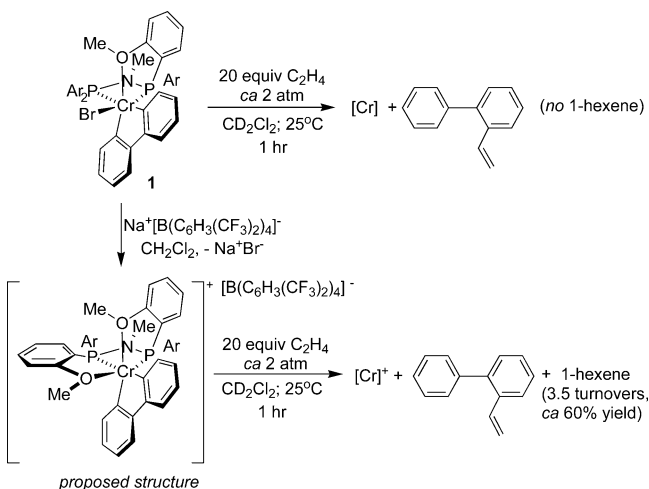
We present herein studies aiming to provide new details concerning the mechanism of the formation of 1-hexene from ethylene with the chromium/PNP⁰⁴ system. Part of this work was communicated previously.¹⁹ Here we discuss in detail labeling experiments that distinguish between metallacyclic and Cossee-type mechanisms. Oligomerization experiments with partially labeled ethylene explain the observed selectivity for 1-hexene in the C6 fraction. Studies of olefin reaction with a model biphenyldiyl chromacycle address questions of regioselectivity of insertion into a metallacyclopentane and β -H elimination/3,7-hydrogen shift from metallacycloheptane product. Relative rates of olefin insertion into biphenyldiyl chromacycle are discussed.

Results and Discussion

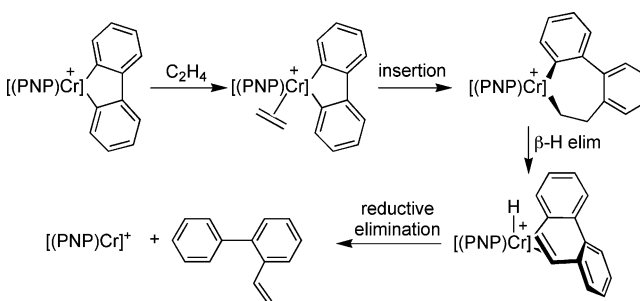
Neutral versus Cationic Species in the Trimerization of Ethylene and 2-Butyne. Most of the systems reported to perform selective trimerization of ethylene to 1-hexene involve the use of large excess of activators, mainly alkylaluminum-oxanes. Alkylaluminumoxanes act both as alkylating agents to convert metal halides to metal alkyls, as well as halide or alkide abstracting agents to generate cationic metal complexes. Given the large excess normally employed for these reagents, the nature of the in situ generated species capable of performing ethylene trimerization is not clear. The chromium biphenyldiyl species (**1**, Scheme 3) provides a useful starting material to answer the question of whether a cationic or neutral species is required for catalytic activity.²¹ Halide abstraction from this complex occurs readily with Na[B(C₆H₃(CF₃)₂)₄]. In this context, a solution of complex **1** was placed under ethylene, in a J-Young tube. Within 1 h, the formation of vinylbiphenyl was observed by ¹H NMR spectroscopy and GC–MS (gas chromatography–mass spectrometry). No formation of 1-hexene was observed under these conditions. In a different experiment, a cationic species was generated by halide extraction with Na[B(C₆H₃(CF₃)₂)₄] in situ and then was placed under ethylene. Under these conditions, formation of vinylbiphenyl as well as of 1-hexene was observed by spectroscopy. These experiments indicate that a cationic species is required for the catalytic generation of 1-hexene.

The formation of vinylbiphenyl suggests a likely mechanism for the initiation reaction (Scheme 4). The starting chromium biphenyldiyl species coordinates ethylene followed by insertion to generate a biphenyldiyl chromacycloheptane species. β -H

Scheme 3



Scheme 4



elimination occurs to generate a chromium–alkenyl-hydride which, upon reductive elimination, leads to the formation of vinylbiphenyl. It is notable that vinylbiphenyl is formed from both neutral and cationic chromium precursors. This indicates that the chromium center can coordinate ethylene, presumably by displacing the labile ether donor, insert, β -H eliminate, and reductively eliminate in the neutral form. The generated metal byproduct would be a chromium(I) species. If this byproduct is neutral, then ethylene trimerization does not occur. Multiple reasons could reside behind the ability of the cationic species to turn over—a more electrophilic metal center may be necessary for ethylene coordination and oxidative coupling to generate a new metallacyclopentane, an additional coordination site may be needed for this process, or the low-coordinate neutral chromium(I) species is more likely to deactivate by forming dimeric species via halide bridges. Alternatively, a neutral metallacyclopentane could form but not insert ethylene further due to steric and electronic differences compared to the chromium biphenyldiyl species.

To further test the role of neutral versus cationic chromium species in trimerization catalysis, the reaction with 2-butyne was investigated (Scheme 5). We envisioned that alkynes would be more reactive toward oxidative coupling and allow catalytic turnover even with neutral chromium species. Exposure of a solution of the neutral species **1** to 2-butyne resulted in the formation of 9,10-dimethylphenanthrene but no hexamethylbenzene. If halide abstraction is performed first, however, the formation of 9,10-dimethylphenanthrene as well as the catalytic formation of hexamethylbenzene is observed. Hence, mirroring the behavior of ethylene in this system, 2-butyne is trimerized only by the cationic species, possibly due to related reasons.

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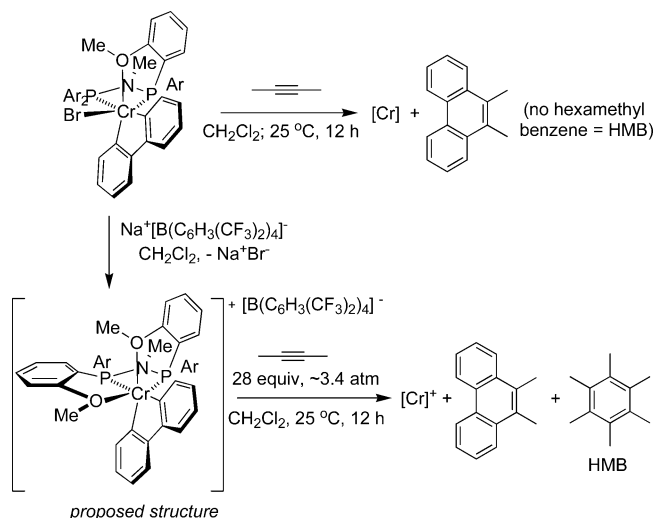
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Scheme 5



With respect to the mechanism of initiation and catalytic trimerization, two pathways are possible (Scheme 6). The biphényldiyl chromium species could react with the alkyne by an insertion or a Diels–Alder mechanism,⁴⁷ although this alternative appears less likely in this case because it disrupts the aromaticity of two arenes. In either case, reductive elimination generates a cationic chromium(I) species. This intermediate coordinates two molecules of alkyne and, upon oxidative coupling, generates a chromacyclopentadienyl species. Another alkyne molecule can react with the chromacyclopentadiene intermediate via the insertion or the Diels–Alder pathway, to form the alkyne trimer upon reductive elimination.

Although catalytic trimerization of alkynes and the cotrimerization of alkynes and olefins have applications in synthesis,^{48–50} to our knowledge, the potential of olefin trimerization catalysts to perform alkyne trimerization has not been reported. Chromium systems have been used as catalysts (but not optimized systems) and as stoichiometric variants for the study of the mechanism of alkyne trimerization.^{51–53} More recently, in situ prepared neutral biphényldiyl chromium species have been reported to undergo reaction with alkynes to generate the corresponding phenanthrene derivatives.⁵⁴ One recent application involves a zirconium/chromium system for the cotrimerization of alkynes with nitriles and isocyanates.⁵⁵ This system is proposed to involve the formation of a neutral chromacyclopentadiene species, which reacts with π -bonds to lead to the formation of cotrimers. Although these systems are stoichiometric in chromium, the current results indicate that the development of catalytic applications for organic synthesis may be possible, one approach being to develop cationic chromium systems.

Crossover Experiments with the Cr(PNP⁰⁴) System for Ethylene Trimerization. The biphényldiyl chromium species

provides a system that can catalytically generate 1-hexene upon stoichiometric activation and allows for further studies of the mechanism of the trimerization of ethylene. Our first studies were directed toward designing a test to distinguish the two mechanistic proposals for 1-hexene formation: metallacyclic versus Cossee-type mechanism. A mixture of C₂H₄ and C₂D₄ (1:1) was trimerized with the cationic biphényldiyl chromium species. Formation of *d*₀ and *d*₄ vinylbiphenyl was observed along with the generation of four 1-hexene isotopologs, C₆H₁₂, C₆D₄H₈, C₆D₈H₄, and C₆D₁₂, in a 1:3:3:1 ratio (see the Supporting Information). Alternative preparations of the catalytic system (complex **1** activated with excess methylalumoxane (MAO)); the in situ prepared system comprised of a toluene solution of CrCl₃(THF)₃, PNP⁰⁴, and excess MAO; or CrPh₃-(PNP⁰⁴) activated with [H(OEt₂)] [B(C₆H₃(CF₃)₂)₄]²⁰ led to a similar distribution of isotopologs, indicating that the same mechanism occurs in all these cases.

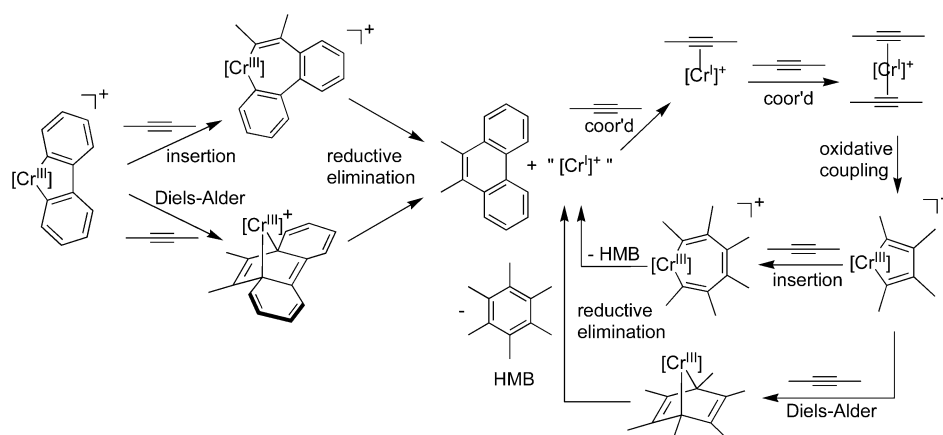
To account for the observed distribution of 1-hexene isotopologs the two proposed mechanisms need to be analyzed more closely. The metallacyclic mechanism can generate intermediates with both hydrogen and deuterium in the β -position (Scheme 7). Hence β -Z (Z = H or D, blue) elimination would move either a hydrogen or a deuterium from the alkyl chain to the chromium center. However, in the subsequent reductive elimination step the transferred Z atom would be returned to the same alkenyl chain. The net effect involves no hydrogen/deuterium scrambling between different molecules of 1-hexene. Of course, the alternative mechanism, concerted 3,7-H shift with loss of 1-hexene, effects the same transformation. As a consequence of either, only isotopologs bearing even numbers of deuteriums and hydrogens are expected from the metallacyclic mechanism. Taking into account the possible routes to access each of the isotopologs, we find that the distribution corresponds to the binomial expansion coefficients—for the trimerization reaction the calculated ratio is 1:3:3:1 (Scheme 7). Hence, the metallacyclic mechanism is consistent with the experimental results.

As described earlier, the Cossee-type mechanism also involves hydride or deuteride intermediates. Upon ethylene insertion the initial Z (Z = H or D) moves from the metal center, to the end of the linear alkyl chain (Scheme 8). Two further ethylene insertions ensue, but unlike the metallacyclic mechanism, the atom (Z', Z' = H or D) abstracted in the metal-hexyl species to give 1-hexene is not the same as the initially metal bound one (Z). As a consequence, scrambling of deuterium and hydrogen between [C₂Y₄]₃ (Y = H, D) units may occur. Hence, isotopologs bearing odd numbers of hydrogens and deuteriums are expected for the Cossee-type mechanism. The various possibilities to access 1-hexene isotopologs by this mechanism lead to a much broader distribution—10 isotopologs can be formed theoretically, with six of them containing odd numbers of hydrogens and deuteriums. This is not observed experimentally. Hence, the present experiment supports the metallacyclic mechanism and is not consistent with the Cossee-type mechanism.

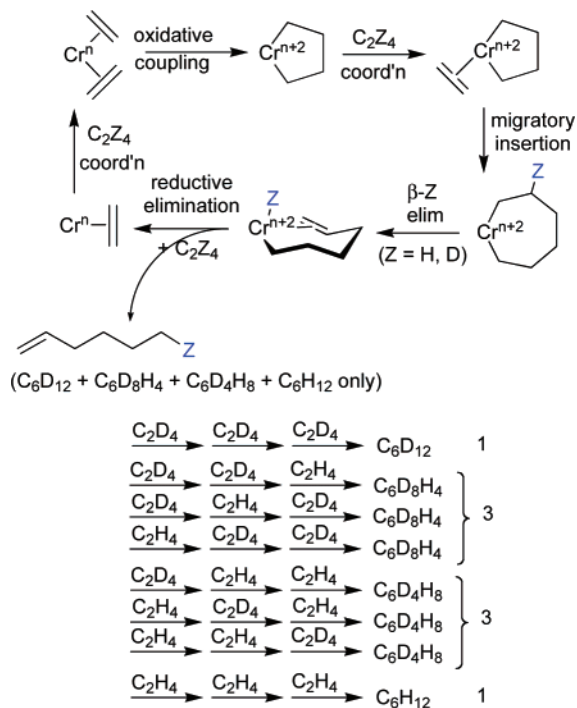
Crossover Experiments with the SHOP Catalyst. The above experimental test is able to distinguish between metallacyclic and Cossee-type mechanisms for any type of olefin oligomerization and is not limited to trimerizations. In fact, other research groups have used this test since our initial report.^{7,56,57} To document the outcome of this experiment under the

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Scheme 6



Scheme 7



conditions of a Cossee-type mechanism, the above test was performed with a nickel-based nonselective ethylene oligomerization catalyst, Ni(Ph₂PCH₂COO)(PPh₃)(Ph).⁵⁸ Formation of a broad distribution of α -olefins was observed (see the Supporting Information). Analysis of the C₆ fraction reveals an isotopolog distribution reflecting the predicted one. Interestingly, slightly more of the isotopologs enriched in hydrogen are present in this fraction. A bar plot showing the expected and observed isotopolog distributions for the metallacyclic and Cossee-type mechanism is shown in Figure 1. This plot highlights the fact that the chromium trimerization reaction gives a better match between the predicted and isotopomer distributions. This is due to the fact that trimerization dominates in this case, and little “leaching” of deuteriums or hydrogens to another oligomer fraction occurs. For the SHOP oligomerization, however, there

is a branching point for each intermediate metal–alkyl species (Scheme 1): ethylene insertion can occur to increase the chain length or β -H elimination can occur to generate the corresponding α -olefin. Although ethylene insertion is expected to have a small, secondary isotope effect, the β -H elimination will have a larger, primary isotope effect; the latter will be the main contributor to the isotope effects on the isotopolog distributions. Every time the last inserted ethylene is C₂D₄, the metal alkyl will have a slower rate of β -Z elimination leading to a higher probability for insertion of another monomer with the net effect that higher olefins carry more deuterons. This isotope effect on the isotopolog distribution cannot occur if only one oligomer is formed, as in the selective formation of 1-hexene, because there are no branching points. However, a similar enrichment with hydrogens in the lower oligomers is expected even for a metallacyclic mechanism, if it is not fully selective for one of the oligomers. Indeed, this effect has been reported for the metallacyclic nonselective ethylene oligomerization with chromium catalysts.⁵⁷ In that case, simulation of the observed distributions in the low oligomers gave the best fit when an isotope effect was included. For the selective trimerization and tetramerization of ethylene with a Cr(PNP) system, it was reported that more deuterium was incorporated in the C₈ than in the C₆ fraction.⁷ This is well accounted for by the above proposal invoking primary isotope effects for β -H elimination (or 3,7-H shift) step.⁵⁹

Reactions with 1,2-Dideuteroethylene. Trimerization of partially deuterated ethylene has provided further insight into the mechanism of formation of 1-hexene with these (PNP^{O4})Cr catalysts. *cis*- and *trans*-ethylene-*d*₂ were trimerized using the cationic biphenyldiyl chromium precursor. The volatile materials, consisting of 1-hexenes, CD₂Cl₂, and unreacted ethylene, were vacuum transferred to a J-Young tube and analyzed by NMR spectroscopy. The olefinic region of the ¹H NMR spectra reveals two types of isotopomers with either two hydrogens or two deuteriums at the 1 and 2 positions of 1-hexene, both with a [=CDH] terminal methylene group. Due to the *cis* stereochemistry for both insertion of ethylene into chromium–carbon bond of the metallacyclopentane and β -H elimination (or the 3,7-H shift alternative), upon conversion of ethylene to 1-hexene

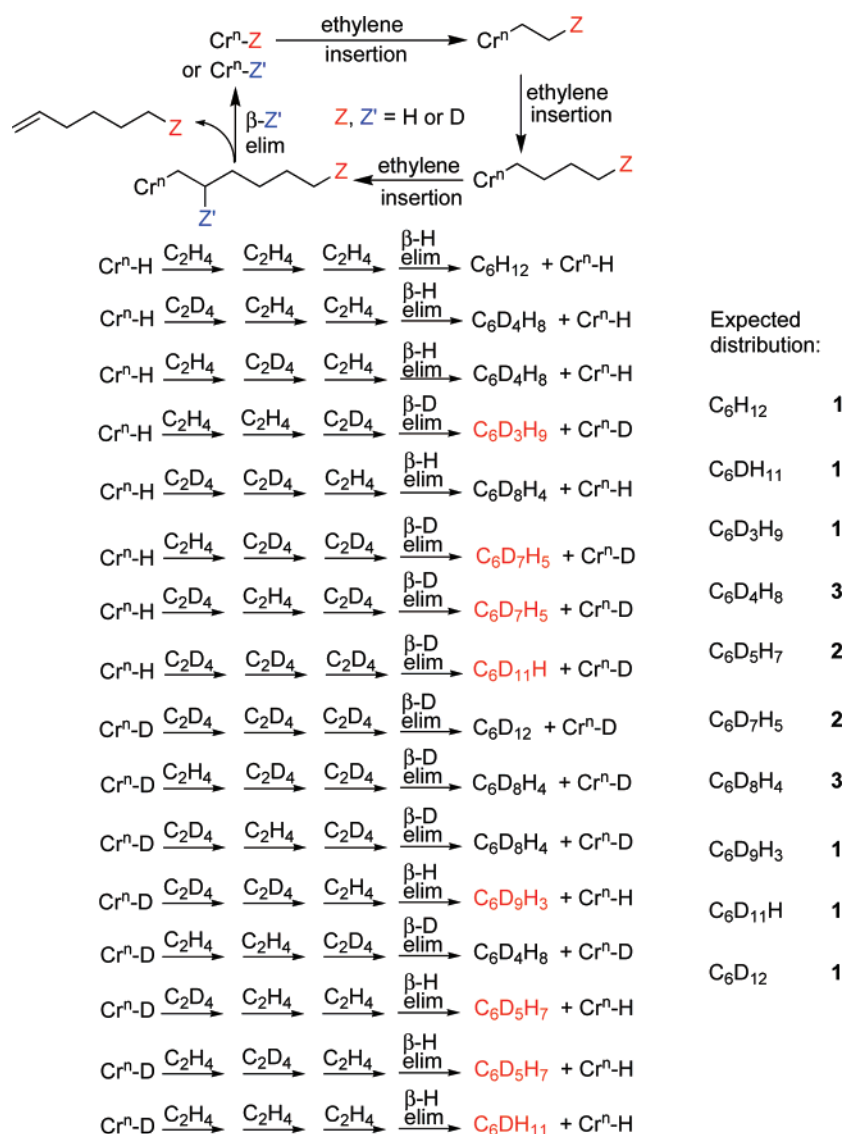
(56) Tomov, A. K.; Chirinos, J. J.; Long, R. J.; Gibson, V. C.; Elsegood, M. R. *J. Am. Chem. Soc.* **2006**, *128*, 7704–7705.

(57) Tomov, A. K.; Chirinos, J. J.; Jones, D. J.; Long, R. J.; Gibson, V. C. *J. Am. Chem. Soc.* **2005**, *127*, 10166–10167.

(58) Peuckert, M.; Keim, W. *Organometallics* **1983**, *2*, 594–597.

(59) The rationale proposed in the literature for the different isotope distributions in the C₆ and C₈ fractions involves a secondary isotope effect for the formation of the metallacyclopentane intermediate. This isotope effect, however, should be small and inverse and should affect both the C₆ and C₈ fractions, which is not the case.

Scheme 8



the geometry around the double bond is inverted. For example, *cis*-ethylene- d_2 leads to the formation of 1-hexene that has the two deuteriums or hydrogens trans to each other. The ratio of the two observed isotopomers for the trimerization of *cis*-ethylene- d_2 was found to be 3.1(1) at 25 °C, 3.7(4) at 0 °C, and 3.6(1) at -25 °C (reactions performed in Schlenk flasks).⁶⁰ The ratio of the two observed isotopomers for the trimerization of *trans*-ethylene- d_2 was found to be 4.1(1) at 25 °C.

Analysis of the metallacyclic mechanism in the context of the trimerization of 1,2-ethylene- d_2 indicates that the steps leading to the formation of the chromacycloheptane should not be affected significantly compared to nondeuterated ethylene—only small, secondary isotope effects are expected. The chromacycloheptane intermediate so generated has one hydrogen and one deuterium on each carbon in the ring when it reaches the branching point between β -H and β -D eliminations (Scheme 9). These two pathways are completely analogous; only one will be described in detail. Upon β -H elimination, a chromium—

alkenyl-hydride species is formed which can undergo reductive elimination to generate a 1-hexene isotopomer with a [=CDH] end group. Alternatively, the chromium—alkenyl-hydride species could perform a 2,1-reinsertion into the [Cr—H] bond to lead to the formation of a methyl-chromacyclohexane. From this intermediate, β -D elimination from the exo position generates a chromium—alkenyl-hydride species. Reductive elimination leads to a 1-hexene isotopomer with a [=CH₂] end group. Experimentally, only 1-hexene isotopomers with a [=CDH] end group are observed, without any detectable isotopomers with [=CH₂] or [=CD₂] end groups.

These results of the trimerization of 1,2-ethylene- d_2 indicate that the reductive elimination from chromium—alkenyl-hydride (or the concerted 3,7-H transfer) is fast compared to 2,1-reinsertion into the [Cr—H] bond (Scheme 9). This has important consequences on the purity of the resulting trimerization product. If 2,1-H insertion were a competitive process then the resulting chromacyclohexane could conceivably undergo β -H elimination from intracyclic CH bonds, followed by reductive elimination, leading to the formation of 2-hexene, an undesired byproduct. In the context of the trimerization of 1,2-ethylene- d_2 , the

(60) The values reported in the initial communication (ref 19) are somewhat different, due to the use of short recycling delays in the ¹H NMR spectroscopy experiments. Current values were measured with recycling delays of 250 s.

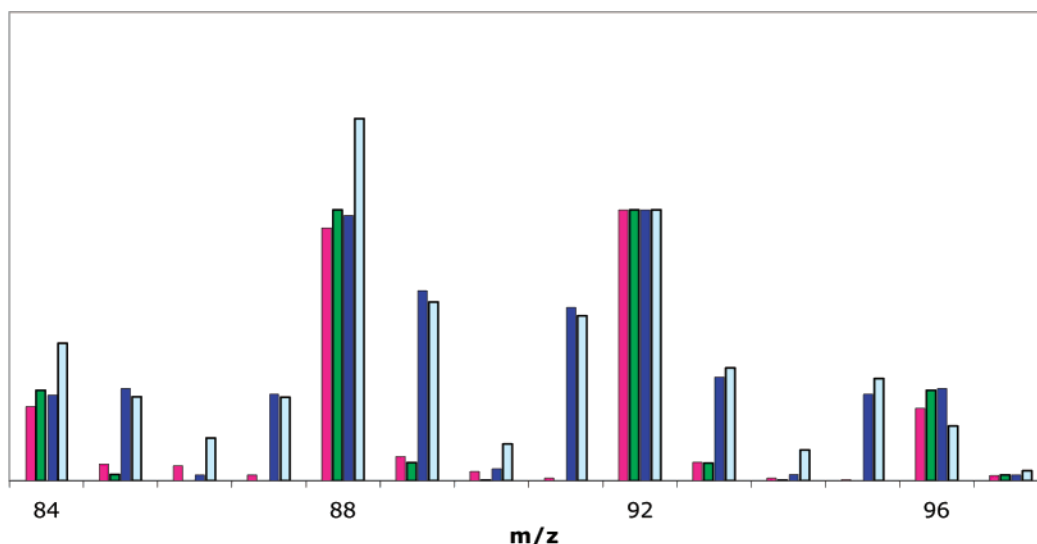
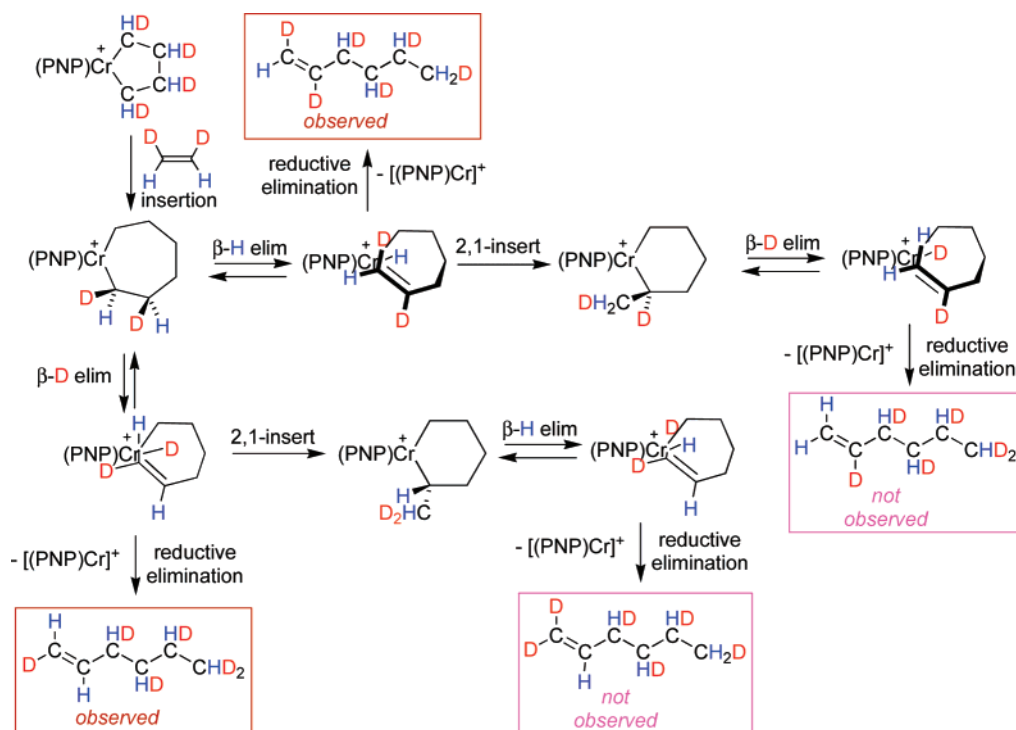


Figure 1. Experimental MS data for a chromium ethylene trimerization reaction (red), simulated isotopolog distribution for a mechanism involving metallacyclic intermediates (green), simulated isotopolog distribution for a Cossee-type mechanism (blue), and experimental MS data for a nickel ethylene oligomerization reaction (light blue). All intensities are normalized to same value at $m/z = 92$.

Scheme 9

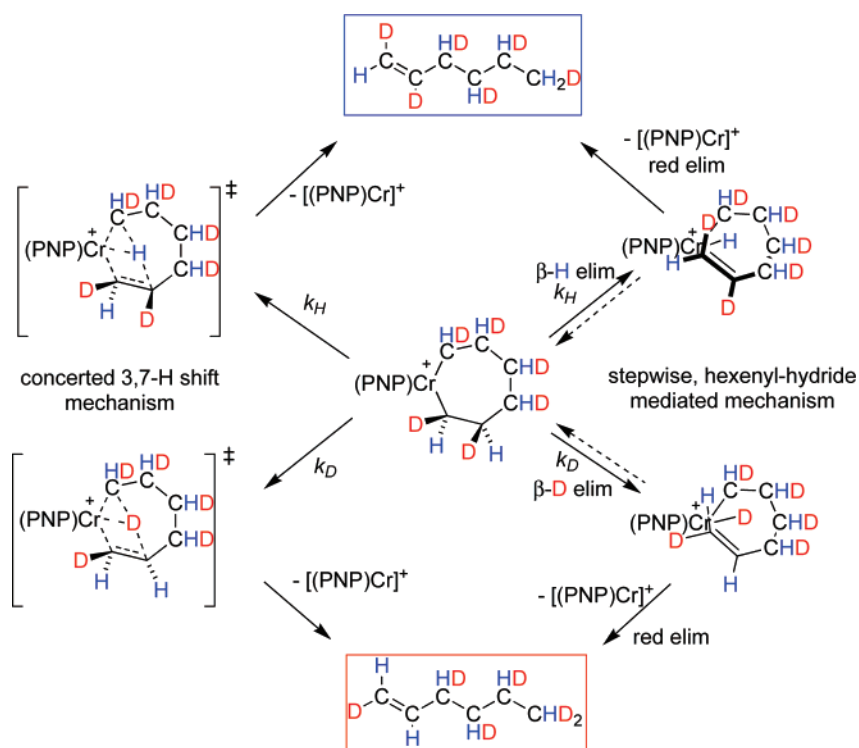


possibility of a 1,2-reinsertion into the [Cr–H] bond of the chromium-alkenyl-hydride species becomes an interesting question. Analysis of the relative stereochemistry of the hydrogens at the α , β , and γ positions of the metallacycloheptane indicates that such process is inconsequential to the isotopomer distribution in the products (see the Supporting Information), and hence, the present experiment does not interrogate the possibility of a 1,2-H insertion. However, this transformation does not affect the selectivity for 1-hexene in the C6 fraction.

An alternative explanation for the selective formation of the observed isotopomers of 1-hexene in the trimerization of 1,2-ethylene- d_2 involves concerted 3,7-H (or D) shifts instead of

stepwise β -H (or D) elimination followed by reductive elimination (Scheme 10).^{39–46} It is clear that if a true chromium hydride is *not* formed, as in the 3,7-H shift mechanism, then no selectivity issues remain relative to olefin reinsertion. A number of computational studies have indicated that the 3,7-H shift is more energetically favorable than a stepwise mechanism for titanium, tantalum, and chromium ethylene trimerization systems.^{39–46} It is important to note, however, that catalytic systems closely related to the present system generate byproducts that likely arise via intermediate β -H elimination steps.^{7,22,29} The observed isotope effects could possibly provide an indication of which of the two pathways from chromacycloheptane to 1-hexene is operative. In the case of the stepwise mechanism,

Scheme 10



two situations can be envisioned. If β -H elimination is fast and reversible with respect to reductive elimination, then the observed ratio of isotopomers reflects a composite of an equilibrium isotope effect for the β -H elimination and the kinetic isotope effect for the reductive elimination. If β -H elimination is slow relative to the subsequent reductive elimination, then the ratio of isotopomers reflects the kinetic isotope effect for the β -H elimination elementary step. In the case of the 3,7-H shift, the ratio of isotopomers represents the kinetic isotope effect for this process. In either case, the ratio of isotopomers represents the intrinsic overall isotope effect for the formation of 1-hexene from the chromacycloheptane. Reasoning that a 3,7-H shift may have a significant tunneling contribution leading to unusually large kinetic deuterium isotope effects, we investigated the temperature dependence. Only a modest variation was observed over a 50 K range, suggesting no significant tunneling component to the process. Thus, the results of our experiments are equally consistent with either the concerted or the stepwise mechanism. The difference between the observed isotope effect for the trimerization of *cis*-ethylene- d_2 (3.1(1)) versus *trans*-ethylene- d_2 (4.1(1)) is apparently real, but somewhat surprising, since both ethylenes should give the same value, if only primary isotope effects are involved.⁶¹

Interestingly, the present diphosphine framework (and more generally, PNP phosphines with either four ortho alkyl substituents or at least one ortho ether group) is capable of rendering the reaction very selective for the formation of 1-hexene in the C6 fraction, with essentially no isomerization coming from chain walking or insertions of the pendant olefin. Two explanations could be envisioned. One possibility invokes the steric bulk of the ligand favoring the transition state for 3,7-H shift over β -H elimination. Conversely, if β -H elimination does occur, reductive elimination is very fast compared to isomerization. Again, the sterics of the ligand (or the ability of pendant donors to compete

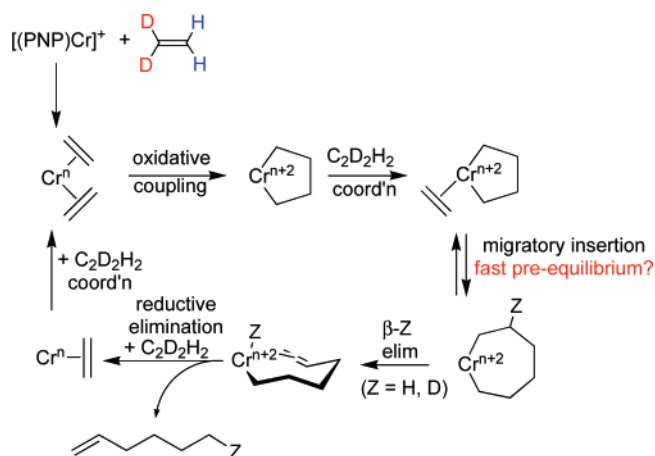
for coordination sites) would slow the coordination of the pendant olefin and the hydride reinsertion.

Reactions with 1,1-Dideuteroethylene. The trimerization of *gem*-ethylene- d_2 was performed under conditions identical to those for *cis*- and *trans*-ethylene- d_2 . The formation of two types of olefin isotopomers of 1-hexene was observed, depending on the terminal methylene group, [=CD₂] or [=CH₂]. Because in both cases the allylic position can bear either hydrogens or deuteriums, the corresponding signals are complicated by the overlap of different coupling patterns. The integrals corresponding to the peaks for the vinylic protons provide the ratio (1.3-1)) between the two possible double-bond isotopomers.

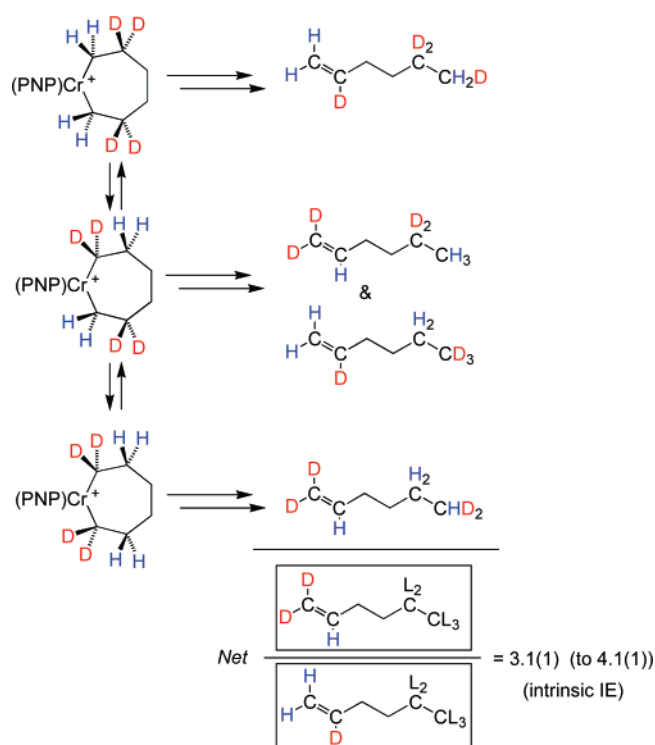
The outcome of the trimerization of *gem*-ethylene- d_2 can be used to investigate the reversibility of the formation of chromacycloheptane. In the context of the metallacyclic mechanism, the reverse process would involve an elimination of ethylene to generate a chromacyclopentane-ethylene species (Scheme 11). Three cases can be distinguished. If the formation of the chromacycloheptane is reversible and fast compared to subsequent steps, then the various chromacycloheptane isotopomers can interconvert rapidly (Scheme 12). Such rapid equilibration will lead to a distribution of 1-hexene isotopomers according to the intrinsic isotope effect for the conversion of chromacycloheptane to 1-hexene which was measured to be 3.1(1) for *cis*-ethylene- d_2 (4.1(1) for *trans*-ethylene- d_2) at room temperature. Conversely, if formation of chromacycloheptane is irreversible, and there is sufficient asymmetry such that β -H elimination occurs selectively from one end of the alkanediyl group (Scheme 13), no isotope effect is expected (assuming negligible secondary isotope effects). However, if formation of

(61) The relative integrals of the methyl region vs the olefinic region can be used to check the isotope effects determined from the olefinic region. The measured ratios of methyl vs smallest olefin peak are 9.2(1) (for *trans*-ethylene trimerization) and 8.1(6) (for *cis*-ethylene); the calculated ratios are 9.2(1) and 7.2(1), respectively.

Scheme 11



Scheme 12



chromacycloheptane is irreversible and β -H elimination can occur equally from either end of the alkanediyl group then the different types of chromacycloheptanes need to be treated separately (Scheme 14). The ones with all the same atoms (H or D) on the β -carbon can generate only one type of 1-hexene isotopomer leading to a 1:1 ratio of the two possible ones (stemming from the 1:1 probability of forming the two corresponding chromacycloheptane isotopomers). The metallacycloheptane displaying both hydrogens and deuteriums in the β -position are expected to β -eliminate according to the intrinsic isotope effect (3.1(1) to 4.1(1)). Upon accounting for the statistical populations of different chromacycloheptane isotopomers this analysis leads to an expected isotope effect of 1.7(1) to 1.9(1). The observed isotope effect is 1.3(1), indicating that the metallacycloheptane is formed irreversibly. This isotope effect is not conclusive with respect to symmetry of the two ends of the metallacycloheptane. It is possible that a dynamic process exchanges the two ends of the alkanediyl moiety at a

rate similar to conversion to 1-hexene. This would lead to an isotope effect intermediate between the symmetric and the nonsymmetric and static cases.⁶²

Reaction of Cationic Species with α -Olefins. Access to a biphenyldiyl chromium species, a model of the metallacycloheptane intermediate in the mechanism of the ethylene trimerization reaction, allows for selectivity studies relevant to olefin cotrimerization. In principle, olefin cotrimerization could lead to diverse olefin isomers of the same number of carbon atoms. For instance, cotrimerization of 1-butene with two ethylenes can lead to the formation of seven C8 isomers (not counting double-bond stereoisomers), depending on the nature of the metallacycloheptane formed, the regioselectivity of α -olefin insertion, and the regioselectivity of β -H elimination. Although the preparation of olefin mixtures is desirable for some applications, the selective generation of only one isomer generally is more valuable. In this context, a better understanding of the selectivity of different steps of the cotrimerization reaction is desirable. Starting directly from a model of a chromacycloheptane allows for a systematic study of the α -olefin insertion and β -H elimination of a subset of cotrimerization possibilities (Scheme 15).

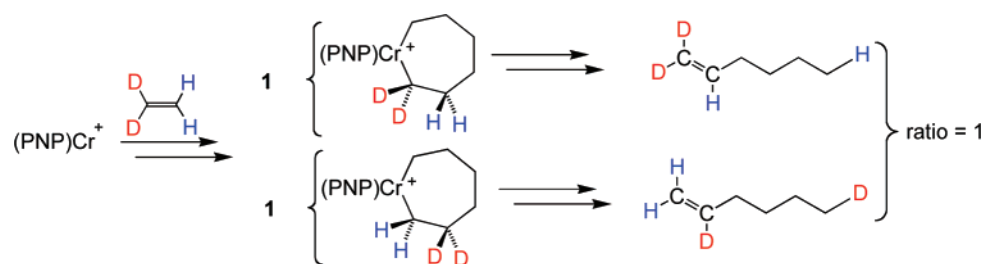
The cationic biphenyldiyl chromium species was prepared in situ as described above and was exposed to various olefins. The reaction was quenched, the mixture was filtered through silica gel, and the nonvolatile species were analyzed by ^1H NMR spectroscopy and GC-MS. Only products stemming from stoichiometric olefin insertion into the biphenyldiyl chromium moiety were observed under these conditions. No α -olefin trimers were detectable.⁶³ Reactions of this cationic biphenyldiyl chromium species with α -olefins such as propene or 1-butene lead to the formation of only one product, that corresponding to the 1,2-insertion of olefin. The chromacycloheptane resulting from a 1,2-insertion of α -olefins has only one β -hydrogen; hence, the selectivity of β -H elimination cannot be tested in this process, given that the formation of the metallacycloheptane intermediate is irreversible. Reaction with internal olefins however, necessarily generates chromacycloheptanes with two types of β -hydrogens—endocyclic and exocyclic carbons (b and c in Scheme 16). Again formation of only one product is observed; this corresponds to β -H elimination from the ring position. It is interesting to note that the ring position is statistically disfavored versus the exocyclic position by 3-fold. However, in this case, the ring position also corresponds to a weaker, benzylic CH bond.

The above reaction, employing *E*-2-butene and forming *E*-2-biphenyl-2-butene, could occur via two mechanisms as described before (Scheme 10). The metallacycloheptane intermediate can undergo either a concerted hydride shift or β -H elimination followed by reductive elimination. These two possibilities apply

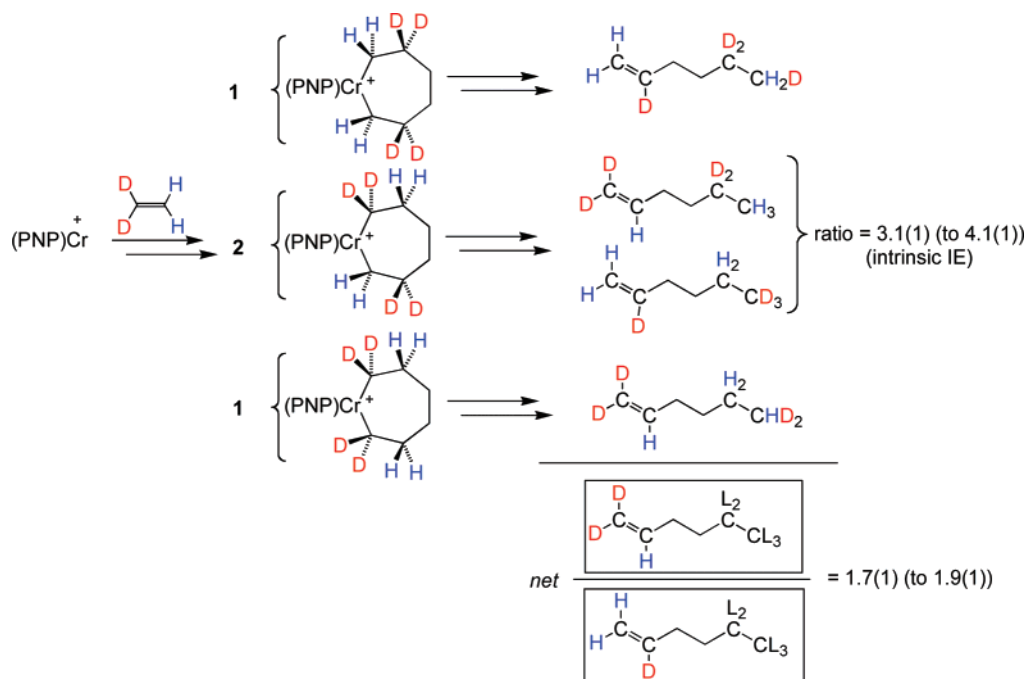
(62) The ratio of methyl vs olefinic integrals (5.0(1)) is consistent with symmetric metallacycloheptane (calculated 5.1 to 5.6 compared to 3 in the case of unsymmetric metallacycloheptane), whereas the IE from the olefinic region gives an ambiguous outcome. This difference suggests that other effects, such as secondary isotope effects (both in the formation of the metallacycloheptane as well as for the β -H elimination), may be important.

(63) Upon quenching this mixture with water, it is found, by ^{31}P and ^1H NMR spectroscopy, that the diphosphine is altered to unidentified products. These products are not observed spectroscopically prior to quenching. Furthermore, the major phosphine species observed upon workup is also one of the compounds produced, according to ^{31}P NMR spectroscopy, if the same experiment is performed with phosphine and $\text{Na}[\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4]$ in the absence of chromium species. This suggests that any free phosphine produced may react with species stemming from $\text{Na}[\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4]$.

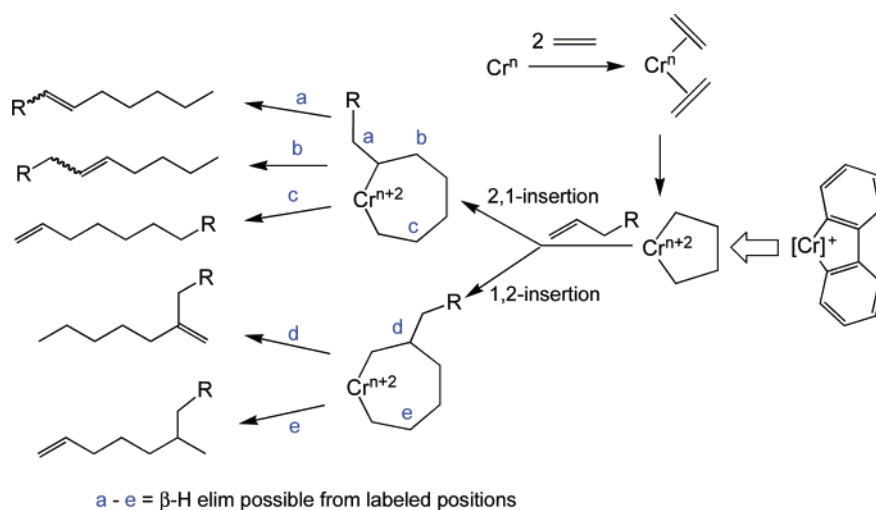
Scheme 13



Scheme 14



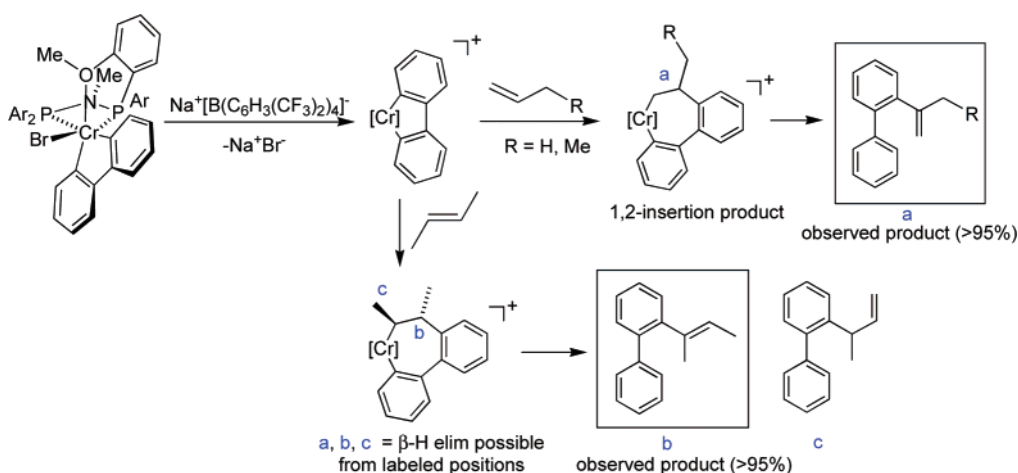
Scheme 15



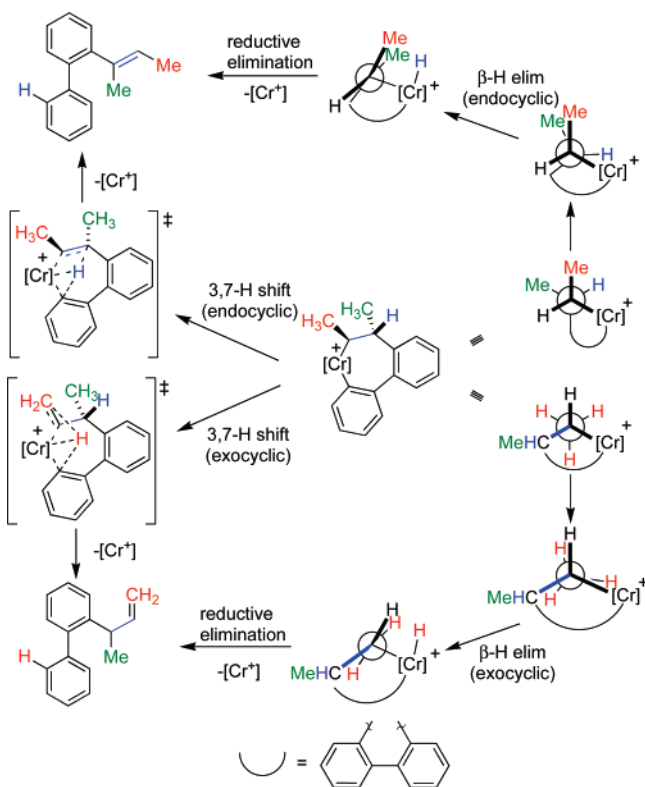
for both β -positions (endocyclic and exocyclic). The hydride shift could occur either in the ring, as a 3,7-H shift (Scheme 17, top left), or exocyclic, as a reductive β -H abstraction (Scheme 17, bottom left). The exocyclic reductive β -H abstraction represents the acyclic version of the 3,7-H shift; this has not been commonly invoked over β -H elimination/reductive elimination of linear dialkyl species, but recently it has been computed to be the preferred route for the conversion of

titanium(IV)-methyl-propyl species to titanium(II)-propylene and methane.⁴¹ It is difficult to speculate on which of the two positions would preferentially undergo reductive hydride shift; this is a problem well suited for computational analysis. Alternatively, the β -H elimination mechanism could occur from both endocyclic and exocyclic positions (Scheme 17, right). Because β -H elimination requires a near zero dihedral angle for the β -C-H and Cr-C bonds, it is expected that the ring

Scheme 16



Scheme 17



β -H elimination would encounter a higher barrier than the exocyclic process. In this context, the formation of only the product stemming from endocyclic hydride shift/elimination may suggest that the working mechanism involves a 3,7-H shift.

Competitive Olefin Insertion Experiments. Competition experiments between various olefins for insertion into the cationic chromacyclopentane mimic derived from **1** provides an opportunity to examine the relative rate. Accordingly, the cation derived from **1** was generated in situ in a J-Young NMR tube, and two olefins were condensed in at -196°C . More than a 10-fold excess of each olefin relative to biphényldiyl chromium complex was utilized. This procedure allowed the measurement of the approximate initial ratio in solution of the two olefins, the amounts consumed for the stoichiometric insertion reaction being negligible. Upon completion of the reaction, volatile materials were removed under vacuum, and the remaining

Table 1. Relative Insertion Rates of Insertion of Various Olefins into a Cationic Chroma–Biphényldiyl Moiety

olefin	relative insertion rate
ethylene	13000
1-butene	660
propene	620
4-methyl-1-pentene	190
3-methyl-1-butene	62
styrene	31
<i>cis</i> -2-butene	16
<i>trans</i> -2-butene	1

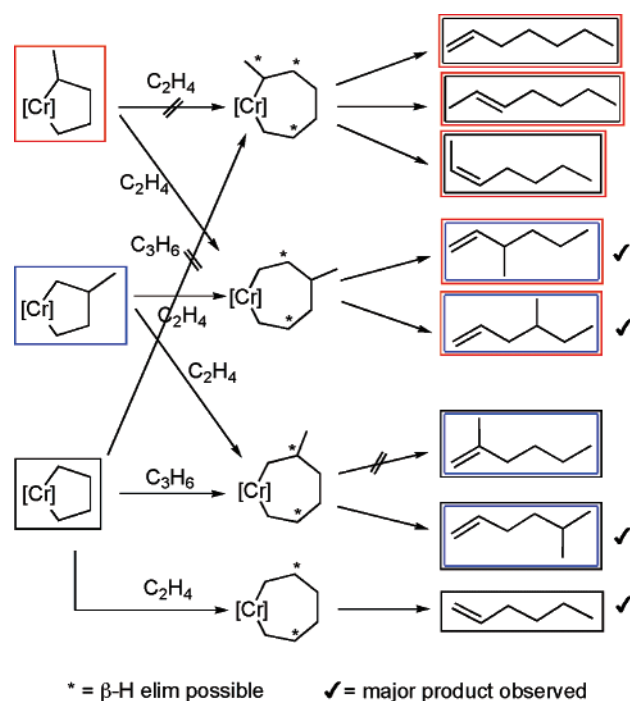
biphényl derivatives were inspected by ^1H NMR spectroscopy to provide the ratio of chromacycles generated by the insertion of different olefins. The relative rates of olefin insertion into the biphényldiyl chromium cation were calculated from the initial ratio of starting olefins and the final ratio of biphényl olefin species (Table 1). The measurements involving ethylene present a problem: trimerization to generate 1-hexene occurs upon initiation via the biphényldiyl chromium species, leading to a substantial decrease in the concentration of ethylene. This error was minimized by recording the initial olefin ratio upon warming the sample to room temperature in the NMR probe. Because the formation of the chromacycloheptane species is irreversible, these measurements reflect the relative insertion rates and do not reflect any subsequent steps (3,7-H shifts or β -H elimination followed by reductive elimination).

Generally, the relative insertion rates increase with decreasing size of the olefin, likely due to steric reasons. Ethylene inserts more than 20 times faster than linear α -olefins, consistent with the observed good selectivity of homotrimerization over cotrimerization in the presence of α -olefin (1-hexene) product. The relative rates of insertion mirror the trends observed for the rates of olefin insertion into zirconium hydrides.⁶⁴ Internal olefins are slower than α -olefins, with *trans*-2-butene significantly slower than *cis*-2-butene. Although the relative order of rates of insertions are probably similar for the parent chromacyclopentane, it is important to note that the model system derived from **1**, being a dibenzovariant, is substituted, more rigid, and involves different hybridization at the carbon centers compared to the parent, which may lead to different values for the actual catalytic system.

Trimerization of a Mixture of Ethylene and Propylene. To test the selectivity results obtained from stoichiometric

(64) Chirik, P. J.; Bercaw, J. E. *Organometallics* **2005**, *24*, 5407–5423.

Scheme 18



reactions of α -olefins with a model of chromacyclopentane, the cotrimerization of ethylene and propylene was performed. A large excess of propylene was used to ensure detectable levels of cotrimer. Propylene was chosen as a cotrimerization partner because all the C7 olefins are commercially available, allowing for comparison against authentic samples. The reaction was performed starting both with **1** upon halide abstraction (CH_2Cl_2) and with $\text{Cr}(\text{PNP}^{\text{O}4})\text{Cl}_3$ upon activation with MAO (toluene). Upon quenching, an aliquot was investigated by GC-MS. 3-Methyl-1-hexene, 4-methyl-1-hexene, 5-methyl-1-hexene (obtained in similar amounts), and 1-hexene were found to be the major products in both cases.

Analysis of various cotrimerization possibilities (Scheme 18) shows that three types of chromacyclopentanes and four types of chromacycloheptanes can be formed (including the parent, unsubstituted ones). Multiple routes can be envisioned to some olefin products. None of the major products observed come from 2,1-insertions of propylene into chromacyclopentane or from β -H elimination/shift from exo-C-H bonds, consistent with the conclusions concerning selectivity above. It is worth noting, however, that selectivities in the catalytic system can be determined in part by steps prior to chromacycloheptane formation, such as the chromacyclopentane generation, which is not addressed in the present experiments.

Conclusions

Mechanistic studies relevant to the catalytic trimerization of ethylene have been performed using a chromium(III) system supported by diphosphine ligand $\text{PNP}^{\text{O}4} = (o\text{-MeO-C}_6\text{H}_4)_2\text{-PN}(\text{Me})\text{P}(o\text{-MeO-C}_6\text{H}_4)_2$. A model biphenyldiyl chromium complex was used as a well-defined precursor to a model chromacyclopentane for a number of studies. Catalytic trimerization of ethylene and 2-butyne is accomplished with a cationic chromium species but not with a neutral one, indicating that a cationic species is likely required for catalysis. Trimerization of a 1:1 mixture of C_2D_4 and C_2H_4 with the chromium system

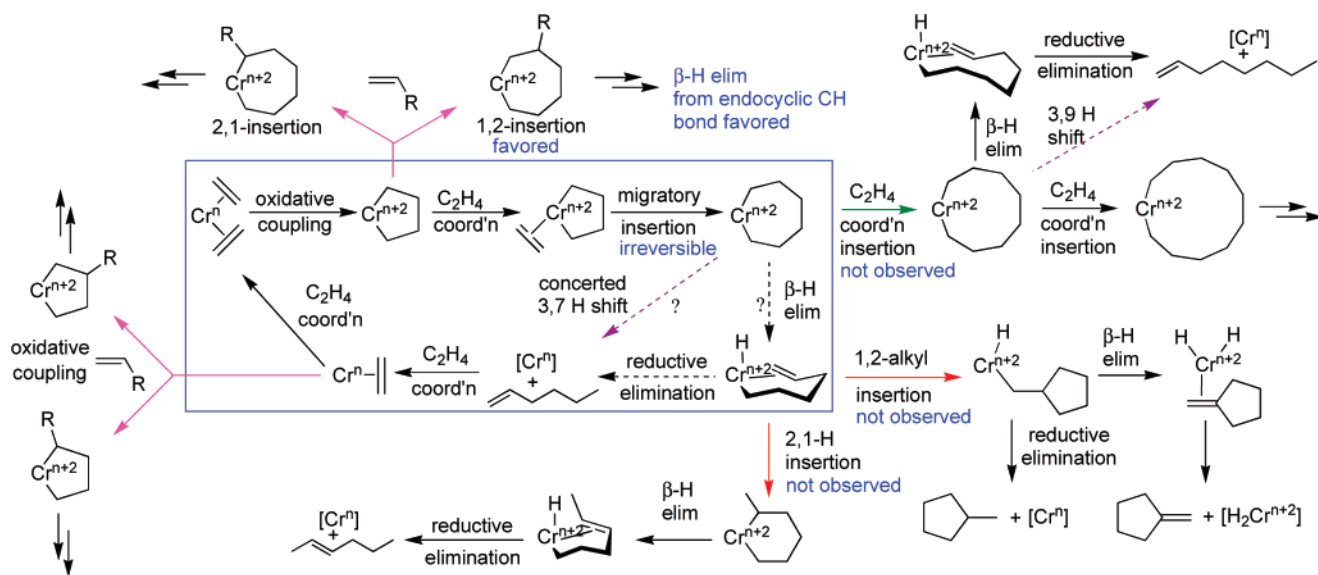
leads to isotopologs of 1-hexene without H/D scrambling, a result that supports a metallacyclic mechanism and is inconsistent with a Cossee-type mechanism. When the same study is performed with a nickel nonselective oligomerization catalyst it gives approximately the expected, broader distribution of 1-hexene isotopologs (with H/D scrambling). These results indicate that oligomerization of mixtures of C_2D_4 and C_2H_4 and analysis of isotopolog distribution in the products is a versatile and useful test for distinguishing between metallacyclic and Cossee-type mechanisms of olefin oligomerization.

Trimerization of *trans*- and *cis*-ethylene- d_2 interrogates the formation of 1-hexene from chromacycloheptane. This experiment results in isotopomers corresponding to fast reductive elimination of the putative chromium-hydride-alkenyl species compared to isomerization pathways. It is also consistent with concerted 3,7-H shift. This effect probably stems from the steric or coordinating properties of the ortho substituents and is likely important for the good selectivity for 1-hexene in the C6 fraction observed with this catalyst system. The trimerization of *gem*-ethylene- d_2 occurs with an isotope effect consistent with the irreversible formation of chromacycloheptane.

Reaction of a biphenyldiyl chromium cation derived from **1** with higher olefins has allowed for selectivity studies. α -Olefin insertion into the chromacyclopentane model occurs with 1,2-regioselectivity, whereas β -H elimination in model chromacycloheptanes occurs from endocyclic CH bonds over exo-CH bonds. Although the selectivities observed in the stoichiometric system show some promise for the selective cotrimerization of olefins, our catalytic experiments with ethylene/propylene mixtures illustrate the complexity of the full system. The products of the catalytic cotrimerization experiment are consistent with direction (i.e., 1,2- or 2,1-) and relative rates for insertion determined in the stoichiometric studies. Our measurements of relative rates of insertion into a biphenyldiyl chromium moiety for different olefins reveal that ethylene is significantly faster than α -olefins, consistent with the good selectivities for ethylene homotrimerization in the presence of 1-hexene product.

The findings described here, along with previous reports, allow for a more comprehensive picture of the transformations related to the formation of 1-hexene with chromium catalysts (Scheme 19). Although the metallacyclic mechanism explains the selective formation of 1-hexene, there are many mechanistic pathways that could lead to a diverse selection of products. Examples of side reactions include (a) additional ethylene insertions (green arrow), (b) hydride or alkyl reinsertion into intermediate pendant olefins (red arrows), and (c) incorporation of the product α -olefin into the metallacyclic intermediates (magenta arrow). The chromacycloheptane intermediate could further insert ethylene to generate larger metallacycles (a), if ethylene insertion can compete with β -H elimination. In this regime, ring expansion is favored by higher concentrations (pressures) of ethylene.^{22,29} Furthermore, if the preference for β -H elimination from each of the resulting metallacycles is similar, then a Shultz-Flory distribution is expected.^{56,57} If β -H elimination is faster than ethylene insertion in the chromacycloheptane intermediate (b), then a chromium hydride alkyl complex forms. Given the presence of a pendant olefin, hydride reinsertion might well occur to generate a chromacyclohexane which in turn could β -H eliminate from the ring to lead to the chain-walked product, with an internal double bond (2-hexene).

Scheme 19



Our labeling studies do not show evidence of hydride reinsertion product. This finding is consistent with a mechanism involving a 3,7-H shift which bypasses the formation of a chromium hydride. It is important to note, however, that evidence for the formation of intermediate chromium-alkenyl-hydride complexes has been presented for the system competent for both ethylene trimerization and tetramerization.^{7,22,29} In that case, the observation of methylcyclopentane and methylenecyclopentane as major side products is an indication of pendant olefin insertion into intermediate alkyl species followed by either reductive elimination (methylcyclopentane) or β -H elimination (methylenecyclopentane). The cotrimerization of α -olefin product with ethylene (c) is a minor side reaction, relevant in particular at high conversions when the concentration of α -olefin product is increased.⁵ The efficient incorporation of styrene into trimers with ethylene has been reported recently.⁶⁵ Further exploration is needed to understand the selectivity of chromacyclopentane formation in mixtures of olefins as well as regioselectivity of insertion in asymmetric chromacycloheptane.

Experimental Section

General Considerations and Instrumentation. All air- and moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques or in a drybox under a nitrogen atmosphere. Solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl or by the method of Grubbs.⁶⁶ Dichloromethane-*d*₂ was purchased from Cambridge Isotopes and distilled from calcium hydride. Other materials were used as received. Methylaluminumoxane was purchased from Aldrich. ¹H and ¹³C NMR spectra were recorded on Varian Mercury 300 or Varian INOVA-500 spectrometers and, unless otherwise indicated, at room temperature. Chemical shifts are reported with respect to internal solvent: 7.27 and 77.23 (t) ppm (CDCl₃); 5.32 (t) and 54.00 (q) ppm (CD₂Cl₂); for ¹H and ¹³C data.

Trimerization of Ethylene with 1 upon Halide Abstraction. Dichloromethane-*d*₂ was vacuum transferred to a J-Young tube or Schlenk flask charged with **1** (8–34 mg, 10–42 μ mol, 1 equiv) and NaB[C₆H₃(CF₃)₂]₄ (10.5–45 mg, 12–51 μ mol, 1.2 equiv). The mixture

was warmed to room temperature using a water bath followed by mixing (via mechanical rotation for NMR tubes or magnetic stirring for flasks) for 10 min. The mixture turned brown as the starting materials dissolved. Ethylene (128.2 mL at 30–125 torr, 200–860 μ mol, 17.5–23 equiv) was condensed in (~2.3–3.8 atm in the vessel at room temperature). The reaction mixture was mixed for 1–1.5 h at room temperature during which the mixture turned brown-green. *o*-Vinyl-biphenyl and 1-hexene were detected by ¹H NMR spectroscopy. Relative to the amount of *o*-vinyl-biphenyl observed, about 3.5 equiv of 1-hexene is formed (ca 60%).

Reaction of 1 with Ethylene. Dichloromethane-*d*₂ was vacuum transferred to a J-Young tube charged with **1** (8.1 mg, 10.1 μ mol, 1 equiv). Ethylene (43.48 mL at 87 torr, 200 μ mol, 20 equiv) was condensed in (~2 atm in the tube at room temperature). The mixture was warmed to room temperature using a water bath, then mixed by mechanical rotation for 1 h. During this time the mixture achieved a brown-green color. *o*-Vinyl-biphenyl was detected by ¹H NMR spectroscopy, but no 1-hexene was observed. After an additional 1 h of mixing the mixture turned brown-red, but no 1-hexene was formed according to ¹H NMR spectroscopy.

Trimerization of 2-Butyne with 1 upon Halide Abstraction. Dichloromethane was vacuum transferred to a 10 mL round-bottom Schlenk tube charged with **1** (31.8 mg, 39.6 μ mol, 1 equiv) and NaB[C₆H₃(CF₃)₂]₄ (42 mg, 47.6 μ mol, 1.2 equiv). The mixture was warmed up to room temperature using a water bath, followed by stirring for 10 min. 2-Butyne (128.2 mL at 160 torr, 1.1 mmol, 23.2 equiv) was condensed in. The reaction mixture was allowed to mix for 12 h. Upon opening to air, the reaction was quenched with 1 mL of aqueous CO₃²⁻/HCO₃⁻ solution. The mixture was transferred to a scintillation vial and centrifuged. The organic layer was separated and filtered through silica gel, then volatile materials were removed under vacuum. The residue was analyzed by ¹H NMR spectroscopy in CDCl₃ and GC-MS to reveal the presence of hexamethyl benzene and 9,10-dimethylphenanthrene.

Reaction of 2-Butyne with 1. Dichloromethane was vacuum transferred to a 10 mL round-bottom Schlenk tube charged with **1** (65.6 mg, 81.7 μ mol, 1 equiv). 2-Butyne (128.2 mL at 220 torr, 1.5 mmol, 18.5 equiv) was condensed in. The reaction mixture was allowed to mix for 12 h at room temperature. Upon opening to air, the reaction was quenched with 1 mL of aqueous CO₃²⁻/HCO₃⁻ solution. The mixture was transferred to a scintillation vial and centrifuged. The organic layer was separated and filtered through silica gel, then volatile materials were removed under vacuum. The residue was analyzed by

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^1H NMR spectroscopy in CDCl_3 and GC–MS. Hexamethyl benzene was absent by both analytical methods. 9,10-Dimethylphenanthrene was identified as the major product by ^1H NMR spectroscopy in CDCl_3 and GC–MS.

Trimerization of a $\text{C}_2\text{D}_4/\text{C}_2\text{H}_4$ Mixture with **1 Activated with $\text{NaB}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4$.** Dichloromethane- d_2 was vacuum transferred to a J-Young tube charged with **1** (9.2 mg, 11.4 μmol , 1 equiv) and $\text{NaB}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4$ (12.2 mg, 13.8 μmol , 1.2 equiv). The mixture was warmed up to room temperature using a water bath, followed by mixing (via mechanical rotation) for 10 min. The mixture turned brown upon the starting materials dissolving. A 1:1 mixture of C_2D_4 and C_2H_4 (128.2 mL at 29 torr, 200 μmol , 17.5 equiv) was condensed in (~ 2.4 atm in the tube at room temperature). The reaction mixture was allowed to mix for 1 h at room temperature during which time it achieved a brown-green color. The reaction vessel was cooled in a dry ice/acetone bath and degassed. Following removal of ethylene, the mixture was allowed to reach room temperature and volatile materials were vacuum transferred to a round-bottom flask and analyzed by GC–MS. The 1-hexene fraction shows a 1:3:3:1 distribution of isotopomers (C_6H_{12} , $\text{C}_6\text{H}_8\text{D}_4$, $\text{C}_6\text{H}_4\text{D}_8$, and C_6D_{12}). The solid residue was partitioned between water and dichloromethane, and the organic fraction was analyzed by GC–MS to reveal the presence of d_0 - and d_4 -*o*-vinylbiphenyl and biphenyl.

Trimerization of a $\text{C}_2\text{D}_4/\text{C}_2\text{H}_4$ Mixture with **1 Activated with MAO.** Compound **1** (8.2 mg, 10.1 μmol , 1 equiv) was suspended in toluene (30 mL), and the mixture was cooled to -78 °C in a dry ice/acetone bath. Under counterflow of argon, the Teflon stopcock was replaced with a rubber septum, and MAO solution (10% in toluene, $d = 0.875$ g/mL, 2.4 mL, 300 equiv) was added via syringe. The septum was replaced with the Teflon stopcock. The mixture was degassed briefly and placed under 1:1 $\text{C}_2\text{D}_4/\text{C}_2\text{H}_4$ mixture (~ 2.3 atm static pressure, 10 mmol, 1000 equiv) while warming up to room temperature in a water bath. The reaction mixture was allowed to stir for 1.5 h. An aliquot was collected, the reaction was quenched with water, and the mixture was analyzed by GC–MS. The 1-hexene fraction resolves in a quartet showing a 1:3:3:1 distribution of isotopomers (C_6H_{12} , $\text{C}_6\text{H}_8\text{D}_4$, $\text{C}_6\text{H}_4\text{D}_8$, and C_6D_{12}). d_0 - and d_4 -*o*-vinylbiphenyl do not resolve on the GC trace but are both present according to the mass spectrum.

Trimerization of a $\text{C}_2\text{D}_4/\text{C}_2\text{H}_4$ Mixture with $\text{CrCl}_3(\text{THF})_3/\text{PNP}^{\text{O}4}$ Activated with MAO. A solution of $\text{CrCl}_3(\text{THF})_3$ (6 mg, 16 μmol , 1 equiv) in dichloromethane (1 mL) was added to a dichloromethane solution (1 mL) of **1** (8.3 mg, 16 μmol , 1 equiv). The reaction mixture was allowed to stir for 1 h at room temperature. Volatile materials were removed in vacuo, and toluene (40 mL) was added. The resulting mixture was cooled down in a dry ice/acetone bath, and the Teflon stopcock was replaced with a rubber septum under counterflow of argon. MAO solution (10% in toluene, $d = 0.875$ g/mL, 3.2 mL, 300 equiv) was added via syringe, then the septum was replaced with the Teflon stopcock. The mixture was degassed briefly and placed under 1:1 $\text{C}_2\text{D}_4/\text{C}_2\text{H}_4$ mixture (~ 1.4 atm static pressure at room temperature, 1.4 mmol, 875 equiv) while warming up to room temperature in a water bath. It was allowed to stir for 2.5 h; the mixture turned pale green. An aliquot was collected, the reaction was quenched with water, and the mixture was analyzed by GC–MS. The 1-hexene fraction displays a 1:3:3:1 distribution of isotopomers (C_6H_{12} , $\text{C}_6\text{H}_8\text{D}_4$, $\text{C}_6\text{H}_4\text{D}_8$, and C_6D_{12}).

Trimerization of *cis*-, *trans*-, and *gem*- $\text{C}_2\text{H}_2\text{D}_2$. Dichloromethane- d_2 was vacuum transferred to a J-Young tube or Schlenk flask charged with **1** (8–34 mg, 10–42 μmol , 1 equiv) and $\text{NaB}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4$ (10.5–45 mg, 12–51 μmol , 1.2 equiv). The mixture was warmed up to room temperature using a water bath followed by mixing (via mechanical rotation for NMR tubes or magnetic stirring for flasks) for 10 min. The mixture turned brown upon the starting materials dissolving. Labeled ethylene (128.2 mL at 30–125 torr, 200–860 μmol , 17.5–23 equiv) was condensed in (~ 2.3 – 3.8 atm in the vessel at room temperature). The reaction mixture was allowed to mix for 1–1.5 h at room temperature during which the mixture turned brown-green.

Subsequently, the reaction mixture was cooled in a dry ice/acetone bath and degassed. Following removal of ethylene, the mixture was allowed to warm to room temperature, and volatile materials were vacuum transferred to a J-Young tube and analyzed by ^1H and ^{13}C NMR spectroscopy. Isotope effects obtained from the ratio of the integrals corresponding to the olefinic peaks: 3.1, 3.2, 3.1 (298 K, *cis*- $\text{C}_2\text{H}_2\text{D}_2$), 4.0, 4.1 (298 K, *trans*- $\text{C}_2\text{H}_2\text{D}_2$), 1.3, 1.3 (298 K, *gem*- $\text{C}_2\text{H}_2\text{D}_2$), 4.0, 3.4 (273 K, *cis*- $\text{C}_2\text{H}_2\text{D}_2$), 3.6, 3.6 (248 K, *cis*- $\text{C}_2\text{H}_2\text{D}_2$). Ratios of the methyl integral versus the smallest olefinic peak integral: 7.7, 8.8, 7.7 (298 K, *cis*- $\text{C}_2\text{H}_2\text{D}_2$), 9.2, 9.2 (298 K, *trans*- $\text{C}_2\text{H}_2\text{D}_2$), 5.0, 4.9 (298 K, *gem*- $\text{C}_2\text{H}_2\text{D}_2$). The solid residue was partitioned between water and dichloromethane, and the organic fraction was analyzed by GC–MS to reveal the presence of *d*₂-*o*-vinylbiphenyl and biphenyl. See the Supporting Information for ^1H NMR spectra of the olefin region of trimers resulted from different ethylene- d_2 isotopomers and couplings obtained from these spectra.

Reaction of **1 with Higher Olefins upon Halide Abstraction.** These experiments were performed with propylene, 1-butene, *cis*- and *trans*-2-butene, and styrene. The following procedure is typical: Dichloromethane (2 mL) was vacuum transferred to a Schlenk flask charged with **1** (37 mg, 46.0 μmol , 1 equiv) and $\text{NaB}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4$ (49 mg, 55.3 μmol , 1.2 equiv). The mixture was warmed up to room temperature using a water bath followed by magnetic stirring for 10 min. The mixture turned brown upon the starting materials dissolving. Propylene (128.2 mL at 160 torr, 1.1 mmol, 24.6 equiv) was condensed in. (In the case of styrene, the olefin was added via syringe, in the glove-box.) The reaction mixture was allowed to mix for 24 h at room temperature during which the mixture turned green. Upon opening to air, the reaction was quenched with 1 mL of aqueous $\text{CO}_3^{2-}/\text{HCO}_3^-$ solution. The mixture was transferred to a scintillation vial and centrifuged. The organic layer was separated and filtered through silica gel, then volatile materials were removed under vacuum. The residue was analyzed by NMR spectroscopy in CDCl_3 and GC–MS. With respect to diphosphine at the end of the reaction: ^1H NMR (300 MHz, CDCl_3) δ : 2.65, 2.68 (two br singlets, 3H, NCH), 3.66, 3.73 (two br singlets, 12H, OCH₃). ^{31}P NMR (121 MHz, CDCl_3) δ : 29.6, 54.9 (major, doublets, $J_{\text{PP}} = 122$ Hz), 19.2, 37.9 (minor, doublets, $J_{\text{PP}} = 9$ Hz). The same major peaks in ^{31}P NMR spectrum are observed when a solution (CH_2Cl_2) of $\text{PNP}^{\text{O}4}$ and $\text{NaB}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4$ (1.1 equiv) is stirred for 36 h, then the reaction quenched with water. The nature of the resulting biphenyl olefin was determined from the aliphatic and olefin peaks in the ^1H NMR spectrum. 2-Vinyl-biphenyl, 2-(1-phenylvinyl)-biphenyl, and 2-*i*-propenyl-biphenyl were identified using literature reports. The remaining of the biphenyl derivatives are presented below.

2-(1-*i*-Propenyl-vinyl)-biphenyl. Obtained from 3-methyl-1-butene. ^1H NMR (500 MHz, CDCl_3) δ : 0.82 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6H, CH_3), 1.95 (app h, $^3J_{\text{HH}} = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 5.10 (dd, $^3J_{\text{HH}} = 0.4$ Hz, $^2J_{\text{HH}} = 1.5$ Hz, 1H, = CHH), 5.14 (app t, $^2J_{\text{HH}} = ^3J_{\text{HH}} = 1.5$ Hz, 1H, = CHH).

2-(1-Ethyl-vinyl)-biphenyl. Obtained from 1-butene. ^1H NMR (500 MHz, CDCl_3) δ : 0.82 (d, $^3J_{\text{HH}} = 7.3$ Hz, 3H, CH_3), 1.91 (q, $^3J_{\text{HH}} = 7.3$ Hz, 2H, CH_2CH_3), 5.08 (m, 1H, = CHH), 5.10 (app q, $J_{\text{HH}} = 1.4$ Hz, 1H, = CHH).

2-(*E*-1-Methyl-propenyl)-biphenyl. Obtained in the reaction with *trans*-2-butene. ^1H NMR (500 MHz, CDCl_3) δ : 1.53 (app q, 3H, = $\text{C}(\text{Ar})\text{CH}_3$), 1.67 (dq, $^5J_{\text{HH}} = 1.1$, $^3J_{\text{HH}} = 6.8$ Hz, 1H, = $\text{CH}(\text{CH}_3)$), 5.55 (qq, $^4J_{\text{HH}} = 1.5$ Hz, $^3J_{\text{HH}} = 6.8$ Hz, 1H, = CHCH_3). NOE experiment: magnetization of the 1.53 ppm signal does not transfer to the 5.55 ppm signal.

2-(*Z*-1-Methyl-propenyl)-biphenyl. Obtained in the reaction with *cis*-2-butene. ^1H NMR (500 MHz, CDCl_3) δ : 1.43 (app d, $^5J_{\text{HH}} = 1.2$, $^3J_{\text{HH}} = 6.7$ Hz, 3H, = CHCH_3), 1.73 (app q, $^5J_{\text{HH}} \approx ^4J_{\text{HH}} = 1.2$ Hz, 1H, $\text{C}(\text{Ar})\text{CH}_3$), 5.44 (app q, $^4J_{\text{HH}} = 1.2$ Hz, $^3J_{\text{HH}} = 6.6$ Hz, 1H, = $\text{CH}(\text{CH}_3)$). NOE experiment: magnetization of the 1.73 ppm signal transfers at 5.44 ppm signal.

2-(1-*i*-Butyl-vinyl)-biphenyl. Obtained in the competition between 4-methyl-1-pentene and propene. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 0.67 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6H, CH_3), 1.32 (m, $\text{CH}(\text{CH}_3)_2$), 1.68 (overlap with propylene peak, 2H, $=\text{C}(\text{Ar})\text{CH}_2$), 5.10 (m, overlap with propylene peak 1H, $=\text{CHH}$), 5.14 (app d, $J_{\text{HH}} = 2.2$ Hz, 1H, $=\text{CHH}$).

Reaction of 1 with Mixtures of Olefins upon Halide Abstraction.

The following procedure is typical: Dichloromethane- d_2 (~ 0.6 mL) was vacuum transferred to a J-Young tube charged with **1** (15.4 mg, $19.2 \mu\text{mol}$, 1 equiv) and $\text{NaB}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4$ (25.5 mg, $28.8 \mu\text{mol}$, 1.5 equiv). The mixture was warmed up to room temperature using a water bath followed by mechanical rotation of the tube for 10 min. The mixture turned brown upon the starting materials dissolving. Propylene (55.39 mL at 80 torr, 0.24 mmol, 13 equiv) and 1-butene (55.39 mL at 80 torr, 0.24 mmol, 13 equiv) were condensed in. In the case of styrene, the olefin was added first via syringe, in the glovebox, to a frozen dichloromethane mixture prepared as above. The mixture was kept frozen, connected to a high-vacuum line, and the second olefin was condensed in. Upon adding in the second olefin, the NMR tube was sealed and warmed up to room temperature under water flow. The $^1\text{H NMR}$ spectrum of the crude mixture was recorded after 1–2 h of mechanical spinning to give the ratio of unreacted olefin starting materials dissolved in solution. The reaction mixture was allowed to spin for 24 h at room temperature, then the reaction was quenched with 1 mL of aqueous $\text{CO}_3^{2-}/\text{HCO}_3^-$ solution. The mixture was transferred to a scintillation vial and centrifuged. The organic layer was separated and filtered through silica gel, then volatile materials were removed under vacuum. The residue was analyzed by $^1\text{H NMR}$ spectroscopy in CDCl_3 to give the ratio of biphenyl-olefin products and their identity. From the ratio of initial excess olefins in solution and the ration of products, the relative insertion rate was calculated. Competition experiments between propylene and 1-butene, 4-methyl-1-pentene, styrene, 3-methyl-1-butene, and *cis*-2-butene were performed. The order of addition was varied for 1-butene (ratio = 1.1 in both cases), and 3-methyl-1-butene (ratio = 10 and 13) and was found to have just a small influence on the results of the experiment. *trans*-2-Butene was found to be too slow to compete with propylene, and the competition experiment was performed with *cis*-2-butene. The results are presented in Table 1. To check the relative rates obtained from propylene competition experiments, different mixtures of olefins were utilized—*cis*-2-butene and 3-methyl-1-butene (ratio = 1/3.3); styrene and 3-methyl-1-butene (ratio = 1/1.2).

Ethylene Oligomerization with $\text{Ni}(\text{Ph}_2\text{PCH}_2\text{COO})(\text{PPh}_3)(\text{Ph})$. A benzene (2 mL) solution of the Ni complex (1 mg) was placed in a thick-walled Schlenk tube equipped with a screw-in Teflon adaptor. The solution was degassed, and then ethylene was condensed in (128.8 mL, 630 torr). The flask was immersed in a water bath and agitated

until the solution was thawed, then the reaction flask was immersed in an oil bath preheated at 73 °C. The reaction mixture was stirred vigorously for 5 min, then frozen, and the reaction was quenched with water. The organic layer was analyzed by GC–MS. Fractions C_4 – C_{24} are observable, with the corresponding isotopologs.

Cotrimerization of Ethylene and Propylene Using 1 as Catalyst Precursor.

Dichloromethane (2 mL) was vacuum transferred to a 7 mL Schlenk tube charged with **1** (16.4 mg, $20.4 \mu\text{mol}$, 1 equiv) and $\text{NaB}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4$ (22 mg, $24.8 \mu\text{mol}$, 1.2 equiv). The mixture was warmed up to room temperature using a water bath followed by stirring for 10 min. The mixture turned brown upon the starting materials dissolving. Propylene (55.39 mL at 430 torr, 1.29 mmol, 63 equiv) and ethylene (55.39 mL at 60 torr, 0.18 mmol, 8.8 equiv) were condensed in. The flask was sealed and warmed up to room temperature under water flow. The reaction mixture was stirred at room temperature for 24 h, then the reaction was quenched, and the mixture was analyzed by GC–MS. The major products formed are 1-hexene, 3-methyl-1-hexene, 4-methyl-1-hexene, and 5-methyl-1-hexene. These were compared against the GC–MS data of original samples, available commercially.

Cotrimerization of Ethylene and Propylene Using $\text{CrCl}_3(\text{PNP}^{\text{O}4})$ as Catalyst Precursor.

Compound $\text{CrCl}_3(\text{PNP}^{\text{O}4})$ (10.1 mg, $14.9 \mu\text{mol}$, 1 equiv) was suspended in toluene (30 mL), in a 170 mL Schlenk tube fitted with a screw-in Teflon stopper. The flask was connected to a high-vacuum line, placed under Ar, and MAO (10% in toluene, $d = 0.875$ g/mL, 3.0 mL, 300 equiv) was added via syringe. Then the reaction mixture was cooled to -78 °C and degassed. Propylene (3 times 128.2 mL at 800 torr, 16.6 mmol, 1.1×10^3 equiv) and ethylene (128.2 mL at 100 torr, 0.69 mmol, 46 equiv) were condensed in. The flask was sealed and warmed up to room temperature under water flow. The reaction mixture was stirred at room temperature for 36 h, then the reaction was quenched and the mixture was analyzed by GC–MS. The major products formed are 1-hexene, 3-methyl-1-hexene, 4-methyl-1-hexene, and 5-methyl-1-hexene. These were compared against GC–MS data of original C7 samples, available commercially.

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Supporting Information Available: Spectroscopic data for experiments with labeled ethylene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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