

Some Mechanistic and Synthetic Aspects of the Interaction
of Lewis Acids with Bis-Cyclopentadienyltitanium(IV)
Alkyls and Bis-Cyclopentadienyltitanacyclobutanes

Thesis by
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In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California

1982
(Submitted June 3, 1982)

ABSTRACT

Titanocene dichloride has been shown to react cleanly with two equivalents of AlMe_3 to produce the Lewis acid stabilized titanium methylene $\text{Cp}_2\overline{\text{TiCH}_2\text{AlMe}_2\text{Cl}}$ (1). Due to the interest in the utility of this complex in Wittig-type chemistry, in the metathesis of olefins, and in the synthesis of titanacyclobutanes, a study of the mechanism of formation of the complex was carried out. The proposed mechanism for formation of 1 involves an intramolecular proton abstraction by an Al-Me bond from a Ti-CH₃ group in the intermediate $\text{Cp}_2\text{TiMeCl} \cdot \text{AlMe}_3$. The effect of Cp-ring substitution and halide substitution on the reaction rate along with a deuterium isotope effect of 3 and a large negative entropy of activation were consonant with the proposed mechanism.

Specifically labelled titanacyclobutanes were prepared, and the cleavage reaction with AlMe_2Cl to yield 1 was studied. It was found that cleavage occurred with a secondary deuterium isotope of 1.2 to 1.6 (depending upon the titanacyclobutane) and exhibited bimolecular kinetics. Surprisingly, the stereochemistry of the titanacyclobutanes was completely scrambled before cleavage to 1 and olefin. A mechanism for this isomerization was proposed to involve a rapid and reversible transmetallation of a Ti-C bond with AlMe_2Cl , producing a 3-aluminapropyl-titanocene chloride. Following rapid inversion at the carbon adjacent to aluminum, the racemized 3-aluminapropyltitanocene chloride could cleave to 1 or close to yield isomerized titanacyclobutane.

The β, β -disubstituted titanacyclobutanes proved to be good sources of the Cp_2TiCH_2 unit, as indicated by their ready formation of bis- μ -CH₂-bis- Cp_2Ti (2). Some chemistry and photochemistry of 2 are reported.

The Cp_2TiCH_2 moiety is readily trapped with transition metal or main group metal Lewis acids such as Cp^*TiCl_3 or Me_3SnCl to produce compounds such as $[\text{Cp}_2\text{TiCl}] - \mu - \text{CH}_2 - [\text{Cp}^*\text{TiCl}_2]$ (3) and $\text{Cp}_2\text{Ti}(\text{CH}_2\text{SnMe}_3)\text{Cl}$. Cp_2TiCH_2 may also be trapped as the methylene phosphine adduct $\text{Cp}_2\text{Ti}(=\text{CH}_2)\text{PEt}_3$ (4).

The compounds 2 and 3 react with CO to yield insertion products which contain bridging ketene ligands which were characterized spectroscopically. Compound 4 also reacts with CO to produce the mononuclear ketene $\text{Cp}_2\text{Ti}(\eta^2\text{-CH}_2\text{CO})$ in low yield.

Throughout this Thesis,
Cp and Cp* designate the ligands
 $\eta^5\text{-C}_5\text{H}_5$ and $\eta^5\text{-C}_5\text{Me}_5$, respectively.

ACKNOWLEDGMENTS

I would like to thank Bob Grubbs for providing the opportunity to come to Caltech and do a little organometallic chemistry. I also thank all of the friendly people at Caltech, past and present, who made the transition to Caltech so simple. I owe special thanks to Steve Buchwald who spent many long hours helping to put this thesis into recognizable English, and to Henriette Wymar for her excellent typing. I would also like to thank my parents for their faith and support. And lastly, to Rosalie, who provided the light at the end of the tunnel.

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CHAPTER 1

An Investigation of the Reaction of Bis-Cyclopentadienyltitanium Dichloride with Trimethylaluminum.
Mechanism of an α -Hydrogen Abstraction Reaction.

INTRODUCTION

Since Ziegler's discovery^{1, 2} that ethylene could be polymerized at low temperature and pressure to a high molecular weight polymer using a catalyst formed from the reaction of an early transition metal halide such as TiCl_4 and aluminum alkyls, there has been a keen interest in the nature of the interaction of the aluminum alkyls with the transition metal center and its ligands. The insolubility of catalysts derived from TiCl_4 has made mechanistic studies difficult, and has led to a large effort to synthesize soluble polymerization catalysts.³

One such soluble catalyst for the polymerization of ethylene is the system $\text{Cp}_2\text{TiCl}_2/\text{AlR}_{3-n}\text{X}_n$ ($n = 0, 1, 2$; $\text{R} = \text{alkyl}$, $\text{X} = \text{halide}$).⁴ This catalyst system has become the best characterized (in terms of the kinetics of polymerization and subsequent side reactions)^{3a} of those studied.

In the mid-1960's several groups studied the reaction of Cp_2TiCl_2 with AlMe_3 and noticed that methane was evolved and that the organometallic product contained $\text{Ti-CH}_2\text{-Al}$ units.⁵

Schrock's isolation of tantalum alkylidene compounds⁶ and the possible role of such early transition metal alkylidenes in the catalysis of the olefin metathesis reaction stimulated Tebbe to reinvestigate the $\text{Cp}_2\text{TiCl}_2/\text{AlMe}_3$ system. This led to Tebbe's isolation and characterization of the Lewis acid-stabilized titanium methylene, $\text{Cp}_2\text{Ti}\overline{\text{CH}_2\text{AlMe}_2\text{Cl}}$, and other derivatives.⁷

Tebbe's methylene compound demonstrated olefin metathesis activity, and reacted with internal acetylenes to produce the titanacyclo-

butenes $\text{Cp}_2\overline{\text{TiCRCR}'\text{CH}_2}$.⁸ Tebbe also demonstrated that $\underline{7}$ was very reactive with organic carbonyl compounds, transferring a methylene unit to ketones⁷ and esters to produce olefins and vinyl ethers, respectively. Tebbe also showed that $\underline{7}$ reacted with propylene to form isobutylene. As part of a reinvestigation of this methanation reaction with unsymmetrical (mixed-ring) analogues of $\underline{7}$,¹² it was discovered that $\underline{7}$ reacted with mono-substituted olefins under certain conditions to cleanly produce titanacyclobutanes.^{10a} These titanacyclobutanes derived from $\underline{7}$ have been the center of intense investigation in Grubbs' laboratory with respect to their properties as well defined olefin metathesis catalysts^{10b} and their utilization in organic synthesis.^{9,11} The synthesis of $\underline{7}$ in large quantities for this research provided impetus for the work described herein.

This chapter details an investigation into the mechanism of formation of $\underline{7}$. This study was initiated to provide information regarding the interaction of aluminum alkyls with a transition metal center and its ligands and lend insight into the apparent α -H abstraction involved in formation of $\underline{7}$ from Cp_2TiCl_2 and AlMe_3 . Such mechanistic information would prove valuable in extending the synthesis to the formation of higher alkylidene units.

RESULTS

Preparation of the "Mixed-Ring" Titanocenedichlorides

The "mixed-ring" titanocenedichlorides (i. e., those compounds having one substituted and one non-substituted cyclopentadienyl ligand) were prepared by reaction of CpTiCl_3 with the lithium salt of a substituted cyclopentadienide. The mixed-ring compounds prepared were $\text{Cp}'\text{CpTiCl}_2$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{Me}$) 1, $(\text{Cp}^{\text{tms}})\text{CpTiCl}_2$ ($\text{Cp}^{\text{tms}} = \text{C}_5\text{H}_4\text{SiMe}_3$) 2, IndCpTiCl_2 (Ind = indenyl) 3, $\langle\text{Cp}\rangle\text{CpTiCl}_2$ ($\langle\text{Cp}\rangle = 1, 2, 4$ -trimethylcyclopentadienyl) 4, $[\text{Cp}]\text{CpTiCl}_2$ ($[\text{Cp}] = 1, 3$ -diphenylcyclopentadienyl) 5, and $\text{Cp}^*\text{CpTiCl}_2$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) 6. The latter compound was prepared by reaction of Cp^*TiCl_3 with CpLi . An attempt was made to prepare (1, 2, 4-triphenylcyclopentadienyl) CpTiCl_2 . This compound proved unstable to hydrolysis during work-up and could not be isolated in pure form.

In many of these preparations, not only was the anticipated mixed-ring compound observed, but also Cp_2TiCl_2 and often $\overline{\text{Cp}}_2\text{TiCl}_2$ ($\overline{\text{Cp}} =$ substituted Cp). For example, the preparation of $\text{Cp}'\text{CpTiCl}_2$ often resulted in a statistical mixture of Cp_2TiCl_2 , $\text{Cp}'\text{CpTiCl}_2$, and $\text{Cp}'_2\text{TiCl}_2$. This problem was partially circumvented by slow addition of an ether slurry of $\text{Cp}'\text{Li}$ to a cold ether solution of CpTiCl_3 . At best, the crude reaction mixtures contained at least 10% Cp_2TiCl_2 [commercial $(\text{MeC}_5\text{H}_5)_2$ contains approximately 4% $(\text{C}_5\text{H}_6)_2$]³⁹ which could be fractionally crystallized from $\text{Cp}'\text{CpTiCl}_2$. Typically, the synthesis of other mixed-ring compounds resulted in formation of less than 10% Cp_2TiCl_2 . In one preparation of $\text{Cp}^*\text{CpTiCl}_2$ from Cp^*TiCl_3 and CpLi , the ratio of $\text{Cp}^*\text{CpTiCl}_2$ to $\text{Cp}_2^*\text{TiCl}_2$ was approximately 2:1.

Fractional crystallization provided pure Cp* CpTiCl₂. ¹H NMR spectral data for these mixed-ring compounds are listed in Table 1.

Preparation of the Mixed-Ring Methylenes.

Reaction of toluene solutions of the mixed-ring titanocene dichlorides with more than two equivalents of AlMe₃ resulted in the formation of analogues of 7 (eq. 1). The reactions proceeded in poor to moderate



($\overline{\text{Cp}}$ = a substituted cyclopentadienyl)

yields for the mixed-ring compounds with the exception of IndCpTiCl₂. ¹H NMR spectroscopy of the reaction of IndCpTiCl₂ with AlMe₃ indicated extensive decomposition had occurred, although there were resonances in the δ 7-8 region, indicative of formation of Ti-CH₂-Al species. With the exception of Cp' Cp $\overline{\text{TiCH}_2\text{AlMe}_2\text{Cl}}$ 8 and [Cp] Cp $\overline{\text{TiCH}_2\text{AlMe}_2\text{Cl}}$ 11, the titanium methylene compounds were oils which crystallized only slowly, if at all. If allowed to stand undisturbed in a drybox, both $\langle \text{Cp} \rangle \text{Cp} \overline{\text{TiCH}_2\text{AlMe}_2\text{Cl}}$ 10 and Cp* Cp $\overline{\text{TiCH}_2\text{AlMe}_2\text{Cl}}$ ¹² 12 crystallized over a period of several weeks. ¹H NMR spectral data are listed in Table 2.

Reaction of Cp₂TiCl₂, Cp₂TiMeCl, and Cp₂TiMe₂ with AlMe₃ and AlMe₂Cl.

Reactions were followed by ¹H NMR spectroscopy. Due to their lability, the aluminum alkyl adducts of the titanium species could not be isolated. ¹H NMR data for the reaction products described below appear in Table 3.

One equivalent of AlMe₃ reacts rapidly with Cp₂TiCl₂ to form Cp₂TiMeCl · AlMe_{3-n}Cl_n as was indicated by the appearance of a new

TABLE 1.

 ^1H NMR Spectral Data for Mixed-Ring Titanocenedichlorides

Compound	Solvent	Chemical Shift (δ)*		
$\text{Cp}'\text{CpTiCl}_2$ (1)	CDCl_3	6.54	s	(C_5H_5)
		6.33	m	($\text{C}_5\text{H}_4\text{Me}$)
		2.33	s	($\text{C}_5\text{H}_4\text{Me}$)
$\text{Cp}^{\text{tms}}\text{CpTiCl}_2$ (2)	CDCl_3	6.54	s	(C_5H_5)
		6.78	J = 2Hz	($\text{C}_5\text{H}_4\text{TMS}$)
		6.57		
		0.32	s	($\text{C}_5\text{H}_4\text{TMS}$)
IndCpTiCl_2 (3)	CDCl_3	6.21	s	(C_5H_5)
		7.36-7.68	m	(C_6 ring, Ind)
		6.67	d J = 3.5	(C_5 ring, Ind)
		6.88	t "	
$\langle\text{Cp}\rangle\text{CpTiCl}_2$ (4)	CDCl_3	6.43	s	(C_5H_5)
		6.26	s	($\text{C}_5\text{H}_2\text{Me}_2\text{Me}$)
		2.12	s	($\text{C}_5\text{H}_2\text{Me}_2\text{Me}$)
		2.07	s	($\text{C}_5\text{H}_2\text{Me}_2\text{Me}$)
$[\text{Cp}]\text{CpTiCl}_2$ (5)	CDCl_3	6.33	s	(C_5H_5)
		7.40-7.71	m	($\text{C}_5\text{H}_3\text{Ph}_2$)
		6.96	d J = 1Hz	($\text{C}_5\text{H}_2\text{HPh}_2$)
$\text{Cp}^*\text{CpTiCl}_2$ (6)	CDCl_3	6.25	s	(C_5H_5)
		2.04	s	(C_5Me_5)

*Chemical shifts relative to residual protio-solvent resonances.

 CHCl_3 at $\delta 7.24$, CH_2Cl_2 at $\delta 5.32$.

TABLE 2.

NMR Spectral Data for Titanocene-Methylene Compounds in C_6D_6 .

Compound	Chemical Shift (δ)*		
$Cp_2\overline{TiCH_2AlMe_2Cl}$ (7)	1H : 8.28	s	(CH ₂)
	5.67	s	(C ₅ H ₅)
	-0.28	br. s	(AlMe ₂)
	^{13}C : 188		(CH ₂)
	114		(C ₅ H ₅)
$Cp' Cp\overline{TiCH_2AlMe_2Cl}$ (8)	1H : 8.12	ABq J = 6.9Hz	(CH ₂)
	5.78, 5.39	m	(C ₅ H ₄ Me)
	5.66	s	(C ₅ H ₅)
	1.66	s	(C ₅ H ₄ Me)
	-0.32, -0.36	2s, br	(AlMe ₂)
$Cp^{tms}\overline{CpTiCH_2AlMe_2Cl}$ (9)	8.47, 8.24	2d, J = 6.5Hz	(CH ₂)
	6.17	m	(C ₅ H ₄ TMS)
	5.72	s	(C ₅ H ₅)
	0.01	s	(C ₅ H ₄ TMS)
	-0.28, -0.32	2s, br	(AlMe ₂)
$\langle Cp \rangle Cp\overline{TiCH_2AlMe_2Cl}$ (10)	1H : 7.99, 7.54	2d, J = 6.8Hz	(CH ₂)
	5.47, 5.13	2d, J = 0.6Hz	(1, 2, 4-C ₅ H ₂ Me ₃)
	5.72	s	(C ₅ H ₅)
	1.76, 1.63, 1.46	3s	(1, 2, 4-C ₅ H ₂ Me ₃)
	^{13}C : 180.6		(CH ₂)
	112.9		(C ₅ H ₅)
	16.3, 14.2		(C ₅ Me ₃ H ₂)

TABLE 2 (continued)

Compound	Chemical Shift (δ)*		
[Cp]CpTiCH ₂ AlMe ₂ Cl (11)	7.2-6.8	m	(1,3-C ₅ H ₃ Ph ₂)
	6.4-6.1	m	(1,3-C ₅ H ₃ Ph ₂)
	5.62	s	(C ₅ H ₅)
	8.23	ABq J = 0.5Hz	(CH ₂)
	.27	s, br	(AlMe ₂)
Cp [*] CpTiCH ₂ AlMe ₂ Cl (12)	¹ H: 7.57, 6.94	2d, J = 7.3Hz	(CH ₂)
	5.66	s	(C ₅ H ₅)
	1.59	s	(C ₅ Me ₅)
	-0.19, -0.36	2s, br.	(AlMe ₂)
	¹³ C: 173.9	(J = 125Hz)	(CH ₂)
	113.6		(C ₅ H ₅)
	121.8		(C ₅ Me ₅)
	12.6		(C ₅ Me ₅)

*Shifts relative to C₆D₅H at δ 7.15. ¹³C shifts relative to C₆D₆ at δ 128.0

TABLE 3

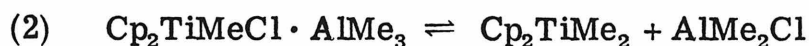
¹H NMR Spectral Parameters for Methyltitanium and Aluminum Mixtures

	Cp Resonance (δ)	Ti-Me Resonance (δ)*
Cp ₂ TiMeCl	5.81	0.82
Cp ₂ TiMe ₂	5.67	0.06
Cp ₂ TiCl ₂ + 1AlMe ₃	5.79	0.94
Cp ₂ TiMeCl + AlMe ₂ Cl	5.79	0.94
Cp ₂ TiMeCl + 2AlMe ₃	5.73	0.90
Cp ₂ TiCl ₂ + 2AlMe ₃	5.79	0.92

*Spectra recorded in C₆D₆; referenced to C₆D₅H, δ 7.15.

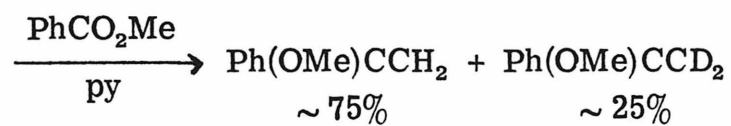
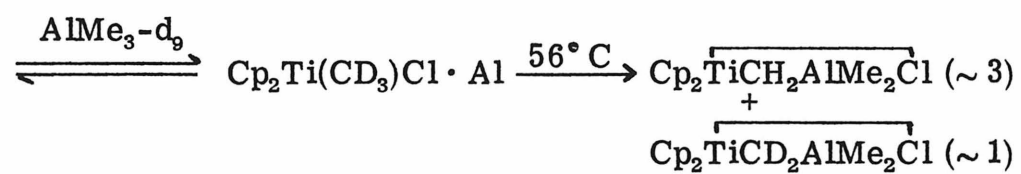
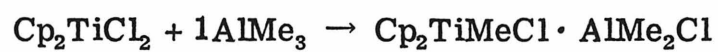
Cp resonance at δ 5.79 (10H) and a methyl resonance at δ 0.94 (3H). An identical spectrum was obtained when one equivalent of AlMe_2Cl was allowed to react with Cp_2TiMeCl . Heating these solutions to 56°C for 19h resulted in the formation of a 30% yield of a 6:1 mixture of $\text{Cp}_2\text{TiCH}_2\text{AlMeClCl}$ and $\underline{7}$. Further heating resulted in formation of a homogeneous blue-green solution which exhibited a broad ^1H NMR spectrum.

Reaction of 1.21 equivalents AlMe_3 with Cp_2TiMeCl resulted in formation of a mixture of 78% $\text{CpTiMeCl} \cdot \text{AlMe}_{3-n}\text{Cl}_n$ ($\cdot \text{Al}$ designates $\text{AlMe}_{3-n}\text{Cl}_n$) and 22% CpTiMe_2 . Similarly, when 1.19 equivalents of AlMe_2Cl was allowed to react with Cp_2TiMe_2 , a mixture of 87% $\text{Cp}_2\text{TiMeCl} \cdot \text{Al}$ and 13% Cp_2TiMe_2 was observed, the ratio $[\text{Cp}_2\text{TiMe}_2][\text{AlMe}_2\text{Cl}] / [\text{Cp}_2\text{TiMeCl}][\text{AlMe}_3]$ was 0.06 for both solutions.³⁷ When these solutions were heated to 65°C for 6h, an 80% yield of $\underline{7}$ was formed by way of eq. 2 and 3.



Reaction of Cp_2TiCl_2 with greater than two equivalents of AlMe_3 resulted in formation of $\text{Cp}_2\text{TiMeCl} \cdot \text{Al}$. Heating these solutions to 65° resulted in the formation of $\underline{7}$ according to eq. 1 at the same rate at which the reaction of Cp_2TiMe_2 with AlMe_2Cl proceeds.

Scheme 1



The reaction of Cp_2TiCl_2 with one equivalent AlMe_3 followed by one equivalent of $\text{AlMe}_3\text{-d}_9$ gave rise to a ^1H NMR spectrum which indicated that $\text{Cp}_2\text{Ti}(\text{CH}_3)\text{Cl} \cdot \text{Al}$ and $\text{Cp}_2\text{Ti}(\text{CD}_3)\text{Cl} \cdot \text{Al}$ were present in a 1:1 ratio (Scheme 1). This solution was heated to 56°C and the extent of reaction was monitored by ^1H NMR spectroscopy. As the reaction progressed $\underline{7}$ was preferentially formed relative to $\underline{7\text{-d}_2}$ in a ratio of 2.9:1. The sample was quenched with methylbenzoate and pyridine⁹ producing 1-methoxy-1-phenylethylene- d_0 and -d_2 in a ratio of $2.9 \pm 0.1 : 1$, indicating the reaction proceeds with a moderate primary deuterium isotope effect. Close examination of the vinylic AB quartet indicated that no 1-OMe-1-Ph=CHD is formed and demonstrated that only $\text{Ti-CH}_2(\text{CD}_2)\text{-Al}$ groups and no Ti-CHD-Al groups were present upon reaction with methylbenzoate in the presence of pyridine.

Examination of the Kinetics of Titanium-Methylene Formation.

Kinetics data for the reaction of Cp_2TiCl_2 with greater than 2 equivalents of AlMe_3 in C_6D_6 at 53°C were obtained using varying concentrations of Cp_2TiCl_2 and AlMe_3 . The reaction exhibited second-order kinetics and fit the rate law (eq. 4):

$$(4) \quad -d[\text{Cp}_2\text{TiMeCl} \cdot \text{Al}] / dt = k_{\text{obs}} [\text{AlMe}_3] [\text{Cp}_2\text{TiMeCl} \cdot \text{Al}].$$

Second-order plots were linear over more than two half-lives.¹³

Selected kinetics data are listed in Table 4.

An increase of 40-50% in k_{obs} was observed when CD_2Cl_2 was employed as solvent.

Activation parameters were derived from kinetics data obtained at 38, 57, and 72°C and are listed in Table 5.

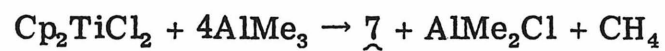
TABLE 4

Kinetics Data for the Reaction $\text{Cp}_2\text{TiCl}_2 + 4\text{AlMe}_3 \xrightarrow{53^\circ\text{C}} \text{7} + \text{AlMe}_2\text{Cl} + \text{CH}_4$

$[\text{TiMeCl}\cdot\text{Al}]_{t=0}$	$[\text{AlMe}_3]_{t=0}$	$k_{\text{obs}} \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$
0.2 M	1.4 M	1.6 ± 0.5 Solvent: C_6D_6
0.1	0.7	1.8 "
0.2	0.7	2.3 ± 0.3 "
0.2	0.6	3.4 Solvent: CD_2Cl_2

TABLE 5

Activation Parameters for the Reaction



T °C	k _{obs}
38	7.7×10^{-5}
57	3.3×10^{-4}
72	1.1×10^{-3}

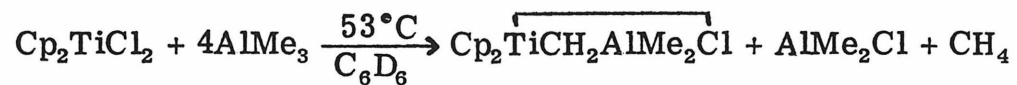
$$\Delta H^\ddagger = 16 \pm 0.2 \text{ kcal}\cdot\text{mol}^{-1}, \Delta S^\ddagger = -26 \pm 1 \text{ e.u.}$$

$$\Delta G_{330}^\ddagger = 25 \pm 1 \text{ kcal}\cdot\text{mol}^{-1}$$

Kinetics data were also obtained for certain mixed-ring compounds¹⁴ and are listed in Table 6. The data for Cp_2TiCl_2 , $\text{Cp}'_2\text{TiCl}_2$, and Cp_2TiBr_2 are included for comparison. An attempt was made to examine the reaction of Cp_2TiF_2 with greater than two equivalents of AlMe_3 , however, this reaction proceeds rapidly to produce Cp_2TiMe_2 which is then converted to at least 40% $\text{Cp}_2\text{TiCH}_2\text{AlMe}_2\text{F}$ in 1h at 65°C . Further heating converts this material into $\text{Cp}_2\text{TiCH}_2\text{AlFMeF}$ and other unidentified products. Monitoring of the reaction by ^1H NMR spectroscopy proved unsuitable for kinetics analysis, as the C_5H_5 resonance corresponding to the product(s) were fairly broad and overlapped the C_5H_5 resonance of Cp_2TiMe_2 .

TABLE 6

Observed Rates of the Reaction

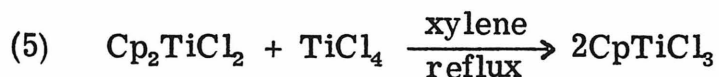


Compound	$k_{\text{obs}} \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$
Cp_2TiCl_2	23
$\text{Cp}^{\text{tms}}\text{CpTiCl}_2$	8
$\text{Cp}'_2\text{TiCl}_2$	7
$[\text{Cp}]\text{CpTiCl}_2$	12
$\langle\text{Cp}\rangle\text{CpTiCl}_2$	3
$\text{Cp}^*\text{CpTiCl}_2$	1
Cp_2TiBr_2	17 (measured at 57.5° C)

DISCUSSION

Synthesis of the Titanocenedichlorides.

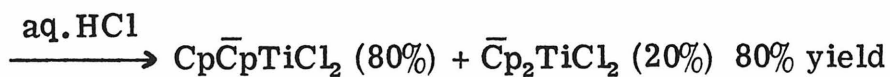
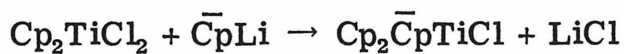
As mentioned above, synthesis of mixed-ring titanocene dichlorides often resulted in production of Cp_2TiCl_2 and $\bar{\text{Cp}}_2\text{TiCl}_2$ ($\bar{\text{Cp}}$ = substituted Cp) as significant by-products. Dormond *et al.*,¹⁵ reported that ring exchange occurs when Cp_2TiCl_2 is reacted with one or two equivalents of $\text{Li}\bar{\text{Cp}}$; hydrolysis of the reaction mixtures with aqueous HCl gave good yields of $\text{Cp}\bar{\text{Cp}}\text{TiCl}_2$ and $\bar{\text{Cp}}_2\text{TiCl}_2$, respectively. It was suggested that the sterically smaller and less electron-donating Cp ligand is selectively hydrolyzed from the metal center (Scheme 2). They do not mention the observation of any Cp_2TiCl_2 in the reaction mixture and Scheme 2 is unable to account for the formation of Cp_2TiCl_2 which was observed in the work reported here. An alternative explanation for the ring exchange via a bridging Cp intermediate is outlined in Scheme 3. Such a ring exchange may occur in the reaction of Cp_2TiCl_2 and TiCl_4 ¹⁶ (equation 5) but must have a higher activation energy than



for the reaction of CpTiCl_3 with $\bar{\text{Cp}}\text{Li}$ which undergoes apparent ring exchange at or below room temperature.⁴⁰ The possibility also exists that the ring exchange proceeds through a Cp bridging a titanium and a $\text{Li}\bar{\text{Cp}}$ as depicted in Scheme 4. The ability of lithium alkyls to form aggregates is well known.^{17a}

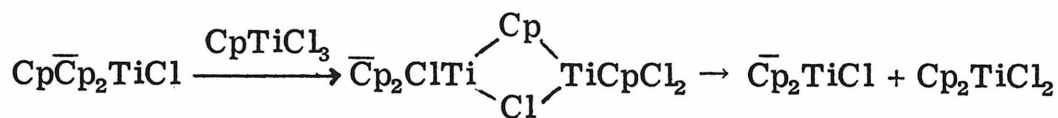
Tuli *et al.*,¹⁸ report that the reaction of CpTiCl_3 and $\text{Cp}'\text{Ti}$ proceeds to yield $\text{Cp}'\text{CpTiCl}_2$ in greater than 85% yield. Thallium

Scheme 2

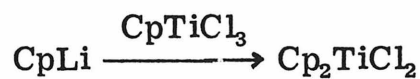
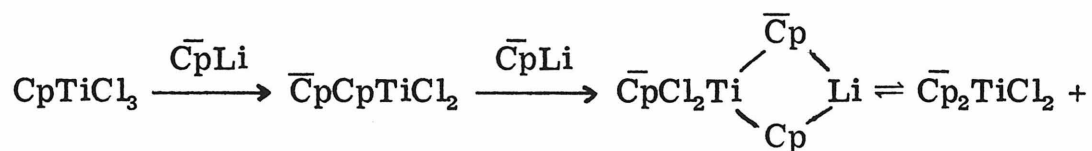


85% yield. Dormand, et al.

Scheme 3



Scheme 4



alkyls may be less prone to aggregation,^{17b} and therefore are less likely to undergo ring exchange similar to that proposed in Scheme 4. However, CpTi is also not as reactive as the lithium analogs, and may react more slowly with CpCpTiCl₂ to yield the species CpCpTiCl.

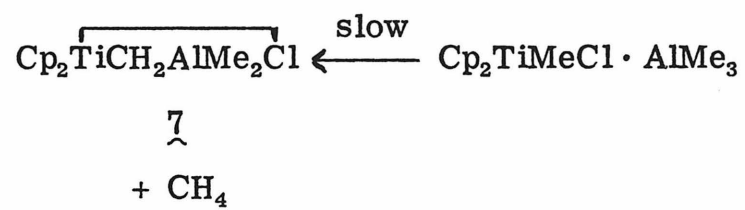
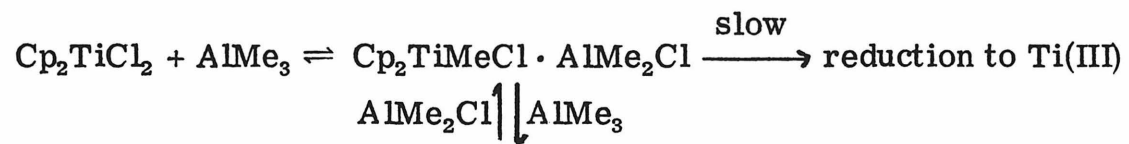
Reaction of Cp₂TiCl₂, Cp₂TiMeCl, and Cp₂TiMe₂ with Aluminum Alkyls.

Reaction of Cp₂TiCl₂ with one equivalent of AlMe₃ proceeds rapidly to yield a solution having the stoichiometry Cp₂TiMeCl · AlMe₂Cl. The aluminum is assumed to complex to the chlorine on titanium.¹⁹ This complexation is weak, as the aluminum may be removed to yield Cp₂TiMeCl by pumping on the solutions or by complexation with an ether.

Addition of one equivalent of AlMe₃ to "Cp₂TiMeCl · AlMe₂Cl" produces only slight changes in the ¹H NMR spectrum, and Cp₂TiCH₂AlMe₂Cl 7 is slowly formed along with methane and AlMe₂Cl.

The results of these reactions are summarized in Scheme 5, which indicates that one AlMe₃ methylates Cp₂TiCl₂. If no additional AlMe₃ is added to this mixture, only small amounts of titanium methylene compounds are slowly formed, and after long reaction times there is apparent formation of a Ti(III) species.²² When one additional equivalent of AlMe₃ is added, it is proposed that AlMe₃-AlMe₂Cl exchange occurs producing an equilibrium concentration of Cp₂TiMeCl · AlMe₃, which then in a slow step extrudes CH₄ forming 7, requiring the observed second-order kinetics. 7 is also produced from the reaction of either Cp₂TiMe₂ with AlMe₂Cl, or Cp₂TiMeCl with

Scheme 5



AlMe_3 . These two reactions proceed at the same rate as Cp_2TiCl_2 with 2AlMe_3 . This suggests that the necessary stoichiometry for formation of $\underline{7}$ is $\text{Cp}_2\text{TiMeCl} \cdot \text{AlMe}_3$, and that all of the above species are in equilibrium.

Throughout this chapter, the Ti-Al species have been described as 1:1 adducts, primarily for simplicity of presentation. It should be noted, however, that due to the tendency of aluminum methyl and chloroaluminummethyl compounds to form dimers, the formation of 1:2 Ti-Al adducts cannot be ruled out.

The observation of a deuterium isotope effect $k_{\text{H}}/k_{\text{D}} = 2.9$ and a large, negative activation entropy of approximately -26 e.u. are consistent with the cyclic transition state complexes depicted in Figure 1. Polarization of the Ti-Cl bond by aluminum as in the resonance structure \underline{B} would be expected to increase the basicity of the Al-CH₃ bonds, and concomitantly increase the acidity of the TiCH₃ α -hydrogens.⁴⁴ Extrusion of CH₄ would then lead to the observed product $\underline{7}$.

The 50% increase in k_{obs} when the solvent is changed from C_6D_6 to CD_2Cl_2 , a solvent of higher dielectric constant,²³ is also consistent with an increase in dipole moment in the transition state.

Based on "hard-soft" considerations,²⁴ an aluminum center should polarize a Ti-Br bond less than a Ti-Cl bond. If resonance structure \underline{B} in Figure 1 is important, then reaction of Cp_2TiBr_2 with two equivalents of AlMe_3 should proceed relatively slowly to $\text{Cp}_2\text{TiCH}_2\text{AlMe}_2\text{Br}$, and in fact, under identical conditions, Cp_2TiBr_2 is converted to $\text{Cp}_2\text{TiCH}_2\text{AlMe}_2\text{Br}$ at 35-40% of the rate at which $\underline{7}$ is formed. Due to experimental difficulties, the rate at which Cp_2TiF_2

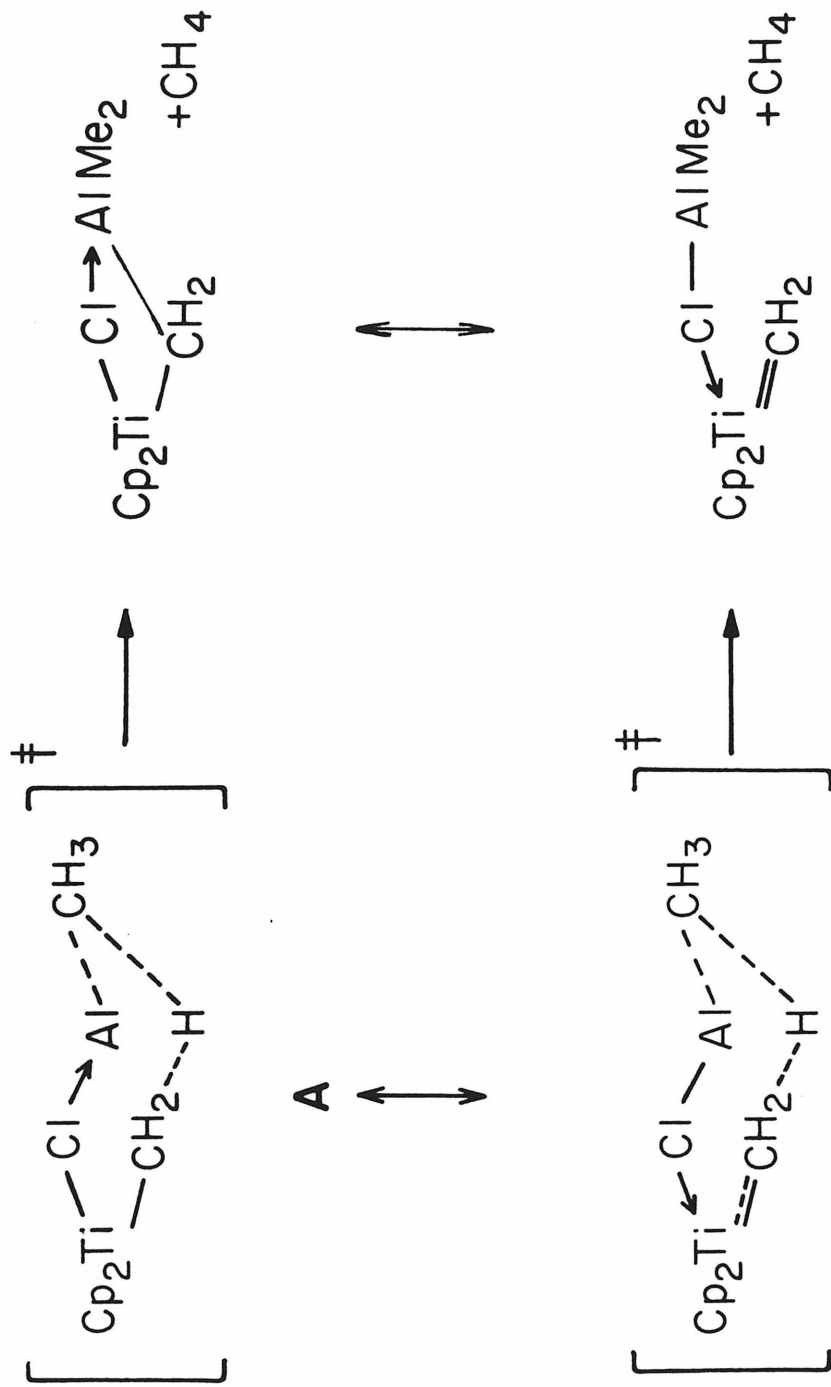
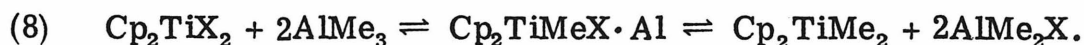


Fig. 1

reacts with AlMe_3 to produce the corresponding titanium methylene compound could not be determined accurately. That the aluminum halide bond polarization in these reactions is important is indicated by the very rapid formation of Cp_2TiMe_2 and AlMe_2F from the reaction of Cp_2TiF_2 with four equivalents of AlMe_3 . Apparently, the position of equilibrium of equation 8 lies in the center for $\text{X} = \text{Cl}, \text{Br}$ but far to the right for $\text{X} = \text{F}$. The subsequent reaction of Cp_2TiMe_2 with AlMe_2F



proceeds to a titanium methylene complex at at least the same rate as observed for the Cp_2TiCl_2 reaction.

In an attempt to investigate the effect of larger and more electron-donating or accepting ligands on the rate of the titanium methylene formation reaction, the mixed-ring compounds were synthesized and the kinetics of their reaction with AlMe_3 measured. These data are tabulated in Table 6 and appear in approximate order of increasing size of the substituted cyclopentadienyl ligand. With the exception of $[\text{Cp}]$, k_{obs} varies inversely with the steric bulk and also with the relative donor ability²⁵ of the substituted cyclopentadienyl ligand. $[\text{Cp}]$ can be considered to be a relatively electron-withdrawing ligand in comparison to the other ligands. Thus, there appear to be two trends demonstrated in the rate data for the mixed ring compounds. One is that a dramatic decrease in k_{obs} is seen with increasing steric bulk of the ligand, and the second being a decrease in k_{obs} with increasing donor strength of the ligand. A better donor ligand would tend to decrease the Lewis acidity of the titanium center in structure B

(Fig. 1) and concomitantly decrease the acidity of the Ti-Me hydrogens. One might speculate that IndCpTiCl_2 would react with excess AlMe_3 to generate the analogous titanium methylene at a rate approximately equal to that of Cp_2TiCl_2 . Unfortunately, IndCpTiCl_2 does not react cleanly with AlMe_3 . This is perhaps related to the relative ease with which the η^5 -indenyl ligand can "slip" to η^3 -indenyl.

In summary, it is proposed that the reaction of Cp_2TiCl_2 with two equivalents of AlMe_3 proceeds to an intermediate $\text{Cp}_2\text{TiMeCl} \cdot \text{Al}$ which goes on to produce $\underline{7}$ via an intramolecular attack of a strong base (Al-Me) on the activated α -hydrogen of the titanium methyl group. This mechanistic course is similar to that observed in the intermolecular proton abstraction from $\text{Cp}_2\text{TaMe}_2^+$ with a strong base to yield $\text{Cp}_2\text{TaCH}_2(\text{Me})$.²⁶ The latter proceeds with a deuterium isotope effect of 3, which is similar in magnitude to that reported here.

Other reactions which proceed via similar 6-center mechanisms are the "ene" reaction,⁴² and the protonolysis of trialkylborons with carboxylic acids.⁴³ Both of these reactions proceed with deuterium isotope effects of approximately 3. The "ene" reaction exhibits activation entropies of -30 to -40 e.u., similar to that reported here (-26 e.u.).

EXPERIMENTAL

General Considerations. All manipulations of air and/or moisture sensitive compounds were performed using glove box and standard high vacuum or Schlenk line techniques. Argon used in Schlenk work was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. Diethyl ether, C_6D_6 (Merck, Sharp and Dohme) C_6H_6 , toluene, tetrahydrofuran, and hexane were dried and deoxygenated by stirring over CaH_2 , degassed, and were vacuum transferred onto purple sodium-benzophenone ketyl. Solvents for Schlenk work were vacuum transferred from sodium-benzophenone ketyl solutions into dry vessels equipped with teflon needle valve closures and stored under Ar. CD_2Cl_2 was dried over CaH_2 and deoxygenated by several freeze-pump-thaw cycles. Solvents used for recrystallization of the titanocene dichlorides were used as received.

Trimethylaluminum (Alfa), dimethylaluminum chloride (Texas Alkyls), and $AlMe_3$ (2M in toluene, Aldrich) were used as received. Cp_2TiCl_2 (Strem or Boulder Scientific) was purified by Soxhlet extraction with dichloromethane. This material was then recrystallized from toluene for the kinetics studies. $TiCl_4$ (Alfa) was used as received. Methylcyclopentadiene and cyclopentadiene dimers, and indene were purchased from Aldrich. $AlMe_3-d_9$,²⁷ $Cp_2TiMeCl$,²⁸ Cp_2TiMe_2 ,²⁸ Cp_2TiBr_2 ,²⁹ HCp^{tms} ,³⁰ HCp^* ,³¹ $H(Cp)$,³² $H[Cp]$,³³ and 1,2,4-triphenylcyclopentadiene³⁴ were prepared by literature methods. Lithium-t-butoxide was prepared from the reaction of t-BuOH with n-BuLi followed by purification by sublimation.

Lithiumcyclopentadienides (except Li[Cp] and Li(1,2,4-triphenylcyclopentadienide)) were prepared by dissolving the cyclopentadiene in degassed n-hexane followed by slow addition of 1.1 equivalent of 1.6 M n-BuLi/hexane (Aldrich). Li[Cp] was prepared by reaction of a benzene solution of H[Cp] with 1.1 equivalents of n-BuLi/hexane. Li(1,2,4-triphenylcyclopentadienide) was prepared similarly using toluene as solvent. The lithium cyclopentadienide suspensions thus prepared were transferred under Ar onto a medium frit via cannula, washed repeatedly with n-hexane, and dried under high vacuum. CpTiCl₃¹⁶ and Cp*TiCl₃³⁵ were prepared by literature methods and purified by sublimation.

¹H NMR spectra were recorded using a Varian EM-390 or a JEOL FX-90Q. Probe temperatures were calculated by measuring $\Delta\nu_{\text{MeOH}}$.³⁶ Chemical shifts are with respect to residual protio-solvent resonances.

Preparation of Cp'CpTiCl₂ (1). Several syntheses of this compound appear in the literature.^{15,16b} Due to the irreproducibility of these preparations, the following preparation is included here.

A suspension of Cp'Li (0.86 g, 10 mmole) in ether (20 mL) was slowly added dropwise via cannula to a stirred solution of CpTiCl₃ (2.193 g, 10 mmole) in 30 mL ether at 0° C under Ar. The bright yellow solution slowly deposited a red microcrystalline powder. After the addition was complete, the mixture was allowed to warm to room temperature. Stirring was continued for 30 min before approximately half of the ether was removed in vacuo, and 10 mL of 9M aqueous HCl was added. The red solids were filtered and washed with 9M aqueous

HCl until the washings were colorless. The solids were washed several times with cold ether and dried to yield 2.1-2.4 g (80-90%) of a mixture of $\text{Cp}'\text{CpTiCl}_2$ which typically contained 10-20% of both Cp_2TiCl_2 and $\text{Cp}'_2\text{TiCl}_2$. Fractional crystallization of this mixture from hot toluene yielded 60-70% $\text{Cp}'\text{CpTiCl}_2$ as red needles which contained approximately 5-10% Cp_2TiCl_2 . Performing the reaction at room temperature or with a 50% excess of $\text{Cp}'\text{Li}$ results in near statistical mixtures of Cp_2TiCl_2 , $\text{Cp}'\text{CpTiCl}_2$, and $\text{Cp}'_2\text{TiCl}_2$.

^1H NMR, 1, CDCl_3 : δ 6.54, s (Cp), 6.73, m ($\text{C}_5\text{H}_4\text{Me}$), δ 2.33, s ($\text{C}_5\text{H}_4\text{Me}$).

Preparation of $\text{Cp}'_2\text{TiCl}_2$. A slurry of LiCp' (8.7 g, 101 mmole) in ether was slowly added to an ether solution of TiCl_4 (5.5 mL, 50 mmole) under Ar at 0°C. The solution was stirred for 30 min and worked up as for 2. The resulting solids were recrystallized from hot toluene to yield $\text{Cp}'_2\text{TiCl}_2$ (8.3 g, 60%). This material contained ca. 7% Cp_2TiCl_2 (and probably a larger amount of 1). A small amount of this material was recrystallized from toluene, and then chloroform to yield a material which contained no Cp_2TiCl_2 ; m.p. = 215-219° (decomp). Lit.³⁹ 217-218° C (decomp). This material probably contained a small amount of 1.

^1H NMR, $\text{Cp}'_2\text{TiCl}_2$, CDCl_3 : δ 6.30, m ($\text{C}_5\text{H}_4\text{Me}$), 2.27, s ($\text{C}_5\text{H}_4\text{Me}$).

Preparation of $\text{Cp}^{\text{tms}}\text{CpTiCl}_2$ (2). A solution of $\text{Cp}^{\text{tms}}\text{Li}$ (1.24 g, 8.6 mmole) in 10 mL THF was slowly added via cannula to a solution of CpTiCl_3 (1.89 g, 8.6 mmole) in 10 mL THF under an Ar atmosphere at room temperature. After the addition was complete, the red solution was stirred for 30 m. The solvent was removed in vacuo to leave a

pinkish-orange powder. The solids were scraped onto a frit, and washed with 6 M aqueous HCl until the washings were colorless. The solids were then washed with 2×5 mL of ethanol and 2×5 mL of ether. The red powder was recrystallized from hot CHCl₃/hexane to yield 2.1 g (76%) of deep red needles. No Cp₂TiCl₂ was observed by ¹H NMR.

¹H NMR, 2, CDCl₃: δ 6.54, s (Cp), 6.78, 6.57, 2t, J = 2 Hz (C₅H₄TMS), 0.32, s (C₅H₄TMS).

Preparation of IndCpTiCl₂ (3). This compound was prepared as for 2. Yields were typically in the range of 40-50% of a red-brown powder which contained ca. 15% Cp₂TiCl₂. This impurity could be removed almost completely (ca. 3% remained) by washing with ether.

¹H NMR, 3, CDCl₃: δ 6.21, s (Cp), 7.68-7.36, m (C₆ indenyl ring), 6.88, t, J = 3.5 Hz, 6.67, d, J = 3.5 Hz (C₅ indenyl ring).

Preparation of <Cp>CpTiCl₂ (4). This preparation is a modification of de Boer's method.¹² <Cp>Li (2.28 g, 20 mmole) and CpTiCl₃ (4.38 g, 20 mmole) were allowed to react under the same conditions described for 2 (<Cp>Li is insoluble in THF, however), and worked up as for 2. <Cp>CpTiCl₂ can be recrystallized from hot CHCl₃ or toluene to give scarlet plates. Yield: 2.72-3.25 g (48-56%). Typically, 5% or less of Cp₂TiCl₂ is observed in the crude reaction mixture under these conditions.

¹H NMR, 4, CDCl₃: δ 6.43, s (Cp), 6.26, s (C₅H₂Me₃), 2.12, s (C₅H₂MeMe₂), 2.07, s (C₅H₂MeMe₂).

Preparation of [Cp]CpTiCl₂ (5). A solution of [Cp]Li (0.61 g, 2.7 mmole) in 10 mL THF ([Cp]Li solutions appear to transmit red and fluoresce blue) was slowly added via cannula to a solution of

CpTiCl_3 (592 mg, 2.7 mmole) in 10 mL THF under Ar at room temperature. The purple-red solution was stirred for 30 min and the solvent was removed in vacuo. The reaction mixture was extracted with a 1 : 1 benzene/dichloromethane mixture. Evaporation of the solvent yielded a dark purple-red microcrystalline powder. Extensive washing of this powder with EtOH and ether yielded 215 mg (20%) of 5. ^1H NMR, CD_2Cl_2 : δ 6.33, s (Cp), 7.71-7.40, m ($\text{C}_5\text{H}_3\text{Ph}_2$), 6.96, d, $J = 1$ Hz ($\text{C}_5\text{HH}_2\text{Ph}_2$).

Preparation of $\text{Cp}^*\text{CpTiCl}_2$ (6). This preparation is a modification of de Boer's method.^{12, 41} A suspension of CpLi (0.72 g, 10 mmole) in 10 mL THF was added slowly via cannula to a stirred solution of Cp^*TiCl_3 (2.9 g, 10 mmole) in 10 mL THF under an Ar atmosphere at ambient temperature. The reaction mixture was stirred for 30 m and worked up as for 2. Examination of the crude reaction product indicated less than 5% $\text{Cp}_2^*\text{TiCl}_2$ was present (^1H NMR). Recrystallization of the red powder from hot toluene gave 1.47 g (46%) of pure 6 as deep red columnar crystals. A small amount was recrystallized from CHCl_3 for kinetics experiments, m.p. 184-185° C decomp). Lit.⁴¹ 185-186° C. ^1H NMR, CDCl_3 : δ 6.25, s (Cp), 2.04, s (C_5Me_5).

Attempted preparation of (1, 2, 4-Triphenylcyclopentadienyl) CpTiCl_2 . This reaction was performed similarly to the preparation of 2, except ether was used in place of THF. In this manner Li(1, 2, 4-triphenylcyclopentadienide) (ca. 1.47 mmole) was allowed to react with CpTiCl_3 (307 mg, 1.4 mmole). A purple-red solid precipitated, and after 30 m of stirring, the solvent was removed in vacuo, and the reaction mixture was hydrolyzed with dilute aqueous HCl. An immediate

reaction occurred to give a green solution and yellow solids. The yellow solids were identified as 1,2,4-triphenylcyclopentadiene by TLC. No further attempts were made to prepare this compound.

Preparation of Cp_2TiF_2 . This is a procedure modified from the preparation of Cp_2ZrF_2 .²⁹ Cp_2TiCl_2 (2.5 g, 10 mmole) and $\text{Li}(\text{O}-t\text{Bu})$ (1.61 g, 20 mmole) were dissolved in 20 mL THF and allowed to stir for 24 hr under Ar at room temperature to give a yellow-orange solution. The solvent was removed in vacuo and the resulting oil was extracted with petroleum ether. The pet ether extracts were filtered under Ar through a fine frit. The petroleum ether was removed in vacuo, leaving a yellow-orange liquid. ^1H NMR spectroscopy of this liquid dissolved in C_6D_6 showed it to be $>90\%$ $\text{Cp}_2\text{Ti}(\text{O}-t\text{Bu})_2$ (δ 5.98, s, 10H; δ 1.16, s, 21H). The liquid was dissolved in 20 mL ether, and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (2.7 ml, 22 mmole) was slowly added by syringe. A pale orange powder precipitated rapidly. The powder was washed exhaustively with ether and dried in vacuo. The product proved to be too insoluble for NMR analysis in CDCl_3 and C_6D_6 . Addition of one drop of D_2O to these suspensions in NMR tubes resulted in rapid dissolution of the orange suspension to give a yellow solution of Cp_2TiF_2 as verified by ^1H NMR spectroscopy. The rest of the orange powder (probably $\text{Cp}_2\text{TiF}(\text{BF}_4)$ or $\text{Cp}_2\text{Ti}(\text{BF}_4)_2$) was treated with 15 mL MeOH to yield a yellow powder which was washed once with 2 mL MeOH followed by washing with ether. The yellow solid was dried in vacuo, and sublimed at 120°C at $<1\ \mu\text{m}$ Hg onto a water cooled probe. Yield: 1.2 g (56%) of fluffy, bright yellow powder. A small portion was recrystallized from hot toluene to yield fluffy yellow needles.

^1H NMR: δ 6.41, t, $J_{\text{FH}} = 1.71$ Hz. A small doublet (ca. 5% of total signal) appears at δ 6.49, $J = 1.71$ Hz.

Preparation of $\text{Cp}'\text{CpTiCH}_2\text{AlMe}_2\text{Cl}$ (8). This compound was prepared using the method of Tebbe⁷ for 7. AlMe_3 (9 mL 2M AlMe_3 in toluene, 18 mmole) was added via syringe to an Ar flushed flask containing 1 (2.34 g, 8.9 mmole). The resulting deep red solution was stirred for 40 h at room temperature. The solvent and the byproduct AlMe_2Cl were removed in vacuo to yield a deep red oil. The oil was dissolved in 10 mL toluene, and more AlMe_3 was added (1 mL of 2M toluene solution, 2 mmole). This solution was stirred for ca. 12 h. Removal of the solvent in vacuo resulted in an oil which slowly solidified to a waxy mass. This mass was extracted with 40-50 mL of n-hexane. The combined extracts were concentrated and cooled to -50°C to obtain 8 as a powder. The powder was washed once with 2-3 mL of hexane and pumped dry under high vacuum. Yield 530 mg (20%). This product contained ca. 5-10% 7 due to the presence of a small amount of Cp_2TiCl_2 in 1.

Preparation of $\langle\text{Cp}\rangle\text{CpTiCH}_2\text{AlMe}_2\text{Cl}$ (10). The preparation and isolation of this compound as a crystalline solid was first accomplished by de Boer¹² and it is this method which was reproduced and is reported here. AlMe_3 (4.6 mL of 2M toluene solution, 9.2 mmole) was added via syringe into an Ar flushed flask containing 4 (1.34 g, 4.6 mmole). The deep red solution was stirred for 28 h at room temperature. The volatiles were removed to yield a sticky solid which consisted of a 60:40 mixture of 10 and $\langle\text{Cp}\rangle\text{CpTiMeCl}$ as determined by ^1H NMR spectroscopy. AlMe_3 (1.84 mmole) and 4 mL toluene were added to the

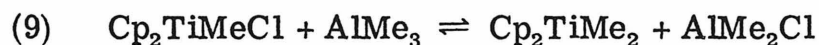
reaction flask, and the mixture was stirred for 24 h at 45° C. Several such cycles were repeated until no $\langle \text{Cp} \rangle \text{CpTiMeCl}$ was observed. After this extended reaction time, the resulting oil contained a significant amount of toluene-insoluble red solids.¹³ The insoluble solids were filtered, and the volatiles removed from the supernatant giving a deep red oil. The oil was triturated with hexane yielding a deep red mass of solids. The solids were extracted with hot hexane. The solvent was removed from the extracts yielding an oil which slowly crystallized to yield 890 mg of 10 which was ca. 85% pure by ¹H NMR spectroscopy. 500 mg of this material was dissolved in 50 mL hot hexane and filtered. The supernatant was concentrated to 15 mL and cooled to -50° C to yield 110 mg of pure 10 as a pale red powder.

Reactions of Cp_2TiCl_2 , Cp_2TiMeCl , Cp_2TiMe_2 , and Cp_2TiF_2 with Alkylaluminums. Reactions were carried out in 5 mm NMR tubes capped with plastic caps or with latex septa (Wilmad Glass). All reactions were performed utilizing a total Ti concentration of 0.2 M in C_6D_6 solvent. Aluminum reagents were introduced via microsyringe. The compositions of reaction mixtures were measured by ¹H NMR spectroscopy and are considered accurate to within 5%.

Reaction of Cp_2TiMeCl with 1 equivalent AlMe_2Cl . A NMR tube was loaded with Cp_2TiMeCl (23 mg, 0.1 mmole), 10 μL AlMe_2Cl (0.11 mmole), and 500 μL C_6D_6 . The ¹H NMR spectrum was recorded (δ 5.79 (10 H), δ 0.94 (3 H), δ -0.14 (6.6 H)) and the sample was then placed in a bath maintained at 56° C. After 1 h, a trace of $\overline{\text{Cp}_2\text{TiCH}_2\text{AlMeClCl}}$ was detected (δ 7.62, $\text{TiCH}_2\text{-Al}$). After 19 h at 56° C, a 30% yield of 7 and $\overline{\text{CpTiCH}_2\text{AlMeClCl}}$ in a ratio of 1 : 5 was

observed. The spectral lines were broad. After 30 h, the sample solution had turned blue-green, and no sharp features remained in the ^1H NMR spectrum. Identical results were obtained when Cp_2TiCl_2 (25 mg, 0.1 mmole) was allowed to react with AlMe_3 (10 μL , 0.1 mmole).

Reaction of Cp_2TiMe_2 with AlMe_2Cl . A NMR tube was loaded with Cp_2TiMe_2 (20 mg, 1 mmole), AlMe_2Cl (ca. 1 mmole), and 400 μL C_6D_6 . The sample rapidly turned deep red upon contact of AlMe_2Cl with the yellow Cp_2TiMe_2 solution. The ^1H NMR spectrum indicated the presence of $\text{Cp}_2\text{TiMeCl} \cdot \text{Al}$ (δ 5.73, Cp; δ 0.90, CH_3) and Cp_2TiMe_2 (δ 5.69, Cp; δ 0.05, CH_3) in the ratio of 87:13. A broad peak was also observed at δ -.23 ($\text{AlMe}_{3-n}\text{Cl}_n$). Integration of the methyl resonances showed the relative amounts of methyl containing species to be 2.60 ($\text{Cp}_2\text{TiMeCl} \cdot \text{Al}$), 0.77 (Cp_2TiMe_2), and 9.72 ($\text{AlMe}_{3-n}\text{Cl}_n$). From these integrals, the concentrations of the titanium species were calculated to be $[\text{Cp}_2\text{TiMeCl}] = 0.17 \text{ M}$ and $[\text{Cp}_2\text{TiMe}_2] = 0.03 \text{ M}$. For simplicity, the reaction under consideration was assumed to be (equation 9)



and the concentrations of AlMe_3 and AlMe_2Cl were calculated to be 0.87 M and 0.32 M, respectively. This yields an "equilibrium ratio"³⁷ of 0.06.

Similarly, when Cp_2TiMeCl (22 mg, 0.1 mmole) was allowed to react with AlMe_3 (ca. 1 mmole), the ratio $\text{Cp}_2\text{TiMeCl} \cdot \text{Al}:\text{Cp}_2\text{TiMe}_2:\text{AlMe}_{3-n}\text{Cl}_n$ was 2.34:1.34:10.2, corresponding to an "equilibrium ratio" of 0.06. Both samples were heated to 65°C. After 6 h, there

had been 80% conversion to $\underline{7}$.

Reaction of Cp_2TiCl_2 with 2 Equivalents of AlMe_3 . A suspension of Cp_2TiCl_2 (25 mg, 0.1 mmole) in 500 μL C_6D_6 was allowed to react with AlMe_3 (20 μL , 0.2 mmole) in a NMR tube yielding a deep red solution. The ^1H NMR spectrum indicated that formation of $\text{Cp}_2\text{TiMeCl} \cdot \text{AlMe}_{3-n}\text{Cl}_n$ had occurred (^1H NMR: δ 5.79, 10 H, Cp's; δ 0.92, 3 H, TiMe). This solution was heated to 65° C. After 6 h, $\underline{7}$ had been formed in 80% conversion.

Measurement of the Deuterium Isotope Effect. Cp_2TiCl_2 (25 mg, 0.1 mmole) was suspended in 500 μL C_6D_6 in a NMR tube. 10 μL AlMe_3 (0.1 mmole) was added via syringe along with 142 μL of a 0.7 M toluene solution of $\text{AlMe}_3\text{-d}_9$ (0.1 mmole). ^1H and ^2H NMR spectra of the solution were recorded. The integrals of the species $\text{Cp}_2\text{TiMeCl} \cdot \text{AlMe}_{3-n}\text{Cl}_n$ were: Cp (10.0), CH_3 (1.5), and AlMe (7.5). Integration of the ^2H spectrum gave a ratio of $\text{TiCD}_3:\text{AlCD}_3$ of approximately 3:13 (the signals were somewhat overlapped). The sample was placed in a bath maintained at 56° C. The progress of the reaction was monitored frequently by ^1H NMR spectroscopy. After 2 h there had been a 37% conversion to $\underline{7}$ (and $\underline{7}\text{-d}_n$). The ratio of the integrals of the cyclopentadienyl resonances to the titanium methylene resonance was 10:1.49. The resonance at δ 8.28 was sharp, and did not exhibit any apparent coupling to deuterium. After 44 h, the conversion to $\underline{7}$ and $\underline{7}\text{-d}_n$ was complete, and methylbenzoate (19 μL , 0.15 mmole) and pyridine (12 μL , 0.15 mmole) were added to the sample. ^1H NMR spectroscopy confirmed that the reaction had yielded 1-methoxy-1-phenylethylene: ^1H NMR: OMe, δ 3.33; $=\text{CH}_\text{A}\text{H}_\text{B}$, δ 4.63, d, δ 4.06,

d, $J_{AB} = 2.8$ Hz. The relative integrals of the methoxy group and the vinylic hydrogens was $1.49 \pm 0.1 : 1$. No 1-Ph-1-OMe=CHD could be detected by examining the center of each vinylic doublet, even with resolution enhancement of the spectrum. The limit of detection is estimated to be $\pm 10\%$.

Measurement of the Kinetics of the Reaction $Cp_2TiCl_2 + Excess AlMe_3$. A 5 mm NMR sample tube was loaded with Cp_2TiCl_2 (25.0 mg, 0.10 mmole) and taken into a dry box. The walls of the NMR tube were washed down with 400 μ L C_6D_6 , and $AlMe_3$ (40 μ L, 0.42 mmole) was added via syringe. The sample was capped, removed from the dry box, and agitated briefly to allow dissolution and formation of $Cp_2TiMeCl \cdot Al$. The sample was placed in the probe of the JEOL FX-90Q maintained at 53° C and spectra were obtained at regular intervals. An effective concentration of $AlMe_3$ at $t = 0$ was calculated from the relative integrals of the C_5H_5 and Ti-Me signals of $Cp_2TiMeCl \cdot Al$ and the total integral of the $AlMe$ signal. Least squares analysis of second-order plots of $\ln kt$ vs. t yielded the rate constants. This procedure was repeated for several concentrations of the titanium and aluminum reagents and at several different temperatures. Activation parameters were obtained from least squares analysis of $\ln k/T$ vs. $1/T$ plots.

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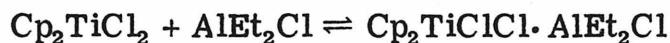
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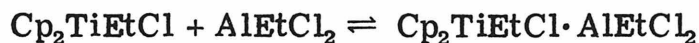
References and Notes (continued)

toluene insoluble solids can be isolated which have high reactivity towards acetone forming isobutylene, or with DMAP in the presence of olefins yielding titanocyclobutanes. Ott, K. C., Grubbs, R. H., unpublished results.

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$K = 140 \text{ M}^{-1}$. Fink,²¹ has shown that the forward rate of reaction



is diffusion controlled, and that the equilibrium constant

$K = 5 \times 10^3 - 5 \times 10^4$ at 240 K.

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concentrations. An equilibrium constant would be difficult to estimate due to the complex equilibria involving all of the aluminum compounds.

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CHAPTER 2

The Stereochemical Consequence of the Interaction of
Dimethylaluminum Chloride with Bis-Cyclopentadienyltitana-
cyclobutanes. Mechanism of Titanacyclobutane Isomerization.

INTRODUCTION

The role of the cocatalyst in the olefin metathesis¹ and Ziegler-Natta polymerization^{7a} reactions is poorly understood. It is generally accepted that the cocatalyst (usually a main group metal alkyl) serves to alkylate the transition metal complex (typically a metal halide). Little else is known about the subsequent role of the cocatalyst.

It is observed that many widely diverse olefin metathesis catalyst systems (typically a 2nd or 3rd row early transition metal complex with a Lewis acid cocatalyst) yield the same stereochemical results for a given substrate. This indicates that the ligands (or cocatalyst) associated with the transition metal center are not a factor in determining the stereochemistry of the product olefins.² There are a few systems reported, however, which give results which indicate that the ligands (or cocatalyst) are a determining factor in the stereochemical outcome. For example, the ring opening metathesis of cyclopentene is catalyzed by a variety of transition metal complexes to produce polypentenamer (equation 1). The system $WF_6/Al_2Et_3Cl_3$ ³ with an Al/W



ratio of greater than 4 produces a polypentenamer with greater than 90% trans-double bonds. The same system with an Al/W ratio less than 1 polymerizes cyclopentene to greater than 80% cis-polypentenamer. How the Lewis acid cocatalyst interacts with the catalyst in this system is unknown. A cocatalyst-free system, $W(CO)_5(CPh_2)_2$, polymerizes cyclopentene to greater than 90% cis-polypentenamer.⁴ The preceding

examples indicate that the type of ligand and the oxidation state of the metal^{5,6} in addition to the presence of a cocatalyst and its concentration are factors in determining the stereochemical outcome of the metathesis reaction in certain catalyst systems.

Katz has suggested that the stereochemical dependence of the olefin metathesis reaction in the presence or absence of a cocatalyst may be due in part to a reversible Lewis acid induced cleavage of a transient metallacyclobutane to a 3-metallapropyl cation. Rotation and reclosure of this intermediate would lead to loss of stereochemistry.⁴ Katz also suggests that since some systems show no dependence of product stereochemistry on cocatalyst concentration there may be steric and/or electronic factors which determine the susceptibility of a metallacyclobutane to cleavage to a metallapropyl cation.

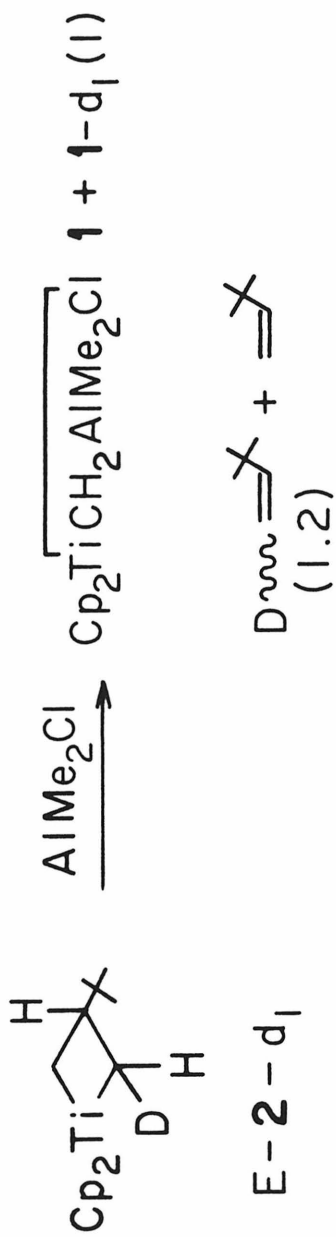
Many Ziegler-Natta catalysts are similar in composition to olefin metathesis catalysts (Ziegler-Natta catalysts are typically a first-row early transition metal halide with an alkylaluminum cocatalyst). Certain syndiotactic specific catalysts are sensitive to the cocatalyst concentration^{7b} with respect to the degree of syndiotacticity of the resultant polymer, indicating that the Lewis acid cocatalyst is a factor in determining the product stereochemistry.

Due to the nature of the olefin metathesis and Ziegler-Natta catalyst systems, the importance and scope of the interaction of the cocatalyst with the active catalytic site is difficult to determine.

Reported here is an investigation of the interaction of a Lewis acid cocatalyst with a well-defined olefin metathesis catalyst. Lee and Grubbs'^{8a,c} investigation of the metathesis reaction catalyzed by

$\text{Cp}_2\overline{\text{TiCHDCH(t-Bu)CH}_2}(\text{E-}\underline{\underline{2}}\text{-d}_1)$ led to the surprising observation that when $\text{E-}\underline{\underline{2}}\text{-d}_1$ was cleaved with AlMe_2Cl to yield $\text{Cp}_2\overline{\text{TiCH}_2\text{AlMe}_2\text{Cl}}$ ($\underline{\underline{1}}$) and $\underline{\underline{1}}\text{-d}_1$, the deuterated 3,3-dimethyl-1-butene produced was a 1:1 mixture of the E and Z isomers (Scheme 1). Consequently, Lee found that $\text{E-}\underline{\underline{2}}\text{-d}_1$ in the presence of AlMe_2Cl was rapidly and completely isomerized before cleavage to $\underline{\underline{1}}$ and $\underline{\underline{1}}\text{-d}_1$. The mechanism of the Lewis acid interaction with the titanacyclobutanes $\text{Cp}_2\overline{\text{TiCH}_2\text{CRR}'\text{CH}_2}$ is described. A preliminary account of this work has appeared.^{8b}

Scheme 1



RESULTS

Preparation of $\underline{3}$, $\underline{4}$, $\underline{4-d_1}$, $\underline{5}$, and $\underline{5-d_1}$. The preparation of $\overline{\text{E-CpTi CHDCD(tBu)CH}_2}$ ($\underline{3}$) was accomplished by an olefin metathesis reaction of E-3, 3-dimethyl-1-butene-1, 2- d_2 with the thermally labile metallacycle $\overline{\text{Cp}_2\text{TiCH}_2\text{CMe}_2\text{CH}_2}$ ($\underline{6}$) producing $\underline{3}$ and isobutylene in excellent yields and with complete retention of configuration. The metallacycles $\overline{\text{Cp}_2\text{TiCH}_2\text{CMe(iPr)CH}_2}$ ($\underline{4}$), E- $\underline{4-d_1}$, $\overline{\text{Cp}_2\text{TiCH}_2\text{CMePhCH}_2}$ ($\underline{5}$) and Z- $\underline{5-d_1}$ were prepared by the "conventional" route⁹ involving reaction of the corresponding olefin with $\overline{\text{Cp}_2\text{TiCH}_2\text{AlMe}_2\text{Cl}}$ ($\underline{1}$) in the presence of a Lewis base such as dimethylaminopyridine.

In contrast to $\underline{2}$, where only one equivalent of olefin is required to obtain good yields of pure metallacycle, large excesses (3-4 fold) of olefin are required to prepare $\underline{4}$ and $\underline{5}$ in good yields. One problem encountered in using a large excess of α -methylstyrene in the preparation of $\underline{5}$ is the inability to pump the excess olefin away from $\underline{5}$ at low temperatures. This leads to decomposition of the metallacycle. Even when $\underline{5}$ has been isolated and purified, the addition of α -methylstyrene results in decomposition of the metallacycle.

Particular care is required during the preparation of these β - β -disubstituted metallacycles due to their thermal lability.¹⁰ This characteristic leads to significant stereochemical scrambling during synthesis of the deuterium labelled metallacyclobutanes $\underline{4-d_1}$ and $\underline{5-d_1}$. Even when the reaction mixtures were maintained at or below -40°C and were worked up rapidly, $\underline{4-d_1}$ was isolated as a 4.9 : 1 mixture of E- and Z-isomers, and $\underline{5-d_1}$ was isolated as a 4.3 : 1 mixture of the Z- and E- isomers.

Isomerization Reactions.

When a 0.18M solution of $\underline{3}$ was allowed to react with 0.1 equivalents of AlMe_2Cl , $\underline{3}$ was rapidly equilibrated (requiring less than 10s) yielding a 1:1 mixture of E- and Z- $\underline{3}$. No $\underline{1}$, $\underline{1-d}_1$ or olefin was detected. The ^1H NMR spectra of $\underline{3}$ before and after isomerization are presented in Figures 1 and 2, respectively.

Interestingly when $\underline{3}$, which contained a very small amount of diethyl ether (less than 2%; incompletely removed reaction solvent), was allowed to react with 0.6 equivalents of AlMe_2Cl , the isomerization of E- $\underline{3}$ to Z- $\underline{3}$ was very slow, and only 15% of the Z-isomer was observed after 2 hr. at room temperature. A mixture of identical composition was obtained when $\underline{3}$ was allowed to react with 1.3 equivalents of $\text{AlMe}_2\text{Cl} \cdot \text{Et}_2\text{O}$ at room temperature for 2 hr.

A solution of $\underline{5-d}_1$ was prepared at low temperature, and the Z:E ratio was monitored. After 30 min at approximately -20°C , the ratio had changed from 74:26 to 64:36, and was accompanied by the appearance of 17% Z- and E- α -methylstyrene- d_1 in the ratio of 64:36.

The metathesis of 14.5 equivalents Z- α -methylstyrene- d_1 catalyzed by $\underline{5}$ was monitored by ^1H NMR spectroscopy at 0°C by observing the relative ratio of the vinylic hydrogens corresponding to E- and Z- β -deutero- α -methylstyrene. The initial rate of metathesis (productive plus non-productive; i. e., the rate of metathesis is twice the rate of isomerization) was calculated to be 1.2 turnovers $\text{Ti}^{-1} \text{min}^{-1}$. The metathesis proceeded less rapidly after 30 min at 0°C , and the solution had changed in color from pale red to brown.

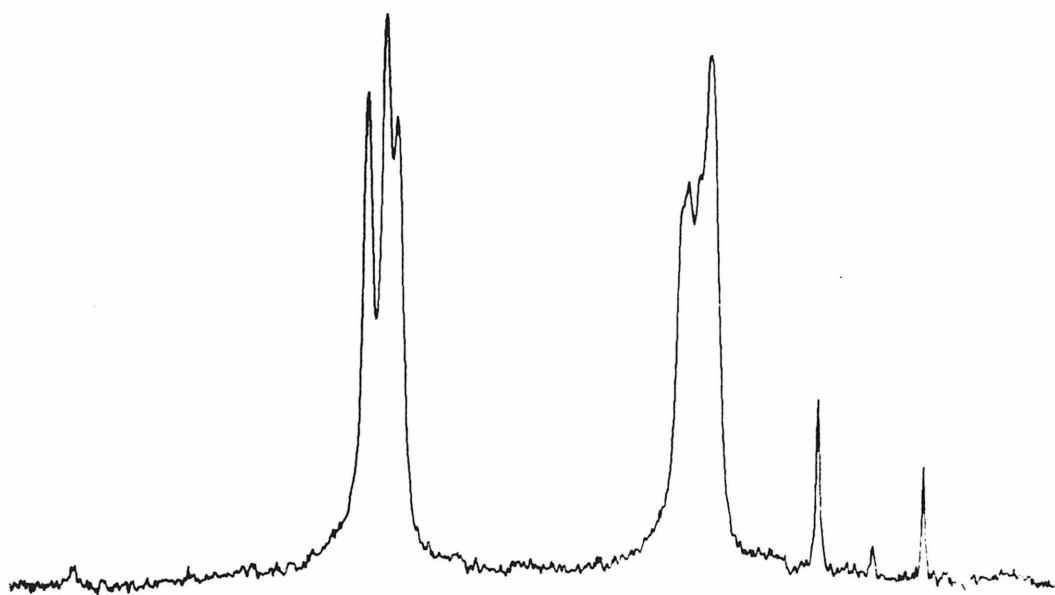


Fig. 2

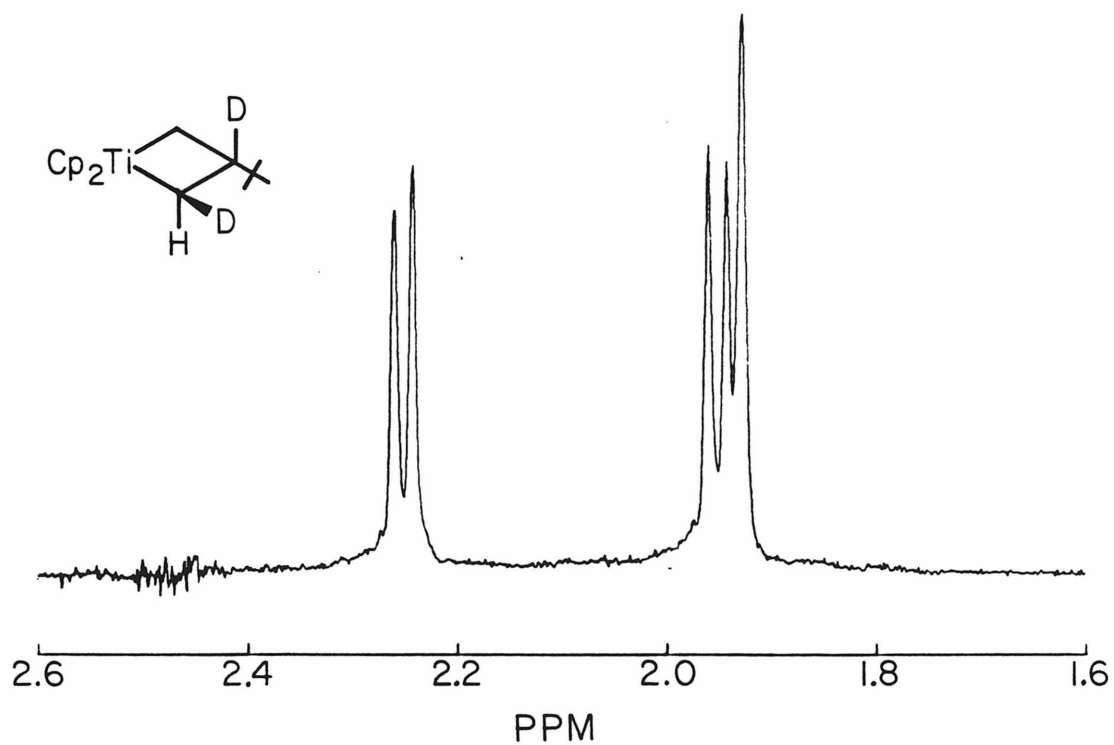


Figure 1 (Bottom). 500 MHz ^1H NMR spectrum of the methylene region of $E\text{-}\underline{3}$ in C_6D_6 , ambient temperature.

Figure 2 (Top). After addition of 0.1 equiv. AlMe_2Cl .

When solutions of $\underline{4}$ -d₁ or $\underline{5}$ -d₁ were allowed to react with excess AlMe₂Cl at low temperature, the olefin which was produced was a 1 : 1 mixture of E- and Z- isomers. In some experiments where less than stoichiometric amounts of AlMe₂Cl were used, the metallacycle that remained was also a 1 : 1 mixture of Z- and E- isomers. In all experiments involving $\underline{4}$ -d₁ or $\underline{5}$ -d₁, the ratio of the resulting $\underline{1}$ -d₁ to deuterated olefin was 1.0 : 1.6.

A competition experiment was performed to insure that all of the isomerization of $\underline{4}$ -d₁ and $\underline{5}$ -d₁ was AlMe₂Cl induced, and not simply due to thermal nonstereoselective olefin metathesis. This experiment was carried out by reacting slight excesses of AlMe₂Cl with $\underline{5}$ in the presence of 1 to 2.6 equivalents of Z- α -methylstyrene-d₁ and monitoring the amount of $\underline{1}$ -d₁ formed. No $\underline{1}$ -d₁ was detected under any circumstances; however, some isomerization (2-13%) of the deuterated α -methylstyrene was observed.

A crossover experiment was performed to determine the extent of intermolecularity of the isomerization. When $\underline{3}$ was reacted with excess AlMe₂Cl at 50° C for 1 hr, GC/MS of the volatiles indicated that only 3,3-dimethyl-1-butene-d₁ and -d₂ were produced. None of the d₀ - nor d₃-olefins were detected.

The kinetics of the reaction of $\underline{2}$ with a slight excess of AlMe₂Cl to produce $\underline{1}$ and 3,3-dimethyl-1-butene was also studied. Second-order plots of the reaction were linear to greater than 80% completion. The observed second-order rate constant at 294 K was $5.8 \pm 1.7 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. An Eyring plot of $\ln(k/T)$ vs. $1/T$ yielded the activation parameters $\Delta S^\ddagger = -38 \pm 1 \text{ e.u.}$ and $\Delta G_{294}^\ddagger = 20 \pm 1 \text{ kcal-mole}^{-1}$.

DISCUSSION

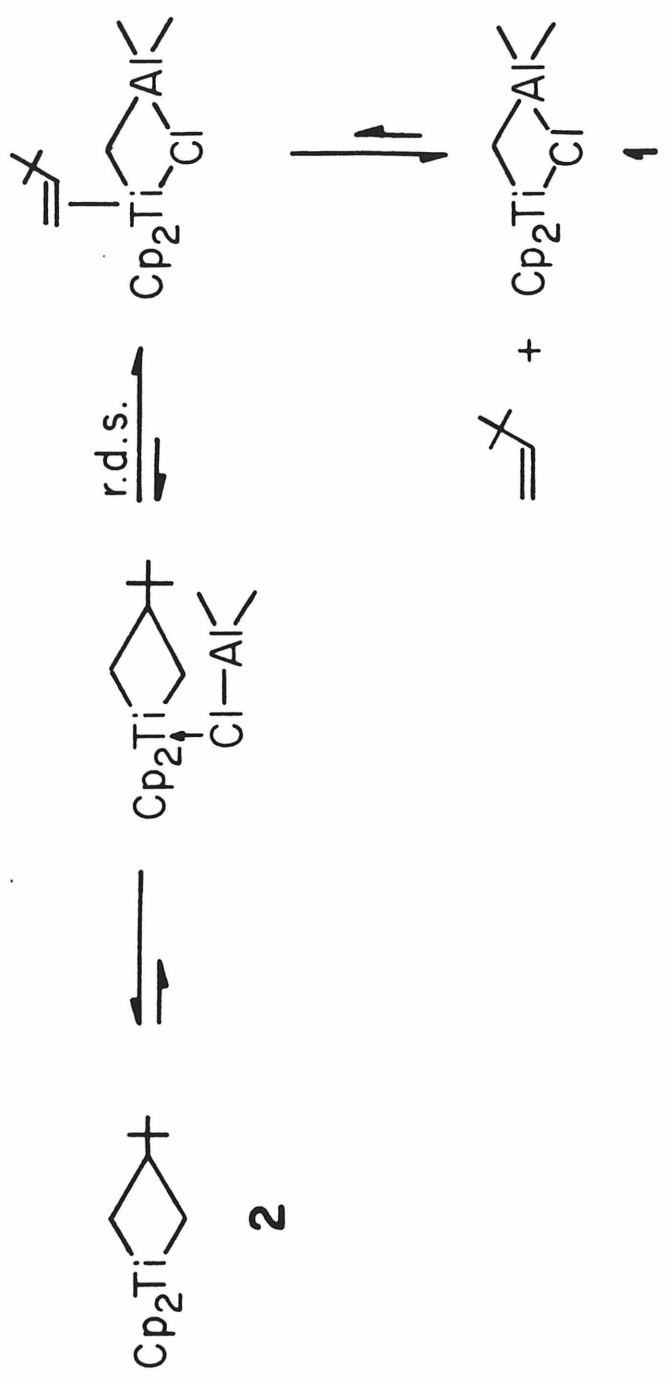
The AlMe_2Cl catalyzed isomerization of $\underline{3}$ to a 1 : 1 mixture of E- and Z-isomers occurs before the formation of detectable amounts of olefin or $\underline{1}$.¹² The rate of AlMe_2Cl induced isomerization of E- $\underline{2}$ -d₁ is several orders of magnitude faster than the rate of thermal isomerization, which has a $t_{\frac{1}{2}} \approx 2$ hr at 50° C.¹³

A study of the kinetics of the reaction of $\underline{2}$ with AlMe_2Cl was initiated to probe the interaction of AlMe_2Cl with titanacyclobutanes. The kinetics data indicated that the reaction was first-order in both $\underline{2}$ and AlMe_2Cl with a fairly large negative activation entropy (-38 e.u.). The kinetics, along with information concerning the activity of $\underline{1}$ as an olefin metathesis catalyst,¹⁴ are consistent with the mechanism depicted in Scheme 2. The existence of the olefin- $\underline{1}$ complex is inferred from Tebbe's olefin metathesis results. The magnitude of ΔS^\ddagger is consistent with an ordered transition state and may reflect significant Al-C and Ti-Cl bond formation.

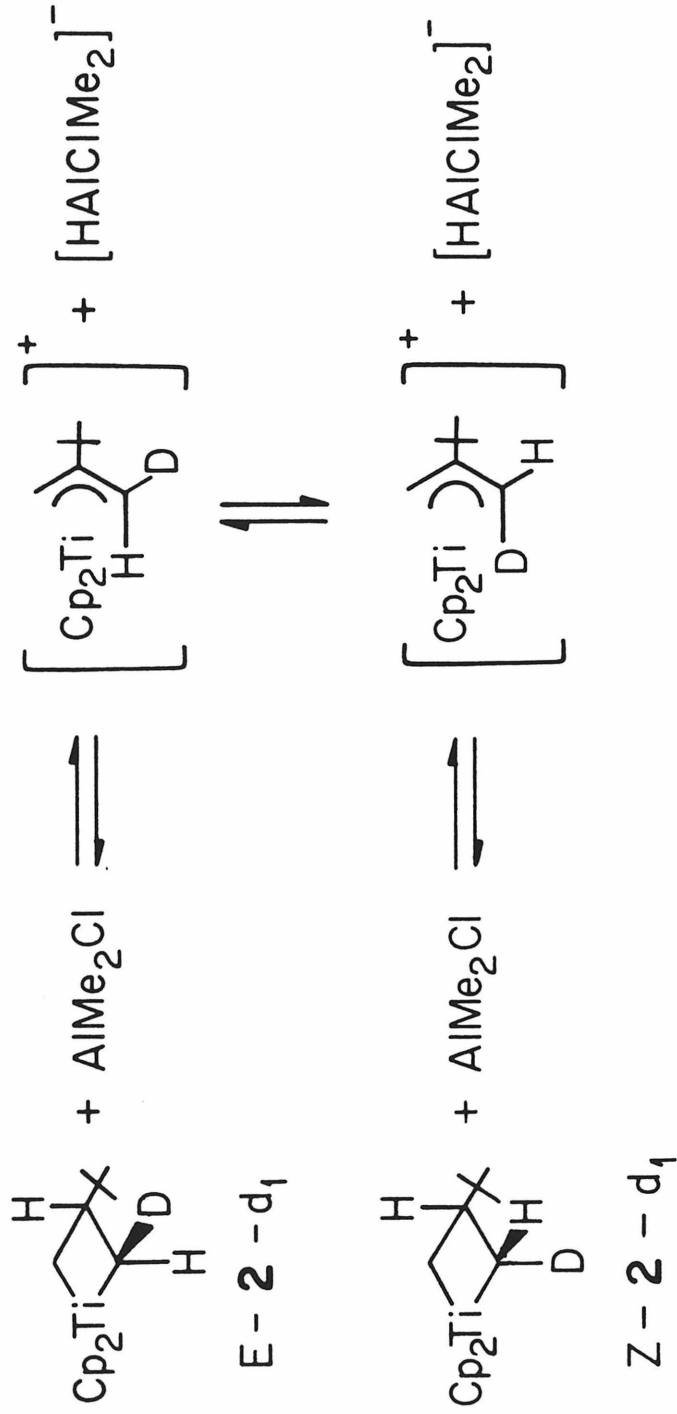
It was originally considered that preceding the cleavage of E- $\underline{2}$ -d₁ to $\underline{1}$ and $\underline{1}$ -d₁, a reversible AlMe_2Cl -mediated β -hydrogen abstraction occurred to yield a titanocene allyl cation and an aluminum hydride anion. This mechanism is depicted for E- $\underline{2}$ -d₁ in Scheme 3. A rotation of a C-C bond via an η^3 - to η^1 -allyl rearrangement followed by closure to titanacyclobutane¹⁵ would result in isomerization of the titanacyclobutane.

To investigate whether the β -H was involved in the isomerization, the labelled titanacyclobutanes $\underline{4}$ -d₁ and $\underline{5}$ -d₁ were prepared. The thermal lability of these β - β -disubstituted titanacyclobutanes results in

Scheme 2



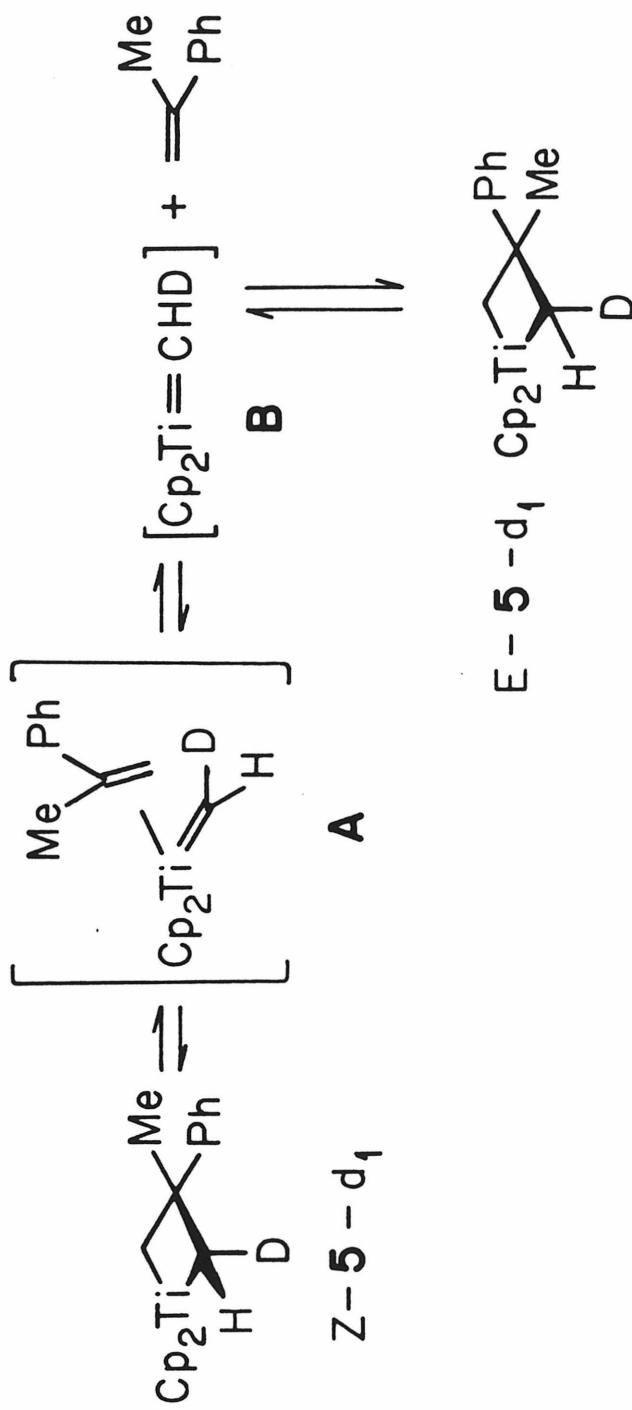
Scheme 3



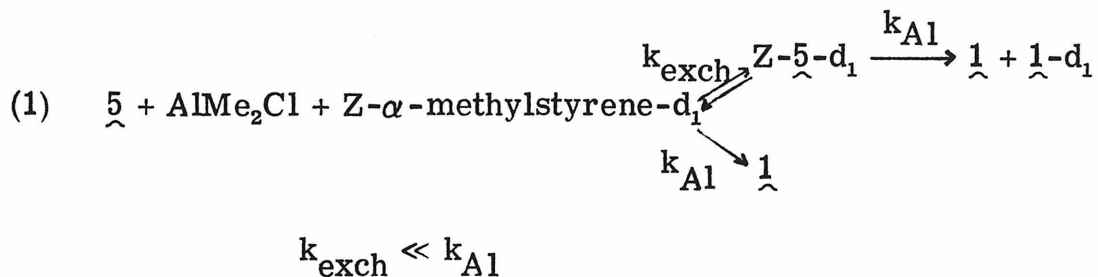
moderately rapid isomerization of the deuterium labelled compounds even at -20°C . A plausible mechanism¹⁶ for the thermal isomerization of $\underline{5}\text{-d}_1$ is represented in Scheme 4. It is proposed that the rate determining step involves opening of the titanacyclobutane to the methylene-olefin complex \underline{A} which is in equilibrium with the methylene complex \underline{B} and olefin. The olefin can return in either of two orientations with respect to the TiCHD unit resulting either in return to $\text{Z-}\underline{5}\text{-d}_1$ or in isomerization to $\text{E-}\underline{5}\text{-d}_1$. This is consonant with the observation that $\text{E-}\underline{2}\text{-d}_1$ isomerizes thermally at half the rate at which diphenylacetylene reacts to form $\text{Cp}_2\text{TiCH}_2\text{CPh}=\text{CPh}$. This suggests that the barrier to rotation of $\text{Cp}_2\text{Ti}=\text{CH}_2$ is greater than the barrier to opening of titanacyclobutane to $\text{Cp}_2\text{Ti}=\text{CH}_2$ and olefin. This latter process has a $\Delta G_{300}^{\ddagger} = 24 \text{ kcal}\cdot\text{mol}^{-1}$.^{8c} The barrier to rotation in $\text{Cl}_2\text{Ti}=\text{CH}_2$ has been calculated¹⁷ to be $19 \text{ kcal}\cdot\text{mol}^{-1}$, which is in disagreement with our results, and may be a rather low estimate.

Reaction of AlMe_2Cl with $\underline{4}\text{-d}_1$ or $\underline{5}\text{-d}_1$ results in immediate cleavage of the titanacyclobutanes to $\underline{1}$ and $\underline{1}\text{-d}_1$. The deuterated olefins (2, 3-dimethyl-1-butene-1- d_1 or α -methylstyrene- d_1) produced were 1 : 1 mixtures of E- and Z-isomers. Due to the rapidity of the cleavage reaction, the stereochemistry of the titanacyclobutanes could not be examined except when less than a stoichiometric amount of AlMe_2Cl was present in solution. In those cases, the titanacyclobutanes were observed to be 1 : 1 mixtures of E- and Z-isomers. However, due to the moderately fast olefin interchange discussed above, the relative contribution of thermal and AlMe_2Cl induced isomerizations could not be determined. Therefore, competition

Scheme 4



experiments were performed. When $\underline{5}$ was allowed to react with AlMe_2Cl in the presence of excess Z - α -methylstyrene- d_1 , no $\underline{1}$ - d_1 was observed, indicating that the reaction of $\underline{5}$ with AlMe_2Cl is much faster than olefin interchange (equation 1).



The above experiments indicate that AlMe_2Cl catalyzes the isomerization of $\underline{4}$ - d_1 and $\underline{5}$ - d_1 at a rate faster than the thermal isomerization. This also suggests that it is unlikely that the β -hydrogen is involved in the AlMe_2Cl catalyzed isomerization of the monosubstituted titanacyclobutanes such as E - $\underline{2}$ - d_1 or $\underline{3}$.

Crossover experiments using $\underline{3}$ were performed to test the intermolecularity of the reaction of $\underline{3}$ with AlMe_2Cl . Any intermolecular process would result in formation of d_0 - or d_3 - $3,3$ -dimethyl- 1 -butene; since neither was detected, it is unlikely that the AlMe_2Cl catalyzed isomerization involves intermediates such as free aluminum hydrides. It is also important to note that there is no α to β hydrogen scrambling in $\underline{3}$ during reaction with AlMe_2Cl .

The evidence presented above leads to the proposal that the isomerization involves a mechanism which scrambles only the α -positions of the titanacyclobutane, and which can ultimately lead to C-C bond cleavage to yield $\underline{1}$. The first step of the isomerization is proposed to be a rapid, reversible transmetalation at the Ti-C bond

(Scheme 5). Such transmetallation reactions have precedent in both Ti¹⁸ and Zr¹⁹ chemistry. The transmetallation apparently requires that aluminum have chloride as a ligand, since AlMe₃ induced catalysis of the titanacyclobutanes is ineffective, whereas AlCl₃ effectively catalyzes the isomerization. The 3-aluminapropyl titanocene chloride can undergo slow C-C bond cleavage to give 1, or rapid, reversible inversion at the carbon adjacent to aluminum followed by reverse transmetallation back to titanacyclobutane. The similarity of this mechanism to Katz,¹⁴ suggestion is apparent.

Inversion at the α -carbon atom in Li, Mg, and Zn alkyls²¹ via an S_{E2} reaction has been demonstrated to be fast on the NMR time scale. Aluminum alkyls also undergo α -carbon inversion on the NMR time scale (Figure 1), but the mechanism is not understood in similar detail.²² Inversion at the α -carbon in triisohexylaluminum is known^{22a} to proceed with first-order kinetics, and manifests very unusual behavior in the presence of Lewis bases. The rate of inversion of triisohexylaluminum is slowed to below detectable levels when either diethyl ether is used as solvent^{21b} or, curiously, when trace amounts of ether^{22a} are added to toluene solutions.²⁸ Analogously, when 3 is allowed to react with 1.3 equivalents of AlMe₂Cl · Et₂O, isomerization is very slow.²³ The same extent of isomerization is observed when 3, which contains traces of diethyl ether, is allowed to react with AlMe₂Cl. The similarity between the lack of alkylaluminum inversion and AlMe₂Cl induced isomerization of titanacyclobutanes in the presence of ether (or obviously, in the presence of DMAP) suggest that both processes may proceed through similar if not identical pathways.

The Lewis acid cocatalyst AlMe_2Cl is proposed to interact directly with a Ti-C bond in the titanacyclobutane metathesis system, which has a dramatic influence on the stereochemistry of the product olefins. Osborn *et al.*,³² have reported that Lewis acids in the $\text{OW}(\text{CH}_2\text{R})_3\text{X}$ system interact with the "spectator" oxide,³³ creating a greater electron deficiency at the metal center facilitating α -hydrogen abstraction and subsequent electrophilic attack by an olefin. Schrock³⁴ has reported that AlCl_3 accelerates the rate of metathesis catalyzed by $\text{OW}(\text{CHCMe}_3)(\text{PEt}_3)_2\text{Cl}$ and suggests that AlCl_3 interacts with or removes completely a Cl^- ligand, creating a vacant coordination site. Thus it appears that there are many types of cocatalyst-catalyst interactions.

Aside from the isomerization reaction discussed above, this work revealed some features concerning the enhanced reactivity of the β,β -disubstituted titanacyclobutanes (4, 5, and 6) versus the β -monosubstituted titanacyclobutanes such as 2.²⁷ The second-order rate constant of the reaction of 2 with AlMe_2Cl was $k \sim 6 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 21°C . The titanacyclobutanes 4, 5, and 6 react with AlMe_2Cl at 0°C at a rate too fast to measure by NMR spectroscopy. 2 reacts with diphenylacetylene to yield $\text{Cp}_2\text{TiCPh}=\text{CPhCH}_2$ with a half-life of approximately 1 hr^{8a, c} at 40°C , while the analogous β,β -disubstituted titanacyclobutanes react with Ph_2C_2 with half-lives of 15-20 min at room temperature.

Similar effects are manifested in the secondary deuterium isotope effects observed in these reactions. The reaction of $\text{E}-\underline{2}-\text{d}_1$ or 3 with AlMe_2Cl (Scheme 1) proceeds with a secondary deuterium isotope

effects of ca. 2.^{8c, 35} These facts may reflect a few features of the transition state of these reactions.

For the reaction with AlMe_2Cl , the larger isotope effect exhibited by the disubstituted titanacyclobutanes may signify a more product or titanium-methylene-olefin-like transition state. The diphenylacetylene reaction is known to exhibit first-order kinetics, and is thought to proceed via the titanium methylene intermediate $\text{Cp}_2\text{Ti}=\text{CH}_2$. For this dissociative pathway, the isotope effects would be expected to be similar for mono- and disubstituted titanacyclobutenes, which is in agreement with our observations.

EXPERIMENTAL

Titanocene dichloride was purchased from Strem Chemicals or Boulder Scientific and purified by Soxhlet extraction with dichloromethane. AlMe_3 (neat) was purchased from Alfa or as a 2M solution in toluene from Aldrich. AlMe_2Cl was purchased from Texas Alkyls. AlCl_3 was purified by sublimation. 3,3-dimethyl-1-butene, 2,3-dimethyl-1-butene, and α -methylstyrene were purchased from Aldrich, and stored over Linde 4Å molecular sieves. Isobutylene purchased from Matheson was used as received. Zirconocene dichloride was purchased from Boulder Scientific. LiAlD_4 was purchased from Merck, Sharp, and Dohme. $\text{Li}(0\text{-}t\text{-Bu})_3\text{AlH}$ was purchased from Aldrich. Dimethylaminopyridine (DMAP) and diphenylacetylene were purchased from Aldrich and recrystallized from hot toluene. Cp_2ZrHCl and Cp_2ZrDCl were prepared by literature methods.^{19a} Phenylacetylene was purchased from Aldrich. *t*-Butylacetylene and *i*-propylacetylene were purchased from Farchan and used as received. Phenylacetylene- d_1 was prepared by deprotonation of phenylacetylene with *n*-BuLi followed by deuterolysis with D_2O .

Dichloromethane was stirred over P_2O_5 or CaH_2 and degassed on a high vacuum line. Pentane, hexane, and petroleum ether were stirred over concentrated H_2SO_4 , then over CaH_2 , and vacuum transferred onto purple sodium-benzophenone ketyl dissolved in a small amount of tetraglyme. Toluene, diethyl ether, and benzene were stirred over CaH_2 and vacuum transferred onto purple benzophenone ketyl. Solvents thus dried and deoxygenated were vacuum transferred

into dry vessels equipped with teflon needle valve closures and stored under Ar. Benzene- d_6 (Merck, Sharp and Dohme) and toluene- d_8 (Aldrich) were dried and deoxygenated by several freeze-pump-thaw cycles of sodium-benzophenone solutions. Dichloromethane- d_2 (Norell, Inc.) was stored over CaH_2 and degassed by several freeze-pump-thaw cycles.

General Procedures

All manipulations of air and/or moisture sensitive compounds were carried out using standard high vacuum, Schlenk line and dry box techniques. Argon used in Schlenk work was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. NMR spectra were recorded with a JEOL FX-90Q (89.60 MHz 1H , 22.53 MHz ^{13}C , 13.76 MHz 2H) or a Bruker WM-500 (500.13 MHz 1H , 76.76 MHz 2H). Kinetics by NMR spectroscopy were run in automated mode on the JEOL FX-90Q. Temperatures were calculated by measuring $\Delta\nu_{MeOH}^{25}$ and were constant to within $\pm 0.1^\circ C$. Difference NOE's¹¹ were measured on the Bruker WM-500. Preparative gas chromatography was performed on a Varian Aerograph Model 920 using 20' Durapak or 6' of 10% saturated $AgNO_3$ /tetra-ethyleneglycol on Chromasorb P. GC/MS was performed on a Kratos MS25.

Preparation of E-3,3-dimethyl-1-butene-1,2- d_2 . This is essentially the method of Schwartz.^{19a} $LiAlD_4$ (144 mg, 3.4 mmole) was added to a solution of Cp_2ZrCl_2 (4g, 13.7 mmole) in THF under Ar. A solution of t-butylacetylene (1.12g, 13.3 mmole) in toluene was slowly added to the resulting THF suspension of Cp_2ZrDCl . The

suspension was stirred overnight and the solvent was removed from the yellow precipitate in vacuo. The precipitate was suspended in 5 ml toluene, and D₂O (250 μL, 13.8 mmole) was added. The resulting white suspension was stirred for several hours and then cooled to 0° C. Approximately half of the reaction liquids were vacuum transferred into a collection bulb containing a few Linde 4Å molecular sieves. The product E-3, 3-dimethyl-1-butene-1, 2-d₂ was separated by preparative gas chromatography (AgNO₃/Chromasorb P, 6', 70° C) and was shown to be >98% deuterated in the 1 and 2 positions (¹H NMR). Yield, 0.95 g, 80%. Variable amounts of additional product may be recovered from the remaining toluene suspension by vacuum transferring the remaining volatiles from the Zr residues.

Preparation of E-2, 3-dimethyl-1-butene-1-d₁ and Z-α-Methyl styrene. These preparations are by the method of Negishi.²⁶ AlMe₃ (3.8 mL, 40 mmole) was added to Cp₂ZrCl₂ (5.84 g, 20 mmole) suspended in 20 mL toluene under Ar. *i*-Propylacetylene (2 mL, 20 mmole) was added to this mixture via syringe. The reaction vessel was closed off from the Ar system, and heated to 45° C for 3h. The volatiles were removed in vacuo, leaving sticky yellow solids which were resuspended in 5 mL toluene. The suspension was cooled to -10° C, and a large excess of D₂O was added slowly. The initial reaction is very vigorous. Addition of D₂O was continued until the yellow color had been discharged. The white suspension was warmed to 0° C, and approximately half of the reaction liquids were vacuum transferred into a receiver containing a few 4Å molecular sieves. The product was isolated by preparative GC (6' AgNO₃/Chromasorb P,

70° C). Yield 1.25 g (74%). The E-2,3-dimethyl-1-butene-1-d₁ was deuterated to greater than 98% in the 1 position (500 MHz ¹H NMR spectroscopy).

Z- α -Methylstyrene was prepared in a similar manner from phenylacetylene-d₁ using CH₂Cl₂ as solvent. After hydrolysis of the reaction with 3M HCl, the product was extracted into ether. The combined ether extracts were dried over MgSO₄, and ether was stripped off leaving 4.1 g (80%) of α -methylstyrene-d₁ which was >95% of the Z-isomer (¹H NMR).

Preparation of 1: The preparation of this compound has been previously described by Tebbe et al.^{14a} A slightly modified procedure is given here. Neat AlMe₃ (21 mL, 220 mmol) was added via cannula to a suspension of Cp₂TiCl₂ (50 g, 200 mmol) in toluene (200 ml) to give a homogeneous red solution. Evolution of methane began immediately. After stirring this solution 48 hr, all volatiles were removed by vacuum distillation into a cold trap (Caution: the AlMe₂Cl evolved reacts violently with protic media and due precautions should be exercised). A small sample of the resulting red crystalline material may be assayed for the presence of Cp₂TiClAlMeClCH₂ (the -CH₂- resonance appears at δ 7.68 as an unresolved AB quartet). This material was converted to 1 by addition of an equivalent amount of AlMe₃ to the reaction mixture, which was redissolved in toluene. The resulting solution was then filtered through a pad of Celite supported on a coarse frit, and concentrated to the point of saturation (~ 150-170 mL total volume). This saturated solution was carefully layered with an equal volume of hexane or petroleum ether and allowed to stand undisturbed

at -20°C for 2-3 days. The supernatant was removed via cannula and the red crystalline mass was washed with several portions of petroleum ether at -20°C . The solids were dried under high vacuum. Typical yields were 30-35 g (53-61%). An additional crop of less pure material (10-15 g) was obtained by condensing the mother liquor as above.

Preparation of $\text{Cp}_2\text{TiCH}_2\text{CH-t-BuCH}_2$ (2). This is an improvement of the original preparation.⁹ To 1 (1 g, 3.5 mmol) dissolved in toluene (6 mL) was added 3,3-dimethyl-1-butene (500 μL , 3.9 mmol) and N,N-dimethylaminopyridine (DMAP) (472 mg, 4 mmol). The resulting red solution was transferred into 60 mL of vigorously stirred -20°C pentane or petroleum ether. The DMAP- AlMe_2Cl adduct precipitated as a yellow-orange mass which was rapidly filtered to give a clear red solution. This solution was evaporated to dryness in vacuo to yield 770-800 mg of 2 (80-83%). This crude material was recrystallized from diethyl ether to give 480 mg (50%) of 2 as red needles. NMR data of 2 have previously been published.⁹

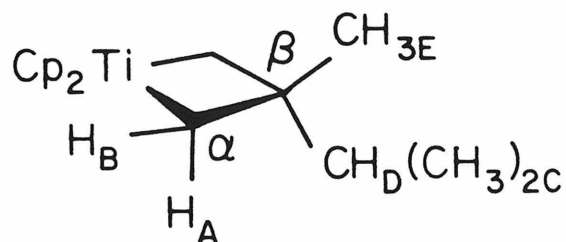
Preparation of $\text{E-Cp}_2\text{TiCHDCD(t-Bu)CH}_2$ (3). To a solution of 6 (238 mg, 0.96 mmole) in Et_2O under Ar at 0°C was added E-3,3-dimethyl-1-butene-1,2- d_2 (150 μL , 1.2 mmole). The solution was stirred for 15 min, and warmed to room temperature. Stirring was continued for 30 min. The solvent was removed in vacuo to yield 3 (240 mg, 90%) as red needles. ^1H NMR spectroscopy indicated that this material consisted solely of the E-isomer. The ^1H NMR assignments of the stereochemistry were in agreement with the assignments based on NOE spectroscopy of 2.

Preparation of 4 and 5: To a suspension of DMAP (427 mg, 4 mmol) and 2,3-dimethyl-1-butene (1.8 mL, 14 mmol) in 3 mL CH₂Cl₂ at -30° C was slowly added a solution of 1 (1.0 g, 3.5 mmol) in 3 mL of CH₂Cl₂. This homogeneous red solution was stirred for 15 min while it was allowed to warm to -10° C. The solution was slowly added dropwise via cannula into 50 mL of vigorously stirred pentane at -30° C. The DMAP-AlMe₂Cl adduct was rapidly filtered, and the resulting clear red solution was evaporated to dryness at or below -10° C to yield 480-770 mg (50-80%) of red powder. This material could be recrystallized from diethyl ether by slowly cooling saturated solutions from 0° to -50° C to yield red needles of 4. NMR data for compound 4 are listed in Table 1.

Compound 5 was prepared similarly, except only 1 equivalent of α -methylstyrene was used. Use of excess olefin leads to decomposition upon attempting to pump the excess α -methylstyrene from the metallacycle. This was circumvented by crystallizing the metallacycle from the pentane-methylene chloride solution at -78° C, and washing the metallacycle free of α -methylstyrene with cold (-50° C) pentane. The material so obtained is of suitable purity for further reactions. Yield 320-420 mg (30-39%). NMR data are listed in Table 1.

Preparation of E-Cp₂TiCHDC(Me)(iPr)CH₂ (4-d₁). To a suspension of DMAP (215 mg, 2 mmole) and E-2,3-dimethyl-1-butene-1-d₁ (900 μ L, 7 mmole) in 2 mL CH₂Cl₂ at -40° C was slowly added via cannula a solution of 1 (500 mg, 1.75 mmole) in 2 mL CH₂Cl₂ under Ar. The resulting homogeneous red solution was stirred for 15 m at -40° C, and added dropwise via cannula into 30 mL of vigorously stirred, cold

Table 1. NMR Data



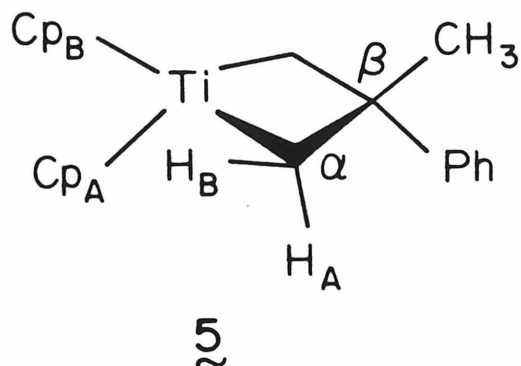
4

500.13 MHz ^1H , -20°C , CD_2Cl_2 , shifts vs. CHDCl_2 at δ 5.320.

δ 5.862, 5.851, 2s (Cp-H), 2.777 d, $J = 9.5$ Hz (H_A^*), 2.047, d, $J = 9.5$ Hz (H_B^*), 0.801, d, $J = 5.5$ Hz, (H_C), 0.753, hep, $J = 5.5$ Hz (H_D), 0.701, s (H_E).

22.53 MHz ^{13}C , gated decoupled, -30°C , CD_2Cl_2 , shifts relative to CDCl_2 at δ 53.8. δ 111.3, 110.7, d of m (Cp's), 79.6, dd, $J = 137$ Hz (C_α), 42.7, d, $J = 130$ Hz (C_D), 25.1 q, $J = 124$ Hz (C_E), 19.4, q, $J = 124$ Hz (C_C), 13.4, s (C_β).

Table 1 (continued)



500.13 MHz ^1H , -20°C , CD_2Cl_2 , shifts vs. CHDCl_2 at δ 5.320. δ 6.011, s ($\text{C}_{\text{P}_\text{A}}^*$), 5.673, s ($\text{C}_{\text{P}_\text{B}}^*$), 2.818, d, $J = 8.8$ Hz (H_A^*) 2.227, d, $J = 8.8$ Hz (H_B^*), 1.058, s (Me), 7.542, 7.429, 7.128, m (Ph).

22.53 MHz ^{13}C , -20°C , CD_2Cl_2 , shifts vs. CD_2Cl_2 at δ 53.8. δ 111.4, 111.2 (Cp's), 73.9 (C_α), 41.2 (Me), 15.8 (C_β), 128.3, 127.8, 126.8, 125.1 (Ph).

*Assignments by difference NOE spectroscopy.

(-50° C) pentane. The DMAP-AlMe₂Cl was rapidly filtered, and the solvent was removed in vacuo from the resulting red solution while maintaining the temperature below -40° C. This procedure yielded 310 mg (64%) of red powder. It is important that a 3-4 fold excess of the olefin be used, otherwise, the yields are poor, and the crude material is less pure. ¹H and ²H NMR spectroscopy indicated that this material was a mixture of the E- and Z- d₁-metallacyclobutanes in the ratio of 4.9 : 1. The ¹H and ²H NMR spectra were consistent with the assignments based on difference NOE results.

Preparation of Z- Cp₂TiCHDC(Me)(Ph)CH₂ (5-d₁). This compound was prepared in an identical manner to 5, except that after ca. 75% of the solvent had been removed and most of the metallacycle was judged to have precipitated, the supernatant was drawn off, and the remaining red powder washed repeatedly with cold (-50° C) pentane to remove any excess olefin. The solids were dried at -40° C under high vacuum. This procedure yielded 5-d₁ (105 mg, 20%) which was judged pure by ¹H NMR spectroscopy. ²H NMR spectroscopy indicated that this material was a mixture of Z- and E- d₁-metallacyclobutanes in the ratio 4.3 : 1. The ¹H and ²H NMR spectra were consistent with the assignments based on difference NOE results for 5.

Preparation of Cp₂TiCH₂CMe₂CH₂ (6). This metallacycle may be prepared as for 4. This metallacycle is considerably more stable than 4 or 5, and may be handled in non-halogenated solvents at room temperature for short periods of time without significant decomposition. Typical yields were 40-80%. The metallacycle can be conveniently purified by crystallization as deep red needles by cooling diethyl ether

solutions of 6 slowly to -50°C .

Isomerization of 3 Catalyzed by AlMe_2Cl . This is similar to the experiment conducted by J. B. Lee,^{8b} only using a catalytic amount of AlMe_2Cl . A solution of 3 (20 mg, 0.072 mmole) in C_6D_6 (400 μL) was prepared in a 5 mm NMR tube. The tube was capped with a latex septum and removed from the dry box. The ^1H NMR spectrum was recorded and indicated that the sample contained only the E- isomer. AlMe_2Cl (7 μL of 1M 0.007 mmole, solution in C_6D_6) was added via syringe. The ^1H NMR spectrum was recorded, and indicated that the ratio of E- and Z-3- d_1 was 1 : 1.

Reaction of 3 with $\text{AlMe}_2\text{Cl}\cdot\text{Et}_2\text{O}$. A solution of 3 (20 mg, 0.072 mmole) was prepared in 500 μL C_6H_6 in a 5 mm NMR tube. The tube was capped with a latex septum, and removed from the dry box. The 76.76 MHz ^2H spectrum was recorded, and indicated that the solution contained only the E-isomer. A solution of AlMe_2Cl (50 μL , 1.84 M, 0.092 mmole) was added to the solution via syringe. The ^2H spectrum indicated that no isomerization had occurred. After 2 hr, 5% of the Z-isomer was observed. Only a few percent 1- d_1 could be observed.

Isomerization of 3 with AlCl_3 . AlCl_3 (10 mg, 0.075 mmole) was added to a C_6D_6 solution of 3 (20 mg, 0.072 mmole). The ^1H NMR spectrum was monitored and indicated that 3 had been isomerized to a 1 : 1 mixture of E- and Z-isomers. There were also indications of decomposition. The suspension slowly turned from its initial red color to brown-green.

Isomerization of $\underline{5-d_1}$. A 5 mm NMR tube was loaded with $\underline{5-d_1}$ (15 mg). The tube was capped with a latex septum and removed from the dry box. 500 μL of toluene was very slowly added to the NMR tube which was nearly completely submerged in a -50°C bath (this must be done to insure that significant decomposition of the metallacycle does not occur). The sample was carefully dissolved while at -50°C . The 76.76 MHz ^2H spectrum was recorded in a NMR probe cooled to ca. -20°C . The ratio of trans- and cis- $\underline{4-d_1}$ was 2.8:1. Approximately 10% of the sample had decomposed to olefin by this time. This sample was allowed to sit in the probe for 30 min, after which the ratio of trans- and cis- $\underline{5-d_1}$ was 1.8:1 (at 17% olefin formation). (The ratio of Z- and E- α -methylstyrene was also 1.8:1.)

Nonstereoselective exchange of Z- α -methylstyrene- $\underline{d_1}$ with $\underline{5}$. $\underline{5}$ (5 mg, 0.016 mmol) was dissolved in 500 μL toluene- $\underline{d_8}$ at -20°C . 30 μL (0.23 mmol, 14.5 equivalents) of Z- α -methylstyrene- $\underline{d_1}$ was injected via syringe. The solution was mixed well at -20°C , and placed in an NMR probe held at 0°C . The extent of isomerization of the olefin was monitored by measuring the ratio of the integrals of the peaks at $\delta 4.98$ and $\delta 5.33$ (Z and E vinylic hydrogen resonances, respectively) by ^1H NMR spectroscopy. After 5 minutes, the ratio Z/E was 3.7:1 corresponding to 1.2 turnovers $\text{Ti}^{-1} \text{min}^{-1}$.

Isomerization of $\underline{4-d_1}$ and $\underline{5-d_1}$ Catalyzed by AlMe_2Cl . A solution of $\underline{4-d_1}$ (15 mg, 0.05 mmole) was prepared at -50°C as described above. ^2H NMR at 76.76 MHz at below -20°C indicated that the solution contained a mixture of E- and Z- $\underline{4-d_1}$ in the ratio of 4.9:1. The solution also contained ca. 5% of a mixture of E- and

Z- 2,3-dimethyl-1-butene-1-d₁. The sample was removed from the probe, and cooled to -50° C. A solution of AlMe₂Cl, 1 M in toluene, (100 μL, 0.1 mmole) was added via syringe, and the sample was replaced in the NMR probe. The ²H spectrum indicated that 1-d₁ had been formed, and that the olefin produced was a mixture of E- and Z- 2,3-dimethyl-1-butene-1-d₁ in the ratio of 1 : 1. Approximately 50% of the metallacycle remained, and was also approximately a 1 : 1 mixture of E- and Z- isomers (natural abundance Ph-CH₂D interferes slightly with the determination of the latter ratio). When all of the metallacycle had reacted, the ratio of (E+Z)-2,3-dimethyl-1-butene-1-d₁ to 1-d₁ was 1.6 : 1.

Similarly, when 5-d₁ (15 mg, 0.048 mmole) was allowed to react with AlMe₂Cl (100 μL of 1 M solution, 0.1 mmole) (initial ratio Z : E 5-d₁ = 4.3 : 1, 5% (Z+E) α-methylstyrene-d₁), the ratio of the Z- and E- α-methylstyrene was 1 : 1, while the ratio of 1-d₁ to (E+Z)-α-methylstyrene was 1.6 : 1.

Reaction of 5 with AlMe₂Cl in the Presence of Z-α-Methylstyrene-d₁. A toluene solution of 5 (10 mg, 0.032 mmole) was prepared at -50° C in an NMR tube as described above. Z-α-Methylstyrene-d₁ (4 μL, 0.031 mmole, 95% Z) was added via syringe, followed by AlMe₂Cl (19 μL of a 2 M toluene solution, 0.038 mmole). The sample was agitated at -50° C, and then shaken vigorously as the tube was warmed to room temperature. ²H NMR spectroscopy indicated that no 1-d₁ was formed. This experiment was repeated several times, and no 1-d₁ was observed. The Z-α-methylstyrene was partially isomerized to the E-isomer to the extent of 2-13 (±3)%.

GC/MS Analysis of the 3, 3-dimethyl-1-butenes Produced on Reaction of 3 with AlMe₂Cl. A flask was loaded with 3 (20 mg, 0.072 mmole) and removed from the drybox. Toluene (300-400 μ L) was vacuum transferred into the flask, and AlMe₂Cl (12 μ L, 14 mmole) was added under a counterflow of Ar. The reaction vessel was closed, and heated at 50° C 1 h. The volatiles were vacuum transferred into a NMR tube. A sample was withdrawn from the NMR tube for GC/MS analysis: m/e (intensity) 87 (114), 86 (1894), 85 (1921), 84 (114), 71 (21, 393), 70 (21, 805), 57 (10, 996), 56 (10, 423), 55 (9, 480), 54 (10, 817), indicating no d₃- or d₀- 3, 3-dimethyl-1-butene was produced.

Kinetics of the Reaction of 2 with AlMe₂Cl. Stock C₆D₆ solutions of 2 (34 mg, 0.125 mmole, 1.00 mL C₆D₆, 0.125 M) and AlMe₂Cl (14 mg, 0.151 mmole, 1.00 mL, 0.151 M) were prepared. Samples for kinetics were prepared by adding a 200 μ L aliquot of the stock solution of 2 by syringe into a 5 mm NMR tube and then freezing the solution at -50° C in the dry box freezer. The sample was removed from the freezer and a 200 μ L aliquot of the AlMe₂Cl stock solution was added by syringe. The tube was rapidly capped, removed from the dry box and refrozen at -50° C. The sample was later thawed, and placed in the NMR probe held at constant temperature. Four measurements of the rate were recorded at 296 K. Activation parameters were derived from additional rate data recorded at 305 K and 279 K. Second-order plots were linear to greater than 80% completion.

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28. A possible mechanism for the triisohexylaluminum inversion was not discussed by Fraenkel.^{22a} The inversion displays first-order kinetics, ruling out an $\text{S}_{\text{E}2}$ mechanism observed for Li, Mg, Zn, etc.^{21a} A possible monomolecular mechanism involves an α -hydrogen migration from an isohexyl to the Al atom. This can be followed by rotation of the $\text{Al}^- \text{-C}^+$ bond, migration of the aluminum hydride back to the α -carbonium center, resulting in inversion at the α -carbon atom. This does not account for the effect of less than stoichiometric amounts of Lewis base. Such α -hydrogen migrations are well known in early transition metal chemistry, having been observed in a tungsten system,²⁹ and crystallographically and spectroscopically in many of Schrock's tantalum alkylidene complexes.³⁰ An α -hydrogen migration has been proposed for aluminum.³¹

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CHAPTER 3

The Preparation and Characterization of a Few
 $M-\mu-CH_2-M$ ($M = Ti, M' = Ti, Zr$) Compounds
and Their Reactions with Carbon Monoxide.

INTRODUCTION

Transition metal methylenes have been implicated as intermediates in the olefin metathesis reaction¹ and the Fischer-Tropsch synthesis.² In both systems, metal methylene dimerizations are thought to be key steps.

Attempts to synthesize metal alkylidene or carbene³ complexes often results in the formation of olefins or metal-olefin complexes which arise from coupling of two alkylidene or carbene groups.⁴ The coupling reactions are generally postulated to involve the bridging of alkylidene groups between two metals. Such a coupling reaction may be involved in a chain termination step of the olefin metathesis reaction. A stable bis-bridging methylene species has been isolated from an olefin metathesis system, and is the subject of this chapter.⁵

Bridging methylene complexes also represent the simplest models of a surface-bound methylene. The chemistry of these species has been the subject of intense interest⁶ due to the implication of the involvement of surface bound methylenes in Fischer-Tropsch chemistry. Oligomerization of methylene groups on metal surfaces to $-(CH_2)_n-$ products and coupling of CO with μ -CH₂ groups to yield bridging ketene functionalities have been proposed to be major C-C bond forming processes in Fischer-Tropsch synthesis.²

The preparation, characterization, and CO coupling reactions of several mono- and bis- μ -CH₂-metal⁷ species are reported herein.

RESULTS

Preparation and Reactivity of Bis- μ -CH₂-[Cp₂Ti(IV)]₂.

The sterically encumbered β - β -disubstituted titanacyclobutanes such as Cp₂Ti $\overline{\text{CH}_2\text{CMe(i-Pr)CH}_2}$ (2) and Cp₂Ti $\overline{\text{CH}_2\text{CMe}_2\text{CH}_2}$ (4) decompose to liberate 2, 3-dimethyl-1-butene or isobutylene, respectively, yielding an intensely permanganate-colored species. Figure 1 shows a ¹H NMR spectrum of a solution containing the products of decomposition of 2. Downfield resonances at δ 8.72 in the ¹H spectrum and at δ 235 (¹J_{C-H} = 125 Hz) in the ¹³C spectrum were observed and are diagnostic for bridging methylenes⁸ or metal-methyldene species. Infrared spectroscopy revealed stretches at 2980 and 2920 cm⁻¹ and are assigned as -CH₂- vibrations. Molecular weight determinations indicated that the intensely purple colored species is a dimer in solution. The reaction chemistry of this dimer (1) follows. The dimer reacts readily with AlMe₂Cl (2 equiv.) producing several color changes before yielding Cp₂Ti $\overline{\text{CH}_2\text{AlMe}_2\text{Cl}}$ in quantitative yield as determined by ¹H NMR spectroscopy. Reaction with trifluoroacetic acid (TFAH) (0.6 equiv.) at low temperature resulted in a near statistical distribution of Cp₂TiMe₂, Cp₂TiMe(TFA), and Cp₂Ti(TFA)₂. Compound 1 reacts only sluggishly in refluxing acetone to produce isobutylene. The above facts lead to the formulation of 1 as bis- μ -CH₂-[Cp₂Ti(IV)]₂. The reluctance of 1 to react with acetone, and the lack of methylene exchange with deuterated olefins rules out 1 as being formulated as [Cp₂Ti=CH₂]₂. Other early transition metal alkylidene species react vigorously with organic carbonyl compounds,¹⁰ and other nucleophilic titanium methylene complexes exchange their methylene groups with terminal olefins.¹¹

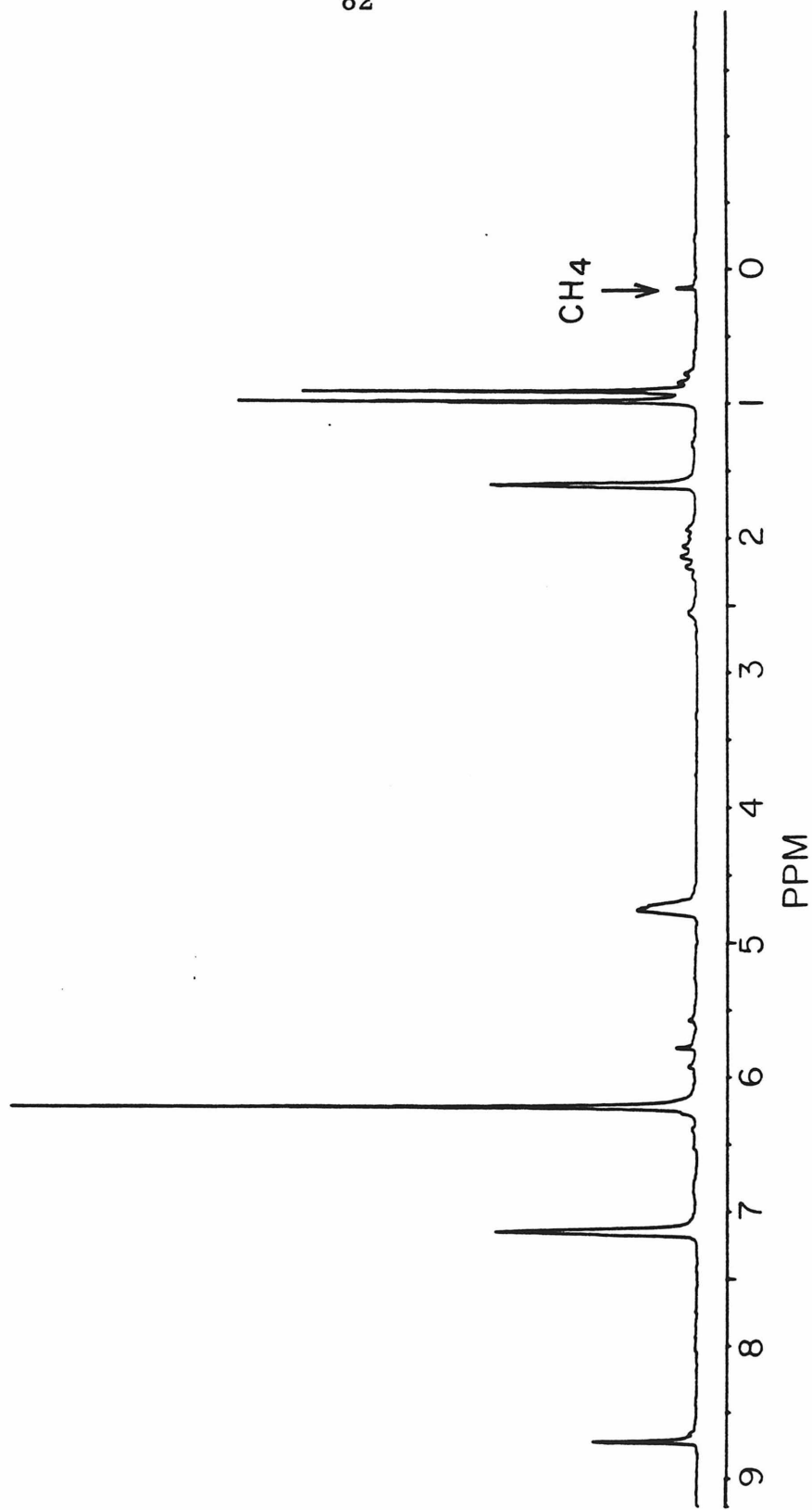
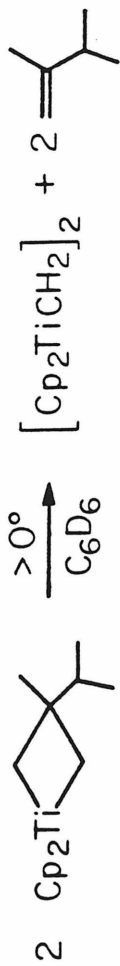


Figure 1. 89.60 MHz ^1H NMR spectrum of the decomposition of 2 after 2 hr in C_6D_6 at room temperature to yield 1 and 2, 3-dimethyl-1-butene.

Compound 1 is surprisingly robust, decomposing only partially after several hours in refluxing toluene. The gaseous decomposition products are methane (92%) and ethane (8%).

When 1 was allowed to react with I₂, Cp₂TiI₂ (¹H NMR) was formed, and ethylene (78%) was liberated along with methane (22%) (GC, NMR).

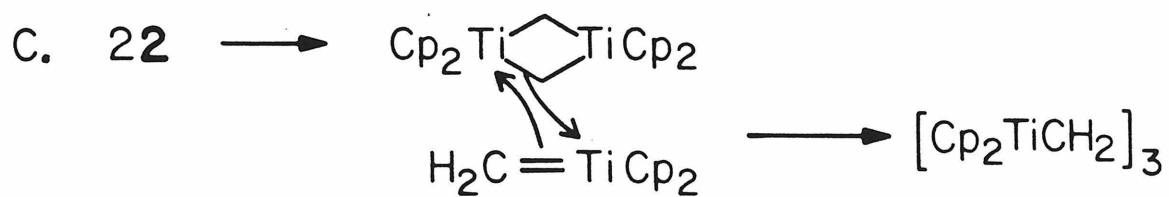
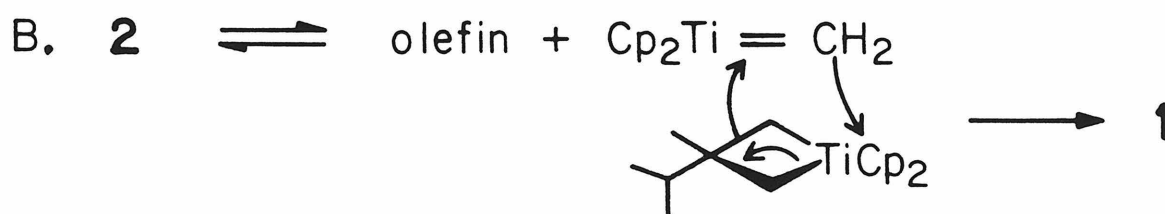
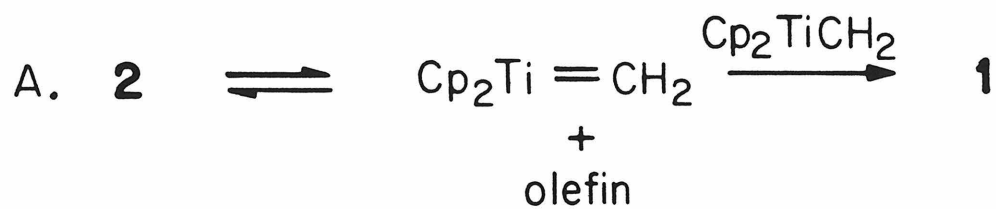
Photolysis of 1 at 30° C also resulted in decomposition to produce ethylene (84%; 80% hydrogenated by Cp₂Ti to ethane).¹² The rest of the hydrocarbon gases produced were CH₄ (15%) and a small amount of propylene. In an attempt to boost the propylene yield, the photolysis of 1 was carried out under an ethylene atmosphere (ca. 1.5 atm). After a few hours the photolysis was stopped. ¹H NMR spectroscopy of the solution indicated that nearly all of 1 had decomposed. A new Cp resonance had grown in (δ 5.89) along with two broad multiplets (δ 1.88, δ 1.28) which integrated 10:4:4. The ethylene resonance was broad and was shifted upfield from δ 5.24 to δ 4.64. These resonances were assigned to the titanacyclopentane $\text{Cp}_2\overline{\text{TiCH}_2(\text{CH}_2)_2\text{CH}_2}$, which exchanges slowly with free ethylene.^{13, 50} Methane and ethane were also observed. The photolysis was allowed to continue until ethylene was no longer detected, and the peaks assigned to $\text{Cp}_2\overline{\text{TiCH}_2(\text{CH}_2)_2\text{CH}_2}$ were absent. GC analysis of the gases above the black solution indicated that a mixture of mostly n-butane (27%), n-butenes (10%), ethane (53%) and CH₄ (9%) had been formed. Traces of ethylene, propane, propylene, and cyclopropane were detected.

Attempts were made to investigate the mechanism of formation of $\underline{1}$. Two possibilities for the formal dimerization are proposed. One involves direct dimerization of two $\text{Cp}_2\text{Ti}=\text{CH}_2$ fragments (Scheme 1, A). The other involves a nucleophilic attack of the methylene of $\text{Cp}_2\text{Ti}=\text{CH}_2$ at the titanium atom of a titanacyclobutane, displacing olefin and forming $\underline{1}$ (Scheme 1, B). The latter appears to be possible due to the fact that another species is observed in solution in low yield when concentrated solutions of $\underline{2}$ are allowed to decompose. This species has ^1H NMR resonances at δ 10.46 (m, br) and δ 5.73 (s, br) with relative integrals of 2:10. This species is tentatively formulated as the trimer $[\text{Cp}_2\text{TiCH}_2]_3$. The signal assigned as the $\mu\text{-CH}_2$ may be broadened by spin-spin coupling of protons which are inequivalent due to the conformation of the Ti_3C_3 ring. This species is proposed to arise from nucleophilic attack of $\text{Cp}_2\text{Ti}=\text{CH}_2$ on $\underline{1}$ (Scheme 1, C).

Assuming that the rate of trapping k_2 is much faster than the back reaction of $\text{Cp}_2\text{Ti}=\text{CH}_2$, both mechanisms predict the observed first-order kinetics ($k_{\text{obs}} = 5 \times 10^{-4} \text{ s}^{-1}$ at 23°C) for the decomposition of $\underline{2}$.

An experiment to distinguish the two possibilities (A and B) was designed. Decomposition of $\text{Cp}_2\text{Ti}\overline{\text{CH}_2\text{CMe(i-Pr)CD}_2}$ ($\underline{2}\text{-d}_2$) to give a mixture of $\underline{1}\text{-d}_{0,2,4}$ was carried out. The deuterium isotope effect on ring-opening of $\underline{2}\text{-d}_2$ is known to be 2.0.¹⁴ With this information, one can predict the relative amounts of ethylenes produced for path A ($4d_0 : 2d_2 : 1d_4$) and path B ($2d_0 : 3d_2 : 1d_4$; this assumes that there is no isotope effect on the reaction of $\text{Cp}_2\text{Ti}=\text{CH}_2$ with the titanacyclobutane). Unfortunately, the GC/MS data were irreproducible from injection to injection, and a spectrum containing only parent ions was not obtained,

Scheme 1



resulting in unreliable ratios.

When 2 was allowed to decompose in the presence of $\text{E-Cp}_2\text{TiCHDCD(t-Bu)CH}_2$ (3-d₂), no deuterium was incorporated into 1, and therefore $\text{Cp}_2\text{Ti=CH}_2$ preferentially inserts into the Ti-C bond of 2 rather than 3-d₂.

Trapping of 'Cp₂TiCH₂' With Other Reagents.

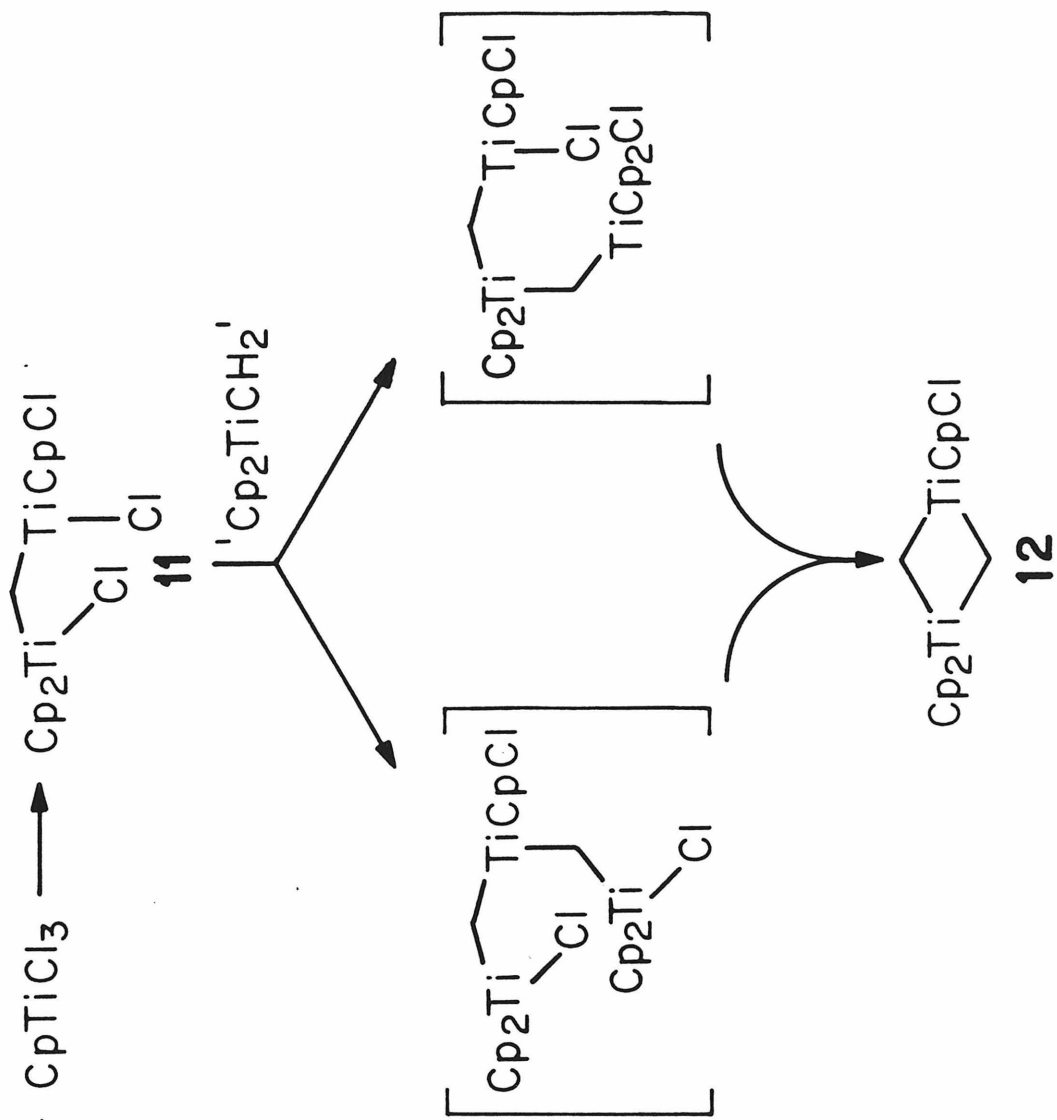
The β - β -disubstituted titanacyclobutanes are convenient sources of the 'Cp₂TiCH₂' moiety ('Cp₂TiCH₂' designates a source of titanium methylene, either Cp₂Ti=CH₂, or titanacyclobutane). With this in mind, 'Cp₂TiCH₂' was trapped with reagents similar to AlMe₂Cl to generate new Lewis acid stabilized metal methylenes. CpTiCl₃ was chosen to be a good candidate. 2 or 4 readily reacted with CpTiCl₃ in C₆D₆ to produce a NMR spectrum with a new set of singlet resonances at δ 6.88, 6.15, and 6.08, integrating 2:10:5, respectively. Resonances due to the corresponding olefin were also observed. An orange solid began to precipitate as the NMR spectra broadened. A new set of broad singlet resonances grew in at δ 7.84 and 6.18, integrating 2:15, respectively. The sample decomposed quickly to a brown-green solution. The first formed species was tentatively assigned as $[\text{Cp}_2\text{TiCl}] - \mu - \text{CH}_2 - [\text{CpTiCl}_2]$ (11). The second formed species may be a dimer or oligomer of 11. Neither of these compounds were isolated due to their thermal lability. A third, less stable species was observed when 4 was allowed to react with 0.5 equivalent of CpTiCl₃. This reaction rapidly yielded a deep violet species which exhibited ¹H NMR signals at δ 8.68, 8.29 (A B

quartet, $J = 6.5$ Hz), 6.78, s, 6.07, s, and 5.84, s, which integrated 2:2:5:5:5, respectively. A very broad resonance (ca. 200 Hz) was observed centered at δ 6.0. No Cp_2TiCl_2 was detected. This species was tentatively assigned as $[\text{Cp}_2\text{Ti(IV)}] - \text{bis-}\mu\text{-CH}_2 - [\text{CpClTi(IV)}]$ (12) having two bridging methylenes between Cp_2Ti and CpTiCl centers. The color of this species and the position of the CH_2 resonances are very similar to that of the closely related 1. This species may arise as depicted in Scheme 5.

It was anticipated that Cp^*TiCl_3 would yield a more robust adduct than CpTiCl_3 . When 2 or 4 was allowed to react with Cp^*TiCl_3 , a rapid reaction occurred. A bright orange crystalline compound was isolated and exhibited ^1H NMR signals at δ 6.61 (s), 6.24 (s), and 1.87 (s) in the ratio of 2:10:15. ^{13}C NMR spectroscopy revealed a resonance at δ 220 (t, $J_{\text{C-H}} = 116$ Hz), in addition to Cp and Cp^* resonances. The infrared spectrum of this compound exhibited stretches at 2960 and 2920 cm^{-1} . This compound is formulated as $[\text{Cp}_2\text{ClTi(IV)} - \mu\text{-CH}_2 - [\text{Cp}^*\text{Cl}_2\text{Ti(IV)}]]$ (5) containing a bridging methylene between Cp_2TiCl and Cp^*TiCl_2 centers. Bright yellow-orange C_6D_6 or CD_2Cl_2 solutions of 5 darkened after 1 hr, and copious amounts of Cp_2TiMeCl and other unidentified Cp^* containing species were formed (^1H NMR).

5 reacted slowly with acetone to produce isobutylene in contrast to $\text{Cp}_2\text{TiCH}_2\text{AlMe}_2\text{Cl}$, which reacts very vigorously. 5 did not react with 3,3-dimethyl-1-butene in the presence of donor solvents such as pyridine or THF to yield $\text{Cp}_2\text{TiCH}_2\text{CH(t-Bu)CH}_2$. No chemical shift changes were observed in the ^1H NMR spectrum when pyridine,

Scheme 5



THF, or PEt_3 was added to solutions of $\underline{5}$.

The reaction of Cp^*TiCl_3 with $\text{Cp}_2\overline{\text{TiCH}_2\text{CH}(\text{t-Bu})\text{CH}_2}$ is slow at 50°C in C_6D_6 , and $\underline{5}$ decomposes under these conditions. No reaction occurs between $\underline{1}$ and Cp^*TiCl_3 at 60°C in C_6D_6 .

The compound $[\text{Cp}_2\text{ClTi(IV)}] - \mu - \text{CH}_2 - [\text{Cp}^*\text{Cl}_2\text{Zr(IV)}]$ ($\underline{6}$) was isolated as maroon crystals in a manner completely analogous to that employed for the isolation of $\underline{5}$. Deep maroon solutions of $\underline{6}$ are surprisingly much less thermally stable than $\underline{5}$. $\underline{6}$ is also far less soluble being nearly insoluble in C_6D_6 . This property suggests that $\underline{6}$ is oligomeric. CD_2Cl_2 solutions of $\underline{6}$ exhibit a ^1H NMR signal at $\delta 9.43$ along with other resonances assigned to the Cp and Cp^* ligands. $\underline{6}$ decomposes quite rapidly in CD_2Cl_2 at room temperature to yield an orange solution containing a large amount of Cp_2TiMeCl and other unidentified Cp^* containing products (^1H NMR). Addition of THF or PEt_3 to C_6D_6 suspensions of $\underline{6}$ does not solubilize the complex.

A wide variety of other reagents were tried as traps for the ' Cp_2TiCH_2 ' moiety. Among them were $(\text{PPh}_3)_3\text{RhCl}$, $\text{CpFe}(\text{CO})_2\text{I}$, Cp_2^*ScCl , Me_3SnCl , Me_2SnCl_2 , Me_3SiCl , and CH_3I . Cp_2^*ScCl , Me_3SiCl , and MeI did not react with $\underline{2}$ or $\underline{4}$. The dimer $\underline{1}$ was obtained in moderate yield from these mixtures. The product from the reaction of $\underline{4}$ with Me_3SnCl was isolated in good yield and was identified as $\text{Cp}_2\text{TiCH}_2\text{SnMe}_3(\text{Cl})$.¹⁵ Reaction with Me_2SnCl_2 yielded an analogous product.

Phosphines trap ' Cp_2TiCH_2 ' as the yellow compounds $\text{Cp}_2\text{Ti}(=\text{CH}_2)\text{PR}_3$. These compounds exhibit identical NMR spectra to complexes which Schwartz has generated in solution by reaction of $\text{Cp}_2\overline{\text{TiCH}_2\text{AlMe}_2\text{Cl}}$ with phosphines in the presence of hexamethylphosphoramide.¹⁶

2 reacted with 1 equiv. PEt_3 to produce an equilibrium mixture of 2 and $\text{Cp}_2\text{Ti}(=\text{CH}_2)\text{PEt}_3$ (9) in the ratio of ca. 5:95 (^1H NMR). Addition of 1 equivalent of PEt_3 to 4 resulted in an equilibrium mixture of 4 and 9 in the ratio of 70:30. Addition of 3,3-dimethyl-1-butene to either of these mixtures resulted in quantitative conversion to $\text{Cp}_2\text{Ti}\overline{\text{CH}_2\text{CH}(\text{t-Bu})\text{CH}_2}$.

A C_6D_6 solution of the phosphine methylene 9 decomposed slowly at room temperature to yield 1 in moderate yield (^1H NMR). In contrast to the decomposition of 2 in the absence of phosphines, methane and a significant amount of ethylene were also produced (GC, NMR).

The phosphine-methylene complexes were isolated as deep-yellow oils which when triturated with pentane gave fluffy yellow powders. In this manner $\text{Cp}_2\text{Ti}(=\text{CH}_2)\text{PMe}_2\text{Ph}$ (10) was isolated in good yield. The phosphine-methylene species have low-field CH_2 resonances at ca. δ 12.5 which are coupled to the phosphorous nuclei with $J_{\text{P-H}} = 6\text{-}7$ Hz, in agreement with Schwartz' observations.

Reaction of 1, 5, and 9 with CO.

A C_6D_6 solution of 1 was sealed under an atmosphere of CO in a NMR tube. A new set of resonances grew in at δ 5.71 (s), 3.73 (d, $J = 1.5$ Hz), and 3.65 (d, $J = 1.5$ Hz) which integrated 10:1:1. This product is tentatively assigned as bis- η^2 - μ -(0, C1)-OC=CH₂-bis-[Cp₂Ti(IV)] (8) (Fig. 2). 8 decomposed slowly (hours), until only $\text{Cp}_2\text{Ti}(\text{CO})_2$ was observed in 60% yield (^1H NMR). No other resonances were observed. Acidolysis of fresh or decomposed solutions with trifluoroacetic acid or anhydrous HCl produced several Cp-containing species (^1H NMR). No fragments which might have arisen from the

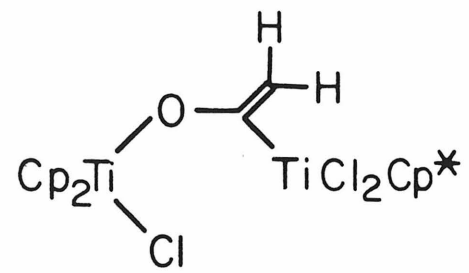
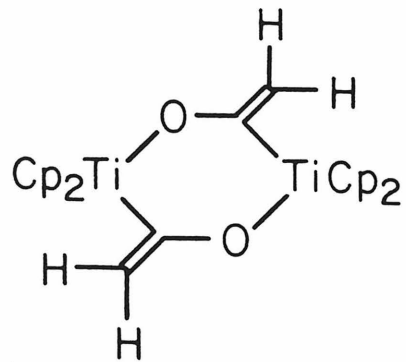
**7****8**

Fig. 2

μ -CH₂CO moiety were detected.

Reaction of CO with 5 produced a single product in 80-90% yield (¹H NMR) which is similar to 8. This new species is assigned as [Cp₂ClTi(IV)]- η^2 - μ -(0, C1)-OC=CH₂-[Cp*Cl₂Ti(IV)] (7) (Fig. 2) based on the following data. The ¹H NMR spectrum in CD₂Cl₂ at -20° C revealed two singlets at δ 4.69 and 4.30 which integrated to 1 proton each with respect to a 10 proton singlet at δ 6.41 and a 15 proton singlet at δ 2.25. The ¹³C spectrum of the same sample exhibited a double doublet (J = 10 Hz) at δ 215 along with another double doublet (J_{CH} = 155 Hz) at δ 132. These resonances are assigned as C1 and C2 of the μ -OC¹=C²H₂ moiety, respectively. An identical product is obtained upon reaction of Cp₂Ti(η^2 -CH₂CO)¹⁷ with Cp*TiCl₃.

Irradiation of the Cp* protons of 7 resulted in NOE enhancement of the downfield vinylic resonance at δ 4.69. Irradiation of the Cp protons did not result in any enhancement of either vinylic resonance. These NOE results suggest that the Cp₂Ti fragment is bonded to the oxygen of the OC¹=C²H₂ moiety, and the Cp*TiCl₂ fragment is bonded to C1.

Attempts to alkylate or hydrogenate 7 were unsuccessful.

1 and 5 reacted rapidly at low temperature with CH₃NC (1 equiv.) to yield products which did not exhibit interpretable ¹H NMR spectra.

Reaction of a maroon solution of 6 in CD₂Cl₂ with CO resulted in a rapid color change to deep orange. The ¹H NMR spectrum of this mixture revealed only broad resonances in the Cp and Cp* regions. No species analogous to 7 were identified.

Reaction of the phosphine-methylene complex 9 with CO yielded a mixture of products. The ^1H NMR spectrum of this mixture indicated that $\text{Cp}_2\text{Ti}(\text{CO})_2$ had been formed in ca. 30% yield. Another species with a Cp resonance at δ 5.66 (10H) and 2 singlets at δ 4.84 (1H) and δ 3.88 (1H) was identified as $\text{Cp}_2\text{Ti}(\text{CH}_2\text{CO})$ by direct comparison with the spectrum of an authentic sample.³⁰ This complex was present in 20% yield along with three or four other unidentified Cp-containing species.

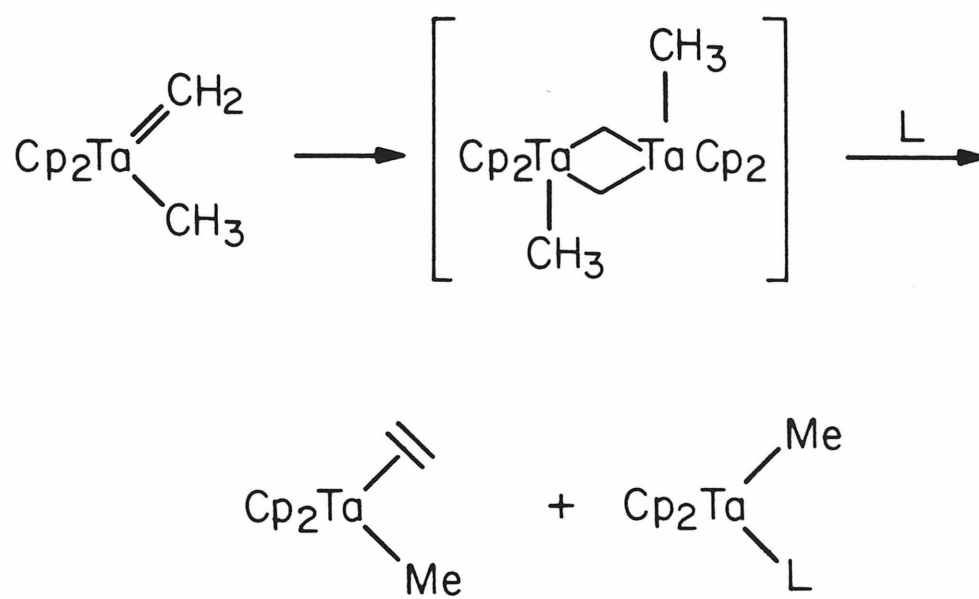
DISCUSSION

Physical and chemical characterization of $\underline{1}$ suggest that the compound is a bis- μ -methylene complex which arises from formal head to tail dimerization of two Cp_2TiCH_2 fragments. Steric and electronic factors favor a 1,3- rather than a 1,2-dititanacyclobutane in this system. The structure of $\underline{1}$ is very likely to be similar to the bis- μ - SiH_2 analogue $[\text{Cp}_2\text{TiSiH}_2]_2$, isolated from the reaction of Cp_2TiCl_2 with KSiH_3 and structurally characterized¹⁸ by X-ray analysis.

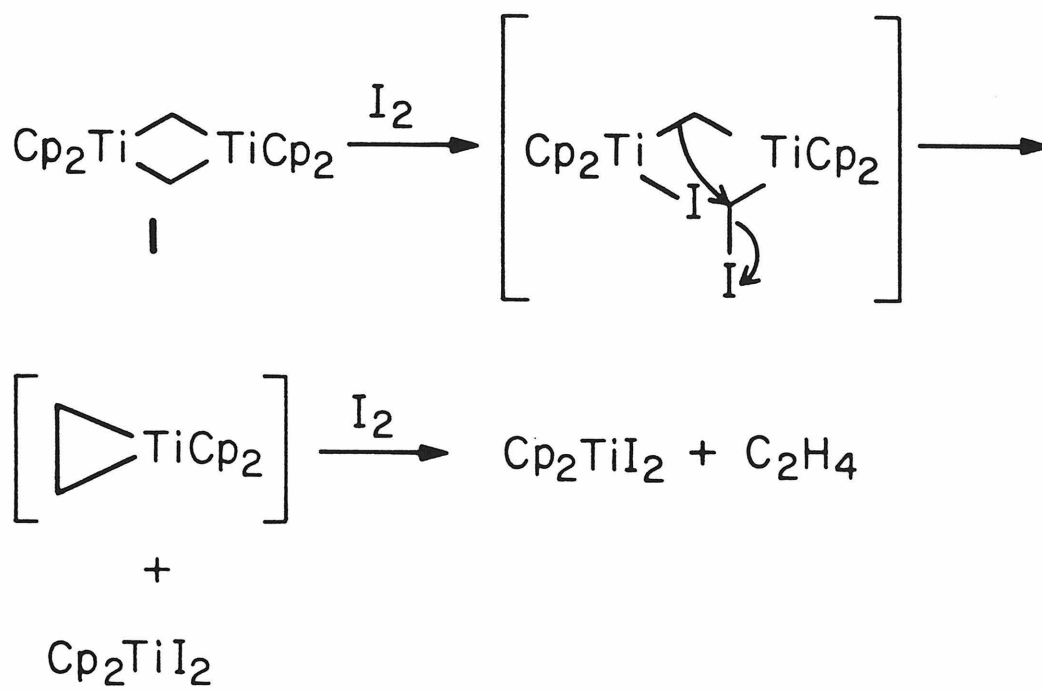
The ' Cp_2TiCH_2 ' dimerization is reminiscent of the thermal decomposition of $\text{Cp}_2\text{Ta}(\text{CH}_2)\text{Me}$ which yields $\text{Cp}_2\text{Ta}(\text{C}_2\text{H}_4)\text{Me}$ and $\text{Cp}_2\text{TaMe}(\text{L})$ in the presence of a trapping ligand L .^{4b} This reaction is postulated to proceed through a 1,3-ditantalacyclobutane (Scheme 2) which cleaves to yield the tantalum ethylene product. The titanium dimer $\underline{1}$ prefers not to thermally cleave to yield ethylene which would require the extrusion of the high energy Cp_2Ti fragment. When a reasonable leaving group is provided in place of Cp_2Ti , $\underline{1}$ does react to yield ethylene as the major decomposition gas. This is the case when $\underline{1}$ is allowed to react with I_2 yielding Cp_2TiI_2 and C_2H_4 . The course of this reaction is likely to be similar to that postulated for the reaction of titanacyclobutanes with I_2 to yield Cp_2TiI_2 and cyclopropanes (Scheme 3).¹⁹ The reaction of the titanacyclopropane intermediate with excess iodine would produce the observed ethylene and Cp_2TiI_2 .

Thermally, $\underline{1}$ does not incorporate deuterium from labelled terminal olefins. The decomposition of titanacyclobutanes to $\underline{1}$ therefore represents a chain termination reaction in this olefin metathesis system.

Scheme 2



Scheme 3



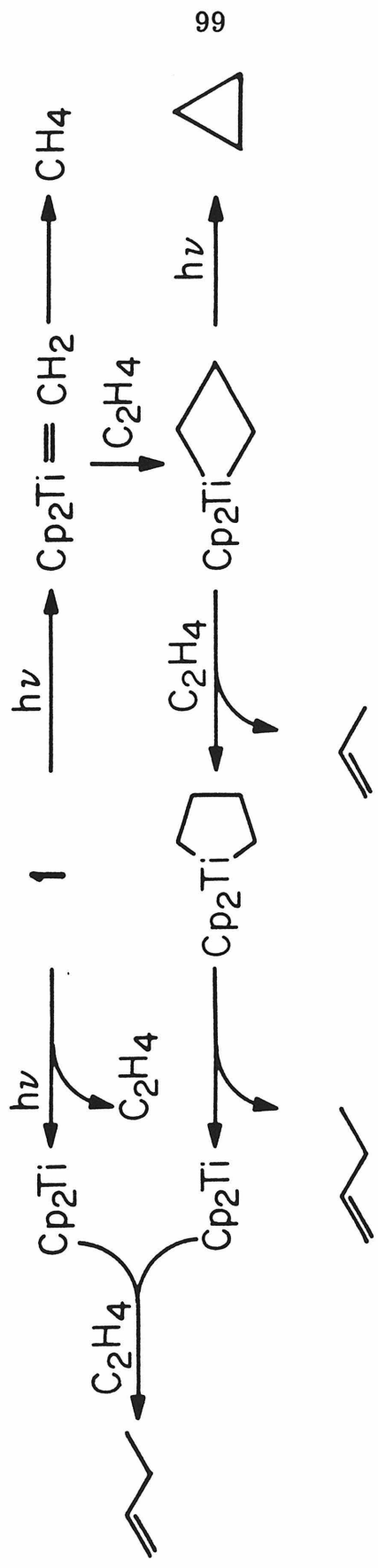
The mechanism by which $\underline{1}$ is formed (Path A or B, Scheme 1) could not be determined by examination of the kinetics. The crossover experiment designed to examine the deuterium incorporation into $\underline{1}$ failed due to instrumental limitations. Based on the chemistry of the titanacyclobutanes with ambiphilic reagents such as AlMe_2Cl , mechanism B appears more reasonable. The formation of $[\text{Cp}_2\text{TiCH}_2]_3$ also supports this mechanism. The lack of detectable crossover between $\underline{2}$ and $\underline{3-d}_2$ is due to a difference of 2-3 kcal-mol⁻¹ for metallacycle cleavage between the mono and β,β -disubstituted titanacyclobutanes.⁴⁹ Mechanism A, on the other hand, involves what appears to be a highly improbable event - the dimerization of two $\text{Cp}_2\text{Ti}=\text{CH}_2$ units which are in very low concentration. It is doubtful that the lifetime of $\text{Cp}_2\text{Ti}=\text{CH}_2$ is sufficient to achieve this trapping reaction.

The bis- μ -methylene $\underline{1}$ has been proposed to be an intermediate in the well studied, but poorly understood, photo- and thermal decomposition of Cp_2TiMe_2 .²⁰ Methane, traces of ethylene and ethane, and Cp_2Ti species are the only products of this decomposition. The proposed mechanism involves α -hydrogen abstraction by one methyl group, producing CH_4 and $\text{Cp}_2\text{Ti}=\text{CH}_2$. This fragment subsequently abstracts hydrogen from the Cp rings, or, as Rausch²⁰ suggested, dimerizes to $\underline{1}$, which then decomposes to yield methane and Cp_2Ti . Since decomposition of $\underline{1}$ produces significant amounts of ethane and ethylene photochemically or thermally, $\underline{1}$ can be ruled out as a possible intermediate in the decomposition of Cp_2TiMe_2 .

Photochemical decomposition of $\underline{1}$ produced a small amount of propylene. It was thought that the propylene could arise from the ethylene produced on decomposition inserting into a Ti-C bond of unreacted $\underline{1}$. This would give an $\eta^2\text{-}\mu\text{-(C1,C3)}$ -propyl species, which could then undergo β -hydrogen elimination to yield propylene. Such a transformation has been observed in an $\eta^2\text{-}\mu\text{-(C1,C3)}$ -propyl-dicobalt compound.²¹ A closer examination of the products formed when $\underline{1}$ was photolysed under an atmosphere of ethylene suggests that the propylene arose from cleavage of $\underline{1}$ to $\text{Cp}_2\text{Ti}=\text{CH}_2$. $\text{Cp}_2\text{Ti}=\text{CH}_2$ can be trapped with ethylene to yield $\text{Cp}_2\overline{\text{TiCH}_2\text{CH}_2\text{CH}_2}$ which is known to react further with ethylene, extruding propylene.¹³ A small amount of cyclopropane was observed which is also indicative of formation of a small amount of $\text{Cp}_2\overline{\text{TiCH}_2\text{CH}_2\text{CH}_2}$.²² The photodecomposition of $\underline{1}$ under ethylene produced significant amounts of 1-butene and butane. The C_4 products arise from catalytic dimerization of ethylene by Cp_2Ti ¹² which is formed by one of several pathways (Scheme 4). The intermediate metallacyclopentane was observed by ^1H NMR spectroscopy. β -Hydrogen elimination in the metallacyclopentane yields 1-butene and regenerates Cp_2Ti . All of the olefinic products are slowly hydrogenated to saturated hydrocarbons by Cp_2Ti .¹²

It was found that not only can ' Cp_2TiCH_2 ' dimerize (and perhaps trimerize), but it can also be trapped by a variety of ambiphilic reagents,⁵² and phosphines. The reaction of ' Cp_2TiCH_2 ' with an M-X (M = metal, metalloid; X = halide) bond very likely proceeds through a four-centered transition state. This is similar to the insertion of XCH_2ZnX into Si, Sn, Pb, Hg and Ge halide bonds to produce $\text{M-CH}_2\text{X}$.²³

Scheme 4



The compounds resulting from insertion of ' Cp_2TiCH_2 ' into Cp^*TiCl_3 , Cp^*ZrCl_3 , and Me_3SnCl were isolated. ' Cp_2TiCH_2 ' was not found to insert into Cp_2^*ScCl , probably due to the tremendous steric limitation imposed by the Cp^* ligands. ' Cp_2TiCH_2 ' was also not observed to insert into C-X and Si-X bonds, most likely due to the reluctance of silicon and particularly carbon to undergo frontside displacement in the proposed four-centered transition state.

' Cp_2TiCH_2 ' was also trapped as phosphine adducts which are analogous to the zirconium analogues reported by Schwartz.^{16b} The $\text{Cp}_2\text{Ti}(=\text{CH}_2)(\text{PR}_3)$ complexes react with olefins to yield equilibrium mixtures of titanacyclobutanes and the phosphine methylene complex. The position of equilibrium depends upon the steric natures of the olefin and probably the phosphine, with bulky olefins displacing the equilibrium towards the phosphine methylene complex.

The thermal decomposition of the phosphine methylene complexes produces 1 in moderate yields, and also produces a small amount of ethylene. Ethylene is not observed on decomposition of titanacyclobutanes,⁵¹ and therefore the phosphine must be affecting the mode of dimerization of the ' Cp_2TiCH_2 ' units. It is proposed that some of the time, the phosphine methylene complex dimerizes in a head-to-head arrangement to produce an $\eta^2-\mu-\text{C}_2\text{H}_4$ ligand which is readily lost as ethylene (Fig. 3). Such an arrangement is postulated to be responsible for the formation of ethylene from the reaction of Cp_2TiCl_2 with AlEt_3 .⁴⁸ The similar reaction of Cp_2ZrCl_2 with AlEt_3 yields a $\eta^2-\mu-\text{C}_2\text{H}_4$ complex which has been structurally characterized.

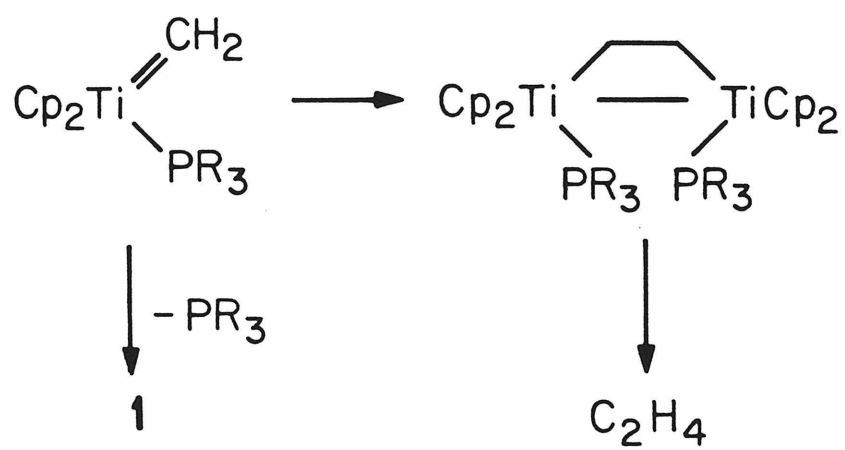


Fig. 3

Reactions of the Methylene Compounds with CO.

Reaction of the μ -methylene compounds bis- μ -CH₂-[Cp₂TiCH₂]₂ and [Cp₂TiCl]- μ -CH₂-[Cp^{*}TiCl₂] with CO resulted in the formation of unstable complexes described as having bis- or mono- bridging ketene (or as α -metalated enolate) ligands. These ligands are proposed to arise from the rearrangement of intermediate acyl complexes. Examples of migratory insertions of CO into metal carbon bonds to yield metal acyl complexes are well known for most d and some f transition elements.²⁵ Early transition metal acyls having fewer than 18 valence electrons and which are highly oxophilic²⁶ tend to exhibit η^2 -bonding of the acyl via interaction of the acyl oxygen lone pairs with the metal atom.²⁷ This η^2 -acyl bonding mode manifests itself in adding considerable carbene character to the metal-carbon bond.²⁸ These features result in rapid rearrangement of the intermediate η^2 -acyl to a bridging ketene as is illustrated for the reaction of 5 with CO (Scheme 6). A similar rearrangement has been observed for Cp₂^{*}Th(COCH₂TMS) (Cl),²⁹ which when heated rearranges to Cp₂^{*}ThCl(OC(TMS)=CH₂). Interestingly, only one of two possible products is observed when 5 is allowed to react with CO. Either CO preferentially coordinates and inserts into only one of the two possible Ti-C bonds, or insertion occurs at either Ti-C bond with one insertion being reversible. The 'hard' Lewis acid character of the Cp^{*}TiCl₂ center relative to the 'softer' Cp₂TiCl center would lead to preferential coordination and insertion of CO into the Cp₂Ti-C bond. This would result ultimately in the formation of the observed Cp₂Ti-O arrangement (Scheme 6).

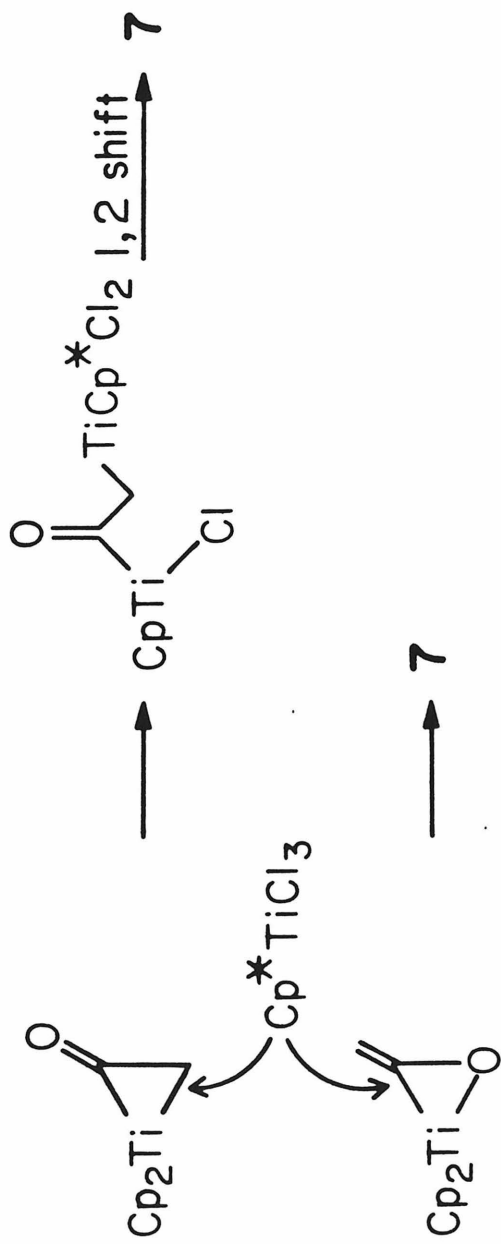
The insertion of Cp^*TiCl_3 into $\text{Cp}_2\text{Ti}(\eta^2\text{-OCCH}_2)$ also yields $\underline{7}$. The η^2 -ketene is thought to be in equilibrium via its O, C and C, C bound isomers.³⁰ Insertion of Cp^*TiCl_3 into the Ti-C bond of either isomer would result in $\underline{7}$ (Scheme 7).

The reaction chemistry of the μ -ketene (or α -metalated enolate) ligand remains undefined. Attempted alcoholysis, protonolysis, alkylation, and hydrogenolysis failed. Preliminary results indicate that $\underline{5}$ does react with ketones and aldehydes to give organometallic aldol condensation products.³¹

There is little direct evidence of CO insertion into other compounds containing bridging methylenes, even though most bridging methylenes known at present contain CO as ligands. Keim³² has reported that $\mu\text{-CH}_2\text{-Fe}_2(\text{CO})_8$ reacts to form methyl acetate in the presence of methanol via the postulated formation of an $\eta^2\text{-}\mu(\text{C1}, \text{C2})\text{-CH}_2\text{C=O}$ moiety. Shapley and Geoffroy³³ have characterized a triosmium cluster compound which contains a ketenylidene ligand. This compound arises from thermolysis of $\text{Os}_3(\text{CO})_{11}(\mu\text{-CH}_2)$ involving an apparent carbonylation of the μ -methylene ligand. A transformation which may involve the reverse of the reactions described above is the formation of $\mu\text{-CH}_2\text{-}\mu\text{-CO-}[\text{Cp}^*\text{Cr}]_2$ ³⁴ which was isolated from a mixture of CrCl_2 , Cp^*H , and the lithium enolate of acetaldehyde which was generated accidentally in situ from THF and $n\text{-BuLi}$. A $\mu\text{-CH}_2\text{CO}$ species may be involved in this reaction, which subsequently decarbonylates to yield the observed product.

Carbon monoxide was also observed to react with the terminal methylene phosphine complexes to give a low yield of $\text{Cp}_2\text{Ti}(\eta^2\text{-CH}_2\text{CO})$ ³⁰

Scheme 7



which arises from the coupling of the methylene with CO, apparently via an unobserved $\text{Cp}_2\text{Ti}(=\text{CH}_2)(\text{CO})$ complex. Similar CO insertions into terminal metal methylenes have been observed for the $\text{Mn}=\text{CPh}_2$,³⁵ $\text{Mo}\equiv\text{Mo}=\text{CPh}_2$,³⁶ $\text{Mn}(\text{anthronyl})$,³⁷ and $\text{W}(=\text{C}(\text{OMe})\text{Ph})$ ³⁸ complexes yielding coordinated or free ketenes.

The β,β -disubstituted titanacyclobutanes have been shown to be good sources of ' Cp_2TiCH_2 ' for the syntheses of $\mu\text{-CH}_2$ complexes, which are precursors of $\eta^2\text{-}\mu\text{-CH}_2\text{CO}$ complexes. Clearly, the potential for further study in this area exists.

The reactivity of ' Cp_2TiCH_2 ' with other electrophilic or ambiphilic organometallic reagents is yet to be explored. ' Cp_2TiCH_2 ' may provide interesting organometallic chemistry via reaction with organometallic substrates such as $\text{CpFe}(\text{CO})_2\text{CHR}^+$ or $\text{CpW}(\text{CO})_3(\text{C}_2\text{H}_4)^+$.

EXPERIMENTAL

2, 3-Dimethyl-1-butene-1, 1-d₂ and 3, 3-dimethyl-1-butene-1, 1-d₂ were prepared by carboalumination^{39, 41} of i-propylacetylene-d₁ and hydrozirconation^{40, 41} of t-butylacetylene-d₁, respectively, and dried over Linde 4Å molecular sieves.

The titanacyclobutanes $\text{Cp}_2\overline{\text{TiCH}_2\text{CMe(i-Pr)CH}_2}$ (2), $\text{Cp}_2\overline{\text{TiCH}_2\text{CMe(iPr)CD}_2}$ (2-d₂), $\text{Cp}_2\overline{\text{TiCH}_2\text{CMe}_2\text{CH}_2}$ (4), $\text{E-Cp}_2\overline{\text{TiCHDCD(t-Bu)CH}_2}$ (3-d₂), and $\text{Cp}_2\overline{\text{TiCH}_2\text{AlMe}_2\text{Cl}}$ were prepared as previously described.⁴¹

CpTiCl_3 ,⁴² Cp^*TiCl_3 ⁴³ and Cp^*ZrCl_3 ⁴⁴ were prepared by literature methods. Cp_2^*ScCl was a gift from Mr. M. E. Thompson. AlMe_2Cl (Texas Alkyls) was used as received.

Trifluoroacetic acid, acetone, methyl iodide and chlorotrimethylsilane were dried over 4Å molecular sieves prior to use. Ethylene, carbon monoxide, and hydrogen were used as received. Triethylphosphine and dimethylphenylphosphine (Strem) were used as received. Methyl isocyanide was a gift from Prof. J. E. Bercaw.

THF-d₈, C₆D₆, and toluene-d₈ were vacuum transferred from sodium-benzophenone ketyl. CD₂Cl₂ was stored over CaH₂ and degassed by several freeze-pump-thaw cycles.

Aromatic hydrocarbon solvents were pre-dried over CaH₂ and vacuum transferred onto sodium benzophenone ketyl. Aliphatic hydrocarbon solvents were stirred over concentrated H₂SO₄, dried over CaH₂, and vacuum transferred onto sodium benzophenone ketyl containing a small amount of tetraglyme. Solvents thus dried and deoxy-

generated were vacuum transferred into dry vessels equipped with teflon needle valve closures and stored under Ar.

General Procedures

All manipulations of air and/or moisture sensitive compounds were carried out using standard high vacuum, Schlenk line, and dry box techniques. Argon used in Schlenk work was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. NMR spectra were recorded with a Varian EM-390, JEOL FX-90Q, or Bruker WM-500. Kinetics by ^1H NMR spectroscopy were obtained in automated mode on the JEOL FX-90Q. Temperatures were calculated by measuring $\Delta\nu_{\text{MeOH}}^{45}$ and were constant to within $\pm 0.1^\circ\text{C}$. Difference NOE's were measured on the Bruker WM-500. Infrared spectra were obtained on a Beckman IR 4240 spectrophotometer.

Analyses were performed by Schwarzkopf Analytical, Inc. The molecular weight of $[\text{Cp}_2\text{TiCH}_2]_2$ was measured cryoscopically in C_6H_6 by a standard procedure, and also by Signer's method.⁴⁶

Preparation of bis- μ - CH_2 -bis(Cp_2TiIV) (1). A solution of $\text{Cp}_2\text{TiCH}_2\text{AlMe}_2\text{Cl}^{47}$ (1.0 g, 3.5 mmole) in CH_2Cl_2 (3 mL) was slowly added via cannula to a suspension of N,N-dimethylaminopyridine (472 mg, 3.9 mmole) and 2,3-dimethyl-1-butene (2 mL, 16.2 mmole) in CH_2Cl_2 (3 mL) at -20°C under Ar. The resulting homogeneous red solution was slowly added via cannula to 30 mL of vigorously stirred pentane at -20°C under Ar. The resulting DMAP- AlMe_2Cl precipitate was rapidly filtered. The solvent was removed from the resulting clear red filtrate in vacuo. The resulting red powder (2) was dissolved in

toluene (8 mL) at -10°C , and the solution was allowed to warm to room temperature. After standing at room temperature for 18 hr, the purple solution was slowly cooled to -10°C . The mother liquor was removed from the resulting purple platelets via cannula, and the crystalline mass was washed with cold toluene (1 mL) followed by n-hexane (3×3 mL). The purple crystals of 1 were dried in vacuo to yield 790 mg (59%). Calculated for $\text{TiC}_{11}\text{H}_{12}$: C, 68.77; H, 6.30. Found: C, 68.88; H, 6.55. ^1H NMR, C_6D_6 , shifts relative to $\text{C}_6\text{D}_5\text{H}$ at δ 7.15: δ 8.72 (CH_2), 6.22 (Cp). ^{13}C , CD_2Cl_2 , shifts relative to $\underline{\text{CD}_2\text{Cl}_2}$ at δ 53.8: δ 235.2, t, $J = 126$ Hz (CH_2), 112.2, d, $J = 174$ Hz (Cp). IR, C_6D_6 solution: 3100, (w, br), 2980, 2920 (m, sh), 1445 (w, br), 1020 (s, sh), 810 (w, br), 790 (s, br), 435 (s, sh). Molecular weight: Calculated for $[\text{Cp}_2\text{TiCH}_2]_2$ 384; found 396 ± 30 cryoscopic in C_6H_6 ; 427 ± 20 (Signer's method).⁴⁶ The visible spectrum exhibits a fairly intense, symmetrical absorption at 530 nm.

Reaction of 1 with AlMe_2Cl . AlMe_2Cl (20 μL , 0.2 mmole) was added via syringe to a solution of 1 (20 mg, 0.05 mmole) in C_6D_6 (400 μL) in a 5 mm NMR tube. The solution changed in color from purple to brown to green to red in about 15 seconds. ^1H NMR spectroscopy revealed that the reaction had proceeded cleanly to yield $\text{Cp}_2\overline{\text{TiCH}_2\text{AlMe}_2\text{Cl}}$ and a small amount of $\text{Cp}_2\overline{\text{TiCH}_2\text{AlMeClCl}}$.

Reaction of 1 with 3,3-Dimethyl-1-butene-1,1- d_2 . 3,3-dimethyl-1-butene-1,1- d_2 (2 μL , 0.02 mmole) was added via syringe to a solution of 1 (15 mg, 0.04 mmole) in C_6D_6 (400 μL). The mixture was monitored by ^1H NMR spectroscopy. After 2 days at 55°C , no 3,3-dimethyl-1-

butene-d₂ was detected, and the CH₂ to Cp ratio of 1 was 2 : 10.

Protonolysis of 1. A sample of 1 (1.7 mg, 0.044 mmole) was placed into solution with 400 μL C₆D₆ in an NMR tube. The sample tube was capped with a septum, and removed from the dry box. The sample was cooled to -78° C, and trifluoroacetic acid (4 μL, 0.052 mmole) was added via syringe. The sample was agitated while maintained below -50° C. The ¹H NMR spectrum at -30° C indicated that Cp₂TiMe₂, Cp₂TiMe(TFA), and Cp₂Ti(TFA)₂⁹ were formed in the ratio of 1 : 1.1 : 1.7. Excess 1 was also observed.

Thermolysis of 1. A toluene-d₈ solution of 1 (10 mg in 400 μL) was prepared in an NMR tube and sealed. The sample was placed in a bath maintained at 100° C for 12 hr. At this point ¹H NMR spectroscopy indicated that a trace of 1 remained. Two other signals were observed at δ 0.79 (C₂H₆) and δ 0.15 (CH₄). The tube was opened under N₂, and a sample for gas chromatography was withdrawn. GC analysis (Poropak Q, 6', 110° C, FID) indicated that the gas phase contained a mixture of CH₄ (92%), C₂H₆ (8%), and a trace (< 0.2%) of C₂H₄.

Reaction of 1 with Acetone. A (CD₃)₂CO solution of 1 (12 mg in 400 μL) was prepared in an NMR tube, and the tube was sealed. There was no apparent reaction after 15 min at ambient temperature as judged by ¹H NMR spectroscopy. The sample was then heated to 40° C for 35 min. No appreciable reaction had occurred at this time. After heating to 50° C for 15 min, some isobutylene was detected (δ 4.68). After 12 hr at 50° C, reaction had occurred to yield pale green solids and a pale yellow solution. Broad signals were observed in the ¹H NMR spectrum.

GC indicated that the gas phase contained CH_4 (93%), C_2H_6 (1%), isobutylene (5%) and C_2H_4 (trace).

Photolysis of $\underline{1}$. A solution of $\underline{1}$ (12 mg) in C_6D_6 (400 μL) was prepared in a pyrex NMR tube and the tube was sealed. The sample was placed in a photolysis well (Hanovia 450 W medium pressure Hg lamp) approximately 20 mm from the source. The sample was maintained at below 30°C during photolysis. After 12 hr of photolysis, the solution was purplish black, and ^1H NMR spectroscopy indicated most of $\underline{1}$ had decomposed. The tube was opened under an N_2 atmosphere, and a gas sample was withdrawn. GC of the gases indicated a mixture of CH_4 (16%), C_2H_4 (3%), C_2H_6 (80%), and C_3H_8 (1%).

Photolysis of $\underline{1}$ in the Presence of C_2H_4 . An NMR tube was loaded with $\underline{1}$ (15 mg). An 'O'-ring adapter and reflon needle valve adapter were attached to the NMR tube, and the tube was removed to the vacuum line. C_6D_6 was vacuum transferred into the tube at -78°C . The tube was vented to 700 mm Hg of C_2H_4 and sealed. The sample was placed in the photolysis well ca. 20 mm from the source. The sample was maintained at 18°C during photolysis. After 10 hr of photolysis, the sample was removed. ^1H NMR spectroscopy indicated that most of $\underline{1}$ had decomposed. A peak at δ 5.89 had grown in along with 2 broad multiplets at δ 1.88 and δ 1.28 and integrated ca. 10:4:4. An intense singlet at δ 0.79 (C_2H_6), a smaller singlet at δ 0.15 (CH_4), and a broad peak at δ 4.64 (C_2H_4) was observed. After 30 hr of photolysis, the peaks at δ 5.89, δ 1.88, δ 1.28, and δ 4.64 had disappeared, while the singlets at δ 0.79 (C_2H_6) and δ 0.15 (CH_4) remained. The

solution was greenish-black in color. The tube was opened, and a gas sample was withdrawn. GC analysis indicated that the gas was a mixture of CH_4 (9%), C_2H_4 (<1%), C_2H_6 (53%), C_3H_8 , C_3H_6 (<1%), C_4H_8 (10%), and C_4H_{10} (27%), along with a trace of cyclopropane.

Reaction of $\underline{1}$ with Iodine. A C_6D_6 solution of $\underline{1}$ (12 mg in 400 μL) was prepared in an NMR tube. The tube was capped with a latex septum and removed from the box. A saturated solution of I_2 (sublimed) in 20 μL C_6D_6 was added to the sample. An immediate reaction occurred, and dark solids precipitated. ^1H NMR spectroscopy indicated that Cp_2TiI_2 had been formed (δ 6.03) along with C_2H_4 (δ 5.24) and CH_4 (δ 0.15). GC of the gas phase indicated that CH_4 (22%) and C_2H_4 (78%) were present.

Generation of $\underline{1-d_{0,2,4}}$ Followed by Reaction with Iodine.

A 10 mL round-bottom flask was loaded with a stirbar and $\underline{2-d_2}$ (20 mg, 0.072 mmole) and attached to a teflon needle valve adapter. Approximately 1 mL of p-xylene was vacuum transferred onto the titanacyclobutane at -20° . The reaction vessel was opened to a cold trap to remove the olefin as it was formed, and the sample was warmed to room temperature. The p-xylene was replenished at regular intervals. The reaction was allowed to proceed for 3.5 hr. The p-xylene was then removed in vacuo. The purple residue was dissolved in C_6D_6 . ^1H NMR spectroscopy indicated the presence of $\underline{1}$. No titanacyclobutane remained. A saturated C_6D_6 solution of I_2 (200 μL) was added to the NMR sample. ^1H NMR indicated that ethylene had been formed. GC/MS of the gas phase revealed the following mass spectrum for the ethylenes: Measured mass (% intensity base) 33 (0.3), 32 (21.4),

31 (3.1), 30 (74.0), 29 (29.9), 28 (100.0), 27 (66.2), 26 (47.7), 25 (8.9), 24 (3.9). Several sample injections were made and gave widely varying relative intensities at the high and low ends of the mass envelope.

Reaction of 2 with E-Cp₂TiCHDCD(t-Bu)CH₂ (3-d₂). An NMR tube was loaded with 2 (20 mg, 0.072 mmole) and 3-d₂ (20 mg, 0.072 mmole). C₆H₆ was vacuum transferred into the NMR tube at -78° C, and the tube was sealed. The sample was shaken vigorously as the solvent thawed. The sample was allowed to react at room temperature for 2 hr. ²H NMR spectroscopy revealed that no 1-d₁ was formed, and that approximately 5% at Z-3-d₂ had formed from the remaining E-3-d₂.

Kinetics of the Reaction of 2 to Form 1. An NMR tube was loaded with 2 (20 mg, 0.072 mmole) and capped with a latex septum. Toluene-d₈ was slowly added to the chilled (-50° C) NMR tube, and dissolved at that temperature. Anisole (1 μL) was then added as an internal standard. The sample was placed in an NMR probe at 23° C. The rate of reaction was monitored by comparison of the Cp resonances of 2 versus the anisole methyl resonance. First-order plots were linear to three half-lives, and the slope yielded the first-order rate constant $k = 5 \times 10^{-4} \text{ s}^{-1}$.

Preparation of μ-CH₂-[Cp₂TiCl][Cp*TiCl₂] (5). A small Schlenk tube was loaded with Cp₂TiCH₂CMe₂CH₂ (4) (200 mg, 0.81 mmole) and Cp*TiCl₃ (233 mg, 0.81 mmole). The reaction vessel was cooled to -20° C, and toluene (4 mL) was added slowly. The reaction mixture was warmed to 0° C while stirring. Approximately 30 min were required for complete dissolution of the Cp*TiCl₃. After stirring the mixture for

1 hr at 0° C, the dark yellow-orange solution was warmed to room temperature. Pentane (10 mL) was added slowly to the stirred toluene solution to precipitate red-orange crystalline 5. This material was washed with a small amount of cold toluene followed by pentane (3 × 1 mL). The red-orange crystals were dried in vacuo to yield 210-310 mg (54-80%). This material may be further purified by recrystallization from CH₂Cl₂/petroleum ether mixtures as orange cubic crystals. ¹H NMR, C₆D₆, shifts relative to C₆D₅H at δ 7.15: δ 6.61, s (CH₂), 6.24, s (Cp), δ 1.87, s (Cp*). ¹³C, C₆D₆, shifts relative to C₆D₆ at δ 128.0, gated decoupled: δ 219.6, t, J = 116 Hz (CH₂), 129.6, s (C₅Me₅), 117.0, d, J = 164 Hz (Cp), 13.4, q, J = 127 Hz (C₅Me₅). IR, CH₂Cl₂ solution (cm⁻¹): 2960, 2920 (m, sh), 1485, 1445 (m, sh), 1380 (s, sh), 1020 (s, sh), 825 (vs, sh), 770 (m, br), 465 (w, sh), 415 (m, br). Attempted elemental analysis gave unsatisfactory results. Calculated for C₂₁H₂₇Ti₂Cl₃: C, 52.38; H, 5.65; Cl, 22.08; Ti, 19.89. Found: C, 43.34; H, 4.38; Cl, 19.71; Ti, 19.55.

Preparation of μ -CH₂-[Cp₂TiCl][Cp*ZrCl₂] (6). 4 (200 mg, 0.81 mmole) and Cp*ZrCl₃ (300 mg, 0.9 mmole) were allowed to react at 0° C in toluene (6 mL) for 1 hr. The resulting maroon microcrystalline powder was filtered and washed repeatedly with cold toluene. The solids were dried in vacuo to yield 260 mg (61%) of 6. This material was too insoluble in C₆D₆ to obtain a ¹H NMR spectrum. It is somewhat soluble in CD₂Cl₂ and THF-d₈, but decomposed fairly rapidly to yield Cp₂TiMeCl and unidentified Cp* containing products (¹H NMR). ¹H NMR, CD₂Cl₂, shifts relative to CH₂DCl₂ at δ 5.32: δ 9.43, s (CH₂), 6.33,

s (Cp), 2.07, s (Cp^{*}). The material from above was dissolved in CH₂Cl₂ (8 mL) at 0° C, filtered, concentrated to ca. 2 mL, and cooled to -50° C. Maroon crystals deposited from the orange solution. The crystals were washed with cold toluene and dried in vacuo to yield 25 mg (5%). Calculated for C₂₁H₂₇Cl₃TiZr: C, 48.05; H, 5.18. Found: C, 48.07; H, 5.07. IR, fluorolube mull, (cm⁻¹): 3110 (w, sh), 2980, 2960 (m, sh), 2800 (m, sh), 1480 (m, sh), 1430 (s, br), 1380 (s, sh).

Reactions of 1, 5 and 6. The reactivity of 5 and 6 was investigated using NMR tube scale reactions. A typical reaction with CO is described here. A 5 mm NMR tube was loaded with 5 (10 mg, 0.021 mmole). O-ring and needle valve adapters were attached to the tube. A deuterated solvent was vacuum transferred into the tube at -196° C. The tube was vented to 300 torr CO, and the tube sealed. The compound [Cp₂ClTi(IV)]-η²-μ-(0, C1)-OC=CH₂-[Cp^{*}Cl₂Ti(IV)] (7) was formed when the tube was shaken briefly at room temperature.

¹H NMR 7, CD₂Cl₂, shifts relative to CHDCl₂ at δ 5.32: δ 6.41, s (Cp's), 4.69 (A), 4.30 (B), 2s (C=CH_AH_B), 2.25, s (Cp^{*}); in C₇D₈, -20° C, shifts relative to C₇D₇H at δ 2.09: δ 6.17, s (Cp's), 4.89, 4.82, 2s (C=CH_AH_B), 1.99, s (Cp^{*}). ¹³C gated decoupled, -20° C, CD₂Cl₂, shifts relative to CD₂Cl₂ at δ 53.8: 215.1, dd, J = 10 Hz (C=CH_AH_B), 132.1, dd, J = 155 Hz (C=CH_AH_B), 117.1, d of m, J = 177 Hz (Cp's), 107.3, br s (C₅Me₅), 13.0, q, J = 127 Hz (C₅Me₅). Difference ¹H NOE spectroscopy, CD₂Cl₂, -20° C: Irradiation of the Cp^{*} resonance enhanced the downfield vinylic resonance at δ 4.69. Irradiation of the Cp resonance resulted in no enhancement of either resonance.

Reaction of 1 with CO. Following the procedure described above, 1 was reacted with an excess of CO. A set of resonances assigned to bis- η^2 - μ -(0, C1)-OC=CH₂-bis[Cp₂Ti(IV)] (8) were observed. ¹H NMR, C₆D₆, shifts relative to C₆D₅H at δ 7.15: δ 5.71, s (Cp's), 3.73, d, J = 1.5 Hz, 3.65, d, J = 1.5 Hz (C=CH_AH_B) integrating 10:1:1, respectively. Copious amounts of Cp₂Ti(CO)₂ were also observed (δ 4.57, Cp's).

Reaction of 2 and 4 with PEt₃. A NMR tube was loaded with 2 (12 mg, 0.043 mmole). The tube was capped with a latex septum. The tube was cooled to 0° C, and C₆D₆ was added slowly. PEt₃ (7 μ L, 0.047 mmole) was added by syringe. The sample was shaken vigorously at room temperature. The reaction was monitored by ¹H NMR spectroscopy. After 10 min, the reaction had reached equilibrium, and Cp₂Ti(CH₂)PEt₃ (9) and 2 were observed in the ratio of ca. 95:5. The solution had changed from pinkish-red to yellow. ¹H NMR, 9, C₆D₆, shifts relative to C₆D₅H at δ 7.15: δ 12.19, d, J = 5.9 Hz (CH₂), 5.37, d, J = 2 Hz (Cp's), 1.4-1.05, m (PEt₃).

Reaction of 4 with PEt₃ (ca. 1:1) resulted in an equilibrium mixture of 4 and 9 in a ratio of 70:30.

Preparation of Cp₂Ti(CH₂)PMe₂Ph (10). A small Schlenk tube was loaded with 4 (200 mg, 0.81 mmole). The vessel was cooled to 0° C and toluene (6 mL) was added via syringe. PMe₂Ph (120 mg, 0.87 mmole) was added via syringe. The vessel was then partially evacuated and opened to a cold trap to remove the isobutylene produced. The reaction mixture was allowed to warm to room temperature. After

stirring for 15 min, the volatiles were removed to yield a deep yellow oil. The oil was triturated with pentane (3 mL) to yield a yellow powder which was washed repeatedly with pentane. The yellow solids were dried in vacuo to yield 220 mg of 10 (83%). ^1H NMR, C_6D_6 , shifts relative to $\text{C}_6\text{D}_5\text{H}$ at δ 7.15: δ 12.34, d, $J_{\text{P-H}} = 6.8$ Hz (CH_2), 7.08, s (PMe_2Ph), 5.38, d, $J = 1.5$ Hz, (Cp's), 1.11, d, $J = 5.9$ Hz (PMe_2Ph). This material was estimated to be greater than 90% pure by ^1H NMR spectroscopy.

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