Synthesis, Structure, and Reactions of Stable Titanacyclopentanes

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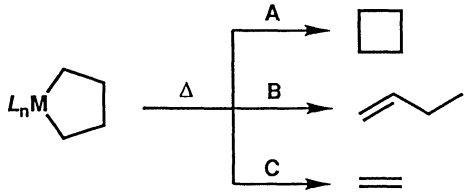
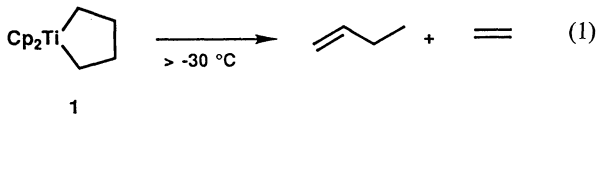
Titanacyclic compounds of the formula $Cp^*_2Ti(CH_2CH_2C(CH_2CHR)CH_2)$ (**5a**; R=H and **5b**; R=C_6H_5, Cp^*=pentamethylcyclopentadienyl), the first stable titanacyclopentanes, have been prepared by the reaction of bis(pentamethylcyclopentadienyl)titanium–ethylene complex (**3**) with methylenecyclopropanes (**4**), and their structures were determined based on both spectroscopic data and X-ray crystallography. Complex **5b** crystallized in space group $P2_1/a$ (Z=4) with cell constants, a=21.832(3), b=8.580(1), c=14.759(2) Å, β=96.81(1)°, U=2744.9(6) Å^3 (4261 reflections, R=0.053). The reaction of **5** with carbon monoxide afforded spiro[2.4]heptan-5-ones in 98% yield. The thermal decomposition of **5** has been investigated, and possible mechanisms of the reactions have been proposed based on deuterium-labeled experiments. A novel formal reductive elimination of organic ligands giving 1-phenylspiro[2.4]hexane has been observed in the thermolysis of **5b**. A structure–reactivity relationship has been discussed.

The chemistry of metallacyclic compounds has been the subject of considerable interest since many synthetically important organic reactions mediated by transition-metal complexes proceed via metallacyclic intermediates.[1] Although numerous metallacyclic compounds have been known, only a limited number of such compounds of the first transition series elements have been isolated and characterized.[2,3] Metallacyclopentanes, when they are heated in solution or in solid state, suffer from several kinds of thermal reactions which can be classified into three modes of reactions (paths A, B, and C), as shown in Scheme 1. A simple reductive elimination produces cyclobutane (mode A), while a β-hydrogen elimination followed by a reductive elimination (mode B) gives rise to 1-butene. The third important reaction is the β-carbon–carbon bond fission (mode C) giving two moles of olefins, which is sometimes reversible; an oxidative coupling of two olefins on a metal gives back metallacyclopentanes. The product distribution varies depending on the nature of metals, ligands, and other experimental conditions. Usually, compounds of the late transition elements suffer from mode A and B reactions, while those of the early transition elements tend to decompose by paths B and C.

Bis(cyclopentadienyl)titanacyclopentane (**1**) (Cp= cyclopentadienyl) has been known to be unstable in solution, even at −30 °C, and all attempts to isolate **1** have been unsuccessful. A facile β-elimination reaction (mode B reaction) and a β-carbon–carbon bond fission (mode C reaction) giving 1-butene and ethylene, respectively, might be the major reason of its instability (Eq. 1).[3] Isolation of complex **2** (Cp^*=pentamethylcyclopentadienyl) is also very difficult because it is in equilibrium with ethylene complex **3** and free ethylene (Eq. 2). Here, a selective cleavage of the β-C–C bond is the main pathway of decomposition.[3c] We thought that if a strained olefin is used in place of ethylene, this equilibrium will be forced to shift to the left-hand side so that the strain of the olefin would be released. Such an effect would stabilize the titanacyclopentane **2**. For the purpose of carrying out detailed structure–reactivity studies on this class of compounds, we have investigated this subject. We describe here the isolation, structures, and some reactions concerning new stable titanacyclopentanes derived from **3** and methylenecyclopropanes **4**.[4]



Scheme 1.

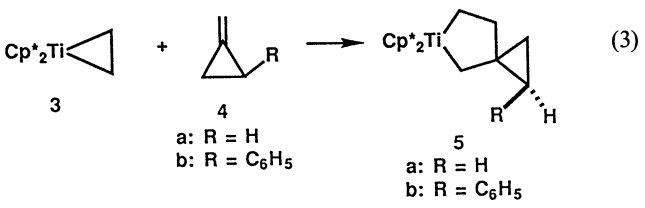


(1)

(2)

Results and Discussion

Synthesis and Characterization of Stable Titanacyclopentanes 5. Decamethyltitanocene–ethylene complex **3** has been conveniently prepared in 43% isolation yield by a reaction of $Cp^*_2TiCl_2$ and two equivalent of butyllithium under atmospheric pressure of ethylene. When a mixture of **3** and an excess amount of methylenecyclopropane (**4a**) in hexane was stirred at −10 °C for 48 h under an argon atmosphere, titanacyclopentane **5a** was obtained as orange needles in 65% yield after recrystallization of the crude product from hexane at



(3)

−80 °C (Eq. 3). Complex **5a** melted at 156—158 °C with decomposition, while slowly decomposing in toluene at 95 °C ($t_{1/2}$=91 min).

The structure of **5a** was supported by its spectral data. The ^{1}H NMR spectrum of **5a** in toluene-d_8 showed that each methylene proton is magnetically equivalent and exhibited no substantial change down to −90 °C; this indicates that the conformational change of the titanacyclopentane ring is rapid, even at −90 °C. Similarly, the phenyl derivative **5b** was prepared as deep-red prisms in 83% yield by treatment of **3** with 2-phenyl-1-methylenecyclopropane (**4b**) at 20 °C for 48 h. The half-life of **5b** in toluene at 95 °C is ca. 3 min. The structure of **5b** was determined by its spectral data and X-ray crystallography.

The molecular structure of **5b** is shown in Fig. 1. Selected bond distances and angles are summarized in Tables 1 and 2. Complex **5b** is monomeric and has the coordination geometry of a distorted tetrahedron defined by two pentamethylcyclopentadienyl ligands and two carbon atoms of the metallacyclopentane ring. The bond lengths of 1.513(5) Å for C(3)–C(4), 1.529(5) Å for C(3)–C(7), and 1.527(4) Å for C(6)–C(7) are comparable, which is in contrast with the fact that the stable metallacyclopentanes of the first transition elements such as Fe,[2g] Co,[2c,5] and Ni[2a,b,6] have a tendency for the bond distances of C_β—C_β' to usually be shorter than those of C_α–C_β. This relatively long C_β–C_β' bond distance in **5b** might be related to an easy cleavage of the C_β–C_β' bond of titanacyclopentanes. The five-membered ring of **5b** is fixed in a puckered form and the C(1)–C(3) bond occupies a pseudoequatorial position. The C(4)–Ti–C(6) angle is 80.6(1)°, showing that this angle is considerably distorted from the ideal value of 110° calculated for Cp_2TiH_2.[7] This deformation of

Table 1. Selected Bond Distances (Å) and Their esd's for **5b**[a]

Ti–C4	2.214(3)	Ti–C6	2.189(3)
Ti–Cp1	2.483(3)	Ti–Cp2	2.449(3)
Ti–Cp3	2.451(3)	Ti–Cp4	2.442(3)
Ti–Cp5	2.468(3)	Ti–Cp11	2.490(3)
Ti–Cp12	2.480(3)	Ti–Cp13	2.431(3)
Ti–Cp14	2.472(3)	Ti–Cp15	2.441(3)
Ti–Cp*1	2.146	Ti–Cp*2	2.150
C1–C2	1.516(5)	C1–C3	1.536(4)
C1–CB1	1.483(6)	C2–C3	1.509(5)
C3–C4	1.513(5)	C3–C7	1.529(5)
C6–C7	1.527(4)		
CB1–CB2	1.378(7)	CB1–CB6	1.384(5)
CB2–CB3	1.380(7)	CB3–CB4	1.351(6)
CB4–CB5	1.360(7)	CB5–CB6	1.395(6)
Cp1–Cp2	1.412(4)	Cp1–Cp5	1.408(4)
Cp1–Cp6	1.510(5)	Cp2–Cp3	1.409(4)
Cp2–Cp7	1.508(5)	Cp3–Cp4	1.416(4)
Cp3–Cp8	1.510(5)	Cp4–Cp5	1.404(5)
Cp4–Cp9	1.514(5)	Cp5–Cp10	1.516(5)
Cp11–Cp12	1.408(4)	Cp11–Cp15	1.417(4)
Cp11–Cp16	1.511(4)	Cp12–Cp13	1.411(4)
Cp12–Cp17	1.509(5)	Cp13–Cp14	1.422(4)
Cp13–Cp18	1.501(5)	Cp14–Cp15	1.403(4)
Cp14–Cp19	1.491(5)	Cp15–Cp20	1.502(5)

a) Cp*1 and Cp*2 are the centroids of two cyclopentadienyl rings, Cp1–Cp5 and Cp11–Cp15, respectively.

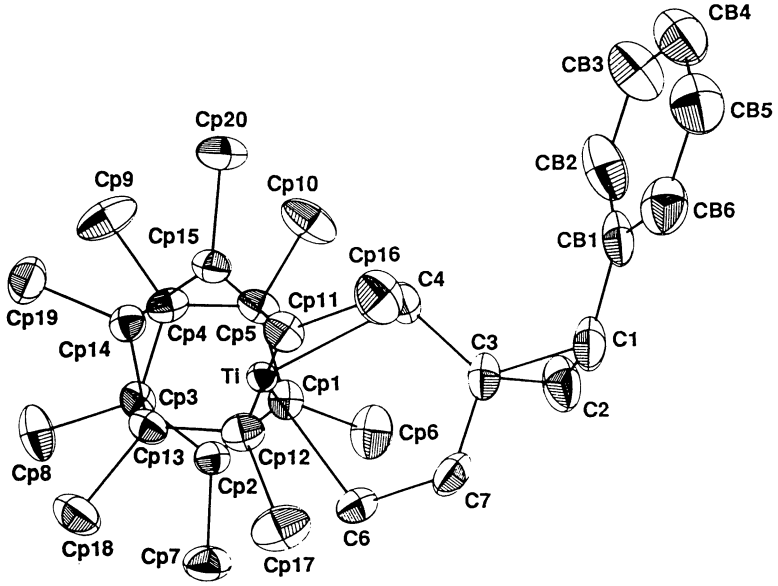


Fig. 1. ORTEP drawing of **5b** with the labeling scheme. The hydrogen atoms were omitted for clarity.

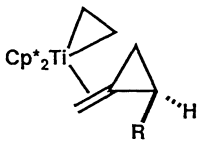
Table 2. Selected Bond Angles (degree) and Their esd's for **5b**[a]

C4–Ti–C6	80.6(1)	C4–Ti–Cp*1	106.3
C4–Ti–Cp*2	106.1	C6–Ti–Cp*1	105.9
C6–Ti–Cp*2	105.8	Cp*1–Ti–Cp*2	137.6
C2–C1–C3	59.2(2)	C2–C1–CB1	122.7(4)
C3–C1–CB1	122.9(3)	C1–C2–C3	61.1(2)
C1–C3–C2	59.7(2)	C1–C3–C4	121.3(3)
C1–C3–C7	115.2(3)	C2–C3–C4	120.0(3)
C2–C3–C7	116.3(3)	C4–C3–C7	114.0(3)
C3–C4–Ti	109.8(2)	C7–C6–Ti	107.2(2)
C3–C7–C6	109.0(3)		
C1–CB1–CB2	124.8(3)	C1–CB1–CB6	119.7(4)
CB2–CB1–CB6	115.5(4)	CB1–CB2–CB3	122.7(4)
CB2–CB3–CB4	120.7(5)	CB3–CB4–CB5	118.8(4)
CB4–CB5–CB6	120.5(4)	CB1–CB6–CB5	121.8(4)
Cp2–Cp1–Cp5	107.7(3)	Cp2–Cp1–Cp6	125.4(3)
Cp5–Cp1–Cp6	126.5(3)	Cp1–Cp2–Cp3	108.1(3)
Cp1–Cp2–Cp7	126.3(3)	Cp3–Cp2–Cp7	125.1(3)
Cp2–Cp3–Cp4	107.9(3)	Cp2–Cp3–Cp8	124.7(3)
Cp3–Cp3–Cp8	125.5(3)	Cp3–Cp4–Cp5	107.8(3)
Cp3–Cp4–Cp9	126.8(3)	Cp5–Cp4–Cp9	123.7(3)
CP1–Cp5–Cp4	108.5(3)	Cp1–Cp5–Cp10	126.9(3)
Cp4–Cp5–Cp10	123.9(3)		
Cp12–Cp11–Cp15	107.5(3)	Cp12–Cp11–Cp16	126.2(3)
Cp15–Cp11–Cp16	125.1(3)	Cp11–Cp12–Cp13	108.5(3)
Cp11–Cp12–Cp17	126.9(3)	Cp13–Cp12–Cp17	122.9(3)
Cp12–Cp13–Cp14	107.6(2)	Cp12–Cp13–Cp18	124.2(3)
Cp14–Cp13–Cp18	127.1(3)	Cp13–Cp14–Cp15	107.7(3)
Cp13–Cp14–Cp19	125.8(3)	Cp15–Cp14–Cp19	124.6(3)
Cp11–Cp15–Cp14	108.5(3)	Cp11–Cp15–Cp20	124.8(3)
Cp14–Cp15–Cp20	126.3(3)		

a) Cp*1 and Cp*2 are the centroids of two cyclopentadienyl rings, Cp1–Cp5 and Cp11–Cp15, respectively.

angle C(4)–Ti–C(6), however, is not considered to destabilize the complex very much, since the difference in the total energy of the complex was calculated to be only within 3 kcal mol^{-1} over the range 75—130°.[5]

Complex **5** can be considered to arise from a mixed-ligand complex of type **6** by oxidative coupling of the



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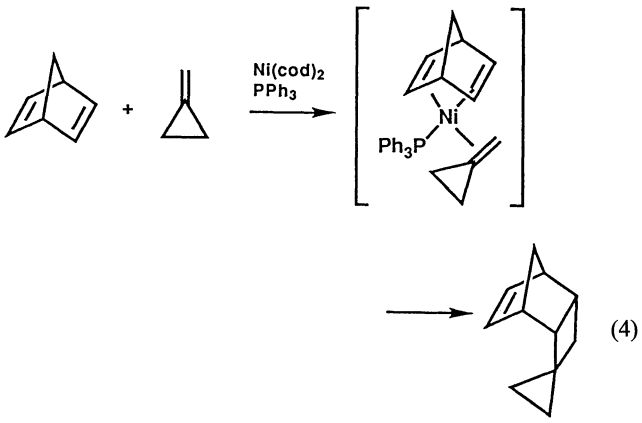
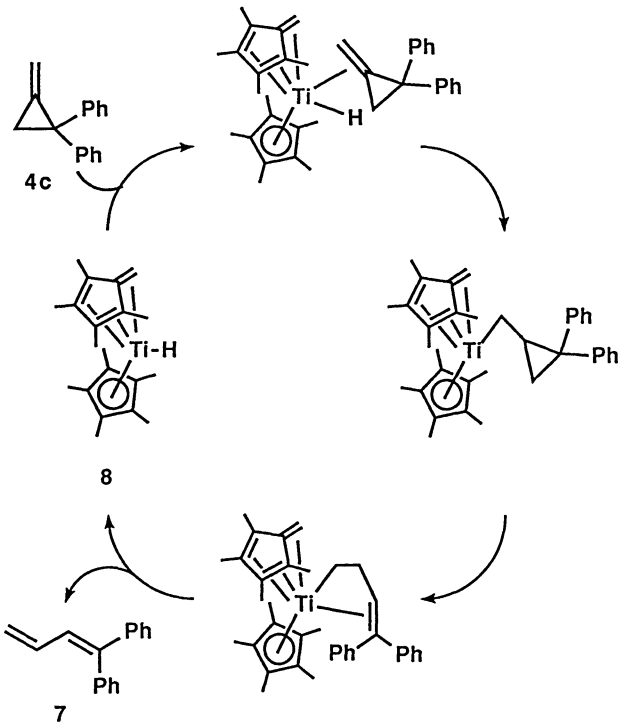
two ligands on titanium or by migratory insertion of the olefin into the Ti–C bond.[8] Selective formation of a related mixed-ligand complex has been proposed for a [2+2] cyclocoupling of norbornadiene and methylenecyclopropane (Eq. 4), in which a subtle balance of the coordination abilities of the two olefins is considered to be an important factor.[9] On the other hand, another possible mechanism is a direct [2+2] suprafacial reaction of the olefinic part of methylenecyclopropane and the strained Ti–C bond of **3**.[8a]



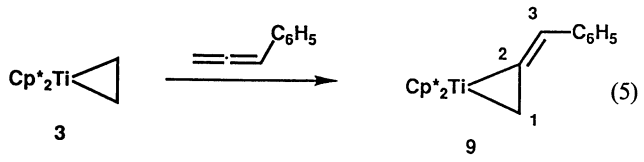
(4)

When 2,2-diphenyl-1-methylenecyclopropane (**4c**) was stirred with **3** in toluene at room temperature, no reaction took place, which can be ascribed to a steric repulsion between bulky pentamethylcyclopentadienyl ligands and two phenyl substituents of **4c**. At an elevated temperature (70 °C), however, **4c** isomerized catalytically to 1,3-butadiene derivative **7** in quantitative yield (Scheme 2). The catalytic conversion of **4c** to **7** can be viewed as proceeding by the mechanism shown in Scheme 2, which involves a cyclopropylmethyl—3-butenyl rearrangement. Titanium hydride **8** is considered to be a catalytically active species.[10,11]

The reaction of **3** with phenylallene has also been investigated; only a ligand-exchange reaction occurred to give a new titanocene–phenylallene complex **9** (Eq. 5). The structure of **9** was determined by a comparison



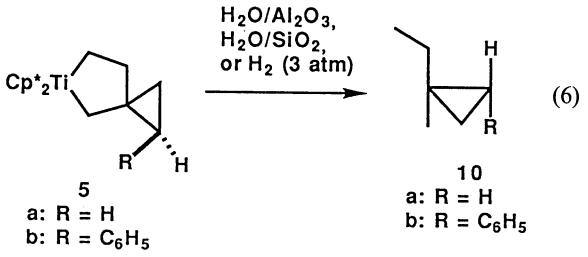
Scheme 2.



(5)

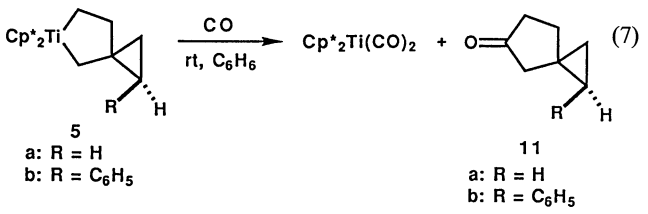
of the ^{1}H and ^{13}C NMR chemical shift values as well as the C–H coupling constants of **9** and those of free phenylallene.[3c,7] No stereochemical assignment has been performed, though the structure of a sterically less-hindered isomer has been tentatively presented. Phenylallene was released from **9** when it decomposed upon exposure to air.

Reactions of 5a and 5b. Complexes **5** are quite stable in dilute hydrochloric acid. However, when a benzene solution of **5a** was treated with silica gel or alumina, a smooth hydrolysis occurred to give 1-ethyl-1-methylcyclopropane (**10a**) in 96% yield (Eq. 6). A similar treatment of **5b** in benzene with silica gel afforded *r*-1-ethyl-1-methyl-*t*-2-phenylcyclopropane (**10b**) in 88% yield. Compounds **10a** and **10b** were also obtained in quantitative yields when **5a** and **5b** were treated with hydrogen (3 atm).



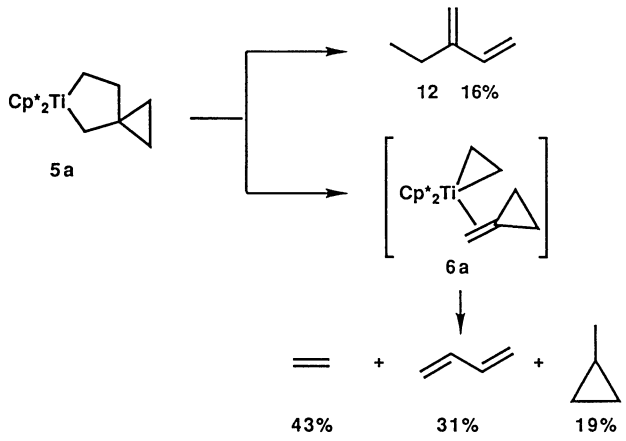
(6)

When **5a** or **5b** in hexane was exposed to three atmospheric pressure of carbon monoxide at room temperature, cyclopentanone derivative **11a** or **11b** was obtained in almost quantitative yields, respectively (Eq. 7).[12,13] This is in contrast with the reported fact that the reaction of complex $Cp^*_2TiCH_2(CH_2)_2CH_2$ (**2**) with carbon monoxide did not give cyclopentanone, but resulted in the formation of ethylene and $Cp^*_2Ti(CO)_2$.[3c]

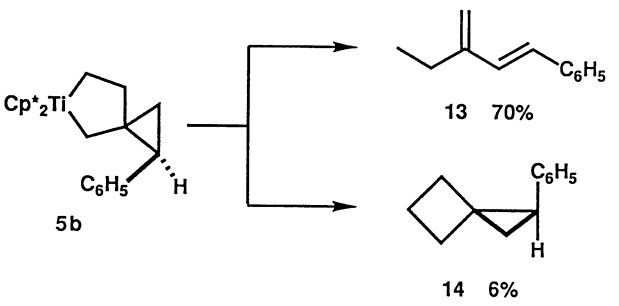


(7)

Thermal Decompositions of 5a and 5b. Thermal reactions of complexes **5** were carried out by rapidly heating a solid sample at 200 °C under reduced pressure; the resulting organic products were collected and analyzed. The results are summarized in Schemes 3 and 4. Two pathways were observed for **5a**, in which a β-carbon–carbon bond cleavage occurred predominantly to give ethylene (43%), butadiene (31%), and methylcyclopropane (19%) (Scheme 3). 1,3-Diene **12** (16%) was also obtained, which is considered to arise from a cleavage of the C(1)–C(3) bond of the spiro[2.4]heptane ring. No products arising from a simple β-hydrogen elimination were detected. In contrast, the thermolysis of complex **5b** did not undergo via the β-carbon–carbon bond fission, but gave 1,3-diene **13** in 70% yield (Scheme 4). Interestingly, the reductive elimination product, a cyclobutane derivative **14** (6%), was also obtained. To our knowledge, this is the first example of a direct reductive elimination of cycloalkanes from the metallacycles of group-4 transition metals. Recently, an oxidative decomposition of titanacyclobutanes has been reported to give cyclopropanes.[14] The remarkable differences in the reaction modes observed for **5a** and **5b** might be partly attributed to the presence of a weak benzylic carbon–carbon bond in **5b**. Another possible factor is the fact that the bulky phenyl substituent deforms the titanacyclopentane ring so that it occupies a pseudoequatorial position, which might make the β-carbon–carbon bond fission more difficult to occur. A similar structure–reactivity relationship has been discussed for the transition-metal-catalyzed valence isomerization of 1,8-bishomocubane.[15]

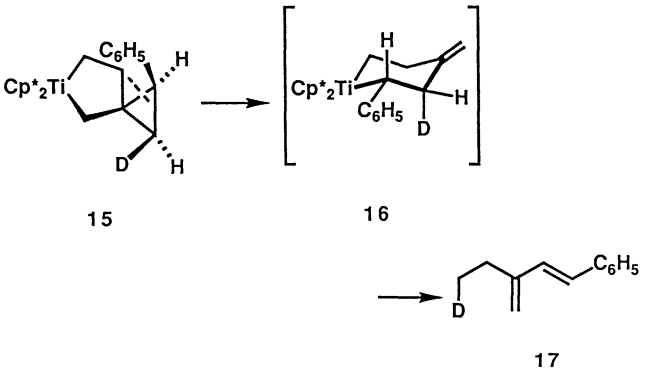


Scheme 3.

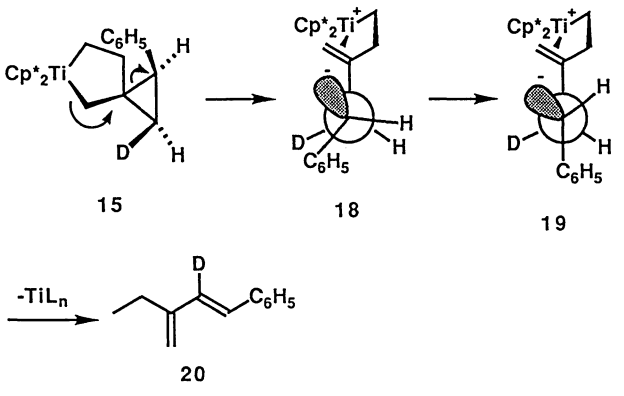


Scheme 4.

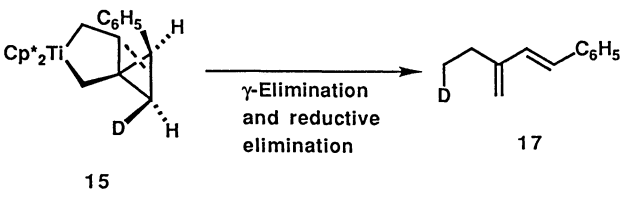
The formation mechanism of the 1,3-dienes **12** and **13** is worthy of further consideration. Three machanisms, Schemes 5—7, can be considered, a priori, whose stereochemical courses are shown for deuterium-labeled complex **15**. Mechanism A shown in Scheme 5 involves an initial rearrangement of complex **15** to **16**, followed by β-hydrogen elimination and reductive elimination. The formation of six-membered metallacycle **16** can be accounted for by a skeletal rearrangement from a cyclopropylmethyl to a 3-butenyl structure.[16] A number of examples of this type of rearrangements have so far been presented for the transition-metal-catalyzed reactions of methylenecyclopropanes.[17–21] From **16**, in which the bulky phenyl substituent occupies an equatorial position, the 1,3-diene **17** with deuterium at the terminal position will be formed by an elimination of the axial deuterium atom followed by a reductive elimination reaction.



Scheme 5.



Scheme 6.

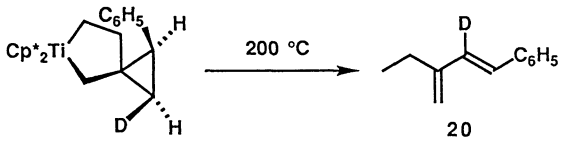


Scheme 7.

Mechanism B is illustrated in Scheme 6. This reaction is initiated by a heterolytic cleavage of the Ti–C bond, giving zwitterionic species **18**. In the next step, this eclipsed conformer **18** proceeds to a more stable gauche conformer **19** by least motion, so that the phenyl substituent at C(1) comes to the *s*-trans position. Subsequent trans hydride abstraction by titanium gives an alkyltitanium hydride species, and reductive elimination affords the 1,3-diene product **20** with deuterium at the 2-position.

Mechanism C (Scheme 7) involves a direct γ-elimination of one of the two C(2) methylene hydrogens, leading to **17**. Here, deuterium abstraction by titanium is also expected, since the Ti–D distance (4.39 Å) is shorter than that of Ti–H (4.74 Å). This mechanism can not be ruled out, even though such an elimination process seems to be unlikely in view of the long distances between Ti and these hydrogens.

In order to obtain information concerning the reaction mechanism, we studied the stereochemical course of the reaction using deuterium-labeled complex **15**. When isolated complex **15** was heated at 200 °C under vacuum, 1,3-diene **20** was obtained as the major product. Thus, the formation of **20** could be reasonably explained by mechanism B shown in Scheme 6.



(8)

As a result, all of the three reactions (A—C illustrated in Scheme 1) are possible for titanacyclopentanes **5**, and the product distributions are highly dependent on the substituent on the metallacycles. The difference in the conformation of the five-membered ring of **5** as well as the presence of substituents in the ring may, at least in part, be a factor which controls the reaction modes.

Experimental

General. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out by the use of the standard Schlenk technique under an argon atmosphere purified through a BASF-Catalyst R3-11 column. All solvents were purified by distillation under argon after drying over calcium hydride or sodium benzophenone ketyl. ^{1}H NMR spectra were recorded on a Varian EM-390 (90 MHz), a JEOL EX 270 (270 MHz), or a JEOL GX400 (400 MHz) spectrometer. ^{13}C NMR spectra were measured on a JEOL EX 270 (67.5 MHz) or a JEOL GX400 (100 MHz) spectrometer. Other spectra were recorded by the use of the following instruments: IR, Hitachi 295; low-resolution mass and high-resolution mass spectra, JEOL D300 (70 eV); gas chromatographic (GLC) analyses, Hitachi 263-30 equipped with a flame ionization detector. Elemental analyses were performed by

the Wako Pure Chemical Ind. Ltd. All melting points were measured in sealed tubes and uncorrected. Methylenecyclopropane,[22] 2-phenyl-1-methylenecyclopropane,[23] and 2,2-diphenyl-1-methylenecyclopropane[23] were prepared by the modified literature methods. Cyclobutanone was obtained from Aldrich Chem. Co.

Preparation of Decamethyltitanocene-Ethylene Complex 3. To a solution of $Cp^*_2TiCl_2$ (2.65 g, 6.8 mmol) in toluene (100 mL) was added dropwise a solution of butyllithium (15 mmol) in hexane (10 mL) at −78 °C. The reaction mixture was exposed to an atmospheric pressure of ethylene; the temperature was then allowed to rise to 20 °C. After stirring the mixture for a period of 2 days, all volatiles were removed under reduced pressure. The resulting residue was extracted with hexane (200 mL); the hexane solution was then filtered through a pad of Celite 545. The filtrate was concentrated to ca. 30 mL, and the solution was kept at −20 °C overnight to afford the ethylene complex **3** (1.01 g, 43% yield) as light-green crystals, whose NMR spectral data were superimposable with those reported.[3c]

Preparation of 5a. To a solution of decamethyltitanocene–ethylene complex **3** (0.43 g, 1.24 mmol) in hexane (50 mL) (0.43 g, 1.24 mmol) cooled at −70 °C was added methylenecyclopropane (**4a**) (2 mL, excess) by a trap-to-trap method. When the reaction mixture was slowly warmed up to −20 °C during 2 h, the light-green color changed to orange. This homogeneous solution was further stirred at −20 °C for a period of 48 h. The resulting deep-red solution was concentrated under reduced pressure; crystallization of the residue from hexane at −80 °C gave **5a** (0.32 g, 65% yield) as orange needles, mp 156—158 °C (decomp). ^{1}H NMR (400 MHz, C_6D_6) δ=0.37 (s, $2H_1$ and $2H_2$), 0.62 (s, $2H_4$), 0.63 (t, $2H_6$, $J_{6,7}$=6.8 Hz), 1.79 (t, $2H_7$), and 1.87 (s, C_5Me_5). ^{13}C NMR (100 MHz, C_6D_6) δ=12.32 ($C_5\mathit{Me}_5$, J_{C-H}=126 Hz), 20.48 (C_1 and C_2, 157 Hz), 25.01 (C_3), 41.59 (C_7, 123 Hz), 63.48 (125 Hz) and 65.60 (125 Hz) for C_4 and C_6, and 120.82 (C_5Me_5). IR (KBr) ν 3045 (w), 2960 (s), 2880 (s), 2800 (s), 1492 (w), 1434 (m), 1375 (s), 1314 (w), 1260 (w), 1180 (m), 1017 (m), 992 (m), 827 (w), 801 (w), 626 (w), 587 (w), 532 (w), 479 (w), 440 (w), 400 (m), and 370 (w) cm^{-1}. Mass spectrum m/z, 400 (M^+), 398 ($M^+ - 2$), 318 ($M^+ - C_6H_{10}$, base peak), 181 ($M^+ - 219$). Exact mass spectrum m/z, Calcd for $C_{26}H_{40}{}^{48}$Ti: M, 400.2609. Found: m/z 400.2584. Found: C, 77.56; H, 9.58%. Calcd for $C_{26}H_{40}$Ti: C, 77.98; H, 10.07%.

Preparation of 5b. A light-green solution of **3** (1.68 g, 4.86 mmol) and 2-phenyl-1-methylenecyclopropane (**4b**) (1.0 mL, 6.3 mmol) in hexane (50 mL) was stirred at 20 °C. After 48 h, a deep-red solution was obtained. All volatiles were removed under reduced pressure and the resulting residue was crystallized from hexane at −80 °C to give **5b** (1.92 g, 83% yield) as red plates. An analytical sample of **5b** was obtained by recrystallization from toluene at −80 °C as deep-red prisms, mp 122—124 °C (decomp). ^{1}H NMR (400 MHz, C_6D_6) δ=−0.13 (ddd, H_{6a}, $J_{6a,6b}$=11.0 Hz, $J_{6a,7b}$=5.5 Hz, and $J_{6a,7a}$=5.5 Hz), 0.09 and 0.39 (ABq, $2H_4$, $J_{4a,4b}$=11.9 Hz), 0.88 (dd, H_{2cis}, $J_{1,2cis}$=6.1 Hz and $J_{2cis,2trans}$=4.1 Hz), 0.97 (dd, H_{2trans}, $J_{1,2trans}$=8.6 Hz), 1.33 (ddd, H_{6b}, $J_{6b,7a}$=11.0 Hz, $J_{6b,7b}$=5.8 Hz), 1.53 (ddd, H_{7a}, $J_{7a,7b}$=12.3 Hz), 1.63 (dd, H_1), 1.69 (s, C_5Me_5), 1.87 (s, C_5Me_5), 2.31 (ddd, H_{7b}), 7.10—7.30 (m, C_6H_5). Stereochemical assignments of the ring methylene protons have not been performed. ^{13}C NMR (100 MHz, C_6D_6) δ= 12.08 ($C_5\mathit{Me}_5$, J_{C-H}=127 Hz), 12.33 ($C_5\mathit{Me}_5$, 127 Hz), 28.74 (C_2, 157 Hz), 34.17 (C_1, 154 Hz), 34.85 (C_3), 44.15 (C_7, 122 Hz), 55.36 (C_4, 125 Hz), 64.98 (C_6, 123 Hz), 120.89 (C_5Me_5), 121.02 (C_5Me_5), and aromatic carbons at 124.49, 127.49, 128.38, and 142.52. IR (KBr) ν 3045 (w), 2970 (s), 2900 (s), 2800 (s), 1640 (m), 1601 (m), 1497 (m), 1445 (m), 1378 (s), 1304 (w), 1077 (w), 1063 (w), 1019 (m), 821 (m), 774 (m), 737 (m), 697 (s), 636 (m), 401 (w) cm^{-1}. Mass spectrum m/z, 476 (M^+), 318 ($M^+ - C_{12}H_{14}$), 158 ($M^+ - Cp^*_2Ti$), 129 ($M^+ - 347$, base peak). Exact mass spectrum m/z, Calcd for $C_{32}H_{44}{}^{48}$Ti: M, 476.2921. Found: m/z 476.2900. Found: C, 80.17; H, 9.95%. Calcd for $C_{32}H_{44}$Ti: C, 80.65; H, 9.31%.

X-Ray Structure Determination of 5b. Deep-red crystals of **5b** were grown from a saturated toluene solution at −20 °C overnight. The crystals were mounted in thin-walled glass capillaries under argon and then flame-sealed. Pertinent details concerning the data collection and the final cell dimensions, which were obtained from a least-squares refinement of 2θ values of 50 independent reflections in the range of $19°<2\theta<30°$, are given in Table 3.

The 4261 unique raw intensity data were converted to values of the structure factor by corrections for Lorentz and polarization effects. Inspection of the standard three reflections ((8 0 0), (0 4 0), and (0 0 4)) measured after every 50 reflections showed no systematic variation in the intensity. A systematic absence, (h 0 l) with h=odd and (0 k 0) with k=odd, indicated the space group $P2_1/a$.

The location of the titanium atom was determined by a direct method (MULTAN-78 program).[25] A series of standard block-diagonal least-squares refinements and Fourier syntheses revealed the remaining carbon atoms as an anisotropic temperature factor. The hydrogen atoms were located both by the difference Fourier syntheses and calculations. All non-hydrogen atoms as an anisotropic and hydrogen atoms as an isotropic temperature factor were refined to $R=\sum||F_o|-|F_c||/\sum|F_o|=0.053$ and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0.056$. A weighting scheme, $1/w=\sigma_c{}^2+(0.015|F_o|)^2$, was employed. A final difference Fourier map indicated that no

Table 3. Crystal Data and Data Collection Parameters of **5b**

Formula	$C_{32}H_{44}$Ti
Fw	476.58
Crystal system	Monoclinic
Space group	$P2_1/a$
a/Å	21.832(3)
b/Å	8.580(1)
c/Å	14.759(2)
β/deg	96.81(1)
U/Å^3	2744.9(6)
Z	4
D_{calcd}/g cm^{-3}	1.154
Crystal size/mm	0.22×0.32×0.40
μ(Mo $K\alpha$)/cm^{-1}	3.42
Diffractometer	Rigaku AFC-5
Scan type	ω–2θ
Scan range/deg	1.1+0.5 tan θ
bkgd/sec	8 at each end of the scan
Scan speed/deg min^{-1}	3
Data collected	$\pm h$, k, l
$2\theta_{max}$/deg	60.0
No. of reflctns	4938
No. of unique reflctns, $\|F_o\|>3\sigma(F_o)$	4261
No. of variables	475
R	0.053
R_w	0.056

significant residual peak remained. The selected bond lengths and angles are listed in Tables 1 and 2, respectively.

Catalytic Isomerization of 2,2-Diphenyl-1-methylenecyclopropane (4c). A sealed NMR tube containig complex **3** (2.0 mg, 0.057 mmol) and 2,2-diphenyl-l-methylenecyclopropane (**4c**) (35 mg, 0.17 mmol) in toluene-d_8 (0.5 mL) was heated at 70 °C for a period of 1 h. The light-green color changed to orange. ^{1}H NMR spectrum showed that **4c** was converted to 1,1-diphenyl-1,3-butadiene (**7**),[26] which was isolated by preparative TLC (Merck silica gel 60 F_{254}). **7**: ^{1}H NMR ($CDCl_3$) δ=5.12 (dd, H_3, $J_{2,3}$=10.1 and $J_{3,4}$=1.8 Hz), 5.38 (dd, H_4, $J_{2,4}$=16.8 Hz), 6.44 (ddd, H_2, $J_{1,2}$=11.0 Hz), 6.71 (d, H_1). ^{13}C NMR ($CDCl_3$) δ=118.48 (C_4, J_{C-H}=158 Hz), 127.26 (160 Hz), 127.37 (160 Hz), 127.44 (160 Hz), 128.03 (160 Hz), 128.06 (160 Hz), 130.27 (162 Hz), 128.39 (C_3, 155 Hz), 134.85 (C_2, 156 Hz), 139.53, 141.96, 143.02. Mass spectrum m/z, 206 (M^+, base peak), 191 ($M^+ - 15$), 178 ($M^+ - 28$), 165 ($M^+ - 41$). Exact mass spectrum, m/z, Calcd for $C_{16}H_{14}$: M, 206.1095, Found: m/z 206.1076.

Reaction of 3 with Phenylallene. To a solution of **3** (140 mg, 0.405 mmol) in toluene (10 mL) was added dropwise phenylallene (304 mg, 2.62 mmol) in toluene (5 mL) at −50 °C. This solution was stirred at room temperature overnight. The color of the solution turned from light-green to red. The resulting solution was concentrated in vacuo; the residue was then dissolved in hexane (5 mL). Upon cooling the solution at −20 °C, complex **9** (90 mg, 75% purity, 38% yield) precipitated as a green powder. In spite of repeated recrystallization from hexane, no pure sample of **9** could be obtained. ^{1}H NMR (C_6D_6) δ=1.67 (s, $2C_5Me_5$), 2.60 (d, H_3, $J_{1,3}$=3.3 Hz, H_3), 5.12 (d, H_1), 7.0—7.5 (m, C_6H_5). ^{13}C NMR (C_6D_6) δ=11.60 ($C_5\mathit{Me}_5$, J_{C-H}=126 Hz), 86.54 (C_3, 147 Hz), 119.53 (C_5Me_5), 120.83 (C_1, 156 Hz), 244.15 (C_2), 124.56 (160 Hz), 126.05 (146 Hz), 128.43 (158 Hz), and 142.00 (aromatic carbons).

Oxidation of complex **9** by O_2 in C_6D_6 afforded phenylallene in quantitative yield (by ^{1}H NMR).

Hydrolysis of 5a. A solution of **5a** (24 mg, 0.06 mmol) in octane (5 mL) was treated with Al_2O_3 (0.5 g) at room temperature. The orange-red color changed immediately to pale-yellow. GLC analysis indicated that 1-methyl-1-ethylcyclopropane (**10a**) was formed in 96% yield. An authentic sample of **10a** was prepared by the Simmons–Smith[27] methylenation of 2-methyl-1-butene. ^{1}H NMR ($CDCl_3$) δ=0.22 (m, cyclopropane ring protons, 4H), 0.92 (t, CH_3CH_2, J=7.32 Hz), 1.02 (s, CH_3), 1.25 (q, $CH_3\mathit{CH}_2$). ^{13}C NMR ($CDCl_3$) δ=10.82 ($\mathit{C}H_3CH_2$, J_{C-H}=125 Hz), 12.61 (cyclopropane ring carbons, 158 Hz), 16.30 (C_1), 22.19 (CH_3, 126 Hz), 31.97 ($CH_3\mathit{C}H_2$, 124 Hz). Mass spectrum m/z, 84 (M^+), 69 ($M^+ - CH_3$, base peak).

Hydrolysis of 5b. Complex **5b** (64 mg, 0.13 mmol) in benzene (5 mL) was treated with Al_2O_3 (0.5 g) to give 1-ethyl-1-methyl-2-phenylcyclopropane (**10b**) in 88% yield (determined by ^{1}H NMR). The stereochemistry of **10b** was determined to be the *r*-1-ethyl-*t*-2-phenyl isomer by a comparison of its GLC retention time and the ^{1}H NMR spectrum with those of the authentic sample.

Preparation of (*E*)- and (*Z*)-2-Methyl-1-phenyl-1-butene. The title compounds have been reported as being a mixture of *E* and *Z* isomers.[28] These isomers were separated by preparative GLC (DIDP, 140 °C, 0.6 kg cm^{-1}). *Z*-isomer: ^{1}H NMR ($CDCl_3$) δ=1.09 (t, $CH_2\mathit{CH}_3$, J=7.63 Hz), 1.88 (s, CH_3), 2.24 (q, CH_2CH_3), 6.25 (s, -CH=), 7.18—7.31 (m, C_6H_5). ^{13}C NMR ($CDCl_3$) δ=12.74 (C_4, J_{C-H}=127 Hz), 23.43 (CH_3, 134 Hz), 25.43 (C_3, 124 Hz), 124.73 (C_1, 153 Hz), 125.72 (162 Hz), 127.93 (158 Hz), 128.39 (155 Hz), 138.48, 140.92. *E*-isomer: ^{1}H NMR ($CDCl_3$) δ=1.11 (t, CH_3CH_2, J=7.63 Hz), 1.86 (s, CH_3), 2.18 (q, $CH_3\mathit{CH}_2$), 6.26 (s, olefinic proton), 7.15—7.32 (m, C_6H_5). ^{13}C NMR ($CDCl_3$) δ=12.65 (C_4, J_{C-H} =127 Hz), 17.60 (CH_3, 127 Hz), 33.24 (C_3, 127 Hz), 123.51 (C_1, 151 Hz), 125.63 (160 Hz), 127.88 (160 Hz), 128.72 (157 Hz), 138.69, 140.70. The stereochemistry was determined on the basis of ^{13}C NMR spectrum.[29] Mass spectrum m/z, 146 (M^+), 131 ($M^+ - CH_3$, base peak).

Preparation of *r*-1-Ethyl-1-methyl-*c*-2-phenylcyclopropane and *r*-1-Ethyl-*t*-2-phenyl Isomers.[30] Both isomers of the title compound were prepared by the Simmons–Smith methylenation[27] of (*E*)- and (*Z*)-2-methyl-1-phenyl-1-butene, respectively. *c*-2-Phenyl isomer: ^{1}H NMR ($CDCl_3$) δ=0.74 (dd, H_{3t}, $J_{3t,3c}$=5.89 Hz), 0.79 (t, CH_3CH_2, J=7.48 Hz), 0.84 (dd, H_{3c}), 0.93 and 1.13 (ABX pattern, $CH_3\mathit{CH}_2$), 1.21 (s, CH_3), 1.95 (dd, H_2, $J_{2,3t}$=8.24 and $J_{2,3c}$=5.80 Hz), 7.18—7.35 (m, C_6H_5). ^{13}C NMR ($CDCl_3$) δ=10.60 (CH_3, J_{C-H}=124 Hz), 17.20 (C_3, 157 Hz), 23.89 (CH_3, 125 Hz), 24.04 (C_1), 26.52 (CH_2, 123 Hz), 30.42 (C_2, 158 Hz), 125.30 (162 Hz), 127.66 (160 Hz), 128.81 (160 Hz), and 140.02 for aromatic carbons. *t*-2-Phenyl isomer **10b**: ^{1}H NMR ($CDCl_3$) δ=0.76 (s, CH_3), 0.76—0.80 (m, H_{3t} and H_{3c}), 1.03 (m, $CH_2\mathit{CH}_3$), 1.32 and 1.53 (ABX pattern, CH_2CH_3, J=6.1 and 12.0 Hz), 1.87 (t, H_2, J=6.0 Hz), 7.17—7.30 (m, C_6H_5). ^{13}C NMR ($CDCl_3$) δ=10.93 (CH_3, J_{C-H}=125 Hz), 17.09 (CH_3, 125 Hz), 17.58 (C_3, 157 Hz), 23.91 (C_1), 28.74 (C_2, 158 Hz), 33.84 (CH_2, 123 Hz), 125.30 (160 Hz), 127.69 (160 Hz), 128.87 (160 Hz), 148.15 for aromatic carbons. The mass spectrum of the trans and cis mixture m/z, 160 (M^+), 145 ($M^+ - CH_3$), 131 ($M^+ - C_2H_5$, base peak). Exact mass spectrum m/z, Calcd for $C_{12}H_{16}$: M, 160.1252. Found: m/z 160.1252.

Reaction of 5a with H_2. After placing a solution of **5a** (32 mg, 0.081 mmol) in octane (4 mL) into a glass pressure bottle, hydrogen was introduced up to 3 atm. After 20 h at room temperature, 1-ethyl-1-methylcyclopropane (**10a**) was obtained in 86% yield (GLC). The structure was identified by a comparison of the GLC retention time and the ^{1}H NMR spectrum with those of the authentic sample.

Reaction of 5b with H_2. After placing a solution of **5b** (37 mg, 0.078 mmol) in hexane (10 mL) into a glass pressure bottle, hydrogen was introduced up to 3 atm. Then, after stirring the mixture at room temperature for 40 h, the orange-red solution turned to orange. *r*-1-Ethyl-1-methyl-*t*-2-phenylcyclopropane (**10b**) was obtained in 88% yield (GLC).

Reaction of 5a with CO. An orange solution of **5a** (131 mg, 0.327 mmol) in hexane (10 mL) was placed in a glass pressure bottle (100 mL); carbon monoxide (3 atm) was then pressured. After stirring at room temperature for 45 min, the starting complex was converted to spiro[2.4]heptan-5-one (**11a**) in 98% yield, the structure of which was confirmed by a comparison of the ^{1}H, ^{13}C, mass, and IR spectra with the reported ones.[31]

Reaction of 5b with CO. A solution of complex **5b** (99.3 mg, 0.21 mmol) in toluene (10 mL) was placed in an autoclave. Carbon monoxide was then pressured to 30 atm. After 20 min at room temperature, the decrease in the CO pressure stopped. 1-Phenylspiro[2.4]heptan-5-one (**11b**) was obtained in 98% yield (GLC) which was isolated by preparative GLC (SE-30, 220 °C) separation. **11b**: ^{1}H NMR ($CDCl_3$) δ=1.13 (d, H_2, $J_{1,2}$=7.64 Hz), 1.91 and 2.04 (ABq, H_4), 2.05 (ABX,

$2H_7$), 2.12 (t, H_1), 2.41 (t, $2H_6$, $J_{6,7}$=7.78 Hz), 7.05—7.28 (m, C_6H_5). ^{13}C NMR ($CDCl_3$) δ=16.58 (C_2, J_{C-H}=159 Hz), 27.40 (C_3), 28.61 (C_1, 158 Hz), 33.69 (132 Hz), 39.32 (131 Hz), and 42.05 (131 Hz) for C_4, C_6, and C_7, 125.92 (160 Hz), 127.73 (158 Hz), 128.15 (158 Hz), and 138.69 for aromatic carbons, 217.79 (C_5). IR (neat) ν 1747 cm^{-1} (C=O). Mass spectrum m/z, 186 (M^+), 142 ($M^+ - 44$), 129 ($M^+ - 57$), 91 ($M^+ - 95$, base peak). Exact mass spectrum m/z, Calcd for $C_{13}H_{14}O$: M, 186.1045. Found: m/z 186.1045.

Thermolysis of 5a. The isolated complex **5a** (21 mg, 0.053 mmol) was placed in a Schlenk tube and rapidly heated up to 200 °C under reduced pressure in an oil bath. The products were condensed into an NMR tube, and the tube was sealed. ^1H NMR and GLC analysis (Durapak) indicated that methylcyclopropane[32] (19%), butadiene (31%), 2-ethyl-1,3-butadiene **12** (16%), and ethylene (43%) were obtained. These compounds were also analyzed by GC-Mass spectroscopy.

Thermolysis of 5b. Complex **5b** (146 mg, 0.31 mmol) was heated at 200 °C under reduced pressure, and the volatile products were condensed on a liquid-nitrogen cold finger. GLC and ^1H NMR analysis indicated that 1-phenyl-3-ethyl-1,3-butadiene (**13**)[33] (70%) and 1-phenylspiro[2.3]hexane (**14**) (6%) were obtained. The structure of **12** was determined by a comparision of the ^1H NMR and GLC retention time with those of an authentic sample. **13**: ^1H NMR ($CDCl_3$) δ=1.18 (t, CH_2CH_3, J=7.5 Hz), 2.37 (q, CH_2CH_3), 5.09 and 5.14 (=CH_2), 6.60 (d, H_1, J=16.3 Hz), 6.84 (d, H_2), 7.21—7.45 (m, C_6H_5). ^{13}C NMR ($CDCl_3$) δ=12.68, 24.66, 115.03, 126.31, 127.24, 127.66, 128.48, 137.42, 147.64. Mass spectrum m/z, 158 (M^+), 143 ($M^+ - CH_3$), 129 ($M^+ - C_2H_5$, base peak). Exact mass spectrum m/z, Calcd for $C_{16}H_{14}$: M, 158.1095. Found: m/z 158.1089.

Preparation of Benzylidenecyclobutane. In an 80 mL Schlenk tube equipped with a magnetic stirring bar was stirred a solution of cyclobutanone (1.0 g, 14 mmol) dissolved in 20 mL of THF. This was cooled to −60 °C; then a solution of benzylmagnesium chloride (15 mmol) in THF (20 mL) was added dropwise over 0.5 h. When the addition was completed, the homogeneous solution was slowly warmed to room temperature over a period of 2 h. The reaction mixture was poured into ice-water, and the mixture was extracted with three 50-mL portions of ether. The crude alcohol was treated with 6 equiv H_2SO_4 at 70—80 °C for 2 h. The products were extracted with ether (50 mL). The ether layer was washed with aq $NaHCO_3$ and dried over sodium sulfate. Crude benzylidenecyclobutane (0.77 g, 37% yield) was obtained by short-path distillation and used without further purification. ^1H NMR ($CDCl_3$) δ=2.09 (m, $CH_2CH_2CH_2$), 2.87 (t, $CH_2CH_2CH_2$, J=7.8 Hz), 3.03 (t, $CH_2CH_2CH_2$, J=7.9 Hz), 6.06 (s, olefinic proton), 7.11—7.31 (m, C_6H_5).

Preparation of 1-Phenylspiro[2.3]hexane (14). A mixture of benzylidenecyclobutane (0.75 g, 5.2 mmol), diiodomethane (3.0 g, 11 mmol), and zinc–copper (2.49 g, 38 mmol) in ether (40 mL) was heated at reflux for 30 h. The solution was filtered and the solid was washed with two 30-mL portions of ether. The filtrate and washings were treated with aq. sodium hydrogencarbonate (30 mL, twice), and then with saturated aq. sodium chloride. The ether layer was dried over sodium sulfate. Short-path distillation yielded a colorless oil (0.46 g). A GLC analysis indicated that the product was contaminated with several impurities. Preparative GLC separation (DIDP column) gave a pure sample of **14**. ^1H NMR ($CDCl_3$) δ=0.85 (dd, H_{2trans}, $J_{1,2trans}$=8.85 Hz, $J_{2cis,2trans}$=5.49 Hz), 1.06 (dd, H_{2cis}, $J_{1,2cis}$=5.80 Hz), 1.83 (dd, H_1), 1.89—2.27 (m, cyclobutane methylene protons), 6.95—7.27 (m, C_6H_5). ^{13}C NMR ($CDCl_3$) δ=16.49 (C_5, J_{C-H}=138 Hz), 20.44 (C_2, 160 Hz), 26.38 (132 Hz) and 31.35 (135 Hz) for C_4 and C_6, 28.08 (C_1, 158 Hz), 28.54 (C_3), 124.88 (161 Hz), 126.49 (158 Hz), 127.84 (158 Hz), and 141.28 for aromatic carbons. IR (KBr) ν 3058 (m), 3020 (m), 2978 (m), 2942 (s), 2920 (s), 2848 (m), 1602 (m), 1498 (s), 1452 (m), 1204 (w), 1107 (w), 1086 (w), 1062 (w), 1037 (w), 918 (w), 833 (w), 787 (w), 761 (m), 741 (m), 702 (s) cm^{-1}. Mass spectrum m/z, 158 (M^+), 143 ($M^+ - CH_3$), 130 ($M^+ - C_2H_4$, base peak), 115 ($M^+ - C_3H_7$), 104 ($M^+ - C_4H_6$). Exact mass spectrum m/z, Calcd for $C_{12}H_{14}$: M, 158.1095. Found: m/z 158.1099.

Preparation of *cis*-3-Deuterio-2-phenyl-1-methylenecyclopropane (*cis*-4b-d_1). This compound was prepared by essentially the same method as that described in the literature.[24] Only modification is used for the preparation of *cis*-3-deuterio-1,1-dibromo-2-phenylcyclopropane with a phase-transfer catalyst system.[23a]

Thermolysis of 15. Complex **15** has been thermally decomposed as described for **5b**. 2-Deuterio-1-phenyl-3-ethyl-1,3-butadiene (**20**) was obtained. Within the limit of ^1H NMR detection, deuterium was only located at the C(2) position. The deuterium content of **20** was 88%.

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References

1) J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, "Principles and Applications of Organotransition Metal Chemistry," University Science Books, Mill Valley, California (1987), Chap. 9.

2) For example: a) S. Takahashi, Y. Suzuki, K. Sonogashira, and N. Hagihara, *J. Chem. Soc., Chem. Commun.*, **1976**, 839. b) M. J. Doyle, J. McMeeking, and P. Binger, *J. Chem. Soc., Chem. Commun*, **1976**, 376. c) Y. Wakatsuki, K. Aoki, and H. Yamazaki, *J. Am. Chem. Soc.*, **101**, 1123 (1979). d) R. J. McKinney, T. H. Tulip, D. L. Thorn, T. S. Coolbaugh, and F. N. Tebbe, *J. Am. Chem. Soc.*, **103**, 5584 (1981). e) J. B. Lee, K. C. Ott, and R. H. Grubbs, *J. Am. Chem. Soc.*, **104**, 7491 (1982). f) P. Diversi, G. Ingrosso, and A. Lucherini, *Inorg. Synth.*, **22**, 171 (1983). g) E. Lindner, E. Schauss, W. Hiller, and R. Fawzi, *Angew. Chem., Int. Ed. Engl.*, **23**, 711 (1984). h) S. A. Cohen and J. E. Bercaw, *Organometallics*, **4**, 1006 (1985).

3) a) J. X. McDermott, M. E. Wilson, and G. M. Whitesides, *J. Am. Chem. Soc.*, **98**, 6529 (1976). b) R. H. Grubbs and A. Miyashita, *J. Chem. Soc., Chem. Commun.*, **1977**, 864. c) S. A. Cohen, P. R. Auburn, and J. E. Bercaw, *J. Am. Chem. Soc.*, **105**, 1136 (1983).

4) A part of this work has been communicated: K. Mashima and H. Takaya, *Organometallics*, **4**, 1464 (1984).

5) P. Diversi, G. Ingrosso, A. Lucherini, W. Porzio, and M. Zocchi, *Inorg. Chem.*, **19**, 3590 (1980).

6) P. Binger, M. J. Doyle, C. Krüger, and Y.-H. Tsay, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **34b**, 1289 (1979).

7) J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 1729 (1976).

8) a) M. L. Steigerwald and W. A. Goddard, III, *J. Am. Chem. Soc.*, **107**, 5027 (1985). b) A. Stockis and R.

Hoffmann, *J. Am. Chem. Soc.*, **102**, 2952 (1980), and the references cited therein.

9) R. Noyori, T. Ishigami, N. Hayashi, and H. Takaya, *J. Am. Chem. Soc.*, **95**, 1674 (1973).

10) M. Akita, H. Yasuda, K. Nagasuna, and A. Nakamura, *Bull. Chem. Soc. Jpn.*, **56**, 554 (1983).

11) M. Akita, H. Yasuda, and A. Nakamura, *Bull. Chem. Soc. Jpn.*, **57**, 480 (1984).

12) For compound **1**, an insertion of carbon monoxide followed by a reductive elimination reaction to give cyclopentanone has been reported.[3a]

13) J. M. Manriquez, D. R. McAlister, R. D. Sanner, and J. E. Bercaw, *J. Am. Chem. Soc.*, **100**, 2716 (1978).

14) a) R. H. Grubbs and W. Tumas, *Science*, **243**, 907 (1989). b) M. J. Burk, W. Tumas, M. D. Ward, and D. R. Wheeler, *J. Am. Chem. Soc.*, **112**, 6133 (1990). c) M. J. Burk, D. L. Staley, and W. Tumas, *J. Chem. Soc., Chem. Commun.*, **1990**, 809.

15) R. Noyori, M. Yamakawa, and H. Takaya, *J. Am. Chem. Soc.*, **98**, 1471 (1976).

16) Anion rearrangement: D. J. Patel, C. L. Hamilton, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 5144 (1965). Radical rearrangement: A. Effio, D. Griller, K. U. Ingold, A. L. J. Beckwith, and A. K. Serelis, *J. Am. Chem. Soc.*, **102**, 1734 (1980).

17) Transition-metal catalyzed reactions of methylenecyclopropanes in the presence of olefinic substrates give a variety of homo- and cross-coupling products,[18–21] for which mechanisms involving similar type of rearrangements have been proposed.[18,21]

18) a) H. Takaya, N. Hayashi, T. Ishigami, and R. Noyori, *Chem. Lett.*, **1973**, 813. b) P. Binger, A. Brinkmann, and P. Wedemann, *Chem. Ber.*, **116**, 2920 (1983).

19) a) R. Noyori, T. Odagi, and H. Takaya, *J. Am. Chem. Soc.*, **92**, 5780 (1970). b) R. Noyori, Y. Kumagai, I. Umeda, and H. Takaya. *J. Am. Chem. Soc.*, **94**, 4018 (1972). c) R. Noyori, M. Yamakawa, and H. Takaya, *Tetrahedron Lett.*, **1978**, 4823.

20) a) P. Binger, *Angew. Chem., Int. Ed. Engl.*, **11**, 309 (1972). b) P. Binger, *Synthesis*, **1973**, 427.

21) a) P. Binger, M. J. Doyle, and R. Benn, *Chem. Ber.*, **116**, 1 (1983). b) P. Binger, T. R. Martin, R. Benn, A. Rufinska, and G. Schroth, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **39b**, 993 (1984).

22) R. Köster, S. Arora, and P Binger, *Synthesis*, **1971**, 322.

23) a) L. Skattebøl, G. A. Abskharoun, and T. Greibrokk, *Tetrahedron Lett.*, **1973**, 1367. b) K. Kitatani, T. Hiyama, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **50**, 3288 (1977). c) S. Arora and P. Binger, *Synthesis*, **1974**, 801.

24) A. R. Pinhas, A. G. Samuelson, R. Risemberg, E. V. Arnold, J. Clardy, and B. K. Carpenter, *J. Am. Chem. Soc.*, **103**, 1668 (1981).

25) MULTAN-78 and UNICS-III program system of Computer Center of IMS.

26) U. Schöllkopf and F. Gerhart, *Angew. Chem., Int. Ed. Engl.*, **7**, 805 (1968).

27) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

28) a) D. Seyferth and J. Fogel, *J. Organomet. Chem.*, **6**, 205 (1966). b) C. Rüchardt and H. Trautwein, *Chem. Ber.*, **98**, 2478 (1965).

29) L. Hevesi, J. B. Nagy, A. Krief, and E. G. Derouane, *Org. Mag. Reson.*, **10**, 14 (1977).

30) W. Engel, E. Seeger, H. Teufel, and H. Machleidt, *Chem. Ber.*, **104**, 248 (1971).

31) A. Sonoda, I. Moritani, J. Miki, T. Tsuji, and S. Nishida, *Bull. Chem. Soc. Jpn.*, **45**, 1777 (1972).

32) M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 1886 (1960).

33) J. Mulzer, U. Kühl, and G. Brüntrup, *Tetrahedron Lett.*, **1978**, 2953.