Kinetics and Stereochemistry of the Titanacyclobutane–Titanamethylene Interconversion. Investigation of a Degenerate Olefin Metathesis Reaction

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Abstract: Analysis of the kinetics of the reaction of dicyclopentadienyltitanacyclobutane **3** with diphenylacetylene to produce the dicyclopentadienyltitanacyclobutene **7** indicated that the exchange is first order in **3** and zeroth order in Ph—C≡C—Ph over a wide range of concentrations. The kinetics and stereochemistry of olefin exchange along with a large secondary isotope effect are consonant with the reaction proceeding via rate-limiting ring opening of **3** to Cp₂Ti=CH₂ and olefin (free or complexed), followed by rapid trapping by incoming olefin or acetylene. The complex **3** and its analogues are effective catalysts for the olefin metathesis reaction of terminal olefins.

Introduction

The mechanism of the metal-catalyzed olefin metathesis reaction[1] has been intensively studied for many years, and a consensus has emerged that metal alkylidenes and metallacyclobutanes are plausible intermediates in this reaction. The syntheses and isolation of metal alkylidene complexes and studies of their reactions with olefins have convincingly demonstrated the intermediacy of such species in metathesis.[2] In contrast, the evidence for the involvement of the metallacyclobutane intermediates has not been as well documented and is largely indirect. To date, examples of well-characterized complexes in this class are rare, being limited to only a few transition metals.[3] Recently, we reported the isolation of a titanacyclobutane[4] from an olefin metathesis system.[2a] In this paper we present detailed studies of

the reactions of this class of metallacyclobutanes that are related to the mechanism and stereoselectivity of the olefin metathesis reaction.

Results and Discussion

Titanacyclobutane **3**, synthesized from the well-defined me-

(1)

(Cp = η⁵-C₅H₅)
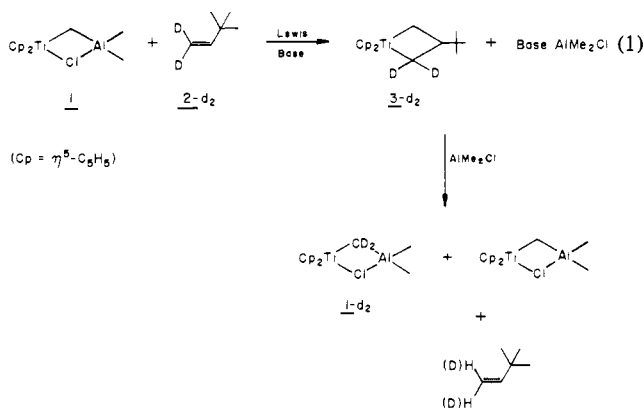
tathesis catalyst **1**, undergoes the reactions required of a metathesis intermediate. When **3**-*d₂* was treated with AlMe₂Cl (eq 1), deuterium was incorporated into **1** in a second-order reaction.[5]

Equation 1 represents a reasonable mechanism for the Lewis-acid-catalyzed route for metathesis involving **1** as the chain-carrying species. We now have found that complex **3** is also an

(1) For recent reviews on the olefin metathesis reaction, see: Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* 1979, *17*, 449. Grubbs, R. H. *Prog. Inorg. Chem.* 1978, *24*, 1. Katz, T. J. *Adv. Organomet. Chem.* 1977, *16*, 283.

(2) (a) Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* 1979, *101*, 5074. (b) Klabunde, U.; Tebbe, F. N.; Parshall, G. W.; Harlow, R. L. *J. Mol. Catal.* 1980, *8*, 37. (c) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* 1980, *102*, 6149. (d) Wengrovius, J.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Young, W. J. *Ibid.* 1980, *102*, 4515. (e) Schrock, R.; Rocklage, S.; Wengrovius, J.; Rupprecht, G.; Fellman, J. *J. Mol. Catal.* 1980, *8*, 73.

(3) (a) Adam, G. J. A.; Davies, S. G.; Ford, K. A.; Ephritikhine, M.; Todd, P. F.; Green, M. L. H. *J. Mol. Catal.* 1980, *8*, 15. (b) Anderson, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* 1978, 446. (c) Foley, P.; Whitesides, G. M. *J. Am. Chem. Soc.* 1979, *101*, 2732. (d) Tulip, T. H.; Thorn, D. L. *Ibid.* 1981, *103*, 2448. (e) Puddephatt, R. J. *Coord. Chem. Rev.* 1980, *33*, 149. (f) Klinger, R. J.; Huffmann, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* 1982, *104*, 2147.

(4) (a) Lee, J. B.; Howard, T. R.; Grubbs, R. H. *J. Am. Chem. Soc.* 1980, *102*, 6876. (b) Lee, J. B., et al. *Ibid.* 1981, *103*, 7358.

(5) For a detailed examination of the reaction of titanacyclobutanes with aluminum reagents, see: Ott, K. C.; Lees, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* 1982, *104*, 2942.
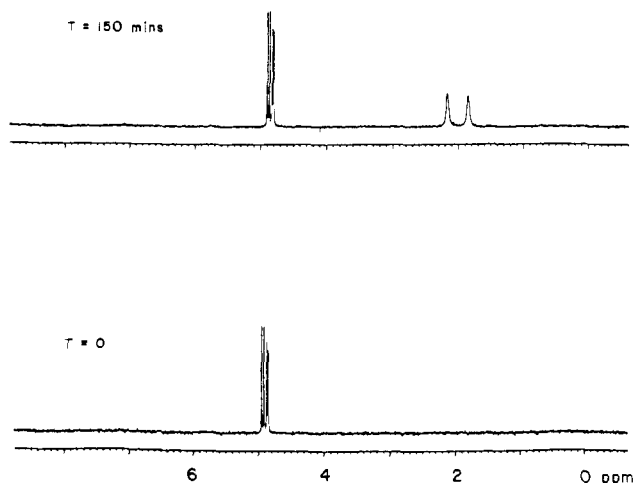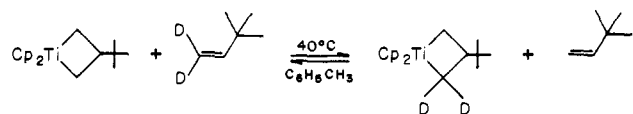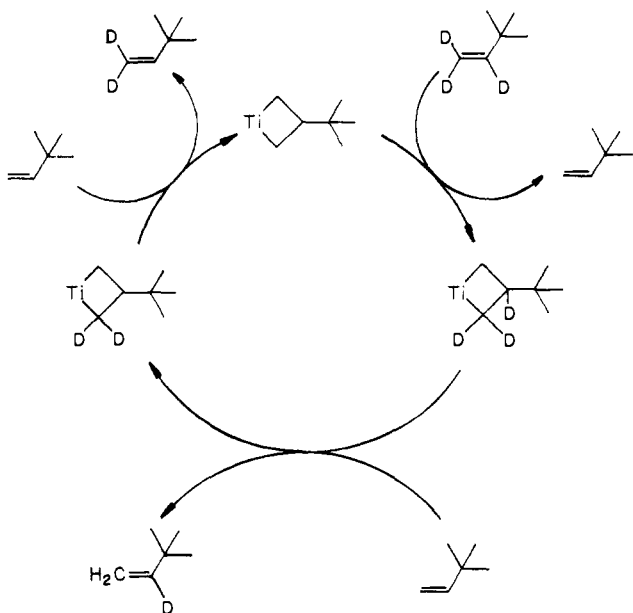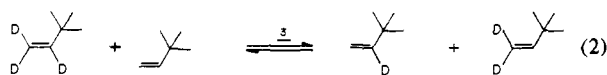
7492 *J. Am. Chem. Soc., Vol. 104, No. 26, 1982*

Lee, Ott, Grubbs

Figure 1. ^{2}H NMR spectra (76.77 MHz) of the reaction


Scheme I

effective catalyst for the methylene exchange of monosubstituted terminal olefins in the absence of $AlMe_2Cl$. Thus, **3** catalyzes the degenerate metathesis of 3,3-dimethyl-1-butene (**2**-d_0) and 3,3-dimethyl-1-butene-*1,1,2*-d_3 (**2**-d_3) (eq 2).


All of the intermediate labeled metallacyclobutanes and olefins are observable by NMR spectroscopy, and the olefins are also analyzed by GC/MS. For example, an equimolar solution of **3** and **2**-d_2 was heated to 40 °C and examined periodically by ^{2}H NMR spectroscopy. The spectra (Figure 1) show depletion of deuterated olefin and incorporation of deuterium into the cis and trans α positions of the metallacyclobutane (δ 1.86 and 2.17, respectively) in equal amounts. The exchange of methylene groups is extensive after 4 h at 40 °C. Thus, the stepwise exchange of labeled and unlabeled **2** can be represented by the catalytic cycle depicted in Scheme I.

In the series of β,β-disubstituted metallacyclobutanes such as **4** and **5**, analogous exchange reactions are observed but typically occur much more rapidly and at lower temperatures (<0 °C) than
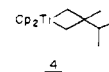
Scheme II
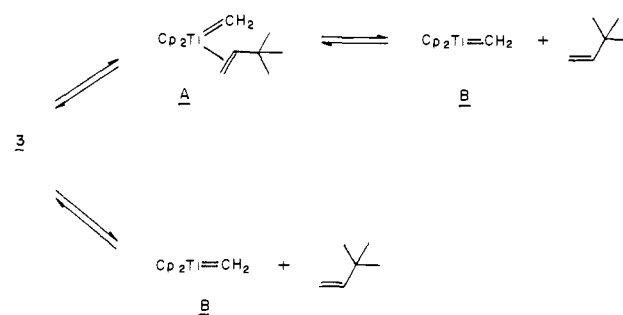
for monosubstituted **3**. When a 13-fold excess of (*Z*)-α-methylstyrene-d_1 was allowed to exchange with **5** (eq 3), the
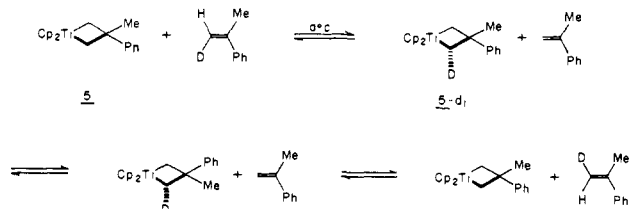
(3)

deuterated *E* and *Z* metallacyclobutanes were observed to appear along with (*E*)-α-methylstyrene-d_1. Reaction was complete within 4 h at 0 °C. The initial rate of exchange was measured to be 1.2 turnovers per minute per Ti. It is significant to note that the catalysis is accomplished without the addition of a cocatalyst. To the best of our knowledge, these are the first examples of metathesis reactions catalyzed by a metallacyclobutane.

Other olefins have been found to exchange with **3** and **4**, to yield the analogous metallacyclobutanes (eq 4, 5). The position of
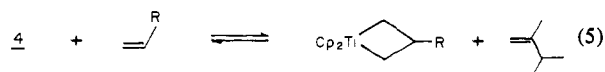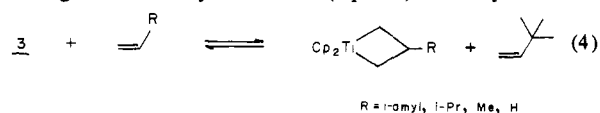
equilibrium in these systems is apparently determined by the steric nature of the olefins involved. A one to one mixture of **4** and **2** reacts to form **3** quantitatively as determined by ^{1}H NMR spectroscopy. In fact, **4** is such a labile metallacycle that **6**, the methylene dimer, can be isolated in high yields by allowing solutions of **4** to warm to room temperature (eq 6). Only small
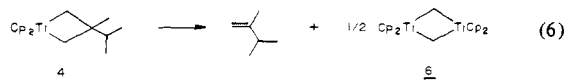
amounts of **6** are observed by ^{1}H NMR spectroscopy upon thermolysis of **3** at 80 °C for 4 h in C_6D_6, reflecting the relative stability of **3** with respect to **4** and **5**. No exchange of methylene groups is observed when **6** is heated with **2**-d_2. Thus, **6** represents the chain-termination product in this metathesis system as has been suggested in other systems.[6]

(6) Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 5922.
(7) Lauher, J. W.; Hoffmann, R. *J. Am. Chem.* **1976**, *98*, 1729.
(8) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.
(9) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521.

Scheme III

Table I. Inhibition of Added Olefin[a]

$[2]_{t=0}$, M	$10^5 k_{obsd}$, s^{-1}	$[2]_{t=0}$, M	$10^5 k_{obsd}$, s^{-1}
0.17	8.8	0.77	7.6
0.38	8.2		

[a] $[3]_{t=0}$ = 0.155 M, [PhC≡CPh] = 0.59 M, T = 40 °C.

There are a number of mechanistic alternatives for the olefin exchange reactions described above. By analogy to the conventional metathesis mechanism, the reactive species may be an olefin-free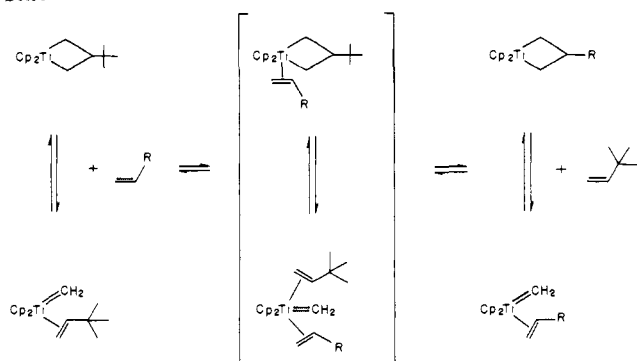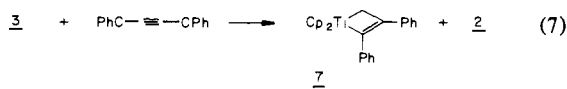 titanium–methylene intermediate B (Scheme II). This complex could be generated either directly from **3** or through the intermediacy of a titanium–methylene–olefin complex A. The presence of B in this reaction system seems plausible in view of the formation of **6** from **4** (eq 6). Alternatively, such a reactive and presumably unstable species need never be involved. Thus, processes involving the direct attack of an olefin on **3** or A become attractive pathways for these exchange reactions[1] (Scheme III).

To probe the nature of the reactive intermediates in the reactions depicted in eq 3 and 4, we examined the kinetics of the irreversible reaction of **3** with diphenylacetylene, which yields the titanacyclobutene **7** and **2** (eq 7).[2c,4a] With the use of ^{1}H NMR spec-
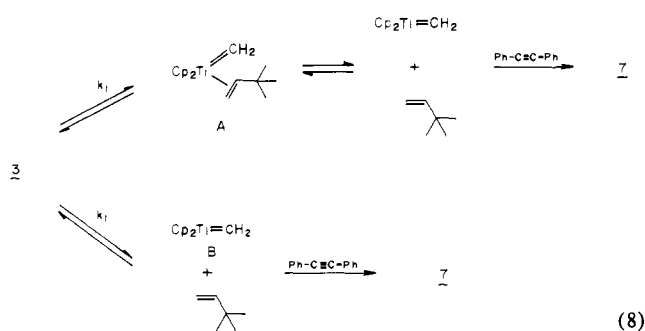

troscopy to monitor the reaction, kinetic data were obtained at 40 °C in benzene-d_6. The reaction rate was found to be first order in **3** for at least 3 half-lives and independent of [PhC≡CPh] over a wide range of relative concentrations with k_{obsd} = 9.2 × 10^{-5} s^{-1} (see Experimental Section). Rate data were obtained at several temperatures between 30 and 60 °C. The activation parameters calculated from the least-squares fits to the Arrhenius plots are $\Delta H^{\ddagger}$ = 26.9 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 8.9 eu. The reaction rate was slightly inhibited by the addition of **2** (Table I), suggesting competition of PhC≡CPh and **2** for a reactive intermediate. When **3** was treated with a 4-fold excess of both **2**-d_2 and PhC≡CPh, ^{2}H NMR spectroscopy indicated the formation of a small amount of **3**-d_2 after 1 half-life. When the reaction was carried to completion, **7**-d_2 was observed. A similar experiment was conducted with *trans*-**3**-d_1, **2**, and PhC≡CPh. It was found that the specifically labeled trans metallacyclobutane-d_1 was partially converted to *cis*-**3**-d_1 during the reaction.

The value of k_{obsd} was unaffected by the trapping substrate. Reaction of **3** with 2,2-dimethylpropionaldehyde[12] or Me$_3$SnCl[13] proceeded at the same rate as trapping with diphenylacetylene.

The above observations lead us to believe that the exchange of olefins or acetylenes with **3** proceeds via the ring opening (k_1

(10) Van Horn, D. E.; Negishi, E. *J. Am. Chem. Soc.* **1978**, *100*, 2252.

(11) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.

(12) Reaction of **3** with 2,2-dimethylpropionaldehyde to yield **2** and (Cp$_2$TiO)$_n$ proceeded with k_{obsd} = 9.3 × 10^{-5} s^{-1} at 40 °C: Brown-Wensley, K. Ph.D. Thesis, California Institute of Technology, 1981.

(13) Reaction of **3** with Me$_3$SnCl to yield **2** and Cp$_2$TiCH$_2$SnMe$_3$(Cl) proceeded with k_{obsd} = 9.4 × 10^{-5} s^{-1} at 40 °C: Ott, K. C.; Grubbs, R. H., unpublished observations.

in eq 8) of the titanacyclobutane to a titanium methylene species

B, which is then rapidly trapped by incoming olefin or acetylene to yield titanacyclobutanes or -butenes, respectively. A plot of $1/k_{obsd}$ vs. $[2]/[PhC≡CPh]$ is linear with an intercept of $1/k_1$ and a slope of k_{-1}/k_{1k2}. The measured value for the rate of ring opening (k_1) is 9.1 × 10^{-5} s^{-1}, and the ratio of the rates of trapping by olefin and acetylene (k_{-1}/k_2) is 0.15. This mechanistic interpretation is further supported by the observation of a large secondary isotope effect when **3**-d_2 was allowed to react with PhC≡CPh (eq 9). The ratio of **7** to **2** was 2.2/1.0 ($=k_{H_2}/k_{D_2}$)
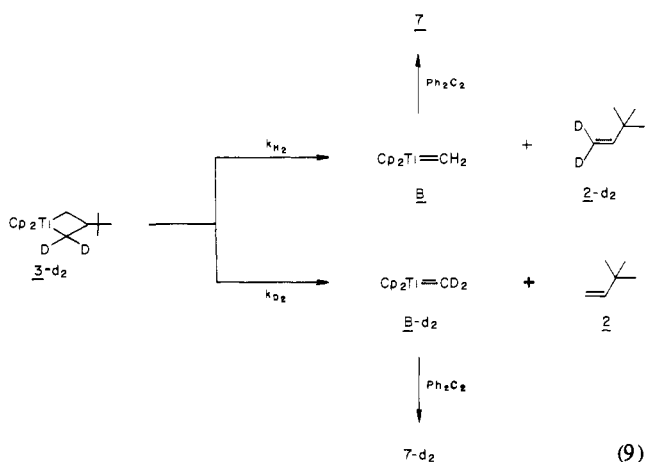
as determined by ^{1}H NMR spectroscopy. Similar reactions with α-**3**-d_1 or α,α,β-**3**-d_3 yielded isotope effects of k_{HD}/k_{H_2} = 1.4 and k_{HD}/k_{D_2} = 1.9, respectively. The magnitude of the isotope effects is consistent with a net decrease in p character of the deuterium-substituted carbon in the transition state (sp^3 methylene → sp^2 carbene). Since this effect is buffered by the corresponding change in the olefin formed when the nondeuterated carbene is generated, the true isotope effect is larger. Although trapping at A represents a viable pathway, it would require the intermediacy of either a titanium–methylene–bis(olefin) complex or a titanium–methylene–olefin–acetylene complex, which are formally 20-electron species. An $\eta^5 \rightarrow \eta^3$ shift of a cyclopentadienyl ligand to achieve an 18-electron configuration alleviates this problem.

The kinetics data do not allow a firm choice to be made between total reaction through B or competitive trapping of both A and B. The following results are most consistent with the former.

When **3**-d_5 was mixed with an equimolar amount of the analogous titanacycle **8** in benzene-d_6, heated to 50 °C (eq 10), and examined periodically by ^{1}H NMR spectroscopy, scrambling of protio- (or deuterio-) methylene units was observed. The spectra show resonances due to incorporation of protons into the α positions of **3**. The observation of **3**-d_3 is consistent with an intermolecular exchange of olefins between **3**-d_5 and **8** occurring through the intermediate B.
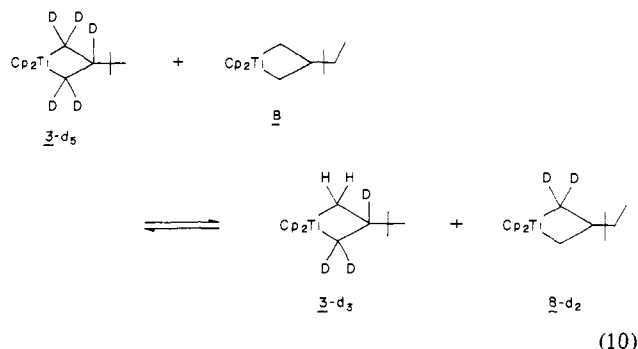
To further distinguish between the two possible intermediates A and B in the presence of substrates, we have studied the metathesis of *trans*-**3**-d_1 with unlabeled olefins. If indeed the olefin or diphenylacetylene exchange proceeds through the unsymmetrical olefin–methylene species A as in Scheme III, there should be retention of stereochemical information in the olefin exchange.

(10)

Scheme IV

If the exchange is followed with ^{2}H NMR spectroscopy, the ratio of (E)-2-d_1 to cis-3d_1 should be 2/1 (Scheme IV). However, if the exchange involves species A, the asymmetry induced by the presence of the olefin in the coordination sphere of the metal and the potential η^3-cyclopentadienyl ring could control the direction of approach of the incoming olefin and induce stereoselectivity in the exchange. It is important to note that $trans$-3-d_1 isomerizes to cis-3-d_1 in the absence of substrate at half the rate at which 3 reacts with diphenylacetylene. It seems unlikely that an intramolecular process involving the rotation of the metal–methylene bond in A is responsible for the isomerization. In dicyclopentadienylmetal–methylene systems, there is a single localized metal orbital that is of proper symmetry to π bond to the methylene ligand.[7] Hence, substantial barriers to free rotation are anticipated in these systems. Indeed, Hoffmann has calculated a barrier of at least 28 kcal mol^{-1} for a hypothetical example, $Cp_2Ti(CH_3)CH_2^-$.[7] Schrock and co-workers have previously reported high barriers to rotation in a number of alkylidene complexes of tantulum and niobium that are structurally analogous to the system presented here.[8] Thus, isomerization of the specifically labeled metallacycle could only be the result of nonstereospecific exchange reactions through a symmetrical methylene species B rather than an intramolecular process. For an examination of the stereochemistry of the olefin exchange reaction $trans$-3-d_1 was allowed to react with excess 2 at 40 °C. After 1 h ^{2}H{^{1}H} NMR spectroscopy showed the signals due to $trans$-3-d_1, cis-3-d_1, $trans$-2-d_1, and cis-2-d_1 at δ 2.17, 1.86, 4.84, and 4.91, respectively. The ratio of $trans$-2-d_1 to cis-3-d_1 was 3.4/1.0. These results are analyzed with use of the intermediates and parameters in Scheme IV to determine if there is stereoselectivity in this reaction ($k_t/k_c = 1$). Since the presence of cis-2-d_1 could have only arisen from the exchange of cis-3-d_1 with 2-d_0, the expression for the total concentration of cis-3-d_1 must also allow for this secondary reaction. It is also necessary to account for the loss of deuterium due to the formation of $trans$-3-d_1, albeit the correction is minimal (Scheme IV, path A). The approximate expression for the concentration of cis-3-d_1 is, thus $[cis$-3-$d_1]_{tot}$ = $[cis$-3-$d_1]$ + $[cis$-2-$d_1]$ + $^1/_2[cis$-2-$d_1]$. Therefore, the correct ratio of $[trans$-2-$d_1]/[cis$-3-$d_2]_{tot}$ was 2.6/1.0. This value can be related to the desired ratio k_t/k_c as shown by eq I–V. The

$$d[trans\text{-}2\text{-}d_1]/dt = k_{H_2}[trans\text{-}3\text{-}d_1] \qquad (I)$$

$$d[cis\text{-}3\text{-}d_1]_{tot}/dt = k_{HD}[trans\text{-}3\text{-}d_1]\left(\frac{k_c}{k_c + k_t}\right) \qquad (II)$$

$$\frac{d[trans\text{-}2\text{-}d_1]}{d[cis\text{-}3\text{-}d_1]_{tot}} = \frac{k_{H_2}}{k_{HD}}\left(\frac{k_c + k_t}{k_c}\right) = 2.6 \qquad (III)$$

$$\frac{k_c + k_t}{k_c} = 2.6\left(\frac{k_{HD}}{k_{H_2}}\right) = 1.9 \qquad (IV)$$

$$k_t/k_c = 0.9 \qquad (V)$$

required k_{H_2}/k_{HD} value was obtained from the reaction of $trans$-3-d_1 with diphenylacetylene. The ratio $k_t/k_c = 0.9$ indicates little, if any, stereoselectivity in the overall exchange. Values significantly different from 1 would have suggested that the reaction proceeded through A. In another experiment designed to
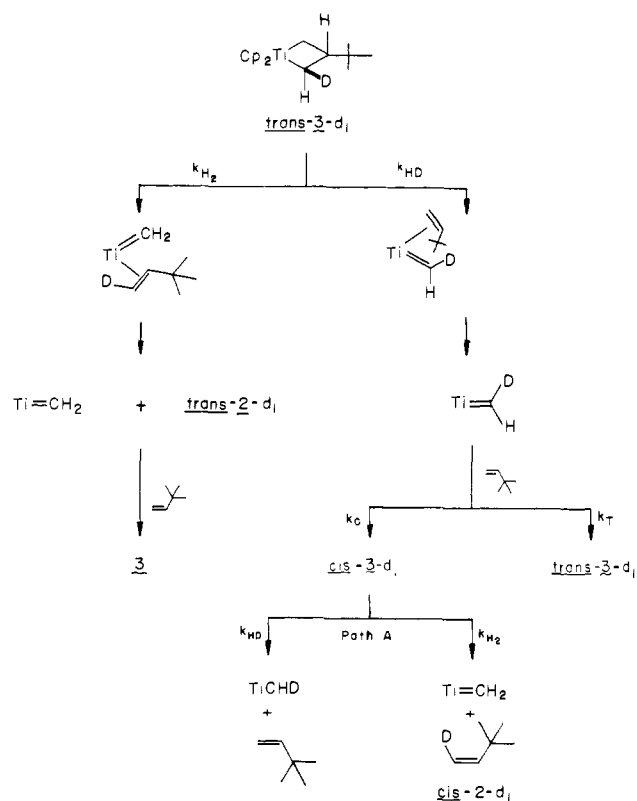
investigate the possibility of stereoselectivity in the exchange reaction, the reaction of $trans$-3-d_1 with 3,3-dimethyl-1-pentene (isoamylethylene) was studied (eq 11).

(11)
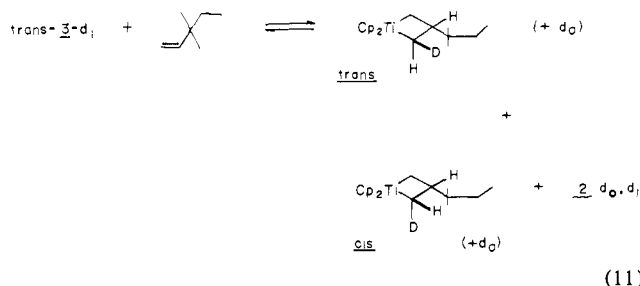
When this reaction is quenched with diphenylacetylene (which displaces the olefin with retention of stereochemistry (see Experimental Section) and the amount and stereochemistry of the product olefins, particularly those of the labeled 3,3-dimethyl-1-pentene, are observed, the degree of stereoselectivity in the overall exchange can be determined. In this case, correction of the isotope effect would not be necessary. The results of this experiment indicated that the 2-d_1 evolved contained only a trace of the Z isomer and that only a minimal amount of isomerization of the starting metallacycle had occurred. The deuterated 3,3-dimethyl-1-pentene consisted of a nearly equal mixture of the Z and E isomers, demonstrating that there is no measurable stereoselectivity in the interchange of 2 for 3,3-dimethyl-1-pentene. It appears that, in this system, the outgoing olefin imposes little, if any, stereochemical preference upon the incoming olefin. The results above, coupled with previous observations, are most consistent with the olefin exchange occurring via the intermediacy of $Cp_2Ti=CH_2$ (B).

Conclusions

The work described herein demonstrates that the exchange of olefins and acetylenes in this titanacyclobutene system proceeds through a rate-limiting ring opening to a metal–methylene intermediate, which can be trapped by a variety of substrates. We feel that the titanacyclobutenes open to the titanium–methylene–olefin complex A, which can reversibly lose olefin to

The Titanacyclobutane–Titanamethylene Interconversion

J. Am. Chem. Soc., Vol. 104, No. 26, 1982 7495

produce the titanium–methylene complex B. This high-energy intermediate is then rapidly trapped by a suitable substrate to yield products in a fast step. Intermediate B dimerizes to yield **6** in the absence of a suitable substrate and represents the chain-termination step of this metathesis system. Although the data do not require the intermediacy of A, we favor its existence on the reaction pathway from titanacyclobutane to the titanium–methylene complex B.

The resting state of the titanium metathesis system lies on the metallacyclobutane side rather than the metal–alkylidene side as has been observed in the well-defined tantalum[2e] and tungsten[2d,e] metathesis systems.

We are unable at present to address the question of the stereoselectivity in the exchange reaction of an olefin with a titanium–alkylidene species such as $Cp_2Ti=CHR$. We are presently investigating possible routes to α-substituted metallacyclobutanes that allow the study of the geometry of the approach of an olefin to a Cp_2TiCHR moiety.

Experimental Section

Materials. Titanocene dichloride was purchased from Strem Chemicals or Boulder Scientific and purified by Soxhlet extraction with dichloromethane. $AlMe_3$ was purchased from Aldrich Chemical Co. as a 2 M solution in toluene or from Alfa as the neat liquid. 3,3-Dimethyl-1-butene, 2,3-dimethyl-1-butene, and α-methylstyrene were purchased from Aldrich. 3,3-Dimethyl-1-pentene was purchased from ICN Pharmaceuticals. Deuterated olefins were prepared by literature methods[9,10] and purified by preparative GC. All olefins were deried over Linde 4 A molecular sieves. (Dimethylamino)pyridine (DMAP, Aldrich) was recrystallized from hot toluene. Diphenylacetylene (Aldrich) was recrystallized from hot toluene. Dichloromethane was dried over P_2O_5 or CaH_2 and degassed on a vacuum line. Pentane, hexane, and petroleum ether were stirred over H_2SO_4, dried over CaH_2, and vacuum transferred onto purple sodium–benzophenone ketyl. Solvents thus dried and deoxygenated were vacuum transferred into dry vessels equipped with Teflon needle valve closures and stored under Ar. Benzene-d_6 (Merck Sharp and Dohme) and toluene-d_8 (Aldrich) were dried and deoxygenated by freeze-pump-thawing sodium–benzophenone ketyl solutions. Dichloromethane-d_2 (Norell, Inc.) was dried over CaH_2 and degassed by freeze-pump-thawing.

General Procedures. All manipulations of air- and/or moisture-sensitive compounds were carried out with use of standard Schlenk or vacuum line techniques. Solids were transferred in a N_2-filled Vacuum Atmospheres Dri-Lab equipped with an MO-40-1 purification train and a DK-3E Dri-Kool. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4 A molecular sieves. NMR spectra were recorded on a JEOL FX-90Q (89.60 MHz, H; 22.53 MHz, ^{13}C; 13.76 MHz, ^{2}H) or a Bruker WM-500 (500.13 MHz, ^{1}H; 76.76 MHz, ^{2}H) spectrometer. Kinetics by NMR spectroscopy were typically run in the automated mode on the JEOL FX-90Q. Temperatures were measured with use of $\Delta\nu_{MeOH}$ and were constant to within ±0.1 °C. Difference NOE's were measured on the Bruker WM-500. Preparative gas chromatography was performed on a Varian Aerograph Model 920 using 20-ft columns of Durapak or 6-ft columns of 10% satd. $AgNO_3$ in tetraethylene glycol on Chromasorb P. GC/MS was performed on a Kratos MS25.

Preparation of 1. The preparation of this compound has been previously described by Tebbe et al.[11] A slightly modified procedure is given here. Neat $AlMe_3$ (42 mL, 440 mmol) was added via cannula to a suspension of Cp_2TiCl_2 (50 g, 200 mmol) in toluene (200 mL) to give a homogeneous red solution. Evolution of methane began immediately. After this solution was stirred 48 h, all volatiles were removed by vacuum distillation into a cold trap (Caution: the $AlMe_2Cl$ evolved reacts violently with protic media and due precautions should be exercised). A small sample of the resulting red crystalline material may be assayed for the presence of $Cp_2TiClAlMeClCCH_2$ (the $-CH_2-$ resonance appears at δ 7.68 as an unresolved AB quartet). This materials was converted to **1** by addition of an equivalent amount of $AlMe_3$ to the reaction mixture, which was redissolved in toluene. The resulting solution was filtered through a pad of Celite supported on a coarse frit and concentrated to the point of saturation ($\sim$150–170 mL total volume). This saturated solution was carefully layered with an equal volume of hexane or petroleum ether and allowed to stand undisturbed at -20 °C for 2–3 days. The supernantant was removed via cannula and the red crystalline mass washed with several portions of petroleum ether at -20 °C. The solids were dried under high vacuum. Typical yields were 30–35 g (53–61%). An additional crop of less pure material (10–15 g) was obtained by condensing the mother liquor as above.

Preparation of 3. To **1** (1 g, 3.5 mmol) dissolved in toluene (6 mL) was added 3,3-dimethyl-1-butene (500 μL, 3.9 mmol) and then (dimethylamino)pyridine (DMAP, 472 mg, 4 mmol). The resulting red solution was transferred into 50 mL of vigorously stirred, cold (-20 °C) pentane or petroleum ether. The DMAP–$AlMe_2Cl$ adduct precipitated as a yellow-orange mass, which was rapidly filtered to give a clear red solution. This solution was evaporated to dryness by vacuum distillation to yield 770–800 mg of **3** (80–83%). This crude material was recrystallized from diethyl ether to give 480 mg (50%) of **3** as red needles. *trans*-3-d_1 and 3-d_2 were prepared similarly with use of *trans*-3,3-dimethyl-1-butene-*1*-d_1 or 3,3-dimethyl-1-butene-*1,1*-d_2, respectively. 3-d_5 was prepared from 3,3-dimethyl-1-butene-*1,1,2*-d_3 and 1-d_2. NMR data of **3** have previously been published.[4] Compound **8** was prepared by analogous methods with use of 3,3-dimethyl-1-pentene and characterized by ^{1}H NMR and protonolysis.

Preparation of 4 and 5. To a cold (-30 °C) suspension of DMAP (427 mg, 4 mmol) and 2,3-dimethyl-1-butene (1.8 mL, 14 mmol) in 3 mL of CH_2Cl_2 was slowly added a solution of **1** (1.0 g, 3.5 mmol) in 3 mL of CH_2Cl_2. This homogeneous red solution was stirred for 15 min while it was allowed to warm to -10 °C. The solution was slowly dripped into 50 mL of vigorously stirred pentane at -30 °C. The DMAP–$AlMe_2Cl$ adduct was rapidly filtered, and the resulting clear red solution was evaporated to dryness at or below -10 °C to yield 480–770 mg (50–80%) of red powder. This material could be recrystallized from diethyl ether by cooling saturated solutions from 0 to -50 °C to yield red needles of **4**. NMR data have been previously reported.[6]

Compound **5** was prepared similarly, except only 1 equiv of α-methylstyrene was used. Use of excess olefin leads to decomposition upon attempting to pump the excess α-methylstyrene from the metallacycle. This was circumvented by crystallizing the metallacycle from the pentane-methylene chloride solution at -78 °C and then washing the metallacycle free of α-methylstyrene with cold (-50 °C) pentane. The material so obtained is of suitable purity for further reactions; yield 320–420 mg (30–39%). ^{1}H NMR (CD_2Cl_2, -20 °C) shifts vs. residual CHDCl$_2$: δ 5.32, 6.011 (5 H, Cp$_A$); 5.673 (5 H, Cp$_B$); 2.818 (d, $J = 8.8$ Hz, 2 H, H$_A$, H$_B$); 2.227 ($J = 8.8$ Hz, 2 H, H$_A$); 1.058 (3 H, Me); 7.542, 7.249, 7.128 (m, 5 H, Ph). Assignments of H$_A$, H$_B$, Cp$_A$, and Cp$_B$ were accomplished by difference NOE methods. ^{13}C NMR (CD_2Cl_2, -20 °C) chemical shifts vs. CD_2Cl_2: δ 53.8; 111.4; 111.2 (Cp's); 73.9 (C$_\alpha$); 41.2 (Me); 15.8 (C$_\beta$); 128.3, 127.8, 126.8, 125.1 (Ph). Both **4** and **5** are thermally labile and were not characterized by elemental analysis.

Metathesis of 2-d_3 and 2-d_0. 2-d_3 (0.330 mmol) and 2-d_0 (0.326 mmol) were added to **3** (0.108 mmol) in 600 μL of toluene in a 5-mm NMR tube. The tube was cooled to 77 K and sealed. The sample was then heated to 40 °C for 13 h. The tube was then opened under an inert atmosphere, and the neohexenes were vacuum transferred into another vessel for GC/MS analysis; m/e 87, 86, 84, and 84 for 2-d_3, 2-d_2, 2-d_1, and 2-d_0 were observed in the ratio 1/1/1.2/1.8.

Nonstereoselective Exchange of (Z)-α-Methylstyrene-d_1 with 5. **5** (5 mg, 0.016 mmol) was dissolved in 400 μL of toluene-d_8 at -20 °C. A 30-μL amount (0.23 mmol, 14.5 equiv) of (Z)-α-methylstyrene-d_1 was injected via syringe. The solution was mixed well at -20 °C and placed in an NMR probe held at 0 °C. The extent of isomerization of the olefin was monitored by measuring the ratio of the integrals of the peaks at 4.98 and 5.33 ppm (*E* and *Z* vinylic hydrogen resonances, respectively) by ^{1}H NMR spectroscopy. After 5 min, the ratio Z/E was 3.7/1 corresponding to 1.2 turnovers per minute per Ti.

Kinetics of the Reaction of 3 with Diphenylacetylene To Produce $Cp_2TiCH_2C(Ph)C(Ph)$ (7). Stock solutions of **3** and diphenylacetylene in C_6D_6 were prepared by weighing the appropriate amount of each reactant into a 2-mL volumetric flask. The solids were then dissolved with C_6D_6. An appropriate aliquot of each solution was withdrawn via syringe and transferred into a 5-mm NMR tube. The tube was sealed under vacuum and chilled until the sample was placed into a NMR spectrometer probe maintained at 40 °C. After sufficient time was allowed for the sample to come to thermal equilibrium in the probe, spectra were recorded periodically. The disappearance of starting material was monitored by observing the upfield cyclopentadienyl resonance of the product **7** at δ 5.65. This procedure was followed for several concentrations of **3** (0.036–0.21 M) and diphenylacetylene (0.056–0.79 M). The activation parameters were derived from the kinetics data obtained at 30–60 °C.

Kinetics of the Reaction of 3 with Diphenylacetylene in the Presence of Excess 2 To Produce 7. Stock solutions of **3** and diphenylacetylene were prepared in C_6D_6. Aliquots of **3** and diphenylacetylene were syringed into a 5-mm NMR tube. Aliquots of **2** were then added via syringe along with enough C_6D_6 to bring the concentration of Ti and Ph_2C_2 to 0.155 and 0.590 M, respectively. The sample tube was then sealed and chilled until the sample was placed into the NMR probe held at a con-

stant temperature of 40 °C. Kinetics data were then derived from ^{1}H NMR spectra as described above. The results of this experiment are tabulated in Table I.

Reaction of 3 or *trans*-3-d_1 with Diphenylacetylene in the Presence of 2-d_2 or 2. 3 (20 mg, 0.073 mmol) was placed in a 5-mm NMR tube along with diphenylacetylene (52 mg, 0.289 mmol). The tube was then attached to a Teflon stopcock with a ground-glass joint, cooled to -50 °C, and degassed. A 500-μL amount of toluene along with 37 μL of 2-d_2 (0.289 mmol) was then vacuum transferred into the tube. After the contents were warmed to room temperature and mixed well, the tube was placed in a constant-temperature bath maintained at 40 °C. After ca. 1 half-life, ^{2}H NMR spectroscopy indicated that 4% of the total deuterium had been incorporated into the metallacycle. After 7 h, the reaction had proceeded to completion, and 1.7% of the deuterium had been incorporated into 7. Exactly the same procedure was followed for the reaction of *trans*-3-d_1 with diphenylacetylene in the presence of 2. After 7 h, ^{2}H NMR spectroscopy indicated that the deuterated 3,3-dimethyl-1-butene contained 7.5% of the cis isomer.

Reaction of *trans*-3-d_1 with Diphenylacetylene. *trans*-3-d_1 (21 mg, 0.076 mmol) was placed into a 5-mm NMR tube attached to a ground-glass joint along with diphenylacetylene (54 mg, 0.3 mmol). A Teflon needle valve adapter was attached and the apparatus evacuated on a vacuum line. Approximately 500 μL of toluene was vacuum transferred into the tube, and the tube was sealed. The tube was heated to 40 °C. After 2 h (ca. 1 half-life), ^{2}H NMR spectroscopy showed *trans*-2-d_1 (δ 4.84), 7-d_1 (δ 3.38), and *trans*-3-d_1 (δ 2.17). Only a trace of *cis*-3-d_1 and no *cis*-3-d_1 could be detected. After 12 h at 40 °C, the reaction was complete, and the ratio of *trans*-2-d_1 to 7-d_1 was 1.37/1.0.

Reaction of 3-d_2 with Diphenylacetylene. A mixture of 21 mg of 3-d_2 (0.076 mmol) and 54 mg (0.30 mmol) of diphenylacetylene was loaded into a 5-mm NMR tube attached to a ground-glass joint. A Teflon needle valve adapter was attached and the apparatus evacuated on a vacuum line. Approximately 500 μL of toluene was vacuum transferred into the tube, and the tube was sealed. The sample was heated at 40 °C for 12 h. ^{2}H NMR spectroscopy indicated that the ratio of 2-d_2 to 7-d_2 was 2.2/1.0.

Reaction of 3-d_5 with 8. A mixture of 14 mg of 3-d_5 (0.049 mmol) and 14 mg of 8 (0.048 mmol) was loaded into a 5-mm NMR tube attached to a ground-glass joint. A Teflon stopcock was then attached, and the tube was evacuated on a vacuum line. Approximately 500 μL of benzene-d_6 was vacuum transferred into the tube, and the tube was sealed. The tube was heated to 50 °C. After 1 h, ^{1}H NMR spectroscopy indicated resonances due to protons incorporating into the α positions of 3, at δ 2.17, 1.86.

Metathesis of *trans*-3-d_1 with 2. This reaction was run with molar ratios of *trans*-3-d_1 to 2 of 2/1 and 10/1. *trans*-3-d_1 (21 mg, 0.076

mmol) was loaded into a 5-mm NMR tube attached to a ground-glass joint. A Teflon stopcock was attached, and the tube was evacuated. A 500-μL of amount of toluene and 2 (20 μL, 0.155 mmol) were vacuum transferred into the tube. The tube was heated at 40 °C for 1 h. ^{2}H{^{1}H} NMR spectroscopy indicated that the ratio of *trans*-2-d_1 (δ 4.84) to *cis*-3-d_1 (δ 1.86) was 3.4/1. The ratio of *trans*-2-d_1 to *cis*-2-d_1 was 18.7/1. When the experiment was repeated with a molar ratio of *trans*-3-d_1 to 2 of 10/1, after 1 h at 40 °C, the ratio of *trans*-2-d_1 to *cis*-3-d_1 was 3.5/1, and the ratio of *trans*-2-d_1 to *cis*-2-d_1 was 14/1.

Metathesis of *trans*-3-d_1 with 3,3-Dimethyl-1-pentene. *trans*-3-d_1 (120 mg, 0.433 mmol) was loaded into a small Schlenk tube. 3,3-Dimethyl-1-pentene (425 mg, 4.33 mmol) and 1.5 mL of toluene were added via syringe. The mixture was then cooled to -196 °C and evacuated. Then it was heated to 40 °C for 65 min. All volatiles were removed in vacuo. The metallacycles were dried at room temperature an additional 1 h under high vacuum. Diphenylacetylene (232 mg, 1.3 mmol) was added to the Schlenk tube along with 1.0 mL of toluene. The mixture was then heated to 40 °C for 12 h. All volatiles were vacuum transferred into another vessel. The volatiles contained 2 (d_0 and d_1) and 3,3-dimethyl-1-pentene (d_0 and d_1) as determined by GC/MS. The 3,3-dimethyl-1-butenes were separated from the 3,3-dimethyl-1-pentenes by preparative GC (Durapak, 120 C, 20 ft). ^{2}H{^{1}H} NMR spectroscopy of 3,3-dimethyl-1-pentene showed two signals of approximately equal intensity at δ 4.89 and 4.92. In the ^{2}H spectrum two overlapping doublets were observed. The peak entered at δ 4.89 had J(H–D) = 2.56 Hz, and the peak at δ 4.92 had J(H–D) = 1.59 Hz. From the magnitude of the coupling constants, the δ 4.89 and 4.92 peaks are assigned to *cis*-3,3-dimethyl-1-pentene-*1*-d_1 and to *trans*-3,3-dimethyl-1-pentene-*1*-d_1, respectively. Examination of deuterated 2 by ^{2}H NMR spectroscopy indicated only a trace of *cis*-2-d_1 had been formed during the reaction.

Preparation, Properties, and Kinetics of the Reaction with Tributyltin Hydride of Manganese(0) Radicals Mn(CO)₃(R₃P)₂[1a]

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Abstract: Persistent manganese(0) radicals, Mn(CO)₃L₂·, where L = P(*n*-Bu)₃, P(*i*-Bu)₃, P(*i*-Pr)₃, or P(O-*i*-Pr)₃, have been prepared by a photochemical route. The radicals exhibit absorptions in the 600–1200-nm range, ascribed to transitions involving largely metal-centered orbitals. Reaction with CCl₄ gives rise to the corresponding Mn(CO)₃L₂Cl, predominantly the 2,4-L₂-1-Cl isomer. The most likely geometry of the radicals is a distorted square pyramid, with phosphorus ligands in trans-basal positions. Reaction of Mn(CO)₃L₂· with HSuBu₃ gives rise to mainly Mn(CO)₃L₂H, with small amounts of Mn(CO)₃L₂SnR₃. The reaction is first order each in Mn(CO)₃L₂· and HSnR₃ and appears to proceed via a simple H atom transfer. The bimolecular rate constants at 20 °C in hexane are 10.7, 0.786, 0.110, and 2.0 × 10⁻³ M⁻¹ s⁻¹ for L = P(*n*-Bu)₃, P(*i*-Bu)₃, P(O-*i*-Pr)₃, and P(*i*-Pr)₃, respectively.

There has been a lively interest during the past few years in the properties of metal carbonyl radicals.[2] For the most part,

such radicals, which are most conveniently formed by metal–metal bond homolysis, atom transfer, or electron transfer, are not