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Intermediates for the Degenerate and Productive Metathesis of Propene Elucidated by the Metathesis Reaction of (Z)-Propene-1-d_1

Katsumi Tanaka,*† Ken-ichi Tanaka,*‡ Harutoshi Takeo,§ and Chi Matsumura§

Contribution from the Research Institute for Catalysis, Hokkaido University, Kita-Ku, Sapporo 060, Japan, The Institute for Solid State Physics, The University of Tokyo, Minato-ku 106, Japan, and the National Chemical Laboratory for Industry, Yatabe, Ibaraki 305, Japan. *Received September 8, 1986*

Abstract: Intermediates for productive and degenerate metathesis of propene were elucidated by using (Z)-propene-1-d_1 on molybdenum oxide catalysts activated with SnMe$_4$. Productive metathesis of (Z)-propene-1-d_1 yielded 2-butene with cis:trans < 1 and ethylene-$1,2$-d_2 with cis:trans = 1 on the catalysts. This result suggests that the mono-methyl-substituted metallacyclobutanes have no preferential configuration, while the 1,2-dimethylmetallacyclobutanes prefer to take the trans configuration. Degenerate metathesis between (Z)-propene-1-d_1 and propene-d_6 yielded (E)-propene-1-h_1 in 80% selectivity. On the basis of these results, the ethylidene species is deduced as the dominant intermediate for the degenerate metathesis of propene. It is assumed in a proposed mechanism that (1) the rate-determining step for the productive metathesis is the reaction of propene with $Mo{=}CH{-}CH_3$ and (2) the degenerate and productive metatheses of propene are competitive in the reaction of propene with $Mo{=}CH{-}CH_3$, but they bring about no mutual inhibition, because the degenerate metathesis does not change the population of the $Mo{=}CH{-}CH_3$ intermediate.

Metal carbene and metallacyclobutane have been accepted as intermediates in the homogeneous metathesis catalysts.[1] If olefin metathesis reaction on heterogeneous catalysts is occurring via the same intermediates, the productive metathesis of propene should involve alternative reaction of propene with methylidene and ethylidene as shown in Scheme III. The degenerate metathesis of propene which occurs simultaneously with the productive metathesis may also be caused by the reaction of either ethylidene or methylidene intermediate with propene. Then an interesting question arises: which intermediate contributes predominantly to the degenerate metathesis of propene? This is a general problem on methylene exchange of α-olefin by the metathesis reaction. To solve this problem, Casey et al. studied the methylene-exchange reaction between (Z)-1-decene-1-d_1 and 1-octene-$1,1$-d_2 in a homogeneous catalytic system, and they ruled out the possibility of methylidene intermediate on the basis of stereospecific retention of the methylene conformation.[2] With respect to the predominant intermediates for the degenerate metathesis of propene, ethylidene intermediate has also been proposed on other experimental grounds.[3,4] In this paper, the participation of alkylidene intermediates for the degenerate metathesis reaction of propene and the preferable configuration of metallacyclobutanes with methyl substituents were proved by measuring stereospecificity in the metathesis reaction of (Z)-propene-1-d_1, propene-d_6, and *cis*- and *trans*-2-butenes on MoO$_3$/TiO$_2$–SnMe$_4$ and MoO$_{3-x}$/TiO$_2$–SnMe$_4$. As was reported in our previous paper, these catalysts are highly active for olefin metathesis reaction being accompanied by neither hydrogen scrambling nor olefin isomerization.[5] This characteristic constitutes a determining advantage for the mechanistic studies using deuterium-labeled olefins.

Experimental Section

Catalyst. The starting material was obtained by immersing β-titanic acid, TiO$_2$H$_2$O, into an aqueous solution of ammonium paramolybdate, (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, and was dried at 120 °C in the air for 12 h. The β-titanic acid was prepared by boiling the water solution with α-titanic acid precipitate at 100 °C for 12 h, which was obtained by reacting titanium tetrachloride, TiCl$_4$, with concentrated aqueous ammonia, NH$_4$OH, in an ice bath followed by washing the precipitate with water until no chlorine was detected.[6] A fully oxidized MoO$_3$/TiO$_2$ was obtained by oxidizing the starting material with O$_2$ at 500 °C for 1 h, which contained 6.7 wt % of MoO$_3$. The partially reduced MoO$_{3-x}$/TiO$_2$ ($0.1 < x < 0.7$) was prepared by reoxidizing a fully reduced MoO$_x$/TiO$_2$ with an equimolar mixture of N$_2$O and H$_2$ with total pressure of about 300 torr (1 torr = 133.3 Pa) at 200 °C for 1 h.[7] The catalyst was evacuated at 500 °C for 1 h prior to the reaction with SnMe$_4$.

The SnMe$_4$ vapor (1 torr/0.1 g of catalyst) diluted with He (about 60 torr) was reacted with the catalyst for 30 min at room temperature and was evacuated at the same temperature for 30 min. The catalysts treated by SnMe$_4$ are denoted as MoO$_3$/TiO$_2$–SnMe$_4$ and MoO$_{3-x}$/TiO$_2$–SnMe$_4$.

Reactants. a. (Z)-Propene-1-d_1. (Z)-propene-1-d_1 was obtained by the hydrogenation of methylacetylene-1-d_1 ($DC{\equiv}C{-}CH_3$) on Pd/CaCO$_3$ (reduced with H$_2$ at 200 °C for 1 h) at 0 °C. The propene obtained by that reaction was composed of 6.9% of d_0 and 93.1% of d_1 species. The purity of the Z form in propene-1-d_1 was 90%.

b. *cis*- and *trans*-2-Butene-d_8. *cis*- and *trans*-2-butene-d_8 (d_7, 5.2%; d_8, 94.8%) were obtained by deuteriation of butadiene-d_6 (commercially available) on ZnO (Kadox 15, 450 °C evacuated for 1 h) at room temperature followed by isomerization at the same temperature. Each butene was separated by a gas chromatograph, trapped, and then purified by vacuum evaporation to remove water.

c. Propene-d_6. Commercially available propene-d_6 (d_5, 2.8%; d_6, 97.2%) was used without further purification.

Reaction and Product Analysis. The metathesis reaction was carried out at room temperature in a closed glass circulation system with a volume of 260 mL using 20–45 torr of olefin on a 0.01–0.5-g catalyst. The composition of ethylene, propene, and *cis*- or *trans*-2-butene was analyzed by an on-line gas chromatograph, where a 13-m stainless steel column (3-ϕ i.d.) in which Sebaconitrile (25%) on Uniport C (60∼80 mesh) was packed. Distribution of deuterium in olefins was determined by a mass spectroscopic analysis with low ionization voltage (10∼14 V). The distribution of deuterium atom in propene-d_1 and in propene-h_1 (propene-d_5) was determined by a microwave spectroscopic analysis. The analysis of *cis*- and *trans*-ethyelne-$1,2,$-d_2 was made by using infrared absorption bands at 842 and 727 cm^{-1}.[8]

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† Hokkaido University.

‡ The University of Tokyo.

§ National Chemical Laboratory for Industry.

(1) Rooney, J. J.; Stewart, A. *Catalysis*; Kemball, C., Ed.; Specialist Periodical Report; The Chemical Society: London, 1977; Vol. 1, Chapter 8. Grubbs, R. H. *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Ed.; Pergamon: New York, 1982; Vol. S, Chapter 54. Ivin, K. J. *Olefin Metathesis*; Academic: New York, 1983. Casey, C. P. *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1985; Chapter 4.

(2) Casey, C. P.; Tuinstra, H. E. *J. Am. Chem. Soc.* **1978**, *100*, 2279.

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(4) Sasaki, M.; Tanaka, K.; Tanaka, K.; Toyoshima, I. *J. Chem. Soc., Chem. Commun.* **1986**, 764.

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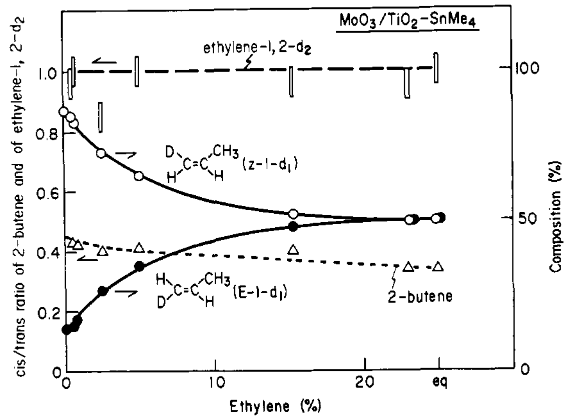
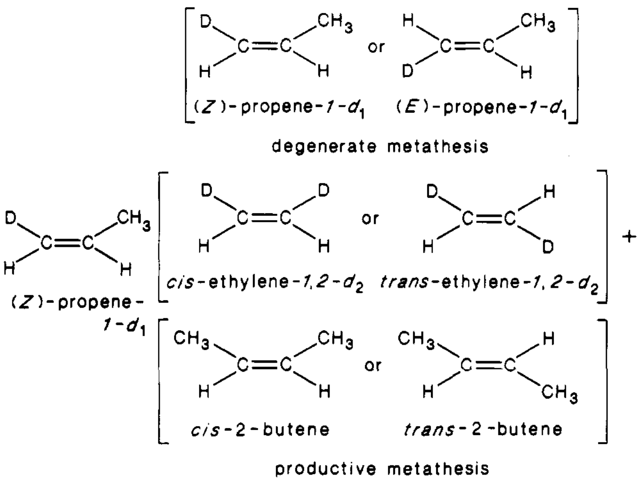


Figure 1. Metathesis reaction of (Z)-propene-1-d_2 on the MoO_3/TiO_2-$SnMe_4$ catalyst. Cis:trans ratio of ethylene-$1,2$-d_2 (□) and that of 2-butene (△). Composition of Z (○) and E isomer (●) in propene-1-d_1.

Results and Discussion

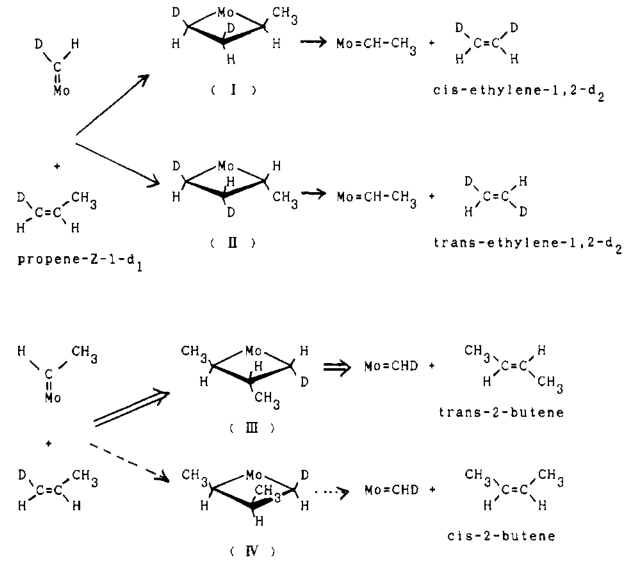
Metathesis Reaction of (Z)-Propene-1-d_1. On MoO_3/TiO_2–$SnMe_4$ and MoO_{3-x}/TiO_2–$SnMe_4$, two types of metathesis reactions, degenerate and productive, occur simultaneously. The degenerate metathesis of propane proceeds faster (more than 1 order of magnitude) than the productive metathesis.[5]



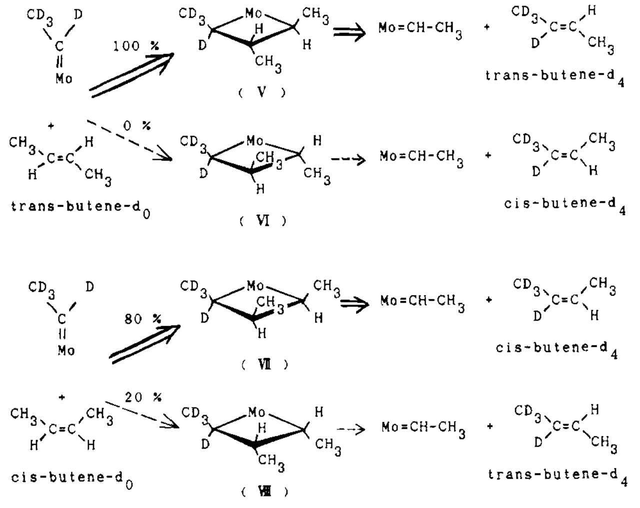
As illustrated in the reaction scheme, the degenerate metathesis reaction of (Z)-propene-1-d_1 gives either (Z)-propene-1-d_1 or (E)-propene-1-d_1, while productive metathesis yields *cis*- and *trans*-ethylene-$1,2$-d_2 and *cis*- and *trans*-2-butene. The cis:trans ratios in both ethylene-$1,2$-d_2 and 2-butene obtained by metathesis of (Z)-propene-1-d_1 at room temperature on the MoO_3/TiO_2–$SnMe_4$ catalyst are shown in Figure 1. It is clear that the cis and trans isomers of ethylene-$1,2$-d_2 were formed in equal amount, whereas the formation of *trans*-2-butene was preferred to that of *cis*-2-butene (cis/trans = 0.45 ± 0.02). A similar result was obtained with the MoO_{3-x}/TiO_2—$SnMe_4$ catalyst; that is, the cis:trans ratio in ethylene-$1,2$-d_2 was unity while the cis:trans ratio in 2-butene was 0.20 ± 0.02 in the initial stage of the reaction.

The cis–trans isomerization of ethylene-$1,2$-d_2 as a consecutive secondary reaction can be ruled out, since a cross metathesis between $^{13}C_2H_4$ and C_2H_4 was strongly suppressed in the presence of propene.[4] Therefore, the cis:trans ratio in ethylene-$1,2$-d_2 shown in Figure 1 indicates nonselective *cis*- and *trans*-ethylene-$1,2$-d_2 formation in the productive metathesis of (Z)-propene-1-d_1. This fact implies that the following two reaction routes via 1-methylmetallacyclobutane (I and II displayed in Scheme I) occur equally. While, then the two reaction paths through the intermediates III and IV contribute equally to the productive metathesis, the cis:trans ratio in the produced 2-butene is unity.[9] For this reason, both values of 0.45 and 0.20 (the former is larger than the equilibrium value 0.30 ± 0.02 and the latter is smaller) indicate trans preferential 2-butene formation on these catalysts; that is, the 1,2-dimethylmetallacyclobutane prefers to take the trans configuration (III).

Scheme I



Metathesis Reaction of *cis*- and *trans*-2-Butene Using d_0 and d_8 Isomers. When a 1:1 mixture of *trans*-2-butene-d_0 and *trans*-2-butene-d_8 was reacted on the MoO_3/TiO_2–$SnMe_4$ and MoO_{3-x}/TiO_2–$SnMe_4$ catalysts, *trans*-2-butene-d_4 was formed with almost 100% selectivity, while an equimolar mixture of *cis*-2-butene-d_0 and *cis*-2-butene-d_8 gave *cis*-2-butene-d_4 in 80% selectivity.[5] It was already observed in homogeneous phase that *trans*-olefins give a higher retention of conformation than *cis*-olefins in the metathesis of RCH=CHMe.[10] It is significant to point out that the conformation-retaining metathesis was confirmed on the heterogeneous catalysts by labeling experiments. Such retention of conformation of the starting olefin is well explained by the cis preferential configuration (V, VII) of the 1,3-dimethyls in the metallacyclobutane intermediates, as shown below.[7]



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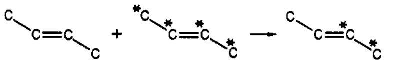
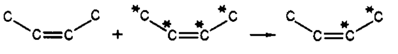
(8) Crawford, B. L., Jr.; Lancaster, J. E.; Inskeep, R. G. *J. Chem. Phys.* **1953**, *21*, 678. Pinchas. S.; Laulicht, I. *Infrared Spectra of Labelled Compounds*; Academic: New York, 1971; p 85.

(9) (a) It is reasonable to assume that the stereoselectivity for the metathesis reaction of α-olefins is expressed by the cis:trans ratio of the produced internal olefins instead of the deviation from thermodynamical equilibrium ratio. The same statement is shown in the following paper: (b) Leconte, M.; Basset, J. M. *Ann. N. Y. Acad. Sci.* **1980**, *333*, 165.

(10) (a) Hughes, W. B.; *J. Chem. Soc., Chem. Commun.* **1969**, 431. (b) Leconte, M.; Basset, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7296. (c) Garnier, F.; Krausz, P. *J. Mol. Catal.* **1980**, *8*, 91. (d) Ofstead, E. A.; Lawrence, J. P.; Senyek, M. L.; Calderon, N. *Ibid.* **1980**, *8*, 227. (e) Leconte, M.; Taarit, B.; Bilhou, Y.; Basset, J. M. *Ibid.* **1980**, *8*, 263. (f) Bosma, R. H. A.; Xu, X. D.; Mol, J. C. *Ibid.* **1982**, *15*, 187.

Table I. Turnover Frequencies for the Structure-Retaining Metathesis Reaction on the MoO_3/TiO_2–$SnMe_4$ and MoO_{3-x}/TiO_2–$SnMe_4$ Catalysts[a]

reaction	MoO_3/ TiO_2– $SnMe_4$	MoO_{3-x}/ TiO_2– $SnMe_4$
	4.4×10^{-2}	5.0×10^{-2}
	1.1×10^{-3}	6.2×10^{-3}

[a] *C, CD or CD_3, catalyst, 10~50 mg, reaction, room temperature; turnover frequency, molecules of Mo^{-1} s^{-1}.

As was discussed in the productive metathesis of (*Z*)-propene-*1*-d_1, 1,2-dimethyls seem to prefer the trans configurations. If this is the case for the 1,2,3-trimethyl-substituted metallacyclobutanes, the 1,2-trans and 1,3-cis configurations of the methyls (V) will be most preferable. Higher preservation of the trans conformation (100%) than the cis (80%) in the metathesis reaction of 2-butene seems to support this rule. In this reaction scheme, we adopted a flat structure for the metallacyclobutane skeletons since it is sufficient to describe our results. A significant subject is to consider whether the metallacyclobutane skeleton is puckered or flat. So far the two metallacyclobutanes showing activity to metathesis-like reactions have been isolated by two groups, and the structures of these metallacyclobutanes were determined by X-ray diffraction.[11,12] The result given by Grubbs et al. gave impact on us, because the titanacyclobutane has a flat structure contrary to our expectation.[11] On the other hand, Schrock et al. succeeded to isolate a tungustenacyclobutane with puckered structure.[12] These results may imply that the metallacyclobutane ring is rather flexible, and the bulky ligands probably stabilize the puckered skeleton structure of metallacyclobutanes as conjectured by Schrock et al.[12] In conformity with these facts, it is essentially interesting to remember that *cis*- and *trans*-ethylene-d_2 are equally formed on our catalysts via 1-methylmetallacyclobutanes (I and II). This fact indicates that the 1-methylmetallacyclobutanes equally contribute to the reaction and are indistinguishable. Such a phenomenon is difficult to interpret if the 1-methylmetallacyclobutane has a puckered structure. While, if 1,3-dimethylmetallacyclobutanes take the flat structure, it is rather difficult to explain why the 1,3-dimethyls prefer to take cis configurations (V, VII, XI) but the puckered structure can explain them with 1,3-diequatorial orientation.[13] The 1,3-diequatorial interaction was first discussed to interpret stereospecificity of 2-pentene metathesis.[14] Leconte and Basset carried out metatheses of various acyclic olefins with Cr-, W-, and Mo-based homogeneous catalysts and found that the stereoselectivity is independent of the metals. On the basis of these results, they concluded that the puckered structures with (a) 1,3-diaxial interaction and (b) 1,2-equatorial-axial interaction are preferable.[9b,10b] Casey and co-workers pointed out the importance of configurations possessing the fewest axial substituents on the α-carbons in the ring by the olefin metathesis on the $(CO)_5W{=}C(C_6H_5)(CH_3)$ complex.[15] It is significant to stress that the origin of stereoselectivity seems to be the same in solution and on solid surfaces. However, it is still an unsettled problem, which should be solved, whether the substituents make influence on the puckering of metallacyclobutane or not.

The turnover frequencies for the struture-retaining metathesis in 2-butene on these catalysts are shown in Table I, where the turnover frequency was obtained by assuming that all Mo cations participate in the reaction. It is noteworthy that the conformation-retaining metathesis of *trans*-2-butene occurs 8–40 times faster than that of *cis*-2-butene, because *trans*-olefins such as *trans*-2-pentene undergo the metathesis reaction rather slowly with homogeneous catalysts.[16]

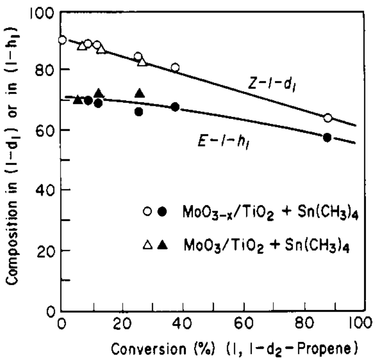
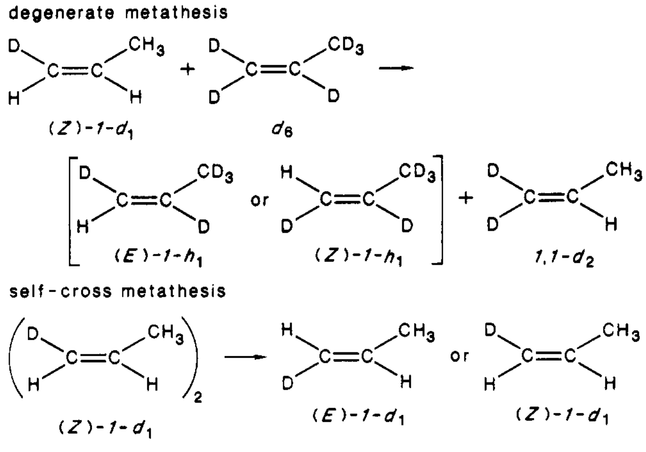


Figure 2. Fraction of *Z* isomer in propene-*1*-d_1 (○, △) and that of *E* isomer in propene-*1*-h_1 (●, ▲) formed in the degenerate methathesis reaction between (*Z*)-propene-*1*-d_1 and propene-d_6 (○, ●: MoO_{3-x}/TiO_2–$SnMe_4$. △, ▲: MoO_3/TiO_2–$SnMe_4$). Conversion is represented as the equilibrium of degenerate metathesis being 100%.

Metathesis Reaction between (*Z*)-Propene-*1*-d_1 and Propene-d_6. The degenerate metathesis of propene occurs in general faster than the productive metathesis, and it was 10 times faster on the MoO_3/TiO_2–$SnMe_4$ and 27 times on the MoO_{3-x}/TiO_2–$SnMe_4$ catalyst.[5] If we consider the fact that both ethylidene and methylidene intermediates coexist on the catalysts during the productive metathesis of propene, an interesting question is whether the degenerate metathesis of propene is caused by an ethylidene- or a methylidene-exchange reaction.

$$C{=}C{-}C + {}^*C{=}{}^*C{-}{}^*C \rightarrow {}^*C{=}C{-}C + C{=}{}^*C{-}{}^*C$$

In order to solve this question, the metathesis reaction of a 1:1 mixture of (*Z*)-propene-*1*-d_1 and -d_6 was performed over the two catalysts. The following two types of degenerate metathesis reactions should occur.



The degenerate metathesis between (*Z*)-propene-*1*-d_1 and -d_6 yields propene-*1,1*-d_2 and either (*E*)-propene-*1*-h_1 or (*Z*)-propene-*1*-h_1. As shown in Figure 2, the fraction of *Z* isomer in propene-*1*-d_1 decreased linearly with conversion (measured by propene-*1,1*-d_2 formation). The fraction of *E* isomer in propene-*1*-h_1 (propene-d_5), however, had a constant value of 72% in the initial stage of reaction on these catalysts. The linear decrease of (*Z*)-propene-*1*-d_1 is undoubtedly due to the self-cross metathesis of (*Z*)-propene-*1*-d_1 to (*E*)-propene-*1*-d_1. The purity of the *Z*

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[11] For structure, see: Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358. For reactivity, see: Lee, J. B.; Ott, K. C.; Grubbs, R. H. *Ibid.* **1982**, *104*, 7491.

[12] Scaverian, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771.

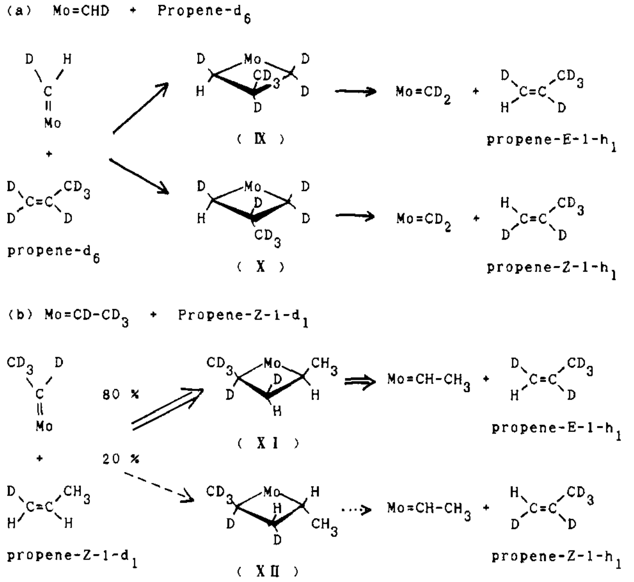
[13] Calderon, N.; Lawrence, J. L.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449.

[14] Katz, T. J.; MaGinnis, J. *J. Am. Chem. Soc.* **1975**, *97*, 1592.

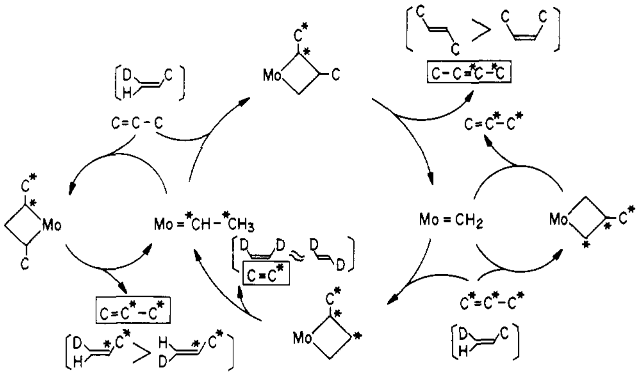
[15] Casey, C. P.; Albin, L. D.; Brukhardt, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2733.

[16] Calderon, N.; Ofstead, E. A.; Ward, J. P.; Judy, W. A.; Scott, K. W. *J. Am. Chem. Soc.* **1968**, *90*, 4133. Hughes, W. B. *J. Chem. Soc., Chem. Commun.* **1969**, 431. Basset, J. M.; Bilou, J. L.; Mutin, R.; Theolier, A. *J. Am. Chem. Soc.* **1975**, *97*, 7376. Bilou, J. L.; Basset, J. M.; Mutin, R.; Graydon, W. F.; *Ibid.* **1977**, *99*, 4083.

Scheme II



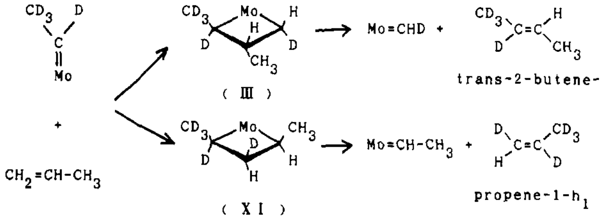
Scheme III



isomer in the reactant propene-*1*-d_1 used in the experiment was 90%, and the conformation retained in the degenerate metathesis is calculated to be 80%. This fact indicates that the intermediates in the degenerate metathesis should have the retained methylene congfiguration. The formation of the *E* or *Z* isomer of propene-*1*-h_1 is caused by either reaction a or reaction b as shown in Scheme II.

If the degenerate metathesis of propene was caused by the reaction of Mo=CH$_2$ intermediates with propene, selective formation of (*E*)-propene-*1*-h_1 should occur only via the 2-methylmetallacyclobutane intermediate (IX). 1-Methylmetallacyclobutanes (I and II) have no specific configuration as was proved by the nonselective formation of *cis*- and *trans*-ethylene-*1,2*-d_2 from (*Z*)-propene-*1*-d_1. Probably, 1-methyl- or 2-methylmetallacyclobutane would give the same results if one assumes that in general monosubstituted metallacyclobutanes have no preferred configuration. Taking account of this fact, mechanism a via 2-methylmetallacyclobutane intermediates is ruled out. Consequently, the reaction with Mo=CH—CH$_3$ will bring about selective formation of (*E*)-propene-*1*-h_1, because the 1,3-dimethyls in metallacyclobutane prefer to take the cis configuration (XI), as is the case of cometathesis reaction of 2-butene-d_0 and -d_8 (V, VII).

Overall Mechanism of Propene Metathesis Reaction. The overall reaction mechanism of propene metathesis taking place on the catalysts can be expressed by Scheme III, where the metathesis reaction of (*Z*)-propene-*1*-d_1 and the degenerate metathesis between (*Z*)-propene-*1*-d_1 and propene-d_6 are displayed in parentheses. From this reaction scheme, predominant contribution of the ethylidene route to the degenerate metathesis may be correlated to the rate-determing step of the productive metathesis reaction; that is, the slow step in the productive route is the reaction of ethylidene (Mo=CH—CH$_3$) with propene, and the reaction of methylidene (Mo=CH$_2$) with propene may be much faster than that with ethylidene. As a result, the Mo=CH$_2$ changes instantaneously to Mo=CH—CH$_3$, which results in lowering the population of Mo=CH$_2$ and increasing that of Mo=CH—CH$_3$. According to this mechanism, the productive metathesis and the degenerate metathesis of propene are competitive reactions of propene with Mo=CH—CH$_3$. It is important to point out that the degenerate metathesis is 1 order faster than the productive metathesis, but no mutual retardation is induced, because the degenerate metathesis regenerates ethylidene intermediates and changes little the population of Mo=CHCH$_3$.



Acknowledgment. We are indebted to Prof. R. H. Grubbs of the California Institute of Technology who suggested to us the measurement of the cis:trans ratios in ethylene-*1,2*-d_2 at the Sixth International Symposium on Olefin Metathesis (ISOM-6), Hamburg, 1985.