

α -Agostic Interactions and Olefin Insertion in Metallocene Polymerization Catalysts

ROBERT H. GRUBBS* AND GEOFFREY W. COATES†

Contribution No. 9144 from The Arnold and Mabel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Received September 25, 1995

Introduction

In the 40 years since the discovery of transition metal catalysts for olefin polymerization by Ziegler and Natta,^{1,2} a substantial amount of research has been directed toward understanding the basic mechanistic steps of this important industrial process. Attention has focused in particular on the process of monomer enchainment, which is generally agreed to occur through olefin coordination^{3–5} followed by insertion into a metal–carbon bond. Four general mechanistic proposals for the nature of this insertion have emerged (Scheme 1). The first is alkyl migration to the coordinated olefin^{6–10} and is known as the Cossee–Arlman mechanism. The second model, proposed by Rooney and Green,^{11,12} involves an oxidative 1,2-hydrogen shift from the α -carbon of the polymer chain, generating a metal–alkylidene hydride. This species then reacts with an olefin to generate a metallacyclobutane, and reductive elimination completes the propagation sequence. Somewhat intermediate to the first two proposals is a mechanism proposed by Green, Rooney, and Brookhart^{13–15} where a hydrogen atom on the α -carbon of the growing polymer chain interacts with the metal center throughout the catalytic cycle. This three-center, two-electron covalent bond, termed an “agostic interaction”,^{15,16} occurs when the hydrogen atom is simultaneously bonded to both a carbon and a metal atom. The fourth mechanistic possibility is olefin insertion where an α -hydrogen interacts with the metal center only during the transition state of the C–C bond forming step. This mechanism is a hybrid of the Cossee–Arlman and modified Green–Rooney mechanisms.

Agostic interactions are of general interest in organometallic chemistry since they often lead to C–H activation.^{17,18} Concerning polymerization catalysts, it has been proposed that an understanding of the factors which control β -agostic interactions will yield better control of catalyst activity¹⁹ and polymer molecular weights.^{20–22} The α -agostic interaction is of particular interest since it might dramatically lower the activation barrier to olefin insertion²³ and influence the stereochemical outcome of the olefin insertion

step.^{23–27} Brintzinger has proposed that an α -agostic interaction rigidifies the transition state of a C_2 -symmetric catalyst undergoing propylene insertion, thereby increasing the isotacticity of the resulting polypropylene (Figure 1).^{23,24} Specifically, the α -agostic interaction firmly orients the polymer chain into the open sector of the catalyst structure to minimize interactions between the alkyl substituent of the monomer and the ligand/polymer array during olefin insertion. In addition, Guerra has proposed that the high syndiospecificity of C_s -symmetric catalysts²⁸ for propylene polymerization results from a γ -agostic structure which persists in the catalytic species after olefin insertion.²⁹ Several theoretical studies suggest

* E-mail: RHG@starbase1.caltech.edu.

† E-mail: coates@CCO.caltech.edu

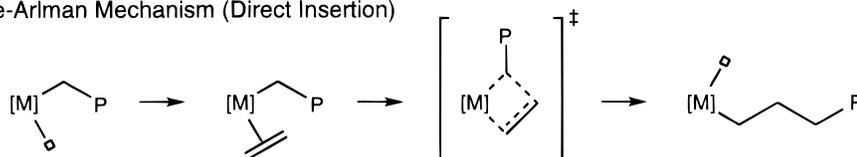
- (1) Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. *J. Am. Chem. Soc.* **1955**, *77*, 1708–1710.
- (2) Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H. *Angew. Chem.* **1955**, *67*, 426, 541.
- (3) Brookhart, M.; Volpe, A. F., Jr.; Lincoln, D. M.; Horváth, I. T.; Millar, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 5634–5636.
- (4) Wu, Z.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 5867–5868.
- (5) Casey, C. P.; Hallenbeck, S. L.; Pollock, D. W.; Landis, C. R. *J. Am. Chem. Soc.* **1995**, *117*, 9770–9771.
- (6) Breslow, D. S.; Newburg, N. R. *J. Am. Chem. Soc.* **1959**, *81*, 81–86.
- (7) Cossee, P. *Tetrahedron Lett.* **1960**, No. 17, 12–16.
- (8) Cossee, P. *Tetrahedron Lett.* **1960**, No. 17, 17–21.
- (9) Cossee, P. *J. Catal.* **1964**, *3*, 80–88.
- (10) Arlman, E. J.; Cossee, P. *J. Catal.* **1964**, *3*, 99–104.
- (11) Green, M. L. H. *Pure Appl. Chem.* **1978**, *50*, 27–35.
- (12) Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* **1978**, 604–606.
- (13) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 1410–1411.
- (14) Laverty, D. T.; Rooney, J. J. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 869–878.
- (15) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395–408.
- (16) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1–124.
- (17) Ginzburg, A. G. *Russ. Chem. Rev.* **1988**, *57*, 1175–1193.
- (18) Gleiter, R.; Hyla-Kryspin, I.; Niu, S. Q.; Erker, G. *Organometallics* **1993**, *12*, 3828–3836.
- (19) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443–1444.
- (20) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566–1577.
- (21) Resconi, L.; Piemontesi, F.; Franciscano, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025–1032.
- (22) Guo, Z.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1994**, *13*, 1424–1432.
- (23) Proscen, M. H.; Janiak, C.; Brintzinger, H. H. *Organometallics* **1992**, *11*, 4036–4041.
- (24) Röhl, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 279–280.
- (25) Lee, I.-M.; Gauthier, W. J.; Ball, J. M.; Iyengar, B.; Collins, S. *Organometallics* **1992**, *11*, 2115–2122.
- (26) Burger, B. J.; Cotter, W. D.; Coughlin, E. B.; Chacon, S. T.; Hajela, S.; Herzog, T. A.; Köhn, R.; Mitchell, J.; Piers, W. E.; Shapiro, P. J.; Bercaw, J. E. In *Ziegler Catalysts*; Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds.; Springer-Verlag: Berlin, 1995; pp 317–331.
- (27) Yu, Z.; Chien, J. C. W. *J. Polym. Sci., Part A* **1995**, *33*, 125–135.
- (28) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255–6256.

Robert H. Grubbs was born near Possum Trot, KY, in 1942. He received his B.A. and M.S. degrees from the University of Florida working with M. Battiste and his Ph.D. from Columbia University for work with Ronald Breslow. After a postdoctoral year with James P. Collman at Stanford he joined the faculty at Michigan State University in 1969. In 1978 he moved to the California Institute of Technology, where he is now the Victor and Elizabeth Atkins Professor of Chemistry.

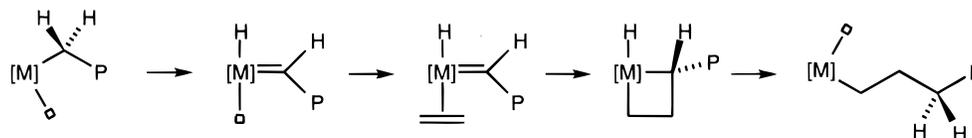
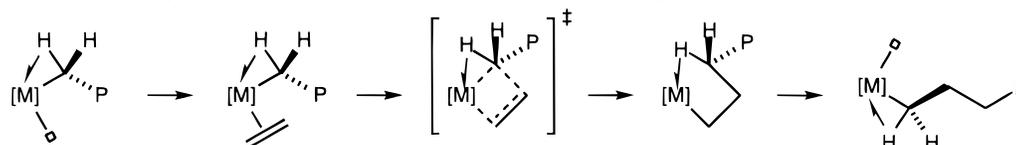
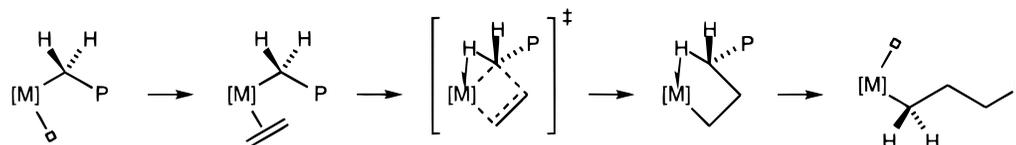
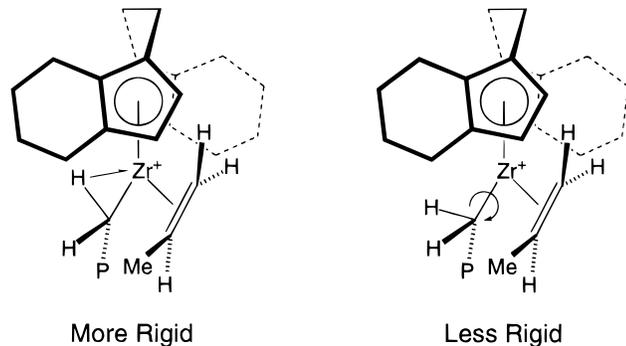
Geoffrey W. Coates was born in 1966 in Evansville, IN. He obtained a B.A. degree in chemistry from Wabash College in 1989 working with Roy G. Miller and a Ph.D. in organic chemistry from Stanford University in 1994. His thesis work, under the direction of Robert M. Waymouth, investigated the stereoselectivity of metallocene-based Ziegler–Natta catalysts. He is currently a NSF postdoctoral fellow with Robert Grubbs at the California Institute of Technology.

Scheme 1^a

Cossee-Arlman Mechanism (Direct Insertion)



Green-Rooney Mechanism (Hydride Shift)

Modified Green-Rooney Mechanism (Ground and Transition State α -Agostic Interaction)Transition State α -Agostic Mechanism^a "P" denotes a polymer chain.**Figure 1.** Proposed species preceding insertion for isospecific catalysts with and without α -agostic interactions.

that γ -agostic interactions are present following insertion^{30–32} and that these contacts can be relatively long lasting.^{33–35} This interaction might serve to stabilize the catalytic species (both geometrically and electronically) between the insertion and monomer coordination steps and result in a regular alternation between *si*- and *re*-preferring sites (Figure 2).

(29) Cavallo, L.; Guerra, G.; Vacatello, M.; Corradini, P. *Macromolecules* **1991**, *24*, 1784–1790.

(30) Kawamura-Kuribayashi, H.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1992**, *114*, 8687–8694.

(31) Kawamura-Kuribayashi, H.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1992**, *114*, 2359–2366.

(32) Meier, R. J.; van Doremale, G. H. J.; Iarlori, S.; Buda, F. *J. Am. Chem. Soc.* **1994**, *116*, 7274–7281.

(33) Woo, T. K.; Fan, L.; Ziegler, T. *Organometallics* **1994**, *13*, 2252–2261.

(34) Fan, L.; Harrison, D.; Woo, T. K.; Ziegler, T. *Organometallics* **1995**, *14*, 2018–2026.

(35) Woo, T. K.; Fan, L.; Ziegler, T. In *Ziegler Catalysts*; Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds.; Springer-Verlag: Berlin, 1995; pp 291–315.

Although significant advances in understanding classical Ziegler–Natta catalysts at the molecular level have been made,³⁶ the heterogeneous nature of these systems impedes detailed investigations. More recently, the development of well-defined, homogeneous metallocene catalysts has created new opportunities for mechanistic studies. In order to distinguish among possible mechanisms, a homogeneous system was designed in our laboratory that probed the presence of an α -agostic interaction through the isotopic perturbation of stereochemistry (*vide infra*).³⁷ In this study it was concluded that, for the system examined, there was not a significant effect due to an α -agostic interaction on either the rate or stereochemistry of olefin insertion, thus ruling out the modified Green–Rooney mechanism. Also, a substantial amount of evidence presently available (X-ray, IR, NMR)^{15,16} indicates that β -agostic^{3,20,22,26,38,39} (not α -agostic)⁴⁰ structures characterize ground states for this class of catalysts.

Recently, neutral group III and cationic group IV metallocene alkyls have been established to be the active catalysts in olefin polymerization.^{41,42} Since

(36) For three recent reviews, see: Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds. *Ziegler Catalysts*; Springer-Verlag: Berlin, 1995. *Macromol. Symp.* **1995**, *89*, 1–586. Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143–1170.

(37) Clawson, L.; Soto, J.; Buchwald, S. L.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 3377–3378.

(38) Jordan, R. F.; Bradley, P. K.; Baenziger, N. C.; LaPointe, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1289–1291.

(39) Mashima, K.; Nakamura, A. *J. Organomet. Chem.* **1992**, *428*, 49–58.

(40) Sterically crowded complexes which either lack β -hydrogens or have only one β -hydrogen have in some cases been shown to adopt α -agostic ground-state structures.^{22,39}

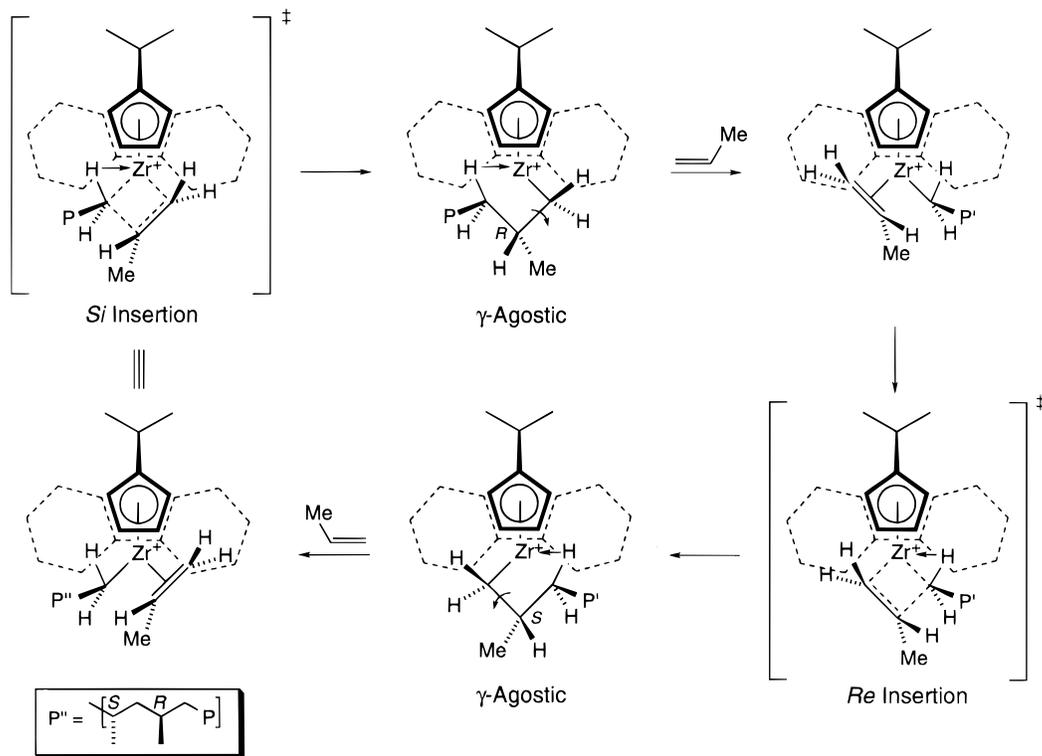


Figure 2. Proposed origin of syndiospecificity in C_2 -symmetric catalysts.

these complexes have no d-electrons, they cannot undergo formal oxidative addition at the metal center,¹⁵ as is required for metal-alkyl to metal-alkylidene hydride conversion in the Green-Rooney mechanism. Thus the leading proposals for these $14e^-$, d^0 metal-alkyl catalysts are the direct insertion (Cossee-Arlman) and transition state α -agostic assisted insertion mechanisms. For other catalyst systems, all four proposals remain mechanistic possibilities.

In the 10 years since our initial report, studies have been conducted with related catalyst systems using isotopically labeled substrates to probe for α -agostic interactions during olefin insertion. In some cases an effect is observed, but in others, it is not. The intent of this paper is to briefly summarize the literature where the effects of isotopic substitution on stereochemistry and reaction rates are used to probe for α -agostic interactions during olefin insertion. After a brief description of the α -agostic interaction in terms of the well-studied β -secondary kinetic isotope effect of organic chemistry, we will present an explanation which accounts for the presence and absence of isotopic perturbations in d^0 -metallocene systems.

Isotope Effects on α -Agostic Interactions

The two leading mechanistic proposals for olefin insertion in metallocene-based catalysts differ only by an α -agostic interaction in the transition state. Let us assume for a moment that olefin insertion proceeds with α -agostic assistance. Then this step would be expected to exhibit a secondary isotope effect when α -hydrogen atoms are replaced with deuterium atoms, since no bonds to the isotopic atoms are broken or formed during that step.⁴³ As a result, the reaction

coordinate will not be affected by the substitution. However, the bridging hydrogen or deuterium should resonate at a lower frequency than the corresponding nonbridging atom, causing a narrowing of the gap between hydrogen and deuterium zero-point energies in the transition state.⁴⁴ Since the C-D bond has the lower zero-point energy in both the ground and transition states, there will be a preference for hydrogen over deuterium in the agostic interaction,⁴⁵ and the insertion will exhibit a $k_H/k_D \geq 1$. Theoretical studies predict a k_H/k_D value of ≈ 1.25 for $M-H-C_\alpha$ versus $M-D-C_\alpha$ transition states.²³

Secondary isotope effects are typically measured by directly determining reaction rates or by competition studies of isotopically labeled substrates. In complex organometallic systems, large uncertainties in kinetic measurements often render it impossible to directly determine rate differences between isotopically related substrates, especially since the magnitudes of secondary isotope effects are typically small ($k_H/k_D < 1.4$). Although competition experiments have been employed to determine isotope effects in Ziegler-Natta systems, such studies can be complicated by isotope effects on not only the insertion step but the rate of catalyst generation as well.

Isotopic Perturbation of Stereochemistry in Metallocene-Based Systems

A more direct and precise method to investigate α -C-H interactions with the metal center during the C-C bond forming step is the isotopic perturbation

(43) Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; Robert E. Krieger: Malabar, FL, 1987; pp 170-201.

(44) Lowery, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; pp 238-240.

(45) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726-7727.

(41) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74-84.

(42) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325-387.

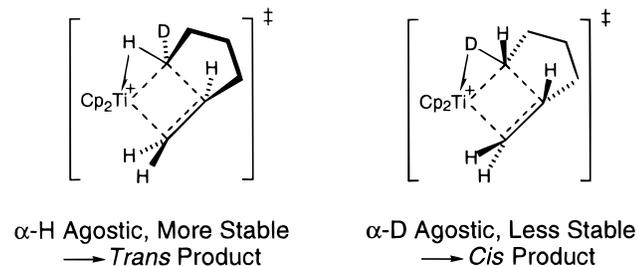


Figure 3. Stereochemistry of transition states involving $\alpha\text{-H}$ and $\alpha\text{-D}$ agostic interactions for activated titanocene 5-hexenyl- $1\text{-}d_1$ chloride.

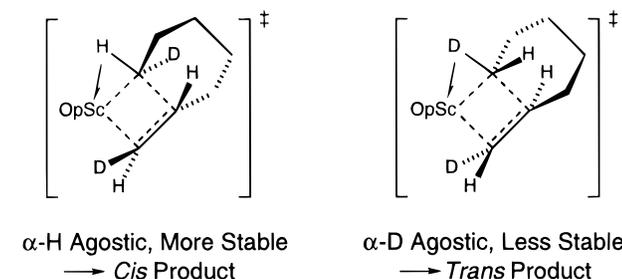
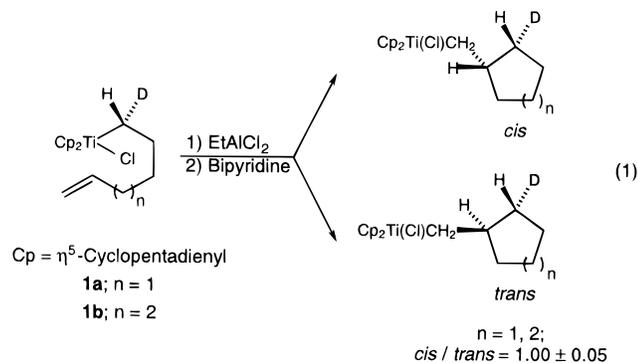


Figure 4. Stereochemistry of transition states involving $\alpha\text{-H}$ and $\alpha\text{-D}$ agostic interactions for scandocene-based hydrocyclization of (*E,E*)-1,5-hexadiene- $1,\beta\text{-}d_2$.

of stereochemistry. The first investigation of this effect was the study of the cyclization of unsaturated metal alkyls by Grubbs *et al.*³⁷ In this study, racemic titanocene 5-hexenyl- $1\text{-}d_1$ chloride (**1a**) was reacted with EtAlCl_2 at -100°C , and the stereochemistry of the cyclization products was determined (eq 1). Due



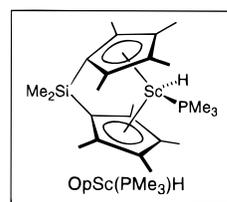
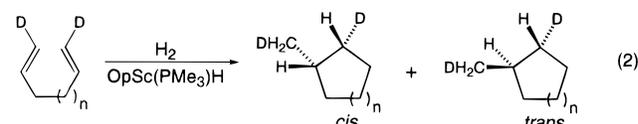
to the conformational preference of the incipient ring, a *cis* fusion of the bicyclic transition state is predicted. In the absence of an $\alpha\text{-agostic}$ interaction the *trans/cis* ratio should be 1/1, whereas the presence of an $\alpha\text{-agostic}$ interaction should produce an excess of the *trans* isomer (Figure 3). A *trans/cis* ratio of 1.00 ± 0.05 was found in this case, as well as in an experiment involving the closely related complex titanocene 6-heptenyl- $1\text{-}d_1$ chloride (**1b**). These results clearly demonstrate that a ground-state $\alpha\text{-agostic}$ interaction does not exert a strong influence on the rate or stereochemistry of olefin insertion in this system as is required by the Green–Rooney and modified Green–Rooney mechanisms (Scheme 1).⁴⁶

More recently, Bercaw and Piers adapted this mechanistic probe to neutral scandium-based systems

(46) This result is also consistent with a double $\alpha\text{-agostic}$ interaction where both the $\alpha\text{-H}$ and $\alpha\text{-D}$ interact equally with the metal center. However, such a transition state is unlikely for steric reasons ($\alpha\text{-H} \leftrightarrow \text{Cp}$ and $\beta\text{-C} \leftrightarrow \text{olefin}$ repulsions), and theoretical studies⁴⁷ find no electronic preference for the “double” interaction.

(47) Janiak, C. *J. Organomet. Chem.* **1993**, 452, 63–73.

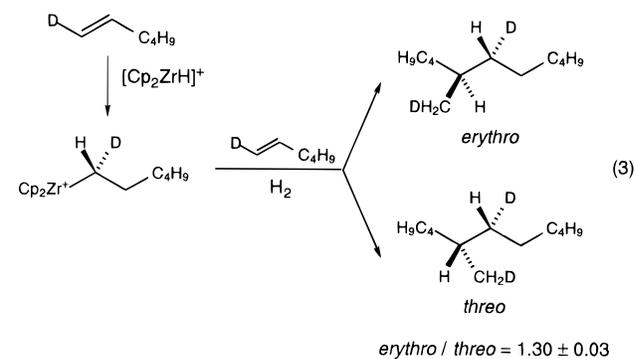
through the catalytic hydrocyclization of *trans*-deuterated α,ω -dienes (eq 2).⁴⁸ Insertion of one olefin of



$n = 1; trans / cis = 1.23 \pm 0.01$
 $n = 2; cis / trans = 1.12 \pm 0.01$

the diene into the Sc-H bond yields a species similar to **1**; then cyclization and hydrogenolysis yield the methylcyclopentane product. Spectroscopic analysis by $^2\text{H}\{^1\text{H}\}$ NMR reveals a *trans/cis* ratio of 1.23 ± 0.01 for the cyclopentane product ($n = 1$) and, interestingly, an inverse *cis/trans* ratio of 1.12 ± 0.01 for the cyclohexane product ($n = 2$).²⁶ The reversal in *cis/trans* stereochemistry for the longer diene was attributed to a chair-like conformation of the incipient ring in the transition state, creating a *trans*-fused bicycle (Figure 4). Studies of other scandocene and ytrocene catalysts showed similar perturbations of stereochemistry.²⁶ Subsequent studies involving the insertion of 2-butyne- $1,1,1\text{-}d_3$ into a Sc-CH_3 bond did not exhibit a measurable steric kinetic deuterium isotope effect, suggesting that the isotope effects in the cyclization reaction were not steric in origin.⁴⁹ These results provide solid evidence that $\alpha\text{-agostic}$ interactions occur during olefin insertion in these neutral group III systems.⁵⁰

Brintzinger and Krauledat have reported an acyclic version of the isotopic perturbation of stereochemistry technique by carrying out the hydrodimerization of deuterated 1-hexene with methylaluminumoxane (MAO)-activated zirconocene dichloride (Cp_2ZrCl_2)⁵¹ (eq 3). In



this experiment, an *erythro/threo* ratio of 1.30 ± 0.03 was measured, again consistent with an $\alpha\text{-agostic}$ assisted insertion as shown in Figure 5. Bercaw has recently reported a similar *erythro/threo* ratio of 1.27

(48) Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, 112, 9406–9407.

(49) Cotter, W. D.; Bercaw, J. E. *J. Organomet. Chem.* **1991**, 417, C1–C6.

(50) There is also evidence for the $\gamma\text{-agostic}$ assistance of β -methyl elimination (microscopic reverse of $\alpha\text{-agostic}$ assisted olefin insertion into a Sc-C bond) in scandocene–isobutyl complexes. Hajela, S. Ph.D. Thesis, California Institute of Technology, 1995.

(51) Krauledat, H.; Brintzinger, H. H. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 1412–1413.

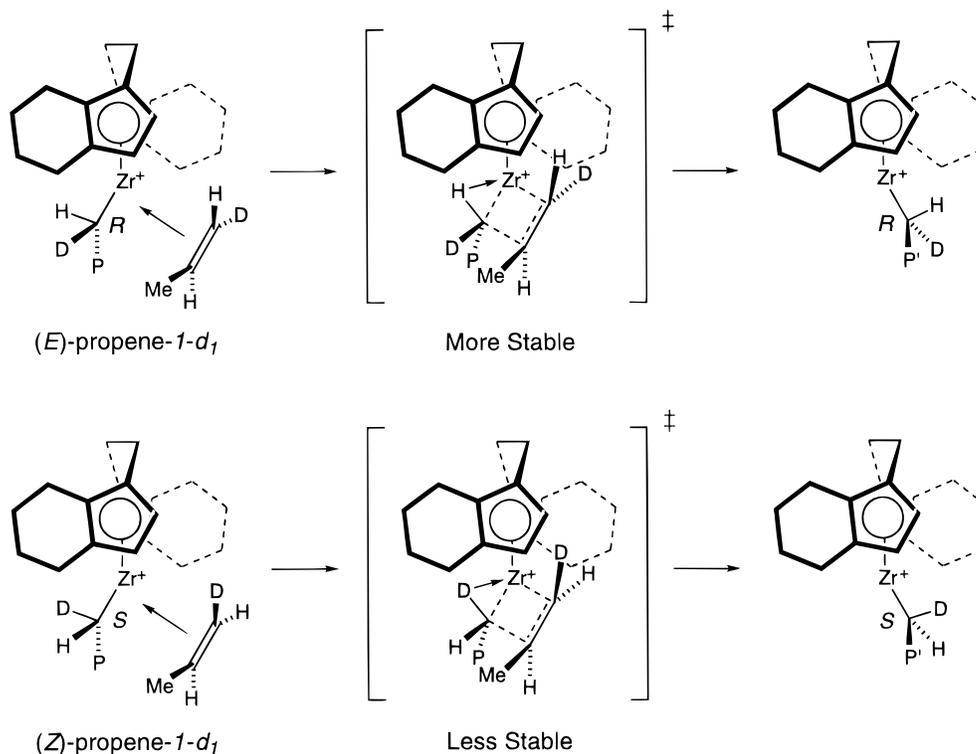


Figure 6. Stereochemistry of transition states involving α -H and α -D agostic interactions for the polymerization of (*E*)- and (*Z*)-propene-1- d_1 using a C_2 -symmetric zirconocenes activated with MAO.

predict α -agostic interactions, while others do not.^{18,23,27,30–35,47,54–61} Since the origin of these discrepancies is not currently apparent, one way to gain insight is to look to physical organic chemistry, where secondary isotope effects have been studied in detail for over 40 years.^{43,62,63} We propose that the transition-state α -agostic interaction as observed in these systems is closely related to the well-studied β -secondary isotope effect of the solvolysis of alkyl halides,⁶⁴ where the carbocation is replaced by an electrophilic metal atom (Figure 7).⁶⁹ In the following section, we

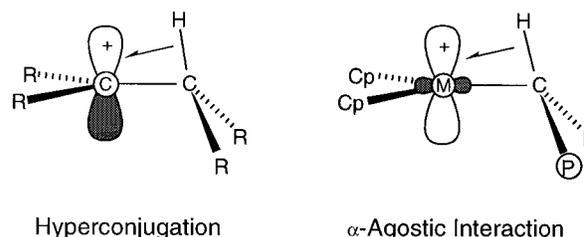


Figure 7. A comparison of hyperconjugation and α -agostic interactions.

will briefly review the factors which govern these secondary isotope effects that are relevant to the catalytic systems discussed.

Hyperconjugative Stabilization of Carbonium Ions by β -Hydrogens

Kinetic isotope effects (KIEs) are among the most powerful tools available to chemists for elucidating the nature and structure of transition states of chemical reactions. A substantial amount of work has centered on studying the secondary effect of hydrogen and deuterium in the β -position of substrate undergoing nucleophilic substitution (S_N) reactions. These studies have shown that hyperconjugation is the principal source of the observed β -deuterium isotope effect, and that the magnitude of the KIE depends on (1) the mechanism of the reaction; (2) the magnitude of

(69) A controversial aspect of hyperconjugation is whether the stabilizing β -CH bond is formally distorted toward the carbocation, in exact analogy to the distortion of the α -agostic interaction.^{70,71} We prefer to think of the interaction in terms of σ - π delocalization, where a continuum between no distortion and bridging exists.⁶⁶ Regardless of the exact geometries, we propose that the factors which determine secondary isotope effects in both of the systems should be the same.

(70) Lowery, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; pp 429–432.

(71) Capon, B.; McManus, S. P. *Neighboring Group Participation*; Plenum Press: New York, 1976; Vol. 1, pp 31–43.

(54) Fujimoto, H.; Yamasaki, T.; Mizutani, H.; Koga, N. *J. Am. Chem. Soc.* **1985**, *107*, 6157–6161.

(55) Jolly, C. A.; Marynick, D. S. *J. Am. Chem. Soc.* **1989**, *111*, 7968–7974.

(56) Castonguay, L. A.; Rappé, A. K. *J. Am. Chem. Soc.* **1992**, *114*, 5832–5842.

(57) Weiss, H.; Ehrig, M.; Ahlrichs, R. *J. Am. Chem. Soc.* **1994**, *116*, 4919–4928.

(58) Yoshida, T.; Koga, N.; Morokuma, K. *Organometallics* **1995**, *14*, 746–758.

(59) Woo, T. K.; Fan, L.; Ziegler, T. *Organometallics* **1994**, *13*, 432–433.

(60) Koga, N.; Yoshida, T.; Morokuma, K. In *Ziegler Catalysts*; Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds.; Springer-Verlag: Berlin, 1995; pp 275–289.

(61) Jensen, V. R.; Børve, K. J.; Ystenes, M. *J. Am. Chem. Soc.* **1995**, *117*, 4109–4117.

(62) Sunko, D. E.; Hehre, W. J. *Prog. Phys. Org. Chem.* **1983**, *14*, 205–246.

(63) Westaway, K. C. In *Isotopes in Organic Chemistry*; Buncl, E., Lee, C. C., Eds.; Elsevier: Amsterdam, 1987; Vol. 7, pp 275–392.

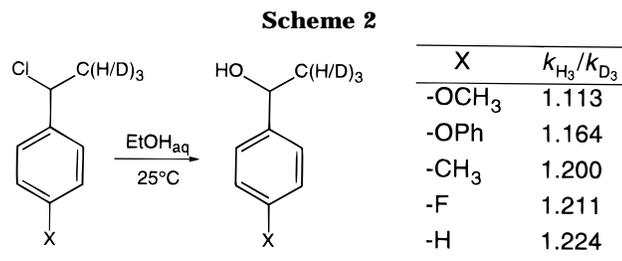
(64) Hehre has viewed distortions in metal carbene complexes in terms of hyperconjugation.⁶⁵ Berndt has compared the σ - π delocalization of nonclassical methyleneboranes to hyperconjugation,⁶⁶ Eisenstein has recently invoked hyperconjugation to explain the preference for β -methyl elimination over β -hydrogen elimination in certain early transition metal systems,⁶⁷ and Reed has similarly described the hyperconjugative stabilization of silylium cations.⁶⁸

(65) Francl, M. M.; Pietro, W. J.; Hout, R. F., Jr.; Hehre, W. J. *Organometallics* **1983**, *2*, 281–286.

(66) Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 985–1009.

(67) Sini, G.; Macgregor, S. A.; Eisenstein, O.; Teuben, J. H. *Organometallics* **1994**, *13*, 1049–1051.

(68) Xie, Z.; Bau, R.; Benesi, A.; Reed, C. A. *Organometallics* **1995**, *14*, 3933–3941.



charge buildup in the transition state; and (3) the geometrical relationship of the β -hydrogens and the carbon atom undergoing substitution.

The magnitude of the β -secondary KIE is used to distinguish between concerted ($\text{S}_{\text{N}}2$) and carbocation ($\text{S}_{\text{N}}1$) reaction mechanisms.^{43,63} Whereas the amount of positive charge on the α -carbon of the $\text{S}_{\text{N}}2$ transition state is small, there is considerable positive charge buildup in an $\text{S}_{\text{N}}1$ reaction. Since β -hydrogen atoms stabilize the $\text{S}_{\text{N}}1$ carbocation through hyperconjugative interactions better than β -deuterium atoms, the KIE for these reactions is substantial. Theoretical calculations and experimental results reveal that a $k_{\text{H}}/k_{\text{D}} \geq 1.07$ per β -D suggests a $\text{S}_{\text{N}}1$ reaction mechanism, while a $k_{\text{H}}/k_{\text{D}}$ of ≤ 1.05 per β -D indicates $\text{S}_{\text{N}}2$ displacement.⁶³ For example, the hydrolysis of *tert*-butyl chloride exhibits a $k_{\text{H}}/k_{\text{D}}$ of 1.33 (for β -D₃),⁷² while ethyl tosylate shows a much smaller $k_{\text{H}}/k_{\text{D}}$ of 1.02 (for β -D₃).⁷³ In addition, it has been demonstrated that the β -KIE is sensitive enough to determine the changes in electron density caused by subtle changes in substituents.⁷⁴ Shown in Scheme 2 is the reaction between para-substituted 1-phenylethyl chlorides in 50% ethanol at 25 °C. The $k_{\text{H}}/k_{\text{D}}$ (for β -D₃) runs from 1.113 for the electron-donating methoxy group to 1.224 for the unsubstituted compound. This trend suggests that the need for hyperconjugative stabilization increases as the stabilizing effect of the substituent decreases, thereby increasing the observed KIE.

Also consistent with the hyperconjugative stabilization model is the dependence of the magnitude of the KIE on the orientation of the stabilizing C_{β} -H bond relative to the carbonium ion center.⁷⁵ The degree of interaction is proportional to $\cos^2 \theta$, where θ is the dihedral angle between the C_{β} -H bond and the empty 2p atomic orbital.⁷⁶ Hence it has been experimentally determined that maximum KIEs are found when the dihedral angle is 0°, and minimum values are obtained at 90° (Figure 8).⁷⁵

Parallelism of α -Agostic and Hyperconjugative Interactions

Reexamination of the transition-state α -agostic effect observed in the isotopic perturbation of stereochemistry in light of the results discussed above for organic β -KIEs suggests many similarities. We propose that the transition states for polymerization and solvolysis are closely related, and the factors concern-

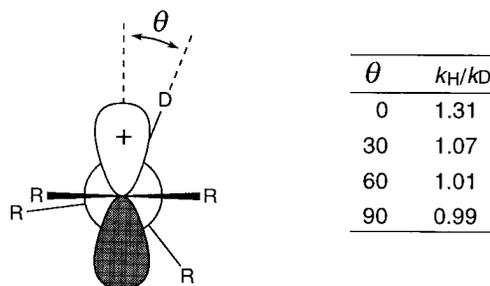
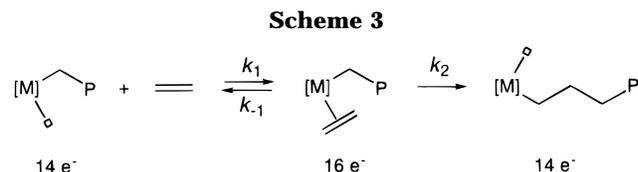


Figure 8. Effect of the dihedral angle (θ) between the C_{β} -H bond and the empty 2p orbital on $k_{\text{H}}/k_{\text{D}}$.



ing the developing electron deficient center are similar as well. In organic systems, the stabilization is known as hyperconjugation, whereas in organometallic systems it is an α -agostic interaction. In both instances, the reaction mechanism, the electrophilicity of the cation, and the angle of the C-H bond should determine the magnitude of the observed KIE.

It is now accepted that the catalytically active species in metallocene-based polymerization systems is a 14-electron metal-alkyl, $[\text{Cp}_2\text{MR}]^{n+}$ (M = group IV metal, $n = 1$; M = group III metal, $n = 0$),³⁹ which coordinates the olefinic monomer prior to insertion (Scheme 3). Since the olefin adduct is not normally observed, the steady-state approximation can be used to write the rate equation for the propagation sequence (eq 8). Inspection of eq 8 reveals that a KIE due to a

$$\text{propagation rate} = \frac{k_1 k_2 [\text{M}][=]}{k_{-1} + k_2} \quad (8)$$

(transition-state) α -agostic assisted insertion can be observed *only* when $k_2 \leq k_{-1}$ and that maximum effects will be observed when $k_2 \ll k_{-1}$. If olefin coordination is rate-determining ($k_2 > k_{-1}$), then an isotope effect will *not* be observed, even if an α -agostic assisted insertion exists.^{37,49,77} Goddard and Bercaw have noted that olefin insertion in the scandium cases is most likely rate-determining, which is substantiated by the observed KIEs in all olefin insertions involving scandium catalysts.⁷⁷ The only scandium-based example that does not exhibit a KIE is the alkyne insertion reaction, which Bercaw has proposed to arise from a rate-limiting alkyne binding step.⁴⁹ What remains to be explained is why some reactions involving group IV catalysts exhibit a KIE, while others do not. We believe that there are two possible explanations for this result. As can be seen in Table 1, the only group IV-catalyzed reactions which do not exhibit KIEs are intramolecular cyclization reactions. An

(72) Shiner, V. J., Jr.; Murr, B. L.; Heinemann, G. *J. Am. Chem. Soc.* **1963**, *85*, 2413–2416.

(73) Leffek, K. T.; Llewellyn, J. A.; Robertson, R. E. *Can. J. Chem.* **1960**, *38*, 2171–2177.

(74) Shiner, V. J., Jr.; Buddenbaum, W. E.; Murr, B. L.; Lamaty, G. *J. Am. Chem. Soc.* **1968**, *90*, 418–426.

(75) Shiner, V. J., Jr.; Humphrey, J. S. *J. Am. Chem. Soc.* **1963**, *85*, 2416–2419.

(76) Sunko, D. E.; Szele, I.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 5000–5004.

(77) Bierwagen, E. P.; Bercaw, J. E.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1994**, *116*, 1481–1489.

(78) Gonzales, J. S. Doctoral Thesis, California Institute of Technology, 1984.

(79) Austin, R. G.; Welborn, H. C. (Exxon). PCT Int. Appl. WO 88 04-673, 1988; *Chem. Abstr.* **1988**, *109*, 130214c.

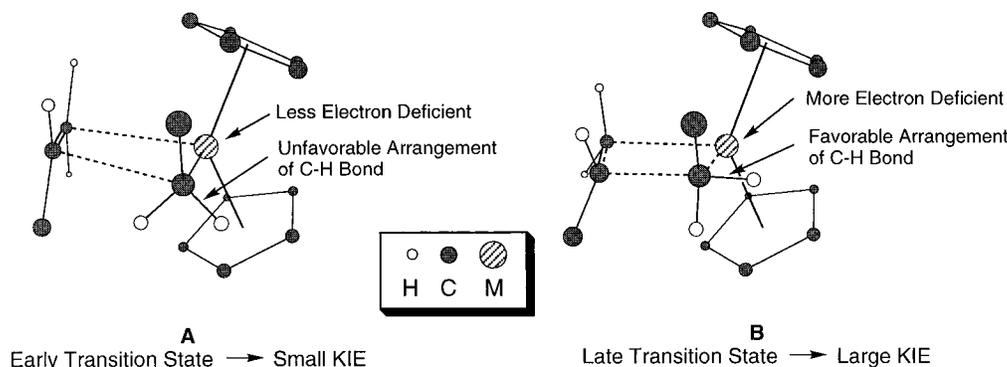
(80) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* **1987**, *109*, 6189–6191.

(81) Kaminsky, W.; Ahlers, A.; Möller-Lindenhof, N. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1216–1218.

Table 1. Summary of α -KIE Effects in Metallocene-Catalyzed Insertion Reactions

entry	eq	reactn type	catalyst system	insertion ^a	qualitative rate ^b	KIE
1	1	cyclization	Ti/AlEtCl ₂	intra	very fast ^c	1.00
2	2	cyclization	Sc	intra	slow ^d	1.12–1.23
3	3	dimerization	Zr/MAO	inter	slow ^e	1.30
4	3	dimerization	Sc	inter	slow ^f	1.27
5	4	cyclization	Zr/MAO	intra	very fast ^g	1.01
6	5	alkyne insertion	Sc	inter	slow ^h	0.98
7	6	cyclization	Ti/MgX ₂	intra	slow ⁱ	1.25
8	6	cyclization	Ti/MAO	intra	fast ^j	0.91
9	7	polymerization	Zr/MAO	inter	slow ^k	1.30

^a Intra, intramolecular; inter, intermolecular. ^b There is a lack of kinetic data for many of these reactions. However, the productivities of these systems (turnovers of substrate per mole of catalyst per hour/initial substrate concentration) can be used to establish the lower limits for the rates of olefin insertion. ^c Cyclization of titanium compound (**1a**) in the presence of ethylene at 0 °C yields cyclopentyl-capped polyethylene oligomers.⁷⁸ Thus olefin cyclization occurs in less than the time required for ethylene insertion, which is 95 ms (38 000 h⁻¹) in this system. ^d Productivity = 135 h⁻¹ M⁻¹.⁴⁸ ^e Productivity = 14 h⁻¹ M⁻¹.⁵¹ ^f In 1 h at 25 °C, the catalyst converted 45 equiv of 1-pentene selectively to the dimer.⁴¹ ^g There is not sufficient experimental data to estimate the rate of cyclization in this system. However, zirconocene-catalyzed copolymerization of 1,5-hexadiene and ethylene yields soluble polymers with cyclopentane rings in the main chain. Calculations reveal that cyclization in this system is extremely rapid, occurring in less than 0.38 ms (9.4 × 10⁶ h⁻¹).⁷⁹ ^h The rate of insertion is presumably very slow, since this reaction can be monitored by NMR.⁴⁹ ⁱ Slow relative to entry 8. ^j Fast relative to entry 7. ^k Productivities for this system range from 364 to 340 h⁻¹ M⁻¹.^{80,81}

Scheme 4

explanation for this is that tethering the olefin causes a decrease in the magnitude of rate constant k_{-1} (relative to k_2),⁴ which makes olefin binding rate-limiting. As a result, a KIE due to a transition-state α -agostic interaction cannot be detected, even if the contact is present, since it has no effect on the rate or stereochemistry of olefin insertion.

A further explanation of the unpredictable presence and absence, as well as the magnitude, of α -agostic derived KIEs in these group IV systems is the following. As the insertion proceeds, the metal center loses electron density, as the formal electron count of the complex changes from 16e⁻ to 14e⁻ (Scheme 3).³⁹ One of the factors that determines the amount of charge buildup in the transition state is the timing of the transition state. In this exothermic reaction, a fast reaction will have an early transition state. Such a transition would be expected to have only a small buildup of positive charge and poor overlap of the α -C–H bond with the electrophilic metal, resulting in a small KIE (Scheme 4A). Conversely, a slow reaction (late transition state) would be expected to have a large KIE (Scheme 4B). This synopsis is consistent with the observed isotope effects for the metallocene-catalyzed examples summarized in Table 1. Fast systems, such as the group IV intramolecular cyclizations, exhibit no isotope effect. However, slow systems, such as those involving neutral group III complexes or intermolecular reactions, exhibit substantial isotope effects. As can be seen in Table 1, the only slow system that does not exhibit an isotope effect is the alkyne insertion reaction (entry 6). This result

is likely due to a rate-limiting alkyne coordination step.⁴⁹ This analysis provides a consistent picture of the α -agostic effect as hyperconjugation and provides a rationale for the variation of the KIEs from 1.0 to 1.3.

Conclusion

The two leading mechanisms of olefin insertion in d⁰-metallocene polymerization catalysts are (1) direct insertion of the coordinated olefin and (2) an α -agostic assisted olefin insertion. Transition-state α -agostic interactions are of particular interest since they are expected to have a strong impact on the stereospecificity and rate of olefin insertion. The use of isotope labeling studies to probe the nature of the olefin insertion (*via* stereochemistry and reaction rates) has been reviewed. In some instances α -isotope effects are found, which is strong evidence that α -C–H bonds are intimately involved in the transition state of the insertion step. However, in other closely related systems, no isotope effects are found. Two factors are proposed to account for the variability of the observed isotope effects. The first factor to consider is mechanism. Since there does not appear to be an α -agostic interaction before or during olefin complexation (as is required by the Green–Rooney and modified Green–Rooney mechanisms), only if the insertion step is rate-limiting can there be an agostic-derived isotope effect. If olefin binding is rate-limiting, transition-state α -agostic interactions may be present but will not significantly affect either the rate or stereochemistry

of olefin insertion. The second key factor is the nature of the transition state of olefin insertion. We propose that the observed α -agostic interaction is an organo-metallic version of hyperconjugation. The factors which govern the secondary isotope effects in organic systems are also responsible for the magnitudes of these effects in olefin insertion reactions. The magnitude of charge buildup and α -C-H bond geometry will determine the magnitude of the isotope effect when an α -agostic interaction is present.

It has been shown that systems with high reaction rates typically do not exhibit α -isotope effects. In such systems, the barriers to both olefin coordination and olefin insertion must be relatively small and both of these factors contribute to low isotope effects. If coordination is rate-limiting and there are no α -agostic interactions in the ground state, a KIE will not be found. If insertion is rate-limiting, the transition state

will be early, resulting in a small amount of charge buildup, poor overlap with the α -C-H bonds, and hence a small KIE. Systems with low reaction rates typically exhibit α -isotope effects. This is strong evidence that olefin insertion is rate-limiting in these reactions. We believe that these factors provide an explanation for the range of KIEs observed in olefin insertion reactions involving d^0 -metallocene complexes.

This work was generously supported by a grant from the NSF. We thank Prof. J. E. Bercaw, Prof. H. H. Brintzinger, Dr. S. N. Brown, Prof. M. L. H. Green, Prof. W. E. Piers, and Prof. J. J. Rooney for helpful discussions and comments. G.W.C. gratefully acknowledges a Noyes Postdoctoral Fellowship from Caltech and a NSF Postdoctoral Fellowship.

AR9501683