solvents are complex and depend both on the solute–solvent hydrogen bonding and dielectric relaxation. The heteroatom lone pair hydrogen bonding in the absence of dielectric effects can often lead to *red* shifts.

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α "Agostic" Assistance in Ziegler-Natta Polymerization of Olefins. Deuterium Isotopic Perturbation of Stereochemistry Indicating Coordination of an α C–H Bond in Chain Propagation

Warren E. Piers and John E. Bercaw*

Contribution No. 8177, Arnold and Mabel Beckman
Laboratories of Chemical Synthesis
California Institute of Technology
Pasadena, California 91125

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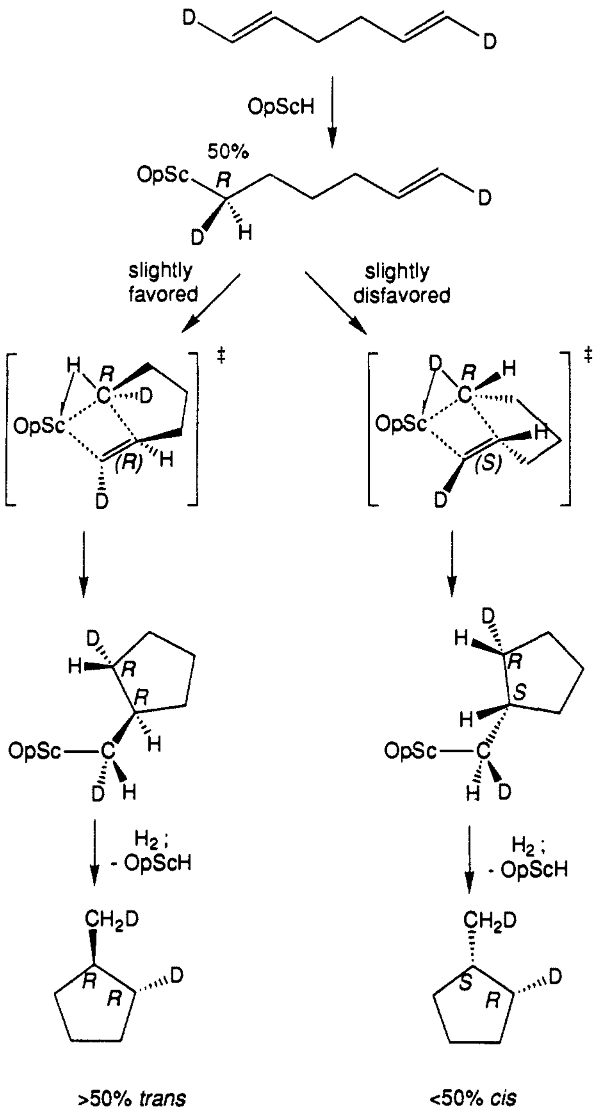
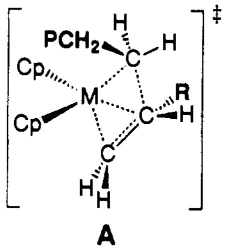
The well-defined, homogeneous Ziegler–Natta olefin polymerization systems that have been reported recently provide an unprecedented opportunity to investigate the mechanism of this important process. New systems[1] include (1) single-component catalysts such as cationic group 4 metallocenes[2] or the isoelectronic, neutral group 3 or lanthanide metallocene hydrides or alkyls[3] and (2) highly active, two-component systems consisting of "methylalumoxane" in combination with a group 4 metallocene derivative, which, with suitable modification of the cyclopentadienyl ligands, may exhibit remarkable iso-or syndiospecificities.[4] While a consensus appears to be developing that in all these systems the active catalysts are the 14-electron, d^0 (or d^0f^n) metallocene alkyls, Cp_2MR (M = lanthanide or group 3 transition metal) or $[Cp_2MR]^+$ (M = group 4 transition metal), the mechanism for chain propagation and the geometry of the transition state for olefin insertion into the metal–carbon bond have not yet been unequivocally established.

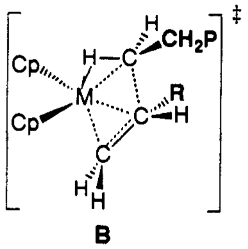
The Cossee mechanism and a staggered arrangement of alkyl and olefin substituents (A) generally have been assumed in rationalizing the stereospecificity of propene polymerization by these metallocene catalyst systems.[5] The most popular alternative suited to d^0 metal complexes, the "modified Green–Rooney mechanism", invokes α C–H coordination to assist olefin insertion,[6] a quite different transition-state geometry (B).

Scheme I



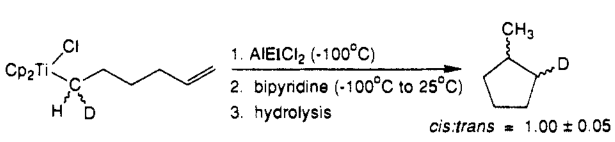


A



B

In a cleverly conceived experiment, Grubbs et al.[7] probed for an α agostic interaction in the transition state for olefin insertion. Racemic *1*-d_1-5-hexenylchlorotitanocene was prepared and found to undergo $AlCl_2(CH_2CH_3)$-induced cyclization to a mixture of *cis*- and *trans-2*-d_1-cyclopentylmethyl stereoisomers (eq 1). Any



(1)

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[1] A class of one-component ethylene-polymerization catalysts based on late-transition-metal complexes of the type $[(\eta^5\text{-}C_5Me_5)(L)M(C_2H_4)(R)]^+$ (M = Co, Rh; L = phosphine or phosphite) has also been developed. See: Brookhart, M.; Volpe, A. F., Jr.; Lincoln, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5634–5636 and references cited therein.

[2] (a) Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892–2906. (b) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728–2729. (c) Taube, R.; Krukowa, L. *J. Organomet. Chem.* **1988**, *347*, C9. (c) Eshuis, J. J. W.; Tan, Y. Y.; Teuben, J. H. *J. Mol. Catal.*, submitted.

[3] (a) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337. (b) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566–1577. (c) Jeske, G.; Lauke, H.; Mauermann, H.; Sweptson, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

[4] (a) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (b) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 635–6364. (c) Ewen, J. A.; Jones, R. L.; Razavi, A. *J. Am. Chem. Soc.* **1988**, *110*, 6255–6256. (d) Erker, G.; Nolte, R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *29*, 629. (e) Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Dong, S.; Chien, J. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 2030–2031. (f) Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 4953–4954.

[5] (a) Pino, P.; Galimberti, M. *J. Organomet. Chem.* **1989**, *370*, 1–7. (b) Pino, P.; Cioni, P.; Wei, J.; Rotzinger, B.; Arizzi, S. Recent Developments in Basic Research on the Stereospecific Polymerization of α-Olefins. In *Transition Metal Catalyzed Polymerization: Ziegler-Natta and Metathesis Polymerization*; Quirk, R. P., Ed.; Cambridge Press: New York, 1988; pp 1–24 and references cited therein. (c) Jolly, C. A.; Marynick, D. S. *J. Am. Chem. Soc.* **1989**, *111*, 7968–7974. (d) Waymouth, R.; Pino, P. *J. Am. Chem. Soc.* **1990**, *112*, 4911–4914.

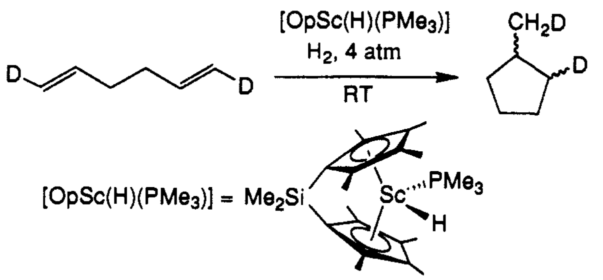
[6] (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Brookhart, M.; Green, M. L. H.; Wong, L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

[7] Clawson, L.; Soto, J.; Buchwald, S. L.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 3377–3378.

0002-7863/90/1512-9406$02.50/0

α agostic assistance in the insertion step is expected to favor the trans product (vide infra). Hydrolysis and ^{2}H NMR analysis of the resultant mixture of deuteriomethylcyclopentanes revealed a 1.00 ± 0.05 ratio of trans:cis products, arguing against an α agostic assisted insertion in their system, however.

The scandium hydride, $\{(\eta^5\text{-}C_5Me_4)_2SiMe_2\}Sc(PMe_3)H$ ("$OpSc(PMe_3)H$"), cleanly catalyzes the hydrocyclization of 1,5-hexadiene to methylcyclopentane.[8] In light of some very recent theoretical results favoring transition state B,[9] we have adapted this *catalytic* hydrocyclization reaction along the lines of the Grubbs experiment to probe for α agostic assistance with the scandium system. *trans,trans-1,6-d_2*-1,5-Hexadiene was employed as substrate, and as expected, $OpSc(PMe_3)H$ cleanly catalyzes its hydrocyclization to a mixture of *cis-* and *trans-d_2*-methylcyclopentane (eq 2).[10] $^2H\{^1H\}$ NMR analysis reveals a (1.19 ± 0.04):1 ratio of trans:cis products at 25 °C (see supplementary material).[11]

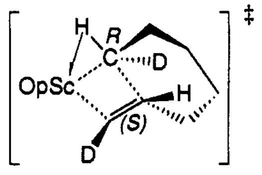


(2)

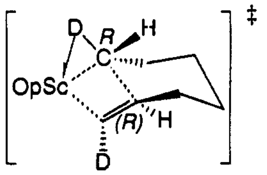
Assuming that an α agostic interaction is, in fact, responsible,[12] the excess of *trans-d_2*-methylcyclopentane may be rationalized as shown in Scheme I. Addition of achiral α,ω-diene to achiral OpScH yields a precisely 50:50 mixture of *R* and *S 1,6-d_2*-5-hexenyl–scandium complexes. Due to ring strain there should a strong preference for cis fusion of the pseudo 4,5 ring system in the transition state for olefin insertion.[13] As shown in Scheme I for the *R* isomer only, the face selection for insertion of the pendant olefin then depends on whether H or D occupies the α agostic position. The expected preference for H to occupy the bridging position[14] leads to excess of the *R,R* (trans) product. A similar analysis for the *S* enantiomer leads to the same conclusion: the trans isomer (in that case *S,S*) is produced in excess, if an α agostic interaction assists olefin insertion into the Sc–C bond (see supplementary material for full analysis).

Additional experiments support the supposition that the partitioning of stereochemistry is due to a kinetic deuterium isotope effect operating at the α methylene of the $[OpScCHDCH_2CH_2CH_2CH{=}CHD]$ intermediate: (1) the trans:cis ratio varies in a normal enthalpic manner with temperature (1.07 ± 0.03 at 120 °C, 1.19 ± 0.04 at 25 °C, 1.26 ± 0.03 at −10 °C); (2) hydrocyclization of *cis,cis-1,6-d_2*-1,5-hexadiene affords a ratio of 1.20 ± 0.04, indicating that insertion of the pendant olefin is not influenced by the geometry about its double bond; and (3) similarly, *trans-1-d1*-1,5-hexadiene gives the same trans:cis ratio of 1.19 ± 0.02 with the single deuteron partitioned equally (^{2}H NMR) between methyl and ring positions of the d_1-methylcyclopentane product.

For longer chain diolefins, simple hydrogenation to α,ω-d_2-alkanes competes with hydrocyclization. Reaction of $OpSc(PMe_3)H$ with neat 1,5-heptadiene at −4 °C in the presence of 1 atm of H_2 leads to an approximately 60:40 mixture of methylcyclohexane and *n*-heptane. 1,7-Octadiene is converted exclusively to *n*-octane. Nonetheless, the partial hydrocyclization of *trans,trans-1,7-d_2*-1,6-heptadiene allowed us to ascertain the ratio of *trans-* to *cis-d_2*-methylcyclohexane products. We find a (1.21 ± 0.5):1 ratio of *cis-d_2*-methylcyclohexane:*trans-d_2*-methylcyclohexane, although the analysis is less accurate due to overlap of the *cis*-D resonance with that for the methyl deuterons in the ^{2}H NMR spectrum (see supplementary material). This reversal of trans:cis ratio is entirely consistent with the expectation that face selectivity for pendant olefin approach would be opposite to that for formation of the five-membered ring. The developing six-membered ring adopts a chair-like conformation, and the pseudo bicyclic transition state is now trans fused. Thus, as illustrated below, preferential H in the α agostic position leads to the cis isomer.



slightly favored



slightly disfavored

Our results provide good evidence for the modified Green–Rooney pathway for chain propagation with these Ziegler–Natta systems.[15] Moreover, they suggest a rationale for the apparent requirement that active catalysts be 14-electron alkyl derivatives with *two* vacant orbitals: one to accommodate the incoming olefin, another for the α agostic interaction.[16]

Acknowledgment. We thank Professors Bob Grubbs, Tom Flood, Maurice Brookhart, and Dennis Dougherty for helpful discussions. We also thank Professor Hans Brintzinger for providing us with information prior to publication. This work was supported by the USDOE Office of Basic Energy Sciences (Grant No. DE-FG03-85ER113431), by Exxon Chemicals Americas, and by Shell Companies Foundation. W.E.P. thanks the National Sciences and Engineering Research Council of Canada and the Izaak Walton Killam Foundation for postdoctoral fellowship support.

Supplementary Material Available: Experimental details for the preparation of the substrates used, ^{2}H NMR measurements, gas chromatographic separations, and complete versions of Scheme I for *trans,trans-1,6-d_2*-1,5-hexadiene and *trans,trans-1,7-d_2*-1,6-heptadiene hydrocyclizations (8 pages). Ordering information is given on any current masthead page.

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

(9) H. H. Brintzinger, private communication.

(10) In a typical procedure, a 10–15-mg sample of $OpSc(PMe_3)H$ was loaded into a 150-mL thick-walled reactor equipped with a 4-mm Kontes needle valve. Toluene (4 mL) was added in vacuo, the scandium complex dissolved with warming, and ca. 100 equiv of rigorously dried *trans,trans-1,6-d_2*-1,5-hexadiene and 1 atm of H_2 were added at −196 °C. The reactor was warmed to room temperature and stirred for 30 min at 25 °C. Excess dihydrogen was removed by two freeze–pump–thaw cycles, and all volatile organic compounds were vacuum transferred away from the catalyst residue for analysis by ^{2}H NMR and GC.

(11) ^{1}H-coupled ^{2}H spectra, while not entirely base-line resolved, gave the same ratio of trans:cis, confirming that NOEs for ^{2}H are insignificant.

(12) An alternative, less likely possibility is that the excess trans isomer results from the smaller size of deuterium in a more conventional transition state such as A. "Steric" kinetic deuterium isotope effects of 1.16 ± 0.03 have been observed for extremely crowded transition states; see: Melander, M.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley-Interscience: New York, 1980; p 189. On the other hand, the 1.00:1 ratio observed by Grubbs and co-workers at −100 °C would appear to rule out a substantial contribution from steric effects.

(13) Although strained, some trans alicyclic bicyclo[3.2.0]heptane compounds have been prepared: Meinwald, J.; Anderson, P.; Tufariello, J. J. *J. Am. Chem. Soc.* **1966**, *88*, 1301 and references cited therein.

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

(15) Brintzinger and Krauledat have very recently observed a 1:(1.28 ± 0.02) ratio of threo-erythro *5-methyl,6-d_2*-5-methylundecane isomers in the hydrodimerization of *trans-1-d_1*-1-hexene with the $(\eta^5\text{-}C_5H_5)_2ZrCl_2$/methylalumoxane system (Krauledat, H.; Brintzinger, H. H. *Angew. Chem.*, submitted).

(16) β agostic interactions have been identified as the preferred *ground-state* structures for $Cp^*_2ScCH_2CH_3$ and for the cations $[Cp^*(L)CoCH_2CH_2R]^+$ and $[Cp_2(PMe_3)ZrCH_2CH_2R]^+$ (refs 1 and 8; Jordan, R. F.; Bradley, P. K.; Baenziger, N. C.; LaPointe, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1289). Our results implicate the (less stable due to ring strain) α agostic arrangement in the *transition state* for C–C bond formation. Thus, we tentatively conclude that β agostic structures characterize ground states and α agostic structures transition states for chain propagation. On the other hand, the 1.00:1 ratio observed by Grubbs et al. could be taken as an indication that α agostic assistance is not *required* for C–C bond formation.