Catalytic Isomerization and Disproportionation of Olefins Promoted by Group 4/d⁰ Benzamidinate Complexes

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Abstract: The group 4/d⁰ benzamidinate complexes *cis*-[*p*-CH₃-C₆H₄C(NSiMe₃)₂]₂Zr(CH₃)₂ (**1**), C_3-tris([*N*-trimethylsilyl][*N′*-myrtanyl]benzamidinate)zirconium chloride (**2**) and *cis*-[*p*-CH₃C₆H₄C(NSiMe₃)₂]₂Ti(CH₃)₂ (**3**) were found to be active catalytic precursors, in the presence of MAO (methylalumoxane), for the isomerization of aliphatic olefins (1-octene, 2-*E*-octene, 3-methyl-1-butene, 2-methyl-1-butene, allylbenzene) and the disproportionation of 1,4- and 1,3-cyclohexadienes. The active species was found to be the cationic hydride complex obtained for aliphatic olefins by the insertion of the methyl ligand with concomitant β-hydrogen elimination, and for the alicyclic dienes by an activation of the allylic hydrogen and accompanying elimination of methane. Kinetic studies and Eyring analysis for the isomerization of allylbenzene show that the reaction is first order in both complex and olefin with $\Delta H^\dagger = 17.8(6)$ kcal·mol⁻¹ and $\Delta S^\dagger = -25.1(2)$ eu. These findings support the epimerization mechanism proposed for these types of cationic complexes, in the polymerization of propylene, toward isotactic polypropylene. To the best of our knowledge, this is the first study in which high oxidation state group 4 complexes are able to induce the catalytic isomerization of olefins or the disproportionation of cyclic olefins.

Introduction

Recently, increased attention has been given to the chemistry of complexes containing non-Cp-spectator ligands, such as chelating benzamidinate complexes.[1,2] For early-transition complexes, the bis(benzamidinate) dichloride group 4 complexes (**A**) are obtained as racemic mixtures of C_2-symmetry *cis*-

Ar = CH₃C₆H₄
R′ = R = TMS
M = Zr (**1**), Ti (**3**)

R = TMS
R′ = [myrtanyl group]
M = Zr (**2**)
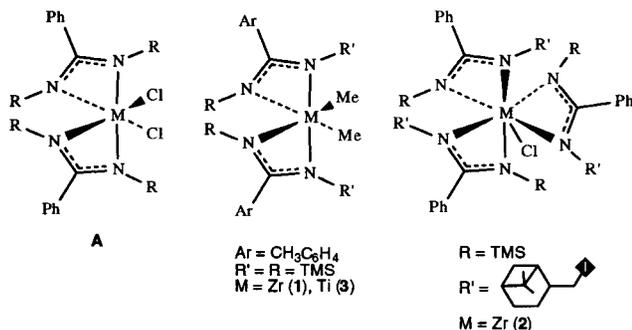
octahedral structures and, when activated with methyl alumoxane (MAO), were found to produce active catalytic cationic complexes for the polymerization of ethylene, propylene, norbornene, and for the cyclooligomerization of 1,5 hexadiene.[3]

Interestingly, we have shown that, when the polymerization was carried out at atmospheric pressure, polypropylene was produced as an atactic oil, instead of the expected isotactic

polymer. When the polymerization was conducted at high monomer concentration, a highly isotactic polypropylene (mmmm > 99%, mp = 153 °C) was obtained.[4] The resulting atactic polypropylene was mechanistically rationalized by an intramolecular epimerization reaction of the growing polypropylene chain at the last inserted monomeric unit. This was found to be faster (at low monomer concentrations) than the stereoregular insertion of propylene (Scheme 1a).[5]

Additional corroboration indicating that the mechanism presented in Scheme 1a is responsible for the stereo defects in

(2) For group 4 complexes, see: (a) Müeller, E.; Müeller, J.; Olbrich, F.; Bruser, W.; Knapp, W.; Abeln, D.; Edelmann, F. T. *Eur. J. Inorg. Chem.* **1998**, 87. (b) Stewart, P. J.; Blake, A. J.; Mountford, P. *Organometallics* **1998**, *17*, 3271. (c) Hagardon, J. R.; Arnold, J. *Organometallics* **1998**, *17*, 1355. (d) Hagardon, J. R.; Arnold, J. *Inorg. Chem.* **1997**, *36*, 2928. (e) Ciruelo, G.; Cuenca, T.; Gomez, R.; Gomez-Sal, P.; Martin, A.; Rodriguez, G.; Royo, P. *J. Organomet. Chem.* **1997**, *547*, 287. (f) Hagardon, J. R.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **1997**, 3087. (g) Richter, J.; Belay, M.; Brieser, W.; Edelmann, F. T. *Main Group Met. Chem.* **1997**, *20*, 191. (h) Hagardon, J. R.; Arnold, J. *J. Am. Chem. Soc.* **1996**, *118*, 893. (i) Gomez, R.; Green, M. L. H.; Haggitt, J. L. *J. Chem. Soc., Dalton Trans.* **1996**, 939 and references therein. For group 5 complexes, see: (j) Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics*, **1998**, *17*, 4090. (k) Stewart, P. J.; Blake, A. J.; Mountford, P. *Inorg. Chem.* **1997**, *36*, 1982. (l) Dawson, D. Y.; Arnold, J. *Organometallics*, **1997**, *16*, 1111. For group 13 complexes, see: (m) Duchateau, R.; Meetsma, A,; Teuben, J. H. *J. Chem. Soc., Chem. Comun.* **1996**, 223. (n) Barker, J.; Blacker, N. C.; Phillips, P. R.; Alock, N. W.; Errington, W.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1996**, 431.

(3) (a) Richter, J.; Edelmann, F. T.; Noltemeyer, M.; Schmidt, H.-G.; Shmulinson, M.; Eisen, M. S. *J. Mol. Catal. Part A* **1998**, *130*, 149. (b) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1995**, *14*, 1827. (c) Walther, D.; Fischer, R.; Görls, H.; Koch, J.; Schweder, B. *J. Organomet. Chem.* **1996**, *508*, 13. (d) Walther, D.; Fischer, R.; Friedrich, F.; Gebhardt, P.; Görls, H. *Chem. Ber.* **1996**, *129*, 1389. (e) Gómez, R.; Duchateau, R.; Chernega, A. N.; Meetsma, A.; Edelmann, F. T.; Teuben, J. H.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1995**, 217. (f) Herskovics-Korine, D.; Eisen, M. S. *J. Organomet. Chem.* **1995**, *503*, 307.

(4) Volkis, V.; Shmulinson, M.; Averbuj, C.; Lisovskii, A.; Edelmann, F. T.; Eisen, M. S. *Organometallics* **1998**, *17*, 3155.

(1) For some group 3 and lanthanide complexes, see: (a) Edelmann, F. T.; Richter, J. *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 157. (b) Hagardon, J. R.; Arnold, J. *Organometallics* **1996**, *15*, 984. (c) Edelmann, F. T. *Top. Curr. Chem.* **1996**, *179*, 113 and references therein. (d) Duchateau, R.; van Wee, C. T.; Meetsma, A.; van Duijnen, P. Th.; Teuben, J. H. *Organometallics* **1996**, *15*, 2279. (e) Duchateau, R.; van Wee, C. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2291. (f) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403 and references therein.

Scheme 1. (a) Proposed Mechanism for the Intramolecular Epimerization Reaction of the Growing Polypropylene Chain at the Last-inserted Monomeric Unit and (b). Plausible Mechanism for the Expected Isomerization of Olefins

(a)

(b)
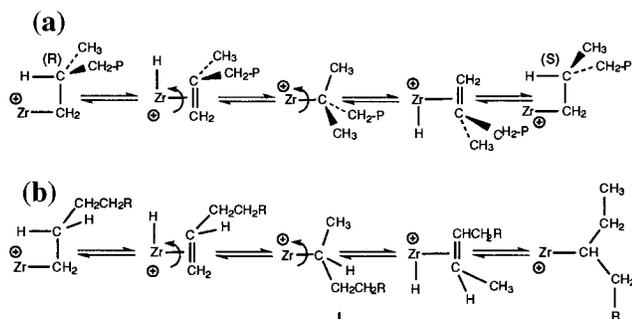
polypropylene obtained by C_2-symmetry early transition metal octahedral complexes was obtained by reacting the active benzamidinate early transition metal hydride complexes with an α-olefin which has an extremely low rate of polymerization (Scheme 1b).

Thus, a β-hydrogen elimination is expected to occur either from the terminal methyl group at the α-position in complex **1** (Scheme 1b), causing no change in the alkene, or from the α-position at the chain (CH_2-CH_2-R group), inducing isomerization of the double bond. The efficacy of complementary symmetric octahedral "template" ligation or even that of a C_3 ligation, raises conceptual questions of applicability to the isomerization of double bonds promoted by group IV/d^0 complexes. In this paper we report the reactivity and selectivity of some well-defined early transition metal *rac*-benzamidinate complexes with C_2- and C_3-symmetry in the isomerization and disproportionation of alkenes. In addition to kinetic, thermodynamic, and mechanistic studies, we present here the spectroscopic characterization of the products obtained in stoichiometric reactions, allowing a rationalization of some of the key organometallic intermediates. To the best of our knowledge, this is the first example in which organometallic group 4/d^0 complexes are able to perform catalytic isomerization and disproportionation of alkenes.[6]

Results and Discussion

The reaction of *cis*-[*p*-CH_3-C_6H_4C($NSiMe_3$)$_2$]$_2$Zr(CH_3)$_2$ (**1**)[4] or C_3-tris([*N*-trimethylsilyl][*N*′-myrtanyl]benzamidinate)zirconium chloride (**2**)[7] with an excess of MAO in toluene (catalyst: MAO = 1:400) catalyzes the isomerization of 1-octene (cat: olefin = 1:180; TON = ca. 25 h^{-1} at 90 °C) yielding 2-(*E*)-

octene, 2-(*Z*)-octene, 3-(*E*)-octene, and 4-(*E*)-octene (Table 1, entries 1, 2). The Z-isomer was formed exclusively with 2-octene indicating that the enthalpy of activation toward both geometrical isomers is similar. Starting from the 2-(*E*)-octene isomer (Table 1, entries 3, 4), the isomerization proceeds toward the 3-(*E*)-octene and 4-(*E*)-octene products as well as similar amounts of 2-(*Z*)-octene, as found for the reaction with 1-octene, but without traces of 1-octene. This result strongly argues for an equilibrium between the two 2-octene isomers. Moreover, for complex **1**, the amount of the different isomerization products for either starting alkene is similar, supporting the equilibrium process proposed in Scheme 1b.

The isomerization of 3-methyl-1-butene yields the two possible isomers 2-methyl-2-butene and 2-methyl-1-butene. We have also studied the isomerization of 2-methyl-1-butene to investigate if 2-methyl-1-butene is formed via the consecutive isomerization from 2-methyl-2-butene. Thus, the isomerization of 2-methyl-1-butene affords 2-methyl-2-butene in almost the same yield (72%) as does 3-methyl-1-butene (Table 1, entries 5, 6), again supporting an equilibrium between the different products, as expected from Scheme 1b. In Scheme 1b, the cationic hydride complex is proposed as the active species, whereas our starting isomerization catalysts are the corresponding alkyl complexes.[8] We decided to study the formation of this hydride complex, by performing the reaction with a small excess of olefin. In the reaction of complex **1** with MAO and 5 equiv of 1-octene, similar stoichiometric amounts of 2-(*E*)-nonene and 3-(*E*)-nonene were trapped and characterized. This result clearly indicates that the methyl complex inserts regioselectively into the olefin followed by a β-hydrogen elimination leading to the formation of the active hydride complex (eq 1).[9]

(1)
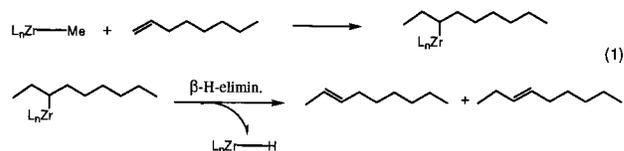
We decided to investigate whether this catalyst might isomerize cyclic 1,3- and 1,4-dienes and induce their disproportionation reactions to aromatic compounds. Reaction of 1,4-cyclohexadiene with **1**/MAO does indeed give benzene, cyclohexene, and cyclohexane with no trace formation of the conjugated 1,3-isomer or the methylated cyclic compounds (Table 1, entry 7). In contrast, for 1,3-cyclohexadiene, in addition to the disproportionation products, 1,4-cyclohexadiene, saturated and unsaturated dimers, trimers, and tetramers were also found. A plausible mechanism for the disproportionation of 1,4-cyclohexadiene is described in Scheme 2. In this mechanism, the cationic form of complex **1**, which was obtained by the reaction of **1** and MAO,[4] is activated by the allylic hydrogen, producing methane and the active cyclohexadienyl complex **B**. Elimination of a hydrogen in a 1,4-fashion[10] produce benzene and the hydride complex **C**. Complex **C** may either insert into 1,4-cyclohexadiene or cyclohexene, forming complex **D** or **E**, respectively. Allylic activation of complex **D** or **E** by 1,4-cyclohexadiene allows the formation of cyclohexene and cyclohexane, respectively.

(5) (a) Busico, V.; Cipullo, R.; Caporaso, L.; Angelini, G.; Segre, A. L. *J. Mol. Catal. Part A* **1998**, *128*, 53 and references therein. (b) Busico, V.; Brita, D.; Caporaso, L.; Cipullo, R.; Vacatello, M. *Macromolecules* **1997**, *30*, 3971. (c) Busico, V.; Caporaso, L.; Cipullo, R.; Landriani, L.; Angelini, G.; Margonelli, A. Segre, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 2105. (d) Leclerc, M.; Brinzinger, H. H. *J. Am. Chem. Soc.* **1996**, *118*, 9024 and references therein. (e) Leclerc, M.; Brinzinger, H. H. *J. Am. Chem. Soc.* **1995**, *117*, 1651. (f) Busico, V.; Cipullo, R. *J. Am. Chem. Soc.* **1994**, *116*, 9329.

(6) The stoichiometric isomerization of olefins via the hydrozirconation reaction is well-known, see: (a) Schwartz, J. *Pure Appl. Chem.* **1980**, *52*, 733 and references therein. (b) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333 and references therein. (c) Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115. For group 4 complexes, the catalytic isomerization of alkenes is known only for low-valent complexes, see: (a) Ohff, A.; Burlakov, V. V.; Rosenthal, U. *J. Mol. Catal. Part A* **1996**, *105*, 103. (b) Rao, S. A.; Periasamy, M. *J. Organomet. Chem.* **1988**, *342*, 15 (c) Yanlong, Q.; Jiaqui, L.; Weihua, X. *J. Mol. Catal.* **1986**, *34*, 31. (d) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136.

(7) Averbuj, C.; Tish, E.; Eisen, M. S. *J. Am. Chem. Soc.* **1998**, *120*, 8640.

(8) See refs 4 and 7 for the formation of the corresponding cationic benzamidinate complexes.

(9) 2-Methyl-1-octene is also an expected isomer although it was not detected either due to a difference in reactivity favoring the 2,1-insertion or because the methyl elimination of such an organometallic moiety is much faster than the β-hydrogen elimination. For the polymerization of propylene catalyzed by octahedral complexes we have shown that the methyl elimination is the only effective termination pathway at atmospheric pressure. See ref 4.

Table 1. Distribution Ratio for the Isomerization of Olefins Promoted by Benzamidinate Complexes Activated with MAO

entry	catalyst	substrate	products (%)			
1	**1**	1-octene	2-(*Z*)-octene (15.9)	2-(*E*)-octene (24.3)	3-(*E*)-octene (41.3)	4-(*E*)-octene (18.5)
2	**2**	1-octene	2-(*Z*)-octene (20.3)	2-(*E*)-octene (53.4)	3-(*E*)-octene (23.8)	4-(*E*)-octene (2.5)
3	**1**	2-*E*-octene	2-(*Z*)-octene (13.5)	2-(*E*)-octene (27.0)	3-(*E*)-octene (41.6)	4-(*E*)-octene (17.9)
4	**2**	2-*E*-octene	2-(*Z*)-octene (14.3)	2-(*E*)-octene (31.2)	3-(*E*)-octene (37.8)	4-(*E*)-octene (16.7)
5	**1**	3-methyl-1-butene	2-methyl-2-butene (76.0)	2-methyl-1-butene (24.0)		
6	**1**	2-methyl-1-butene	2-methyl-2-butene (72.0)	2-methyl-1-butene (28.0)		
7	**1**	1,4-cyclohexadiene	benzene (55.5)	cyclohexene (43.1)	cyclohexane (1.4)	
8	**1**	1,3-cyclohexadiene	benzene (24.3)	cyclohexene (21.1)	cyclohexane (4.3)	1,4-cyclohexadiene (4.1) dimers (20.4) trimers (17.7) tetramers (8.1)
9	**1**	allylbenzene	*trans*-β-methylstyrene (68.0)	*cis*-β-methylstyrene (32.0)		
10	**2**	allylbenzene	*trans*-β-methylstyrene (90.0)	*cis*-β-methylstyrene (10.0)		
11	**3**	allylbenzene	*trans*-β-methylstyrene (100)			

Scheme 2. Plausible Mechanism for the Disproportionation of 1,4-Cyclohexadiene

It is important to point out the mechanistic difference between the two cyclic dienes. The insertion of 1,3-cyclohexadiene with complex **C** may follow two routes: (1) preferential formation of the allylic organometallic moiety **F**, which seems to be responsible for the formation of higher oligomers, or (2) formation of the intermediate **D**. β-hydrogen elimination from complex **D** will yield 1,4-cyclohexadiene and the starting hydride complex **C** (eq 2). [11]

We have observed two different pathways that are effective for *rac*-octahedral benzamidinate complexes yielding the cationic active hydride complex. For aliphatic alkenes, an insertion reaction between the Zr—CH$_3$ complex and the double bond followed by β-hydrogen elimination; and for alicyclic dienes,

activation of the allylic hydrogen in the starting substrate with the concomitant elimination of methane. A final question concerns the mechanistic pathway for an alkene, such as allylbenzene, with both a benzylic and an allylic position. Thus, the isomerization of allylbenzene to *cis*- and *trans*-β-methylstyrene was studied with complexes **1**, **2**, and with the analogous complex *cis*-[*p*-CH$_3$-C$_6$H$_4$C(NSiMe$_3$)$_2$]$_2$Ti(CH$_3$)$_2$ (**3**) (Table 1, entries 9–11). In contrast to the well-known isomerization of allylbenzene catalyzed by late transition metal complexes in which the isomerized products are in equilibrium,[12] no equilibrium between the products is achieved for our octahedral complexes (entries 9 and 11). This result indicates that the insertion of the cationic hydride complex does not occur at the conjugated double bonds, but only with the starting material. To elucidate which of the two possible mechanisms is responsible for the formation of the hydride complex, the reaction of complex **1**/MAO and 10 equiv of allylbenzene was carried out. Besides the expected isomerization products, 1-phenyl-2-butene, 1-phenyl-1-butene, and 2-methyl-3-phenyl-1-propene were obtained in similar amounts (ca. 30–34%), with no traces of methane. The formation of these three compounds is in agreement with insertion of the methyl ligand into the double bond of the starting allylbenzene with no regioselectivity and the subsequent β-hydrogen elimination, producing the cationic hydride complex (eq 3).

Kinetic measurements on the isomerization of allylbenzene with **1** were undertaken by in situ ^{1}H NMR spectroscopy. The reaction was monitored with constant catalyst concentration until complete substrate consumption. The disappearance of the benzylic ^{1}H resonance (doublet at $\delta = 3.10$ ppm) and the appearance of the methyl ^{1}H resonance of the product (doublet at $\delta = 2.08$ ppm) were followed and normalized. The kinetic shows a linear dependence of the rate of the reaction on allylbenzene concentration over a ~10-fold substrate concentration range, which indicates a first order dependence of the catalytic rate on substrate concentration under these conditions (Figure 1).

(10) The 1,4-elimination producing benzene is favored over an isomerization of the organometallic complex with consecutive 1,2-elimination. If isomerization occurs before the elimination, an intermediate complex similar to the one obtained for the disproportionation of 1,3-cyclohexadiene would be expected, leading also to oligomeric products. For favoring 1,4-eliminations over 1,2-eliminations in alicyclic compounds see: Mandelbaum, A. *Mass Spectrom. Rev.* **1983**, *2*, 223.

(11) In Scheme 2, the allylic activation of either complexes **D** and **E** by cyclohexene is possible, although it seems not to be a competing reaction since complex **F** would be formed allowing oligomerization products.

(12) Crabtree, R. H. In *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons Inc.: New York, 1988; Chapter 9.

(13) No isomerization products were observed in blank reactions, performed under the same conditions, for both olefin and cyclic olefins with MAO.

Figure 1. Plot of the observed reaction rate vs allylbenzene concentration for the isomerization of allylbenzene with complex **1** as the precatalyst in toluene-d_8. The line represents the least-squares fit to the data points.
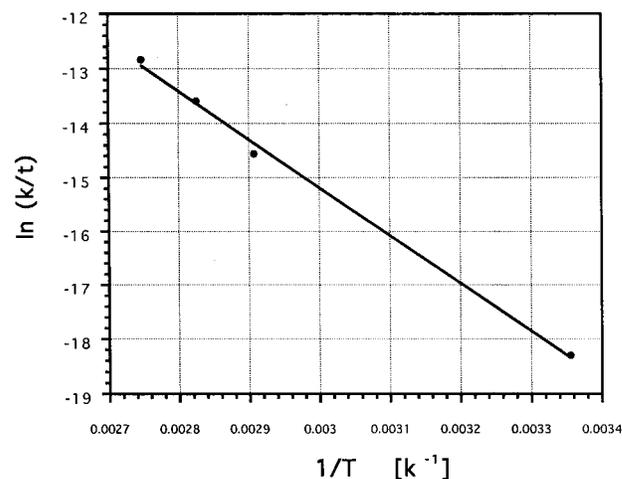

Figure 2. Plot of the observed reaction rate vs catalyst concentration for the isomerization of allylbenzene with complex **1** as the precatalyst in toluene-d_8. The line represents the least-squares fit to the data points.

When the concentration of the allylbenzene is maintained constant and the concentration of the precatalyst is varied over a 10-fold concentration range, a plot of reaction rate vs precatalyst concentration indicates that the reaction is first-order dependent in precatalyst (Figure 2).

The rate law expression for the isomerization of allylbenzene promoted by the precatalyst **1** is given by eq 4.

$$\nu = k[L_nZr\text{-}H]^1[\text{allylbenzene}]^1 \qquad (4)$$

An enthalpy of activation, $\Delta H^{\ddagger} = 17.8$ (6) kcal·mol^{-1}, and a large negative entropy of activation, $\Delta S^{\ddagger} = -25.1$ (2) e.u., characterize the activation parameters derived from an Eyring analysis for the isomerization of allylbenzene (Figure 3). These parameters suggest a highly ordered transition state with considerable bond making to compensate for bond breaking.

A plausible mechanism for the isomerization of allylbenzene is given in Scheme 3. This mechanism consists of two well-established elementary reactions: (1) insertion of a hydride M−H σ-bond as a turnover-limiting step and (2) rapid β-hydrogen elimination of the products.

Figure 3. Eyring plot for the isomerization of allylbenzene to *trans*-β-methylstyrene with complex **1** as the precatalyst in toluene-d_8. The line represents the least-squares fit to the data points.

Scheme 3
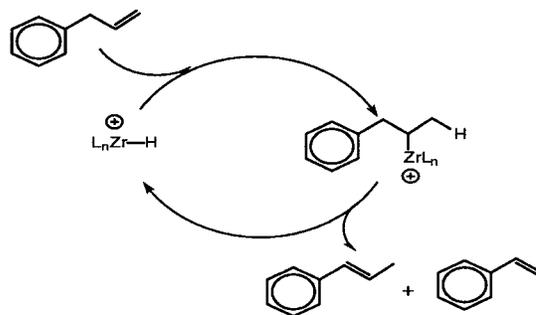
The results presented here demonstrate for the first time that early transition metal octahedral cationic complexes are active catalysts for the isomerization of alkenes by a mechanism that consists of several Zr−H insertions and β-hydrogen eliminations to the most stable alkene (Saytzeff rule). In addition, these complexes are active in the disproportionation of cyclic dienes, producing the active cationic hydride species by a mechanism that consists of activation of an allylic hydrogen in the starting diene with the concomitant elimination of methane.

Experimental Section

Materials and Methods. All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line, or interfaced to a high-vacuum (10^{-5} Torr) line, or in a nitrogen-filled Vacuum Atmospheres glovebox with a medium capacity recirculator (1−2 ppm O$_2$). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Hydrocarbon solvents (toluene-d_8, benzene-d_6) were distilled under nitrogen from Na/K alloy. All solvents for vacuum line manipulations were stored in vacuo over Na/K alloy in resealable bulbs. α-Olefins (1-octene, 2-octene, 1,3- and 1,4-cyclohexadiene, 3-methyl-1-butene, 2-methyl-1-butene, and allylbenzene) (Aldrich) were dried and stored over activated molecular sieves (4 Å), degassed, and freshly vacuum-distilled. Complexes **1**, **2**, and **3** were prepared according to literature procedures.[4] NMR spectra were recorded on Bruker AM 200 and Bruker AM 400 spectrometers. Chemical shifts for ^{1}H-NMR and ^{13}C-NMR are referenced to internal solvent resonances and are reported relative to tetramethylsilane. GC/MS experiments were conducted in a

(14) (a) *The Aldrich Library of NMR Spectra*; Pouchert, C. J., II, Ed.; Aldrich Chemical Co.: Milwaukee, WI; 1983; Vols. 1, 2. (b) *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*; Pouchert, C. J., Behnke, J. Eds.; Aldrich Chemical Co.: Wilwaukee, WI; 1993.

GCMS (Finnigan Magnum) spectrometer. The NMR experiments were conducted in Teflon valve-sealed tubes (J-Young) after vacuum transfer of the liquids in a high-vacuum line.

Kinetic Study of the Isomerization of Allylbenzene. In a typical experiment, a NMR sample was prepared as described in the typical NMR scale catalytic reactions section but maintained at −78 °C until kinetic measurements were started. The sealed tube was heated in a temperature-controlled oil bath and at suitable time intervals NMR data were acquired using eight scans with a long pulse delay to avoid saturation of the signal. The kinetic studies were usually monitored by the intensity changes in the substrate resonances and in the product resonances over 3 or more half-lives. The substrate concentration (C) was measured from the area (A_s) of the [1]H-normalized signal of the solvent (A_b). All the data collected could convincingly fit ($R > 0.98$) by least squares to eq 5 where C_o ($C_o = A_{so}/A_{bo}$) is the initial concentration of substrate and C (A_s/A_b) is the substrate concentration at time, t.

$$mt = \log(C/C_o) \tag{5}$$

The ratio of catalyst to substrate was accurately measured by using stock solutions of both catalyst and substrate. Turnover frequencies (N_t, h^{-1}) were calculated from the least-squares slope (m) of the resulting plots. Typical initial olefin concentrations were in the range 0.42−4.2 M and typical catalyst concentrations were in the range 7.9−7.7 mM.

General Procedure for the Catalytic Isomerization of α-Olefins and the Disproportionation of Cyclic Dienes. In a typical procedure, the specific amount of an olefin or a cyclic diene was vacuum transferred into an J-Young NMR tube containing 10 mg of the specific catalyst and a specific amount of MAO (keeping the ratio catalyst: MAO:olefin as 1:400:180) in 0.6 mL of toluene-d_8.[13] The sealed tube was then heated in an oil bath at 85 °C for 6 h. The organic products were vacuum transferred (10^{-6} mmHg) to another J-Young NMR tube and sealed, and both residue and volatiles were characterized by ^{1}H- and ^{13}C-NMR and 2D-NMR spectroscopy and GC-MS spectroscopy and by comparing with known compounds.[14]