Stereochemical Mechanistic Probe of Substituted α-Methylenetitanacyclobutane Reactivity

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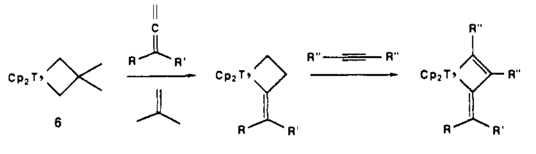
Abstract: The exocyclic double-bond geometry of asymmetrically substituted α-methylenetitanacyclobutanes **4** and -butenes **5** was followed during substitution reactions in order to probe the stereochemistry at titanium during substitution. Treatment of isomeric mixtures enriched in **4b** or **4c** with 3-hexyne gave the same ((1.7 ± 0.1):1) mixture of **5c** and **5b**. The equilibration of **4b** and **4c** in the absence of 3-hexyne was first order with $k_{obsd} = (2.1 \pm 0.2) \times 10^{-4}\ s^{-1}$ at 26 °C, independent of the concentration of ethylene. These results are consistent with a dissociative mechanism via the free vinylidene **7** or a displacement mechanism in which displacements are very fast with respect to closure to the metallacycle ($k_d >$ ca. $100k_c\ M^{-1}$; c = closure and d = displacement).

Titanocene metallacyclobutanes are of current interest for the methylenation of carbonyl compounds[2] and the ring-opening metathesis polymerization of cyclic olefins.[3] Mechanistic studies have shown that substitution reactions of titanocene metallacyclobutanes proceed by an initial rate-determining cleavage to an olefin–titanocene methylidene complex (e.g. **1**, Scheme I), which can then rapidly react with the unsaturated substrate, X = Y, by an S_N2-like displacement mechanism to give the new methylidene complex **2**.[4] However, a competitive S_N1-like dissociative mechanism via the free methylidene **3** was not ruled out. This paper presents a stereochemical probe to distinguish between S_N2- and S_N1-like processes for substituted α-methylenetitanacyclobutanes.

Substituted α-methylenetitanacyclobutanes (e.g. **4a**) have been prepared by the reaction of titanacyclobutanes with 1,1-disubstituted allenes.[5] We found that these species react with alkynes in benzene at 70 °C to give substituted α-methylenetitanacyclobut*enes* (**5**, eq 1). These species are novel in that each of the metallacyclobutene carbons is sp^2 hybridized.[6] Metallacyclobutenes **5** were generated from **6** in greater than 80% yield according to NMR; **5a** was isolated in 48% yield after recrystallization.



(1)

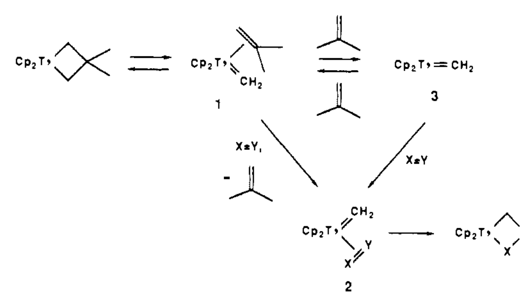
6

4a, R=R'=Me
4b, R=Me, R'=iPr
4c, R=iPr, R'=Me

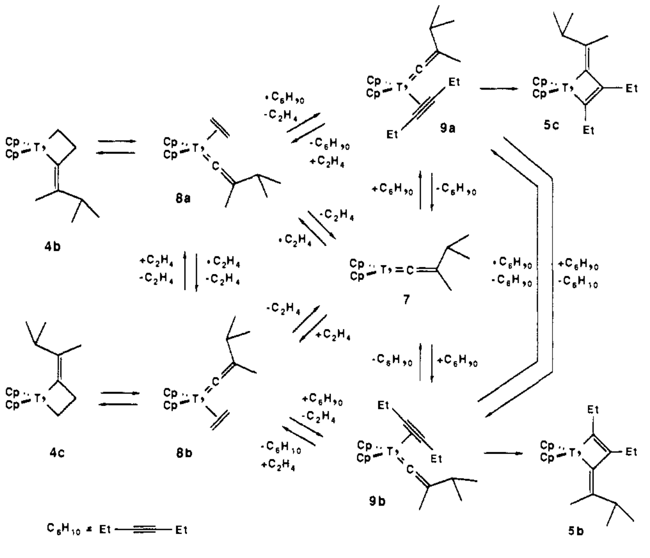
5a, R=R'=Me, R''=Et
5b, R=Me, R'=iPr, R''=Et
5c, R=iPr, R'=Me, R''=Et
5d, R=R'=R''=Me

Asymmetrical substitution of the allene precursor introduces a stereochemical element to this reaction via the geometric isomers of **4** and **5** (Scheme II). A dissociative mechanism via the free vinylidene **7** should scramble the double-bond geometry and give the same mixture of **5b** and **5c** from either **4b** or **4c**. Alternatively, a displacement mechanism may proceed with inversion, **4b** giving **5c** and **4c** giving **5b**. In this fashion, inversion at titanium in the conversion of **8** to **9** corresponds to double-bond isomerization in the conversion of **4** to **5**. A displacement mechanism may also result in scrambling if displacement reactions of the vinylidene adducts **8** and **9** are rapid with respect to metallacycle formation. This analysis assumes that the vinyl substituents in **8** and **9** lie in the plane of the paper,[7] that rotation about the titanium–carbon double bond in **8** and **9** is slow with respect to metallacycle for-

Scheme I



Scheme II



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[1] National Institutes of Health Postdoctoral Fellow, 1986–1987.

[2] Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhart, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733.

[3] (a) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733. (b) Swager, T. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 894.

[4] Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 4880. Contrary to the conclusion derived from section C of this reference, Anslyn and Grubbs have subsequently shown that the titanocene methylidene trimethylphosphine adduct reacts with acetylenes via a dissociative mechanism where dissociation of the phosphine is rate determining. Saturation behavior was observed at nearly neat acetylene trap concentration. Greater than 70% saturation was required in order to see curvature in their pseudo-first-order plots. Phosphine exchange also proceeds by a dissociative mechanism. Details will be reported elsewhere.

[5] Buchwald, S. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 5490.

[6] For a study of substituent effects in metallacyclobutenes see: McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbaugh, T. S.; Tebbe, F. N. *J. Am. Chem. Soc.* **1981**, *103*, 5584.

[7] All of the atoms of the [Ta(H)(=C=CH$_2$)] moiety of Cp$_2$*Ta(H)(=C=CH$_2$) are believed to lie in the same plane: van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347.

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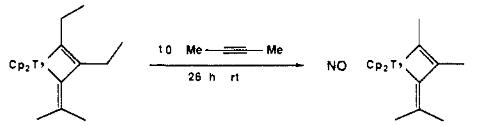
Table I. Isomer Ratios during the Reaction of **4** with 3-Hexyne (Eq 3)

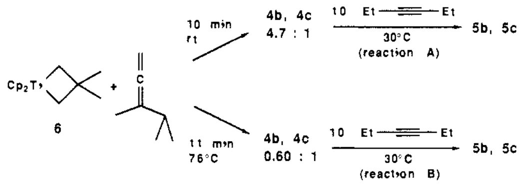
	reaction A			reaction B		
time, h	conversion, %	**4b**:**4c**	**5c**:**5b**	conversion, %	**4b**:**4c**	**5c**:**5b**
initial		4.7			0.60	
0.25	32	3.6	1.8	25	0.56	1.7
0.50	57	3.3	1.7	46	0.53	1.6
0.75	66	2.7	1.6	60	0.48	1.6
1.00	77	2.2	1.6	71	0.43	1.7
1.25	83	1.8	1.7	78	0.44	1.6
1.50	88	1.5	1.7	85	0.38	1.6

mation,[8] and that the free vinylidene **7** is not pyramidal at titanium with a deep potential well.[9] The formation of the substituted α-methylenetitanacyclobutenes is irreversible; **5a** did not exchange with an excess of 2-butyne (eq 2).



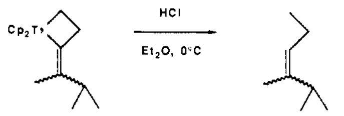
5a 5d (2)

Enriched mixtures of **4b** and **4c** were obtained as the kinetic (4.7:1) and thermodynamic (0.60:1) products of the reaction of metallacycle **6** with 3,4-dimethyl-1,2-pentadiene (eq 3).[10] The



6 (3)

ratio of **4b** and **4c** was determined by NMR of the metallacycles or by GC of the corresponding olefins obtained by protonolysis with HCl (eq 4).[12,13] The enriched mixtures of **4b** and **4c** were



(4)

treated with an excess of 3-hexyne (eq 3), and the starting material (**4**) and product (**5**) isomer ratios were followed by NMR (Table I). In both reactions, the starting material ratio (**4b**:**4c**) decreased with time due to equilibration and/or kinetic enrichment. However, the product ratio (**5c**:**5b**) remained constant ((1.7 ± 0.1):1) at both early and late stages of the reaction from starting materials enriched in either **4b** or **4c**.[14] The stereochemistry of **4** was thus scrambled during its conversion to **5**.

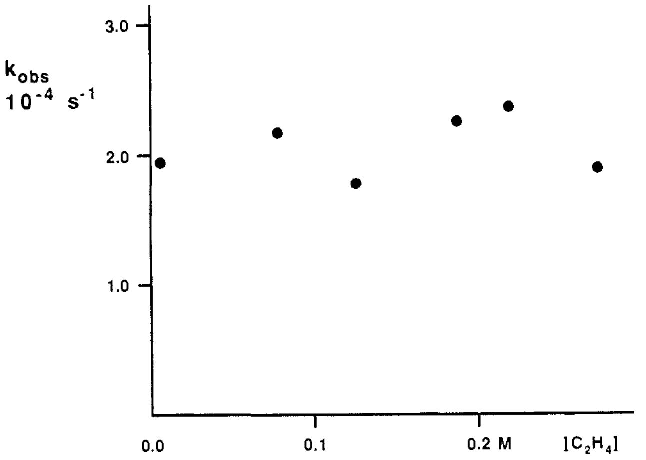


Figure 1. Rate of equilibration of **4b** and **4c** as a function of ethylene concentration.

A second mechanistic probe was found in the dependence of the rate of equilibration of **4b** and **4c** (in the absence of the acetylene) as a function of the concentration of added ethylene. Steady-state kinetic analysis of the system showed that the rate of a dissociative reaction (via the free vinylidene **7**) should be strictly independent of the ethylene concentration (eq 5), while

$$\mathbf{4b} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{8a} \underset{k_{-2}\,C_2H_4}{\overset{k_2}{\rightleftharpoons}} \mathbf{7} \underset{k_{-3}}{\overset{k_3\,C_2H_4}{\rightleftharpoons}} \mathbf{8b} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathbf{4c} \qquad (5)$$

$$\frac{d[4c]}{dt} = \frac{k_1 k_2 k_3 k_4 [4b] - k_{-1} k_{-2} k_{-3} k_{-4} [4c]}{k_{-1} k_{-2} k_{-3} + k_4 k_{-1} k_{-2} + k_3 k_4 k_{-1} + k_2 k_3 k_4}$$

the rate of a displacement reaction should depend on the ethylene concentration (eq 6). The ethylene dependence in eq 6 is most

$$\mathbf{4b} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{8a} \underset{k_{-2}\,C_2H_4}{\overset{k_2\,C_2H_4}{\rightleftharpoons}} \mathbf{8b} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathbf{4c} \qquad (6)$$

$$\frac{d]4c]}{dt} = \frac{k_1 k_2 k_3]4b] [C_2H_4] - k_{-1} k_{-2} k_{-3} [4c] [C_2H_4]}{k_{-1} k_{-2} [C_2H_4] + k_2 k_3]C_2H_4] + k_3 k_{-1}}$$

pronounced at low ethylene concentrations (k_{obsd} increasing with $[C_2H_4]$ from $k_{obsd} = 0$ at $[C_2H_4] = 0$), with saturation occurring at high ethylene concentrations ($[C_2H_4] \gg k_3 k_{-1}/(k_{-1}K_{-2} + k_2 k_3)$). Saturation corresponds to the condition where displacements on **8a** and **8b** by ethylene occur faster than closure to **4b** and **4c**. Experimentally, the equilibration of **4b** and **4c** was found to be first order with $k_{obsd} = (2.1 \pm 0.2) \times 10^{-4}$ s^{-1} at 26 °C over an ethylene concentration range of 0.006–0.27 M (corresponding to 0.03–1.23 equiv of ethylene, Figure 1).[15] This graph fits eq 5 or eq 6 at saturation. For saturation to have been achieved at $[C_2H_4] < 0.006$ M, the rate constants for ethylene displacement on **8a** and **8b** (k_2 and k_{-2}) would have to be considerably greater than the rate constants for closure to the metallacycles (k_3 and k_{-1}): $k_d >$ ca. $100k_c$ M^{-1} (c = closure and d = displacement).[16]

The stereochemical and kinetic experiments are both consistent with a dissociative mechanism or a displacement mechanism in

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[8] The methylene ligand in $Cp_2Ta(CH_3)({=}CH_2)$ does not rotate on the ^1H NMR time scale ($\Delta G^‡ \geq 20$ kcal/mol): (a) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389. The rotational barrier in $Cp_2Ti(CH_3)({=}CH_2)^-$ is calculated to be 28 kcal/mol: (b) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. The rotational barrier in $Cp_2Ti({=}CH_2)$ is calculated to be 36–52 kcal/mol: (c) Gregory, A. R.; Mintz, E. A. *J. Am. Chem. Soc.* **1985**, *107*, 2179. (d) Francl, M. M.; Pietro, W. J.; Hout, R. F., Jr.; Hehre, W. J. *Organometallics* **1983**, *2*, 815. Barriers of this magnitude should be accessible from high-energy intermediates.

[9] $Cp_2Ti({=}CH_2)$ is calculated to be pyramidalized 34° with a small barrier (3 kcal/mol).[8c]

[10] The kinetic ratio of **4b** and **4c** is consistent with a favored approach of titanium to the allene's less hindered (Me) face. A similar selectivity (4.9:1) was observed in the palladium-catalyzed hydrogenation of 3,4-dimethyl-1,2-pentadiene.[11]

[11] Crombie, L.; Jenkins, P. A.; Mitchard, D. A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1081.

[12] 2,3-Dimethyl-3-hexene was stable to the protonolysis conditions. The addition of HCl to olefins is very slow in ether: Hennion, G. F.; Irwin, C. F. *J. Am. Chem. Soc.* **1941**, *63*, 860.

[13] The protonolysis of a vinyl–titanium bond with retention of double-bond geometry was observed in the conversion of 2,3-diphenyltitanacyclobutene to (*Z*)-1,2-diphenyl-1-propene: Meinhart, J. D. Ph.D. Dissertation, California Institute of Technology, 1987.

[14] The observed ratio of **5c** and **5b** is consistent with a favored approach of 3-hexyne to **7**'s less hindered (Me) face. The relative energies of the transition states for closure to the metallacycles (**9a** to **5c** versus **9b** to **5b**) could also account for the ratio if Curtin–Hammett conditions are operative.

[15] The point of lowest ethylene concentration was measured without added ethylene. Presumably this ethylene was produced by a small amount of metallacycle decomposition.

[16] Assuming that the difference between the Me and *i*-Pr vinyl substituents in **4b** and **4c** has only a small effect on the forward and reverse rate constants in eq 6 (i.e. $k_1 \approx k_{-3}$, $k_2 \approx k_{-2} \equiv k_d$, and $k_3 \approx k_{-1} \equiv k_c$; the equilibrium constant of 1.7 implies that the rate constants are of the same order), the rate expression for eq 6 reduces to $d[\mathbf{4c}]/dt \approx k_1[C_2H_4]([\mathbf{4b}] - [\mathbf{4c}])/(2[C_2H_4] + k_c/k_d)$ or $k_{obsd} \approx k_1[C_2H_4]/([C_2H_4] + k_c/2k_d)$. For $[C_2H_4] = 0.006$ M and k_{obsd} at this concentration equal to at least 60% of the value at saturation, then $k_d \geq 110k_c$ M^{-1}. A total of 60% of saturation is a conservative estimate of the lowest value that k_{obsd} could have at the background concentration of ethylene (the left-hand point in Figure 1).

which displacements are fast with respect to closure to the metallacycle. The kinetic experiment is more sensitive in setting a limit on the relative rates of displacement and closure if displacements occur. The limit set by this experiment ($k_d >$ ca. $100k_c$ M^{-1}) sets the ratio at an unlikely high level, implying a dissociative mechanism via the free vinylidene **7**. While few data are available for the direct comparison of displacement and closure rates for vinylidene or methylidene olefin adducts, analogy can be drawn with the corresponding phosphine adducts. A titanocene methylidene phosphine adduct has been shown to react with acetylenes via a dissociative mechanism where dissociation is rate determining.[4] Displacement of phosphine by acetylene is thus very slow (not observed) with respect to closure to the metallacyclobutene. For olefin adducts, displacements of the olefin can occur (leaving-group effects in competitive metallacycle trapping experiments indicated a displacement mechanism for the titanocene methylidene system[4]), so we cannot rule out the possibility that displacements can become fast with respect to closure. It appears that both displacement[4] and dissociative mechanisms are possible with titanocene metallacyclobutanes depending on the substitution pattern. The structures of the organometallic species in this study allowed double-bond geometry to serve a role similar to that which chirality served in distinguishing between S_N1 and S_N2 mechanisms in organic systems.

Experimental Section

The metallacycles were handled under an inert atmosphere by standard drybox and Schlenk line techniques. Benzene, benzene-d_6, pentane, and ether were purified by vacuum transfer from the sodium benzophenone ketyl. Metallacyclobutane **6** was prepared according to the published procedure.[17] 3,4-Dimethyl-1,2-pentadiene[11] was prepared from 2,3-dimethyl-1-butene by Moore's procedure.[18]

Metallacyclobutene 5a. A 46-mg (0.19 mmol) sample of metallacyclobutane **6** was dissolved in 1.0 mL of benzene at room temperature and immediately treated with 16 μL (11 mg, 0.17 mmol) of 3-methyl-1,2-butadiene. After the solution was stirred for 20 min at room temperature, 84 μL (61 mg, 0.74 mmol) of 3-hexyne was added. After the solution was stirred for 15 min at room temperature and 20 min at 70 °C, volatiles were removed under vacuum. The resulting semicrystalline mass was treated with 5 mL of pentane, filtered, and concentrated to a volume of ca. 1 mL. This solution was slowly cooled to −50 °C, producing crystals. This mixture was allowed to stand at −78 °C for 3 h before the solvent was removed by cannula, and the crystals were dried under vacuum, yielding 24.7 mg (48%) of small dark brown clusters: ^{1}H NMR (C_6D_6) δ 5.68 (s, 10 H), 2.51 (q, J = 7.6 Hz, 2 H), 2.20 (q, J = 7.5 Hz, 2 H), 1.90 (s, 3 H), 1.57 (s, 3 H), 0.98 (t, J = 7.6 Hz, 3 H), 0.91 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (C_6D_6) δ 221.89, 188.57, 120.70, 111.12, 95.76, 31.56, 29.70, 22.44, 18.17, 16.67, 13.57. Anal. Calcd for $C_{20}H_{26}Ti$: C, 76.43; H, 8.34. Found: C, 76.47; H, 8.11.

Metallacyclobutenes 5b and 5c. A 28 mg (0.11 mmol) sample of metallacyclobutane **6** was dissolved in 1.0 mL of benzene at room temperature, immediately cooled on an ice bath, treated with 14 μL (10 mg, 0.11 mmol) of 3,4-dimethyl-1,2-pentadiene, and warmed to room temperature with mixing. After the solution was stirred for 12 min, 51 μL (37 mg, 0.45 mmol) of 3-hexyne was added. After the resulting solution was stirred for 4 min at room temperature and 20 min at 70 °C, volatiles were removed under vacuum. The resulting dark brown oil was treated with 3 mL of pentane and filtered. Removal of volatiles under vacuum gave a dark brown oil. ^{1}H NMR (C_6D_6) revealed a 1.7:1 mixture of **5c** and **5b**. **5b**: δ 5.68 (s, 10 H), 3.09 (sept, J = 6.8 Hz, 1 H), 2.49 (q, J = 7 Hz, 2 H), 2.17 (q, J = 7 Hz, 2 H), 1.44 (s, 3 H), 1.11 (d, J = 6.8 Hz, 6 H), 0.96 (t, J = 7 Hz, 3 H), 0.93 (t, J = 7 Hz, 3 H). **5c**: δ 5.69 (s, 10 H), 2.51 (q, J = 7 Hz, 2 H), 2.20 (q, J = 7 Hz, 2 H), 1.76 (s, 3 H), 1.67 (sept, J = 6.8 Hz, 1 H), 1.12 (d, J = 6.8 Hz, 6 H), 0.98 (t, J = 7 Hz, 3 H), 0.90 (t, J = 7 Hz, 3 H). Difference NOE experiment: irradiation at δ 2.195 enhanced δ 1.76 and 3.09 but not δ 1.44 or 1.67.

Metallacyclobutene 5d. A 36-mg (0.15 mmol) sample of metallacyclobutane **6** was dissolved in 450 μL of benzene at room temperature and immediately treated with 14 μL (9.9 mg, 0.15 mmol) of 3-methyl-1,2-butadiene. After the solution stood for 11 min at room temperature, 23 μL (16 mg, 0.29 mmol) of 2-butyne was added. After the resulting solution was heated for 15 min at 76 °C, volatiles were removed under vacuum, giving a dark purple oil: ^{1}H NMR (C_6D_6) δ 5.66 (s, 10 H), 2.05 (s, 3 H), 1.94 (s, 3 H), 1.65 (s, 3 H), 1.56 (s, 3 H).

Treatment of 5a with 2-Butyne. A solution of 4.7 mg (15 μmol) of **5a** in 450 μL of benzene-d_6 in an NMR tube was treated with 12 μL (8.1 mg, 0.15 mmol) of 2-butyne. After the solution stood for 26 h at room temperature, the ^{1}H NMR showed the starting materials without any trace of **5d**.

Protonolysis of 4b and 4c with HCl. A 22-mg (89 μmol) sample of metallacyclobutane **6** was dissolved in 450 μL of benzene at room temperature, immediately cooled on an ice bath, treated with 9.7 μL (7.3 mg, 75 μmol) of 3,4-dimethyl-1,2-pentadiene, and warmed to room temperature with mixing. After the solution stood for 14 min, a 100-μL aliquot of the dark orange-brown solution was injected into a nitrogen-filled test tube containing 1.0 mL of ether and 2.0 mL (ca. 4.6 equiv) of HCl gas rapidly stirred in an ice bath. The ether solution immediately became red-orange and deposited a red-orange precipitate within 1 min. After 2 min, an excess of Na_2CO_3 was added, the mixture was warmed to room temperature, and the supernatant was analyzed by GC (25-m SE-30 capillary column, 35 °C). Peaks corresponding to (*Z*)- and (*E*)-2,3-dimethyl-3-hexene (retention times 5.08 and 5.29 min) were observed in a ratio of 4.65:1. A second aliquot taken after 3.9 h and similarly treated with HCl showed the same peaks in a ratio of 0.61:1.

Treatment of 4b and 4c with 3-Hexyne (Reaction A). A 20-mg (81-μmol) sample of metallacyclobutane **6** was dissolved in 450 μL of benzene-d_6 in an NMR tube at room temperature, immediately cooled in an ice bath, treated with 8.9 μL (6.7 mg, 69 μmol) of 3,4-dimethyl-1,2-pentadiene, and warmed to room temperature with mixing. After the solution was allowed to stand for 10 min, 92 μL (66 mg, 0.81 mmol) of 3-hexyne was added, and the tube was warmed to 30 °C in the NMR probe. ^{1}H NMR spectra were recorded at 15-min intervals as shown in Table I.

Treatment of 4b and 4c with 3-Hexyne (Reaction B). A 20-mg (81 μmol) sample of metallacyclobutane **6** was dissolved in 450 μL of benzene-d_6 in an NMR tube at room temperature, immediately cooled in an ice bath, treated with 11.4 μL (8.5 mg, 89 μmol) of 3,4-dimethyl-1,2-pentadiene, and warmed to room temperature with mixing. After the solution was heated for 11 min at 76 °C, 92 μL (66 mg, 0.81 mmol) of 3-hexyne was added, and the tube was warmed to 30 °C in the NMR probe. ^{1}H NMR spectra were recorded at 15-min intervals as shown in Table I.

Equilibration of 4b and 4c in the Presence of Ethylene. A reaction was required for each data point in Figure 1; the following is illustrative. A 31-mg (0.12 mmol) sample of metallacyclobutane **6** was dissolved in 560 μL of benzene at room temperature, immediately cooled in an ice bath, treated with 14 μL (10 mg, 0.11 mmol) of 3,4-dimethyl-1,2-pentadiene, and warmed to room temperature with mixing. After the solution was stirred 11 min, volatiles were removed under vacuum (9 min). The resulting brown oil was dissolved in 560 μL of benzene-d_6 and transferred via syringe to a nitrogen-filled NMR tube containing 4.2 mL of ethylene gas (measured at room temperature and pressure) in an ice bath. The tube was warmed to room temperature, and ^{1}H NMR spectra were recorded at 15-min intervals over 2.5 h with a final spectrum at 15 h. **4b**: δ 5.30 (s, 10 H), 2.73 (sept, J = 6.8 Hz, 1 H), 2.64 (m, 2 H), 1.67 (s, 3 H), 1.05 (d, J = 6.8 Hz, 6 H), 0.31 (m, 2 H). **4c**: δ 5.32 (s, 10 H), 2.64 (m, 2 H), 2.37 (sept, J = 6.8 Hz, 1 H), 1.65 (s, 3 H), 1.15 (d, J = 6.8 Hz, 6 H), 0.26 (m, 2 H). The concentration of ethylene was determined by integration relative to the metallacycles. The combined concentration of **4b** and **4c** remained constant throughout the reaction as judged by integration relative to the protio solvent peak. A plot of $\ln \{[(\alpha + 1)^{-1} - (\alpha_\infty + 1)^{-1}]/[(\alpha_0 + 1)^{-1} - (\alpha_\infty + 1)^{-1}]\}$ versus time (α = [**4b**]/[**4c**], α_0 = initial ratio, α_∞ = final ratio) was linear for each of the reactions (correlation coefficients ranging from −0.9948 to −0.9994) with the negative of the slope equal to k_{obsd}.[19]

Acknowledgment. We are grateful to the National Institutes of Health, E. I. du Pont de Nemours & Co., and the National Science Foundation (Grant CHE 8520517) for financial support.

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(17) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658.

(18) Moore, W. R.; Ward, H. R. *J. Org. Chem.* **1962**, *27*, 4179.

(19) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper & Row: New York, 1981; p 180.