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# Highly Stereoselective Isomerization of Monosubstituted 1-Alkenes to (*E*)-2-Alkenes by Catalysis of $(C_5Me_5)_2TiCl_2/NaC_{10}H_8$

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The catalyst systems which consist of $MCl_2(C_5R_5)_2$(M=Ti, Zr; R=H, $CH_3$)/$NaC_{10}H_8$, *i*-$C_3H_7MgBr$, *n*-$C_4H_9Li$ or $LiAlH_4$ in 1 : 2 ratio were highly effective for the stereoselective isomerization of monosubstituted 1-alkenes to (*E*)-2-alkenes. Unconjugated dienes were converted to (*E*)- or (*E*,*E*)-dienes. The catalysis of $(C_5Me_5)$-$TiCl_2/NaC_{10}H_8$ was extremely high and resulted in the complete isomerization of 1-alkenes in >99% stereoselectivity within a short period. The use of the bulky $C_5Me_5$ ligand is essential to find out the excellent stereoselectivity. Systems, $(C_5H_5)_2TiCl_2/NaC_{10}H_8$ and $(C_5H_5)_2TiCl_2$/*i*-$C_3H_7MgBr$ showed less selectivity and the catalysis of the corresponding zirconium systems was very poor irrespective of the reducing agents and substrates.

Transition metal catalyzed isomerization of terminal olefins into internal olefins has been extensively studied with metal hydrides,[1] metal carbonyls[2] and others.[3] In general, these catalysts require relatively high temperatures (>50 °C) and result in a mixture of 1-alkenes, (*E*)- and (*Z*)-2-alkenes reflecting the thermodynamic equilibrium. The *Z*/*E* ratio varies in a wide range from 0.1 to 3.5. The reactions in some cases involve the carbon skeletal change[4] and the multiple double bond movement.[2a] Exceptional is [Ir(cyclooctadiene)$(PMePh_2)_2$]$PF_6$ which catalyzes isomerization of allyl ethers to (*E*)-1-propenyl ethers in extreme stereoselectivity at room temperature.[5a] Enantioselective isomerization of allylamines with a Rh(I) complex has also been reported recently.[5b]

We wish to report here the excellent catalysis of low valent titanocene species, "$(C_5Me_5)_2Ti$" and "$(C_5H_5)_2$-Ti", for highly stereoselective isomerization of 1-alkenes to (*E*)-2-alkenes under the mild conditions. Though titanocene species are generally accepted as efficient catalysts for hydrogenation[6] and hydrometalation of olefins,[7] the catalysis for isomerization of olefins has not yet been extensively studied except some works using $(C_5H_5)_2Ti$ species.[8] We found now that these species, especially $(C_5Me_5)_2Ti$, have a good catalysis toward the isomerization of 1-alkenes, allylamines and unconjugated dienes which lead to (*E*)-2-internal alkenes or (*E*,*E*)-dienes. The use of permethylcyclopentadienyl ligand was crucial to observe the high stereoselectivity.

## Results and Discussion

*Catalytic Isomerization of 1-Hexene to (*E*)-2-Hexene.* The catalysts used in this work were generated by reduction of $(C_5Me_5)_2TiCl_2$ (**1**), $(C_5H_5)_2TiCl_2$ (**2**), or $(C_5H_5)_2ZrCl_2$ (**3**) with two equivalents of sodium naphthalene ($NaC_{10}H_8$), *i*-$C_3H_7MgBr$, butyllithium, or $LiAlH_4$. Photolysis of $(C_5Me_5)_2Ti(p\text{-tolyl})_2$ (**4**), $(C_2H_5)_2Ti$-$(p\text{-tolyl})_2$ (**5**), and $(C_5H_5)_2Zr(p\text{-tolyl})_2$ (**6**) were also examined since ultraviolet ray irradiation to these complexes is known to generate low valent metallocene species.[9]

Catalyst systems
Ia $(C_5Me_5)_2TiCl_2/NaC_{10}H_8$
Ib $(C_5Me_5)_2TiCl_2$/*i*-$C_3H_7MgBr$
Ic $(C_5Me_5)_2TiCl_2$/*n*-$C_4H_9Li$
Id $(C_5Me_5)_2TiCl_2/LiAlH_4$
IIIa $(C_5H_5)_2ZrCl_2/NaC_{10}H_8$
IIIb $(C_5H_5)_2ZrCl_2$/*i*-$C_3H_7MgBr$
IIIc $(C_5H_5)_2ZrCl_2$/*n*-$C_4H_9Li$
IIId $(C_5H_5)_2ZrCl_2/LiAlH_4$

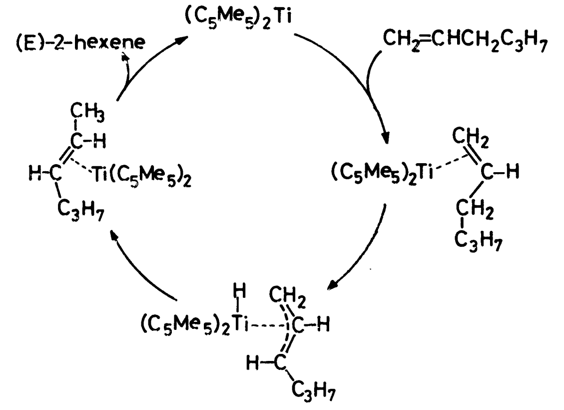
Catalyst systems
IIa $(C_5H_5)_2TiCl_2/NaC_{10}H_8$
IIb $(C_5H_5)_2TiCl_2$/*i*-$C_3H_7$-MgBr
IIc $(C_5H_5)_2TiCl_2$/*n*-$C_4H_9Li$
IId $(C_5H_5)_2TiCl_2/LiAlH_4$
Ie $(C_5Me_5)_2Ti(p\text{-tolyl})_2/h\nu$
IIe $(C_5H_5)_2Ti(p\text{-tolyl})_2/h\nu$
IIIe $(C_5H_5)_2Zr(p\text{-tolyl})_2/h\nu$

The result of isomerization of 1-hexene at 20 °C was listed in Table 1 as a typical example. The distribution of the products was determined by gas chromatographic analysis with authentic samples and the structure of the respective isomers was determined from the chemical shift values of the $^{13}C$-NMR spectra. The rate of isomerization was expressed as turnover max (mol/mol min) since these catalyst systems in many cases have an

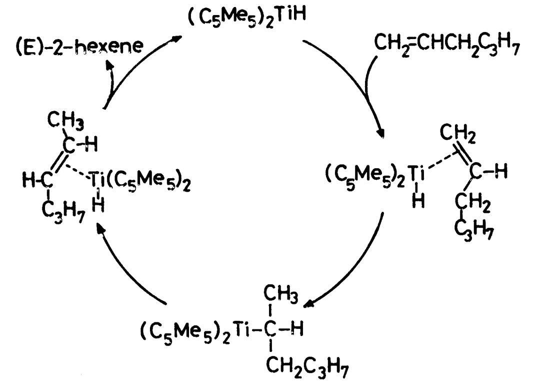
TABLE 1. DISTRIBUTION OF THE PRODUCTS OBTAINED BY ISOMERIZATION OF 1-HEXENE WITH CATALYST SYSTEMS Ia—e, IIa—e, AND IIIa—e AND THEIR RATE OF ISOMERIZATION[a]

| Reducing agent | Solvent | Distribution of (*E*)-2-hexene/(*Z*)-2-hexene/(*E*)-3-hexene(%) and turnover max (parentheses, mol/mol min) | | | | | |
|---|---|---|---|---|---|---|---|
| | | $(C_5Me_5)_2Ti$ System(I) | | $(C_5H_5)_2Ti$ System(II) | | $(C_5H_5)_2Zr$ System(III) | |
| (a) $NaC_{10}H_8$ | THF | 100/0/0 | (128) | 83/17/0 | (>4) | 97/3/0 | ($8\times10^{-3}$) |
| (b) *i*-$C_3H_7MgBr$ | Ether | 100/0/0 | (0.2) | 51/29/20 | (54) | 100/0/0 | ($4\times10^{-2}$) |
| (c) *n*-$C_4H_9Li$ | Ether | 100/0/0 | (0.4) | 73/18/9 | (77) | 99/1/0 | ($1\times10^{-2}$) |
| (d) $LiAlH_4$ | Ether | 100/0/0 | (0.1) | 66/17/17 | (1.3) | No isomerization[b] | |
| (e) $(C_5R_5)_2M(p\text{-tolyl})_2$ | Benzene | No isomerization | | 85/15/0 | (>7)[c] | 100/0/0 | ($2\times10^{-2}$)[c] |

a) Molar ratio of $(C_5R_5)_2MCl_2$(R: H, $CH_3$; M: Ti, Zr)/reducing agent/1-hexene was 1.0/2.0/200. Reaction was carried out at 20 °C for 1 h when Ia—e or IIa—e was used while the reaction with IIIa—e was done for 10 h. The ratio of 1-hexene to a solvent was 1.2/1.0 (v/v). b) Hydroalumination occurred. c) The reproducibility was invariably poor.



Scheme 1.



Scheme 2.

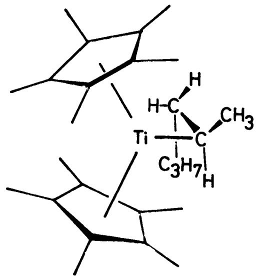
induction period (2—30 min).

1-Hexene was converted to (*E*)-2-hexene quantitatively when 1 mol-% of the catalyst system Ia—d which consists of **1** and $NaC_{10}H_8$(a), *i*-$C_3H_7MgBr$(b), *n*-$C_4H_9Li$(c) or $LiAlH_4$(d) in 1:2 ratio was added at 20 °C under atmospheric pressure. Catalysis of Ia was especially high in comparison to others and >98% of the substrate was converted to (*E*)-2-hexene within 5 min after the addition of the catalyst. The reaction of $(C_5Me_5)_2TiCl_2$ with $NaC_{10}H_8$ is reported to give "$(C_5Me_5)_2Ti$" which equilibrates with $(C_5Me_5)[(C_5(CH_3)_4(CH_2)]TiH$.[10)] Therefore, it seems most likely that the isomerization proceeds following the cycle given in Scheme 1. The coordination of 1-hexene to $(C_5Me_5)_2Ti$ occurs in the initial step and "($\eta^3$-allyl)TiH" species is produced by the successive $\beta$-hydride elimination. Liberation of 2-hexene results in the regeneration of $(C_5Me_5)_2Ti$. A similar $^3\eta$-allyltitanium hydride has been postulated as an intermediate in olefin hydrogenation[8a)] and, actually, $\eta^3$-allylhafnium hydride was recently isolated.[11)]

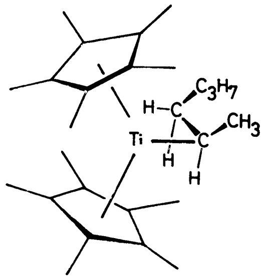
A similar catalytic cycle (1,3-hydrogen shift mechanism) has already been proposed for the isomerization of olefins catalyzed by a Pd(II) complex (though the selectivity was rather poor).[2a)] The coordination of liberated (*E*)-2-hexene to the metal is hindered by the steric effect of permethylcyclopentadienyl ligand. The selective formation of (*E*)-2-hexene may be ascribed to the preferential formation of *syn*-$\eta^3$-allylic titanium hydride species. The X-ray structure of $(C_5H_5)_2Ti$(*syn*-$\eta^3$-butenyl) supports this assumption.[12)]

In contrast to Ia, the turnover max for Ib, Ic and Id was remarkably small. Since the system IIb is known to afford $(C_5H_5)_2TiR$ which readily decomposes at ambient temperature to $(C_5H_5)_2TiH$ by $\beta$-hydride elimination,[13)] the isomerization with Ib—c is best interpreted by the conventional addition-elimination mechanism as shown in Scheme 2.[1c)] Actually, these systems have an induction period (5—30 min) before the largest turnover appears while the catalyst system Ia can initiate the isomerization immediately. Raising the reaction temperature to 60 °C (1—3 min) in the initial stage resulted in the shortening of the induction period which was observed for Ib—d.

Stereocontrol of the product will come from the predominant elimination of *threo*-hydrogen at the $\beta$-carbon. Two intermediates (A) and (B) are conceivable for the adduct, $(C_5Me_5)_2TiH$/1-hexene. However, the placement of (A) will favor over (B) from the steric reasons. If the intermediate assumes the geometry (B), steric repulsion among the $C_5Me_5$ ring, $C_3H_7$ and $CH_3$ group will prevent access of $\beta$-hydrogen to metal while the placement of (A) can diminish the steric repulsion. Hence, $\beta$-hydride abstraction from (A) was estimated to occur preferentially.



**A**

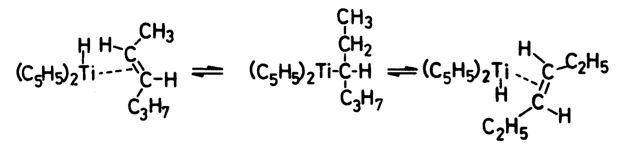


**B**

The catalysis of "$(C_5H_5)_2Ti$" or "$(C_5H_5)_2TiH$" was examined to evaluate the importance of the methyl groups of $C_5Me_5$ in stereoregulation. The catalysis of $(C_5H_5)_2TiCl_2/NaC_{10}H_8$ (IIa) was characterized by the low stereoselectivity (83%) and the diminished activity (turnover max). Isomerization to 3-hexene was not observed. The well-known spontaneous dimerization of $(C_5H_5)_2Ti$ to catalytically inactive $Ti_2H_2(\eta^5\text{-}C_5H_5)_2(\eta^{10}\text{-}C_{10}H_8)$ may be invoked for the lower activity.[14)] When $(C_5H_5)_2Ti$ species were immobilized on a polystyrene matrix to inhibit the dimerization, a significant increase in activity was observed as reported by Bergbreiter *et al.*, though the stereoselectivity remained unchanged (72—85%).[8a)]

Catalysts IIb—d showed a moderate activity. However, the stereoselection was insufficient and, further, these systems caused the isomerization to 3-hexene. The formation of 3-hexene implies that the isomerization takes place following the addition-elimination mechanism shown below.

Photolysis of $(C_5H_5)_2Ti$(*p*-tolyl)$_2$ is also utilized for generation of a catalyst[9)] but both activity and stereocontrol are insufficient. In addition, the reproducibility was poor with respect to the rate of isomerization. All



of the above results indicate that coordination of bulky ligand such as $C_5Me_5$ to metal is crucial to realize this highly stereoselective isomerization. The thermal-stability of Ia gave us an additional advantage in handling the catalyst; no decrease in activity was observed when Ia was kept at 20 °C for 6 h.

We have also examined the catalysis of the corressponding zirconium systems IIa—e and found very poor results irrespective of the reducing agents and substrates. The observed catalysis may be caused by a minute quantities of certain Zr(III) or Zr(II) species formed in the reaction system. Zr(IV) species are generally less readily reduced to Zr(II) or Zr(III) species in comparison to the Ti(IV) species.[15] The poor activity of IIIa—d will be ascribed to such natures existing in zirconium complexes. Photolysis of **6** did not give catalytically active species because **6** is highly resistant to ultraviolet rays under the normal conditions.

Though titanacyclopentane has been proposed as an intermediate in the dimerization of 1-alkenes,[16] any dimerization of alkenes was not observed in the present work.

*Characteristics and the Limitation of Titanocene Species as Catalysts.* Isomerization of a wide range of terminal olefins was examined with Ia to find broad applications. The results are given in Table 2. $C_4$–$C_8$ 1-alkenes were readily converted to (*E*)-2-alkenes within a short time even in the absence of a solvent. Thus, the present system provides a very convenient method for preparation of (*E*)-2-alkenes. Treatment of the products with aq HCl followed by one flash distillation or even one filtration is sufficient to obtain the pure sample. In the similar manner, (*E*)-1-phenyl-1-propene and (*E*)-*N*,*N*-diethyl-1-propenylamine were prepared in good yield from 3-phenyl-1-propene and *N*,*N*-diethyl-2-propenylamine, respectively.

Table 2. Isomerization of mono- and disubstituted alkenes with catalyst system Ia at 20 °C[a)]

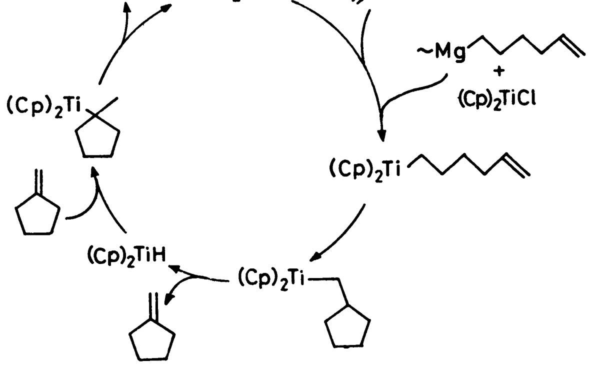
| Substrate | Product | *E*/*Z* ratio<br>% | Conversion<br>% |
|---|---|---|---|
| 1-Butene | 2-Butene | 99/1 | 100 |
| 1-Pentene | 2-Pentene | 100/0 | 99 |
| 1-Octene | 2-Octene | 100/0 | 99 |
| 3-Phenyl-1-propene | 1-Phenyl-2-propene | 99/1 | 100 |
| *N*,*N*-Diethyl-2-propenylamine | *N*,*N*-Diethyl-1-propenylamine | 99/1 | 98 |
| 2-Methyl-1-pentene | Recovered | — | 0 |
| 3-Methyl-1-pentene | Recovered | — | 0 |
| 4-Methyl-1-pentene | 4-Methyl-2-pentene | 99/1 | 25 |
| Allyl phenyl ether | Recovered | — | 0 |
| Allyl acetate | Recovered | — | 0 |

a) Reaction conditions: reaction time, 1 h; ratio of Ia/alkenes, 1/100 (mol/mol); solvent was not used.

In contrast to the results obtained with terminal olefins, internal olefins such as (*E*)- or (*Z*)-isomers of 2-butene, 2-pentene and 3-hexene were completely inert toward the catalyst Ia at 20—50 °C. No isomerization from (*Z*)- to (*E*)- or (*E*)- to (*Z*)-isomer occurred under these reaction conditions. It should be noted, however, that conversion of (*E*)-2-hexene to (*Z*)-2-hexene was observed when the mixture of (*E*)-2-hexene and Ia (100 : 1 molar ratio) was heated to 120 °C for 48 h in a sealed tube. The ratio of (*E*)-, (*Z*)-2-hexene and (*E*)-3-hexene was 94 : 5 : 1. The mechanism may involve ($\eta^3$-allyl)TiH species followed by elimination.

Isomerization of 1-alkenes with an alkyl substituent varying in size was examined using Ia as catalyst. Thus, 2-methyl- and 3-methyl-1-pentene were not isomerized but 4-methyl-1-pentene could be converted to (*E*)-4-methyl-2-pentene in low yield (25% at 20 °C for 12 h). The catalyst IIa has higher catalysis for these olefins; *i.e.*, 3- and 4-methyl-1-pentene were converted quantitatively (>98%) to 3-methyl-2-pentene and 4-methyl-2-pentene, respectively, when the reaction was carried out for 12 h at 20 °C. Catalyst Ia was also inert to 1,3-hexadiene, 5-trimethylsilyl-1,3-pentadiene and 1,5-cyclooctadiene. Addition of a stoichiometric amount (3 mol equivalents to Ia) of alkyl allyl ether, allyl alcohol or allyl acetate resulted in the complete deactivation of the catalyst. This will be due to the cleavage of alkyl allyl ether, allyl ester or vinyl ether which was formed by double bond migration. Further studies are required to clarify the stoichiometric reaction.

*Catalytic Isomerization of Unconjugated Dienes.* The result of isomerization of unconjugated dienes was given in Table 3. The catalyst Ia showed a sufficiently high selectivity for 1,5-hexadiene and 1,7-octadiene, whereas IIa and IIb showed a rather poor selectivity and induced an undesired skeletal isomerization leading to 1-methylcyclopentene. The pathway for formation of 1-methylcyclopentene is interpreted by the catalytic cycle given in Scheme 3. Since $(C_5H_5)_2TiCl_2$ is known to catalyze the hydromagnesiation of olefins,[7b)] the formation of 5-hexenylmagnesium compound is most probable in the initial stage. The resulting magnesium compound is readily converted into 5-hexenyltitanium



Scheme 3.

Table 3. Distribution of the products obtained by isomerization of 1,5-hexadiene and 1,7-octadiene with catalysts Ia, IIa and IIb[a)]

| Catalyst system | Isomerization of 1,5-hexadiene Products/% | | | | Isomerization of 1,7-octadiene Products/% | | | |
|---|---|---|---|---|---|---|---|---|
| | 2,4-Hexadiene | | | 1-Methylcyclopentene | 2,6-Octadiene | | | (*E*)-1,6-Octadiene |
| | (*E*, *E*) | (*E*, *Z*) | (*Z*, *Z*) | | (*E*, *E*) | (*E*, *Z*) | (*Z*, *Z*) | |
| Ia | 99.6 | 0.4 | 0.0 | 0.0 | 96.4 | 0.0 | 0.0 | 3.6 |
| IIa | 78.3 | 15.1 | 0.3 | 6.3 | 41.9 | 43.2 | 10.1 | 4.8 |
| IIb | 56.3 | 15.2 | 0.7 | 27.8 | 35.6 | 45.6 | 13.7 | 5.2 |

a) Reaction conditions: reaction time, 20 °C for 1 h; ratio of Ia to dienes, 1/100(mol/mol). Solvent was not used.

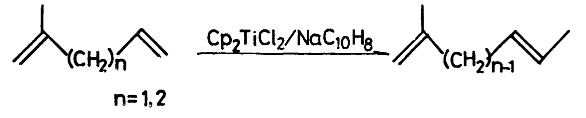
Table 4. Stereocontrolled regioselective isomerization of monosubstituted unconjugated dienes with Ia at 20 °C[a)]

| Substrate | Product | Stereoselectivity/%[b)] | Conversion/%[b)] |
|---|---|---|---|
| 1,4-Pentadiene | (*E*)-1,3-Pentadiene | >99 | 99 |
| (*E*)-1,4-Hexadiene | (*E*, *E*)-2,4-Hexadiene | >99 | 100 |
| 2-Methyl-1,4-pentadiene | (*E*)-2-Methyl-1,3-pentadiene | >99 | 97 |
| 2-Methyl-1,5-hexadiene | (*E*)-2-Methyl-1,4-hexadiene | >99 | 97 |

a) Reaction conditions: reaction time, 20 °C for 2 h; ratio of Ia to dienes, 1/100; solvent was not used. b) Determined by gas chromatographic analysis.

derivative by the metal exchange reaction. Ring closure gives (cyclopentylmethyl)titanium species which releases methylenecyclopentane by the $\beta$-elimination. The isomerization of methylenecyclopentane to 1-methylcyclopentene will follow the addition-elimination mechanism similar to that reported by Lehmkuhl.[17)]

*Stereocontrolled Regioselective Isomerization of Substituted Dienes.* The substrate selectivity observed in the above-mentioned olefin isomerization prompted us to try the regioselective (chemoselective) isomerization of substituted dienes. As shown in Table 4, vinyl groups were shifted to internal (*E*)-type olefins while vinylidene moiety was unaffected. Thus, regio- and stereoselective isomerization of a series of methylpentadienes was established with the catalyst Ia. 4-Vinylcyclohexene was isomerized with the catalyst IIa but not with Ia. A mixture of 4-ethylidenecyclohexene (69%) and 3-ethylidenecyclohexene (31%) were obtained in 91% yield by catalysis of IIa (1 mol%) at 20 °C for 12 h. Recently, quantitative isomerization of vinylcycloalkanes to ethylidenecycloalkanes was accomplished under rather vigorous conditions (180 °C) with the catalyst IId.[8b)] In these reaction conditions, the catalyst IId was also capable of converting 2,5-dimethyl-1,5-hexadiene or bicyclo[4.3.0]-3,7-nonadiene to conjugated 1,3-dienes.[8b—c)]



The extremely good selectivity and chemoselectivity observed in this work utilizing $(C_5Me_5)_2Ti$ species will be valuable for organic syntheses since the isomerization took place under the mild conditions in a short period.

## Experimental

All operations were conducted by Schlenk techniques under an argon atmosphere. $^1$H- and $^{13}$C-NMR spectra were recorded at 100 and 25.05 MHz on a Varian XL-100 and a JEOL FX-90Q spectrometer, respectively. The infrared pectra were recorded on a Hitachi EPI-2 spectrometer. The structure of the products was determined from the chemical shift values of $^{13}$C-NMR spectra referring to the reported data.[18)] The product distribution was determined with a Hitachi Model 163 gas chromatograph. $(C_5Me_5)_2TiCl_2$,[10)] $(C_5H_5)_2TiCl_2$,[19)] and $(C_5H_5)_2ZrCl_2$[19)] were prepared according to the method previously reported. Tetrahydrofuran, diethyl ether and benzene were dried over sodium-potassium alloy and were distilled. All olefins and dienes (Aldrich Chem.) were dried over calcium hydride and purified by distillation.

*Isomerization of 1-Hexene with Ia.* To a stirred suspension of $(C_5Me_5)_2TiCl_2$ (39.0 mg, 0.10 mmol) in 0.8 ml THF was added a solution of $NaC_{10}H_8$ (30 mg, 0.2 mmol) in THF (1 ml) at room temperature. The color of the solution changed into dark yellow green. After stirring for 10 min, mixture was evaporated to dryness and was extracted with pentane (10 ml) at 20 °C. After the removal of the salt with a centrifuge, flash distillation of the pentane extract was performed *in vacuo* to give the species Ia as a green solid (32 mg). To the resulting catalyst species was added 1-hexene (1.25 ml, 10 mmol) at −70 °C and the mixture was immediately warmed to 20 °C to induce the isomerization. A small portion of the reaction mixture was taken out and hydrolyzed to monitor the reaction with a gas chromatograph. After stirring the mixture for 30 min at 20 °C, 6 mol dm$^{-3}$ aq HCl was added and organic layer was distilled to give (*E*)-2-hexene (1.1 ml, 9 mmol). The removal of the salts or solvent was not neccessarily required because the presence of these materials did not affect on catalysis.

*Preparation of Ib—d and IIa—d.* To a mixture of $(C_5Me_5)_2TiCl_2$ (19 mg, 0.05 mmol) and ether (0.5 ml) was added $i$-$C_3H_7MgBr\cdot(OEt_2)_2$(26 mg, 0.1 mmol) in ether (1.5 ml). The mixture was stirred at 20 °C for 10 mix the and precipitates was separated by centrifugation using a specially designed two-necked tube fitted with septum caps. The ether solution was evaporated to dryness to give Ib as a green solid and 1-hexene was added to the solid at 20 °C to induce the isomerization. In essentially the same way for Ia, diethyl ether solution (1.5 ml) of butyllithium (6 mg, 0.1 mmol) or $LiAlH_4$ (4 mg, 0.05 mmol) was allowed to react with $(C_5Me_5)_2TiCl_2$ (0.1 mmol) for 10 min and 60 min, respectively, to generate the catalyst Ic and Id. The ether soluble green solid was used as catalysts. The systems IIa—d were prepared in the similar manner.

*Photolysis of* $(C_5Me_5)_2Ti$(p-*tolyl*)$_2$ *and* $(C_5H_5)_2Ti$(p-*tolyl*)$_2$. $(C_5Me_5)_2Ti$(*p*-tolyl)$_2$ **4** and $(C_5H_5)_2Ti$(*p*-toyl)$_2$ **5** were prepared according to the reported procedures.[9] After the addition of **4** or **5** (1 mmol) to 1-hexene (100 mmol) in benzene (10 ml), ultraviolet ray irradiation was carried out with stirring for 2 h using a high pressure (250 W) mercury lamp.

*Characterization of the Products.* $^{13}$C-NMR assignment of a series of (*E*)- or (*Z*)-olefins and dienes including the products obtained in this paper is already established by Haan *et al.*[18] Therefore, the structure was determined with reference to the reported data. The distribution of the products was analyzed using authentic samples (Aldrich Chem.) with a gas chromatograph fitted with a capillary column, HB-2000 or CW (45 m, Gaschro Kogyo, Co.). When the product was contaminated with isomers, characterization was done after the separation into the respective isomers by a preparative gas chromatograph fitted with a Benton-34 or SiDC-560 column. The geometry of *N*,*N*-diethyl-1-propenylamine was determined by the $^1$H-NMR spectrum referring with the data reported by Sauer.[20] The IR and $^1$H-NMR spectra of 1-methylcyclopentene agreed with the data reported by Becker.[21]

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