

dots) stereoselectively poison the exposed horizontal surfaces within a defect, leading to etch-pit formation. Other surfaces at this site will dissolve unperturbed. Such a process could enhance the depth of the etch pit.

We may conclude that stereoselective etching of a chiral crystal by an optically pure, tailor-made additive provides a means of manually sorting enantiomorphous crystals and of correlating the absolute configuration of the etchant and the etched (or unetched) crystals. Furthermore such etching allows one to directly assign the absolute configuration of chiral desolved additives (e.g., the α -amino acids) by their effect on centrosymmetric crystals (e.g., α -glycine). We have applied this stereoselective etching to other systems such as cinnamide, allopurinol, serine, and glutamic acid hydrochloride and for the assignment of the absolute direction of polar crystals whose constituent molecules are nonchiral, such as the γ -form of glycine, which will be discussed elsewhere.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the U.S./Israel Binational Foundation, Jerusalem, for financial support. We are indebted to Isabella Weissbuch, Dr. Lia Addadi, and Dr. Ziva Berkovitch-Yellin for helpful discussions.

Registry No. (*R*)-Asparagine monohydrate, 5794-24-1; (*S*)-asparagine monohydrate, 5794-13-8; (*R*)-aspartic acid, 1783-96-6; *N*-methyl-asparagine, 7175-34-0; α -glycine, 56-40-6; (*R*)-alanine, 338-69-2.

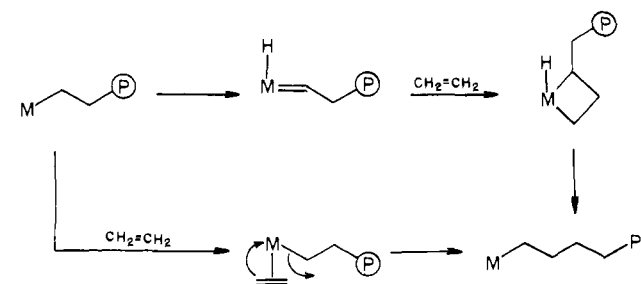
Olefin Insertion in a Metal Alkyl in a Ziegler Polymerization System

Leigh Clawson, Jorge Soto, Stephen L. Buchwald, Michael L. Steigerwald, and Robert H. Grubbs*

Contribution No. 7133, Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91125

Received July 27, 1984

Ziegler-Natta polymerization is the backbone of the polyolefin business and remains as one of the key processes in organometallic chemistry. After more than 30 years of intensive study, many questions concerning the basic steps in this process remain unanswered. Basic to the understanding of this reaction is the mechanism of the insertion of an olefin into a metal-carbon bond. Of the variety of mechanisms that have been proposed, two distinct classes have emerged and have been modeled. Cossee proposed the direct insertion of the olefin into the growing polymer.¹ More recently, Green and Rooney proposed that the reaction proceeds through a metathesis-type mechanism.² The only difference between these two mechanisms is the interaction of a hydrogen on the α -carbon with the metal center in the latter. Before further progress can be made in the understanding of the basic mechanistic and stereochemical steps of this reaction, this division of mechanisms must be established. Excellent models exist for each of the proposed classes of mechanisms.^{3,4}



(1) Cossee, P. *Tetrahedron Lett.* 1960, 17, 12.

(2) Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, J. R. *J. Chem. Soc., Chem. Commun.* 1978, 604.

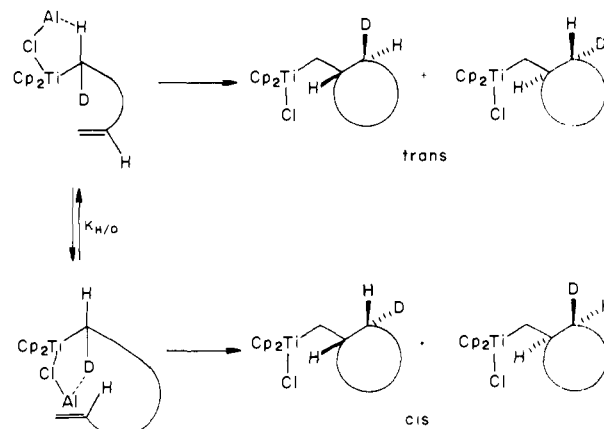
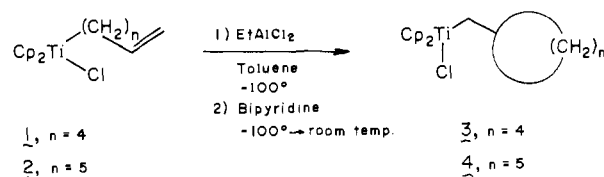


Figure 1.

The first of our approaches required the measurement of a precise kinetic isotope effect on the polymerization of ethylene.⁵ Since no kinetic isotope was observed, the Cossee mechanism was favored since it does not involve α -H activation. However, due to the complexity of the catalytic system and the possibility of the masking of the key carbon-carbon bond-forming step, a more direct approach to the problem was sought. Since in the polymerization of an α -olefin the stereochemistry is set in the carbon-carbon bond-forming step, a system has been developed that will show an *isotope effect on the stereochemistry* of olefin insertion if the α -hydrogens are involved in this key reaction. This is the most direct and precise method to probe for such a C-H interaction.

The best studied of the original Ziegler-type systems is the titanocene ethyl chloride/ethylaluminum dichloride catalyst.⁶ Thus, a series of titanocene alkenyl chlorides were prepared.⁷ The



pendant olefin, appropriately situated for Lewis acid induced intramolecular insertion, provides a high local concentration while maintaining a 1:1 stoichiometry of olefin to metal center. These alkenyl chlorides are stable for long periods at room temperature but cyclize to the corresponding titanocene metallocycloalkanes on treatment with 1-10 equiv of ethylaluminum dichloride at -100

(3) Watson, P. L. *J. Am. Chem. Soc.* 1982, 104, 337.

(4) Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* 1983, 105, 4942.

(5) Soto, J.; Steigerwald, M.; Grubbs, R. H. *J. Am. Chem. Soc.* 1982, 104, 4479. Arguments in this paper suggest that isotopic effects of >1.5 are expected.

(6) Ziegler, K.; Gellert, H. G.; Zosel, K.; Holzkamp, E.; Schneider, J.; Soll, M.; Kroll, W. R. *Ann. Chem.* 1960, 629, 121.

(7) (a) Compounds 1-4 were prepared by treating Cp_2TiCl_2 with the appropriate Grignard reagent at $-30^\circ C$ in THF. After 10 min the solution is warmed to room temperature and stirred for 2 h. After 10 min the solution is concentrated and hexane, the solution is filtered and cooled to $-50^\circ C$ to give red needles in all cases. 1: 1H NMR (C_6D_6) δ 1.0-1.8 (m, 4 H), 1.5 (s, br, 2 H), 2.0 (q, 2 H), 4.97 (d, 1 H, $J = 1$ Hz), 5.12 (dd, 1 H, $J = 6$ Hz, 1 H), 5.85 (s, 10 H), 5.6-6.0 (unresolved dd under Cp peak, 1H); ^{13}C NMR (C_6D_6) δ 33.7, 34.5, 37.2, 72.1, 114.4, 115.6, 139.6. 2: 1H NMR (C_6D_6) δ 1.0-1.9 (m, 6 H), 1.57 (s, 2 H), 2.04 (q, 2 H), 4.97 (d, 1 H, $J = 1$ Hz), 5.12 (dd, 1H, $J = 6$ Hz, 1 H), 5.7-6.0 (unresolved dd under Cp peak, 1 H), 5.78 (s, 10 H); ^{13}C NMR (C_6D_6) δ 28.9, 34.4, 34.9, 37.8, 72.6, 114.4, 115.6, 139.4. (b) 4: 1H NMR (C_6D_6) δ 1.3-1.7 (m, 9 H), 1.66 (d, $J = 5.6$ Hz, 2 H), 5.81 (s, 10 H); ^{13}C NMR (C_6D_6) gated decoupled δ 25.3 (t, $^1J_{CH} = 125.9$ Hz, C(3) and C(4) of cyclopentyl), 37.2 [t, $^1J_{CH} = 131.8$ Hz, C(2) and C(5) of cyclopentyl], 48.3 [d, $^1J_{CH} = 127$ Hz, C(1) of cyclopentyl], 82.5 (t, $^1J_{CH} = 125$ Hz, C(α), 115.5 (d, $J = 174$ Hz, Cp), 4: 1H NMR (C_6D_6) δ 0.8-1.9 (m, 11 H), 1.52 (overlapping d, 2 H, α -CH), 5.81 (s, 10 H, Cp); ^{13}C NMR (C_6D_6) δ 26.8, 27.4, 37.2, 46.0, 82.5, 115.5. Yields of $\sim 90\%$ by 1H NMR based on integration with respect to an internal standard (1,2-dichloroethane) with no other products observed. The cyclized products were spectroscopically identical with the independently prepared authentic compounds.^{7a}

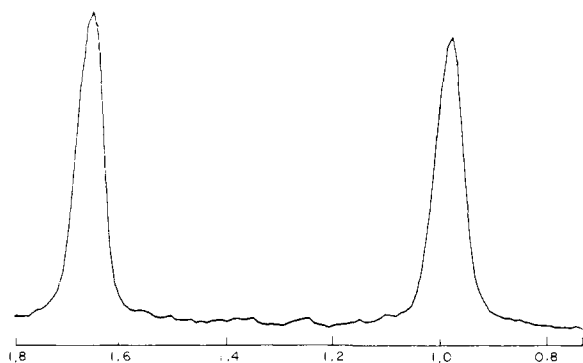


Figure 2. ^2H NMR spectrum of *cis*-methylcyclopentane-2- d_1 (δ 1.01) and *trans*-methylcyclopentane-2- d_1 (δ 1.68), the hydrolysis products obtained in the cyclization of **1**- d_1 .

$^\circ\text{C}$. Quenching with bipyridine at -100°C yields cyclized compounds that are stable at room temperature and can be obtained in greater than 90% yields. To demonstrate that the cyclization occurred under the same conditions as polymerization, the reaction of **1** with ethylaluminum dichloride cocatalyst was carried out in the presence of ethylene at -100°C . After rapid quenching, ethylene oligomers capped with cyclopentyl groups were obtained.⁸

Since this carefully designed polymerization system results in the insertion of an α -olefin into a titanium-carbon bond under polymerization conditions, the measurement of an isotope effect on stereochemistry of polymerization can be accomplished. This represents the most direct and precise method for the study of a step in a catalytic reaction in which a stereocenter is produced.

Insertion of an α -olefin into a metal alkyl bond that is monodeuterated at the α -position generates diastereomers as shown below for one enantiomer. Although there may be a kinetic isotope effect in the Cossee mechanism, the stereochemically determined isotope effect in this situation should be 1.0. If the α -hydrogens are involved in activation prior to insertion, the symmetry of the CHD is broken, and the ratio of diastereomers will reflect the ratio of C-H to C-D activation. This is demonstrated in Figure 1 for one enantiomer and one orientation of the inserting olefin. Choice of olefin orientation is unimportant in the example since, if α -activation is important, *one direction of attack* by the olefin will be highly favored. This is particularly true in this case, since bicyclic transition states are involved. Consequently, if α -CH activation is important in M-C activation and in the control of stereochemistry, the ratio of diastereomers should not equal 1; i.e., there will be an isotope effect reflected in the diastereomer ratio.⁵

This isotope effect on the stereochemistry was measured using the titanocene alkenyl chlorides described above. Cyclization of the α -deuterated analogue at -100°C using EtAlCl_2 produces *cis*-*trans* diastereomers, as shown above. The ^2H spectra of the isomeric organometallic products, as well as the *cis* and *trans* methylcycloalkanes which result from protonolysis of the organometallic are readily distinguishable at 76 MHz.^{9,10} In all cases, the ratio of *cis* to *trans* isomers is 1.00 ± 0.05 (Figure 2). This result demonstrates that α -activation is not a significant effect in either the rate or stereochemistry of this olefin insertion reaction which takes place under polymerization conditions in a polymerization system.

Although Ziegler polymerization and olefin metathesis have been linked from the beginning as related processes, it is now

(8) The oligomers were analyzed by GC-MS and by capillary GC, using authentic products for comparison.

(9) ^2H NMR analysis of the hydrolysis products of the cyclization with **1**- d_1 showed a 1:1 mixture of *cis*-methylcyclopentane-2- d_1 (δ 1.01) and *trans*-methylcyclopentane-2- d_1 (δ 1.68). This is in agreement with literature values. Lipnick, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 2941.

(10) After quenching with bpy, the organometallic product from the cyclization with **2**- d_1 was analyzed by ^2H NMR. The spectrum showed a 1:1 mixture of the *trans* and *cis* products at δ 1.54 and 0.69, respectively. Hydrolysis of the mixture gave again a 1:1 mixture of *trans*-methylcyclohexane-2- d_1 (δ 1.60) and *cis*-methylcyclohexane-2- d_1 (δ 0.80).

apparent from this work and our metathesis studies with titanocene systems that the basic steps are different. Metathesis is the chemistry of titanium carbon double bonds while Ziegler polymerization is that of titanium carbon single bonds.

Acknowledgment. Support of the National Science Foundation (CHE-8214668) and the Southern California Regional NMR Facility (CHE-7916324) is gratefully acknowledged.

2,2-Dimesityl-1-(2,4,6-tri-*tert*-butylphenyl)germaphosphene: The First Stable Compound with a Germanium-Phosphorus Double Bond[†]

Jean Escudie,* Claude Couret,* Jacques Satge,*
Mbolatiana Andrianarison, and
Jean-Dominique Andriamizaka

Laboratoire de Chimie des Organominéraux
U.A. du CNRS No. 477, Université Paul Sabatier
31062 Toulouse, France

Received December 28, 1984

Currently, there is great deal of interest in group 14 and 15 elements in low coordination states. In organophosphorus and organogermanium chemistry, several very interesting new compounds with $p\pi-p\pi$ bonds between heteroatoms have been reported: $\text{P}=\text{C}$,¹ $\text{P}=\text{N}$,^{1b} $\text{P}=\text{P}$,^{2,3} $\text{P}=\text{As}$,² $\text{P}=\text{Sb}$,² and $\text{Ge}=\text{Ge}$.⁴

It seems quite evident that the stability of these compounds is intimately related to the accessibility of the double bond. Indeed, such compounds could be stabilized when reactive sites are protected by bulky substituents.

Metallaphosphenes [$>\text{M}=\text{P}-$, M = group 14 (Si, etc.)] have long been speculated as reactive intermediates and could only be characterized by trapping reactions (M = Si,⁵ Ge,⁶ Sn⁷). Very recently, the first stable silaphosphene ($>\text{Si}=\text{P}-$) has been reported.⁸

In the present paper, we describe the synthesis of 2,2-dimesityl-1-(2,4,6-tri-*tert*-butylphenyl)germaphosphene (**1**), the first stable compound containing a germanium-phosphorus double bond. The highly air-sensitive germaphosphene **1** has been isolated in pure form and characterized by its physicochemical data and its expected trend in chemical reactivity.

The first step in the synthesis of **1** involves the preparation in nearly quantitative yields of (halo)germylphosphines **5** by addition of the lithiophosphine **3** [prepared by reacting *tert*-butyllithium (1.6 M in pentane) with (2,4,6-tri-*tert*-butylphenyl)phosphine (**2**)]

[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)

(1) For a review, see: (a) Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1980**, *20*, 731-744. (b) Fluck, E. *Top. Phosphorus Chem.* **1980**, *10*, 193-284.

(2) For a review, see: Cowley, A. H. *Polyhedron* **1984**, *3*, 389-432. Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Mehrotra, S. K.; Norman, N. C.; Pakulski, M.; Whittlesey, B. R.; Atwood, J. L.; Hunter, W. E. *Inorg. Chem.* **1984**, *23*, 2582-2593.

(3) See also: Escudie, J.; Couret, C.; Ranaivonjatovo, H.; Satge, J.; Jaud, J. *Phosphorus Sulfur* **1983**, *17*, 221-235. Escudie, J.; Couret, C.; Ranaivonjatovo, H.; Satge, J. *J. Chem. Soc., Chem. Commun.* **1984**, 1621-1622.

(4) For a review, see: Satge, J. *Adv. Organomet. Chem.* **1982**, *21*, 241-287. Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141-177. See also: Hitchcock, P. B.; Lappert, M. F.; Miles, J. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 480-482. Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* **1984**, *25*, 4191-4194.

(5) Couret, C.; Escudie, J.; Satge, J.; Andriamizaka, J. D.; Saint-Roch, B. *J. Organomet. Chem.* **1979**, *182*, 9-15.

(6) Couret, C.; Satge, J.; Andriamizaka, J. D.; Escudie, J. *J. Organomet. Chem.* **1978**, *157*, C35-C39. Escudie, J.; Couret, C.; Satge, J.; Andriamizaka, J. D. *Organometallics* **1982**, *1*, 1261-1265.

(7) Couret, C.; Andriamizaka, J. D.; Escudie, J.; Satge, J. *J. Organomet. Chem.* **1981**, *208*, C3-C5.

(8) Smit, C. N.; Lock, F. M.; Bickelhaupt, F. *Tetrahedron Lett.* **1984**, *25*, 3011-3014.