

Substituent Effects on the Cleavage Rates of Titanocene Metallacyclobutanes

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Abstract: The rate of cleavage of titanocene metallacyclobutanes to titanocene methylenedienyl complexes was studied as a function of electron-withdrawing and electron-donating substituents on the cyclopentadienyl rings. The rate of cleavage was found to decrease with electron-donating substituents. Cleavage rates were correlated with the UV spectra of titanocene dichlorides, the $^{47,49}\text{Ti}$ NMR of titanocene complexes, the C-H coupling constants of titanocene methyl chlorides, and the equilibrium constants between titanocene methyl chlorides and dimethyltitanocenes. The mechanism of titanocene metallacyclobutane cleavage is discussed in light of these and past studies.

Several transition-metal alkylidene and methylenedienyl complexes have been found to catalyze olefin metathesis. The mechanism has been extensively studied and has led to the acceptance of a nonpairwise mechanism involving metal alkylidene and metallacyclobutane intermediates.¹ The relative stabilities of the alkylidene versus the metallacycle depends on the metal system. Osborn has found an active homogeneous system in which metal alkylidene complexes are more stable than metallacyclobutanes.² Schrock³ has found an active system, starting with $(\text{RO})_2\text{W}(\text{NR}')(\text{=CH}(t\text{-Bu}))$ complexes, in which the energy differences are probably smaller. The masked titanium methylenedienyl species $\text{Cp}_2\text{TiCH}_2\text{AlMe}_2\text{Cl}$, known as the Tebbe reagent, acts as a slow catalyst for the degenerate metathesis of terminal olefins.⁴ The reaction of the Tebbe reagent with olefins in the presence of Lewis bases allows the isolation of bis(cyclopentadienyl)titanacyclobutanes.⁵ These titanacyclobutanes are catalysts for the degenerate metathesis of terminal olefins, but they are very poor catalysts for the productive metathesis of acyclic internal olefins.^{5c} In these titanacyclobutane systems the metallacycle is the lowest energy intermediate in the metathesis reaction.

Several olefin metathesis systems have been used for ring-opening metathesis polymerization of cyclic olefins.⁶ Specifically, the titanocene metallacyclobutanes have been shown to form a norbornene living polymerization system.⁷ Several other polymers of strained cyclic olefins are also currently being synthesized in our laboratories.⁸ A good understanding of the mechanism of metallacyclobutane cleavage to methylenedienyl coupled with the understanding of the relative energetics between titanocene metallacyclobutanes and titanocene alkylidenes could allow us to control the catalytic activity of these ring-opening metathesis polymerization catalysts.

Table I. Absorption Maxima of Lowest Energy Transitions in the UV-Vis Spectra of Ring-Substituted Titanocene Dichlorides

compd ^a	λ_{max}^b	compd ^a	λ_{max}^b
Cp^*TiCl_2	560	Cp_2TiCl_2	523
$(\text{Cp})_2\text{TiCl}_2$	536	$\text{CpCp}^{\text{Cl}}\text{TiCl}_2$	517
$\text{Cp}^{\text{TMS}}\text{TiCl}_2$	532	$\text{Cp}_2^{\text{Cl}}\text{TiCl}_2$	514
$\text{Cp}'_2\text{TiCl}_2$	528	$\text{CpCp}^{\text{CF}_3}\text{TiCl}_2$	513
$\text{Cp}'\text{CpTiCl}_2$	525	$(\text{Cp})\text{CpTiCl}_2$	510

^a 3.3×10^{-3} M solutions in CHCl_3 . ^b λ in nm.

Table II. $^{47,49}\text{Ti}$ NMR^a of a Number of Titanium Compounds

compd	$\delta(^{47,49}\text{Ti})$, ppm	$\nu_{1/2}(^{49}\text{Ti})$, Hz	$\nu_{1/2}(^{47}\text{Ti})$, Hz
Cp_2TiCl_2	-771.8	44	84
$\text{Cp}'\text{CpTiCl}_2$	-744.8	66	184
$\text{Cp}'_2\text{TiCl}_2$	-719.3	125	235
$\text{Cp}^{\text{TMS}}\text{TiCl}_2$	-747.3	85	257
$(\text{Cp})\text{CpTiCl}_2$	-666.4	107	195
$(\text{Cp})_2\text{TiCl}_2$	-568.5	115	
Cp^*TiCl_2	-442.3	70	213
$\text{Cp}^{\text{Cl}}\text{CpTiCl}_2$	-740.1	110	
$\text{Cp}^{\text{Cl}}_2\text{TiCl}_2$	-708.8	136	
$\text{CpCp}^{\text{CF}_3}\text{TiCl}_2$	-776.7	82	

^a ^{49}Ti (5.51%; $I = 7/2$, $Q = 0.24 \times 10^{-28}$ M²); ^{47}Ti (7.28%; $I = 5/2$, $Q = 0.29 \times 10^{-28}$ M²). See ref 14.

The mechanism of metallacycle cleavage has been studied both theoretically and experimentally. Using the extended-Hückel method, Hoffmann and co-workers⁹ found that the lowest energy structure was "nonclassical". Contrary to experimental observations they find the carbene olefin structure to be lower in energy, by ca. 1 eV, than the metallacyclobutane structure.

Rappé has carried out calculations on a model system in which the cyclopentadienyl groups of the actual system are replaced with chlorines.¹⁰ In these calculations the titanacyclobutane structure was found to be lowest in energy, in agreement with experimental observations. The methylenedienyl-olefin complex was found to be 11.5 kcal mol⁻¹ higher in energy, but essentially no potential energy well was found at this geometry. The free titanocene methylenedienyl and olefin were found to be 10.4 kcal mol⁻¹ above the methylenedienyl-olefin complex.

The mechanism of titanocene metallacyclobutane cleavage has been extensively studied experimentally.¹¹ Competitive trapping experiments and kinetic studies of the reaction of $\text{Cp}_2\text{Ti}(\text{CH}_2)\text{-}$

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Table III. C-H Coupling Constants of Methyl Groups Attached to a Metal Center

compd	J_{CH} , Hz	compd	J_{CH} , Hz
$\text{CpCp}^{\text{CF}_3}\text{TiMeCl}$	129.9	$\text{Cp}'_2\text{TiMeCl}$	128.2
$\text{Cp}^{\text{Cl}}_2\text{TiMeCl}$	129.9	$\langle\text{Cp}\rangle\text{CpTiMeCl}$	127.7
$\text{Cp}^{\text{Cl}}\text{CpTiMeCl}$	129.1	$\text{Cp}^*\text{CpTiMeCl}$	127.2
Cp_2TiMeCl	128.9	$\langle\text{Cp}\rangle_2\text{TiMeCl}$	126.7
$\text{Cp}'\text{CpTiMeCl}$	128.4	$\text{Cp}^*_2\text{TiMeCl}$	126.5

PMe_3 with acetylenes and olefins strongly implicate a titanocene methyldiene π adduct.^{11c}

Since the mechanism of cleavage has been studied very extensively, we undertook a study of substituent effects on metallocycle cleavage in order to further our understanding of the relative energetics between metallocyclobutanes and alkylidenes. These studies are being used in a rational synthesis of better ring-opening polymerization catalysts.

Results

A number of ring-substituted titanocene dichlorides can be readily prepared.¹² The compounds $\text{Cp}'_2\text{TiCl}_2$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{Me}$), $\text{Cp}'\text{CpTiCl}_2$, $\langle\text{Cp}\rangle\text{CpTiCl}_2$ ($\langle\text{Cp}\rangle = 1,2,4\text{-C}_5\text{H}_2\text{Me}_3$), $\langle\text{Cp}\rangle_2\text{TiCl}_2$, $\text{Cp}^*_2\text{TiCl}_2$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$), $\text{Cp}^*\text{CpTiCl}_2$, $\text{CpCp}^{\text{Cl}}\text{TiCl}_2$ ($\text{Cp}^{\text{Cl}} = \text{C}_5\text{H}_4\text{Cl}$), $\text{Cp}^{\text{Cl}}_2\text{TiCl}_2$, $\text{CpCp}^{\text{TMS}}\text{TiCl}_2$ ($\text{Cp}^{\text{TMS}} = \text{C}_5\text{H}_4\text{SiMe}_3$), and $\text{CpCp}^{\text{CF}_3}\text{TiCl}_2$ ($\text{Cp}^{\text{CF}_3} = \text{C}_5\text{H}_4\text{CF}_3$) were prepared for use in this study.

The UV-vis spectra of these ring-substituted titanocene dichlorides were recorded (Table I). They all exhibit a weak absorbance ($\epsilon \sim 200 \text{ M}^{-1} \text{ cm}^{-1}$) between 500 and 560 nm, which in titanocene dichloride has been assigned to a symmetry-forbidden $A_1 \rightarrow A_2$ transition.¹³ This band moves to lower energy as electron-donating substituents are added to the rings and moves to higher energy as electron-withdrawing substituents are added to the rings. The absorption spectra of the compounds having single substituents on the rings are qualitatively similar to the spectrum of titanocene dichloride; in addition to the band between 500 and 560 nm, they exhibit a broad region of absorption between 260 and 410 nm. The compounds with more highly substituted rings, i.e., those with $\langle\text{Cp}\rangle$ and Cp^* ligands, exhibit not only this broad region of absorption but also a band between 470 and 490 nm.

The $^{47,49}\text{Ti}$ NMR spectra of these ring-substituted titanocene dichlorides were also recorded (Table II). Both the ^{49}Ti and ^{47}Ti resonances appear in the same spectrum, with the ^{49}Ti resonance 268.1 ppm downfield of the ^{47}Ti resonance. Due to its higher quadrupole moment, the ^{47}Ti resonance is always broader than the ^{49}Ti resonance. Increasing methyl substitution of the rings causes an increasingly downfield shift of the $^{47,49}\text{Ti}$ resonances. Substitution of the electron-donating TMS (trimethylsilyl) group and the electron-withdrawing Cl and CF_3 groups onto the rings also causes a downfield shift of the $^{47,49}\text{Ti}$ resonances.

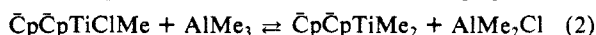
From the ring-substituted titanocene dichlorides the corresponding titanocene methyl chlorides can be prepared in good yield (eq 1). The C-H coupling constants of the methyl group bonded



Cp = substituted or unsubstituted ring

to titanium are included in Table III. The C-H coupling constant decreases with increasing methyl substitution of the cyclopentadienyl rings and increases with electron-withdrawing substituents.

The titanocene methyl chlorides are in equilibrium with dimethyltitanocenes when treated with 1 equiv of trimethylaluminum (eq 2). The equilibrium constants lie further to CpCpTiMe_2 as



electron-withdrawing substituents are substituted on the cyclopentadienyl ligands and lie further to CpCpTiMeCl with increasing

Table IV. Equilibrium Constants for the Reaction in Equation 2

compd	K_{eq}	compd	K_{eq}
$\text{CpCp}^{\text{CF}_3}\text{TiMeCl}$	1.12	Cp_2TiMeCl	0.08
$\text{Cp}^{\text{Cl}}_2\text{TiMeCl}$	1.03	$\text{Cp}'_2\text{TiMeCl}$	0.03
$\text{CpCp}^{\text{Cl}}\text{TiMeCl}$	0.40	$\text{Cp}^*\text{CpTiMeCl}$	<0.01

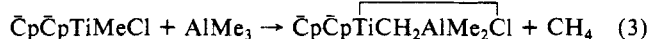
Table V. Kinetic Data for the Equilibration^a

$T, ^\circ\text{C}$	$\text{cis-2} \xrightleftharpoons[k_{-1}]{k_1} \text{trans-2}$	
	$k_1, \times 10^5 \text{ s}^{-1}$	$k_{-1}, \times 10^5 \text{ s}^{-1}$
63.5	7.3	3.5
68.5	16.0	7.7
74.0	27.0	13.0
78.5	40.0	19.0

^a $[\text{Ti}]_m = 0.11 \text{ M}$. For k_1 : $\Delta H^\ddagger = 26 \pm 2 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = -2 \pm 7 \text{ eu}$, $\rho = -0.991$. For k_{-1} : $\Delta H^\ddagger = 25 \pm 3 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = -3 \pm 7 \text{ eu}$, $\rho = -0.990$.

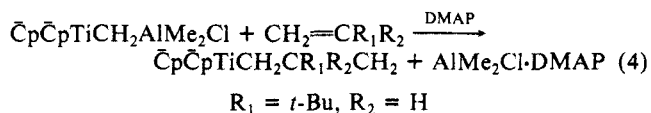
methyl substitution on the cyclopentadienyl ligands. The equilibrium constants are listed in Table IV.

The methyl ring-substituted titanocene methyl chlorides are the best starting materials for the preparation of methyl ring-substituted analogues of the Tebbe reagent (eq 3). The materials

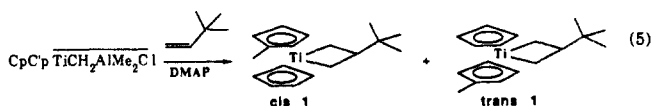


are identical with materials produced by the direct reaction of the titanocene dichlorides with 2 equiv of AlMe_3 .¹² The electron-withdrawing ring-substituted titanocene dichlorides must be used to make the Tebbe reagent.

The ring-substituted Tebbe analogues could be used to synthesize various titanacyclobutanes via modifications of established routes used for the parent system (eq 4). The reaction of



$\text{Cp}'\text{CpTiCH}_2\text{AlMe}_2\text{Cl}$ with neohexene and DMAP ((dimethylamino)pyridine) produces a 1:1 mixture of *trans*-1 and *cis*-1 (eq 5). Apparently this is the equilibrium ratio as it does not change



upon heating, even in the presence of added olefin. Attempts to separate the isomers by crystallization failed; they cocrystallize in the same 1:1 ratio.

Reaction of $\langle\text{Cp}\rangle\text{CpTiCH}_2\text{AlMe}_2\text{Cl}$ with neohexene and DMAP produces a 3.4:1 *trans*-2 to *cis*-2 (eq 6). Attempts to



separate *trans*-2 and *cis*-2 failed. Recrystallization from toluene led to a 3.5:1 *trans*/*cis* ratio of the isomers. Recrystallization from diethyl ether led to a 2.2:1 ratio. These different ratios of *trans*-2 to *cis*-2 are due to different solubilities of the metallocycles in the different solvents and are not due to equilibration during recrystallization. Conducting the metallocycle synthesis at low temperatures did not significantly increase the fraction of *trans*-2 in the reaction mixture.

The 3.4:1 ratio of *trans*-2 to *cis*-2 is a kinetic ratio. Material with this initial ratio was allowed to equilibrate (both with and without added olefin) at various temperatures from 55 to 83 $^\circ\text{C}$. The equilibrium constant $k = [\text{trans-2}]/[\text{cis-2}]$ is essentially invariant at 2.0 over this temperature range. This result indicates that ΔH° and ΔS° for the equilibration of *trans*-2 and *cis*-2 are both small, as expected since *trans*-2 and *cis*-2 have the same number and kinds of bonds and should have similar structures.

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Table VI. Relative Rates of Reaction of $\text{CpCpTiCH}_2\text{CH}(t\text{-Bu})\text{CH}_2$ at 55 °C: $\text{CpCpTiCH}_2\text{CH}(t\text{-Bu})\text{CH}_2 + \text{PhC}\equiv\text{CPh} \rightarrow \text{CpCpTiCH}_2\text{C(Ph)C(Ph)} + \text{CH}_2=\text{CH}(t\text{-Bu})$

Cp	metallacycle	$k_{\text{obsd}} \times 10^5 \text{ s}^{-1}$	rel rate
Cp_2	3	68	16
$\text{Cp}'\text{Cp}$	<i>trans</i> -1	40	9.3
$\text{Cp}'\text{Cp}$	<i>cis</i> -1	40	9.3
Cp'_2	5	10	2.3
$\langle\text{Cp}\rangle\text{Cp}$	<i>trans</i> -2	4.5	1.1
$\langle\text{Cp}\rangle\text{Cp}$	<i>cis</i> -2	4.3	1.0
Cp^{Cl}_2	4	32	7.4

Table VII. Activation Parameters for the Reaction of $\text{CpCpTiCH}_2\text{CH}(t\text{-Bu})\text{CH}_2$ at 55 °C: $\text{CpCpTiCH}_2\text{CH}(t\text{-Bu})\text{CH}_2 + \text{PhC}\equiv\text{CPh} \rightarrow \text{CpCpTiCH}_2\text{C(Ph)C(Ph)} + \text{CH}_2=\text{CH}(t\text{-Bu})$

Cp	metallacycle	$\Delta H^\ddagger$, kcal mol ⁻¹	$\Delta S^\ddagger$, eu
Cp'_2	5	30.1 (6)	15 (2)
$\langle\text{Cp}\rangle\text{Cp}$	<i>trans</i> -2	30.1 (4)	13 (1)
$\langle\text{Cp}\rangle\text{Cp}$	<i>cis</i> -2	28.3 (9)	8 (3)
Cp_2	3	25.0 (5)	10 (2)
Cp^{Cl}_2	4	27.2 (4)	8 (2)

The rate in which a ca. 3.5:1 mixture of *trans*-2/*cis*-2 attains equilibrium in the absence of added olefin was monitored at several temperatures. Forward and reverse rate constants for the equilibration *cis*-2 $\rightleftharpoons$ *trans*-2 could be estimated from these data. The results are shown in Table V. These rate constants are smaller than rate constants observed for trapping reactions of these metallacycles with diphenylacetylene (vide infra). During the equilibrations ca. 5% decomposition of metallacycle occurs, so we cannot rule out that freed olefin, though not observed, may catalyze the equilibration of *trans*-2 and *cis*-2. Qualitatively, the addition of 2 equiv of olefin did not increase the rate of this equilibration. In the presence of 2 equiv of added labeled olefin *cis*-1,2-dideuterio-3,3-dimethylbutene, ca. 8% of the metallacycle incorporated (²H NMR) labeled olefin when a mixture of *trans*-2 and *cis*-2 was heated to 68 °C for 75 min.

All the titanacyclobutanes synthesized for this study are similar spectroscopically to the parent system. In the proton NMR spectra the α -H's of the metallacycle ring resonate in the region 1.8–2.4 ppm and β -H's are in the characteristic high-field region +0.14 to –0.2 ppm. In ¹³C NMR spectra the *tert*-butyl metallacycles show α -C resonances between 67.0 and 68.0 ppm and β -C resonances between 20.0 and 30.0 ppm. The reactivity of these titanacycles is similar to that of the parent metallacycles.

Metallacyclobutenes could be independently synthesized from the reaction of the corresponding Tebbe reagent with diphenylacetylene. One of the most characteristic spectroscopic features of these metallacyclobutenes is the low-field resonance of the sp^2 -hybridized α -carbon in their ¹³C NMR spectra.¹⁵

The irreversibility of the reaction of titanacyclobutenes with carbonyls and acetylenes to form metallacyclobutenes makes these reagents good trapping reagents for kinetic studies. The kinetics of the reaction of the *tert*-butyl metallacycles $\text{Cp}_2\text{TiCH}_2\text{CH}(t\text{-Bu})\text{CH}_2$ (**3**), $\text{Cp}^{\text{Cl}}_2\text{TiCH}_2\text{CH}(t\text{-Bu})\text{CH}_2$ (**4**), $\text{Cp}'_2\text{TiCH}_2\text{CH}(t\text{-Bu})\text{CH}_2$ (**5**), *trans*-1, *cis*-1, *trans*-2, and *cis*-2 with diphenylacetylene were studied. The results are shown in Table VI. Activation parameters for the reaction of **3**, **4**, **5**, and *cis*- and *trans*-2 with diphenylacetylene were derived from kinetics data obtained in a temperature range between 45 and 75 °C and are listed in Table VII.

The reaction of a mixture of *trans*-2 and *cis*-2 with 7 equiv of diphenylacetylene and 10 equiv of labeled olefin 1,2-*cis*-dideuterio-3,3-dimethylbutene was carried out to 60% conversion

Table VIII. Kinetics Data for the Reaction $\text{Cp}_2\text{TiCH}_2\text{CMe}_2\text{CH}_2 + \text{PhC}\equiv\text{CPh} \rightarrow \text{Cp}_2\text{TiCH}_2\text{C(Ph)C(Ph)} + \text{CH}_2=\text{CMe}_2$

Cp	metallacycle	$k_{\text{obsd}} \times 10^4 \text{ s}^{-1}$	rel rate
Cp_2	6	18.7	8.9
Cp'_2	7	2.1	1

Table IX. Kinetics Data for the Reaction $\text{CpCpTiCH}_2\text{CH}(t\text{-Bu})\text{CH}_2 + \text{O}=\text{CMe}_2 \rightarrow \text{CpCpTi}=\text{O} + \text{CH}_2=\text{CMe}_2 + \text{CH}_2=\text{CH}(t\text{-Bu})^a$

Cp	metallacycle	$k_{\text{obsd}} \times 10^5 \text{ s}^{-1}$	rel rate
Cp_2	3	30	15
$\text{Cp}'\text{Cp}$	<i>trans</i> -1	20	10
$\text{Cp}'\text{Cp}$	<i>cis</i> -1	20	10
Cp'_2	5	5	2.5
$\langle\text{Cp}\rangle\text{Cp}$	<i>trans</i> -2	2	1
$\langle\text{Cp}\rangle\text{Cp}$	<i>cis</i> -2	2	1

^a $[\text{Ti}]_{\text{tot}} = 0.16 \text{ M}$, $[\text{O}=\text{CMe}_2]_0 = 0.48 \text{ M}$.

Table X. Kinetics Data for the Reaction $\text{Cp}_2\text{TiCH}_2\text{CMe}_2\text{CH}_2 + \text{O}=\text{CMe}_2 \rightarrow \text{Cp}_2\text{Ti}=\text{O} + 2\text{CH}_2=\text{CMe}_2^a$

Cp	metallacycle	$k_{\text{obsd}} \times 10^4 \text{ s}^{-1}$	rel rate
Cp_2	6	34	7.1
Cp'_2	7	4.8	1

^a $[\text{Ti}]_{\text{tot}} = 0.18 \text{ M}$, $[\text{O}=\text{CMe}_2]_0 = 1.1 \text{ M}$.

of metallacyclobutane to metallacyclobutene at 72 °C. No deuterium incorporation into the metallacyclobutene starting material or the metallacyclobutene product was observed (²H NMR).

The kinetics of the reaction of $\text{Cp}_2\text{TiCH}_2\text{CMe}_2\text{CH}_2$ (**6**) and $\text{Cp}'_2\text{TiCH}_2\text{CMe}_2\text{CH}_2$ (**7**) with diphenylacetylene were studied. The results are shown in Table VIII.

The kinetics of the reaction of *cis*- and *trans*-1, *cis*- and *trans*-2, **3**, and **5** with acetone were studied. The results are shown in Table IX. The relative rates observed are similar to the relative rates observed in the reaction of those metallacyclobutenes with diphenylacetylene.

The kinetics of the reaction of **6** and **7** with acetone were studied. The results are shown in Table X. Again the relative rates are similar to the relative rates of these metallacycles with diphenylacetylene.

Discussion

Substitution of the cyclopentadienyl rings can affect the reactivity of bis(cyclopentadienyl)titanacyclobutenes through steric and electronic effects. Several titanacyclobutenes have been structurally characterized. The substituents on the β -carbon of the metallacyclic ring interact with the cyclopentadienyl rings. In mono- β -substituted metallacycles, the steric interaction is relieved by a rocking of the β -carbon fragment and not by ring puckering, as revealed by the structures of **3** and $\text{Cp}_2\text{TiCH}_2\text{CHPhCH}_2$.^{5b} It has also been found that increasing steric bulk at the β -position increasingly destabilizes the metallacycles.^{11a} Thus, one would expect that increasing the steric bulk of the cyclopentadienyl groups by substitution should destabilize the metallacycles.

We see from the 1:1 ratio of *trans*-1 to *cis*-1 that adding one methyl group to the ring does not have much steric effect. With three methyl groups on a ring steric effects appear; *trans*-2 is ca. 0.5 kcal mol⁻¹ more stable than *cis*-2.

Ring substitution can affect these complexes electronically. Gassman¹⁷ has shown from ESCA data that substitution of two Cp* ligands for the two Cp ligands in titanocene dichloride produces an effect on the titanium core orbitals equivalent to a 0.8-eV reduction at titanium. Thus, electron-donating substituents on the rings increase the electron density at the metal center.

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(15) The low-field ¹³C resonance of sp^2 -hybridized carbons bound to early transition metals is typical.¹⁶

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(17) Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, 2, 1470.

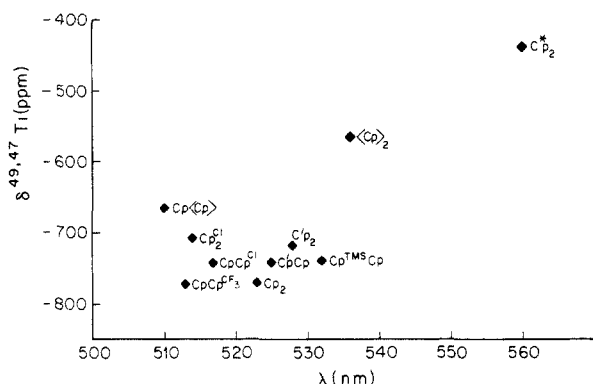


Figure 1. Plot of $\delta^{47,49}\text{Ti}$ vs $\lambda_{\max}$ (lowest energy transition) of a number of ring-substituted titanocene dichlorides.

We have observed from the absorption spectra of various titanocene dichlorides that ring substitution affects the energy difference between the ground and first excited states of these complexes. It seems that electron-donating groups on the rings tend to make this energy difference smaller; there are exceptions to this generalization; cf. the absorption spectrum of $\langle\text{Cp}\rangle\text{CpTiCl}_2$. The UV spectra of the titanocene dichlorides can give at least an indication of relative electron density at the metal center.

NMR chemical shift values are not always an indication of electron density at the atom being observed. A striking example of this is found in the $^{47,49}\text{Ti}$ NMR data for a number of ring-substituted titanocene dichlorides (Table II). Replacing two chlorides in TiCl_4 with more electron-donating cyclopentadienyl rings does shift the Ti resonances upfield as expected, but the titanocene dichloride complex that should be the most electron-rich at titanium, Cp^*TiCl_2 , exhibits the lowest field $^{47,49}\text{Ti}$ resonance. Gassman¹⁸ has found an inverse relationship between core electron binding energy and $^{47,49}\text{Ti}$ chemical shift for Cp_2TiX_2 , $\text{Cp}^*\text{CpTiX}_2$, and Cp^*TiX_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) compounds. Spinney¹⁹ has attributed the counterintuitive chemical shift values found in titanium NMR to large paramagnetic shielding terms. In molecules with low-lying excited states, such as the titanium complexes we have studied, the σ_p term, which acts to deshield the nucleus, can become dominant in determining the observed chemical shifts. The largest contribution to σ_p should arise from the first excited state; $E_n - E_0$ is the smallest for this state. Thus, for systems in which σ_p is playing the major role in determining the observed chemical shifts, there should be a correlation between the lowest energy transition observed in the absorption spectrum and the observed chemical shift (δ should be related to $(E_1 - E_0)^{-1}$ or to $\lambda_{\max}$). Such correlations were found for TiX_4 and Cp_2TiX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).²² A plot of the observed $\delta^{47,49}\text{Ti}$ values vs the wavelength of the observed lowest energy transition in the absorption spectrum of a number of ring-substituted titanocene dichlorides is presented in Figure 1. We do not expect linear correlations since both σ_p and the diamagnetic shielding term, σ_d , will change with substitutions on the rings. In general, it does seem that the lower the energy of the first optical transition, the farther downfield the observed $^{47,49}\text{Ti}$ resonance. In addition, a fairly linear correlation is found among sets of titanocene dichlorides that are substituted with the same substituents.

The C-H coupling constants of methyl groups depend on the amount of s character at carbon in the C-H bonds.²¹ To a first approximation the amount of s character depends on the effective electronegativity of the group to which the methyl group is bonded;

the larger the electronegativity of this group, the lower the s character of its bond with the methyl carbon. This leaves more s character in the C-H bonds, and hence, increasing the electronegativity of the group attached to the carbons should increase the C-H coupling constant observed for a methyl group. Conversely, decreasing the electronegativity of the group attached to carbon should lower the C-H coupling constant. Increasing the electron density at the atom to which the methyl group is bonded effectively lowers the electronegativity and should lower the C-H coupling constant. Such an effect was observed by Yoder²² in his study of the variation of C-H coupling constants of methyl groups in several types of aromatic compounds as a function of substitutions on aromatic rings. He found a linear correlation between J_{CH} and the Hammett σ values of the substituents. Electron-withdrawing substituents increased J_{CH} and electron-donating substituents decreased J_{CH} .

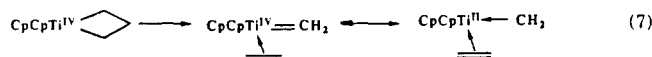
We found similar effects in ring-substituted titanocene methyl chlorides (Table III). Increasing the electron density at Ti by adding methyl groups to the cyclopentadienyl rings causes a lowering of the J_{CH} of the methyl group bonded directly to the metal center. Conversely, substitution of electron-withdrawing chlorides or a trifluoromethyl group on the rings causes an increase in J_{CH} .

Since J_{CH} is a direct relative measure of the hybridization of the Ti-CH₃ bond, of the methods presented here, it best reflects the relative electron density at the metal center. In addition, we have found no exceptions to the predicted trends and, therefore, we view the J_{CH} as the most reliable measure of the electron-donating or -withdrawing nature of the cyclopentadienyl and possibly other ligands.

Since our kinetics were done under saturation conditions, they essentially give us only information about the relative energies of the titanacyclobutanes and the first transition state. We can see how the relative energy difference varies as a function of ring substitution. The data do not let us determine the relative stabilities of metallacycles having different substituents on the cyclopentadienyl rings. Thus, we cannot separate ground-state from transition-state effects.

We see from all our kinetic results that increasing methyl substitution of the rings decreases k_{obsd} . Steric effects seem to be playing a very small part in determining the observed rate; *trans*-1 and *cis*-1 react at the same rate, and *trans*-2 and *cis*-2 react essentially at the same rate. For a number of reasons we rule out isomer equilibration as the cause for the equal values of k_{obsd} for reactions of the *trans* and *cis* isomers of the mixed-ring metallacycles. First, the reactions are carried out under saturation conditions. Closure of carbene-olefin back to metallacycle, which would be required for isomer equilibration, should not be competitive with the trapping reaction. Second, the observed forward and reverse rate constants for the equilibration of *trans*-2 and *cis*-2 were smaller than k_{obsd} values obtained in trapping experiments. Third, the k_{obsd} values for the reaction of *trans*-2 and *cis*-2 with diphenylacetylene were the same whether the material was 3.5:1 *trans*/*cis* to start or 2.2:1 *trans*/*cis* to start. Lastly, while labeled added olefin is incorporated into a *cis*/*trans* mixture of 2 in the absence of added trapping reagent, no labeled olefin is incorporated into starting material or product when a concentration of diphenylacetylene equivalent to that used in the kinetic studies is present.

Electronic effects then seem to play the major role in determining the relative reactivities of the metallacycles studied. The cleavage of a metallacyclobutane to a carbene-olefin complex is formally a reductive process. In a carbene-olefin complex the CH₂ group can be considered either a dianionic donor or a neutral donor. Thus, in these titanium systems we should assign the oxidation state of titanium metallacycles as Ti^{IV} while in the carbene-olefin complex, the titanium can have some Ti^{II} character (eq 7). Hoffman⁹ has studied these systems using the extend-



ed-Hückel method. While quantitatively incorrect, his calculations

(18) Gassman, P. G.; Campbell, W. H.; Macomber, D. W. *Organometallics* 1984, 3, 385.

(19) Kidd, R. G.; Matthew, R. W.; Spinney, H. G. *J. Am. Chem. Soc.* 1973, 94, 6686.

(20) The following discussion is a summary of the discussion found in: Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders: Philadelphia, 1977; pp 198, 283-294.

(21) Levy, G. C.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*; Wiley: New York, 1972; pp 25-28.

(22) Yoder, C. H.; Tuck, R. H.; Hess, R. G. *J. Am. Chem. Soc.* 1969, 91, 539.

lead to a qualitative understanding of this system. He calls the titanacyclobutanes d^0 complexes and carbene-olefin complexes d^2 . A more convincing argument for a reductive process is electron counting. The metallacycles are $16e^-$ species and possess an empty $1a_1$ orbital of largely metal character. In the $18e^-$ carbene-olefin complex this orbital is filled.

In fact, this is the exact reactivity that would be predicted from the Rappé-Upton generalized valence bond calculations.¹⁰ Their calculations predict a metallacycle cleavage to yield a titanocene methyldiene olefin adduct which has some donor olefin character. Their calculations, however, found no energy minimum for this carbene-olefin complex.

By the Hammond²³ postulate the transition state for the endothermic formation of carbene-olefin from metallacycle should most closely resemble the carbene-olefin species. Thus, effects that change the stability of carbene-olefin relative to metallacycle should cause similar changes to the stability of the transition state relative to metallacycle. Since the formation of carbene-olefin from metallacycle involves formal reduction at titanium, increasing the electron density at titanium by increasing the electron-donating ability of the ancillary ligands should destabilize the carbene-olefin relative to the metallacycle. Thus, we predicted that increasing methyl substitution of the cyclopentadienyl rings, making them better donors, should slow cleavage of metallacycle to carbene-olefin. This prediction is observed. All the Cp_2TiCl_2 UV-vis and $Cp_2TiMeCl$ C-H coupling constant data convince us that the methyl substitution on the cyclopentadienyl ligands does increase the electron density on the Ti. Similar effects of ring substitution were observed in the formation of the Tebbe reagent from mixed-ring titanocene dichlorides.¹² In that system increasing methyl substitution of the cyclopentadienyl rings lowered the kinetic acidity of the α -hydrogens of a L_nTi-Me intermediate.

The chloro substitution on the cyclopentadienyl rings should decrease their electron-donating ability, which seems confirmed by the fact that the J_{CH} coupling constant of the methyl bonded to titanium in $Cp^{Cl}_2TiMeCl$ is larger than the corresponding constant in $Cp_2TiMeCl$ (Table III). From our argument we would predict that **4** should react faster with diphenylacetylene than would the plain-ring analogue **3**. It was found, however, that k_{obsd} for the reaction of **4** with diphenylacetylene is smaller than k_{obsd} for the same reaction of **3**. One possible explanation for this result is that while the transition state for the slow step is stabilized by the chloro substitution (relative to the plain-ring transition state), the metallacycle ground state is stabilized to a greater extent. Evidence for this argument is found in the preparation of the Cp^{Cl}_2 analogue of the Tebbe reagent. It is made difficult because of the formation of a large amount of $Cp^{Cl}_2TiMe_2$ in the reaction of $Cp^{Cl}_2TiCl_2$ with $AlMe_3$. In fact, in order to successfully synthesize the Cp^{Cl}_2 analogue of the Tebbe reagent, an extra equivalent of $AlMe_2Cl$ was necessary to shift the equilibrium toward $Cp^{Cl}_2TiMeCl$. This was accomplished by starting with $Cp^{Cl}_2TiCl_2$ and 2 equiv of $AlMe_3$ instead of $Cp^{Cl}_2TiMeCl$ and 1 equiv of $AlMe_3$.

To further elucidate this effect, the equilibrium constants of several $\bar{C}p\bar{C}pTiMeCl$ complexes with $\bar{C}p\bar{C}pTiMe_2$ complexes were measured (eq 2). The K_{eq} increased with decreasing methyl substitution and increased with electron-withdrawing substituents. Since the aluminum reagents are the same in all the equilibria studied, the K_{eq} 's reflect relative thermodynamics of the titanocene methyl chlorides and dimethyltitanocenes. Electron-withdrawing cyclopentadienyl ligands make the titanium center less electropositive, and therefore the complex prefers the more electron-donating methyl than electron-withdrawing chlorine. A second possible explanation is that the chloro-substituted cyclopentadienyl ring is removing s character from the titanium, leaving more d character to form stronger metal-carbon bonds in the metallacycle.²⁵ The other substituted titanocene dichlorides studied do

not readily form Cp_2TiMe_2 . Thus, dialkyls including metallacyclobutanes in the Cp^{Cl}_2Ti system may enjoy special stabilization.

Conclusions

Substitution on the cyclopentadienyl rings of bis(cyclopentadienyl)titanium compounds can exert steric and electronic effects. In the reactions of ring-substituted titanacyclobutanes with trapping reagents steric effects play only a small role in determining the relative rates observed; electronic effects seem to dominate. The electronic effects can be understood from the fact that increasing the electron-donating ability of the substituted rings causes a destabilization of the transition state between metallacycle and carbene-olefin. This destabilization arises from the "reductive" nature of the conversion of metallacycle to carbene-olefin. Some results also indicate that ground-state effects cannot always be ignored. Electron-withdrawing cyclopentadienyl ligands stabilized titanocene dialkyl complexes and therefore stabilized the metallacycles also.

The $^{47,49}Ti$ NMR spectra of these complexes were not a reliable measure of the electron density at the Ti center. The UV-vis and methyl C-H coupling constants, however, did provide an accurate relative measure (with one exception in the UV-vis) of the Ti electron density.

Experimental Section

All manipulations of air- and/or moisture-sensitive compounds were carried out by using standard Schlenk line, vacuum line, and drybox techniques. Argon used in Schlenk work was purified by passage through columns of BASF-RS-11 (Chemalog) and Linde 4-Å molecular sieves.

Routine 1H and ^{13}C spectra were recorded on JEOL FX-90Q or JEOL GX-400 spectrometers. Kinetics by 1H NMR spectroscopy were obtained in automated mode on the JEOL FX-90Q. Temperatures were determined from measurement of $\Delta\nu_{MeOH}$ and were constant to within $\pm 0.1^\circ C$. Difference NOE spectra were measured on either a Bruker WM-500 or the JEOL GX-400. The ring-substituted titanocene methyl chloride Ti-Me C-H coupling constants were measured either from nondecoupled ^{13}C INEPT spectra or from observation of the ^{13}C satellites of the Ti-Me resonance in 1H spectra.

The $^{47,49}Ti$ NMR spectra were recorded on the JEOL GX-400 at 22.52 MHz. The 90° pulse length, 40 μs , was determined from a sample of neat $TiCl_4$ sealed in a 5-mm tube held concentrically in a 10-mm NMR tube filled with 2 mL of $CDCl_3$ as a lock solvent. $^{47,49}Ti$ spectra of the ring-substituted titanium compounds were obtained from saturated solutions of the titanium compounds in 2 mL of $CDCl_3$ held in 10-mm NMR tubes. Deuterium locking was used. The FID data were collected by using 90° pulses and an acquisition time of 0.272 s. The pulse delay between the end of acquisition and the beginning of the next pulse was 1 s. The spectral window was 30 kHz wide and 16K data points were collected, yielding a digital resolution of 3.7 Hz. An exponential line-broadening factor of 10 Hz was applied to the raw FID, which was then Fourier transformed to yield the spectrum. Both ^{49}Ti and ^{47}Ti resonances appear in a single spectrum separated by 268.1 ppm, with the ^{49}Ti resonance downfield relative to the ^{47}Ti resonance. Chemical shifts were referenced relative to external neat $TiCl_4$ by using the convention that positive δ values are downfield. The reported line widths include the 10 Hz of line broadening. No proton decoupling was used as its use produced no effect on the line shape of the resonances.

The UV-vis absorption spectra of the ring-substituted titanocene dichlorides were obtained on an HP 8451A diode array spectrophotometer. Solutions (3.3×10^{-3} M) of the titanocene dichlorides in spectral grade chloroform were prepared in air. The solutions were transferred to 1-cm path length cuvettes, and the absorption spectra were recorded in air. The λ_{max} of the lowest energy transition was located at the point where the first derivative of the spectrum was zero.

The solvents used were treated as follows. Pentane was freed of olefinic impurities by stirring over concentrated H_2SO_4 . It was washed with water, predried over anhydrous $MgSO_4$, and dried with CaH_2 . It was degassed and stirred over sodium benzophenone ketyl solubilized by the addition of a small amount of tetraglyme. Toluene, diethyl ether, tetrahydrofuran, benzene, benzene- d_6 , and toluene- d_8 were degassed and stirred over sodium benzophenone ketyl. All solvents were vacuum transferred into dry storage flasks equipped with Teflon closures and stored under Ar.

Diphenylacetylene (Aldrich) was recrystallized from hot toluene. Trimethylaluminum, 2 M in toluene (Aldrich), was transferred into a storage flask equipped with a Teflon closure and stored under Ar. Titanocene dichloride, Cp_2TiCl_2 (Boulder), was purified by Soxhlet ex-

(23) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

(24) Seetz, J. W. F. C.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 248.

(25) For a discussion of bonding in these systems, see: Rappé, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 297.

traction with CH_2Cl_2 . CpTiCl_3 (Aldrich) was used as received.

The ring-substituted titanocene dichlorides $\text{Cp}^*_2\text{TiCl}_2$, $\text{Cp}^*\text{CpTiCl}_2$, and $(\text{Cp})\text{CpTiCl}_2$ were prepared by a literature method¹² with the modification for the preparation of $\text{Cp}^*\text{CpTiCl}_2$ and $(\text{Cp})\text{CpTiCl}_2$ that solvent chilled to 0°C was added via cannula to a mixture of solid CpTiCl_3 and solid ring-substituted lithium cyclopentadienide. The reaction mixture was allowed to warm slowly to room temperature and stirred at this temperature for 30 min. Workup of these reactions was identical with the literature procedure.¹²

$\text{CpCp}^*\text{TiCl}_2$ and $\text{Cp}^{\text{Cl}}_2\text{TiCl}_2$ were prepared by a literature method.²⁶ $\text{CpCp}^{\text{CF}_3}\text{TiCl}_2$ was also prepared by a literature method.²⁷ $(\text{Cp})_2\text{TiCl}_2$ was prepared in an analogous manner to $\text{Cp}^*_2\text{TiCl}_2$. Cp^*TiCl_3 and $\text{Cp}^*_2\text{TiCl}_2$ were prepared by a literature method²⁸ with the modification that LiCp^* was used in place of NaCp^* .

$\text{Cp}^*\text{CpTiCl}_2$ was prepared by literature method¹² with the modification that solvent chilled to 0°C was added via cannula to a mixture of solid Cp^*TiCl_3 and solid LiCp . The reaction mixture was allowed to warm slowly to room temperature and stirred at this temperature for 30 min. Workup then followed the literature procedure.

All titanocene dichlorides except $\text{Cp}^{\text{Cl}}_2\text{TiCl}_2$ could be recrystallized from either hot toluene or hot chloroform. All were obtained in pure form except $\text{Cp}^*\text{CpTiCl}_2$, which typically contained 5–10% Cp_2TiCl_2 (^1H NMR).

The Tebbe reagent,²⁹ $\text{Cp}_2\text{TiCH}_2\text{AlMe}_2\text{Cl}$, and metallacycles 3 and 6^{11a} were prepared by literature methods.

All NMR tube experiments were prepared in the drybox and capped with a rubber septum.

Preparation of $\text{Cp}^*\text{CpTiMeCl}$ (8). This procedure is analogous to the method³² used to prepare Cp_2TiMeCl . AlMe_3 (7 mL of 2 M AlMe_3 in toluene, 14 mmol) was added via syringe to an Ar-flushed flask containing a solution of $\text{Cp}^*\text{CpTiCl}_2$ (3.27 g, 12.4 mmol) in 30 mL of CH_2Cl_2 at 0°C . The reaction mixture immediately becomes a very dark brown-red. The reaction mixture was stirred for 2.5 h at 0°C . Diethyl ether (15 mL) was then added at 0°C ; the solution immediately changes color from dark brown-red to orange. The solution was warmed to room temperature and all volatiles removed in vacuo. The resulting oily residue was dissolved in 6 mL of CH_2Cl_2 , and 10 mL of diethyl ether was carefully layered on top of the solution. The mixture was slowly cooled to -50°C and orange-red crystals formed. The mother liquor was decanted off, and the crystals were washed with two 5-mL aliquots of diethyl ether and dried in vacuo (yield 1.51 g, 50%). Material typically contains 5–10% Cp_2TiMeCl impurity. ^1H NMR (C_6D_6): δ 5.81 (s, 5 H, Cp), 5.93 (m, 1 H, $\text{C}_5\text{H}_4\text{Me}$), 5.54 (m, 1 H, $\text{C}_5\text{H}_4\text{Me}$), 5.38 (m, 1 H, $\text{C}_5\text{H}_4\text{Me}$), 5.23 (m, 1 H, $\text{C}_5\text{H}_4\text{Me}$), 2.15 (s, 3 H, $\text{C}_5\text{H}_2\text{Me}$), 0.79 (s, 3 H, Ti-Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 123.5, 120.6, 116.3, 113.3, 110.4 ($\text{C}_5\text{H}_4\text{Me}$), 115.3 (Cp), 48.1 (Ti-Me), 16.6 ($\text{C}_5\text{H}_4\text{Me}$).

Preparation of $\text{Cp}^*_2\text{TiMeCl}$. This compound was prepared as for 8. Yield was 73% of orange-red crystals. ^1H NMR (C_6D_6): δ 5.92 (m, 2 H, $\text{C}_5\text{H}_4\text{Me}$), 5.54 (m, 2 H, $\text{C}_5\text{H}_4\text{Me}$), 5.42 (m, 2 H, $\text{C}_5\text{H}_4\text{Me}$), 5.27 (m, 2 H, $\text{C}_5\text{H}_4\text{Me}$), 2.14 (s, 6 H, $\text{C}_5\text{H}_2\text{Me}$), 0.74 (s, 3 H, Ti-Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 120.1, 115.8, 113.2, 110.5 ($\text{C}_5\text{H}_4\text{Me}$), 46.4 (Ti-Me), 16.1 ($\text{C}_5\text{H}_4\text{Me}$).

Preparation of $(\text{Cp})\text{CpTiMeCl}$. This compound was prepared as for 8. Yield was 41% of orange-red crystals. ^1H NMR (C_6D_6): δ 5.84 (s, 5 H, Cp), 5.62 (s, 1 H, $\text{C}_5\text{H}_2\text{Me}$), 5.06 (s, 1 H, $\text{C}_5\text{H}_2\text{Me}$), 1.99 (s, 3 H, $\text{C}_5\text{H}_2\text{Me}$), 1.72 (s, 3 H, $\text{C}_5\text{H}_2\text{Me}$), 1.51 (s, 3 H, $\text{CC}_5\text{H}_2\text{Me}$), 0.73 (s, 3 H, Ti-Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 121.8, 121.2, 115.1 ($\text{C}_5\text{H}_2\text{Me}$), 115.7 (Cp), 47.7 (Ti-Me), 16.0, 14.3, 14.1 ($\text{C}_5\text{H}_2\text{Me}$).

Preparation of $\text{Cp}^*\text{CpTiMeCl}$. This compound was prepared as for 8. Yield was 57% of orange-red crystals. ^1H NMR (C_6D_6): δ 5.78 (s, 5 H, Cp), 1.65 (s, 15 H, C_5Me_5), 0.51 (s, 3 H, Ti-Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 123.7 (C_5Me_5), 116.1 (Cp), 51.0 (Ti-Me), 12.6 (C_5Me_5).

Preparation of $\text{Cp}^*_2\text{TiMeCl}$. This compound was prepared as for 8 with the modification that the initial CH_2Cl_2 solution was stirred for 7 h at 0°C before the diethyl ether was added. Yield was 67% of orange-red crystals. ^1H NMR (C_6D_6): δ 1.77 (s, 30 H, C_5Me_5), 0.22 (s,

3 H, Ti-Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 123.1 (C_5Me_5), 54.4 (Ti-Me), 13.0 (C_5Me_5). Anal. Calcd for $\text{C}_{21}\text{H}_{33}\text{ClTi}$: C, 68.38; H, 9.02. Found: C, 67.38; H, 8.58.

Preparation of $\text{CpCp}^{\text{Cl}}\text{TiMeCl}$. This compound was prepared as for 8. Yield was 72%. ^1H NMR (C_6D_6): δ 5.54 (m, 1 H, $\text{C}_5\text{H}_4\text{Cl}$), 5.46 (m, 1 H, $\text{C}_5\text{H}_4\text{Cl}$), 5.23 (m, 1 H, $\text{C}_5\text{H}_4\text{Cl}$), 5.78 (m, 1 H, $\text{C}_5\text{H}_4\text{Cl}$), 5.77 (s, 5 H, C_5H_5), 0.93 (s, 3 H, Ti-Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 117.3, 115.4, 112.2, 111.3 ($\text{C}_5\text{H}_4\text{Cl}$), 116.5 (C_5H_5), 51.6 (Ti-Me). Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{Cl}_2\text{Ti}$: C, 50.23; H, 4.59. Found: C, 50.51; H, 4.51.

Preparation of $\text{Cp}^{\text{Cl}}_2\text{TiMeCl}$. This compound was prepared as for 8. Yield was 46%. ^1H NMR (C_6D_6): δ 5.80 (m, 2 H, $\text{C}_5\text{H}_4\text{Cl}$), 5.58 (m, 2 H, $\text{C}_5\text{H}_4\text{Cl}$), 5.44 (m, 2 H, $\text{C}_5\text{H}_4\text{Cl}$), 5.23 (m, 2 H, $\text{C}_5\text{H}_4\text{Cl}$), 1.01 (s, 3 H, Ti-Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 117.7, 116.2, 112.9, 112.1, 109.5 ($\text{C}_5\text{H}_4\text{Cl}$), 53.6 (Ti-Me). Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{Cl}_3\text{Ti}$: C, 44.40; H, 3.73. Found: C, 44.16; H, 4.04.

Preparation of $(\text{Cp})_2\text{TiMeCl}$. The compound was prepared as for 8. Yield was 72%. ^1H NMR (C_6D_6): δ 5.52 (d, 2 H, $\text{C}_5\text{H}_2\text{Me}_3$), 5.44 (d, 2 H, $\text{C}_5\text{H}_2\text{Me}_3$), 1.85 (s, 3 H, $\text{C}_5\text{H}_2\text{Me}_3$), 1.68 (s, 3 H, $\text{C}_5\text{H}_2\text{Me}_3$), 1.54 (s, 3 H, $\text{C}_5\text{H}_2\text{Me}_3$), 0.70 (s, 3 H, Ti-Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 128.3, 120.1, 120, 119.5, 118.8 ($\text{C}_5\text{H}_2\text{Me}_3$), 16.3, 13.8, 15.4 ($\text{C}_5\text{H}_2\text{Me}_3$), 57.6 (Ti-Me).

Preparation of $\text{CpCp}^{\text{CF}_3}\text{TiMeCl}$. This compound was successfully synthesized only on an NMR tube scale since it decomposes slowly. $\text{CpCp}^{\text{CF}_3}\text{TiCl}_2$ (10 mg) was dissolved in a 5-mm NMR tube in 0.4 mL of C_6D_6 under N_2 . AlMe_3 (3.5 μL) was syringed in. The reaction turns dark orange. Yield is quantitative by NMR. ^1H NMR (C_6D_6): δ 6.27 (m, 2 H, $\text{C}_5\text{H}_4\text{CF}_3$), 6.18 (m, 2 H, $\text{C}_5\text{H}_4\text{CF}_3$), 5.85 (s, 5 H, C_5H_5), 1.73 (s, 3 H, Ti-Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 118.9 (C_5H_5), 113.5, 116.9, 121.2, 123.2, 131.7 ($\text{C}_5\text{H}_4\text{CF}_3$), 128.7 (q, $\text{C}_5\text{H}_4\text{CF}_3$), 82.5 (Ti-Me).

Preparation of $\text{Cp}^*_2\text{TiCH}_2\text{AlMe}_2\text{Cl}$. AlMe_3 (3 mL of 2 M AlMe_3 in toluene) was added via syringe to a solution of $\text{Cp}^*_2\text{TiMeCl}$ (1.5 g, 5.8 mmol) in 7 mL of toluene at room temperature. The resulting deep brown-red solution was heated to 50°C for 28 h. The volatiles were then removed at room temperature. ^1H NMR of the resulting residue showed $\text{Cp}^*_2\text{TiMeCl}$ was still present. The residue was dissolved in 5 mL of toluene, and 0.6 mL of 2 M AlMe_3 in toluene was added. The reaction mixture was stirred at room temperature for ca. 56 h. The volatiles were removed in vacuo, leaving a red oily residue. The residue was dissolved in 1 mL of toluene, and 5 mL of pentane was layered on top. The mixture was slowly cooled to -20°C to obtain the product as a red powder (yield 725 mg, 39%). ^1H NMR (C_6D_6): δ 7.94 (s, 2 H, $\mu\text{-CH}_2$), 5.91, 5.52, 5.27 (all m, 8 H, tot, $\text{C}_5\text{H}_4\text{Me}$), 1.74 (s, 6 H, $\text{C}_5\text{H}_4\text{Me}$), -0.27 (s, 6 H, Al-Me).

Preparation of $(\text{Cp})\text{CpTiCH}_2\text{AlMe}_2\text{Cl}$. This compound was prepared as for $\text{Cp}^*_2\text{TiCH}_2\text{AlMe}_2\text{Cl}$. Yield was 22% of red powder. Spectral data were identical with the published data.¹²

Preparation of $\text{Cp}^{\text{Cl}}_2\text{TiCH}_2\text{AlMe}_2\text{Cl}$. $\text{Cp}^{\text{Cl}}_2\text{TiCl}_2$ (2.12 g, 6.7×10^{-3} mol) was measured into a medium Schlenk tube and suspended in 60 mL of toluene under Ar at room temperature. A total of 8.5 mL of 2 M AlMe_3 (1.7×10^{-2} mol) in toluene was syringed in and the reaction brought to 50°C for 26 h. The volatiles were removed by vacuum at room temperature for 12 h. The resulting moist solid was extracted with pentane (3×10 mL), and the pentane extracted was pumped dry under vacuum for 12 h. The resulting red solid was dissolved in 10 mL of pentane and slowly cooled to -50°C , yielding 1.1 g of products as a red powder (yield 46%). ^1H NMR (C_6D_6): δ 5.63, 5.52, 5.46, 5.32 (all m, 8 H tot, $\text{C}_5\text{H}_4\text{Cl}$), 8.59 (s, 2 H, $\mu\text{-CH}_2$), 0.34 (s, 6 H, Al-Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 119.7, 113.0, 112.1, 111.8, 111.5 ($\text{C}_5\text{H}_4\text{Cl}$), 199.2 ($\mu\text{-CH}_2$).

Preparation of *cis*- and *trans*- $\text{Cp}^*\text{CpTiCH}_2\text{CH}(t\text{-Bu})\text{CH}_2$ (1). Neohexene (0.51 mL, 8.4 mmol) was added via syringe to a red solution of $\text{Cp}^*\text{CpTiCH}_2\text{AlMe}_2\text{Cl}$ (0.5 g, 1.7 mmol) in 2 mL of toluene cooled to 0°C . DMAP (0.21 g, 1.7 mmol) was added to the solution, which was stirred for 5 min at 0°C and then cooled to -35°C . Pentane (20 mL) was slowly added via syringe to the solution, which was rapidly stirred at -35°C . An orange precipitate formed and the reaction mixture was filtered. The volatiles were removed from the filtrate in vacuo, leaving a red powder. This powder was dissolved in 0.5 mL of toluene at room temperature, and the resulting red solution was cooled to -50°C . A 1:1 mixture of *cis*- and *trans*-1 is isolated as a red powder (yield 0.33 g, 67%). The red powder contains ca. 20% 3. ^1H NMR (C_6D_6) (*trans*-1):³³ δ 5.63 (s, Cp), 5.42, 5.18 (2 m, $\text{C}_5\text{H}_4\text{Me}$); 2.10 (t, $J = 10$ Hz, H_a); 1.94 (t, $J = 10$ Hz, H); 1.72 (s, $\text{C}_5\text{H}_4\text{Me}$); 0.96 (s, CMe_3), 0.06 (qn, $J = 10$ Hz, H_b). ^1H NMR (C_6D_6) (*cis*-1):³³ δ 5.59, 5.30 (2 m, $\text{C}_5\text{H}_4\text{Me}$); 5.46 (s, Cp); 2.18 (t, $J = 10$ Hz, H_a); 1.83 (t, $J = 10$ Hz, H_b); 1.85 (s, $\text{C}_5\text{H}_4\text{Me}$); 0.97 (s, CMe_3), 0.10 (qn, $J = 10$ Hz, H_b). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 123.1, 119.5, 112.5, 111.4, 110.3, 109.7 ($\text{C}_5\text{H}_4\text{Me}$); 110.7, 110.4 (Cp); 67.7, 67.4 ($\alpha\text{-C}$); 34.4, 34.3 (CMe_3); 29.53, 29.5 (CMe_3); 21.5, 20.2 ($\beta\text{-C}$); 16.5, 15.9 ($\text{C}_5\text{H}_4\text{Me}$). The signals could not be assigned to the individual isomers. Attempts to separate the isomers failed.

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Preparation of $\text{Cp}'_2\text{TiCH}_2\text{CH}(t\text{-Bu})\text{CH}_2$. This compound was prepared as for **1**. The yield was 46%. ^1H NMR (C_6D_6):³¹ δ 5.60, 5.33 (2 m, $\text{C}_5\text{H}_4\text{Me}$, Cp'_A); 5.47, 5.23 (2 m, $\text{C}_5\text{H}_4\text{Me}$, Cp'_B); 2.03 (t, $J = 10$ Hz, H_A); 1.80 (t, $J = 10$ Hz, H_B); 0.98 (s, CMe_3); 0.16 (qn, $J = 10$ Hz, H_C). ^{13}C (C_6D_6):³⁵ δ 123.5 (s), 119.4 (s), 112.8 (d), 111.6 (d), 110.3 (d), 109.8 (d) ($\text{C}_5\text{H}_4\text{Me}$); 67.2 (t, $\alpha\text{-C}$); 34.4 (s, C_O), 29.5 (q, C_E), 22.8 (d, $\beta\text{-C}$); 16.3 (q), 15.8 (q) ($\text{C}_5\text{H}_4\text{Me}$).

Preparation of *cis*- and *trans*-(Cp) $\text{CpTiCH}_2\text{CH}(t\text{-Bu})\text{CH}_2$. The method of preparation of **1** was used. Recrystallization from toluene gave a 25% yield of a 3.5:1 mixture of *trans*-2 and *cis*-2. Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{Ti}$: C, 75.46; H, 9.50. Found: C, 75.29; H, 8.79. ^1H NMR (C_6D_6) *trans*-2:³¹ δ 5.68 (s, Cp); 4.89 (s, $\text{C}_5\text{H}_2\text{Me}_3$); 1.95 (t, $J = 10$ Hz, H_B); 1.65, 1.61 (2 s ratio 2:1, $\text{C}_5\text{H}_2\text{Me}_3$); 0.99 (s, CMe_3); -0.19 (qn, $J = 10$ Hz, H_A). One H_A is obscured by (Cp)-Me resonances. $^{13}\text{C}\{^1\text{H}\}$ (C_6D_6): δ 119.8, 117.6, 111.0 ($\text{C}_5\text{H}_2\text{Me}_3$); 110.8 (Cp), 67.9 ($\alpha\text{-C}$); 34.4 (C_E); 29.5 (C_C); 20.9 ($\beta\text{-C}$); 16.0, 13.7 ($\text{C}_5\text{H}_2\text{Me}_3$). ^1H NMR (C_6D_6) *cis*-2:³¹ δ 5.50 (s, Cp); 5.10 (s, $\text{C}_5\text{H}_2\text{Me}_3$); 2.09 (t, $J = 10$ Hz, H_A); 1.69, 1.67 (ratio 2:1, $\text{C}_5\text{H}_2\text{Me}_3$); 1.02 (s, CMe_3); -0.25 (qn, $J = 10$ Hz, H_B). One H_A is obscured by (Cp)-Me resonances. $^{13}\text{C}\{^1\text{H}\}$ (C_6D_6): δ 119.9, 115.8, 114.0 ($\text{C}_5\text{H}_2\text{Me}_3$); 114.9 (Cp), 67.9 ($\alpha\text{-Cp}$), 67.9 ($\alpha\text{-C}$); 24.8 ($\beta\text{-C}$); 16.9, 14.8 ($\text{C}_5\text{H}_2\text{Me}_3$). Attempts to separate the isomers failed. Recrystallization from diethyl ether yielded a 2.2:1 mixture of *trans*-2 and *cis*-2.

Preparation of $\text{Cp}^{\text{Cl}}_2\text{TiCH}_2\text{CH}(t\text{-Bu})\text{CH}_2$. A medium Schlenk tube was charged with 1 g of $\text{Cp}^{\text{Cl}}_2\text{TiCH}_2\text{AlMe}_2\text{Cl}$ (2.8×10^{-3} mol), and then 3 mL of CH_2Cl_2 was syringed in at -30°C . Another medium Schlenk tube was charged with 0.38 g (3.1×10^{-3} mol) of (dimethylamino)pyridine (DMAP), and 3 mL of CH_2Cl_2 was syringed in at -30°C . Neohexene (1.5 mL, 1.2×10^{-2} mol) was added to the DMAP solution, and then this solution was syringed onto the $\text{Cp}^{\text{Cl}}_2\text{TiCH}_2\text{AlMe}_2\text{Cl}$ solution. The reaction was stirred for 15 min at -30°C and then warmed to -10°C over 15 min. The reaction was cooled to -30°C and slowly cannulated into 50 mL of pentane at -30°C . A light orange precipitate formed and the red mother liquor was filtered off by Schlenk filtration. The precipitate was then washed with 10 mL of pentane, and the combined pentane solution was pumped to dryness under vacuum. The resulting red powder was dissolved in 3 mL of toluene and slowly cooled to -50°C . The resulting red powder was isolated by filtration (yield 220 mg, 24%). ^1H NMR (C_6D_6): δ 5.44, 5.39, 5.24, 5.15 (m, 2 H each, $\text{C}_5\text{H}_4\text{Cl}$), 22.17 (t, $J = 10$ Hz, H_A), 2.47 (t, $J = 10$ Hz, H_B), -0.11 (t, $J = 10$ Hz, H_B), 0.92 (s, 9 H, $t\text{-CMe}_3\text{Bu}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 113.1, 110.9, 109.9, 109.0, 108.3 ($\text{C}_5\text{H}_4\text{Cl}$), 76.9 ($\alpha\text{-C}$), 30.2 (CMe_3), 29.2 (CMe_3), 20.1 ($\beta\text{-C}$).

Equilibration Studies of *cis*- and *trans*-1. A 1:1 mixture of *cis*- and *trans*-1 (14 mg) was weighed into an NMR tube and dissolved in 400 μL of C_6D_6 . The tube was heated in an oil bath to 55°C . It was periodically removed and cooled to room temperature to be examined by ^1H NMR spectroscopy. Over days there is no change in the *cis*/*trans* ratio, but the metallacycles gradually decompose. The experiment was repeated with the inclusion of 2 equiv of neohexene; the *cis*/*trans* ratio stayed at 1:1 in this experiment also.

Equilibration of *cis*- and *trans*-2. A 3.5:1 *trans*-2/*cis*-2 mixture (14 mg) was loaded into an NMR tube and dissolved in 400 μL of C_6D_6 (0.11 M solution). The tube was heated to 55°C in an oil bath. The tube was periodically removed from the bath and the sample quickly frozen with liquid nitrogen. The sample was warmed to room temperature, a temperature where equilibration is slow (vide infra), and immediately examined by ^1H NMR spectroscopy. The *trans*-2/*cis*-2 ratio eventually stabilizes at 2.0:1. The procedure was repeated at oil bath temperatures of 65, 75, and 83°C . At these temperatures the *trans*-2/*cis*-2 ratio also stabilizes at 2.0:1. Decomposition of metallacycles is $\leq 5\%$ in the course of experiments at temperatures $\leq 75^\circ\text{C}$; at 83°C decomposition is more

pronounced at ca. 20% over 5 h. However, the *trans*-2/*cis*-2 ratio stays constant after reaching 2.0:1 even during decomposition. At 83°C it appears that one decomposition pathway is the formation of the dimer $[(\text{Cp})\text{CpTi}(\text{CH}_2)]_2$ as the solution turns purple and peaks appear at δ 6.01 (Cp), 7.59, and 7.58 (possibly $\mu\text{-CH}_2$ signals). CH_4 (δ 0.15) was also produced.

The entire procedure was repeated with the inclusion of 12 μL (2 equiv) of neohexene. The *trans*-2/*cis*-2 ratio was the same as before. Qualitatively, the addition of olefin did not greatly affect the rate of isomerization.

Kinetics of Equilibration of *trans*-2 and *cis*-2. A NMR tube was loaded with a 3.5:1 mixture of *trans*-2 and *cis*-2 (14 mg, 0.044 mmol) and 400 μL of C_6D_6 . The sample was placed in the probe of the JEOL FX-90Q maintained at 63.5°C , and spectra were recorded at regular intervals. The relative concentrations of *trans*-2 and *cis*-2 were determined from the integrals of their respective Cp resonances. The resonance due to residual protons of the solvent was used as an internal standard, and it was observed that ca. 8% decomposition of the metallacycles occurs over the experimental period. The combined constant $k_1 + k_{-1}$ was obtained from least-squares analysis of a plot³² of $\ln(X_e - X/X_e)$ vs t , where $X_e = (R_0 - R_e)/(R_e + 1)R_0A_0$ and $X = (R_0 - R_t)/(R_t + 1)R_0A_0$. R_0 is the initial *trans*-2/*cis*-2 ratio, R_e is the equilibrium ratio, R_t is the ratio at time t , and A_0 is the initial concentration of *trans*-2. A_0 does not have to be known explicitly. The individual rate constants k_1 and k_{-1} could then be determined by using the fact that $K = k_1/k_{-1}$. The procedure was repeated at several temperatures and the rate constants were determined. The errors in these constants, as estimated from their standard deviations determined in the least-squares analysis, are on the order of $\pm 5\%$. Activation parameters were obtained from least-squares analysis of $\ln(k/T)$ vs $1/T$ plots.³³

Measurement of the Kinetics of Reaction $\text{CpCpTiCH}_2\text{CH}(t\text{-Bu})\text{CH}_2$ with Diphenylacetylene.³⁴ A NMR tube was loaded with diphenylacetylene (0.33 mmol), metallacycle (0.044 mmol), and C_6D_6 (400 μL). The sample was placed in the probe of the JEOL FX-90Q, maintained at 55°C , and spectra were obtained at regular intervals. For the mixed-ring systems the mole fraction of each isomer of metallacyclobutane³⁵ was determined from the integral of its C_5H_2 signal and the total integral of all C_5H_2 signals. For $\text{Cp}'_2\text{TiCH}_2\text{CH}(t\text{-Bu})\text{CH}_2$ the upfield $\text{C}_5\text{H}_4\text{Me}$ signal and the $\alpha\text{-H}$ signal of the product were used to determine the mole fraction of **5**. With the phenyl region as an internal standard, minimal decomposition of materials occurred during kinetic runs. First-order plots of $\ln X$, where X is the mole fraction of metallacyclobutane, vs t were linear to 3 half-lives. k_{obsd} values were derived from least-squares analysis of these plots. The error in the k_{obsd} values as estimated from their standard deviations found in the least-square analysis was on the order of $\pm 5\%$. At the concentration of titanium species used (0.11 M), it had been determined from experiments with various concentrations of diphenylacetylene that initial concentrations ≥ 0.55 M diphenylacetylene were sufficient to reach saturation. For **2**, **3**, **4**, and **5**, this procedure was repeated at several temperatures. Activation parameters were obtained from least-squares analysis of $\ln(k/T)$ vs $1/T$ plots.

Reaction of **2 with Labeled Olefin.** A NMR tube was loaded with a 3.5:1 mixture of *trans*-2/*cis*-2 (14 mg, 0.044 mmol) and 400 μL of toluene. A solution of 25 mol % *cis*-1,2-dideuterio-3,3-dimethylbutene in toluene (40 μL , 0.986 mmol of olefin) was added via syringe. C_6D_6 (1 mg) was added as an internal deuterium standard. The mixture was heated to 68°C in the probe of the FX-90Q for 75 min, after which time ca. 20% of the labeled olefin had been incorporated into metallacycle as determined by integration of the vinyl deuterium signals of free olefin and the $\beta\text{-D}$ signal of metallacycle in the ^2H NMR spectrum (nondecoupled spectrum).

Reaction of **2 with Labeled Olefin in the Presence of Diphenylacetylene.** A NMR tube was loaded with a 3.5:1 mixture of *trans*-2/*cis*-2 (14 mg, 0.044 mmol), diphenylacetylene (61 mg, 0.34 mmol), and 400 μL of C_6D_6 . A solution of 25 mol % *cis*-1,2-dideuterio-3,3-dimethylbutene in toluene (200 μL , 0.44 mmol of olefin) was added via syringe. The sample was heated to 72°C for 75 min. The tube was placed in an Ar-flushed Schlenk tube, and the septum was pierced with a needle. The Schlenk tube was then evacuated and the volatiles in the NMR tube were removed. The residue in the NMR tube was redissolved in 400 μL of C_6D_6 , with 2 μL of toluene- d_8 added as a deuterium internal standard. The ^1H spectrum of the solution (run with no lock on the GX-400) showed ca. 60% conversion of the metallacyclobutenes **2** to the metallacyclobutene product. The ^2H NMR spectrum showed no deuterium incorporation into either the starting material or the product.

Equilibration of CpCpTiMeCl and CpCpTiMe_2 . A typical experiment involved loading 10 mg of CpCpTiMeCl in an NMR tube in the drybox and dissolving it in 0.4 mL of C_6D_6 . One half of an equivalent of neat AlMe_3 (usually approximately 2 μL) was syringed in and the NMR tube shaken. The equilibria are established immediately. The product and

(33) Since the initial ratio of *trans*-2 to *cis*-3 is very close to its equilibrium value, the accuracy of the rate constants is questionable. The data are presented to indicate the order of magnitude of the rate of equilibration. In light of the kinetic results for the trapping reactions of **2**, the measured activation parameters do not seem unreasonable.

(34) The reaction of these metallacyclobutenes with diphenylacetylene cleanly produces their corresponding metalocyclobutenes having spectral properties identical with those of independently synthesized samples prepared from the ring-substituted Tebbe analogues. No intermediates were observed during the course of the reactions.

(35) Since the *trans* and *cis* isomers of the mixed ring complexes **12** and **13** could not be separated, kinetics data were obtained from samples containing both isomers. For **2** samples with *trans*/*cis* starting ratios of 3.5:1 and 2.2:1 were used and gave identical results.

(36) These metallacycles react with acetone in a Wittig manner, producing isobutene via methylene transfer. No intermediates are observed with ^1H NMR spectroscopy. An oxo polymer is the other product of the reaction; broad resonances in the region δ 6.8–5.2 (Cp ring protons) and also δ 2.5–2.0 (Cp ring methyl groups).

reactant ratios were determined by ^1H NMR integration. The K_{eq} was calculated. Another 1 or 2 μL of neat AlMe_3 was added, and the product ratios and K_{eq} were determined again. The value reported is an average of the two experimental equilibrium constants. The two values were always within 20% of one another.

Preparation of $\text{Cp}'_2\text{TiCH}_2\text{CMe}_2\text{CH}_2$ (7). This compound was prepared as for 6.⁸ Isobutylene (ca. 5 mL) was condensed at -70°C into a flask containing $\text{Cp}'_2\text{TiCH}_2\text{AlMe}_2\text{Cl}$ (2.99 g, 9.6 mmol) and (dimethylamino)pyridine (1.17 g, 9.6 mmol). The resulting paste was dissolved in 15 mL of CH_2Cl_2 . The resulting red solution was warmed to -20°C and added dropwise via cannulas to 100 mL of rapidly stirred pentane cooled to -40°C . An orange solid precipitates out and the mixture is filtered (Schlenk filtration) to yield a red filtrate. The volatiles were removed in vacuo at low temperature ($\leq -10^\circ\text{C}$) and a red residue was left. This residue was dissolved in a minimum of diethyl ether at 0°C , and the resulting red solution was slowly cooled to -50°C , yielding 7 as a red powder (yield 0.67 g, 25%). The product is temperature sensitive and must be stored cold (-40°C) under an inert atmosphere. ^1H NMR (C_6D_6): δ 5.59 (m, 4 H, $\text{C}_5\text{H}_4\text{Me}$), 5.27 (m, 4 H, $\text{C}_5\text{H}_4\text{Me}$), 2.36 (s, 4 H, $\text{TiCH}_2\text{CMe}_2\text{CH}_2$), 1.79 (s, 6 H, $\text{C}_5\text{H}_4\text{Me}$), 1.14 (s, 6 H, $\text{TiCH}_2\text{CMe}_2\text{CH}_2$). $^{13}\text{C}\{^1\text{H}\}$ (C_6D_6): δ 120.7, 112.7, 110.3 ($\text{C}_5\text{H}_4\text{Me}$), 8.31 ($\text{TiCH}_2\text{CMe}_2\text{CH}_2$), 38.0 (TiCH_2), 15.5 ($\text{C}_5\text{H}_4\text{Me}$), 8.8 ($\text{TiCH}_2\text{CMe}_2\text{CH}_2$).

Preparation of $\text{Cp}'\text{CpTiCH}_2\text{C(Ph)C(Ph)}$ (9). A solution of diphenylacetylene (120 mg, 0.69 mmol) in 3 mL of THF at 0°C was added to an Ar-flushed flask containing $\text{Cp}'\text{CpTiCH}_2\text{AlMe}_2\text{Cl}$ (205 mg, 0.69 mmol). The resulting red solution was stirred at 0°C for 0.5 h, gradually becoming deep purple. The reaction mixture was warmed to room temperature and stirred for an additional 15 min. The volatiles were removed in vacuo, leaving a dark purple residue, which was left under dynamic vacuum overnight. The residue was dissolved in 1 mL of toluene and 1 mL of pentane and cooled to -50°C . Dark purple crystals of product were collected (yield 127 mg, 48%). A sample for C,H analysis was obtained by recrystallization from diethyl ether; this sample contained 11% $\text{Cp}'_2\text{TiCH}_2\text{C(Ph)C(Ph)}$ (by ^1H NMR). Anal. Calcd for 89% $\text{C}_{26}\text{H}_{22}\text{Ti}$ and 11% $\text{C}_{25}\text{H}_{22}\text{Ti}$: C, 81.22; H, 6.26. Found: C, 80.93; H, 6.23. ^1H NMR (C_6D_6): δ 7.67–7.24 (m, Ph), 5.72 (s, Cp); 5.56, 5.23 (2 m, $\text{C}_5\text{H}_4\text{Me}$); 3.29, 3.21 (2 d, $J = 17.6$ Hz (α -H)); 1.79 (s, $\text{C}_5\text{H}_4\text{Me}$). $^{13}\text{C}\{^1\text{H}\}$ (C_6D_6): δ 209.1 (α - C_{sp^2}); 147.4, 131.9, 129.6, 128.6, 128.5, 126.2, 126.1, 124.5 (Ph); 125.6, 115.3, 113.7, 110.2, 107.8 ($\text{C}_5\text{H}_2\text{Me}_3$); 111.8 (Cp); 103.5 (β -C); 72.3 (α - C_{sp^3}); 15.7 ($\text{C}_5\text{H}_4\text{Me}$).

Preparation of $\text{Cp}'_2\text{TiCH}_2\text{C(Ph)C(Ph)}$. This compound was prepared as for 9. The yield of dark purple crystalline material was 47%. An analytical sample was obtained from recrystallization from diethyl ether. Anal. Calcd for $\text{C}_{27}\text{H}_{26}\text{Ti}$: C, 81.40; H, 6.58. Found: C, 81.42; H, 6.50. ^1H NMR (C_6D_6): δ 7.49–6.75 (m, Ph); 5.71, 5.52, 5.27 (3 m ratio 2:1:1, $\text{C}_5\text{H}_4\text{Me}$); 3.12 (s, α -H); 1.80 (s, $\text{C}_5\text{H}_4\text{Me}$). ^{13}C (C_6D_6):³⁵ δ 207.9 (s, α -C); 147.2 (s), 138.7 (s), 129.6 (d), 128.4 (d), 126.3 (d), 126.2 (d) (Ph); 125.2 (s), 114.8 (d), 112.8 (d), 110.2 (d), 107.4 (d), ($\text{C}_5\text{H}_4\text{Me}$); 105.6 (s, β -C); 71.1 (t, α -C), 15.8 (q, $\text{C}_5\text{H}_4\text{Me}$).

Preparation of $(\text{Cp})\text{CpTiCH}_2\text{C(Ph)C(Ph)}$. This compound was prepared as for 9. It could only be obtained as an impure oil. ^1H NMR (C_6D_6): δ 7.7–6.7 (m, Ph); 5.78 (s, Cp); 5.53, 5.03 (2 d, $J = 2.4$ Hz, $\text{C}_5\text{H}_2\text{Me}_3$); 3.21, 2.86 (2 d, $J = 11.7$ Hz, α -H); 1.68, 1.67, 1.62 (3 s, $\text{C}_5\text{H}_2\text{Me}_3$). $^{13}\text{C}\{^1\text{H}\}$ (C_6D_6): δ 208.1 (α - C_{sp^2}); 147.2, 139.2, 131.9, 129.7, 126.5, 126.1, 124.4, 123.7 (Ph); 122.4, 119.5, 115.7, 115.2, 112.2

($\text{C}_5\text{H}_2\text{Me}_3$); 111.9 (Cp); 106.0 (β -C); 71.0 (α - C_{sp^3}); 16.1, 14.1, 13.7 ($\text{C}_5\text{H}_2\text{Me}_3$).

Measurement of the Kinetics of Reaction of $\text{CpCpTiCH}_2\text{CH}(\text{t-Bu})\text{CH}_2$ Metallacycles with Acetone.³⁶ The desired metallacycle (0.064 mmol) was loaded into a NMR tube and dissolved in 400 μL of C_6D_6 . Acetone (15 μL , 0.19 mmol) was added to the tube via syringe. The tube was heated to 55°C in an oil bath. It was periodically removed and the sample rapidly frozen with liquid nitrogen; the sample was then warmed to room temperature, a temperature where the reaction is not rapid, and examined by ^1H NMR spectroscopy. The sample was then returned to the oil bath. The ratio of the initial concentration of metallacycle, $[\text{M}]_0$, to the concentration of metallacycle at time t , $[\text{M}]_t$, was measured from the integral of the C_5H_5 signal ($\text{C}_5\text{H}_4\text{Me}$ signal for 5), using the signal due to residual protons of the solvent as an internal standard. The rate constants were determined from the relationship $k = (1/t) \ln ([\text{M}]_0/[\text{M}]_t)$ as an average of several measurements at different times. The estimated error of these values as estimated from the range of the values averaged is on the order of $\pm 10\%$.

Measurement of the Kinetics of Reaction of $\text{Cp}_2\text{TiCH}_2\text{CMe}_2\text{CH}_2$ (6) and $\text{Cp}'_2\text{TiCH}_2\text{CMe}_2\text{CH}_2$ (7) with Acetone.³⁶ Metallacycles 6 (9 mg, 0.036 mmol) and 7 (10 mg, 0.026 mmol) were loaded into a NMR tube and dissolved in 400 μL of toluene- d_8 . The tube was placed in the probe of the FX-90Q maintained at 10°C . Acetone (20 μL , 0.44 mmol) was added via syringe, and NMR spectra were obtained at regular intervals. The ratio of 7 to 6 rapidly grows larger than its initial value of 1:1 as 6 is consumed more rapidly than 7. The concentrations of the two metallacycles as a function of time were determined from the integrals of their α -H signals as well as their β -Me group signals. First-order plots for each metallacycle were linear. The rate constants were determined from a least-squares analysis of these plots. The errors of these constants as estimated from their standard deviations found in the least-squares analysis was on the order of $\pm 10\%$.

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Registry No. *cis*-1, 113110-35-3; *trans*-1, 113215-09-1; *cis*-2, 113110-37-5; *trans*-2, 113215-10-4; 3, 75687-68-2; 4, 113110-38-6; 5, 113110-36-4; 6, 80122-07-2; 7, 113110-39-7; 8, 113110-27-3; 9, 113110-40-0; $\text{Cp}'_2\text{TiCH}_2\text{C(Ph)C(Ph)}$, 113110-41-1; $(\text{Cp})\text{CpTiCH}_2\text{C(Ph)C(Ph)}$, 113110-42-2; $\text{Cp}'_2\text{TiCH}_2\text{AlMe}_2\text{Cl}$, 113110-33-1; $(\text{Cp})\text{CpTiCH}_2\text{AlMe}_2\text{Cl}$, 87739-01-3; $\text{Cp}^{\text{Cl}}_2\text{TiCH}_2\text{AlMe}_2\text{Cl}$, 113110-34-2; $\text{Cp}'\text{CpTiCH}_2\text{AlMe}_2\text{Cl}$, 87729-05-3; $\text{Cp}'_2\text{TiMeCl}$, 107547-98-8; $(\text{Cp})\text{CpTiMeCl}$, 113110-28-4; $\text{Cp}^*\text{CpTiMeCl}$, 113110-29-5; $\text{Cp}^*_2\text{TiMeCl}$, 107534-13-4; $\text{Cp}^{\text{Cl}}\text{CpTiMeCl}$, 113110-30-8; $\text{Cp}^{\text{Cl}}_2\text{TiMeCl}$, 113110-31-9; $(\text{Cp})_2\text{TiMeCl}$, 113132-21-1; $\text{Cp}^{\text{CF}_3}\text{CpTiMeCl}$, 113110-32-0; $\text{Cp}'\text{CpTiCl}_2$, 1282-43-5; $\text{Cp}'_2\text{TiCl}_2$, 1282-40-2; $(\text{Cp})\text{CpTiCl}_2$, 87738-99-6; $\text{Cp}^*\text{CpTiCl}_2$, 38496-87-6; $\text{Cp}^*_2\text{TiCl}_2$, 11136-36-0; $\text{Cp}^{\text{Cl}}\text{CpTiCl}_2$, 94890-69-4; $\text{Cp}^{\text{Cl}}_2\text{TiCl}_2$, 94890-70-7; $(\text{Cp})_2\text{TiCl}_2$, 113110-43-3; $\text{Cp}^{\text{CF}_3}\text{CpTiCl}_2$, 113110-44-4; $\text{Cp}^{\text{TMS}}\text{CpTiCl}_2$, 79269-70-8; Cp_2TiCl_2 , 1271-19-8; Cp_2TiMeCl , 1278-83-7; neohexane, 558-37-2; isobutylene, 115-11-7; diphenylacetylene, 501-65-5; acetone, 67-64-1; *cis*-1,2-dideuterio-3,3-dimethylbutene, 84784-40-7.