temperatures ranging from −50 °C to room temperature using the general procedure which was successful in the case of (*E*)-2,4-pentadienyltrimethylsilane failed to give the desired products. After the usual workup and evaporation of the organic layer to remove solvent a viscous liquid residue invariably remained. No volatile products could be isolated from this material.

Acknowledgment. We are grateful to the U.S. Air Force Office of Scientific Research (NC)-AFSC for generous support of this work.

Registry No. **2**, 72952-73-9; **3**, 72952-63-7; **7**, 73400-23-4; **8**, 79210-77-8; **9**, 79210-79-0; **11** (R = CH_3), 82932-92-1; **11** (R = CH_3) Me_4Si, 82932-94-3; **11** (R = CH_3CH_2), 82932-96-5; **11** (R = CH_3CH_2) Me_4Si, 82932-98-7; **11** (R = $(CH_3)_2CH$), 82933-00-4; **12** (R = CH_3), 82932-93-2; **12** (R = CH_3) Me_4Si, 82932-95-4; **12** (R = CH_3CH_2), 82932-97-6; **12** (R = CH_3CH_2) Me_4Si, 82932-99-8; **12** (R = $(CH_3)_2CH$), 82933-01-5; (*E*)-$(CH_3)_2HSiCH_2CH{=}CHCH\Delta bdCH_2$, 82932-80-7; $CH_2{=}CHCH{=}CHCH_3$, 504-60-9; $CH_2{=}CHCH{=}CHCH_2K$, 51391-25-4; $CH_3CH{=}CHCH{=}CHCH_3$, 592-46-1; $CH_2{=}CHCH{=}CHCH(CH_3)K$, 82932-81-8; $CH_2{=}C(CH_3)CH_2CH{=}CH_2$, 763-30-4; C_2H_5CHO, 123-38-6; C_3H_7CHO, 123-72-8; $(CH_3)_2CHCHO$, 78-84-2; C_4H_9CHO, 110-62-3; $(CH_3)_3CCHO$, 630-19-3; $C_5H_{11}CHO$, 66-25-1; c-$C_6H_{11}CHO$, 2043-61-0; C_6H_5CHO, 100-52-7; $(cH_3)_2CO$, 67-64-1; $(C_2H_5)CO$, 96-22-0; $(C_3H_7)_2CO$, 123-19-3; $CH_3C(O)CH(CH_3)_2$, 563-80-4; $CH_3C(O)CH_2CH(CH_3)_2$, 108-10-1; $(CH_3)_2CHCH_2CH(OC_2H_5)_2$, 3842-03-3; $C_6H_5CH(OCH_3)_2$, 1125-88-8; $(CH_3)_2C(OCH_3)_2$, 77-76-9; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C_2H_5$, 72952-65-9; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C_3H_7$, 82932-82-9; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)CH(CH_3)_2$, 72952-66-0; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C_4H_9$, 82932-83-0; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C(CH_3)_3$, 72952-67-1; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C_5H_{11}$, 82932-84-1; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C_6H_{11}$-*c*, 72952-68-2; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C_6H_5$, 72952-69-3; (*E*)-$CH_2{=}CHCH{=}CHCH_2C(OH)C(CH_3)_2$, 82932-85-2; (*E*)-$CH_2{=}CHCH{=}CHCH_2C(OH)(C_2H_5)_2$, 72952-70-6; (*E*)-$CH_2{=}CHCH{=}CHCH_2C(OH)(C_3H_7)_2$, 72952-71-7; (*E*)-$CH_2{=}CHCH{=}CHCH_2(OH)(CH_3)CH(CH_3)_2$, 82932-86-3; (*E*)-$CH_2{=}CHCH{=}CHCH_2C(OH)(CH_3)CH_2CH(CH_3)_2$, 82932-87-4; (*E*)-$CH_2{=}CH{=}CHCH_2C(OH)(CH_2)_5$, 72952-72-8; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OC_2H_5)CH_2iCH(CH_3)_2$, 82932-88-5; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OCH_3)C_6H_5$, 82932-89-6; (*E*)-$CH_i{=}CHCH{=}CHCH_2C(OCH_3)(CH_3)_2$, 64586-00-1; (*E*)-$CH_2{=}CHCH{=}CHCH_2C(OC_2H_5)(CH_2)_5$, 82932-90-9; $Me_2C{=}CHC(O)Me$, 141-79-7; (*E*)-$CH_2{=}CHCH{=}CHCH_2C(CH_3)_2CH_2C(O)CH_3$, 72952-74-0; 1,4-pentadiene, 591-93-5; cyclohexanone, 108-94-1; cyclohexanone diethyl ketal, 1670-47-9; crotonaldehyde, 4170-30-3; acetaldehyde, 75-07-0; *cis*-3-(trimethylsilylmethyl)-4-acetyl-5,5-dimethylcyclohexene, 82932-91-0; *trans*-3-(trimethylsilylmethyl)-4-acetyl-5,5-dimethylcyclohexene, 82933-02-6.

Titanacyclobutanes: Substitution Pattern and Stability[†,‡]

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The relative stabilities of six alkyl-substituted titanacyclobutanes have been measured. For monosubstituted metallacycles, the substituent prefers the β-position. Addition of a second β substituent, such as CH_3, results in significant destabilization of the metallacycles. The relationship of ground-state stability to reactivity and the structural features influencing the stability are considered.

Introduction

Metallacyclobutanes have been implicated or demonstrated as intermediates in a number of catalytic and synthetic transformations.[1-3] Of major import in these reactions is the effect of substituents on the relative stabilities of the possible metallacyclic intermediates. For example, the selectivity observed in the olefin metathesis reaction has been attributed to differences in stability of the possible metallacyclic intermediates. We recently reported the synthesis of a series of metallacyclobutanes which undergo metathesis reactions. In this report we describe the effect of substituents on the relative stability of a series of titanacyclobutanes and examine the relationship between their relative stability and reactivity.

Experimental Section

Titanocene dichloride was purchased from Boulder Scientific and purified by Soxhlet extraction with dichloromethane. $AlMe_3$ was purchased from Alfa, or as a 2 M solution in toluene from Aldrich.[4] $AlMe_2Cl$ was purchased from Texas Alkyls. 4-(Dimethylamino)pyridine (DMAP) was purchased from Aldrich and recrystallized from hot toluene. 2,3-dimethyl-1-butene and 3,3-dimethyl-1-butene were purchased from Aldrich and stored over Linde 4-Å molecular seives. 2-Methyl-1-butene was purchased from ICN Pharmaceuticals and stored over molecular seives. 3-Methyl-1-butene was purchased from Phillips and stored over molecular seives. Isobutylene was purchased from Matheson and freeze-degassed twice prior to use. Tebbe reagent (**2**) prepared by an established procedure[5] was used for preparative purposes. For equilibrium measurements, **2** was prepared from $Cp_2TiMeCl$ and recrystallized from hexane.[6] $Cp_2\overline{TiCH_2CH(t\text{-}Bu)C}H_2$ (**1a**), $Cp_2\overline{TiCH_2CH(i\text{-}Pr)C}H_2$ (**1b**), and $Cp_2\overline{TiCH_2}\overline{\underline{CHC}}\underline{H(C}H_2)_3$ (**4**)

[†] Dedicated to the memory of Rowland G. Pettit.

[‡] Contribution No. 6706.

(1) (a) Grubbs, R. H. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon Press: New York, in press. (b) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1. (c) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449.

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(3) Ephritikhine, M.; Francis, B. R.; Green, M. L. H.; MacKenzie, R. E.; Smith, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1131.

(4) Toluene solutions of $AlMe_3$ were titrated by using an established procedure. Hagen, D. F.; Leslie, W. D. *Anal. Chem.* **1963**, 814.

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were prepared by established methods[5] (see the preparation of 5 for the general method).

Toluene, diethyl ether, and THF were stirred over CaH_2 and vacuum transferred onto sodium benzophenone ketyl. Pentane and hexane were stirred over concentrated H_2SO_4, washed with water, dried over $CaCl_2$, and vacuum transferred onto sodium benzophenone ketyl in tetraglyme. Dichloromethane was stirred over P_2O_5 and degassed by intermittent pumping on a high vacuum line. The above solvents were vacuum transferred into storage flasks sealed with Teflon screw valves. Benzene-d_6 (Merck, Sharp and Dohme) and toluene-d_8 (Aldrich) were dried and deoxygenated by stirring over sodium benzophenone ketyl.

General Procedures. All manipulations of air- and/or moisture-sensitive compounds were carried out by using standard high-vacuum line Schlenk techniques or in a Vacuum Atmospheres drybox. Argon used in Schlenk work was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4-Å molecular sieves. NMR spectra were recorded on a Varian EM-390 (90-MHz ^1H), a JEOL FX-90Q (89.60-MHz ^1H, 22.53-MHz ^{13}C), or a Bruker WM-500 (500.13-MHz ^1H) instrument. Kinetic and equilibrium measurements were run in the automated mode on the JEOL FX-90Q. Temperatures were measured by using $\Delta\nu_{MeOH}$[7] and were constant to within ±0.1 °C.

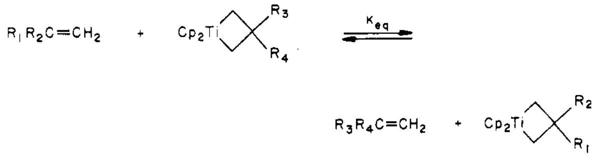
Preparation of $Cp_2TiCH_2{\cdot}AlMe_2Cl$ (2) from Cp_2TiCH_3Cl. Titanocenemethyl chloride[6] (8.15 g, 28.0 mmol) was suspended in 15 mL of toluene in a Schlenk tube. A solution of $AlMe_3$ in toluene (14.6 mL, 28.0 mmol, 1.92 M) was added via syringe, and the mixture was stirred at room temperature in the dark. The reaction was periodically monitored by NMR. After 3 days, a second portion of $AlMe_3$ in toluene (5.84 mL, 11.2 mmol) was added, and the solution was stirred for an additional 3 days. The solvent was removed in vacuo. The crude product was washed with 30 mL of hexane and dried in vacuo overnight. The solid was dissolved in 60 mL of toluene and filtered through a coarse Schlenk frit. Solvent was removed in vacuo until solids began to form. Crystallization was achieved by addition of 10 mL of toluene and careful layering of 45 mL of hexane above the toluene solution, followed by cooling at −20 °C overnight. The supernatant was removed via cannula. The crystalline $Cp_2TiCH_2{\cdot}AlMe_2Cl$ was washed twice with 40 mL of −20 °C pentane and dried in vacuo overnight (4.2 g, 66%). Analysis of the dark red product by NMR, using 1,2-dibromoethane as an internal standard, indicated 94% purity and revealed no $Cp_2TiCH_2{\cdot}Al(CH_3)Cl_2$. A portion of the product (1.85 g) was dissolved in 250 mL of hexane, filtered through a medium Schlenk frit, and concentrated to 150 mL in vacuo. Slow cooling to −50 °C produced large red-brown crystals which were isolated on a coarse Schlenk frit. The product (1.20 g, 65% recovery) is 98% pure by NMR analysis.

Preparation of $Cp_2\overline{TiCH_2CMe_2CH_2}$ (5). Tebbe reagent (2) (2.46 g, 8.63 mmol) was dissolved in 17 mL of CH_2Cl_2 in a Schlenk tube. Isobutylene (100 mmol) was freeze-degassed and condensed into the reaction vessel at −196 °C. DMAP (1.23 g, 10.0 mmol) was added to the stirred solution at −20 °C. The mixture was stirred for 3 min and transfered via cannula into 120 mL of vigorously stirred pentane at 0 °C. The byproducts were removed on a coarse Schlenk frit, and the filtrate was concentrated to 40 mL by removal of solvent in vacuo at 0 °C. The red solution was transferred from a flocculent white precipitate via cannula and concentrated to 20 mL. After the solution was cooled at −78 °C overnight, the supernatant was decanted. The remaining dark red solid was dissolved in 6 mL of toluene at 0 °C and gradually cooled to −50 °C. The resulting solid was washed twice with 5 mL of cold pentane. Residual pentane was removed in vacuo at room temperature over a period of 3 h to give red needles of $Cp_2\overline{TiCH_2CMe_2CH_2}$ (660 mg, 31%): ^1H NMR (toluene-d_8, −10 °C) δ 1.10 (s, 6 H), 2.50 (s, 4 H), 5.51 (s, 10 H); ^{13}C NMR (C_6D_6, 6 °C) δ 5.4 (s), 38.1 (q, J = 123 Hz), 83.5 (t, J = 137 Hz), 110.7 (d, J = 171 Hz).

Equilibrium and Kinetic Measurements. Metallacycles were recrystallized from Et_2O or toluene. Tebbe's reagent (2) was prepared from $Cp_2TiMeCl$ and recrystallized from hexane. Reactions were run in sealed NMR tubes at 40 °C in C_6D_6. For reactions of titanacycles with base–aluminum adducts, samples were prepared by covering a weighed sample of titanacycle with C_6D_6 and layering on a measured amount of standardized (NMR vs. internal 1,2-dibromoethane) base–aluminum adduct in C_6D_6. The samples were immediately removed from the drybox, frozen, and sealed. For reactions with olefin and THF or Et_2O, 2 was weighed into an NMR tube fitted with a gas-measuring bulb, into which the solvent, olefin, and base were introduced by vacuum transfer. After the reaction was complete, the volume of the solution was measured by replacement of the sample with a measured volume of liquid. Integration vs. C_6D_5H indicated no more than 5% decomposition in most cases. Initial concentrations were derived from the weight of titanacycle or 2 and the measured volume. Subsequent values were calculated from NMR integration in a straightforward manner. Analysis of the data is discussed in the text.

Results and Discussion

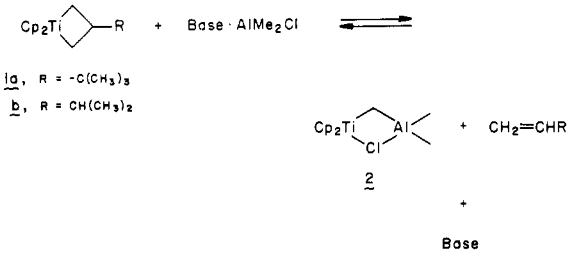
The relative stability of metallacycles vs. the conjugate olefins can be determined by measuring the equilibrium constant K_{eq} in eq 1. Since relative olefin stabilities are readily available, the substituent effect on metallacycle stability can be determined.



(1)

Direct measurement of K_{eq} would be difficult due to the overlapping of NMR signals. Consequently, an accurate, indirect method was used which allows a variety of stabilities to be measured under similar conditions. This method is based on the following observations.

Base adducts of Me_2AlCl react with the metallacycles to release olefin and generate the titanium methylene adduct, 2.[8] The position of equilibrium is controlled by the base strength and the structure of the metallacycle. For example, if the base is (dimethylamino)pyridine, the equilibrium lies almost completely to the left for most olefins,[9] whereas ethers result in equilibrium mixtures which contain significant amounts of 2. The equilibrium shown in eq 2 may be approached from either direction.



(2)

Measurement of the rate of reaction of 1a with 1.0 and 3.0 equiv of $AlMe_2Cl{\cdot}Et_2O$ at low conversion revealed that the reaction is first order in 1a with $k = 9.5\ (\pm\ 0.6) \times 10^{-5}\ s^{-1}$ (40 °C, C_6D_6) and zeroth order in $AlMe_2Cl{\cdot}$base. This is the same as the rate of direct exchange of 1a with other olefins and diphenylacetylene.[10] The rate is consistent with rate-determining formation of titanium methylidene 3 (eq 3) or the corresponding olefin complex.[10] Involvement of free $AlMe_2Cl$ was excluded by the observation that

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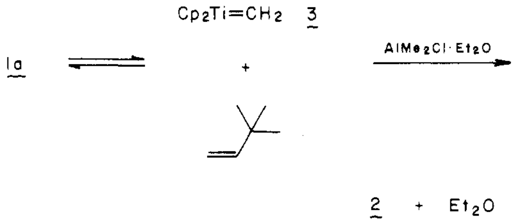
[7] Gordon, A. J.; Ford, R. A. "A Chemist's Companion..."; Wiley-Interscience: New York, 1972; p 103.

[8] (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *Ibid.* **1979**, *101*, 5074. (c) Klabunde, U., Tebbe, F. N.; Parshall, G. W.; Harlow, R. L. *J. Mol. Catal.* **1980**, *8*, 37.

[9] Ott, K. C.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 2942.

[10] Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* in press.



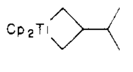
(3)

the rate of reaction of **1a** with 1.0 equiv of $AlMe_2Cl{\cdot}Et_2O$ is unchanged by addition of 0.1 equiv of Et_2O ($k = 9.3 \times 10^{-5}$ s^{-1}, 40 °C, C_6D_6). The rate of reaction of **1a** with $AlMe_2Cl{\cdot}THF$ was somewhat more difficult to measure. In this case, equilibrium favors the reactants, which causes the reaction to be first order over a shorter interval, even under fairly dilute conditions. The measured rate (with 4 equiv of $AlMe_2Cl{\cdot}THF$) is 8.4 (± 1) × 10^{-5} s^{-1} (40 °C, C_6D_6), the same (within experimental error) as the rate of reaction of **1a** with $AlMe_2Cl{\cdot}Et_2O$ and with diphenylacetylene.

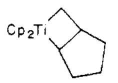
Observation of first-order kinetics for reaction of **1a** with $AlMe_2Cl{\cdot}Et_2O$ and with $AlMe_2Cl{\cdot}THF$ contrasts with the reaction of **1a** with $AlMe_2Cl$, which is second order (first order in each reactant).[9] This suggests that an open coordination site on aluminum is required for direct reaction with **1a**.

The reactions described above provide the basis for measuring the desired equilibrium constants. The required equations are given in Scheme I. The use of bases of different strengths can be used to examine a wide variety of olefins.

Initial experiments performed using the metallacycles derived from 3,3-dimethyl-1-butene (**1a**), 3-methyl-1-butene (**1b**), and cyclopentene (**4**) demonstrated that diethyl ether was a suitable base for measurement of K_{eq} by the method of Scheme I. These and all other equilibrium measurements were carried out at 40 °C in C_6D_6. Results of a typical experiment using **1b** are shown in Figure 1. Plots of ln Q asymptotically approach the equilibrium value ln K_{eq}, which is deduced graphically. Similar plots derived for **1a** and **4** indicate that the order of stability is **4** ≈ **1a** < **1b**. Values of K^{Et_2O} for these metallacycles are 0.33 M (**1a**), 0.091 M (**1b**), and 0.43 M (**4**). Thus the difference in free energy between these titanacyclobutanes is less than 1 kcal mol^{-1}. None of the other possible isomers of **1a,b**, the α-substituted metallacycles, were observed. Consequently, for these bulky alkyls the β isomer is at least 2 kcal mol^{-1} more stable than the α isomer.

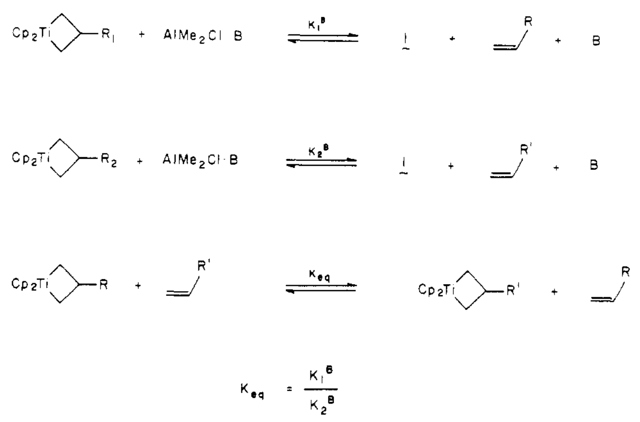


1b



4

Scheme I



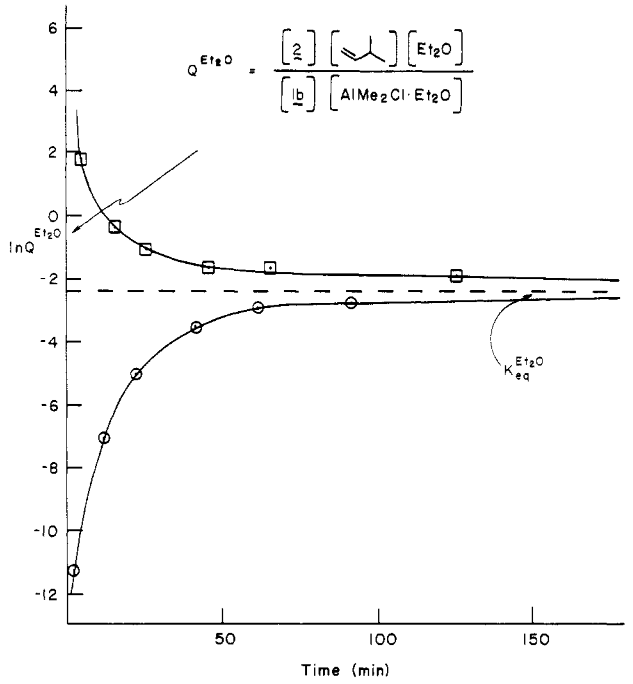


Figure 1. Asymptotic approach to equilibrium of **2** and **1b**: □, represents data from reaction of **2** with 3-methyl-1-butene and Et_2O; ○, indicates reaction of **1b** with $AlMe_2Cl{\cdot}Et_2O$. Both experiments were monitored by ^1H NMR at 40 °C in C_6D_6.

Several β,β-disubstituted metallacycles including $Cp_2TiCH_2CMe_2CH_2$ (**5**), $Cp_2TiCH_2CEtMeCH_2$ (**6**), and $Cp_2TiCH_2C(i\text{-}Pr)MeCH_2$ (**7**) have been prepared.[5,11] These complexes have been found to be far more labile than their monosubstituted counterparts and **4**. Attempts at using Et_2O to measure the stability of these metallacycles failed, because the equilibria (Scheme I) lay almost completely to the right. However, THF was found to serve as convenient base for these measurements. Equilibrium mixtures of the metallacycles and $AlMe_2Cl{\cdot}THF$ were found to be remarkably stable at 40 °C in C_6D_6 solutions. The equilibrium between metallacycle and **2** was achieved without decomposition to $(Cp_2TiCH_2)_2$, the normal product of metallacycle decomposition.[12] Mixtures of **2**, THF, and isobutylene, 2-methyl-1-butene, or 2,3-dimethyl-1-butene reached equilibrium within several minutes. Values of K^{THF} = 0.21 and 2.1 M were obtained for **5** and **6**, respectively. Measurement was less accurate in the case of **7** because the amount of metallacycle formed was small. When 2 equiv of THF and 4 equiv of 2,3-dimethyl-1-butene were used the value $K^{THF} \simeq 8$ M was obtained. The order of stability is thus **7** < **6** < **5**. Replacement of the hydrogens of one of the methyl substituents in **5** with methyl groups results in an increase in steric crowding which destabilizes the complex by ca. 1 kcal/methyl for the first two substitutions (Figure 2). Replacement of a third hydrogen is not possible; addition of pyridine to a solution of **1** and 2,3,3-trimethyl-1-butene resulted in immediate destruction of **1** and formation of an unidentified dark brown solid.

In order to relate these values of K^{Et_2O} and K^{THF}, we determined the extent of reaction of **1a** with $AlMe_2Cl{\cdot}THF$ under relatively dilute conditions. From the value ob-

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[11] Straus, D. A. Ph.D. thesis, California Institute of Technology, 1983.

[12] Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 5922.

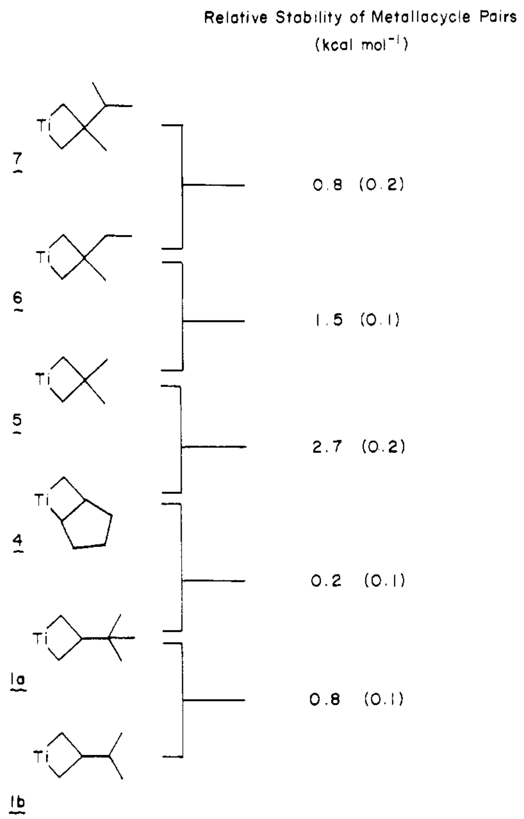

Figure 2. Differences in ΔG between pairs of titanacyclobutanes (40 °C, C_6D_6), calculated from equilibrium constants obtained by the method of Scheme I.

tained, $K^{THF} = 2 \times 10^{-3}$ M, we estimate $K^{Et_2O}/K^{THF} = 160$. The differences in stability of the six titanacyclobutanes, relative to the conjugate olefins and 3, are shown in Figure 2. Part of the difference between mono and disubstituted metallacycles is certainly due to the difference in relative olefin heats of formation.

Stabilities of the titanacyclobutanes derived according to Scheme I are relative to the conjugate olefins. The difference in free energy of formation between these olefins and the corresponding saturated hydrocarbons provides an estimate of the contribution of this difference to K_{eq}. These are $\Delta G_f°$ (3,3-dimethyl-1-butene) (19.53) − $\Delta G_f°$ (3,3-dimethylbutane) (−2.37) = 21.90 kcal mol^{-1} and $\Delta G_f°$ (3-methyl-1-butene) (17.87) − $\Delta G_f°$ (2-methylbutane) (−3.50) = 21.37 kcal mol^{-1}.[13] Thus the more stable metallacycle, **1b**, forms from the more stable olefin. The opposite ordering would be expected if olefin stability was the only determining factor. The greater stability of **1b** relative to **1a**, as measured according to Scheme I, may therefore be attributed to structural features of these metallacycles. Corresponding differences for some other olefin-alkane pairs are as follows:[13] isobutylene, 18.88; 2-methyl-1-butene, 19.01; 2,3-dimethyl-1-butene, 18.41 kcal mol^{-1}. These disubstituted olefins are ca. 2.5–3 kcal mol^{-1} more stable, relative to the corresponding alkanes, than are the monosubstituted olefins. The apparent instability of **5**, **6**, and **7** relative to **1a** and **1b** may be due in part to this effect.

The titanacyclobutanes **1a**, **5**, and $Cp_2\overline{TiCH_2CHPhCH_2}$ (**8**) have been structurally characterized by X-ray diffraction.[14] These structures provide the basis for understanding the relative stability of the titanacyclobutanes. The conformation of the metallacycle ring is nearly planar, and **5** does not show significant distortion from C_{2v} symmetry.[14] In **1a** and **8**, interaction of the CMe_3 or Ph substituent with the Cp rings is relieved by a rocking of the substituted β-carbon in the plane of the ring, instead of puckering. The observation that **1b** and **1a** differ in stability by less than 1 kcal mol^{-1} suggests that this motion, which relieves much of the expected difference (≥2 kcal mol^{-1}), is a relatively low energy distortion. Interaction of the two methyl substituents with the Cp rings cannot be avoided in **5**, and this metallacycle is significantly less stable than **1a** and **1b**. The instability of **6** and **7** and the fact that it has not been possible to observe the β-methyl-β-*tert*-butyl titanacyclobutane suggest that the strain relieved in **1a** by rocking of the central carbon unit is considerable. The rate of the reactions of **1a** and **7** with diphenylacetylene have been measured.[5] Activation energies are $\Delta G^{*} = 24$ and 22 kcal mol^{-1} for **1a** and **7**, respectively, at 27 °C. For these metallacycles $\Delta\Delta G^{*} = 2$ kcal mol^{-1}, compared with $\Delta\Delta G = 5$ kcal mol^{-1} from Figure 2.

It has been observed that the reactivity of a monosubstituted metallacycle decreases as the bulk of the substituent increases.[17] This and the above observations are most consistent with a mechanism, such as rate-determining cleavage to a carbene olefin complex, in which the relief of steric interaction gained by the rocking of the β-methylene is lost in the transition state.

The data presented above provide a precise guide to the factors controlling the stability of these metallaycles that will be useful in predicting the reactions of such species in catalytic and synthetic reactions.[18] The dominate interactions determining the stability of these metallaycles are between the substituents on the metallacycle and the cyclopentadienyl rings. One substituent prefers to occupy the β-position when steric effects are most important. However, when a second substituent is added to the metallacycle ring, the α-position appears to be the preferred substitution site.

Not only will these quantitative measurements of substituent effects provide a guide to metallacycle reactions, both catalytic and stoichiometric, but also they will also be useful in understanding substituent effects in other metallocene systems.

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Registry No. **1a**, 75687-68-2; **1b**, 83314-22-1; **2**, 67719-69-1; **3**, 11068-51-2; **4**, 83314-23-2; **5**, 80122-07-2; **6**, 83314-24-3; **7**, 79389-13-2; **8**, 80122-06-1; Cp_2TiCH_3Cl, 1278-83-7; $AlMe_3$, 75-24-1; isobutylene, 115-11-7.

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(13) $\Delta G_f°$(gas, 25 °C) values from "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds"; American Petroleum Institute, Project 44; Carnegie Institute of Technology: Pittsburgh, PA, 1953.

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