

Mechanistic Studies of the Ethylene Trimerization Reaction with Chromium–Diphosphine Catalysts: Experimental Evidence for a Mechanism Involving Metallacyclic Intermediates

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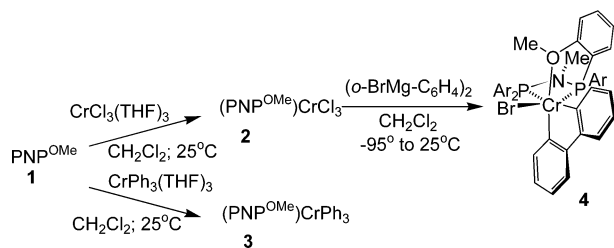
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The oligomerization of ethylene typically leads to a broad range of α -olefins; catalytic systems that are selective for specific desirable alkenes would be of great interest. There have been several recent reports of trimerization of ethylene to 1-hexene with high selectivity.¹ While some ethylene trimerization catalysts are based on titanium and tantalum,^{1,j,k} chromium-based systems generally display higher activity, selectivity, and thermal stability.^{1,b-i} A recent communication describes a catalyst, generated in situ by treating Cr(III) salts with methylalumoxane in the presence of the diphosphine PNP^{OMe} [**1**, PNP^{OMe} = (*o*-MeO-C₆H₄)₂PN(Me)P(*o*-MeO-C₆H₄)₂], that trimerizes ethylene to 1-hexene with unprecedented selectivity and productivity.^{1,c,d} Herein we report the synthesis and characterization of chromium complexes of **1**,² along with some mechanistic investigations of the ethylene trimerization reaction they catalyze.

Reactions of diphosphine **1** (Scheme 1) with suitable chromium(III) etherate complexes afford compounds (PNP^{OMe})CrCl₃ (**2**) and (PNP^{OMe})CrPh₃ (**3**); **2** reacts with *o,o'*-biphenyldiyl Grignard to give (PNP^{OMe})Cr(*o,o'*-biphenyldiyl)Br (**4**). All three are hexacoordinate, displaying (P,P,O)- κ^3 coordination of the diphosphine, established by single-crystal X-ray diffraction as well as ²H NMR.^{3,4} The structures of **3** and **4** (Figure 1) reveal long Cr–O bonds (2.293(2) Å in **3** and 2.337(2) Å in **4**) and significant differences between the two Cr–P bond lengths. The ether-chelated phosphine is closer to chromium by 0.16 Å (**3**) and 0.23 Å (**4**).

Scheme 1



Compounds **3** and **4** constitute well-characterized precursors to the ethylene trimerization catalyst. Activation of **3** with H(Et₂O)₂B-[C₆H₃(CF₃)₂]₄ provides an active catalyst that gives turnover and selectivity to 1-hexene comparable to those observed in the originally reported BP system.^{1c} Compound **4** reacts with NaB-[C₆H₃(CF₃)₂]₄ upon mixing dichloromethane solutions of the reagents, presumably generating a solution of [(PNP^{OMe})Cr(*o,o'*-biphenyldiyl)]⁺. Upon exposure to ethylene, formation of *o*-vinylbiphenyl and 1-hexene is observed by GC–MS and NMR spectroscopy. In contrast, reaction of **4** with ethylene affords only *o*-vinylbiphenyl without 1-hexene formation, suggesting that a cationic species is required for catalytic trimerization activity.

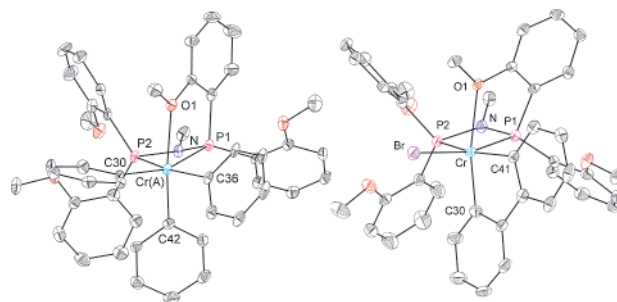
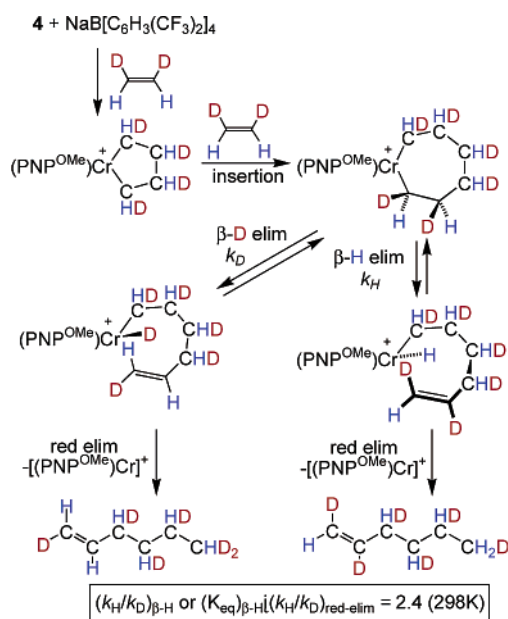


Figure 1. Structural drawings of **3** (left) and **4** (right) with thermal ellipsoids at the 50% probability level.³

A mechanism involving metallacyclic intermediates (Scheme 2) has been favored over a Cossee-type mechanism, in large part because the latter offers no reasonable explanation for highly selective ethylene trimerization.^{1b} In support of the former mechanism, Jolly and co-workers have reported well-characterized chromacyclopentane and chromacycloheptane complexes; the latter decomposes more readily and yields 1-hexene.⁵ On the other hand, no experiment to distinguish between these alternatives has been reported to our knowledge. Trimerization of a 1:1 mixture of C₂D₄ and C₂H₄ provides such a test. The metallacyclic route would give no H/D scrambling—only C₆D₁₂, C₆D₈H₄, C₆D₄H₈, and C₆H₁₂ should be observed—while the Cossee-type mechanism would lead to H/D scrambling and formation of isotopomers containing an odd number of deuterons.^{6a} Addition of an equimolar mixture of C₂D₄/C₂H₄ to the catalyst obtained by activating **3** with H(Et₂O)₂B-[C₆H₃(CF₃)₂]₄ or **4** with NaB-[C₆H₃(CF₃)₂]₄ produces only the isotopomers C₆D₁₂, C₆D₈H₄, C₆D₄H₈, and C₆H₁₂ in a 1:3:3:1 ratio, along with a mixture of vinylbiphenyl-*d*₀ and -*d*₄ from precatalyst system **4**. The same hexene isotopomer distribution is obtained for alternate catalyst preparations,⁷ indicating that the same type of mechanism is in effect for all the cases analyzed.

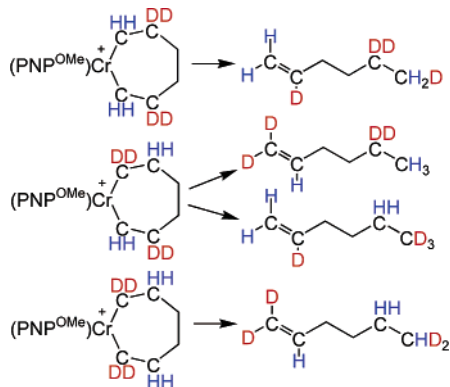
Trimerization of partially deuterated ethylenes has afforded insight into possible processes via analysis of the stereo- and regiochemistry of the products (Scheme 2). Either *cis*- or *trans*-dideuterioethylene leads to a mixture of isotopomers resulting from β -H vs β -D elimination followed by reductive elimination. In both cases a single geometric isomer is observed, with the stereochemistry of the double bond opposite to that of the ethylene starting material; that plus the absence of any isotopomers with terminal =CH₂ or =CD₂ groups rule out any H/D scrambling pathways, such as 2,1-reinsertion, competing with reductive elimination.^{6b} The product distributions indicate a kinetic isotope effect around 2.4 at room temperature.⁸ This value may represent either k_H/k_D for the β -H elimination step, if reductive elimination is faster than reinsertion, or a composite of a reductive elimination kinetic isotope effect and a β -H elimination/insertion equilibrium isotope effect if the opposite is the case.⁹

Scheme 2



Still further mechanistic inferences can be obtained from trimerization of *gem*-dideuterioethylene (Scheme 3).^{6b} Three cases can be distinguished. If the formation of the chromacycloheptane is reversible and fast compared to subsequent steps, then an isotope effect around 2.4, similar to that observed for trimerization of 1,2-dideuterioethylene, should be observed. Conversely, if formation of chromacycloheptane is irreversible, an isotope effect around 1.5 is expected, assuming β -H elimination can occur equally from either end of the alkanediyl group. If, however, there is sufficient asymmetry such that β -H elimination occurs selectively from one end of the alkanediyl group, no isotope effect is expected (assuming negligible secondary isotope effects). The observed isotope effect is 1.3, most consistent with irreversible formation of a symmetric metallacycloheptane.¹²

Scheme 3



While the exact nature of the active catalytic species, the detailed mechanism of ethylene trimerization, and an explanation for the

remarkable selectivity to 1-hexene remain to be elucidated, the findings reported here provide support for a structure based on tridentate PNP^{OMe} coordination and a metallacyclic route. Further studies are in progress.

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Supporting Information Available: Experimental procedures for 2–4 and tables of bond lengths, angles, and anisotropic displacement parameters for their structures; depictions of various mechanisms and description of expected experiment outcome for particular cases; and typical spectroscopic data for experiments with labeled ethylene (PDF). X-ray crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (2) The coordination chemistry of chromium complexes supported by phosphine **1** will be reported in a subsequent full paper.
- (3) Experimental procedures and single-crystal X-ray diffraction studies of 2–4 are presented in the Supporting Information.
- (4) Deuterium labeling of the methoxy group provides a useful spectroscopic handle, as the paramagnetic chromium(III) center produces a characteristic shift for coordinated vs noncoordinated methoxy. La Mar, G. N.; Horrocks, W. D., Jr.; Holm, R. H. *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973.
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- (6) See Supporting Information for analysis of the expected isotopomer distribution and stereochemistry for different possible mechanisms: (a) section S2 and (b) section S4.
- (7) 4/MAO and CrCl₃(THF)₃/PNP^{OMe}/MAO (the original preparation of ref 1c).
- (8) The isotope effect as determined from reactions in stirred flasks is 3.4 at 248 K, 2.5 at 273 K, and 2.4 at 298 K. Somewhat different values are obtained from reactions in sealed NMR tubes, possibly reflecting complications from slow diffusion.
- (9) A series of computational studies on the trimerization reaction with tantalum and titanium catalysts suggest that β -H elimination and reductive elimination may occur in one concerted step involving a metal-assisted hydride transfer (ref 10). Such a process might be expected to involve hydrogen tunneling and manifest unusual kinetic isotope effects (ref 11). The modest isotope effects observed here do not support such a proposal (but do not rule it out, either).
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- (12) The absence of any isotope effect in the product distribution from the mixture of C₂D₄ and C₂H₄ also argues against reversible formation of the chromacycloheptane.

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