Synthesis and Reactivity of Bis(cyclopentadienyl)titanacyclobutanes and Ketene Complexes of Bis(cyclopentadienyl)titanium and Bis(cyclopentadienyl)zirconium

Thesis by

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To Mom, Dad

and Paul

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ABSTRACT

The synthesis of several titanacyclobutanes of the types $Cp_2\overline{TiCH_2CR_2CH_2}$ and $Cp_2\overline{TiCHRCHRCH_2}$ (Cp = η^5-C_5H_5, R = alkyl) is described. The stability of several of these, as well as some metallacycles of the type $Cp_2\overline{TiCH_2CHRCH_2}$, has been measured and is discussed in terms of the structure of these species. The reaction of some titanacyclobutanes with dimethylaluminum chloride in the presence of diethyl ether and tetrahydrofuran was investigated, and is discussed in terms of a scheme for olefin metathesis involving an aluminum co-catalyst. The thermolysis, acidolysis and reactions with bromine and iodine have been studied for a number of these metallacycles. The mechanism of the reaction with iodine is considered in some detail.

Titanacyclobutanes of the type $Cp_2\overline{TiCH_2CHRCH_2}$ and $Cp_2\overline{TiCH_2CR_2CH_2}$ are known to catalyze degenerate metathesis of terminal olefins. The activity of the titanacyclobutanes in non-degenerate olefin metathesis has been investigated here. The titanacyclobutanes have been found to metathesize cis- and trans-2,8-decadiene with some stereospecificity. This process is very inefficient and the reasons for this are discussed in terms of the stability and reactivity of various titanacyclobutanes, which model presumed intermediates in this reaction.

The carbonylation of several titanacyclobutanes has been examined in detail and leads to insertion of two molecules of carbon monoxide to produce cyclic enediolate products in all cases when carbon monoxide is present in excess. Acidolysis and oxidation of these enediolates affords

2-hydroxycyclopentanones and 1,2-cyclopentanediones, respectively. Under conditions where the carbon monoxide concentration is limited, cyclobutanones and titanocene dicarbonyl are formed. A mechanism which explains these observations is presented. Carbon monoxide insertion has been found to proceed with retention of stereochemistry at migrating carbon.

Ketene complexes have been prepared by treatment of chloro and bromo acyl complexes of titanocene, zirconocene and decamethylzirconocene with strong bases. In this manner $(Cp_2Ti(OCCH_2))_n$, $(Cp_2Zr|OCCHC(CH_3)_3|)_2$ and $(\eta^5\text{-}C_5Me_5)_2Zr(OCCH_2)(C_5H_5N)$ have been synthesized. The reactivity of these complexes with hydrochloric acid, hydrogen, ethylene and acetylene is discussed. Reaction of $Cp_2Zr(COCH_3)CH_3$ with CH_2PPh_3 gives the enolate complex $Cp_2Zr(OC(CH_2)CH_3)CH_3$ and PPh_3. Reaction of $Cp_2Zr(COCH_3)CH_3$ with $NaN(TMS)_2$ gives the anion $Cp_2Zr(COCH_2)CH_3^-$, which is alkylated with methyl iodide to produce $Cp_2Zr(COCH_2CH_3)CH_3$.

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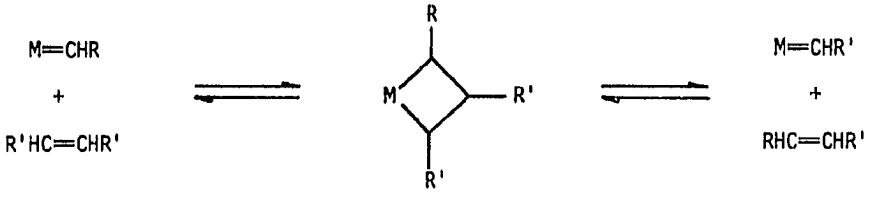
CHAPTER 1

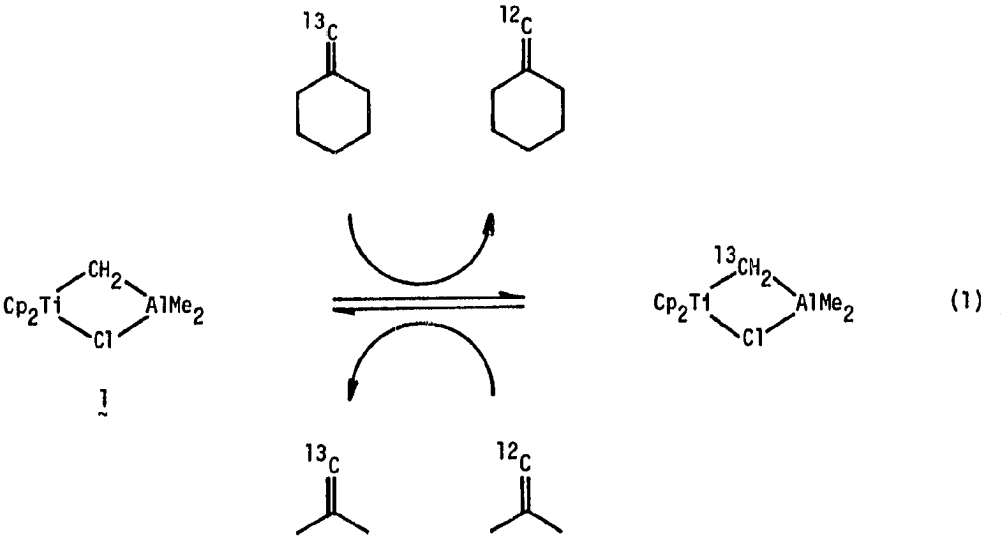
Synthesis, Stability, Structure and Reactivity of Bis(cyclopentadienyl)titanacyclobutanes and their Olefin Metathesis Activity

Introduction

The mechanism of the olefin metathesis reaction has been a subject of considerable research and much controversy over the last fifteen years.[1] The currently accepted mechanism, first proposed by Chauvin,[2] involves exchange of alkylidene units between metal alkylidene complexes and olefins via metallacyclobutane intermediates. Labeling studies provided strong support[3] for this "non-pairwise" exchange process. Recently, metal alkylidene

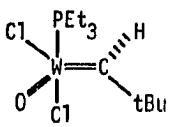


catalysts have been prepared which may be recovered from reaction mixtures with a fragment of the metathesized olefin incorporated. The first such complex was the masked carbene **1**, described by Parshall and Tebbe, which slowly incorporates the methylene unit of 2,2-disubstituted olefins (eq. 1).[4]



(1)

Schrock and co-workers have reported the tungsten oxo-carbene **2**, which was found to catalyze metathesis of terminal and internal olefins at a higher rate than **1**, but far more slowly than commercial systems.[5] Osborn and co-workers have recently prepared highly active tungsten carbene catalysts, such as **3**, which are capable of turnover rates of 3000 min^{-1}.[6]



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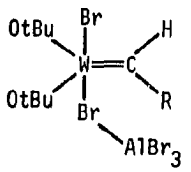
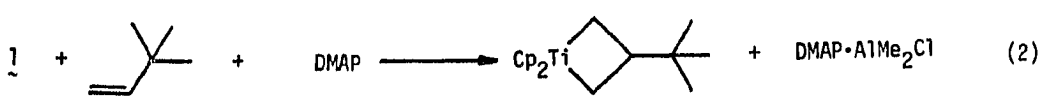


3

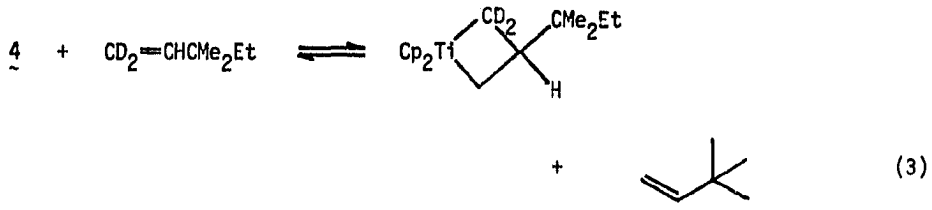
Examples of metallacyclobutanes which undergo the required reactions have only recently been found. The number of metallacyclobutanes reported is small, due to lack of a suitable method for preparation of 1,3-dilithio and di-Grignard precursors.[7] Those which have been prepared are limited to Pt,[8,9] Mo, W,[10] Ru[11] and Fe.[12] None of these have been found to exhibit metathesis activity. Tebbe and Harlow have prepared bis(cyclopentadienyl)-titanacyclobutenes which exchange methylene units with terminal olefins and exchange acetylene fragments with free acetylene.[13] The bis(cyclopentadienyl)titanacyclobutanes, which had been suggested[4,13] as intermediates in olefin metathesis involving titanacyclobutenes and **1**, have been isolated in our laboratory (eq. 2).[14] Monosubstituted titanacycles, such as **4**, has been found to undergo slow exchange with α-olefins (eq. 3).[14-17] The reactivity of these metallacycles is markedly dependent on the substituents.



(2)

4

DMAP = 4-dimethylamino pyridine



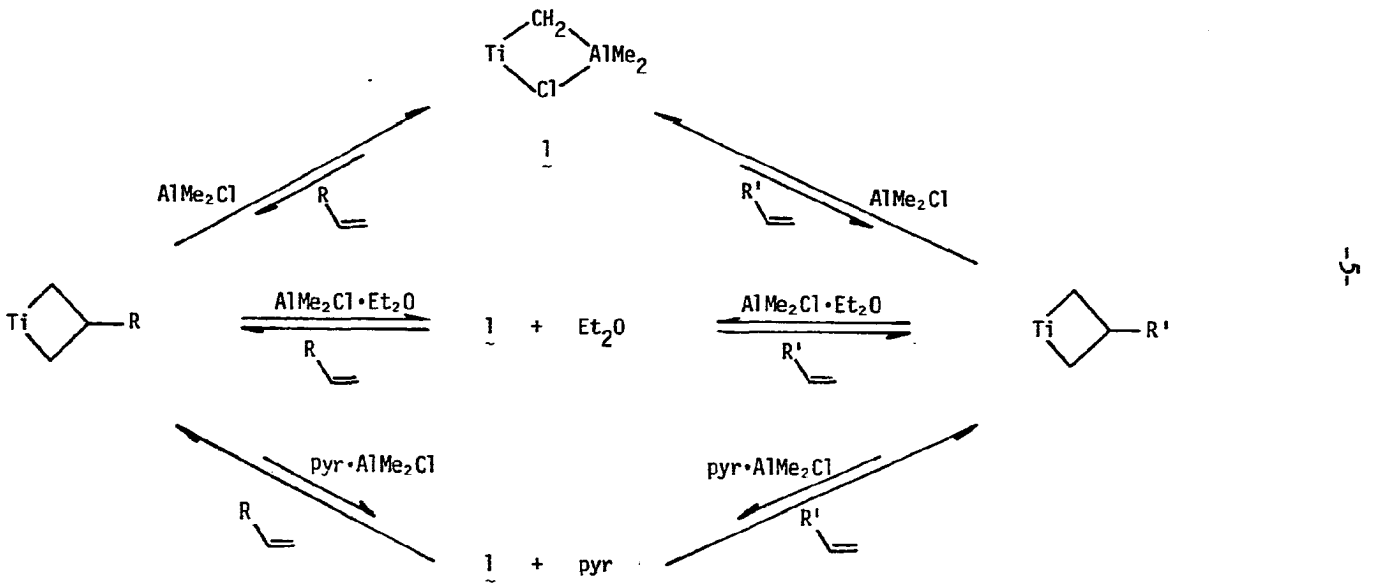
(3)

Results and Discussion

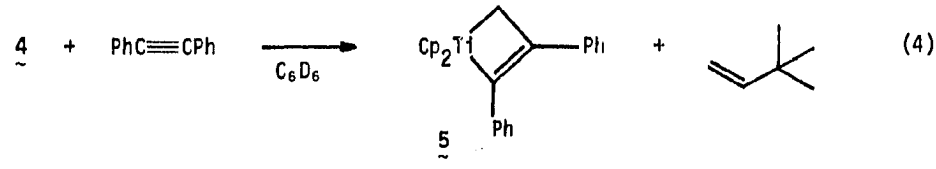
Although bis(cyclopentadienyl)titanacyclobutanes will catalyze metathesis in the absence of a co-catalyst (eq. 3), there remained the question of whether turnover rates would be increased by the presence of a Lewis acid co-catalyst. Rate enhancement might be expected because aluminum alkyl species function as co-catalysts in many highly active non-supported metathesis systems.[18] Those paths which would have to be competitive with direct exchange (e.g., eq. 3) for an increased turnover rate to be realized are illustrated in Scheme I. First, introduction of $AlMe_2Cl$ alone leads to rapid and complete conversion of titanacycle to **1** , which is an inefficient catalyst. On the other hand, addition of strong bases for aluminum,[19] such as pyridine, would deplete the system of **1**, and direct exchange would predominate. Between these extremes, use of a weaker base, such as Et_2O or THF, in conjunction with $AlMe_2Cl$, might allow rapid formation of a significant concentration of **1** and labilize **1** for subsequent metallacycle formation. With the proper choice of base, the aluminum-mediated exchange depicted in Scheme I might compete favorably with the direct reaction. Such an aluminum-assisted exchange was proposed by Tebbe to account for his observation[13a] that the metathesis of **1** is greatly accelerated by ethers, with THF having a greater effect than Et_2O.[20]

To test for acceleration of metathesis by various co-catalysts in the

Scheme I

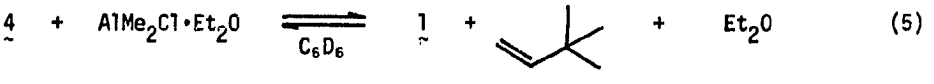

CH2
Ti
AlMe2
Cl
1
AlMe2Cl
R
R'
AlMe2Cl
Ti
R
AlMe2Cl·Et2O
1 + Et2O
AlMe2Cl·Et2O
Ti
R'
R
R'
pyr·AlMe2Cl
pyr·AlMe2Cl
R
R'
1 + pyr

titanacyclobutane system, we chose to study the exchange of diphenylacetylene for neohexene shown in equation 4. The reaction proceeds to completion and formation of 5[13] is conveniently monitored by NMR.[14,15] It was found that the presence of 0.2-0.3 equivalent of $AlMe_2Cl \cdot Et_2O$, $AlMe_2Cl \cdot THF$

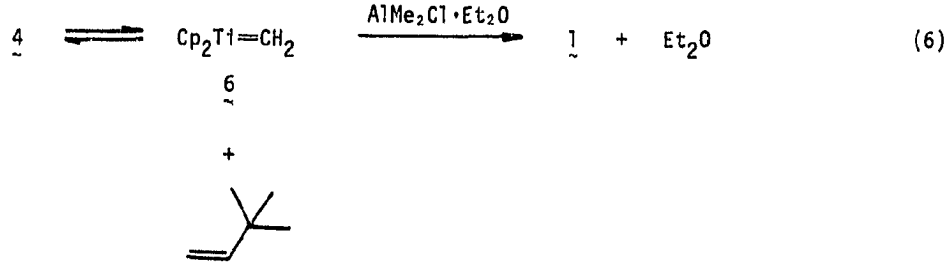


or $AlMe_2Cl \cdot pyr$ produced no significant change in the rate of reaction of 4 with a three- to fourfold excess of diphenylacetylene. The reaction is first order in 4 and proceeds with a rate of 6×10^{-6} s^{-1} at ca. 22°C. Addition of even 2 equivalents of $AlMe_2Cl \cdot THF$ did not alter this exchange rate. Rapid reaction of $AlMe_2Cl$ with 4 led to production of 1 in the absence of bases. In the $AlMe_2Cl \cdot THF$ and $AlMe_2Cl \cdot pyr$ samples, no 1 was detected. However, with 0.3 equivalent $AlMe_2Cl \cdot Et_2O$ present, a small amount of 1 was slowly formed.

The equilibrium shown in the center path of Scheme I was verified by reaction of 4 with 1.0 equivalent of $AlMe_2Cl \cdot Et_2O$ in the absence of diphenylacetylene. The equilibrium (eq. 5) may be approached from either



direction. Measurement of the rate of reaction of 4 with 1.0 and 3.0 equivalents of $AlMe_2Cl \cdot Et_2O$ at low conversion revealed that the reaction is cleanly first order in 4 with k = 9.5 (± 0.6) x 10^{-5} s^{-1} (40°C, C_6D_6). This is the same as the rate of direct exchange (eq. 4),[21] which accounts for the failure of these base-aluminum adducts as co-catalysts. The rate is consistent with rate-determining formation of titanium methylidene 6 (eq. 6).[22] Involvement of free $AlMe_2Cl$ was excluded by the observation that

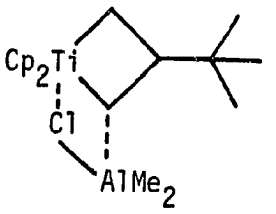


(6)

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

Observation of first-order kinetics for reaction of 4 with $AlMe_2Cl \cdot Et_2O$ and with $AlMe_2Cl \cdot THF$ contrasts with the reaction of 4 with $AlMe_2Cl$, which is second order (first order in each reactant).[23] This suggests that an open coordination site on aluminum is required for direct

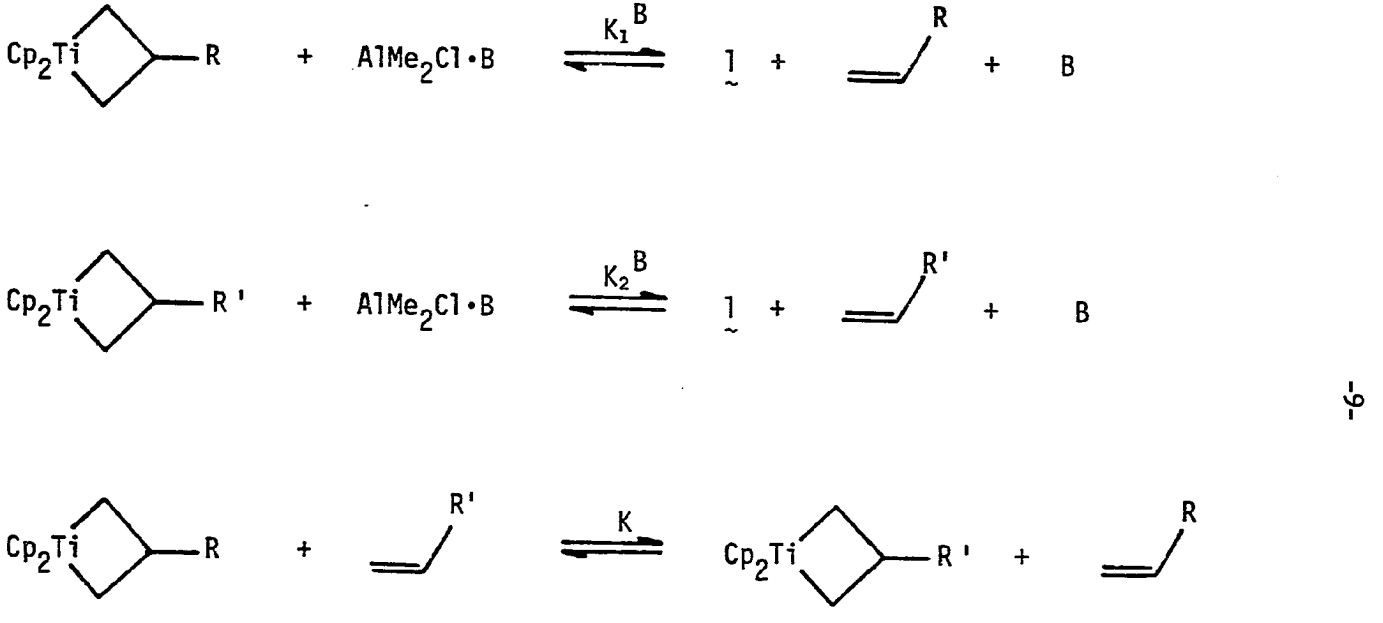
reaction with **4**, and the initial interaction between **4** and $AlMe_2Cl$ may be as depicted below. This is identical with the transition state originally formulated by Tebbe.[4a] The importance of the Cl bridge is implicated by the slower reaction of **4** with $AlMe_3$.[24]



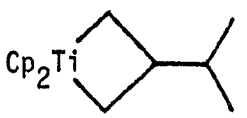
Although the experiments described above have not led to a means of increasing the turnover rate in metathesis reactions of bis(cyclopentadienyl)-titanacyclobutanes, equilibria such as equation 5 have enabled us to measure the relative stabilities of a series of these catalysts. Measurement of the equilibrium constant for a reaction such as equation 3 (direct olefin exchange) would be difficult because of overlapping NMR resonances of the reaction partners. Indirect measurement (Scheme II) provided an accurate method for determining the stability of titanacyclobutanes relative to the olefin from which each is formed. Use of various bases extends the range of species to which this approach may be applied.

Initial experiments were performed using the metallacycles which had been isolated and characterized at that time, those derived from neohexene (**4**), 3-methyl-1-butene (**7**) and cyclopentene (**8**). Diethyl ether was found to be a suitable base for measurement of equilibria involving **4**, **7** and **8**. These and all other equilibrium measurements were carried out at 40°C in C_6D_6.

Scheme II



$$K = \frac{K_1^B}{K_2^B}$$



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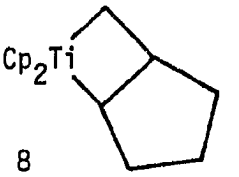


8

Results of a typical experiment are shown in Figure 1. Plots of lnK are linear in free energy and asymptotically approach the equilibrium value, which is deduced graphically. Similar plots derived for **4** and **8** indicate that the order of stability is **8**, **4** < **7**. Values of K^{Et_2O} for these metallacycles are 0.33 (**4**), 0.091 (**7**) and 0.43 M (**8**). The difference in free energy between titanacyclobutane vs **6** plus free olefin varies by less than 1 kcal mol^{-1} for these three species (Fig. 2).

Several β,β-disubstituted metallacycles including $Cp_2\overline{TiCH_2CMe_2CH_2}$ (**9**), $Cp_2\overline{TiCH_2CEtMeCH_2}$ (**10**) and $Cp_2\overline{TiCH_2C(i\text{-}Pr)MeCH_2}$ have been prepared.[25] These complexes have been found to be far more labile than their monosubstituted counterparts and **8**. Attempts at using Et_2O to measure the stability of these metallacycles failed, because the equilibria (Scheme II) lay almost completely to the right. However, THF was found to serve as convenient base for these measurements. The metallacycles were found to be remarkably stable at 40 °C in C_6D_6 solutions containing $AlMe_2Cl{\cdot}THF$; the equilibrium between metallacycle and **1** was achieved without decomposition to the dimer $(Cp_2TiCH_2)_2$.[26] Mixtures of **1**, THF and isobutylene, 2-methyl-1-butene or 2,3-dimethyl-1-butene reached equilibrium within several minutes. Values of K^{THF} = 0.21 and 2.1 M were obtained for **9** and **10**, respectively. Measurement was less accurate in the

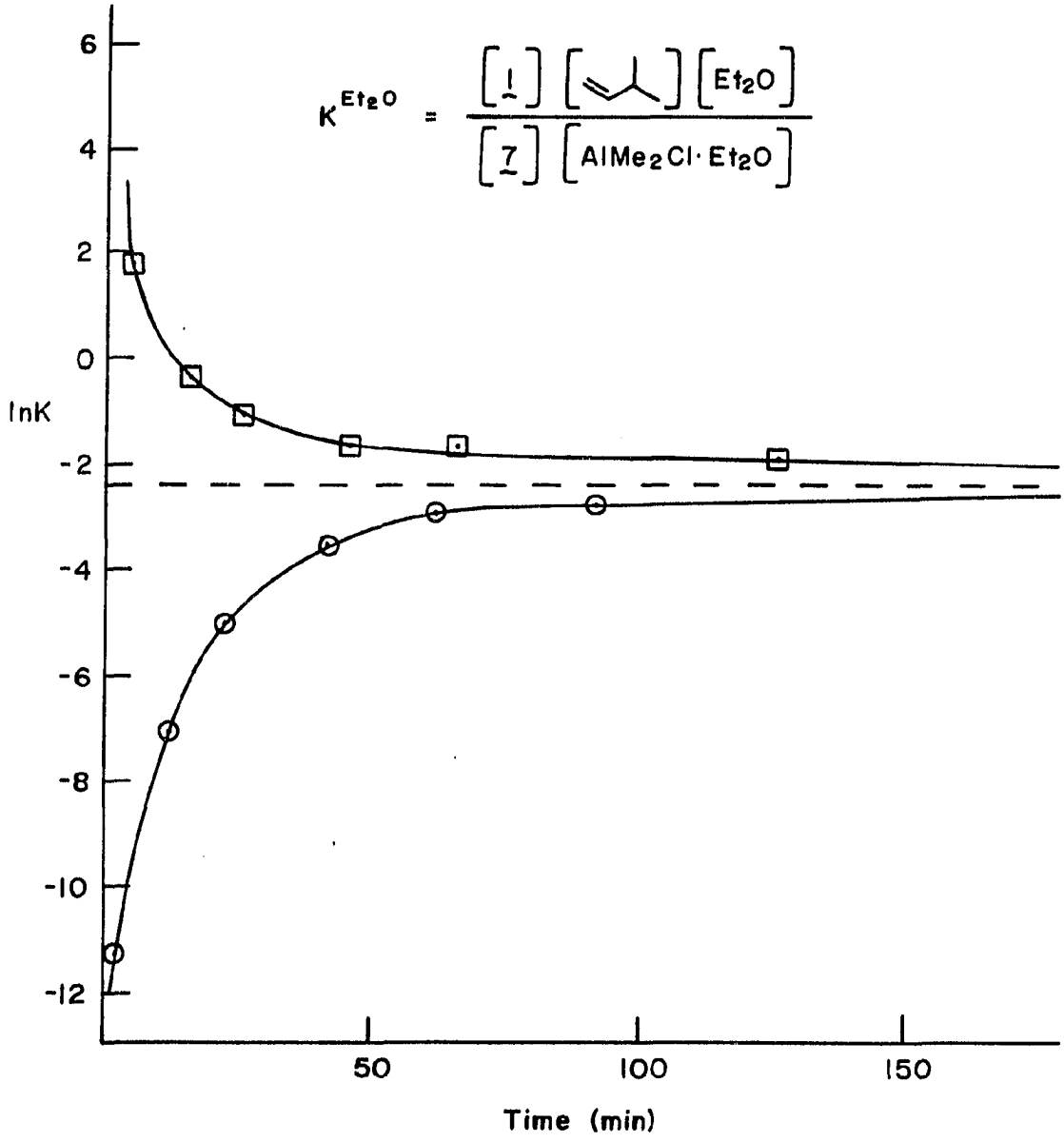


Figure 1. Asymptotic approach to equilibrium of 1 and 7. □ represents data from reaction of 1 with 3-methyl-1-butene and Et_2O. ○ indicates reaction of 7 with $AlMe_2Cl{\cdot}Et_2O$. Both experiments were monitored by ^1H NMR at 40°C in C_6D_6.

case of **11** because the amount of metallacycle formed was small even when 2 equivalents of THF and 4 equivalents of 2,3-dimethyl-1-butene were added. For **11**, $K^{THF} \cong 8$ M. The order of stability is thus **11** < **10** < **9**. Replacement of the hydrogens of one of the methyl substituents in **9** with methyl groups results in an increase in steric crowding which destabilizes the complex by ca. 1 kcal per methyl for the first two substitutions (Fig. 2). Replacement of a third hydrogen is not possible; addition of pyridine to a solution of **1** and 2,3,3-trimethyl-1-butene resulted in immediate destruction of **1** and formation of an unidentified dark brown solid.

In order to relate these values of K^{Et_2O} and K^{THF}, the extent of reaction of **4** with $AlMe_2Cl{\cdot}THF$ was determined under relatively dilute conditions. From the value obtained, $K^{THF} = 2 \times 10^{-3}$ M, we estimate $K^{Et_2O}/K^{THF} = 160$. The differences in stability of the six titanacyclobutanes, relative to the conjugate olefins and **6**, are shown in Figure 2. Part of the difference between mono and disubstituted metallacycles is certainly due to the difference in olefin stability.[31]

The titanacyclobutanes **4**, **9** and $Cp_2\overline{TiCH_2CHPhCH_2}$ **(12)** have been structurally characterized by X-ray diffraction.[27] These structures provide the basis for understanding the relative stability of the titanacyclobutanes. The conformation of the metallacycle ring is nearly planar and **9** does not show significant distortion from C_{2v} symmetry.[28] In **4** and **12**, interaction of the CMe_3 or Ph substituent with the Cp rings is relieved by a rocking motion of the central carbon fragment in the plane of the ring, instead of puckering. The observation that **7** is more stable than **4** by less than 1 kcal mol^{-1} suggests that this motion is a relatively low energy distortion.[31] Interaction

of the two methyl substituents with the Cp rings cannot be avoided in this fashion in **9**, and this metallacycle is significantly less stable than **4** and **7**.[32] The instability of **10** and **11**, and the fact that it has not been possible to observe the β-methyl-β-tert-butyl titanacyclobutane, suggest that the steric strain relieved in **4** by rocking of the central carbon unit is considerable. The rate of reaction of **4** and **11** with diphenylacetylene has been measured.[17] Activation energies are $\Delta G^{\dagger}$ = 24 and 22 kcal mol^{-1} for **4** and **11**, respectively, at 27°C. For these metallacycles $\Delta\Delta G^{\dagger}$ = 2 kcal mol^{-1}, compared with $\Delta\Delta G$ = 5 kcal mol^{-1} from Figure 2. This is consistent with substantial relief of steric strain in the transition state for cleavage of **11**.[34]

Isolation of labile titanacyclobutanes, such as **9**, **10** and **11**, posed a synthetic challenge. However, use of a large excess of olefin at low temperature allowed isolation of **9**. Even the extremely labile **11** has been isolated.[17] The highly symmetrical **9** was a particularly attractve synthetic target. The NMR spectra of **9** and its conjugate olefin are simple and the metallacycle is quite labile ($t_{1/2} \cong 70$ min for reaction with PhCCPh, -10°C, toluene-d_8). Isobutylene is inexpensive and is easily removed after reaction. These features combine to make **9** a useful starting material in organic and inorganic reactions of the Cp_2TiCH_2 fragment.

Diffractable crystals of $Cp_2\overline{TiCH_2CMe_2CH_2}$ (**9**) were obtained by slow cooling of a saturated toluene solution from -10 to -50°C. The X-ray structure was solved by G. Gajda.[27] Full-matrix least-squares refinement (using computer-generated hydrogen positional parameters) led to a final R index of 0.065. The ORTEP drawing of **9** is shown in Figure 3. Selected bond angles of tert-butyl titanacycle **4**, phenyl titanacycle **12** and **9** are presented

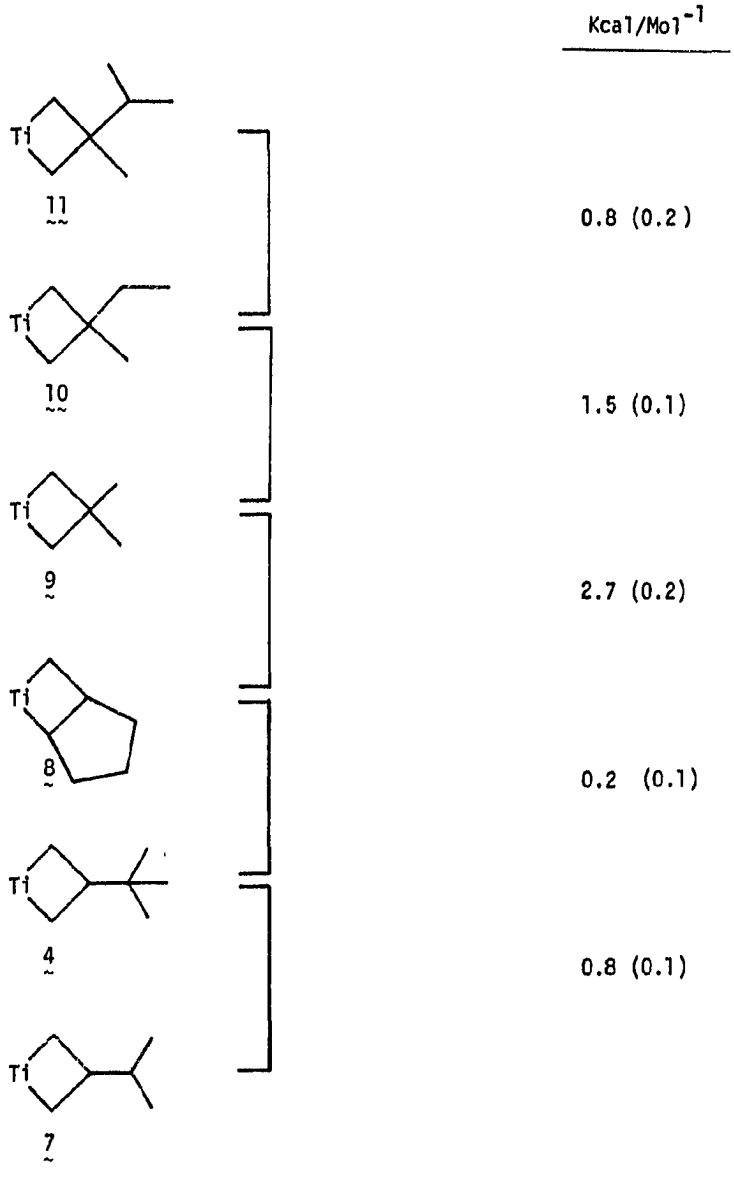


Figure 2. Differences in ΔG for a series of titanacyclobutanes (40 °C, C_6D_6). Calculated from equilibrium constants obtained by the method of Scheme II.

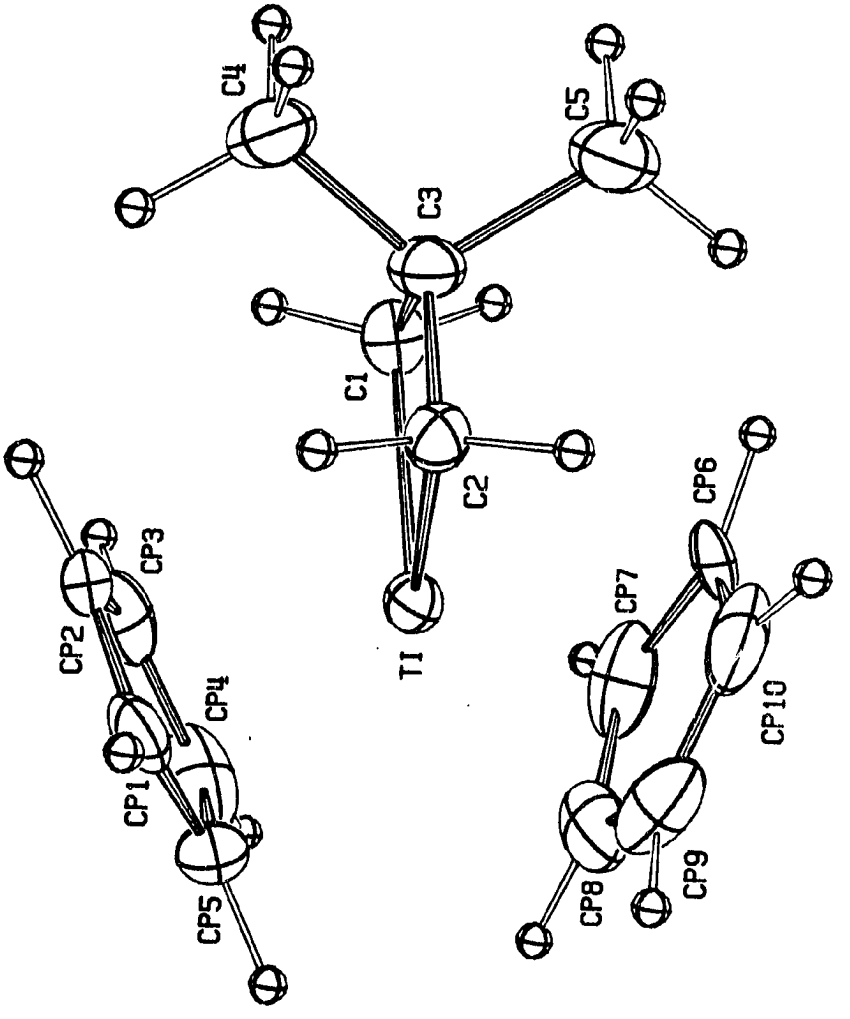


Figure 3. ORTEP drawing of $Cp_2TiCH_2CMe_2CH_2$ (9).

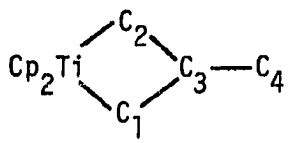
in Table 1. Aside from the previously mentioned rocking of the central carbon (C_3) fragment to relieve crowding of the substituent with the Cp rings in **4** and **12**, the symmetrical **9** (C_{2v}) shows no drastic distortion from the monosubstituted species. The slightly greater Ti-C_1-C_3 and Ti-C_2-C_3 angles in **9** might be due to relief of steric crowding between the methyl groups and the Cp rings. The planarity of these metallacycles has been suggested as a necessary feature for facile C-C bond cleavage in metathesis reactions.[1a]

Apart from use of **9** as a convenient source of Cp_2TiCH_2 (**6**), a number of reactions of this titanacyclobutane have been examined (Fig. 4). Thermolysis produced isobutylene as the only volatile product except trace amounts of methane, ethane and ethylene. Acidolysis gave neopentane with essentially no olefin formation. Bromination afforded 2,2-dimethyl-1,3-dibromopropane in quantitative yield. No hydrocarbon products were produced. This contrasts with iodination of **9**, in which 1,1-dimethylcyclopropane is formed in good yield. The mechanism of reaction of bis(cyclopentadienyl)titanacyclobutanes with halogens has been investigated in detail[36] and is discussed later in this chapter.

The Cp_2TiCH_2 unit, derived from **1** or many of the titanacyclobutanes, is an extremely useful reagent for Wittig-type chemistry.[37] The olefins derived by reaction of ketones with **1** can in turn be converted to β,β-disubstituted metallacycles. The products in Figure 4 could ultimately be derived from acetone in this fashion. Development of these and other synthetic transformations is in progress.

Bis(cyclopentadienyl)titanacyclobutanes have been isolated from a variety of olefins, and those substituted at the β-position(s) undergo degen-

Table 1. Selected Bond Angles and Distances for Metallacycles of the General Type



	4	12	9
	Bond Angles (deg)		
C_1-Ti-C_2	75	75.3	74.8
Ti-C_1-C_3	84	86.0	87.2
Ti-C_2-C_3	85	85.7	87.0
C_2-C_3-C_1	116	112.0	110.9
C_1-C_3-C_4	118	115.9	108.9 (110.3)[a]
C_2-C_3-C_4	115	109.1	111.4 (108.3)[a]
	Bond Distances (Å)		
Ti-Cl	2.16	2.127	2.138
Ti-C_2	2.14	2.113	2.152
C_1-C_3	1.55	1.546	1.59
C_2-C_3	1.53	1.579	1.58
C_3-C_4	1.52	1.521	1.51 (1.44)[a]
Ti-C(η^5)	2.07-2.51	2.36-2.40	2.38-2.44

[a]Corresponding value for the second methyl group.

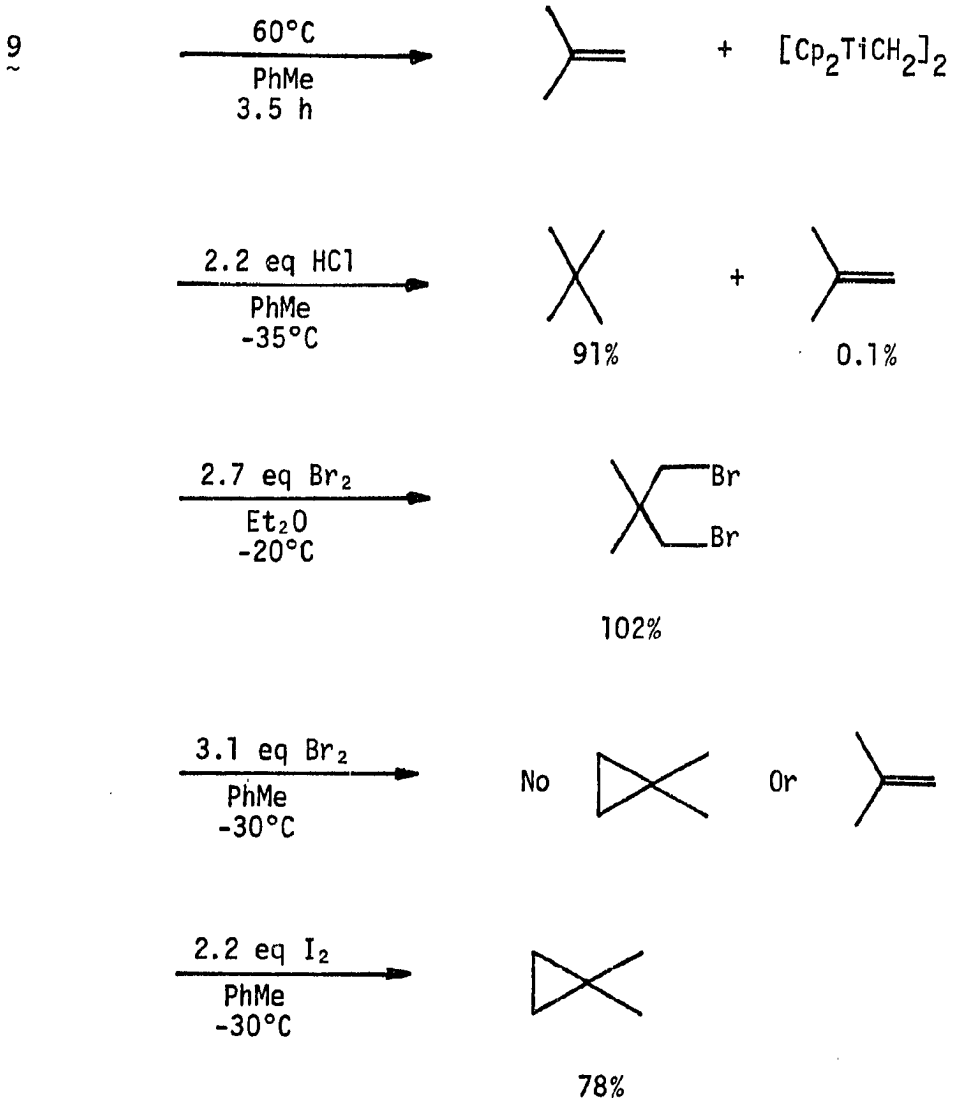

9
60°C
PhMe
3.5 h
+ [Cp2TiCH2]2
2.2 eq HCl
PhMe
-35°C
91%
+
0.1%
2.7 eq Br2
Et2O
-20°C
Br
Br
102%
3.1 eq Br2
PhMe
-30°C
No
Or
2.2 eq I2
PhMe
-30°C
78%

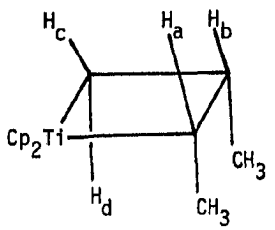
Figure 4

erate olefin metathesis. A requisite for productive metathesis is formation of an $\alpha,\alpha'\beta$-trisubstituted titanacyclobutane, or, at least, an α,β-disubstituted titanacyclobutane. The only previously prepared α,β-disubstituted titanacycle was cyclopentene metallacycle **8**, which cleaves to release cyclopentene and does not appear to produce polypentenamer (i.e., no productive cleavage).[38] Logical targets for synthesis were the α,β-dimethylbis(cyclopentadienyl)titanacyclobutanes **13** (cis) and **14** (trans).

Isolation of titanacyclobutanes had previously been accomplished by precipitation of $AlMe_2Cl{\cdot}DMAP$ with pentane (see eq. 2). This remains the method of choice in most cases. However, preliminary experiments indicated that **13** is highly unstable and is considerably less soluble than most of the titanacycles. To facilitate isolation of such species, a search was made for a base which would form a more soluble aluminum adduct. $AlMe_2Cl{\cdot}NEt_3$ and $AlMe_2Cl{\cdot}N(n\text{-}Bu)_3$ were prepared and found to have reasonably high solubility in toluene-pentane mixtures. Unfortunately, these bases reacted slowly with **1**. Formation of metallacycle **4** in C_6D_6 using a 30% excess of Et_3N requires ca. 15 min at room temperature. With Bu_3N the reaction is slower still. By contrast, the reaction is instantaneous when DMAP is used. This sluggish reaction of trialkylamines is attributed to steric bulk and renders them unacceptable for synthesis of highly unstable species. Primary alkylamines reacted with **1** to form $Cp_2TiMeCl$. The most suitable base tested was 4-tert-butylpyridine which reacts instantaneously at room temperature and forms an $AlMe_2Cl$ adduct of adequate solubility.[39]

Treatment of a toluene solution of **1** and excess cis-2-butene with 4-tert-butylpyridine at low temperature, followed by slow cooling, produced

cis-$Cp_2\overline{TiCHMeCHMeCH_2}$ (13) as small red needles. The product decomposes at room temperature (ca. 1 h). In C_6D_6 solution, 13 decomposes in minutes at room temperature to give a mixture of products with several cyclopentadienyl and methyl resonances. When NMR samples were prepared and analyzed at low temperature, the ^1H NMR spectrum of a single compound, consistent with 13, was obtained (see Experimental Section). Selective homonuclear decoupling was used to aid in assignment of the spectrum. By analogy with β-substituted titanacycles 4 and 7, in which the upfield pair of α-protons are those cis to the β-alkyl substituent,[14] the upfield pseudo-



13

triplet (δ 2.31) is assigned to H_d. The remaining α-protons, H_c and H_d, appear as overlapping multiplets (δ 3.5). The β-hydrogen, H_b, has a characteristic high-field shift (δ 0.03). Of the methyl doublets (δ 1.02, 1.58), that further upfield corresponds with the β-CH_3. The inequivalent Cp rings (δ 5.23, 5.32) have not been assigned. The trans isomer (14) is much more soluble than 13 and had to be prepared using the DMAP procedure. Attempts to recrystallize 14 failed. The ^1H NMR of 14 is similar to that of 13 (see Experimental Section). Retention of olefin stereochemistry in formation of 13 and 14 is presumed because metallacycles derived from stereospecifically deuterated α-olefins form with stereochemical retention in all cases examined.[15,17]

Upon warming to room temperature, toluene-d_8 solutions of **13** underwent rapid isomerization ($t_{1/2}$ < 6 min at 20°C). At least four new Cp resonances and eight new peaks in the methyl region appeared. One of the products is **14**. (Authentic **14** persisted for at least 1 h at 20°C and decomposed in ca. 30 min at 40°C with extreme broadening of the ^1H NMR spectrum.) Also, several broad resonances appeared between δ 0.17 and -0.36 ppm. No further attempt has been made to identify these products, but one obvious possibility is that the cis and trans α,α'-dimethyltitanacyclobutanes are formed. Production of methyltitanacyclopentanes is also possible.

The titanacyclobutane **13** has also been characterized by its reactions (Fig. 5). Acidolysis gave the expected hydrocarbon. Thermolysis afforded a variety of products (indicated in terms of %/Ti, figures for C_1 and C_2 products may be low). Iodination of **13** revealed a high degree of stereoretention in cyclopropane formation.[40] Identification of a diiodide product by GCMS reveals operation of a competitive reaction.

The stereospecificity in iodination of **13** led to examination of the stereospecifically α-deuterated phenyl metallacycle **15** by S. Ho.[36] Contrary to our expectation, there was complete loss of stereochemistry in the phenylcyclopropane products (eq. 7). These seemingly disparate results are reconciled by the mechanism presented in Scheme III. In the first step, iodine adds across the Ti-C bond with retention of configuration[41] to produce **16a** and **b**. These γ-iodoalkyls may give cyclopropanes by an intramolecular nucleophilic displacement. This process should proceed with retention at the α-carbon and inversion at the γ-carbon

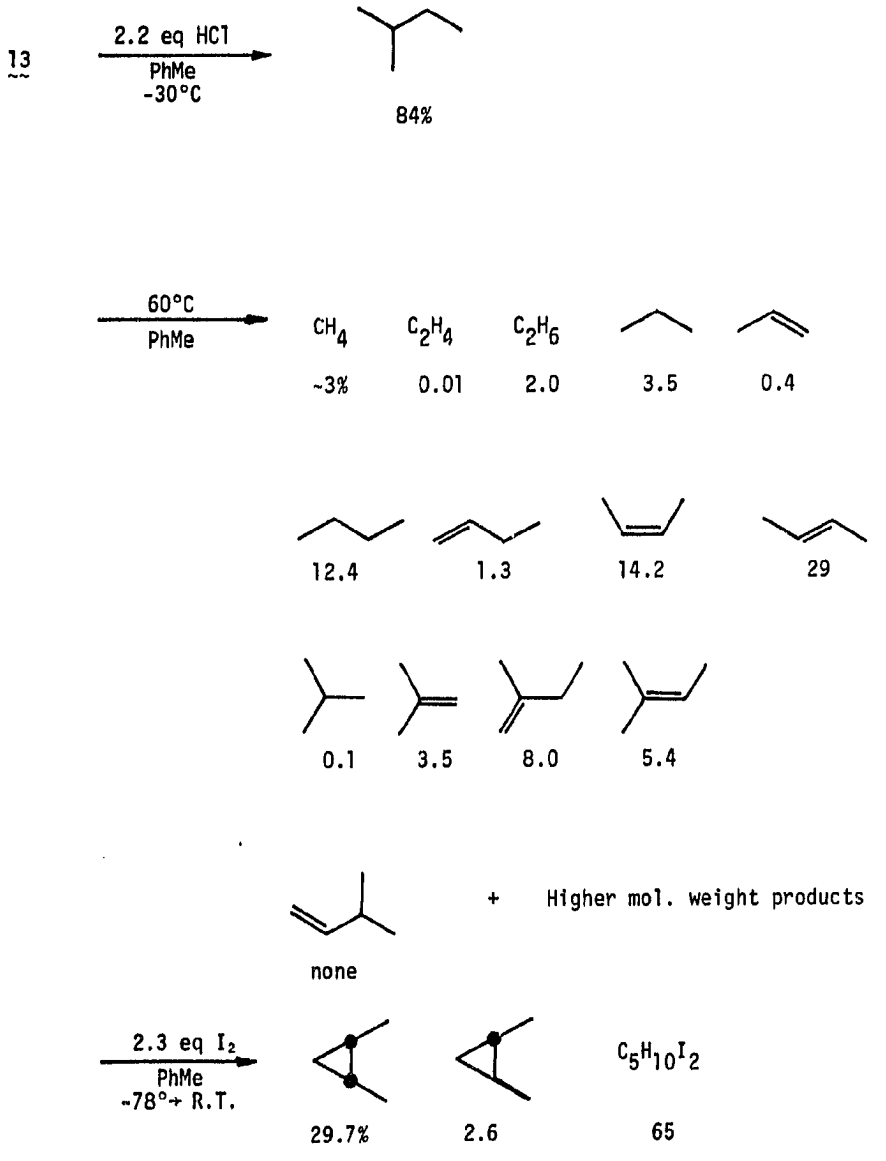
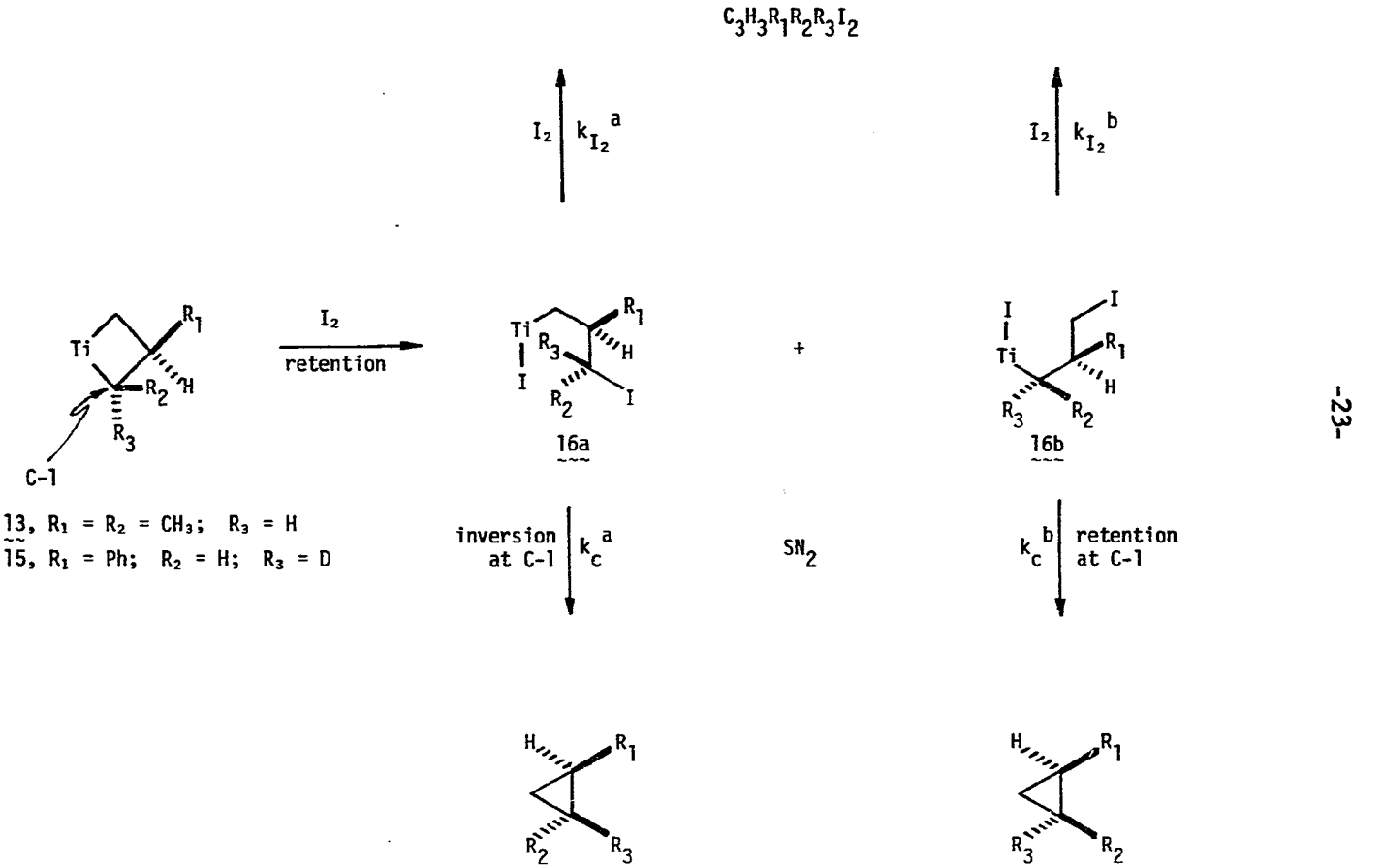
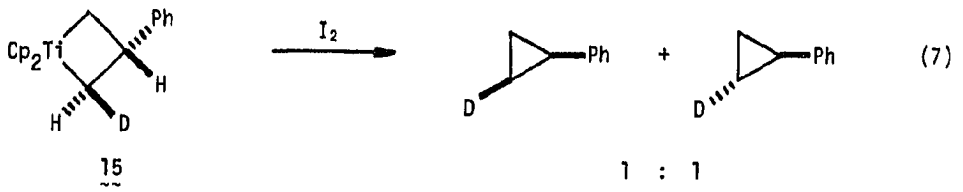

13
2.2 eq HCl
PhMe
-30°C
84%
60°C
PhMe
CH4
C2H4
C2H6
~3%
0.01
2.0
3.5
0.4
12.4
1.3
14.2
29
0.1
3.5
8.0
5.4
+ Higher mol. weight products
none
2.3 eq I2
PhMe
-78°→ R.T.
29.7%
2.6
C5H10I2
65

Figure 5

Scheme III



13, $R_1 = R_2 = CH_3$; $R_3 = H$
15, $R_1 = Ph$; $R_2 = H$; $R_3 = D$

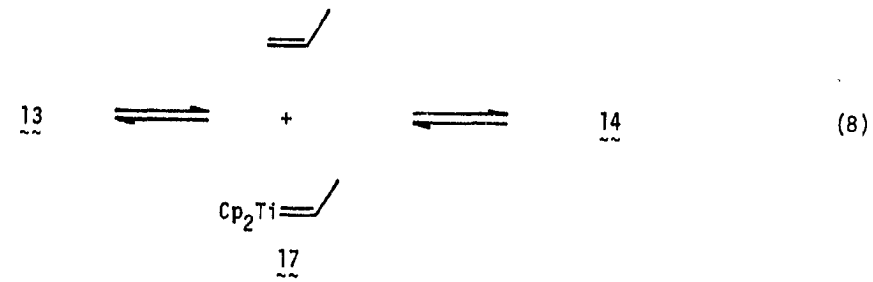


15 (7)

1 : 1

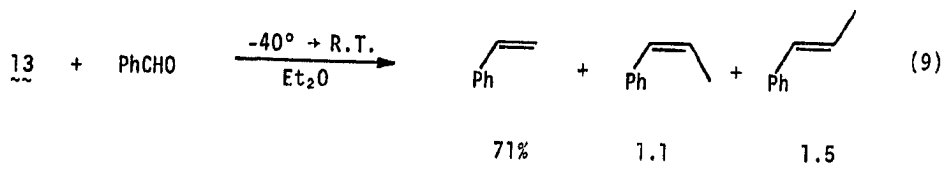
of intermediates **16a** and **b**. In competition with closure is reaction of **16a** and **b** with additional iodine to give diiodide products. Starting with **15**, equal amounts of **16a** and **b** are formed. Since $k_{I_2}{}^a \cong k_{I_2}{}^b$ and $k_c{}^a \cong k_c{}^b$ for these deuterated intermediates,equal amounts of cis- and trans-2-deuteriophenyl-cyclopropane are produced. This interpretation has been confirmed in a detailed study by Ho. She has observed the γ-iodoalkyl intermediates from **15** and determined the stereochemistry of each process along the paths to phenylcyclopropanes and diiodides. In the context of this mechanism, net stereoretention in formation of 1,2-dimethylcyclopropanes from α,β-dimethyl titanacycle **13** could result from preferred formation of **16b**, due to the steric bulk of the α-methyl group. Another cause of this effect might be more rapid displacement of primary vs secondary iodide ($k_c{}^b > k_c{}^a$). If steric crowding disfavors cleavage by I_2, then for iodination of the intermediates, $k_{I_2}{}^b < k_{I_2}{}^a$. Such competitive trapping would enhance stereoretention in the cyclopropane products. Operation of any or all of these effects explains the apparent anomaly of the product ratios from iodination of **13** and **15**. Unfortunately, no γ-iodoalkyl intermediates could be observed by ^1H NMR in the iodination of **13** at -20 °C. Conversion of **16a** and **b** to products appears to be too rapid for observation in this case, even when less than 1 equivalent of I_2 is used. Of interest is the fact no epimerization of **13** to **14** by I_2 occurs.

The thermolysis of **13** (Fig. 5) is noteworthy because of the complex assortment of products evolved. The C_1 and C_2 products are typical of decompositions involving Cp_2TiCH_2 (**6**). Formation of propene might result from cleavage of **13** to give titanium ethylidene **17** (eq. 8). However, interpretation of products in this system requires caution because of the

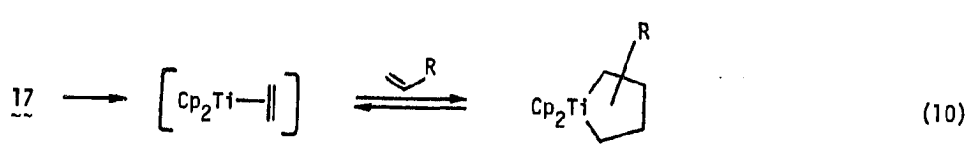


(8)

variety of processes which can occur. Propene might arise <u>via</u> intermediacy of a transient homoallyl hydride, as illustrated in Scheme IV.[42] Although operation of such a mechanism has not been excluded, evidence for the cleavage depicted in equation 8 was obtained from the reaction of **13** with benzaldehyde, which produced β-methyl styrenes (eq. 9). Once propene

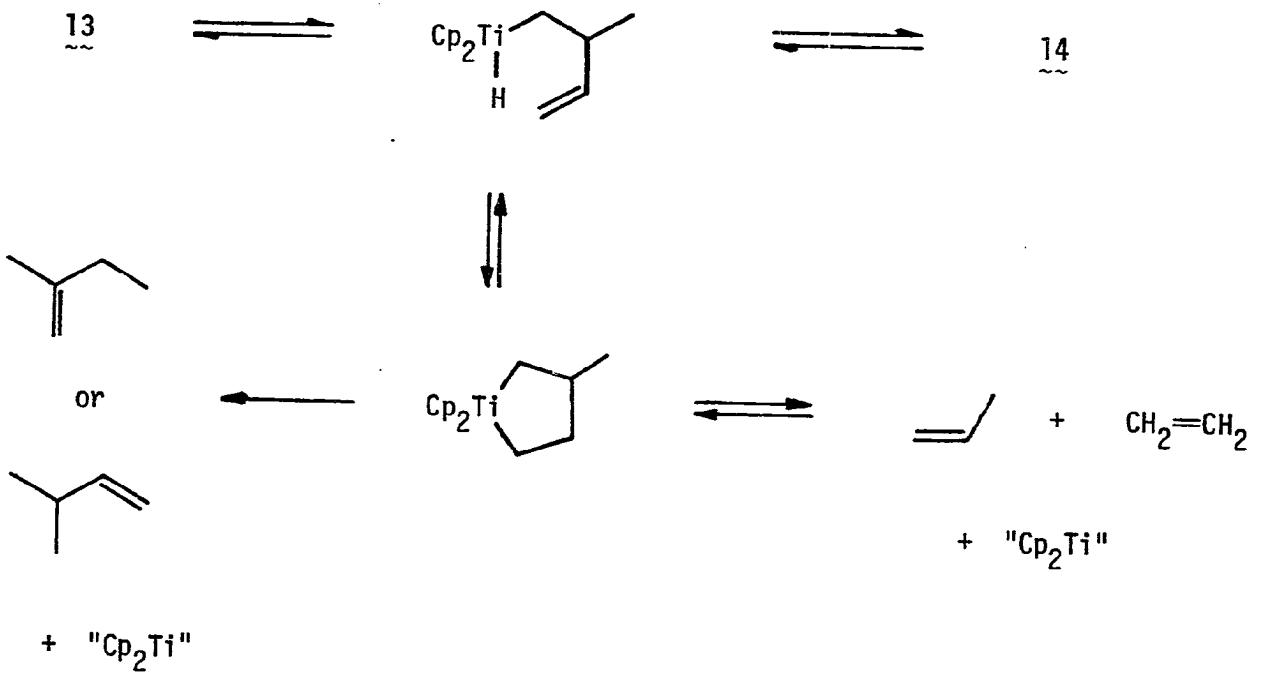


(9)



(10)

Scheme IV

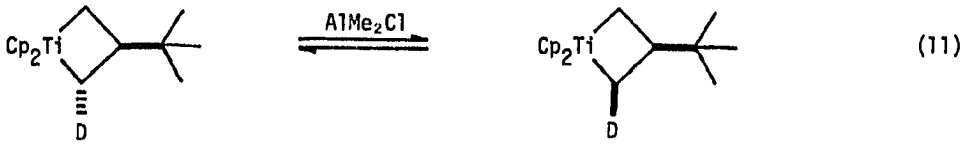


is present, isobutylene and 1-butene could be produced by formation and decomposition of α- and β-methyl-titanacyclobutanes.[43] 1-Butene may also result from isomerization of 2-butenes catalyzed by hydride species.[44] Formation of hydrides in this and related systems is probable in view of the substantial amounts of saturated hydrocarbons observed. One further reaction which can occur is rearrangement of ethylidene **17** to an ethylene complex[46] by hydrogen migration (eq. 10).[47]

The trans-2-butene metallacycle, **14**, is more stable than its cis counterpart, **13**. This is indicated by formation of **14** as a product in the isomerization of **13**; significant amounts of **14** remained after almost all **13** had reacted. Also, thermal decomposition of **14** (monitored by ^{1}H NMR) proceeded without buildup of **13**. Decomposition of **14** was considerably slower than **13**. An attempt was made to measure relative stabilities of **13** and **14** according to Scheme II. Reaction of **1** with THF and cis-2-butene (5°C, C_6D_6) led to extreme line-broadening in the ^{1}H NMR. A few Cp-containing products of unknown composition appeared, but **1** remained largely unconsumed. Detection of **13** was not possible under these conditions due to the poor quality of the ^{1}H NMR spectrum (suggestive of formation of some paramagnetic species) and because the olefin and THF peaks obscured the most diagnostic regions of the spectrum. However, if **13** did form it was present only in small amounts. On the other hand, reaction of **1** with trans-2-butene and THF (5°C, C_6D_6) did lead, after 20 min, to what appears to be an equilibrium concentration of **14**, along with small amounts of unidentified side products. An equilibrium constant was not estimated because of the difficulties noted above, and uncertainty in various concentrations. More

careful experiments might permit accurate measurement of K. However, from the data in hand, we can at least conclude that **14** lies in the range of the β,β-disubstituted titanacycles (Fig. 2). Also, the fact that little if any **13** formed under identical conditions is further evidence of the greater stability of the trans isomer **14**. An additional demonstration of this is reaction of **13** with 5 equivalents of trans-2-butene (-10°C, toluene-d_8) to form **14**. The reaction was monitored by ^{1}H NMR using the resonances of the α-protons. The ratio of **13**:**14** was 1:1 after 30 min and 1:10 after 4 h. By contrast, no reaction of cis-2-butene with **14** was observed at 0°C or even at room temperature.

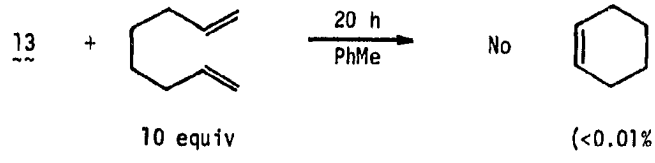
Epimerization of **13** to **14**, demonstrated to occur thermally, allows one to test, at a substituted α-carbon, for the aluminum-catalyzed epimerization which is rapid at low temperature in β-substituted titanacyclobutanes (eq. 11)[23] This catalytic isomerization, which may account for the eventual loss of stereospecificity in commercial metathesis systems, has been investigated in detail and is believed to involve rapid, reversible transmetalation. The reaction is inhibited by trace quantities of Et_2O. Treatment of **13** with $AlMe_2Cl$ (-30°C, toluene-d_8) did not produce **14**. Slow reaction gave **1** as the only organometallic product. Transmetalation could



(11)

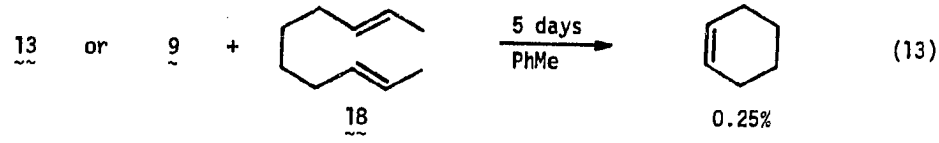
be inhibited by steric crowding at the α-carbon in **13**. Reaction of **13** with $AlMe_3$ also occurred without epimerization, and led to formation of $Cp_2TiCH_2 \cdot AlMe_3$.[4a] The organic products presumably evolved in these reactions were not analyzed.

Having gained some knowledge of the factors which influence the relative stability and reactivity of various titanacyclobutanes, especially **13** and **14**, we proceeded to test for occurrence of non-degenerate metathesis in some well-studied olefin systems. We first examined systems in which cyclohexene would be produced, because this olefin is not consumed (metathesized) in typical commercial catalyst systems, and because double-bond isomers and stereoisomers do not exist for simple cycloalkenes. Accordingly, **13** was treated with excess 1,7-octadiene in toluene at room temperature (eq. 12). The solution remained red and homogeneous. This suggests that a stable, mono-substituted metallacycle is formed. After 20 h, no cyclohexene could be detected in the volatiles. However, reaction of **13**



(12)

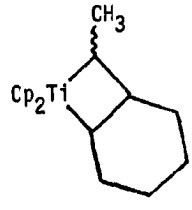
with trans,trans-2,8-decadiene (**18**) (5.7 equiv) in toluene at room temperature (eq. 13) gave a purple solution with some dark solids. Analysis



(13)

of the volatiles (GC and GCMS) revealed a very small amount of cyclohexene. The same amount of cyclohexene resulted when β,β-dimethyl-metallacycle **9** was substituted for **13**.

At this point, we decided to test whether the cyclohexene metallacycle **19** is a viable source of cyclohexene, and how efficient production of cyclohexene from this intermediate would be. Red, crystalline **19** was prepared by the standard method and was characterized by ^{1}H and ^{13}C NMR and by its reactivity (Fig. 6). Acidolysis gave the expected hydrocarbon as the sole product. This metallacycle appears to be more labile than cyclopentene titanacycle **8** and even **9**. In a sealed NMR tube (C_6D_6 solution), ca. 20% decomposition to cyclohexene and $(Cp_2TiCH_2)_2$ occurred in a period of 10 min at room temperature. Thorough analysis of the decomposition products confirmed that cleavage of **19** to give cyclohexene is the preferred path. Formation of no 3-methylcyclohexene indicates that β-elimination of methylene hydrogens in the cyclohexane ring of **19** is unfavorable. Iodination, under the usual conditions, gave a low yield of norcarane.[48] Although the thermolysis products of **19** support it as a viable intermediate in metathesis of trans,trans-2,8-decadiene (**18**), intermediacy of metallacycle **20** must be considered as well.



20

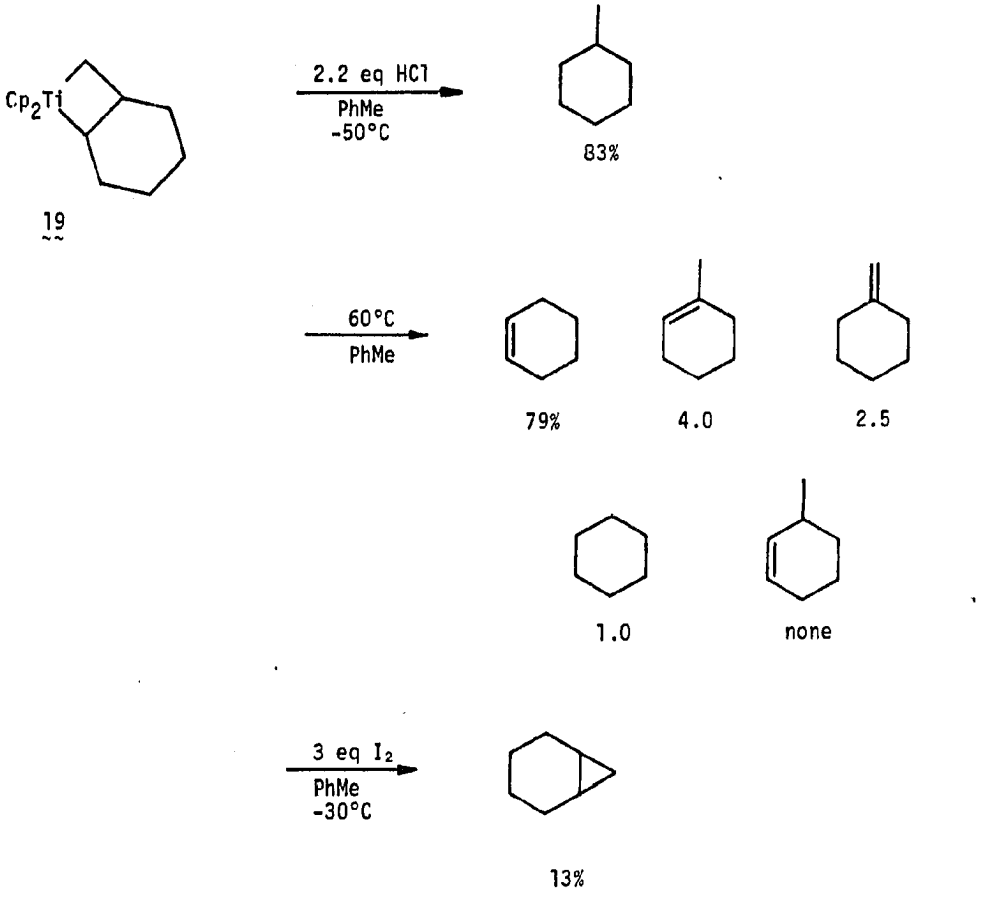
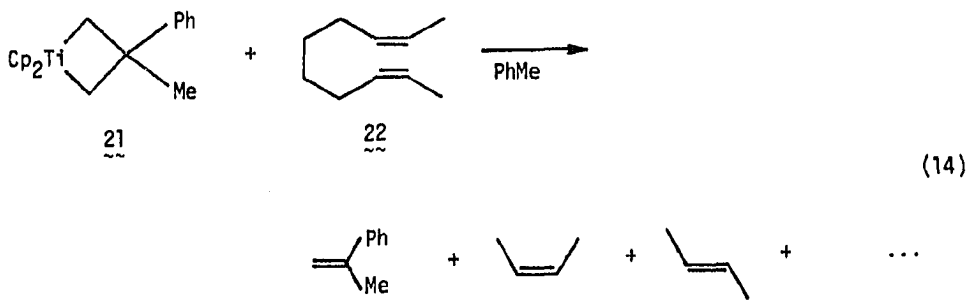

Cp2Ti
19
2.2 eq HCl
PhMe
-50°C
83%
60°C
PhMe
79%
4.0
2.5
1.0
none
3 eq I2
PhMe
-30°C
13%

Figure 6

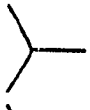
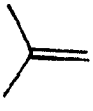
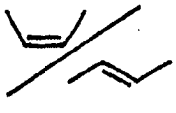
Along with cyclohexene, cis- and trans-2-butene are expected metathesis products of the 2,8-decadienes. For observation of small amounts of 2-butene products by GC, **13** was obviously unsuitable as the starting metallacycle. Even **9** was unacceptable because of the large amount of isobutylene released on decomposition. This problem was avoided by use of the labile metallacycle $Cp_2\overline{TiCH_2CPhMeCH_2}$ (**21**). The first reaction studied was that of **21** with cis,cis-2,8-decadiene[49] (**22**) (eq. 14). A solution of **21** and a sixfold excess of **22** in toluene was stirred in a small Schlenk tube fitted



(14)

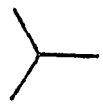
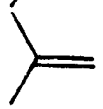
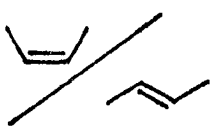
with a latex septum. Aliquots of the gas phase were periodically withdrawn and analyzed. The amounts of C_3 and C_4 products evolved are shown in Table 2. The major C_4 hydrocarbon is a metathesis product, cis-2-butene. Since many commercial metathesis catalysts display stereoretention at low turnover numbers, we decided to examine the reaction of **21** with trans,trans-diene **18** under conditions similar to those used above. The results are shown in Table 3. One striking difference between the reactions of **18** and **22** is the slower rate of appearance of C_3 and C_4 products from **18**. Also notable is the increased production of saturated products (propane and n-butane) in reaction of **18**. There is a dramatic preference for production of

Table 2. Products of Reaction of $Cp_2\overline{TiCH_2CPhMeCH_2}$ **(21)** With cis,cis-2,8-Decadiene **(22)**.

Product* \ Time (min)	5	15	35	70	285
	0.1	0.2	0.3	0.5	0.8
	1.4	3.3	4.9	6.1	8.4
	--	--	--	--	0.1
	tr	0.6	1.1	2.4	2.5
	--	tr	tr	0.1	0.1
	--	tr	tr	0.4	1.0
	1.7	5.0	7.2	9.5	14.6
	--	tr	0.2	0.4	1.1
Ratio 	--	--	35	23	13
Total $C_3 + C_4$	3.2	9.1	13.7	19.4	28.5

*Given as %/Ti. C_1 and C_2 products were present throughout the reaction and were not quantitated. tr = Trace amount. Reaction was run at room temperature.

Table 3. Products of Reaction of $Cp_2\overline{TiCH_2CPhMeCH_2}$ (21) With trans,trans-2,8-Decadiene (18).

Product* \ Time (min)	5	20	45	70	135	340
	0.1	0.1	0.2	0.4	1.0	1.3
	0.3	0.8	1.1	1.9	2.3	3.6
	--	--	tr	tr	tr	tr
	0.2	0.4	0.6	0.8	1.8	5.7
	0.1	0.4	0.8	0.8	0.7	0.7
	--	--	tr	tr	tr	tr
	--	tr	0.1	0.3	0.5	0.4
	--	tr	0.1	0.3	0.9	0.9
Ratio 	--	--	--	1.13	0.51	0.58
Total $C_3 + C_4$	0.7	1.7	2.7	4.5	7.2	12.6

*Given as %/Ti. C_1 and C_2 products were present throughout reaction and were not quantitated. tr = trace amount. The reaction was run at room temperature, except for a 10 min interval following the 45 min aliquot and a 60 min interval after the 70 min aliquot. During these periods the temperature was 45°C.

cis- vs trans-2-butene from metathesis of cis,cis-diene **22**. This contrasts with metathesis of **18**, in which the cis preference is lower and the cis:trans ratio rapidly approaches thermodynamic equilibrium.[45]

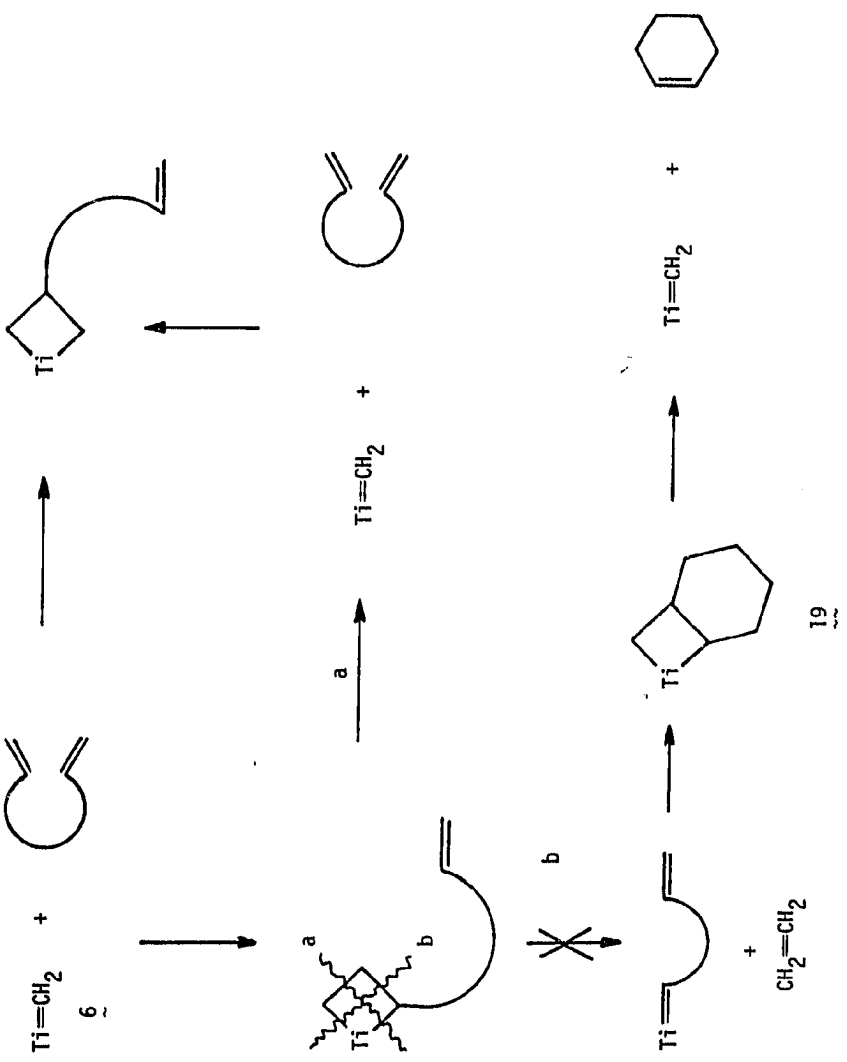
Interpretation of these results must involve caution because of participation of a number of processes beyond those required for metathesis. Facile decomposition of a particular intermediate by these alternate pathways might lead one to conclude that it is disfavored because of the absence of the metathesis product which would otherwise derive from it. Without preparation of individual intermediates it is impossible to correct for this. As a result, no firm conclusions about preferred metallacycle configurations can be drawn.

In considering the metathesis activity observed, we will be concerned with relative rates of cleavage of metallacycle intermediates to give titanium alkylidenes and olefins, rather than with stereoisomeric or regioisomeric preferences in metallacycle formation. This is based on the premise that the alkylidenes are high-energy intermediates and, as such, are nonselective in reaction with incoming olefins. In line with this assumption is the fact that no titanium alkylidene intermediates have been observed in the reactions studied by our group. More important is the observation that for all monosubstituted metallacycles in which both regioisomers are stable enough to be observed, the two form in nearly equal amounts. Examples are the formation of titanacyclobutanes from styrene,[38] propene,[43] and 3,3,3-trifluoropropene.[50] The roughly equal amounts of cis-and trans-β-methylstyrene formed in the reaction of **13** with benzaldehyde (eq. 9) lends further support to this formulation.

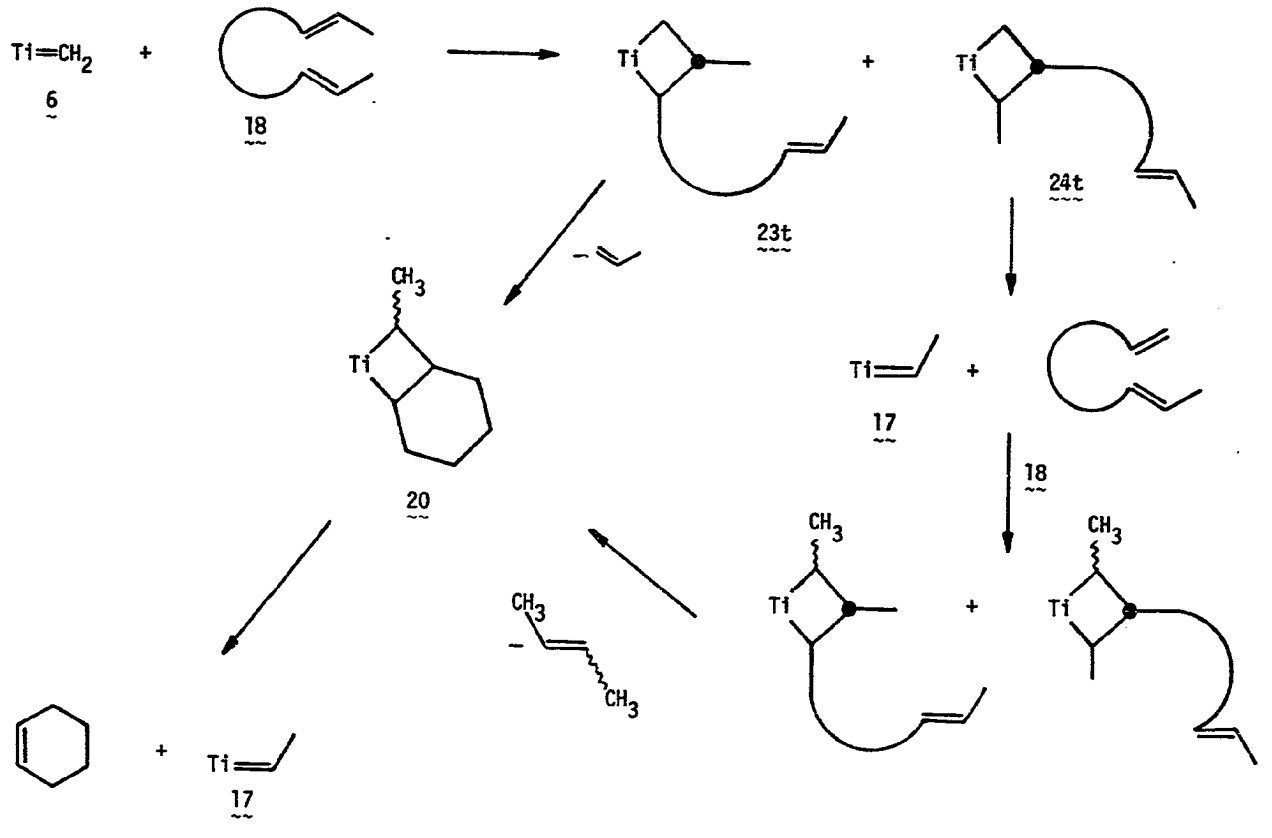
First, the formation of cyclohexene will be considered. This product is detected in the reaction of **13** with the cis,cis diene **18**, but not with 1,7-octadiene. Reaction of **6** with 1,7-octadiene could proceed as in Scheme V. Isomerization of the α-substituted titanacycle to a stable β-substituted species is favored over cleavage to the alkylidene which would close to give **19**. Reactions involving ethylidene **17** (from **13**) should be minor. Formation of trisubstituted metallacycles is expected to be highly unlikely in this reaction. In the decadiene metathesis system (Scheme VI), we may consider the initial reaction to be that of the substrate with Cp_2TiCH_2 (**6**), since involvement of ethylidene **17** generated from **13** is negligible (a conclusion which is supported by the fact that the amount of cyclohexene formed on reaction of **9** and **13** with **18** is identical). In the manner indicated, the trisubstituted metallacycle **20** forms. This metallacycle, which possesses an α-methyl group, might undergo a variety of decomposition processes in addition to cleavage to give cyclohexene.

In the formation of cis- and trans-2-butene from the decadienes (eq. 14, Tables 2 and 3), it is significant that propene is produced early in the reaction. Propene might react with **17** to form metallacycles **13** and **14**, among other products. The 2-butenes could then arise directly from **13** and **14**, without intermediacy of a trisubstituted metallacycle. However, the high cis:trans ratio (and the observation of different degrees of stereoselectivity) in these reactions argues against such a pathway as the major route to the 2-butenes. It is likely that the initial step in the reaction of **21** with dienes **18** and **22** (shown for **18** in Scheme VI) is formation of the disubstituted metallacycles **23** and **24**. The trans isomers (**23t** and **24t**), which form from **18**, might be relatively stable at room temperature, accounting for the

Scheme V



Scheme VI



slower formation of products from **18** than from **22**. Cleavage of **23** is a source of propene. Cleavage of **24** would produce ethylidene **17**. Trapping of **17** by cis,cis diene **22** would give trisubstituted intermediates **25** and **26** (Fig. 7), among other regioisomers. Much more efficient production of cis-2-butene from **25** than trans-2-butene from **26** could explain the high cis:trans ratio in this reaction (Table 2). Similar intermediates, **27** and **28** (Fig. 7), are expected in metathesis of **18**. Slightly more efficient production of cis-2-butene from **28** than trans-2-butene from **27** would account for the data (Table 3). The stereochemical preference in 2-butene formation appears to be lower in metathesis of **18** than of **22**. However, on inspection of Tables 2 and 3, it is evident that hydrogenation of olefinic products occurs to a greater extent, and amounts of C_4 products obtained are lower, in the metathesis of trans,trans-diene **18**. The ratio of cis- to trans-2-butenes is undoubtedly affected to a greater extent by isomerization and reduction in metathesis of **18** than in metathesis of **22**.

At present, we can conclude only that this titanocene system is capable of non-degenerate metathesis and that trisubstituted titanacyclobutanes are likely intermediates in this process. Non-degenerate metathesis is fairly inefficient, due to a variety of decomposition pathways available to intermediates possessing α-alkyl substituents. There does appears to be some stereoselectivity in the metathesis of 2,8-decadienes. In commercial systems, the predominant product is usually of the same stereochemistry as the starting olefin,[51] but in this case cis-2-butene is highly favored from cis and slightly favored from trans starting dienes. It is difficult to make specific statements about the stability of discrete intermediates with the

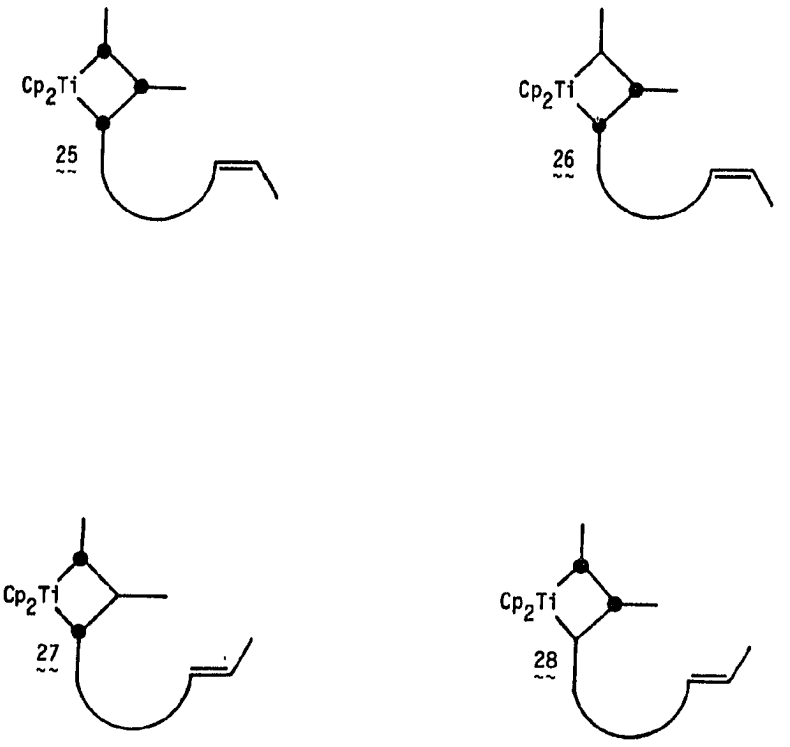
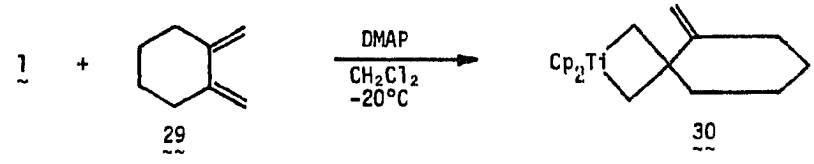


Figure 7. Possible intermediates in decadiene metathesis.

evidence at hand. The most promising approach, if further examination of this system is desired, would employ a new reaction that should make reagents of the type $Cp_2TiCHR{\cdot}AlMe_2Cl$ available.[52] This would allow direct production of trisubstituted metallacycles and could also help to resolve the question of whether α,α'-dimethyltitanacyclobutanes are among the thermal decomposition products of cis-$Cp_2TiCHMeCHMeCH_2$ (13).

Finally, another titanacyclobutane reaction which deserves mention is that of Cp_2TiCH_2 (6) with 1,3-dienes. Formation of titanacyclobutanes from 6 is formally a 2+2 cycloaddition, which is symmetry-forbidden for reaction between two olefins. To explore the orbital symmetry properties of 6, we examined reactions with 1,3-dienes. These reactions could proceed via 2+4 cycloaddition, which would be analogous with the symmetry-allowed Diels-Alder reaction.[53]

Reaction of 1,3-butadiene with 1, under conditions commonly used for preparation of the less stable titanacyclobutanes resulted in a brown suspension rather than the typical clear red titanacycle solution. The products are very thermally unstable, even in the solid state. Some resonances consistent with a titanacyclobutane were found in the ^1H NMR spectrum,[54] but the presence of other products and poor spectral resolution precluded characterization. However, 1,2-bis(methylene)cyclohexane (29) was prepared and found to form a red, microcrystalline product under the same conditions (eq. 15). This product is 30, the result of formal 2+2-



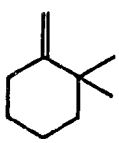
1 + 29 → 30 (15)

cycloaddition. At room temperature, **30** decomposed in the manner typical of β,β-disubstituted titanacyclobutanes (eq. 16). The structure of **30** was

$$\underset{\sim}{30} \xrightarrow[\text{toluene-}d_8]{\text{R.T.}} [Cp_2TiCH_2]_2 + \underset{\sim}{29} \qquad (16)$$

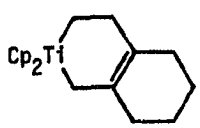
determined by low-temperature ^1H and ^{13}C NMR and by acidolysis (eq. 17). The stability of **30** (although moderate) is surprising in view of the forced interaction of the methylene substituent with the cyclopentadienyl ring.

$$\underset{\sim}{30} \xrightarrow[\substack{Et_2O \\ -40°C}]{\text{2.5 eq HCl}} \qquad (17)$$



Diene **29** is an excellent substrate for Diels-Alder reactions.[55] In spite of this, 2+2 rather than 2+4 cycloaddition (eq. 18) was observed. Reversal of the "usual" orbital symmetry rules, due to participation of d-orbitals in metal-centered reactions, has received theoretical support.[56]

$$\underset{\sim}{6} + \underset{\sim}{29} \not\longrightarrow \qquad (18)$$



Experimental Section

Titanocene dichloride was purchased from Boulder Scientific and purified by Soxhlet extraction with dichloromethane. $AlMe_3$ was purchased from Alfa, or as a 2 M solution in toluene from Aldrich.[57] $AlMe_2Cl$ was purchased from Texas Alkyls. 4-Dimethylaminopyridine (DMAP) was purchased from Aldrich and recrystallized from hot toluene. Diphenylacetylene was purchased from Aldrich and purified by sublimation. 4-tert-Butylpyridine, 2,3-dimethyl-1-butene, 3,3-dimethyl-1-butene and cyclohexene were purchased from Aldrich and stored over Linde 4 Å molecular sieves. Methylenecyclohexane, norcarane, trans-1-phenylpropene and a mixture of cis- and trans-1-phenylpropene were purchased from Aldrich. 1-Methylcyclohexene, 3-Methylcyclohexene, trans,trans-2,8-decadiene, cis-1,2-dimethylcyclopropane and a mixture of cis- and trans-1,2-dimethylcyclopropane were purchased from Chemical Samples Co. 2-Methyl-1-butene was purchased from ICN Pharmaceuticals and stored over molecular sieves. 3-Methyl-1-butene was purchased from Phillips and stored over molecular seives. 1,1-Dimethylcyclopropane was purchased from Pfaltz and Bauer. Methylcyclohexane was purchased from MCB. 1,3-Dibromo-2,2-dimethylpropane was purchased from Fairfield. Isobutylene and cis and trans-2-butene were purchased from Matheson and freeze-degassed twice prior to use. 1,1-Dimethylpropane, 2-methylbutane and 1,3-butadiene were purchased from Matheson. cis,cis-2,8-Decadiene was prepared by Mr. J. McNally according to a published procedure.[49] The decadienes were stored over molecular sieves. 1,2-Dimethylenecyclohexane was prepared in three steps from 1,2-cyclohexanedicarboxylicanhydride.[58] Tebbe reagent (1)

prepared by an established procedure[17] was used for preparative purposes. For equilibrium measurements, **1** was prepared from $Cp_2TiMeCl$ and recrystallized from hexane.[59] $Cp_2\overline{TiCH_2CH(t\text{-}Bu)CH_2}$ (**4**), $Cp_2\overline{TiCH_2CH(i\text{-}Pr)CH_2}$ (**7**), $Cp_2\overline{TiCH_2CPhMeCH_2}$ (**21**) and the cyclopentene titanacycle **8** were prepared by established methods and recrystallized from toluene or diethyl ether.

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

General Procedures. All manipulations of air and/or moisture-sensitive compounds were carried out using standard high vacuum line Schlenk techiques or in a vacuum atmospheres drybox equipped with a -40 °C freezer. Argon used in Schlenk work was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4 Å molecular sieves. NMR spectra were recorded on a Varian EM-390 (90 MHz ^1H), JEOL FX-90Q (89.60 MHz ^1H, 22.53 MHz ^{13}C) or a Bruker WM-500 (500.13 MHz ^1H) instrument. Kinetic and equilibrium measurements were run in the automated mode on the JEOL FX-90Q. Temperatures were measured using $\Delta\nu_{MeOH}$[60] and were constant to within ± 0.1 °C. Gas chromatographic analysis was

performed on a Varian 1400 flame-ionization instrument equipped with a Spectra-Physics System I computing integrator. Analyses were performed using the following columns: 20' Durapak, 10' Porapak Q, 30' 3% SE-30 on 100/120 Supelcoport, or 10' 19% FFAP on 80/100 Chromosorb PAW (unless otherwise indicated).

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

98% pure by NMR analysis ($C_2H_4Br_2$ internal standard).

Preparation of $Cp_2TiCH_2CMe_2CH_2$ (9). Tebbe reagent (1) (2.46 g, 8.63 mmol) was dissolved in 17 mL CH_2Cl_2 in a Schlenk tube. Isobutylene (100 mmol) was freeze-degassed and condensed into the reaction vessel at -196 °C. DMAP (1.23 g, 10.0 mmol) was added to the stirred solution at -20 °C. The mixture was stirred for 3 min and transferred via cannula into 120 mL vigorously stirred 0 °C pentane. The byproducts were removed on a coarse Schlenk frit and the filtrate was concentrated to 40 mL by removal of solvent in vacuo at 0 °C. The red solution was transferred from a flocculent white precipitate via cannula and concentrated to 20 mL. After cooling at -78 °C overnight, the supernatant was decanted. The remaining dark red solid was dissolved in 6 mL toluene at 0 °C and gradually cooled to -50 °C. The resulting solid was washed 2 x 5 mL cold pentane. Residual pentane was removed in vacuo at room termperature over a period of 3 h to give red needles of $Cp_2TiCH_2CMe_2CH_2$ (660 mg, 31%). ^1H NMR (toluene-d_8, -10 °C) δ 1.10 (s, 6H), 2.50 (s, 4H), 5.51 (s, 10H); ^{13}C NMR (C_6D_6, 6 °C) δ 5.4 (s), 38.1 (q, J = 123 Hz), 83.5 (t, J = 137 Hz), 110.7 (d, J = 171 Hz).

Preparation of cis-$Cp_2TiCHMeCHMeCH_2$ (13). Tebbe regent (2.18 g, 7.64 mmol) was dissolved in 20 mL toluene in a Schlenk tube. cis-2-Butene (80 mmol) was freeze-degassed and condensed into the reaction vessel at -196 °C. The solution was stirred at -15 °C and 4-tert-butylpyridine (1.24 mL, 8.1 mmol) was added dropwise via syringe. The solution was stirred at 0 °C for 2 min and placed in a -10 °C bath. The bath was gradually cooled to -50 °C over a 6 h period, followed by an additional 6 h at -78 °C. The supernatant was removed via cannula and the product was washed 3 x 5 mL

-78 °C pentane. Residual pentane was removed in vacuo over a period of 1 h at room temperature to give cis-$Cp_2\overline{TiCHMeCHMeCH_2}$ as a deep red microcrystalline solid (1.05 g, 56%). ^1H NMR (toluene-d_8, -30 °C) δ 0.03 (m, 1H, β-C<u>H</u>CH_3), 1.02 (d, J = 6 Hz, 3H, β-CH_3), 1.58 (d, J = 8 Hz, 3H, α-CH_3), 2.31 (pseudo-triplet, J = 8 Hz, 1H, α-C<u>H</u>H-), 3.47 (m, 2H, α-CH<u>H</u>- and α-C<u>H</u>CH_3-), 5.23 (s, 5H), 5.32 (s, 5H). Assignments were made by selective homonuclear decoupling.

Preparation of trans-$Cp_2\overline{TiCHMeCHMeCH_2}$ (14). Tebbe reagent (3.2 g, 11.2 mmol) was dissolved in 20 mL CH_2Cl_2 in a Schlenk tube. trans-2-Butene (80 mmol) was freeze-degassed and condensed into the reaction vessel at -196 °C. The solution was stirred at -30 °C and DMAP (1.60 g, 13.3 mmol) was added. The soluton was stirred for 3 min at 0 °C and transferred into 150 mL of vigorously stirred -30 °C pentane. The byproducts were removed on a coarse Schlenk frit and the filtrate was stripped of bulk solvent in vacuo at -30 °C. The residue was washed 2 x 10 mL -78 °C pentane and dried in vacuo for 30 min at room temperature. The trans-$Cp_2\overline{TiCHMeCHMeCH_2}$, a red solid (1.5 g, 54%), is very soluble in toluene. Attempts at recrystallization failed, but NMR analysis revealed only trace impurities. ^1H NMR (d_8-toluene, -30 °C) δ -0.80 (m, 1H, β-C<u>H</u>CH_3), 1.04 (d, J = 6 Hz, 3H, β-CH_3), 1.68 (d, J = 6 Hz, 3H, α-CH_3), 2.33 (dd, J = 6, 8 Hz, 1H, α-C<u>H</u>H-), 2.81 (dq, J = 6, 6 Hz, 1H, α-C<u>H</u>CH_3-), 3.05 (dd, J = 8, 9 Hz, 1H, α-CH<u>H</u>-), 5.27 (s, 5H), 5.36 (s, 5H). Assignments were made by selective homonuclear decoupling.

Preparation of Cyclohexene Metallacycle 19. Tebbe reagent (1.25 g, 4.39 mmol) and cyclohexene (1 mL, 8.8 mmol,) were dissolved in 8 mL CH_2Cl_2 in a Schlenk tube. DMAP (0.62 g, 5.08 mmol) was added to the

stirred solution at -20°C. After 5 min, the mixture was transferred dropwise via cannula into 100 mL 0°C pentane. The byproducts were removed on a coarse Schlenk frit and the filtrate was stripped of solvent in vacuo. The residue was dissolved in 4 mL toluene at 0°C and gradually cooled to -50°C. The supernatant was removed via cannula and the solid was washed 2 x 5 mL -50°C pentane and dried in vacuo for 90 min. Cyclohexene metallacycle **19** was collected as a red crystalline solid (200 mg, 17%). ^{1}H NMR (toluene-d_8, -20°C) δ -0.17 (m, 1H), 0.43 (m, 1H), 1.40 (m, 1H), 1.49 (m, 1H), 1.67 (dq, J = 4, 13 Hz, 1H), 1.76 (m, 1H), 1.83 (m, 2H), 1.97 (d, J = 13 Hz, 1H), 2.27 (t, J = 7 Hz, 1H), 3.46 (dd, J = 8, 10 Hz, 1H), 3.64 (dt, J = 4, 12 Hz, 1H), 5.24 (s, 5H), 5.32 (s, 5H); ^{13}C NMR (toluene-d_8, -20°C) δ 4.8 (d), 22.0, 25.6 (t), 32.2 (t), 33.9 (t), 85.4 (t), 95.4 (d), 108.2 (d), 108.8 (d). Multiplicity of the signal at δ 22.0 was not determined, due to overlap of a solvent signal.

Preparation of 1,2-Bis(methylene)cyclohexane Metallacycle 30. Tebbe reagent (1.05 g, 3.68 mmol) and 1,2-bis(methylene)cyclohexane (1.15 g, 10.6 mmol) were dissolved in 10 mL CH_2Cl_2 in a Schlenk tube. Solid DMAP (1.85 g, 15.2 mmol) was added to the stirred solution at -20°C. After 5 min at -20°C, the reaction mixture was cannulated dropwise into 100 mL of vigorously stirred -20°C pentane. The mixture was filtered through a coarse Schlenk frit and the filtrate was concentrated to 10 mL by removal of solvent in vacuo at -10°C. The product was precipitated at -78°C and the supernatant was removed via cannula. The red powder was washed with 10 mL -78°C pentane and dried in vacuo for 90 min at 0°C. Metallacycle **30** (500 mg, 45%) was isolated as a red powder which is stable for at least 24 h at room temperature. A pure sample was obtained by recrystallization from

toluene. ^{1}H NMR (toluene-d_8, -30°C) δ 1.3-1.7 (br, 6H), 2.05 (d, J = 9.7 Hz, 2H), 2.41 (m, 2H), 2.55 (d, J = 9.7 Hz, 2H), 4.80 (s, 1H), 5.05 (s, 1H), 5.57 (s, 5H), 5.65 (s, 5H); ^{13}C (^{1}H) NMR (toluene-d_8, -20°C) δ 18.4, 24.8, 29.9, 36.6, 47.7, 72.1, 104.0, 111.6, 111.9, 159.1.

Acidolysis of 30. Dry HCl gas (1.4 mmol) was vacuum transferred into a stirred suspension of **30** (171 mg, 0.57 mmol) in 2 mL Et_2O at -40°C. After 10 min at -40°C, the volatiles were vacuum transferred from the Cp_2TiCl_2 residue and found (GC analysis) to contain only two high-boiling hydrocarbons in the ratio of 20:1. A sample of the major component was isolated by preparative GC (SE-30) and identified as 1-methylene-2,2-dimethylcyclohexane.[61] ^{1}H NMR (C_6D_6) δ 1.04 (s, 6H), 1.41 (m, 6H), 2.41 (m, 2H), 4.73 (s, 2H).

Acidolysis of 9, 13, and 19. A solution of of the titanacycle (ca. 50 mg) in 2-3 mL toluene, in a Schlenk tube fitted with a teflon needle valve vacuum adaptor, was freeze-degassed three times and stirred at between -40 and -50°C. The Schlenk tube was connected, via the vacuum adaptor, to a glass transfer arm on a high vacuum line. At the other end of the transfer arm was a 30 mL mixing flask containing 2.2 equiv NaCl and fitted with a bent addition tube charged with 1.5 mL concentrated H_2SO_4. The apparatus was degassed in vacuo for 10 min and closed to vacuum. The H_2SO_4 was added, with stirring, to the solid NaCl. The needle valve atop the Schlenk tube was opened and the HCl diffused into the stirred sample solution. Reaction was complete within minutes. The needle valve was closed, and the mixing flask was replaced with a pear-shaped flask, into which the volatiles were vacuum transferred. An internal standard was added and products were

quantitated by GC, using response factors determined with authentic samples.

Thermolysis of 9, 13, and 19. A solution of titanacycle (ca. 50 mg) in 2 mL toluene in a small Schlenk tube, fitted with a teflon needle valve vacuum adaptor, was freeze degassed three times and stirred at 60°C for 1 h. The volatiles were vacuum transferred from the residue and quantitated by GC, using an internal standard and response factors determined with authentic samples. To avoid loss of volatile components, the sample was sealed with a latex septum while still frozen, and stored at -50°C. Gas-liquid distribution was compensated with the aid of careful control experiments. Error due to loss of product is significant only for C_1 and C_2 products (in thermolysis of **13**).

Bromination of 9. A solution of **9** (35.8 mg, 0.144 mmol) in 5 mL Et_2O was vigorously stirred in a small Schlenk tube at -20°C. Bromine (20 μL, 0.39 mmol) was drawn into a piece of polyethylene tubing (Intramedic PE-50) attached to a 50 μL syringe and dispensed into the metallacycle solution. A red-brown solid formed on mixing. The suspension was stirred for several minutes and the volatiles were vacuum transferred with the aid of a heat gun. 1,3-Dibromo-2,2-dimethylpropane was identified and quantitated by comparison with an authentic sample (GC, GCMS). Bromination in toluene solution was performed in a similar manner, to check for hydrocarbon products.

Iodination of 9 and 19. A solution of **9** (66.7 mg, 0.269 mmol) in 2 mL toluene was vigorously stirred at -35°C in a small Schlenk tube. Iodine (150 mg, 0.59 mmol) was added and a dark solid formed immediately. The

solution was allowed to warm to 5°C over a period of 2 h. The volatiles were vacuum transferred and the hydrocarbon products were identified by GC and GCMS comparison with authentic samples and quantitated by GC using measured response factors. No attempt was made to detect iodinated hydrocarbons.

Iodination of **19** was performed in a similar fashion, using 3 equiv of I_2 at -40°C. Norcarane was identified and quantitated by GC comparison with an authentic sample on two different columns.

Iodination of 13. A solution of **13** (81.6 mg, 0.329 mmol) in 30 mL toluene was vigorously stirred at -78°C. A freshly prepared solution of iodine (192 mg, 1.15 mmol) in 10 mL toluene at 0°C was transferred dropwise *via* cannula into the titanacycle solution. A dark solid formed on mixing. The reaction mixture was stirred for 1 h, as the temperature was gradually raised to -50°C. The volatiles were vacuum transferred and dimethylcyclopropane products were identified and quantitated by comparison with authentic samples on two different GC columns using measured response factors.

Another iodination was performed under identical conditions, except that the reaction mixture was washed 2 x 30 mL saturated Na_2SO_3 and filtered through a pad of silica gel. The solvent was reduced to 5 mL *in vacuo*. Only one high-boiling product was detected by GC. This was found to have the composition $C_5H_{10}I_2$ by GCMS. The yield was calculated using 1,6-diiodohexane as an internal standard, with the assumption that $MRF_{product} = 5/6\ MRF_{standard}$.

Reaction of 13 With Benzaldehyde. Benzaldehyde (61 μL, 0.60 mmol) was added *via* syringe to a stirred suspension of **13** (75 mg, 0.30 mmol) in 2

mL Et_2O in a small Schlenk tube at -40°C. No immediate change was observed. As the mixture was allowed to warm to room temperature over a period of 10 min, a yellow precipitate formed. After 1 h at room temperature, the volatile products were vacuum transferred and were identified and quantitated by GC comparison with authentic samples, using measured response factors. Immediate analysis is necessary to avoid polymerization of the styrenes produced.

Metathesis of trans,trans-2,8-Decadiene (18) and cis,cis-2,8-Decadiene (22) by $Cp_2\overbrace{TiCH_2CPhMeCH_2}$ (21). A solution of **21** (46 mg, 0.148 mmol) in 2 mL toluene was stirred in a medium Schlenk tube at -30°C. Diene **22** (150 µL,0.81 mmol) and 20 µL n-pentane were added. The Schlenk tube was fitted with a latex septum wrapped with parafilm, and the closed vessel was stirred at room temperature. Gas samples were withdrawn periodically and analyzed on an 18' x 1/8" 10% DMS on 100/120 Chrom PNAW column at 0°C. After the final aliquot was withdrawn, measured amounts of C-3 and C-4 hydrocarbons were added. Integration of these relative to n-pentane gave an estimate of the quantity of products evolved. Reaction of **21** with diene **18** was carried out under identical conditions except for occasional warming to 45°C. See Tables 2 and 3.

Metathesis of trans,trans-2,8-Decadiene (18) With cis-$Cp_2\overbrace{TiCHMeCHMeCH_2}$ (13). Diene **18** (200 µL, ca. 1.1 mmol) was added via syringe to a stirred suspension of **13** (47 mg, 0.19 mmol) in 1 mL toluene at -40°C in a small Schlenk tube. The mixture was stirred at room temperature for five days and the volatiles were vacuum transferred from the purple residue. Cyclohexene was identified by GC and GCMS comparison with an authentic sample and quantitated in the usual manner.

Attempted Metathesis of 1,7-Octadiene With cis-$Cp_2TiCHMeCHMeCH_2$ (13). 1,7-Octadiene (1.0 mL, 6.8 mmol) was added via syringe to a stirred suspension of **13** (165 mg, 0.665 mmol) in 2 mL toluene at -30 °C. The mixture was stirred at room temperature for 20 h and the volatiles were vacuum transferred from the still-red solution. No cyclohexene was detected by GC (< 0.01%/Ti).

Equilibrium and Kinetic Measurements. Metallacycles were recrystallized from Et_2O or toluene. Tebbe's reagent (**1**) was prepared from $Cp_2TiMeCl$ and recrystallized from hexane. All olefins, Et_2O and THF were dried over 4 Å molecular seives and thoroughly freeze-degassed prior to vacuum transfer. Reactions were run in sealed NMR tubes at 40 °C in C_6D_6. For reactions of titanacycles with base-aluminum adducts, samples were prepared by covering a weighed sample of titanacycle with C_6D_6 and layering on a measured amount of standardized (NMR vs internal 1,2-dibromoethane) base-aluminum adduct in C_6D_6. The samples were immediately removed from the drybox, frozen and sealed. For reactions with olefin and THF or Et_2O, **1** was weighed into an NMR tube fitted with a gas-measuring bulb. The solvent, olefin and base were introduced by vacuum transfer. Reactions were monitored at approximately ten intervals. After reaction, the volume was measured by replacement of the sample with a measured the volume of liquid. Integration of C_6D_6H indicated no more than 5% decomposition in most cases. Initial concentrations were derived from the weight of titanacycle or 1 and the measured volume. Subsequent values were calculated from NMR integration in a straightforward manner. Analysis of the data is discussed in the text.

Reaction of cis-$Cp_2TiCHMeCHMeCH_2$ (13) With $AlMe_2Cl$. Metallacycle 13 (53 mg, 0.21 mmol) was dissolved in C_6D_6, in an NMR tube fitted with a latex septum, at -20°C. The sample was placed in the probe of the JEOL FX-90Q at -30°C and the initial spectrum was recorded. A 0.43 M solution of $AlMe_2Cl$ in C_6D_6 was prepared and 200 µL (0.08 mmol) was added in increments. Slow formation of **1** was observed, but no **14** could be detected (absence of signals in δ 2.8-3.1 ppm region). After several minutes at -30°C, the temperature was raised to 0°C and the remaining $AlMe_2Cl$ reacted to give **1** (in ca. 5 min with no **14** formed).

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(21) The rate of reaction for equation 4 is (9.6×10^{-5} s^{-1}) (**4**) at 40 °C in

C_6D_6.[15]

(22) Intermediacy of a methylidene-olefin complex rather than **6** has not been excluded, but direct olefin exchange is believed to proceed via **6**.[15] To simplify discussion of several systems in this chapter, we frequently refer to free titanium alkylidene species. It should be remembered that existence of these uncomplexed alkylidenes has not been proven.

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dimethyl-1-butene (19.53) $-\Delta G_F°$ 3,3-dimethylbutane (-2.37) = 21.90 kcal/mol^{-1}; $\Delta G_F°$ 3-methyl-1-butene (17.87) $-\Delta G_F°$ 2-methylbutane (-3.50) = 21.37 kcal/mol^{-1}.[32,33] Thus the more stable metallacycle, **7**, forms from the more stable olefin. The opposite ordering would be expected if olefin stability were the only determining factor. The greater stability of **7** relative to **4**, as measured according to Scheme II, may therefore be attributed to structural features of these metallacycles.[35]

(32) Corresponding differences (as in Ref. 31) for some other olefin-alkane pairs are:[33] isobutylene, 18.88; 2-methyl-1-butene, 19.01; 2,3-dimethyl-1-butene, 18.41 kcal/mol^{-1}. These disubstituted olefins are ca. 2-3 kcal/mol^{-1} more stable relative to the corresponding alkanes, than are the monosubstituted olefins.[31] The apparent instability of **9**, **10**, and **11** relative to **4** and **7** may be due in part to this effect.

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

(34) If one considers free energy data for the corresponding olefins,[31,32] which might[35] account for 2-3 kcal/mol^{-1} of the measured difference in stability of **4** and **11**, this rate difference might be interpreted as indicating full relief of steric crowding in the transition state.

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(39) $AlMe_2Cl$·4-tert-Butylpyridine was prepared by mixing the pyridine and $AlMe_2Cl$ in hexane followed by removal of the solvent in vacuo. The white solid (610 mg) was dissolved in 20 mL 2:1 hexane:toluene and cooled to -50 °C. No solid had precipitated after two days.

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(44) The product distribution in Figure 5 is not inconsistent with hydride-mediated isomeriztion.[45]

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CHAPTER 2

Mechanism of Carbonylation of Bis(cyclopentadienyl)titanacyclobutanes

Introduction

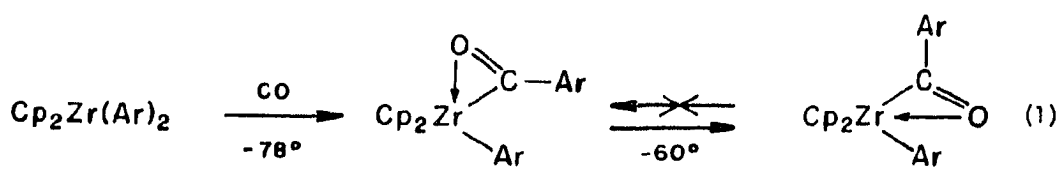
Insertion of carbon monoxide into metal-carbon σ-bonds is among the most widely studied organometallic reactions.[1] Such insertions have been observed for nearly every transition metal. Much of this interest arises from the occurrence of carbon monoxide insertion in useful homogeneous catalytic and stoichiometric transformations[1d,6b] and possibly in heterogeneous processes,[3] including the Fischer-Tropsch synthesis.[4] Among the many points of interest in these investigations have been the factors which influence such migratory insertions and the stereochemical consequence at the migrating carbon center. In general, it has been found that a vacant coordination site for binding of CO is required and that a relatively weak metal-carbon bond strongly favors acyl complex formation. Although a large number of stereospecific CO insertions have been observed, examples in which the stereochemistry at migrating carbon has been unambiguously determined are scarce. Insertion of CO is generally assumed to proceed with retention of configuration, based on the relatively few cases studied.[5]

As recently as ten years ago, no CO insertions into Group IV metal-carbon bonds were known.[1e] This was due to a lack of stable metal alkyl complexes for study. A large number of such alkyl complexes have since been prepared,[6] most of which are metallocene derivatives, and several investigations of CO insertion reactions of these species have been reported.[6a,b,7]

Insertion of CO into titanocene dialkyls is facile, but the alkyl acyl complexes have not been isolated.[7h,8] Reductive elimination occurs under the reaction conditions employed. Thus, carbonylation of $Cp_2Ti(CH_2Ph)_2$

affords $Cp_2Ti(CO)_2$ (1)[9] and dibenzyl ketone.[7h] Similarly, Whitesides reported that carbonylation of $Cp_2TiCH_2(CH_2)_2CH_2$ (2) affords 1 and cyclopentanone.[7f] However, carbonylation of the halo alkyl complexes Cp_2TiRX (R = Me, CH_2Ph, X = Cl; R = Et, X = Cl, I) gives stable halo acyl complexes, $Cp_2Ti(COR)X$.[7g] The acyl ligands in these and all other Group IV metal acyl complexes are η^2 (C,O) bound. This dihapto coordination is characterized by a highly distorted acyl geometry and extremely low C-O stretching frequencies.[7e,g,10] Examples of dihapto-acyl complexes have also been reported for complexes of Groups V, VI and VIII.[12]

The zirconium dialkyls Cp_2ZrR_2 are reversibly carbonylated to produce acyl complexes $Cp_2Zr(COR)R$.[7d] In the case of unsymmetrical dialkyl complexes, insertion of CO occurs at the more sterically hindered alkyl substituent.[6a,11] Low temperature NMR studies of carbonylation of zirconocene dialkyl and diaryl complexes have revealed initial formation of the "oxygen-out" isomer, which subsequently isomerizes to the more stable "oxygen-in" form (eq. 1).[13] Further mechanistic insight has been provided by Schwartz and co-workers, who have demonstrated retention of configuration at migrating carbon for insertion of CO into threo and erythro-$Cp_2Zr(CHDCHDt\text{-}Bu)Cl$.[5b] The alkyl acyl complexes $Cp_2Zr(COR)R$ are inert to further CO insertion, presumably due to blockage of the site for CO



(1)

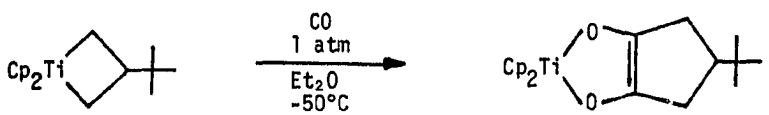
Ar = p-tolyl

coordination by the dihapto-acyl ligand.[7d] Other relevant observations, particularly in the decamethylzirconocene series, will be discussed as appropriate.

Although our interest in Group IV transition-metal acyl chemistry began with our continuing investigation of the reactivity of bis(cyclopentadienyl)titanacyclobutanes,[14] our findings have led to a more general investigation of such species. This area comprises the remainder of this and the following chapter of this thesis.

Results and Discussion

Based on the observation of Whitesides, we had anticipated the formation of cyclobutanones on carbonylation of the titanacyclobutanes. This result would be a synthetically useful process. However, upon carbonylation of titanacyclobutane **3a** (at low temperature in Et_2O under conditions where a relatively high concentration of CO is maintained) the enediolate complex **3b** was produced (eq. 2) along with a trace amount of **1**. This cyclic enediolate is one of a series of such complexes which have been

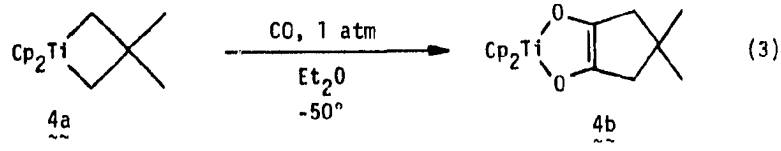


3a 3b (2)

prepared from previously reported[14] titanacyclobutanes (vide infra). These enediolates[15] have been characterized by ^1H and ^{13}C NMR, IR, elemental analysis and/or high-resolution mass spectrometry and by chemical methods. All of the enediolate complexes are deep-purple crystalline solids which are only moderately air-sensitive in the solid state and in solution. The complexes dissolve in benzene, toluene and diethyl ether but are pentane-insoluble. The ^{13}C NMR spectra (C_6D_6) are particularly diagnostic since the oxygen-bound carbons in these complexes appear at δ 142-145 ppm. This is nearly identical with shifts observed for cyclic enediolates of decamethylzirconocene[7b] and decamethylhafnocene.[16] These ^{13}C NMR shifts are in the range typical of olefinic compounds rather than Group IV acyl complexes (ca. 300 ppm).[13b] Characteristic IR stretches occur at

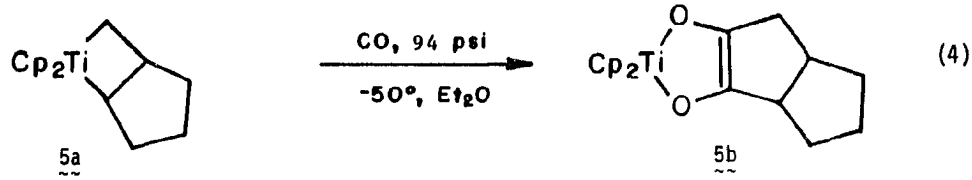
1480-1490 cm^{-1}. Strong M^+ peaks are present in the mass spectra of these products and in all cases Cp_2Ti^+ is the major fragmentation product observed.

Carbonylation of **3a** (eq. 2) goes to completion in less than 30 min (1 atm, -50°C). The isobutylene metallacycle **4a** gives enediolate **4b** under identical conditions (eq. 3). In both reactions, the products are cleanly formed. However, when the reactions are run at higher temperature, or if the CO is allowed to diffuse into stirred solutions of **3a** or **4a** rather than



4a **4b** (3)

being introduced via a dispersion tube, other reactions become competitive. This is evidenced by formation of significant amounts of **1** and extreme broadening of the ^1H NMR spectra of the products obtained upon removal of solvent. The broadened NMR signals presumably result from paramagnetic products, which may be removed by filtration through Florisil. Carbonylation of the cyclopentene titanacyclobutane **5a** is much slower. Under conditions which produce **3b** or **4b** in 30 min, formation of enediolate **5b** is only 15% complete after 4 h, with unreacted **5a** and trace amounts of **1** as



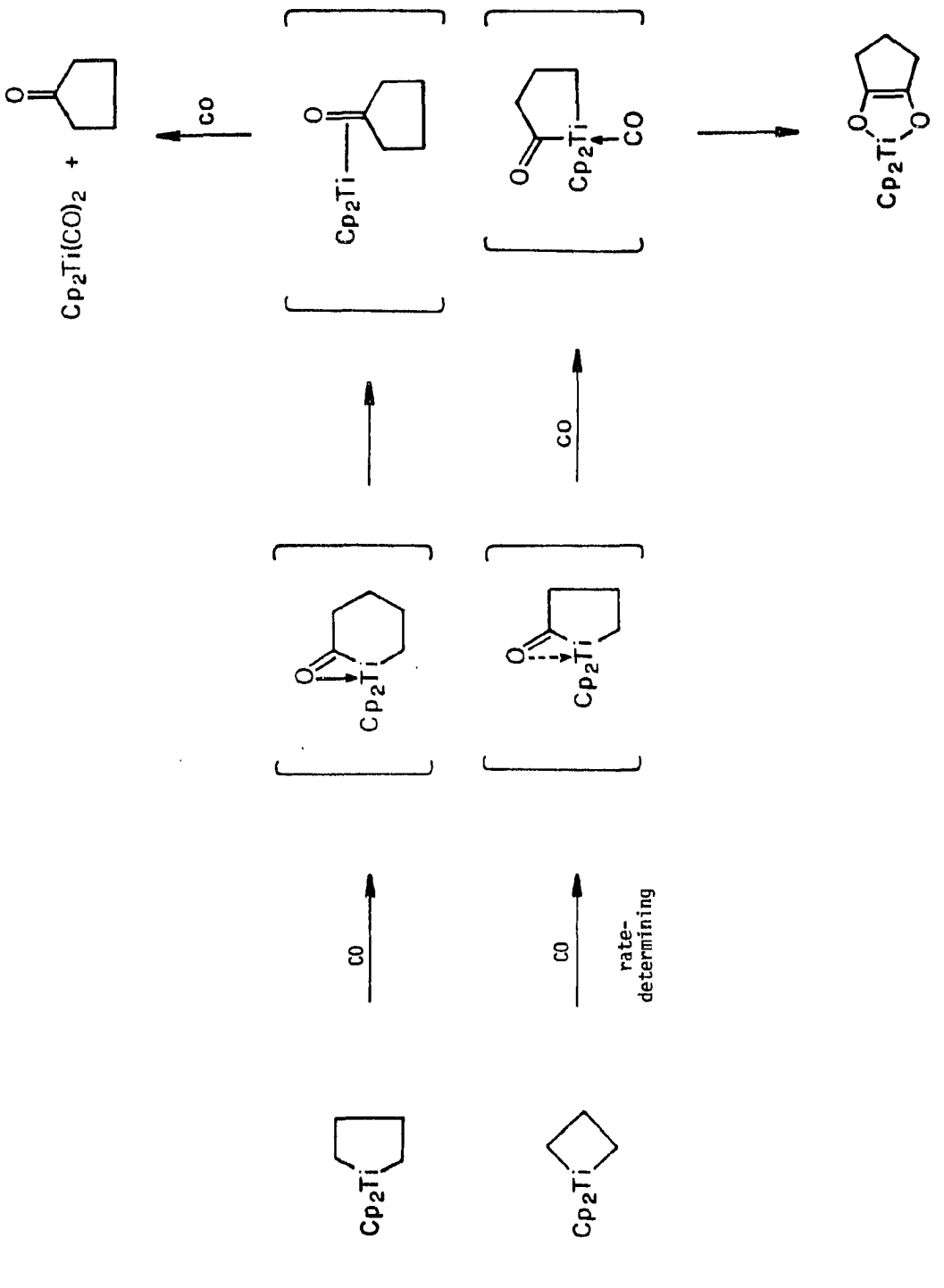
5a **5b** (4)

the only other species present. Under 94 psi CO in a Fischer-Porter bottle, however, **5b** is rapidly and cleanly (< 3% 1) formed (eq. 4).

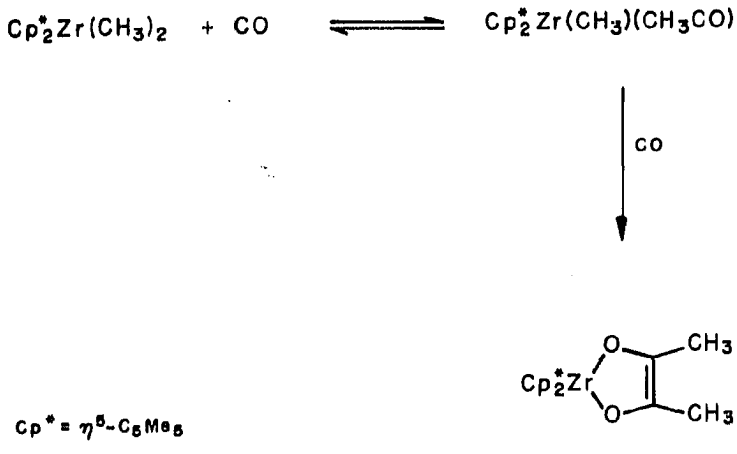
The effect of reaction conditions and titanacyclobutane structure on the course of carbonylation provides some mechanistic insight into this reaction. A mechanism which explains the contrasting behavior of the titanacyclobutanes and titanacyclopentane **2** is presented in Scheme I. Substituents on the titanacyclobutane are omitted for clarity. The difference in these reactions is believed to arise from steric constraints on the initially formed acyl complexes. The cyclic acyl from **2** should be coordinated in the typical dihapto fashion,[17] whereas the homologous acyl intermediates, from the titanacyclobutanes, are expected to tend toward monohapto coordination as a consequence of the smaller ring size. This assertion is supported by examination of molecular models, which show a dramatic difference in the two structures. The "pulling back" of the oxygen in the cyclic acyls allows coordination of a second CO molecule, leading to enediolate products. The first CO insertion is probably rate-determining in the titanacyclobutane case (vide infra). According to this scheme, as the CO concentration is decreased the unstable acyl complex is less efficiently trapped and unimolecular decompositions become more important. The slower reaction of **5a**, compared with **3a** and **4a**, is attributed to further destabilization of the cyclic acyl as a result of additional constraints imposed by the second ring. This is also evident from the molecular models.

Bercaw and co-workers have observed cyclic enediolate formation on carbonylation of $(\eta^5\text{-}C_5Me_5)_2ZrMe_2$ (Scheme II).[7b] These authors have suggested that the oxycarbene resonance structure (Fig. 1), in which the acyl

Scheme I


Cp2Ti
CO
Cp2Ti
CO
rate-
determining
Cp2Ti
Cp2Ti
CO
Cp2Ti
CO
Cp2Ti(CO)2 +
Cp2Ti

Scheme II



group is covalently bonded to the metal via oxygen and the acyl carbon is datively bound, plays an important role in the chemistry of dihapto acyl complexes.[18] This interesting proposal provided the impetus for investigations which are described in the following chapter. Using this concept, the difference in behavior between $(\eta^5\text{-}C_5Me_5)_2ZrMe_2$ and Cp_2ZrMe_2 which undergoes only one insertion, may also be understood in terms of the well-established requirement for coordination of CO prior to insertion. The more strongly donating pentamethylcyclopentadienyl ligands should reduce the tendency of the metal to achieve coordinative saturation via dihapto coordination of the acyl ligand. Also, the larger permethylated rings might destabilize the dative oxycarbene interaction enough that coordination of CO becomes competitive. Such weakening of the oxycarbene

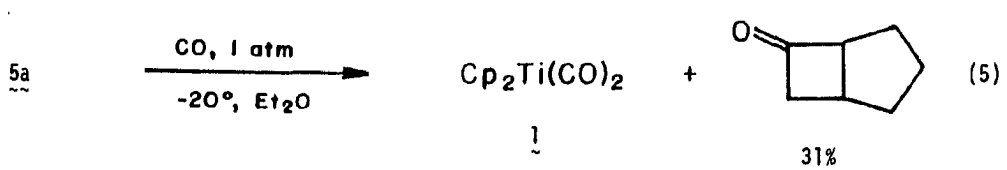
"oxycarbene"

Cp* = η^5-C_5Me_5

Figure 1. Resonance structures for dihapto-acyl complexes after Bercaw, et. al.[7b]

interaction could also play an important role in determining the reactivity of the cyclic acyls derived from the titanacyclobutanes, the acyl form of which is depicted in Scheme I.

One set of products which would be expected in carbonylation of the titanacyclobutanes, under conditions in which CO is limited, are cyclobutanones. Consistent with this expectation, bicyclo(3.2.0)heptan-6-one was formed in low yield when CO was bubbled through an ethereal solution of **5a** (eq. 5). Subsequent experiments indicated that **1** and **5b** form under these conditions. Also formed are minor amounts of Cp-containing materials which cause extensive line-broadening in the ^{1}H NMR. In a similar reaction, the temperature was slowly raised from -40°C to 0°C (3 h). The ^{1}H NMR



(5)

spectrum was sharper and **1** and **5b** were observed in equal amounts along with ca. 5% unreacted **5a**. Bercaw and co-workers have reported formation of $(\eta^5\text{-}C_5Me_5)_2Zr(\overbrace{OC{=}CH(CH_2)_2CH_2}^{}\,)H$ on carbonylation of $(\eta^5\text{-}C_5Me_5)_2\text{-}\overbrace{ZrCH_2(CH_2)_2CH_2}^{}$.[7b] The observation that no additional bicyclo(3.2.0)heptan-6-one is released on treatment of the product of equation 5 with HCl indicates that the ketone is not partially tied up as an enolate complex. No check has been made for cyclobutanone products in carbonylation of other titanacyclobutanes under conditions which promote formation of **1**.

Assignment of the first CO insertion of Scheme I as the rate-determining process in carbonylation of the titanacyclobutanes is based largely on carefully controlled kinetics performed by Dr. S. L. Buchwald. These experiments, in which **5a** was carbonylated at -40°C under 94 psi and under 54 psi of CO for equal lengths of time with otherwise identical conditions, indicated a first order dependance of disappearance of **5a** on CO concentration.[19] Buchwald has also monitored the carbonylation of **4a** by ^{13}C NMR at low temperature using ^{13}C-enriched CO. In the NMR probe it is not possible to bubble CO through the solution. This corresponds, therefore, with the other reactions in which the supply of dissolved CO was limited. No ^{13}C NMR resonances corresponding with an acyl complex (δ ~300 ppm)[13b] or with free ^{13}CO could be observed. The ^1H NMR reveals a number of products of undetermined composition in addition to **4b**, **1**, and isobutylene.[20] Significantly, no ketene complexes (see Chapter 3) were observed. These observations are consistent with rate-determining formation of an unstable cyclic acyl complex which must be rapidly trapped by CO for enediolate

products to be formed.

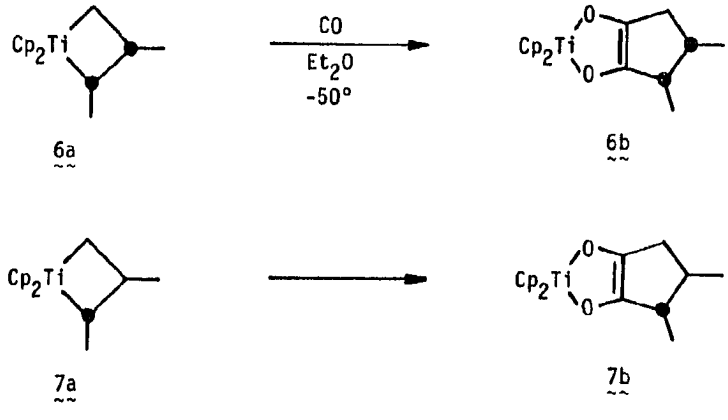
The reductive elimination of cyclopentanone in Scheme I is probably not promoted by carbon monoxide, since it would be difficult to reconcile the CO-dependent partitioning of **5a** between pathways leading to **5b** and to **1** if both reactions involved interception of the cyclic acyl intermediate by processes which are first-order in CO. The cyclopentanone and cyclobutanone complexes, Cp_2Ti(ketone), are probably trapped by CO as Cp_2Ti(ketone)(CO) adducts along the pathway to **1** and free ketone. These adducts would be analogous with $(\eta^5\text{-}C_5Me_5)_2Zr$(aldehyde)(CO) complexes characterized by Roddick and Bercaw.[16] Enolate formation is not observed in the titanacyclobutane reactions (vide supra), probably because of the high strain energy resulting from introduction of a double bond into a four-membered ring.[21]

An attempt was made to promote formation of cyclobutanones in carbonylation of titanacyclobutanes by introduction of a donor ligand which might complete with CO for coordination to the unstable cyclic acyl intermediate. However, addition of 2 equivalents of PMe_3 to an ethereal solution of **3a** did not lead to formation of **1** upon bubbling CO through the solution for 30 min at -50 °C. The only material observed on removal of the volatiles was **3b**.

The stereochemistry of carbon monoxide insertion was determined by carbonylation of cis-$Cp_2TiCHMeCHMeCH_2$ (**6a**) and its trans-isomer (**7a**).[14] Preparative reactions employed **6a** and **7a** prepared from $Cp_2TiCH_2{\cdot}AlMe_2Cl$ and carbonylated without isolation. No difference was observed when isolated **7a** was used. The rate of carbonylation of **6a** and **7a** is roughly the

same as that of **3a** and **4a**. This confirms that the second ring in **5a**, and not simply the 1,2-dialkyl substitution pattern, is responsible for the remarkably slower rate of carbonylation of this metallacycle. Different enediolate products, **6b** and **7b**, are produced from **6a** and **7a**, respectively (Scheme III). Each enediolate is formed exclusively. A toluene-d_8 solution of **6b** was heated to 100°C for 30 min with no apparent change. The stereochemistry of **6b** and **7b** has been determined by difference-NOE experiments[22] (see Experimental Section) and is consistent with retention of configuration as indicated in Scheme III.[25] Thus, at least one of the two successive CO insertions into **6a** and **7a** proceeds with retention. In accordance with experiments involving carbonylation of unsymmetrical zirconocene dialkyl complexes, it is likely that the first insertion occurs at the substituted

Scheme III



position in these titanacycles.[6a,11] This is the first such determination for titanium alkyl complexes and the second for a Group IV metal alkyl. α,β-Disubstituted titanacyclobutanes provide the only existing opportunity to examine the stereochemical course of processes in which titanium-alkyl bonds are cleaved. This feature has also proved useful in examining the mechanism of iodination of titanium-carbon bonds.[23] A number of other applications can be envisioned as well.

In addition to the usual instrumental methods, the enediolates have been characterized by identification of products of chemical degradation. Enediolate **3b**, generated in situ from **3a**, gave a cyclic acyloin, 4-tert-butyl-2-hydroxycyclopentan-1-one, on treatment with HCl at low temperature. Low-temperature oxidative decomposition with iodine afforded the corresponding α-diketone (Fig. 2). Similar treatment of **4b** with bromine produced the expected α-diketone, 4,4-dimethyl-2-hydroxycyclopent-2-en-1-one in 61% isolated yield. The possibility of adapting these reactions to organic synthesis is attractive, especially in view of the experimental difficulty and harsh reaction conditions involved in the acyloin condensation.[24] The overall scheme would involve one-step conversion of a ketone or aldehyde to a titanacyclobutane, which would be carbonylated without isolation (after precipitation and removal of the base-aluminum adduct), and acidolysis of the resulting enediolate to give a cyclic acyloin product. The high-yield in situ production of titanacyclobutanes, which is the basis of this synthesis as well as many other potentially useful synthetic schemes currently under investigation in our laboratory, is evident from equation 6. This sequence has been used successfully in one-step

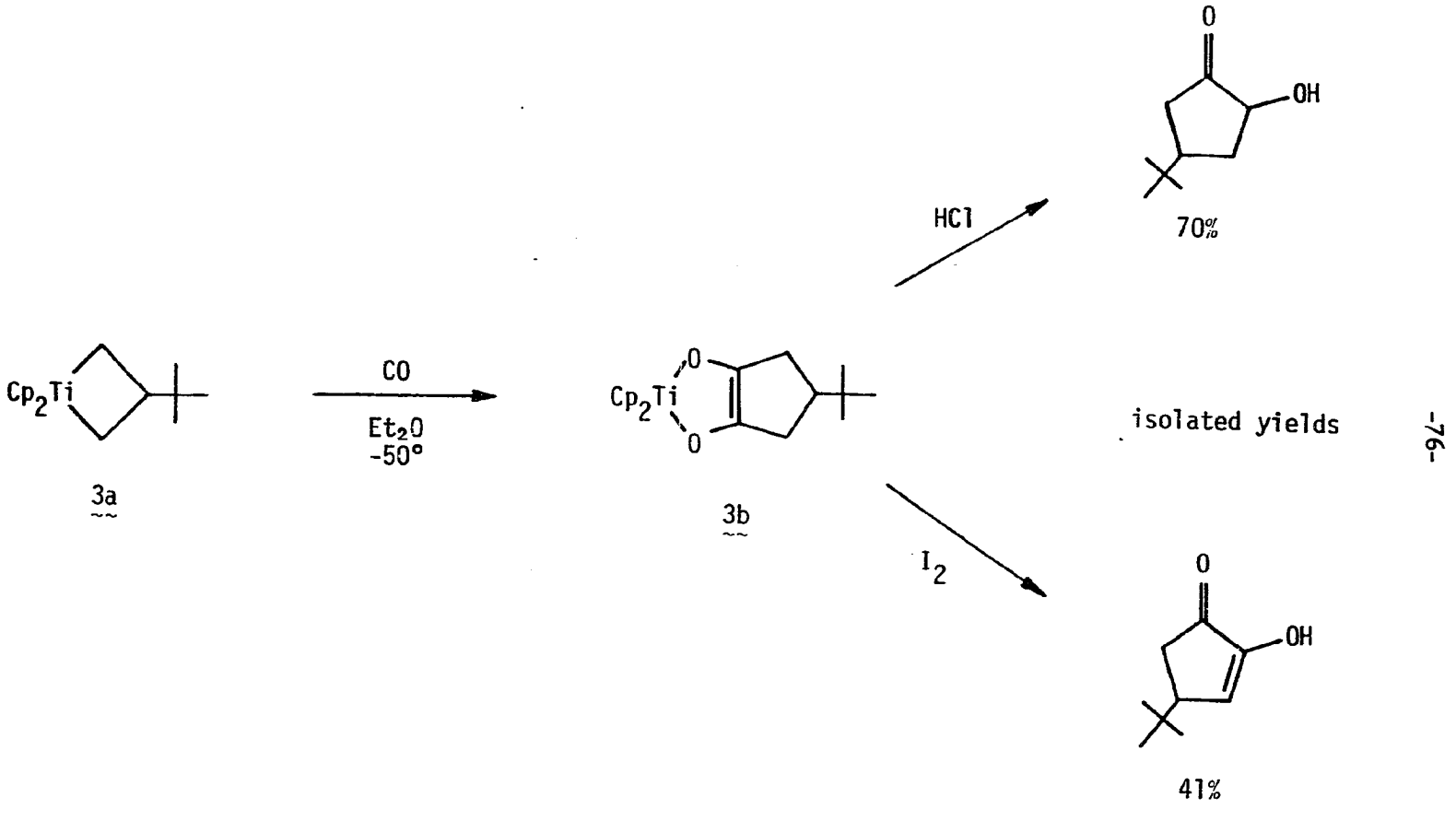
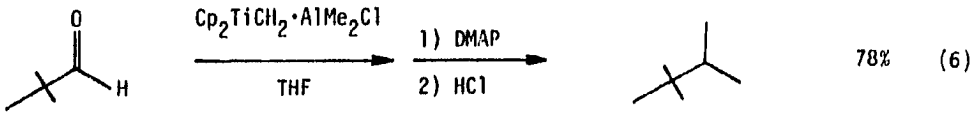

Cp2Ti
CO
Et2O
-50°
3a
Cp2Ti
O
O
3b
HCl
O
OH
70%
I2
O
OH
41%
isolated yields

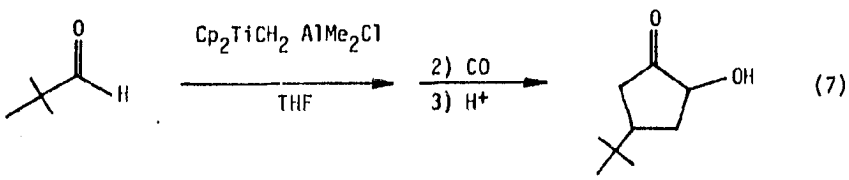
Figure 2



78% (6)

DMAP = 4-dimethylaminopyridine

synthesis of 4-tert-butyl-2-hydroxycyclopentan-1-one from pivalaldehyde as indicated in equation 7. Similar transformations have been employed by Buchwald in the high-yield preparation of spirocyclic acyloins from substituted cyclohexanones. Modification of the techniques involved in these transformations, to improve yields and make the process viable for use in typical synthetic organic laboratories, is in progress.



(7)

54%
isolated

Experimental Section

Pivalaldehyde and 3,3-dimethyl-1-butene were purchased from Aldrich and dried over $MgSO_4$. Cis- and trans-2-butene were purchased from Matheson and were thoroughly freeze-degassed prior to use. Carbon monoxide was purchased from Matheson. 4-Dimethylaminopyridine was purchased from Aldrich and recrystallized from hot toluene. $Cp_2TiCH_2CH(t\text{-}Bu)CH_2$ (**3a**), $Cp_2TiCH_2CMe_2CH_2$ (**4a**), cis-$Cp_2TiCH_2CHMeCHMe$ (**6a**), the cyclopentene titanacyclobutane **5a** and $Cp_2TiCH_2{\cdot}AlMe_2Cl$ ("Tebbe reagent") were prepared by established methods.[14]

Toluene, diethyl ether and THF were stirred over CaH_2 and vacuum transferred onto sodium benzophenone ketyl. Pentane was stirred over concentrated H_2SO_4, washed with water, dried over CaH_2 and vacuum transferred onto sodium benzophenone ketyl in tetraglyme. All solvents were vacuum transferred into flasks sealed with teflon screw valves. Benzene-d_6 (Merck, Sharp and Dohme) and toluene-d_8 (Aldrich) were dried and deoxygenated by stirring over sodium benzophenone ketyl.

General Procedures. All manipulation of air and/or moisture-sensitive compounds was carried out using standard high-vacuum Schlenk techniques or in a Vacuum Atmospheres Dry Box equipped with a -40 °C freezer. Argon used in Schlenk work was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4 Å molecular sieves. NMR spectra were recorded on a Varian EM-390 (90 MHz ^1H) or a JEOL FX-90Q (89.60 MHz ^1H, 22.53 MHz ^{13}C) instrument. Difference NOE spectra were recorded by the staff of the Southern California Regional NMR Facility at Caltech on a Bruker WM-500 (500.13 MHz ^1H). Gas chromatographic analyses were performed

on a Varian 1400 flame ionization instrument equipped with a Spectra-Physics System I computing integrator. Elemental analysis was done by Spang Microanalytical Laboratory or Schwartzkopf Microanalytical Laboratory. High-resolution mass spectra were obtained from the Midwest Center for Mass Spectrometry at the University of Nebraska.

High-pressure carbonylations were carried out in a Fischer-Porter bottle equipped with a Swagelock ball valve and rubber septum, through which solutions were transferred via cannula. Rapid stirring was achieved by use of a 1" x 3/8" stirbar which was shortened to fit the bottle. Carbonylations at 1 atm pressure were performed (unless otherwise indicated) by introduction of CO through a gas dispersion tube which had been oven-dried and flushed with CO for several minutes. Bulb-to-bulb distillation was carried out on a Buchi GKR-50 apparatus.

Preparation of Tert-butylenediolate 3b. A solution of $Cp_2TiCH_2CH(t\text{-}Bu)CH_2$ (**3a**) (380 mg, 1.38 mmol) in 30 mL Et_2O was stirred under 94 psi CO at -50°C for 3 h. The dark solid which formed redissolved at room temperature. The purple solution was filtered and slowly cooled to -78°C. The supernatant was removed via cannula and the purple crystalline solid was washed 2 x 10 mL -78° pentane and dried in vacuo at room temperature to give **3b** (293 mg, 64%). ^1H NMR (C_6D_6) δ 0.77 (s, 9H), 2.35 (m, 5H), 5.55 (s, 5H), 5.71 (s, 5H); ^{13}C (^1H) NMR (C_6D_6) δ 27.2, 31.1, 32.3, 45.0, 109.0, 111.7, 143.3; IR (KBr) 3100, 2960, 2950, 2880, 2850, 1485, 1440, 1370, 1300, 1260, 1230 cm^{-1}. MS (70 eV) 332.126, M^+, 12.8; 267.086, $M^+-C_5H_5$, 2.1; 178.016 m/e, Cp_2Ti^+, 100. MS (70 eV) molecular ion cluster: Nominal m/e, Calculated (Found): 330, 10.5 (10.2); 331, 11.8 (16.5); 332, 100 (100); 333,

28.4 (26.9); 334, 11.1 (10.1). This product may also be prepared by bubbling CO through a -50°C Et_2O solution of **3a** for 30 min.

Preparation of gem-Dimethylenediolate 4b. Carbon monoxide was bubbled through a solution of (**4a**) (75 mg, 0.30 mmol) in 5 mL -50°C Et_2O in a Schlenk tube for a 30 min period. Bubbling was continued as the bath was removed and the deep purple solution was allowed to warm to room temperature over a 10 min period. The solvent was removed in vacuo to give **4b** as a deep purple solid which may be recrystallized from Et_2O. ^1H NMR (C_6D_6) δ 1.09 (s, 6H), 2.31 (s, 4H), 5.61 (s, 10H); ^{13}C NMR (C_6D_6) δ 31.5 (q), 34.2 (s), 44.7 (t), 110.4 (d), 142.7 (s); IR (C_6D_6) 3120, 2960, 2940, 2840, 1490, 1440, 1370, 1310, 1260, 1230 cm^{-1}. MS (70 eV) 304.095, M^+, 15.5; 239.054, $M^+-C_5H_5$, 1.97; 178.016 m/e, Cp_2Ti^+, 100.

Preparation of Tricyclic Enediolate 5b. A solution of the cyclopentene titanacycle **5a** (145 mg, 0.56 mmol) in 50 mL -50°C Et_2O was stirred for ca. 5 h under 94 psi CO at -45°C. The solvent was removed in vacuo at room temperature and the purple solid was washed with 3 mL -78°C pentane. Removal of residual solvent in vacuo afforded **5b**((104 mg, 59%) as a purple powder. The product was contaminated with some impurity which caused high integration values for the upfield portion of the ^1H NMR but which was not detected in the ^{13}C NMR. ^1H NMR (C_6D_6) δ 1.2-1.8 (m, br, several H), 2.15 (m, 1H), 2.41 (m, 2H), 2.67 (m, 2H), 5.41 (s, 5H), 5.79 (s, 5H); ^{13}C (^1H) NMR (C_6D_6) δ 26.6, 30.8, 35.8, 36.0, 37.9, 45.4, 107.1, 113.6, 143.2, 145.8.

Preparation of Cis-Dimethylenediolate 6b. $Cp_2TiCH_2 \cdot AlMe_2Cl$ (1.05 g, 3.68 mmol) was dissolved in 10 mL dichloromethane in a Schlenk tube and cooled to -196°C. Cis-2-butene (40 mmol) was thoroughly freeze-degassed

and vacuum transferred into the reaction vessel. With stirring at -30°C, solid DMAP (0.52 g, 0.43 mmol) was added. After 5 min the mixture was transferred dropwise via cannula into 100 mL vigorously stirred -25°C pentane. The flocculent white precipitate was removed on a coarse frit and the clear red filtrate was stripped of solvent in vacuo at 0°C. The residue was partially dissolved in 60 mL Et_2O at -50°C. Carbon monoxide was bubbled through the stirred mixture for 45 min. Bubbling was discontinued, and the deep purple solution was brought to room temperature and filtered through an 8 cm plug of Florisil. The solvent was removed in vacuo to leave a purple powder, which was washed with 10 mL -50°C pentane. Residual pentane was removed in vacuo and purple **6b** (600 mg, 56%) was collected. The product may be recrystallized from Et_2O. ^1H NMR (C_6D_6) (see Figs. 3 and 4) δ 0.96 (d, J_{H_b} = 8 Hz, β-CH_3), 1.15 (d, J_{H_a} = 8 Hz, α-CH_3), 2.22 (dd, J_{H_b} = 4, J_{H_c} = 16 Hz, H_d), 2.36 (dddq, J_{H_d} = 4, J_{H_c} = 8, J_{H_a} = 8, $J_{\beta CH_3}$ = 8 Hz, H_b), 2.46 (dd, J_{H_b} = 8, J_{H_d} = 16 Hz, H_c), 2.61 (dq, J_{H_b} = $J_{\alpha CH_3}$ = 8 Hz, H_a), 5.54 (s, Cp), 5.75 (s, Cp); ^{13}C (^1H) NMR (C_6D_6) δ 12.7, 17.5, 31.6, 37.0, 38.6, 108.2, 112.9, 142.6, 146.7; IR (KBr) 3100, 2980, 2960, 2940, 2870, 2830, 1480, 1440, 1360, 1330, 1290, 1265, 1250, 1210 cm^{-1}. MS (70 eV) 304.094, M^+, 13.1; 289.071, M^+-CH_3, 0.64; 239.053, M^+-C_5H_5, 1.5; 178.026 m/e, Cp_2Ti^+, 100.

Anal. calcd. for $C_{17}H_{20}O_2Ti$: C, 67.11; H, 6.63; Ti, 15.74. Found: C, 66.38; H, 6.64; Ti, 15.61.

Preparation of Trans-Dimethylenediolate 7b. $Cp_2TiCH_2 \cdot AlMe_2Cl$ (1.00 g, 3.51 mmol) was dissolved in 10 mL dichloromethane in a Schlenk tube and cooled to -196°C. Trans-2-butene (40 mmol) was freeze-degassed and vacuum-transferred into the reaction vessel. With stirring at -30°C, solid

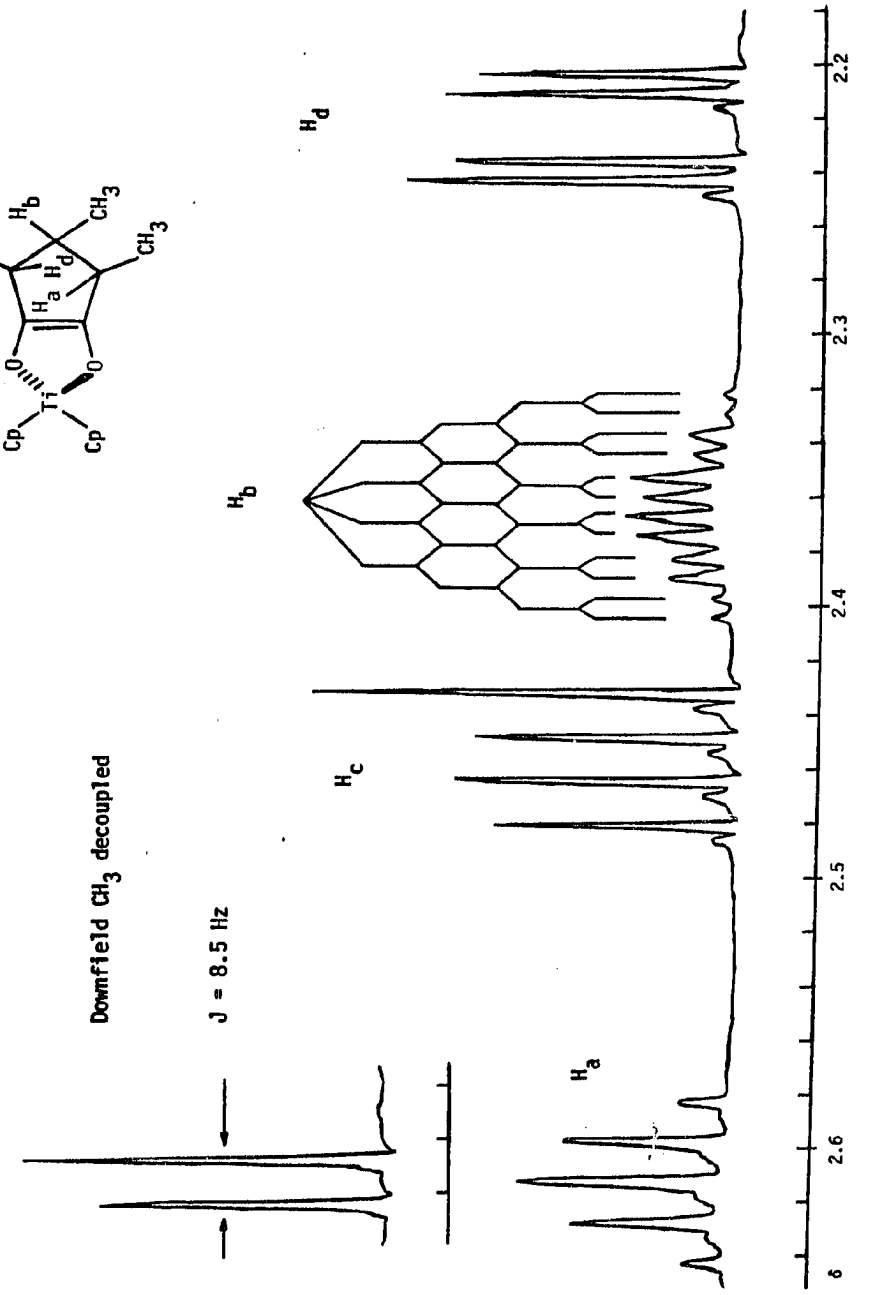
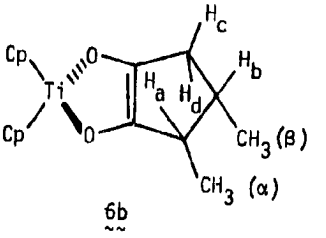


Figure 3. ^1H NMR spectrum (500 MHz) of **6b.**



6b

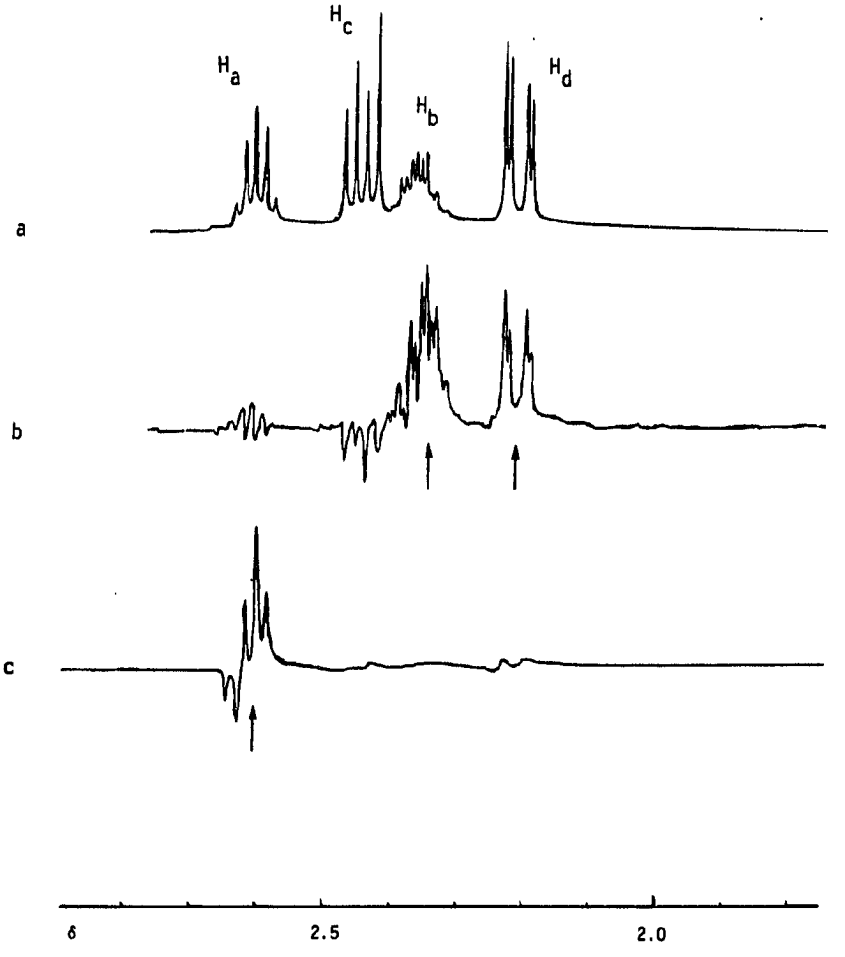


Figure 4. 500 MHz ^{1}H difference NOE spectra of **6b**: a) non-irradiated, b) β-CH_3 irradiated, c) α-CH_3 irradiated. Arrows indicate those peaks for which NOE enhancement is observed.

DMAP (0.50 g, 4.1 mmol) was added. After 3 min, the mixture was stirred at 0°C for 2 min, then cooled to -30°C. The red solution was transferred dropwise via cannula into 100 mL vigorously stirred 0°C pentane. The suspension was filtered on a coarse frit and the clear red filtrate was stripped of solvent in vacuo. The residue was dissolved in 50 mL -50°C Et_2O and carbon monoxide was bubbled through for ca. 30 min. Bubbling was discontinued and the deep purple solution was filtered through an 8 cm plug of Florisil. The solvent was removed in vacuo and the product was washed with 10 mL -78°C pentane and dried in vacuo to give **7b** (650 mg, 58%) as a dark purple powder which may be recrystallized from Et_2O. ^1H NMR (C_6D_6) (see Figs. 5 and 6) δ 1.00 (d, J_{H_b} = 8 Hz, β-CH_3), 1.22 (d, J_{H_a} = 8 Hz, α-CH_3), 1.89 (dddq, $J_{H_a} = J_{H_c} = J_{H_d} = J_{\beta CH_3}$ = 8 Hz, H_b), 1.97 (dd, J_{H_b} = 8 Hz, J_{H_d} = 16 Hz, H_c), 2.17 (dq, $J_{H_b} = J_{\alpha CH_3}$ = 8 Hz, H_a), 2.68 (dd, J_{H_b} = 8, J_{H_c} = 16 Hz, H_d), 5.39 (s, Cp), 5.71 (s, Cp); ^{13}C NMR (C_6D_6) δ 17.0 (q), 20.1 (q), 37.0 (t), 38.6 (d), 43.9 (d), 107.8 (d), 113.2 (d), 142.2 (s), 146.4 (s); IR (KBr) 3100, 2960, 2940, 2910, 2880, 2820, 1485, 1445, 1330, 1280, 1220 cm^{-1}. MS (70 eV) 304.094, M^+, 13.1; 289.071, M^+-CH_3, 0.64; 239.054, M^+-C_5H_5, 1.8; 178.016 m/e, Cp_2Ti^+, 100.

Anal. calcd. for $C_{17}H_{20}O_2Ti$: C, 67.11; H, 6.63; Ti, 15.74. Found: C, 66.41; H, 6.55; Ti, 15.94.

Preparation of Cis-Dimethylenediolate 7b from Cis-$Cp_2TiCH_2CHMeCHMe$ (7a). Titanacycle **7a** (86 mg, 0.35 mmol) was suspended in 20 mL -50°C Et_2O. Carbon monoxide was bubbled through the stirred solution for a 30 min period. The deep purple solution was allowed to warm to room temperature and the solvent was removed in vacuo to give a purple

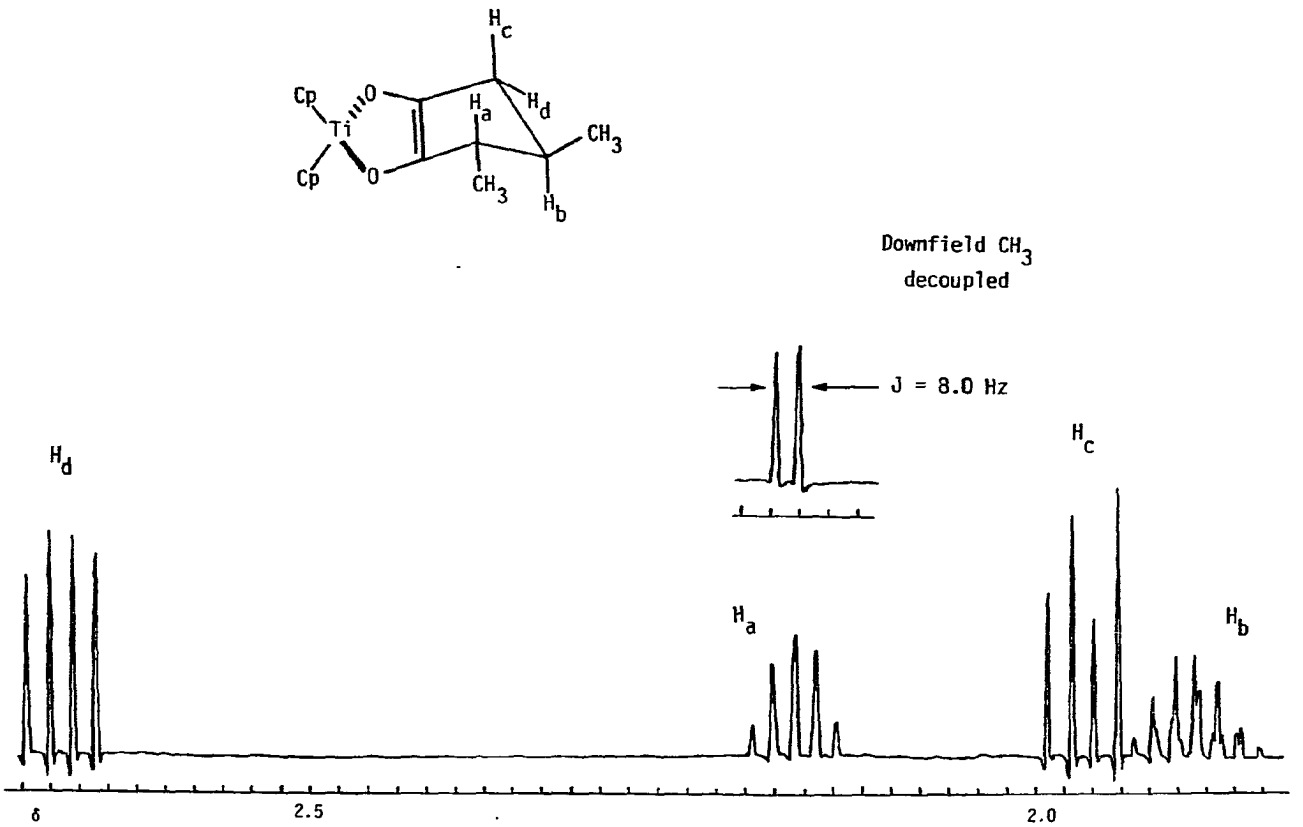
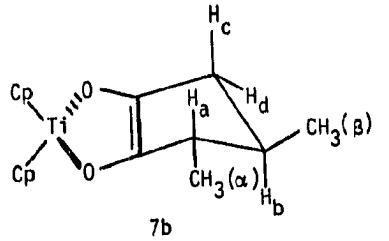


Figure 5. ^{1}H NMR spectrum (500 MHz) of **7b.**



7b

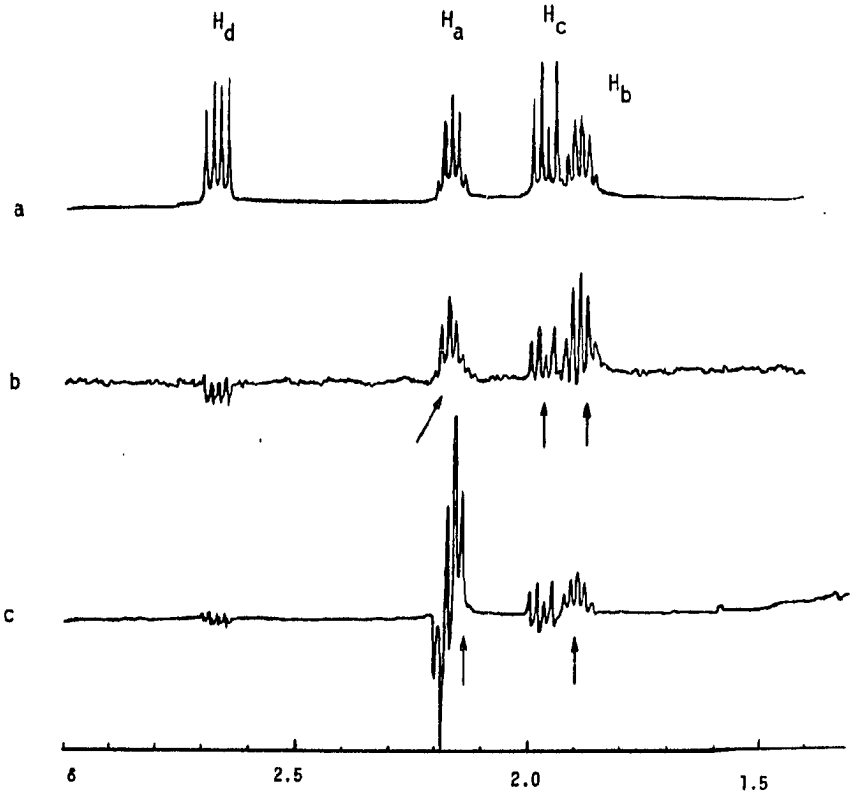


Figure 6. 500 MHz ^{1}H difference NOE spectra of **7b:** a) non-irradiated, b) β-CH_3 irradiated enhancement, c) α-CH_3 irradiated. Arrows indicate those peaks for which NOE enhancement is observed.

powder identical with that obtained directly from $Cp_2TiCH_2 \cdot AlMe_2Cl$ (^1H NMR).

Carbonylation of $Cp_2\overline{TiCH_2CH(t\text{-}Bu)CH_2}$ (3a) Under Conditions of Limited CO Concentration. tert-Butyltitanacyclobutane **3a** (143 mg, 0.52 mmol) was dissolved in 3 mL toluene in a Schlenk tube. The solution was stirred under 1 atm CO at -30 to -20°C over a 30 min period. The mixture was warmed to room temperature and the solvent was removed in vacuo to give a dark solid. ^1H NMR revealed a mixture of **1** and enediolate **3b**, but the spectrum was extremely broad. The product was dissolved in Et_2O and filtered through a plug of Florisil. The residue obtained from the eluate gave a sharp ^1H NMR spectrum which indicated **1** and **3b** in a 2:1 ratio.

Carbonylation of $Cp_2\overline{TiCH_2CH(t\text{-}Bu)CH_2}$ (3a) in the Presence of PMe_3. Metallacycle **3a** (56 mg, 0.20 mmol) was placed in a Schlenk tube in a -50°C bath. A solution of PMe_3 (0.5 mL, 0.4 mmol) in 15 mL Et_2O was cooled to -78°C and transferred onto the metallacycle via cannula. Carbon monoxide was bubbled through the mixture for ca. 30 min at -50°C, 5 min at -30°C and then 2 min at room temperature. The solvent was removed in vacuo to afford pure enediolate **3b** (^1H NMR).

Preparation of Bicyclo[3.2.0]heptan-6-one by Carbonylation of 5a. A solution of the cyclopentene titanacyclobutane **5a** (272 mg, 1.05 mmol) in 30 mL Et_2O was cooled to -15°C. Carbon monoxide was slowly bubbled through as the temperature was gradually raised to 0°C over a 90 min period. The volatiles were vacuum transferred and concentrated to ca. 5 mL by distillation through a short Vigeraux column. Bicyclo[3.2.0]heptan-6-one[26] (12.9 mg, 11%) was isolated as a clear liquid by preparative gas

chromatography on a 6' 10% FFAP on Chrom P column. ^{1}H NMR ($CDCl_3$) δ 1.35-2.25 (m, 6H), 2.37 (pseudo-triplet, 1H), 2.56 (pseudo-triplet, 1H), 2.90 (m, 1H), 3.05-3.38 (8 sharp lines, 1H), 3.52 (m, 1H); IR ($CDCl_3$) 2965, 2878, 1774, 1451, 1388, 1320, 1242, 1199, 1131, 1072, 1021 cm^{-1}. MS (70 eV) 110.073, M^+, 3.7; 82.078, M^+-CO, 19.9; 68.063, M^+-CH_2CO,93.7; 67.056 m/e, M^+-CH_3CO, 100. The non-volatile products were found to include **5b** and **1** (^{1}H NMR).

A second carbonylation was performed in a similar manner, using 140 mg (0.54 mmol) **5a** in 30 mL Et_2O at -20°C for 2 h. 2-Methylcyclohexanone (20 mL) was added as an internal standard and the bicyclo[3.2.0]heptan-6-one produced was quantitated by GC using a 10' 19% FFAP on 80/100 Chrom PAW column and assuming equal molar response factors. Yield, 31%.

Preparation of 2,2,3-Trimethylbutane From Pivalaldehyde. $Cp_2TiCH_2 \cdot AlMe_2Cl$ (500 mg, 1.75 mmol) was dissolved in 2 mL THF at 0°C in a small Schlenk tube. The mixture was immediately transferred via cannula into a stirred -78°C solution of pivalaldehyde (63.5 μL, 0.584 mmol) in 1 mL THF. The solution was stirred for 5 min at -78°C and 5 min at room temperature. Pyridine (155 μL, 1.85 mmol) was added dropwise and the mixture was stirred for 2 min at room temperature. With stirring at -78°C, HCl gas (270 mL, 12 mmol) was introduced in portions via syringe. After the acidolysis was complete, n-octane was added as an internal standard and the product, 2,2,3-trimethylbutane, was quantitated by gas chromatography on a 30' 3% SE-30 on 100/120 Supelcoport column using measured molar response factors. Yield, 74%

A similar procedure, in which DMAP was substituted for pyridine and

the aluminum was removed by precipitation with pentene prior to acidolysis, gave a nearly identical yield (78%).

Preparation of 4-tert-Butyl-2-hydroxycyclopentan-1-one From Pivalaldehyde. $Cp_2TiCH_2 \cdot AlMe_2Cl$ (1.01 g, 3.54 mmol) was dissolved in 3 mL THF at 0°C and was quickly transferred into a stirred solution of pivalaldehyde (130 μL, 120 mmol) in 2 mL THF. The mixture was stirred at room temperature for 5 min. DMAP (500 mg, 4.10 mmol) was added. The solution was stirred for 2 min and the solvent was removed in vacuo. The residue was dissolved in 7 mL dichloromethane and transferred dropwise into 50 mL rapidly stirred 0°C pentane. The mixture was filtered on a coarse Schlenk frit and the filtrate was stripped of solvent in vacuo. The red residue was dissolved in 20 mL Et_2O and cooled to -50°C. Carbon monoxide was bubbled through the solution for 30 min. The Schlenk tube was fitted with a septum and the sidearm was closed. HCl gas (200 mL, 8 mmol) was added via syringe to the stirred, -30°C purple solution. The red solid (Cp_2TiCl_2) which formed was removed on a medium porosity glass frit and washed with 2 x 5 mL Et_2O. The combined filtrate and washings were washed with 20 mL saturated $NaHCO_3$ and 20 mL saturated NaCl and dried over $MgSO_4$. The volume of the ethereal solution was reduced to 2 mL by distillation through a Vigeraux column and the product, 4-tert-butyl-2-hydroxycyclopentan-1-one (101 mg, 54%) was isolated as a white crystalline solid by bulb-to-bulb distillation (110-130°C, 10^{-3} mm). An analytical sample was prepared by recrystallization from hexane. mp 84-85°C. ^1H NMR ($CDCl_3$) δ 0.82 (s, 9H), 1.43 (pseudo-triplet, 1H), 1.8-2.0 (m, 2H), 2.0-2.4 (m, 2H), 4.08 (pseudo-triplet, 1H); IR ($CDCl_3$) 3500, 2970, 2880, 1750, 1100 cm^{-1}. MS (70 eV)

156.115, M^+, 5.5; 155.107, M^+ -H, 5.3; 140.120, M^+ -H_2O, 3.1; 100.052, M^+ -$(CH_3)_2CCH_2$, 66.2; 99.045 m/e, M^+ -$C(CH_3)_3$, 54.2.

Anal. calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 70.03; H, 10.22.

Preparation of 4-tert-Butyl-2-hydroxycyclopentan-1-one From $Cp_2TiCH_2CH(t\text{-}Bu)CH_2$ (3a). Metallacycle **3a** (174 mg, 0.63 mmol) was dissolved in 20 mL Et_2O in a Schlenk tube. Carbon monoxide was bubbled through the solution for 30 min at -50°C. HCl gas (34 mL, 1.39 mmol) was introduced and the mixture was stirred for 20 min at -50°C. The red precipitate was removed on a medium frit. The filtrate was washed with 10 mL saturated $NaHCO_3$ and 10 mL water, dried over $MgSO_4$ and filtered. Most of the solvent was removed by distillation through a short Vigeraux column and the product was isolated by bullb-to-bulb distillation (190°C, 10^{-3} mm) and identified as 4-tert-butyl-2-hydroxycyclopentan-1-one (68.9 mg, 70%).

Preparation of 4-tert-Butyl-2-hydroxycyclopent-2-en-1-one From $Cp_2TiCH_2CH(t\text{-}Bu)CH_2$ (3a). A solution of **3a** (242 mg, 0.877 mmol) in 20 mL Et_2O in a Schlenk tube was cooled to -50°C and CO was bubbled through for 30 min. The bubbling was stopped and the purple solid which formed redissolved upon warming to room temperature. The enediolate solution was transferred into a freshly prepared solution of iodine (600 mg, 2.4 mmol) in 5 mL Et_2O in a second Schlenk tube. Dark brown solids appeared on mixing. The mixture was stirred for 5 min, then washed 2 x 10 mL dil. Na_2SO_3, 1 x 20 mL water and 1 x 10 mL saturated NaCl. The organic layer was dried over $MgSO_4$ and filtered on a medium porosity frit. The filtrate was concentrated

to ca. 1 mL by distillation through a short Vigeraux column. The solution was diluted with 2 mL chloroform and loaded atop a 12 mm x 30 cm silica gel column. A fast-moving impurity was eluted with $CHCl_3$ and the product was eluted with Et_2O. The product fractions were concentrated by distillation through a short Vigeraux column and 4-tert-butyl-2-hydroxycyclopent-2-en-1-one (55.0 mg, 41%) was isolated as a white solid by bulb-to-bulb distillation (120-180°C, 10^{-3} mm). An analytical sample was prepared by recrystallization from hexane. mp. 123-124°C (Lit.[27] 125-127°C). ^1H NMR ($CDCl_3$) δ 0.89 (s, 9H), 2.3 (m, 2H), 2.56 (m, 1H), 5.9 (s, OH), 6.54 (d, J = 2.4 Hz, 1H); IR ($CDCl_3$) 3500, 2970, 2880, 1700, 1660 cm^{-1}. MS (70 ev) 154.100, M^+, 0.5; 139.076, $M^+ - CH_3$, 8.8; 98.036 m/e, $M^+ - (CH_3)_2CCH_2$, 100.

Anal. calcd. for $C_9H_{14}O$: C, 70.09; H, 9.15. Found: C, 69.33; H, 9.10.

Preparation of 4,4-Dimethyl-2-hydroxycyclopentan-1-one From $Cp_2TiCH_2CMe_2CH_2$ (4a). Metallacycle **4a** (120 mg, 0.48 mmol) was dissolved in 3 mL -30°C toluene in a Schlenk tube. The solution was vigorously stirred under 1 atm CO as the temperature was allowed to increase from -30 to -10°C over a 1 h period. The solution was cooled to -50°C and HCl gas (26 mL, 2.2 equiv) was added via syringe. After the solution discolored and a red precipitate had formed, most of the solvent was removed in vacuo. The product, 4,4-dimethyl-2-hydroxycyclopentan-1-one[28] (28.5 mg, 46%) was isolated as a clear liquid by bulb-to-bulb distillation (150°C, 10^{-3} mm). ^1H NMR ($CDCl_3$) δ 1.11 (s, 3H), 1.15 (s, 3H), 1.59 (pseudo-triplet, 1H), 2.15 (m, 2H), 2.33 (m, 1H), 2.79 (s, br, OH), 4.25 (pseudo-triplet, 1H); ^{13}C (^1H) NMR ($CDCl_3$) δ 29.2, 30.4, 31.4, 44.6, 49.7, 74.7, 218.6.

Preparation of 4,4-Dimethyl-2-hydroxycyclopent-2-en-1-one From $Cp_2TiCH_2CMe_2CH_2$ (4a). Metallacycle 4a (141 mg, 0.569 mmol) was dissolved in 4 mL -30°C toulene in a Schlenk tube. The solution was vigorously stirred under 1 atm CO as the temperature was allowed to increase from -30°C to -10°C over a 1 h period. Bromine (32 μL, 0.62 mmol) was added via polyethylene tubing (Intramedic PE50) to the stirred solution at -40°C. Red-brown solids formed upon mixing. The bulk of the solvent was removed in vacuo and the product was further purified by preparative gas chromatography on a 6' 10% FFAP on Chrom P column to give 4,4-dimethyl-2-hydroxycyclopent-2-en-1-one[29,30] (44.5 mg, 61%) as a clear, viscous liquid. ^1H NMR ($CDCl_3$) δ 1.21 (s, 6H), 2.30 (s, 2H), 5.35 (s, br, OH), 6.34 (s, 1H); IR ($CDCl_3$) 3400, 2970, 2880, 1710, 1660 cm^{-1}.

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CHAPTER 3

Synthesis and Reactivity of Ketene Complexes of Bis(cyclopentadienyl)titanium and Bis(cyclopentadienyl)zirconium

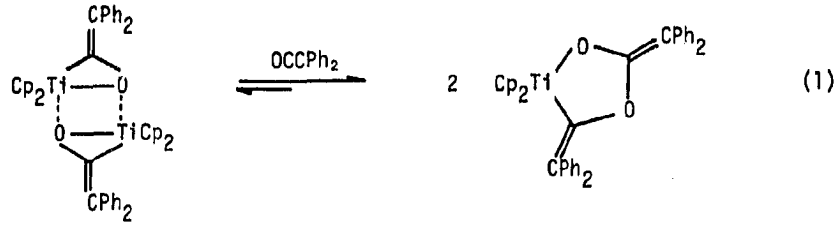
Introduction

Transition metal ketene complexes have been proposed as intermediates in catalytic[1] and stoichiometric[2] reductions of carbon monoxide and as models for the isoelectronic ligand, carbon dioxide.[3,4] Complexes which contain highly stabilized ketene fragments, especially diphenylketene, have generally been prepared by direct reaction of the ketene with a coordinatively unsaturated metal complex[3,5,6] or by carbonylation of metal alkylidenes.[7]

Herrmann has prepared the complex $CpMn(CO)_2(OCCPh_2)$ by reaction of $CpMn(CO)_2(THF)$ with diphenyl ketene.[5] X-ray structure determination has revealed that the diphenylketene ligand is η^2 (C,C) bound.[8] The heterocumulene framework is distorted from linearity in this complex, as is coordinated carbon dioxide.[9] The same complex has been prepared by high-pressure carbonylation of $CpMn(CO)_2(CPh_2)$.[7b] Reaction of 9-diazoanthrone with a mixture of $CpMn(CO)_3$ and $CpMn(CO)_2$ (THF) affords $CpMn(CO)_2$ (η^2-anthronylketene) in good yield.[7a] There is considerable evidence that this reaction proceeds <u>via</u> formation of an unstable anthronylcarbene-manganese species which transfers the carbene ligand to $CpMn(CO)_3$.

Reaction of diphenylketene with coordinatively unsaturated metal complexes has also been used in the preparation of $(Cp_2Ti(OCCPh_2))_2$ and $Cp_2V(OCCPh_2)$ by Floriani and co-workers.[3] In contrast with the η^2 (C,C) bound ketene ligands in $CpMn(CO)_2(OCCPh_2)$ and $(PPh_3)_2Pt(OCCPh_2)$,[6a] the diphenylketene in these complexes is η^2 (C,O) coordinated. This is a

consequence of the oxophilic nature of the early transition metals. As in the other cases studied, the O=C=C unit is highly distorted from linearity upon complexation. The C-O bond length in the titanium complex is in the range of single bonds. This distance in the vanadium analog is considerably shorter, presumably due to the greater electron-donating ability of Cp_2Ti vs Cp_2V. Despite the apparently strong binding of the diphenylketene unit, the titanium complex has been found to undergo reversible insertion of a second diphenylketene unit as shown in equation 1.[3b,c] Acidolysis of $(Cp_2Ti(OCCPh_2))_2$ with excess HCl gave the products of the $CHPh_2$ radical,



(1)

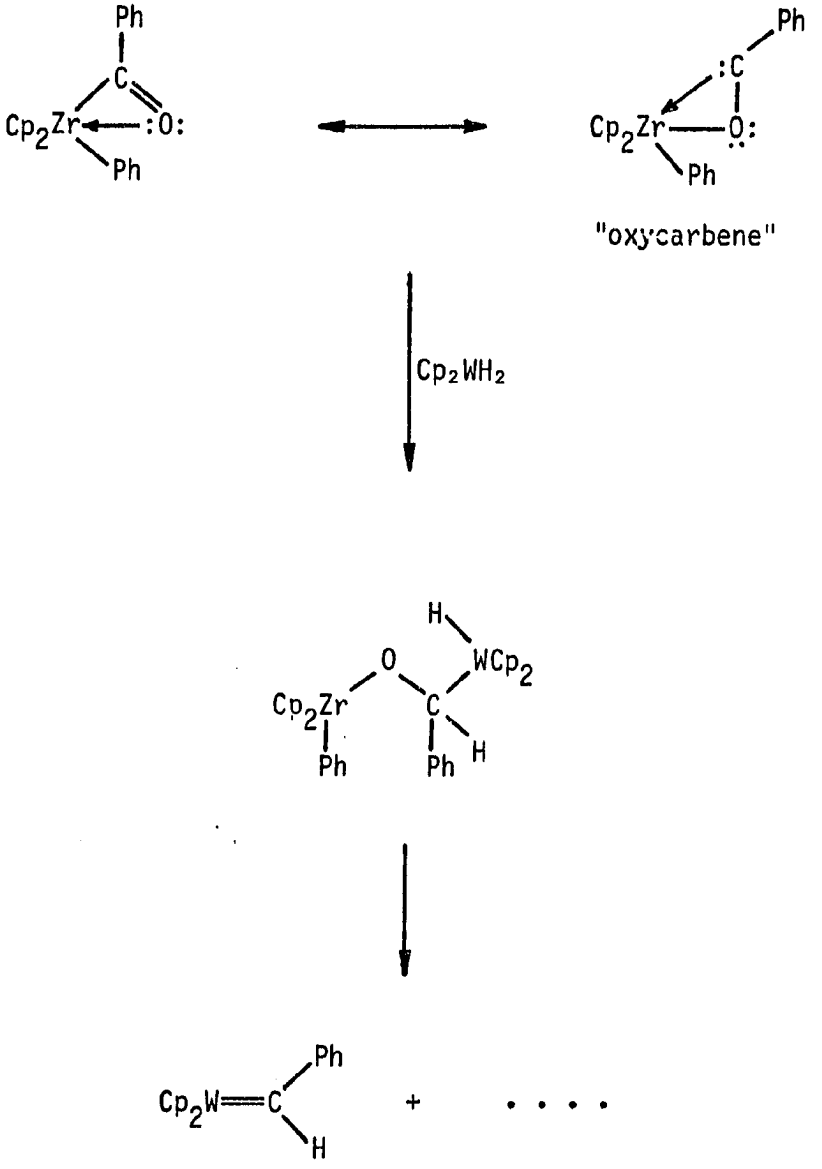
Ph_2CH_2 and $(Ph_2CH)_2$.[3b] This reaction is believed to proceed through decarbonylation of a chloro acyl titanium intermediate to give a benzhydryl complex which is known to decompose by a radical process.

The only reported zirconium ketene complex has very recently been prepared by Lappert and co-workers.[10] These authors have found that the zirconocene dialkyls $Cp_2Zr(CHPh_2)R$ (R = CH_3 or CH_2TMS) are carbonylated under ambient conditions to afford the diphenylketene complex $(Cp_2Zr(OCCPh_2))_2$ and the acyl $Cp_2Zr(COR)(CHPh_2)$ as a co-product. The mechanism of this reaction is not well understood.[11]

Synthesis of stable metal ketene complexes is limited to the above examples. Coupling of metal alkylidenes with CO occurs in a few other cases, but with direct production of free ketene.[12-14] No adducts of ketene, CH_2CO, have been observed, but a complex with a ketene bridge has been proposed as an intermediate in the reaction of $(NEt_4)_2Fe_2(CO)_8$ with $ClCl_2COCl$.[15] Ketenyl complexes (η^2 (C,C)-OCCR) have been produced by coupling of CO with metal alkylidynes.[16] Ketenylidene (OCC) complexes are also known.[17]

Results and Discussion

Our interest in transition metal ketene complexes began when we prepared one by accident in an attempt at developing a new general route to titanium enolate complexes. During our study of the carbonylation of bis(cyclopentadienyl)titanacyclobutanes[18] we became interested in the chemistry of Group IV transition metal acyl complexes.[19] We were especially intrigued with the proposal that the "oxycarbene" resonance structure plays an important role in the chemistry of these η^2 (C,O) acyl complexes.[2,20] This effect has been used by Caulton and co-workers in the synthesis of a tungsten benzylidene (Fig. 1).[21,22] This suggested that it might be possible to transfer a carbene unit to the acyl carbon of $Cp_2Ti(COCH_3)Cl$ (1), providing a general route to enolate complexes. The readily available phosphorous ylides[23a] $CRR'PR_3$" were chosen as the source of the carbene fragment since these reagents may be prepared with a wide variety of substituents.[23b] Methylenetriphenylphosphorane was selected for


Ph
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Cp2Zr
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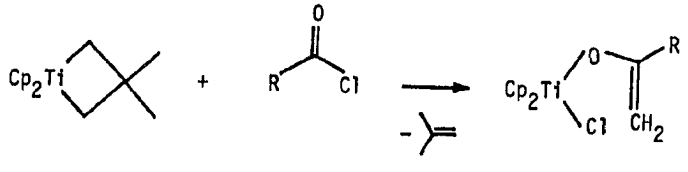
Figure 1

the initial attempt.

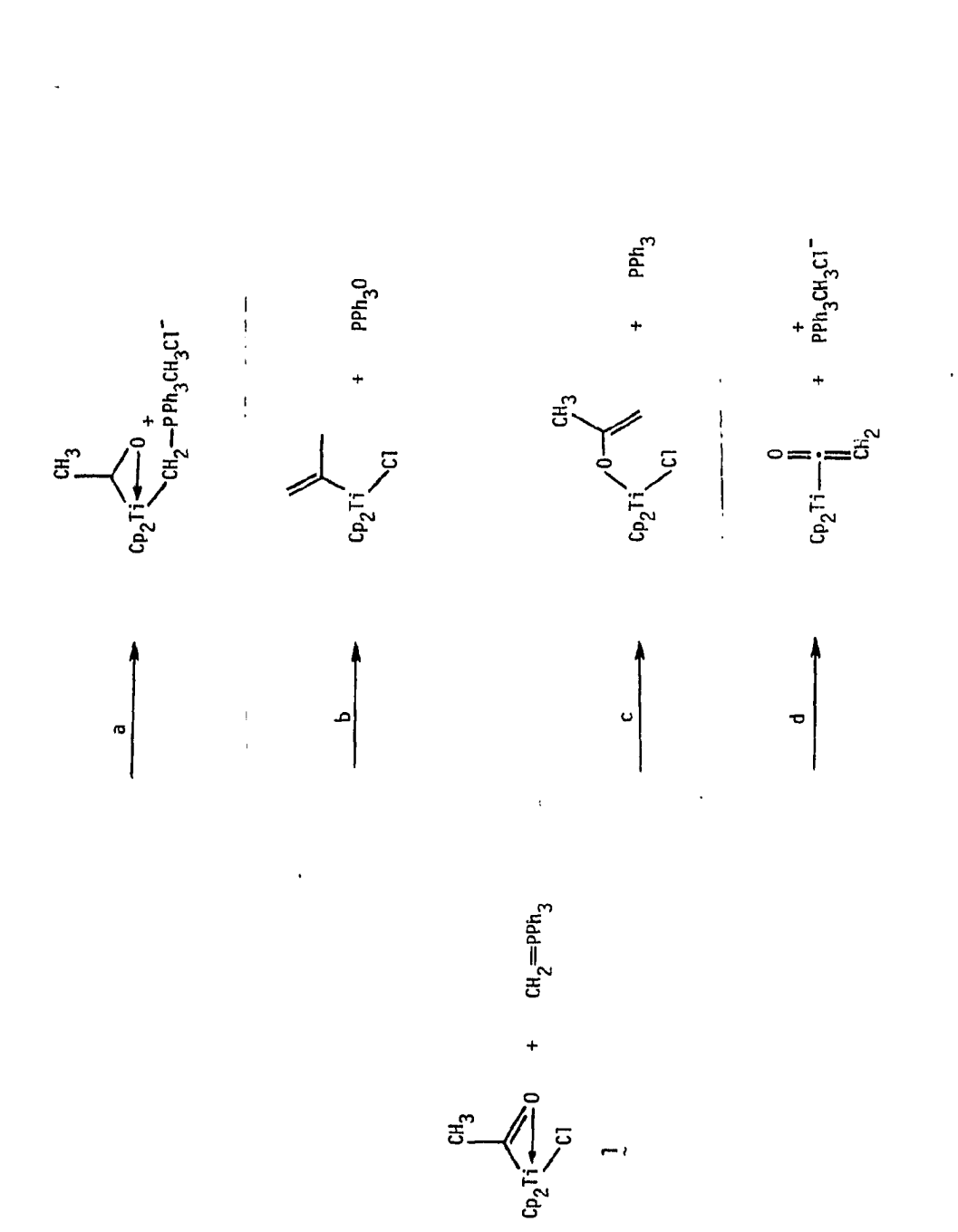
The products which might arise from reaction of 1 with CH_2PPh_3 are shown in Scheme I. Of the possible pathways illustrated, reaction (a) seemed least likely because we expected the η^2-acyl ligand to hinder substitution. Reaction (b), a Wittig-type transformation, and reaction (c), enolate formation, are both unprecedented and would be synthetically useful. Reaction (b) would provide vinyl titanium complexes which might then be used in preparation of reagents of the type $Cp_2TiCRR'\cdot AlR_2''Cl$[24] (R, R', R'' = alkyl). Reaction (c) would complement an enolate synthesis which has recently been developed in our laboratory (eq. 2),[25,26] by introducing substituents at the terminal enolate carbon (using substituted ylides) and perhaps by broadening the range of non-interfering functionality.[23b] Dehydrohalogenation (d) is reasonable in view of the basicity of CH_2PPh_3 and the electron-deficient nature of the acyl ligand in 1.

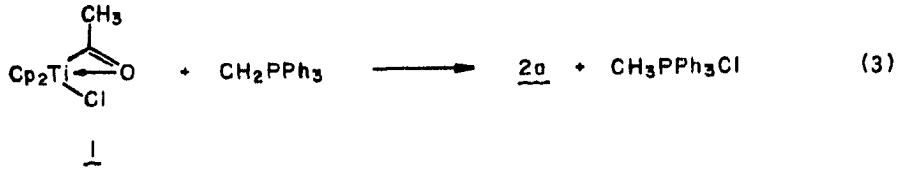


(2)

The acyl complex 1 reacted instantly with CH_2PPh_3 (dichloromethane-ether, -50°C) to give a red solution from which red, microcrystalline **2a** soon precipitated (eq. 3). The byproduct, CH_3PPh_3Cl, precipitated from the supernatant upon addition of Et_2O.[27] Reaction of 1 with $NaN(TMS)_2$ in ether

Scheme I

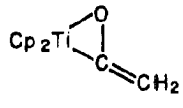




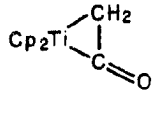
1

also gave **2a**. The product is a moderately air-sensitive solid which is stable at room temperature for several days under an inert atmosphere. This product is sparingly soluble in benzene, toluene and THF, but decomposes rapidly in methylene chloride. In benzene, red **2a** reaches equilibrium with yellow **2b** in a matter of minutes at room temperature. The equilibrium ratio of **2a:2b** is ca. 1:10. The yellow isomer crystallized from benzene solution as large needles. Attempts to obtain crystals suitable for X-ray structure determination have been unsuccessful because the crystals disintegrate outside of solution.

Several lines of evidence suggest that **2a** and **2b** have the basic η^2(C,O) ketene structure shown. The ^{1}H NMR spectrum exhibits inequivalent



2a,b



3

methylene protons for each isomer with chemical shifts and coupling constants in the range typical of vinyl ethers. An η^2 (C,C) ketene (**3**) should show a single methylene resonance. The proposed structure is similar to that of diphenylketene complexes of Ti, V[3] and Zr.[10] Furthermore, both isomers

were cleanly converted to the starting acyl **1** on treatment with one equivalent of HCl gas (toluene, -50°C). Preparation of ^{13}C-enriched **2a** and **2b** showed similar α-carbon ^{13}C NMR shifts (220 and 197 ppm, respectively) for these isomers. These values fall in the range between those of titanium acyl complexes (ca. 300 ppm)[28] and enolates (ca. 170 ppm).[25] It seems likely that **2a** and **2b** exist in oligomeric forms and differ in their mode of aggregation.[29]

Additional evidence for the structure of **2a** and **2b** comes from the reactivity of these complexes with ethylene and acetylene. Complex **2a** reacts readily at room temperature with ethylene (ca. 1 atm, C_6D_6) to give purple **4** and with acetylene to give green **5** (Fig. 2).[30] The same products are formed from **2b**, although much more slowly. Cyclic enolates **4** and **5** have been characterized by ^1H and ^{13}C NMR. Acidolysis of **4** gave 2-butanone (GC, NMR). Complex **2a** also reacts instantly with PMe_2Ph (C_6D_6) to give the highly soluble monophosphine adduct **6** (^1H, ^{13}C NMR). This adduct reacts readily with acetylene to form **5**. The position of the phosphine, adjacent to oxygen, is inferred from the structure of alkyl acyl and chloro acyl complexes of titanocene and zirconocene.[31,32] No ^{31}P coupling was detected in the ^{13}C NMR of this adduct.

Of particular interest is the formation of bridging ketene complexes on reaction of **2a** with $(\eta^2\text{-}C_5Me_5)TiCl_3$ and $CpTiCl_3$ (Scheme II). Ketene adduct **2a** reacted instantly with the former in C_6D_6 at room temperature to produce orange $\mu\text{-}\eta^2$ (C,O)-ketene complex **7**. The same product was formed by carbonylation of $\mu\text{-}CH_2(Cp_2TiCl)((\eta^5\text{-}C_5Me_5)TiCl_2)$.[33] The orientation of the ketene bridge in **7**, determined from NOE experiments performed by

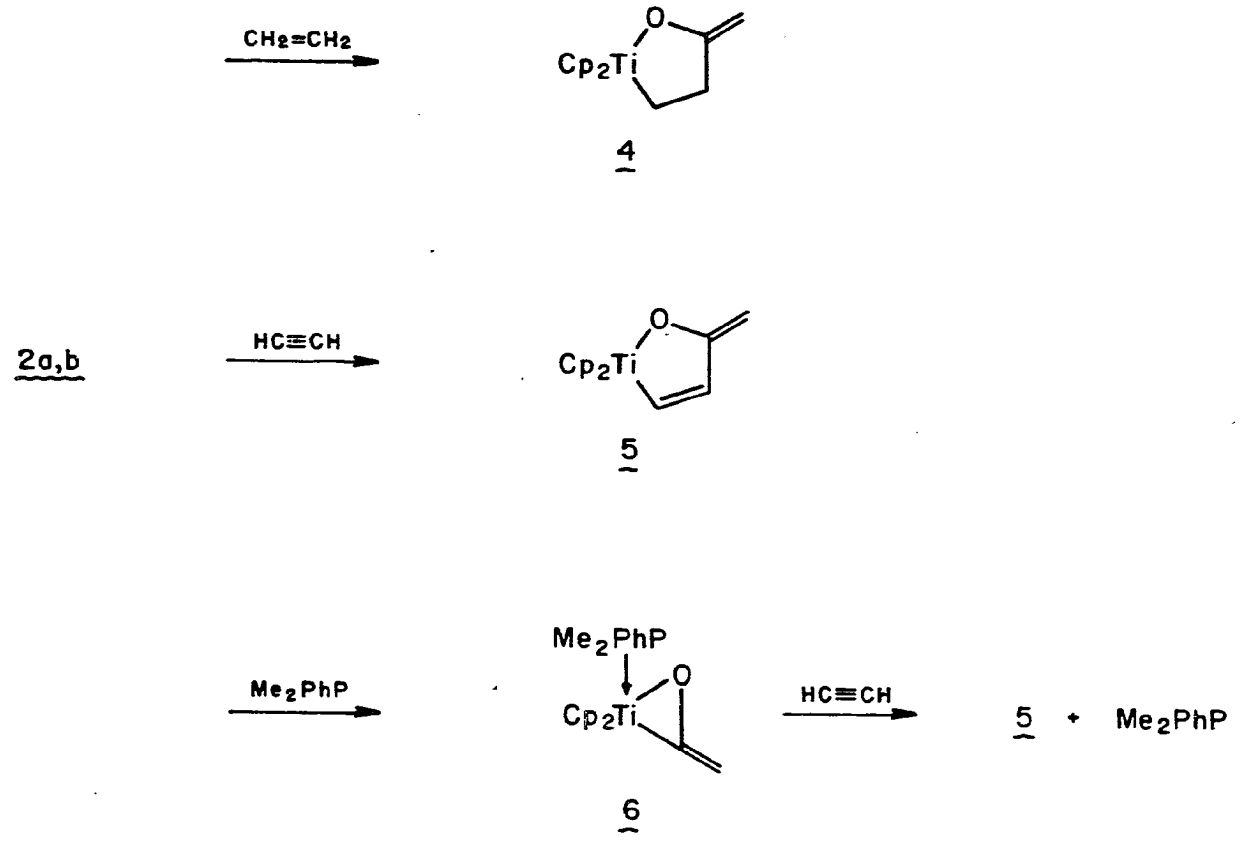
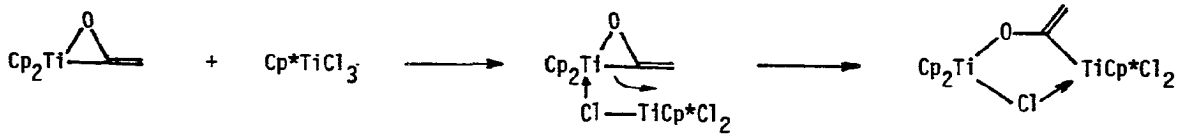

CH2=CH2
Cp2Ti
O
4
2a,b
HC≡CH
Cp2Ti
O
5
Me2PhP
Me2PhP
Cp2Ti
O
6
HC≡CH
5 + Me2PhP

Figure 2

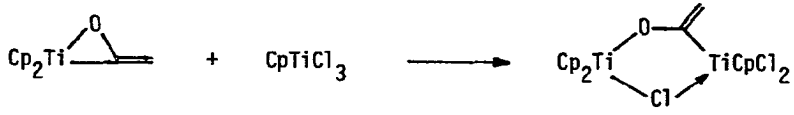
Scheme II



monomeric unit of 2a

7

Cp* = η^5-C_5Me_5



8

Dr. K. Ott, indicates addition of the Ti-Cl bond across the Ti-C bond of **2a**. The μ-η^2 (C,O)-ketene complex from $CpTiCl_3$ was assigned as **8**, by analogy with **7**. This product has not been prepared by carbonylation because the bridging methylene, μ-CH_2-$(Cp_2TiCl)(CpTiCl_2)$, could not be isolated.[33] Reaction of **2a** with other metal halides has not been investigated.

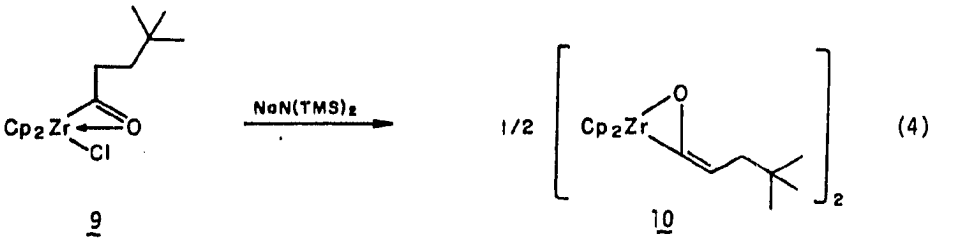
Reaction of ketene complex **2a** with carbon monoxide (room temperature, C_6D_6) led to slow formation of $Cp_2Ti(CO)_2$[34] and a few minor products which have not been identified. No ketene dimer was detected. The fate of the ketene ligand in this reaction is uncertain. Reaction with ^{13}CO (99% ^{13}C-enriched) revealed no ^{13}C incorporation into **2a**. An equilibrium between **2a** and $Cp_2Ti(CH_2)(CO)$ seems unlikely on this basis. Such an intermediate is likely in the low-yield formation of **2a** and **2b** on carbonylation of Cp_2TiCH_2 (phosphine) complexes.[33]

A few other reactions of ketene complex **2a** have been attempted. No reaction was observed on treatment of **2a** with propene or with 2-butyne (room temperature, C_6D_6). This is probably a steric effect. Also, **2a** did not react with methyl iodide under these conditions. This indicates that the β-carbon of this ketene adduct is relatively non-nucleophilic. Reaction of **2a** with acetaldehyde gave intractable products.

The titanium ketene complexes **2a**, **2b**, **7** and **8** are, to the best of our knowledge, the only known transition metal complexes of CH_2CO. The method used by Floriani to prepare $(Cp_2Ti(OCCPh_2))_2$ involves heating diphenylacetylene and $Cp_2Ti(CO)_2$ at 60°C for 1 h.[3b,c] This approach would not be applicable to synthesis of **2a** and/or **2b** because ketene dimerizes under these conditions.[35] In order to explore the generality of dehydrohalogenation

of chloro acyl complexes in metal-ketene synthesis, and to more fully investigate the chemistry of these ketene complexes, we have examined other systems.

The zirconium chloro acyl complexes are readily available using the procedure of Schwartz.[36] The neohexyl group was chosen as the acyl substituent to facilitate NMR analysis and increase product solubility.[37] Treatment of acyl **9** with $NaN(TMS)_2$ in toluene gave the zirconium ketene **10** in high yield (eq. 4). This white crystalline solid is soluble in THF, Et_2O and toluene, but is only sparingly soluble in pentane. It may be handled briefly in air, but must be stored under an inert atmosphere. The complex was characterized by ^1H and ^{13}C NMR, IR and elemental analysis. The ^{13}C



9 **10** (4)

NMR shift of the α-carbon, δ 188 ppm, is similar to that of **2a** and **2b**. The solubility of **10** in benzene permitted cryoscopic molecular weight determination (not possible for **2a** and **2b**), which revealed a dimeric structure (Mol. wt. calcd., 667. Found, 652). This most certainly is achieved by reciprocal metal-oxygen bridges as illustrated for $(Cp_2Ti(OCCPh_2))_2$ in equation 1. The configuration shown in equation 4, in which the neopentyl substituent in **10** is E with respect to the metal, is assumed for steric reasons.

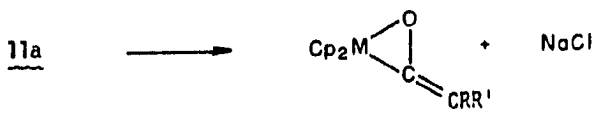
Dimeric ketene **10** is exceptionally unreactive. Treatment with one equivalent of HCl gas (toluene, -50°C) produced **9**, but with nearly equal amounts of Cp_2ZrCl_2 and unreacted **10**. This contrasts with the clean formation of $Cp_2Ti(COCH_3)Cl$ (**1**) on acidolysis of **2a** and **2b**. The complex is inert toward ethylene, acetylene, and hydrogen, even upon prolonged heating (70-100°C, several hours). Pyridine, a good ligand for ketene complexes (vide infra) did not react with **10**, nor did **10** react with ethylene in the presence of pyridine. Tetrabutylammonium fluoride also did not react with **10** or activate it for reaction with ethylene. An attempt to trap the monomer $Cp_2Zr(OCCHCH_2C(CH_3)_3)$ by reaction of **9** with $NaN(TMS)_2$ under ethylene (1 atm) gave only **10**. Dimerization appears to be more rapid than reaction with ethylene.

At this point, our interest turned to the mechanism of the dehydrohalogenation reaction. This base-promoted elimination might occur as a concerted process or it could involve an intermediate anionic ketene adduct, generalized as **11a** in Scheme III.

The feasibility of intermediates such as **11a** has been demonstrated by replacement of the halide leaving group with an alkyl ligand. Accordingly, deprotonation of $Cp_2Zr(COCH_3)CH_3$ with $NaN(TMS)_2$ in Et_2O occurs instantly at -30°C. The product, $Cp_2Zr(COCH_2)CH_3^-Na^+\cdot Et_2O$ (**11b**·Et_2O, Scheme III), precipitates as a white powder. This salt is insoluble in Et_2O and in benzene, but it is highly soluble in THF. The complex blackens in air. It is stable as a solid at room temperature under an inert atmosphere for only a few days, after which it begins to yellow and Cp-containing impurities are produced. The salt has been characterized by ^1H and ^{13}C NMR, IR and by

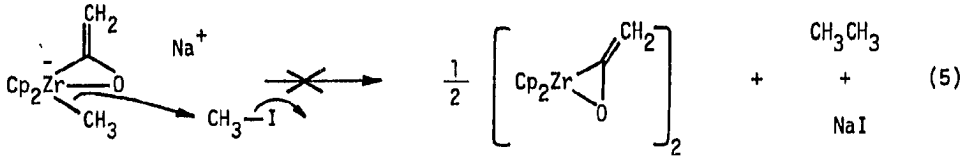
Scheme III

11a, X = Cl
b, X = CH_3, R = R' = H, M = Zr
c, X = CH_3, R = H, R' = CH_3, M = Zr
d, X = CH_3, R = R' = CH_3, M = Zr



elemental analysis. The structure of this anion (Scheme III) was assigned largely on the basis of the similarity of the ^1H and ^{13}C NMR shifts of the ketene fragment with those of **2a, 2b, 10** and other ketene complexes (vide infra). The "oxygen-in" geometry is assumed by analogy with structurally characterized acyl complexes.[31,32] In the ^1H NMR (THF-d_8) of **11b**·Et_2O, the CH_3 group is shifted upfield by 0.6 ppm from the CH_3 of the corresponding acyl complex. These observations are suggestive of high charge density on the metal and a relatively unperturbed ketene moiety.

Although there is no spectroscopic indication of high charge density on the terminal (β) carbon in **11a**·Et_2O, the reactivity of this salt with methyl iodide indicates that this is the nucleophilic site. Reaction with CH_3I at oxygen seemed unlikely on the basis of the oxophilic nature of zirconium.



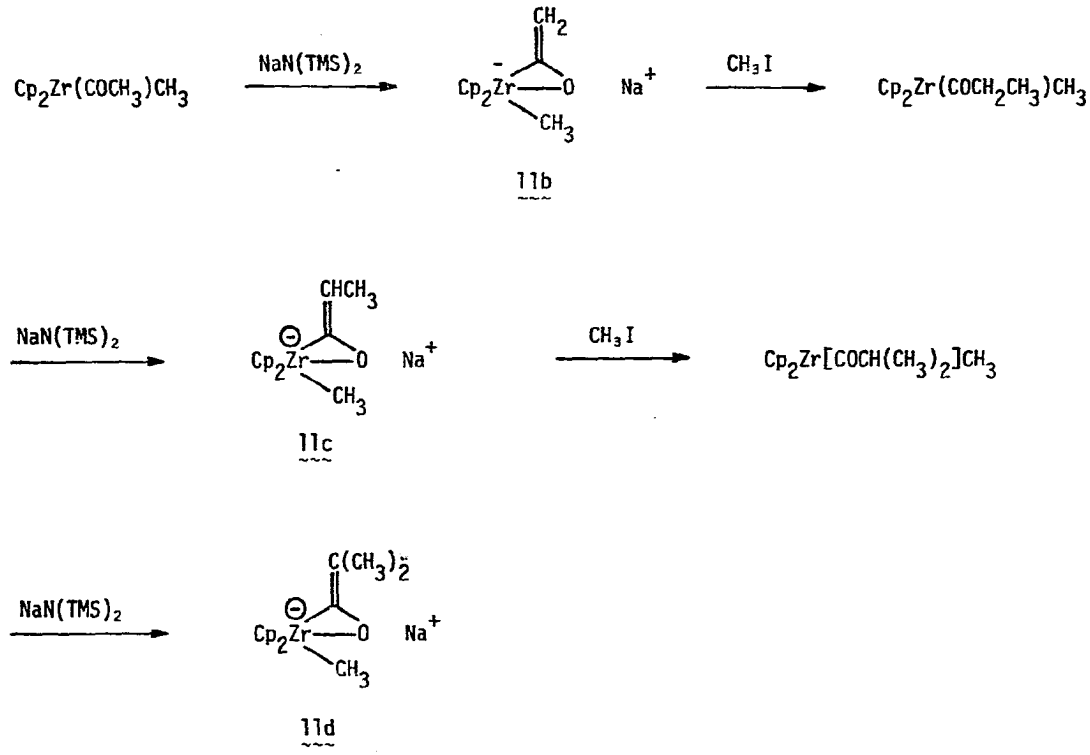
(5)

However, alkylation at the methyl group (eq. 5) was considered a good possibility. Instead, **11b**·Et_2O reacts instantaneously with CH_3I (room temperature, THF-d_8) to give the unsymmetrical alkyl acyl complex $Cp_2Zr(COCH_2CH_3)CH_3$ cleanly and quantitatively by ^1H NMR. This is reminiscent of organic enolate reactions. Sequential treatment with base and CH_3I allows multiple alkylation (Scheme IV). Further reactivity of these anions, including possible reaction with metal halide complexes to give μ-η^2(C,O)-$OCCH_2$ species, remains to be explored. Also, structural characterization of these anionic zirconium complexes would be extremely interesting. This should be facilitated by the observation that slow cooling of a saturated THF solution of **11b**·Et_2O affords **11b**·2 THF as large crystals.

These anionic complexes (e.g., **11b**) appear to be unique.[38] Previous reports of reactions of acyl complexes with bases have generally involved small nucleophilic reagents, especially alkoxides, and metal fragments which form reasonably stable anions. Not surprisingly, in these cases nucleophilic acyl substitution is observed.[39] With the use of bulky non-nucleophilic bases and the proper choice of metal fragment, deprotonation of metal acyl complexes may prove to be a general reaction.

Group IV metal ketene complexes have been of particular interest to

Scheme IV


Cp2Zr(COCH3)CH3
NaN(TMS)2
CH2
Cp2Zr
O
CH3
Na+
CH3I
Cp2Zr(COCH2CH3)CH3
11b
NaN(TMS)2
CHCH3
Cp2Zr
O
CH3
Na+
CH3I
Cp2Zr[COCH(CH3)2]CH3
11c
NaN(TMS)2
C(CH3)2
Cp2Zr
O
CH3
Na+
11d

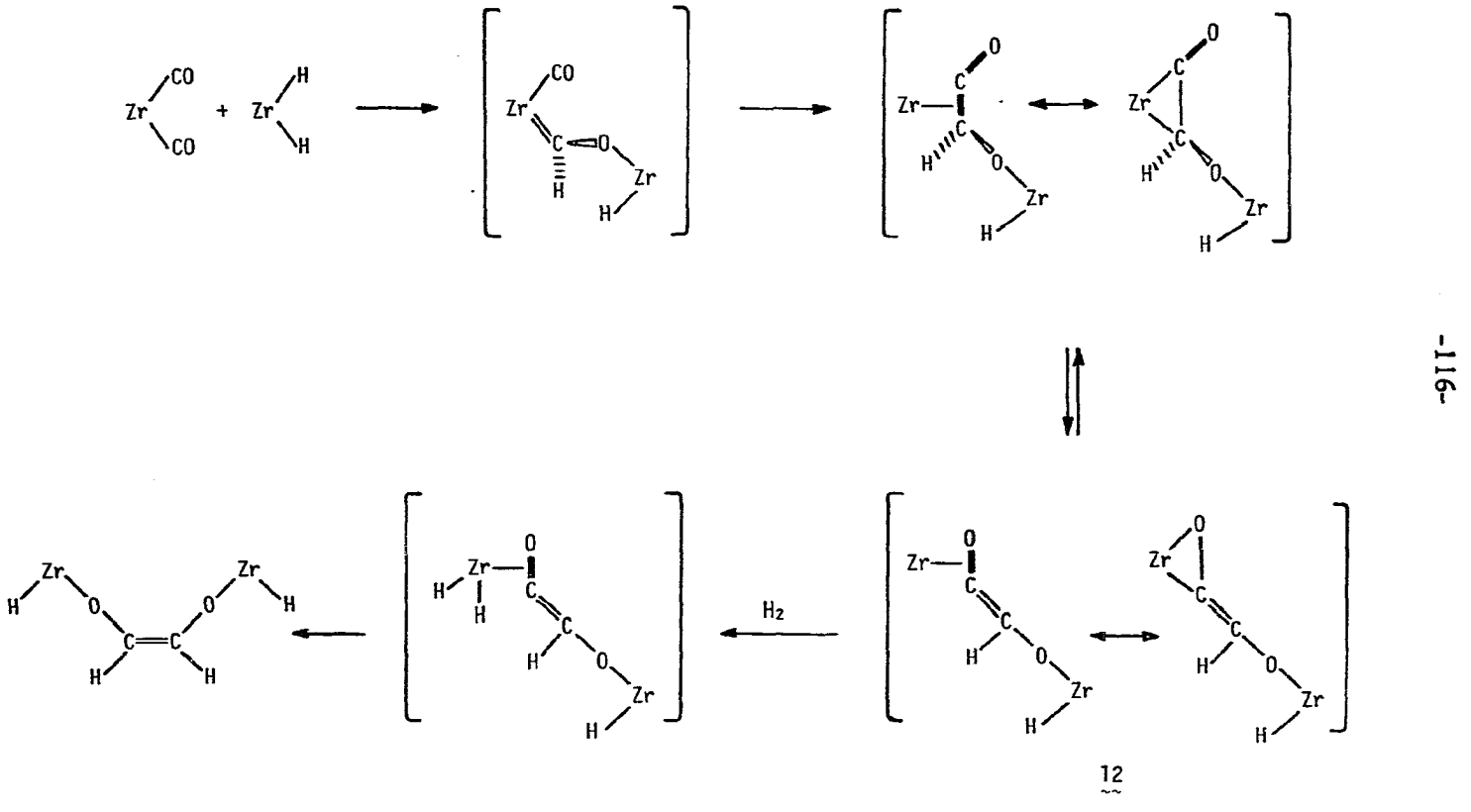
Professor J. E. Bercaw and his group because of the possible intermediacy of such species in a homogeneous reduction of carbon monoxide (Scheme V).[2] The failure of **10** to react with hydrogen, as is required of the intermediate binuclear decamethylzirconocene ketene **12** in Scheme V, was disturbing. It seemed possible that the dimeric structure of **10** was inhibiting its reactivity. To test this possibility we prepared decamethylzirconocene ketene derivatives by the dehydrohalogenation method in collaboration with the Bercaw group. The bulky η^5-C_5Me_5 ligands were expected to prevent dimerization and provide a more suitable model for the proposed ketene intermediate **12.**

Synthesis of $Cp_2^*Zr(COCH_3)Cl$ ($Cp^* = \eta^5$-C_5Me_5) as a precursor to the desired ketene adduct was attempted. Several attempts to methylate $Cp_2^*ZrCl_2$ with one equivalent of CH_3MgCl gave a nearly statistical mixture of $Cp_2^*Zr(CH_3)_2$, $Cp_2^*Zr(CH_3)Cl$ and $Cp_2^*ZrCl_2$. It was not possible to purify the $Cp_2Zr(CH_3)Cl$. The chloro acyl complex obtained by carbonylation of this mixture, $Cp_2^*Zr(COCH_3)Cl$, could not be freed of $Cp_2^*ZrCl_2$ and $Cp_2^*Zr(COCH_3)CH_3$.

The dibromide $Cp_2^*ZrBr_2$ was prepared by treatment of $Cp_2^*ZrCl_2$ with BBr_3 in CH_2Cl_2. Methylation of $Cp_2^*ZrBr_2$ with CH_3MgBr, under the same conditions used for the dichloride, yielded nearly pure $Cp_2^*Zr(CH_3)Br$. Recrystallization from THF gave the methyl bromide as an analytically pure pale green crystalline solid. Carbonylation to give $Cp_2^*Zr(COCH_3)Br$ was straightforward. This pale yellow-green complex slowly decarbonylates in C_6D_6 solution.

Treatment of $Cp_2^*Zr(COCH_3)Br$ with $NaN(TMS)_2$ in C_6D_6 gave a

Scheme V



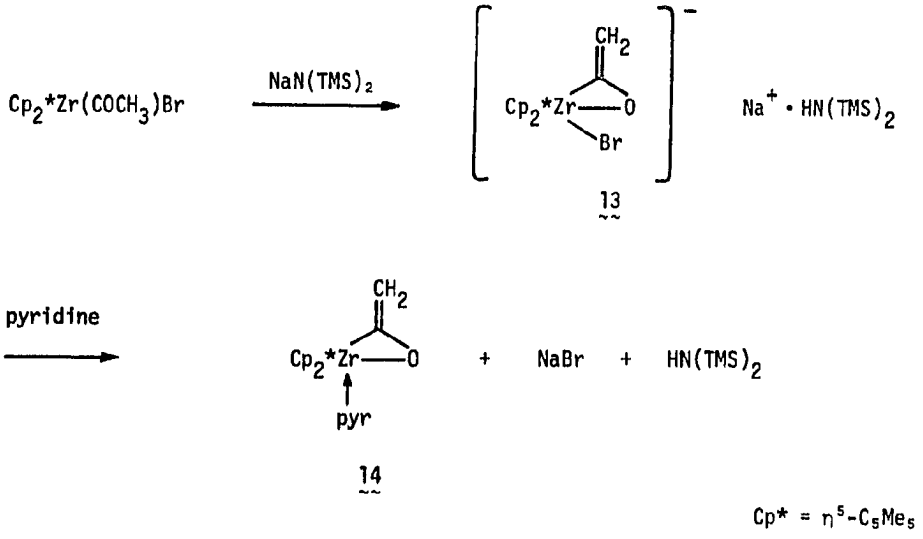
12

From P. T. Wolczanski and J. E. Bercaw, Accts. Chem. Res., 13, 122 (1980). The η^5-C_5Me_5 ligands on these decamethylzirconocene species are omitted for clarity.

clear, pale orange solution, the ^1H NMR of which was consistent with a ketene complex. Attempts at removing this volatile amine in vacuo led to eventual decomposition of the product. However, addition of pyridine to a THF solution of **13** resulted in immediate precipitation of NaBr and formation of a yellow solution from which $Cp_2^*Zr(OCCH_2)(pyr)$ (**14**) was crystallized. This pale yellow product is moderately soluble in benzene and toluene and highly soluble in THF. It has been characterized by ^1H and ^{13}C NMR and by its reactivity (vide infra).

These observations are accounted for in Scheme VI. The first-formed ketene, **13**, is formulated as an anionic bromide adduct. This corresponds with the generalized intermediate **11a** in Scheme III. Apparently, in the η^5-C_5H_5 systems, halide ketene intermediates (**11a**) require the oxygen of a

Scheme VI

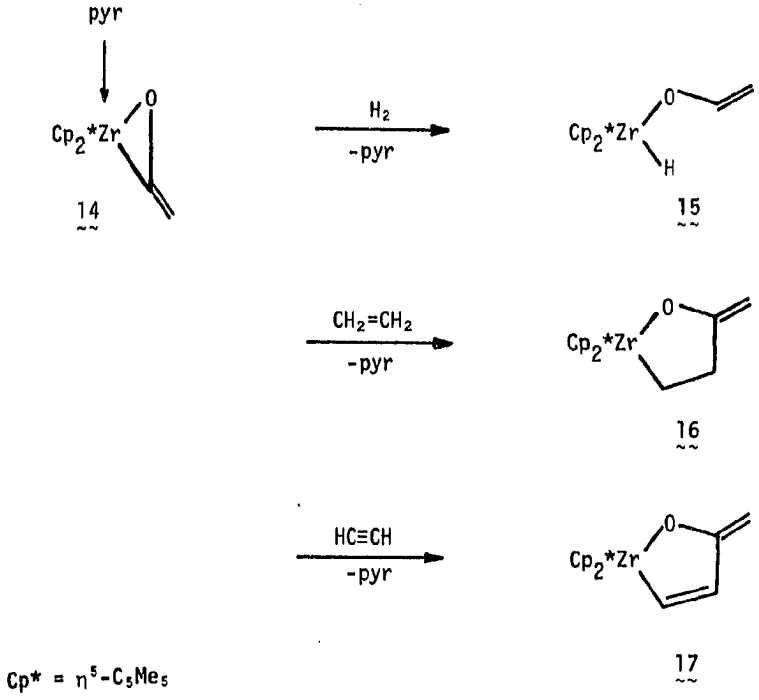


second molecule (either another halide ketene anion or an acyl molecule) to displace the halide ligand. In this fashion, the ketene dimer $(Cp_2Zr|OCCHCH_2C(CH_3)_3|)_2$ (**10**) probably forms without intermediacy of the monomer.[40] In the η^5-C_5Me_5 cases,[41] this bimolecular reaction is blocked and the halide-ketene anion (e.g. **13**) is observed. The similarity of the ^1H NMR spectrum of **13** with neutral ketene adducts is reminiscent of the anion $Cp_2Zr(COCH_2)CH_3^-Na^+$ (**11b**). The amine in **13** plays the role of coordinating the sodium ion as does Et_2O in **11b**·Et_2O. Further support for the structure of **13** has been provided by E. J. Moore, who has prepared the analog $Cp_2^*(OCCHC(CH_3)_3)(Cl)^-Na^+\cdot HN(iPr)_2$ and characterized it by elemental analysis, molecular weight determination and standard spectroscopic methods. An attempt at alkylating **13** with methyl iodide resulted in formation of a mixture of several products; no ethyl group resonances could be detected in the ^1H NMR.

Pyridine displaces the bromide ligand from **13** to give (η^5-C_5Me_5)$Zr(OCCH_2)$(pyr) (**14**). The pyridine ligand in **14** exhibits five inequivalent protons and five inequivalent carbons in the NMR spectra (room temperature, THF-d_8). This indicates that the pyridine does not undergo rapid exchange with the solvent. Also, the complex is stable for at least several hours in vacuo. The effectiveness of pyridine as a ligand is due to its flat shape, which allows it to slip between the pentamethylcyclopentadienyl rings in **14**. X-ray structure determination of **14** is in progress.[42]

Pyridine adduct **14** and the bromide adduct **13** both reacted rapidly with H_2 to produce the enolate hydride $Cp_2^*Zr(OCHCH_2)H$ (**15**), and with ethylene and acetylene to give cyclic enolates **16** and **17**, respectively, as

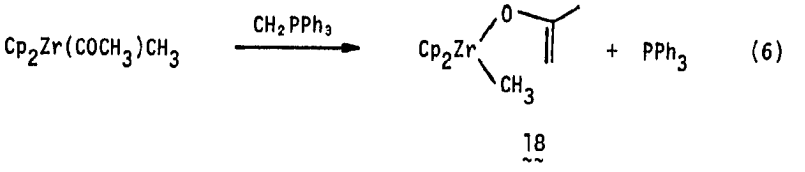
Scheme VII



shown in Scheme VII (ca. 1 atm, room temperature, C_6D_6). These products were characterized by ^1H and ^{13}C NMR. These highly reactive decamethylzirconocene ketene complexes (**13** and **14**) contrast dramatically with the rather inert ketene dimer $(Cp_2Zr|OCCHCH_2C(CH_3)_3|)_2$ (**10**). The reaction with hydrogen provides support for the CO reduction mechanism proposed by Wolczanski and Bercaw (Scheme V).[2]

Recalling our original objective, the development of a new route to enolate complexes, we examined the reaction of $Cp_2Zr(COCH_3)CH_3$ with CH_2PPh_3. Upon mixing the reactants in Et_2O at -50°C, a white precipitate

formed. As the temperature was raised this solid dissolved and gave a pale orange solution. Removal of solvent in vacuo left an orange oil. Analysis by ^{1}H and ^{13}C NMR revealed PPh_3 and what appears to be enolate **18** along with an unidentified product (eq. 6). This reaction is currently being investigated.[43]



(6)

18

Experimental Section

Titanocene dichloride was purchased from Boulder Scientific and purified by Soxhlet extraction with dichloromethane. Zirconocene dichloride was purchased from Boulder Scientific and used as received. Zirconium tetrachloride was purchased from Alfa and purified by sublimation. Carbon monoxide, ethylene, acetylene and 2-butanone were purchased from Matheson. Carbon monoxide-^{13}C (99% enriched) was purchased from MRC-Mound. Methylmagnesium bromide (3 M in Et_2O) was purchased from Aldrich, diluted with Et_2O and standardized by the Gilman procedure.[44] Boron tribromide was purchased from Alfa. $NaN(TMS)_2$ was a gift from T. Coolbaugh. $(\eta^5\text{-}C_5Me_5)TiCl_3$ and $CpTiCl_3$ were gifts from K. Ott. Cp_2ZrHCl,[36] $Cp_2Zr(COCH_3)CH_3$,[32] $Cp_2Ti(CH_3)Cl$[45] and pentamethylcyclopentadiene[46] were prepared by literature methods. CH_2PPh_3 was prepared by the method of Koster[23a] and recrystallized from THF-Et_2O.

Toluene, diethyl ether and THF were stirred over CaH_2 and vacuum transferred onto sodium benzophenone ketyl. Pentane was stirred over concentrated H_2SO_4, washed with water, dried over CaH_2 and vacuum transferred onto sodium benzophenone ketyl in tetraglyme. All solvents were vacuum transferred into flasks sealed with teflon screw valves. Benzene-d_6, toluene-d_8 and THF-d_8 were dried and deoxygenated by stirring over sodium benzophenone ketyl.

General Procedures. All manipulation of air or moisture-sensitive compounds were carried out using standard high-vacuum Schlenk techniques or in a Vacuum Atmospheres drybox equipped with a -40 °C freezer.

Argon used for Schlenk work was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4 Å molecular sieves. NMR spectra were recorded on a Varian EM-390 (90 MHz ^1H) or a JEOL FX-90Q (89.60 MHz ^1H, 22.53 MHz ^{13}C) instrument. Gas chromatographic analysis was performed on a Varian 1400 flame ionization instrument equipped with a Spectra-Physics System I computing integrator. Elemental analysis was done by Spang or Schwartzkopf Microanalytical Laboratories.

Preparation of $Cp_2Ti(COCH_3)Cl$ (1). A solution of $Cp_2Ti(CH_3)Cl$ (3.76 g, 16.5 mmol) in 30 mL toluene was stirred at room temperature under 105 psi CO in a Fischer-Porter bottle. After 16 h the pressure had dropped to 50 psi and the yellow powder which had precipitated was quickly filtered, in air, on a medium porosity frit and washed 2 x 10 mL hexane. Residual solvent was removed in vacuo over a 2 h period to afford $Cp_2Ti(COCH_3)Cl$ as a yellow powder (3.75 g, 89%). The product may be handled in air but should be kept under inert atmosphere for prolonged storage. ^1H NMR ($CDCl_3$) δ 2.93 (s, 3H), 5.74 (s, 10H).

Preparation of $Cp_2Ti(^{13}COCH_3)Cl$ (1-^{13}C). A solution of $Cp_2Ti(CH_3)Cl$ (2.00 g, 8.77 mmol) in 30 mL toluene was stirred at 50°C under 65 psi ^{13}C-enriched CO in a Fischer-Porter bottle. After 12 h the suspension was allowed to cool and the yellow precipitate was quickly filtered, in air, and washed 2 x 10 mL hexane. After removal of solvent for 2 h in vacuo, $Cp_2Ti(^{13}COCH_3)Cl$ was isolated as a yellow powder (1.22 g, 54%). ^1H NMR ($CDCl_3$) δ 2.94 (d, $^2J_{CH}$ = 6.1 Hz, 3H), 5.74 (s, 10H); ^{13}C (^1H) NMR ($CDCl_3$) δ 67.7 (CH_3), 110.5 (Cp), 296.8 (acyl).

Preparation of $(Cp_2TiOCCH_2)_n$ (2a) With CH_2PPh_3. A solution of

$Cp_2Ti(COCH_3)Cl$ (570 mg, 2.23 mmol) in 30 mL CH_2Cl_2 was stirred at -15°C. A suspension of CH_2PPh_3 (570 mg, 2.06 mmol) was transferred via cannula into the cold acyl solution. The mixture instantly became red, and a red microcrystalline solid formed. After addition of 10 mL Et_2O, the solid was allowed to settle. The supernatant was removed via cannula and kept at -25°C. The red solid was washed with 20 mL -25°C Et_2O. Addition of the washing to the supernatant resulted in precipitation of a white solid, which was isolated and identified as CH_3PPh_3Cl (^1H NMR ($CDCl_3$) δ 3.26 (d, J_{PH} = 13.5 Hz), 7.7 (m, br). Mp 218°C (lit.[52] 222-24°C)]. Residual Et_2O was removed in vacuo at 0°C to give $(Cp_2Ti(OCCH_2))_n$ **(2a)** as a red powder (240 mg, 53%). The product is stable in air for periods of ca. 30 min, after which it begins to yellow. The product is insoluble in pentane and Et_2O and is slightly soluble in C_6D_6. It decomposes within several minutes in CH_2Cl_2 at room temperature. Isomerization to an equilibrium mixture with a yellow ketene adduct **(2b)** occurs within ca. 10 min at room temperature in C_6D_6 (ratio **2a:2b** 1:10). ^1H NMR (C_6D_6) δ 3.36 (s, 1H), 4.19 (s, 1H), 5.99 (s, 10H); IR (KBr) 1610 cm^{-1}.

Anal. calcd. for $C_{12}H_{12}OTi$: C, 65.47; H, 5.50; Ti, 21.76 (C:H = 11.90). Found: C, 58.94; H, 4.97; Ti, 20.90 (C:H = 11.86).

Preparation of $(Cp_2Ti(OCCH_2))_n$ (2a) With $NaN(TMS)_2$. This preparation gives the product as a mixture with NaCl. Solid $Cp_2Ti(COCH_3)Cl$ (2.00 g, 7.81 mmol)and $NaN(TMS)_2$ (1.57 g, 8.58 mmol) were combined in a Schlenk tube. At -30°C, 30 mL Et_2O and 5 mL THF were added with stirring. After 30 min the supernatant was forced out through a gas dispersion tube. The red solid was washed with 15 mL Et_2O and stripped

of residual solvent in vacuo for 3 h to give $(Cp_2Ti(OCCH_2))_n$ (2a) as a red powder (1.62 g, yield = 69% if 7.8 mmol NaCl is included).

Preparation of $(Cp_2Ti(OCCH_2))_n$ (2b). A sample of red 2a (193 mg), prepared from $Cp_2Ti(COCH_3)Cl$ and CH_2PPh_3, was stirred in 2 mL benzene for 2.5 h. The benzene was removed via cannula and the yellow solid was washed 1 x 3 mL pentane and dried in vacuo overnight. $(Cp_2Ti(OCCH_2))_n$ (2b) was collected as a yellow powder (112 mg). An analytical sample was prepared by recrystallization from toluene. In C_6D_6 solution, equilibrium with 2a is reached in ca. 1 h at room temperature. ^1H NMR (C_6D_6) δ 3.88 (d, J = 1.5 Hz, 1H), 4.85 (d, J = 1.5 Hz, 1H), 5.66 (s, 10H); IR (KBr) 1610 cm^{-1}.

Anal. calcd. for $C_{12}H_{12}OTi$: C, 65.74; H, 5.50. Found: C, 62.47; H, 5.58.

Preparation of $(Cp_2Ti(O^{13}CCH_2))_n$ (2a-^{13}C and 2b-^{13}C). The red isomer (2a-^{13}C) was prepared by the $NaN(TMS)_2$ procedure described above. In C_6D_6 solution, the two isomers equilibrated. 2a-^{13}C: ^1H NMR (C_6D_6) δ 3.40 (s, br, 1H), 4.18 (d, $^2J_{HC}$ = 10.7 Hz, 1H), 5.99 (s, 10H); ^{13}C NMR (C_6D_6) δ 220.4 (solubility too low to measure coupling in gated spectrum). 2b-^{13}C: ^1H NMR (C_6D_6) δ 3.87 (dd, J_{HH} = 1.5 Hz, $^2J_{HC}$ = 1.0 Hz, 1H), 4.84 (dd, J_{HH} = 1.5 Hz, $^2J_{HC}$ = 11.2 Hz, 1H), 5.66 (s, 10H); ^{13}C NMR (C_6D_6) δ 197.3 (dd, $^2J_{CH}$ = 11.4, 1.2 Hz).

Acidolysis of Ketene Complexes 2a and 2b. A sample of 2a or 2b (ca. 30 mg) was suspended in 5 mL toluene at -30 °C and 1.0 equiv HCl gas (generated from NaCl + H_2SO_4 as described in Experimental Section, Chapter 1) was admitted. After a few minutes the solvent was removed in vacuo. ^1H NMR ($CDCl_3$) revealed only $Cp_2Ti(COCH_3)Cl$.

Reaction of 2a and 2b With Ethylene to Form $Cp_2\overline{TiOC(CH_2)CH_2CH_2}$ (4). Red **2a** (30 mg) was suspended in 500 μL C_6D_6 in an NMR tube with a latex septum. Excess ethylene was added via syringe and over a period of ca. 20 min (with occasional shaking) reaction occurred to give a purple solution (reaction of **2b** is considerably slower, ca. 2 h). The product was decomposed with excess HCl and analyzed by GC (10' 19% FFAP on 80/100 Chrom PAW) and NMR, which both show 50% 2-butanone based on **2a**. The cyclic enolate $Cp_2\overline{TiOC(CH_2)CH_2CH_2}$ (**4**) was stable in solution for at least 24 h. ^1H NMR (C_6D_6) w 1.92 (t, J = 8.2 Hz, 2H), 3.63 (t, J = 8.2 Hz, 2H), 3.86 (br, 2H), 5.83 (s, 10H); ^{13}C (^1H) NMR (C_6D_6) δ 52.5 (-CH_2-), 53.0 (-CH_2-), 78.2 (vinyl CH_2), 115.3 (Cp), 169.9 (vinyl); IR (C_6D_6) 1628 cm^{-1}.

Reaction of 2a, 2b and 6 With Acetylene to Form $Cp_2\overline{TiOC(CH_2)CHCH}$ (5). Red **2a** was suspended in C_6D_6 in an NMR tube. Excess acetylene was added via syringe. Upon shaking, a green solution was formed (**2b** reacts in a similar manner, but requires several minutes). Samples prepared in this manner decomposed in ca. 1 h to give an uncharacterized solid. However, when prepared from phosphine complex **6** solutions of **5** are more stable and dark green crystals form in the NMR tube overnight. ^1H NMR (C_6D_6) δ 4.00 (s, 1H), 4.04 (s, br, 1H), 5.84 (s, 10H), 6.15 (d, J = 8.8 Hz, 1H), 6.97 (d, J = 8.8 Hz, 1H).

Preparation of $Cp_2Ti(OCCH_2)(PMe_2Ph)$ (6). Red ketene complex **2a** (460 mg, 2.09 mmol) was stirred in 10 mL Et_2O at 0°C in a Schlenk tube. Dimethylphenylphosphine (550 μL, 3 mmol) was added via syringe and an instant reaction occurred to give a yellow suspension. After 20 min the supernatant was removed via cannula and the yellow solid was washed 3 x 15

mL pentane. Removal of solvent in vacuo gave $Cp_2Ti(OCCH_2)(PMe_2Ph)$ as a yellow powder (500 mg, 69%). The product was contaminated with ca. 15% **2b**. The phosphine adduct is sparingly soluble in Et_2O and highly soluble in C_6D_6. It is presumed to be monomeric. ^1H NMR (C_6D_6) δ 1.12 (s, br, 6H), 3.99 (s, 1H), 5.26 (s, 10H), 5.35 (s, 1H), 7.1 (m, br, 2H), 7.4 (m, br, 3H). The α-^{13}C labeled complex **6**-^{13}C was prepared as above from **2a**-^{13}C. ^1H NMR (C_6D_6) δ 1.12 (d, $^2J_{HP}$ = 3.5 Hz, 6H), 3.99 (d, $^2J_{HC}$ = 1.5 Hz, 1H), 5.26 (s, 10H), 5.36 (d, $^2J_{HC}$ = 9.6 Hz, 1H), 7.1 (m, br, 2H), 7.4 (m, br, 3H); ^{13}C (^1H) NMR δ 104.0 (Cp), 187.2 (α-^{13}C, no phosphorous coupling). Solutions of **6** begin to darken in ca. 1 h in C_6D_6 solution. This is accompanied by broadening of the ^1H NMR spectrum, which may account for the broad upfield singlet in **6**. After 35 min at room temperature the doublet at δ 1.12 in **6**-^{13}C collapsed to a similar broad signal.

Reaction of 2a With Carbon Monoxide. Red **2a** was suspended in C_6D_6 in an NMR tube and was shaken with excess CO. Slow reaction occurred ($t_{1/2}$ > 3 h) with production of $Cp_2Ti(CO)_2$[34] and a small amount of material with a broad ^1H NMR signal at δ 5.14. Brown solids formed. No ketene dimer was detected. After 1 h under ^{13}CO, no ketene complex resonances were detected by ^{13}C NMR (i.e., no significant incorporation of ^{13}CO into **2a** occured).

Preparation of $Cp_2Zr(COCH_2CH_2C(CH_3)_3)Cl$ (9). Acyl complex **9** was prepared by a modification of the procedure of Carr and Schwartz.[36] A toluene suspension of Cp_2ZrHCl (5.12 g, 19.9 mmol) and 3,3-dimethyl-1-butene (3.2 mL, 24.8 mmol) was stirred in a Schlenk tube for 20 h at room temperature. The reaction mixture was filtered through a medium porosity glass frit and the yellow filtrate was stripped of solvent in vacuo to give a

waxy yellow solid. The solid was dissolved in 55 mL warm 4.5:1 hexane:toluene and transferred into a Fischer-Porter bottle via cannula. The solution was stirred for 3 h under 95 psi CO at room temperature as the white product precipitated. The suspension was cooled to -20 °C for several hours. The bottle was opened to the atmosphere and the white powder was collected on a medium porosity glass frit and washed 2 x 20 mL hexane. After 2 h in vacuo $Cp_2Zr(COCH_2CH_2C(CH_3)_3)Cl$ (**9**) was collected as a white powder (5.84 g, 79%). ^1H NMR (C_6D_6) δ 0.83 (s, 9H), 1.55 (t, J = 7 Hz, 2H), 2.78 (t, J = 7 Hz, 2H), 5.60 (s, 10H); IR (toluene) 1570 cm^{-1} (ν_{CO}).

Preparation of $(Cp_2Zr|OCCHCH_2C(CH_3)_3|)_2$ (10). $Cp_2Zr(COCH_2CH_2C(CH_3)_3)Cl$ (**9**) (2.91 g,7.84 mmol) and $NaN(TMS)_2$ (1.44 g, 7.87 mmol) were dissolved in 40 mL toluene in a Schlenk tube. A colloidal white precipitate formed as the solution was stirred for 2 h at room temperature. The mixture was filtered through a pad of Celite on a coarse frit and washed through with four 10 mL portions of toluene. The clear filtrate was stripped of solvent to give $(Cp_2Zr|OCCHCH_2C(CH_3)_3|)_2$ (**10**) as a white powder (2.29 g, 88%), which was dried in vacuo overnight. An analytical sample was obtained by recrystallization from hot toluene. ^1H NMR (C_6D_6) δ 1.17 (s, 9H), 2.29 (d, J = 7.3 Hz,2H), 5.68 (t, J = 7.3 Hz, 1H), 5.88 (s, 10H); ^{13}C NMR (C_6D_6) δ 30.0 (q, $^1J_{CH}$ = 124 Hz, CH_3), 31.4 (s, CMe_3), 44.6 (t, $^1J_{CH}$ = 127 Hz, CH_2), 99.9 (dt, $^1J_{CH}$ = 146 , $^2J_{CH}$ = 6 Hz, β-CHR), 109.0 (d, $^1J_{CH}$ = 172 Hz, Cp), 187.8 (dt, $^2J_{CH}$ = 8 , $^3J_{CH}$ = 8 Hz, α-C).

Anal. Calcd. for $C_{34}H_{44}O_2Zr_2$: C, 61.21; H, 6.65. Found: C, 59.91; H, 6.74. Molecular weight by cryoscopy in benzene 652. Calcd. 667.

Acidolysis of $(Cp_2Zr|OCCHCH_2C(CH_3)_3|)_2$ (10). Performed as

described for **2a** and **2b** (1.0 equiv HCl gas, -50°C, toluene). ^{1}H NMR revealed a mixture of $Cp_2Zr(COCH_2CH_2C(CH_3)_3)Cl$ (**9**) and unreacted **10**, in roughly equal amounts, after removal of the volatiles.

Acidolysis using 1.0 equiv of HCl gas in an NMR tube at room temperature (C_6D_6) gave equal amounts of **9**, **10**, and $HCOCH_2CH_2(CCH_3)_3$ (identified by ^{1}H NMR: δ 0.57 (s, 9H), 1.12 (t, J = 7 Hz, 2H), 1.75 (t, J = 7 Hz, 2H)), 9.32 (s, br, 1H).

Preparation of $Cp_2Zr(COCH_2)CH_3^-Na^+\cdot Et_2O$ (11b·Et_2O) and 11b·2 THF. A solution of $Cp_2Zr(CH_3)_2$ (1.02 g, 4.06 mmol) was stirred under 1 atm CO for 15-20 min in a Schlenk tube. An additional 75 mL Et_2O was added and the solution was cooled to -20°C. A solution of $NaN(TMS)_2$ (744 mg, 4.06 mmol) in 30 mL Et_2O was transferred <u>via</u> cannula into the pale yellow acyl solution. A white solid precipitated upon mixing. The suspension was stirred at -20°C for 30 min and allowed to settle for 45 min. The clear supernatant was removed <u>via</u> cannula. The solid was washed with 60 mL and with 30 mL Et_2O at -20°C. Residual solvent was removed <u>in vacuo</u> for 30 min at room temperature to give $Cp_2Zr(COCH_2)CH_3^-Na^+\cdot Et_2O$ as a white powder (1.20 g, 79%). The product may be handled at room temperature but must be stored cold. This and similar salts are insoluble in toluene and Et_2O but are highly soluble in THF.[48] ^{1}H NMR (THF-d_8) δ -0.68 (s, 3H), 1.10 (t, J = 7 Hz, 6H), 3.37 (q, J = 7 Hz, 4H), 3.64 (d, J = 2 Hz, 1H), 4.55 (d, J = 2 Hz, 1H), 5.43 (s, 10H); IR (nujol) 1575 cm^{-1}. The Et_2O in 11b·Et_2O may be exchanged with THF to give 11b·2 THF: ^{13}C NMR (THF-d_8) δ 8.8 (q, $^1J_{CH}$ = 115 Hz, CH_3), 74.3 (t, $^1J_{CH}$ = 146 Hz, β-CH_2), 105.2 (d, $^1J_{CH}$ = 170 Hz, Cp), 199.8 (t, $^2J_{CH}$ = 9 Hz, α-C).

Preparation of $Cp_2Zr(COCH_2CH_3)CH_3$. A solution of $Cp_2Zr(CH_3)_2$ (2.33 g, 9.28 mmol) in 60 mL Et_2O was stirred at room temperature under 1 atm CO for 20 min. As the solution was cooled to -25°C, this yellow acyl began to crystallize. A solution of $NaN(TMS)_2$ (2.00 g, 10.9 mmol) in 15 mL Et_2O was added via cannula to the stirred suspension. A white precipitate formed upon mixing. After 15 min at -20°C the supernatant was forced out thorough a gas dispersion tube. The white salt was dissolved in 25 mL THF. The solution was stirred at room temperature and methyl iodide (800 μL, 12.8 mmol) was added via syringe. The solution became pale yellow. After 5 min, the solvent was removed in vacuo. The residue was dissolved in 80 mL Et_2O and filtered on a coarse frit. The filtrate was stripped of solvent in vacuo to give $Cp_2Zr(COCH_2CH_3)CH_3$ as a yellow powder (2.00 g, 73%). An analytical sample was prepared by recrystallization from Et_2O.[49] ^1H NMR (C_6D_6) w 0.53 (s, 3H), 1.05 (t, J = 7 Hz, 3H), 2.55 (q, J = 7 Hz, 2H), 5.32 (s, 10H); IR (KBr) 1530 cm^{-1} (ν_{CO}).

Anal. calcd. for $C_{14}H_{18}OZr$: C, 57.29; H, 6.18. Found: C, 57.09; H, 6.16.

Preparation of $Cp_2Zr(COCH(CH_3))CH_3^-Na^+ \cdot Et_2O$ (11c·Et_2O). A solution of $Cp_2Zr(CH_3)_2$ (1.10 g, 4.38 mmol) in 60 mL Et_2O was stirred at room temperature under 1 atm CO for 15 min, then cooled to 0°C. A solution of $NaN(TMS)_2$ (815 mg, 4.45 mmol) in Et_2O was added via cannula to the chilled acyl solution. A white precipitate formed. After 5 min the mixture was cooled to 0°C and the solvent was forced out through a gas dispersion tube. The salt was washed with 10 mL Et_2O. The precipitate was dissolved in 20 mL THF and methyl iodide (350 μL, 5.6 mmol) was added to

the stirred solution at room temperature. After 5 min the solvent was removed in vacuo. The residue was stirred with 70 mL Et_2O for 20 min and filtered on a coarse frit. A solution of $NaN(TMS)_2$ (800 mg, 4.4 mmol) in 15 mL Et_2O was added to the stirred filtrate at 0°C. A white solid precipitated. After 10 min the supernatant was removed and the white salt was washed with 20 mL cold Et_2O. Residual solvent was removed in vacuo to give $Cp_2Zr(COCH(CH_3))CH_3^-Na^+ \cdot Et_2O$ as a white powder (671 mg, 39%). The product should be stored cold. ^1H NMR (THF-d_8) δ -0.68 (s, 3H), 1.07 (t, J = 7 Hz, 6H), 1.82 (d, J = 6 Hz, 3H), 3.38 (q, J = 7 Hz, 4H), 5.07 (q, J = 6 Hz, 1H), 5.45 (s, 10H).

Preparation of $Cp_2Zr(COCH(CH_3)_2)CH_3$. A solution of $Cp_2Zr(COCH(CH_3)_2)CH_3$ (1.20 g, 4.10 mmol) in 50 mL Et_2O was stirred at -30°C. A solution of $NaN(TMS)_2$ (1.00 g, 5.46 mmol) was added via cannula and a white solid immediately precipitated. After 30 min the solid was allowed to settle for 10 min at -40°C. The solvent was forced out through a gas dispersion tube. The white solid was dissolved in 15 mL THF and methyl iodide (400 µL, 6.4 mmol) was added via syringe at room temperature. After 5 min the solvent was removed in vacuo. The residue was stirred with 30 mL Et_2O and filtered through a pad of Celite. The filtrate was stripped of solvent in vacuo to give $Cp_2Zr(COCH(CH_3)_2)CH_3$ as a yellow powder (750 mg, 59%).[49] An analytical sample was prepared by recrystallization from pentane-Et_2O. ^1H NMR (C_6D_6) δ 0.54 (s, 3H), 1.09 (d, J = 7 Hz, 6H), 2.37 (septet, J = 7 Hz, 1H), 5.37 (s, 10H); IR (KBr) 1520 cm^{-1} (ν_{CO}).

Anal. calcd. for $C_{15}H_{20}OZr$: C, 58.58; H, 6.56. Found: C, 58.58; H, 6.64.

Formation of $Cp_2Zr(COC(CH_3)_2)CH_3^-Na^+$ (11d). $Cp_2Zr(COCH(CH_3)_2)CH_3$ (18 mg, 0.06 mmol) and $NaN(TMS)_2$ (16 mg, 0.09 mmol) were combined in an NMR tube and ca. 400 μL THF-d_8 was added to give a colorless solution. The spectrum was consistent with $Cp_2Zr(COC(CH_3)_2)CH_3^-Na^+$: ^1H NMR (THF-d_8) δ -0.77 (s, 3H), 0.01 (s, TMS), 1.68 (s, 3H), 1.83 (s, 3H), 5.34 (s, 10H).

Preparation of $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$. Prepared by modification of an existing procedure used by Professor J. E. Bercaw and co-workers.[50] Use of isolated C_5Me_5Li, instead of *in situ* preparation, in this procedure was recommended by D. M. Roddick and P. Barger. Zirconium tetrachloride (12.0 g, 51.5 mmol) and C_5Me_5Li (16.0 g, 113 mmol) were suspended in 80 mL toluene in a Schlenk tube fitted with a reflux condensor. The mixture was refluxed for 3 d under an argon atmosphere. Encrustations were occasionally chipped from the walls of the vessel with a spatula. The toluene was removed *in vacuo*. In air, the product was extracted with 200 mL $CHCl_3$. The extract was washed with 100 mL 4 *M* HCl. The acid layer was extracted 4 x 150 mL $CHCl_3$. The combined $CHCl_3$ layers were washed 2 x 200 mL water. The combined water layers were extracted 2 x 100 mL $CHCl_3$. The combined chloroform extracts were dried over $MgSO_4$ at 0°C overnight and filtered on a coarse frit. The yellow filtrate was stripped down to 40 mL on a rotary evaporator and cooled to -50°C overnight. The supernatant was removed *via* cannula and the product was washed 1 x 50 mL cold pentane. After removal of residual solvent *in vacuo* for 90 min, $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$ (18.84 g, 85%) was collected as yellow crystals. An additional 160 mg (1%) was obtained upon cooling of the combined supernatant and washings. ^1H

NMR (C_6D_6) δ 1.84 (s, 30H).

Preparation of $(\eta^5\text{-}C_5Me_5)_2ZrBr_2$.[53] $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$ (2.86 g, 6.62 mmol) was dissolved in 60 mL CH_2Cl_2. With vigorous stirring, BBr_3 (4.5 mL, 7.6 mmol) was added via syringe. The solution became dark, but remained homogeneous. After 10 min at room temperature the solvent was removed. In air, the residue was dissolved in 100 mL warm toluene. A small amount of insoluble black solid was removed by filtration through a medium porosity frit. The pale green filtrate was concentrated to 40 mL in vacuo and stored at -50°C overnight. The supernatant was decanted and the residual toluene was removed in vacuo to afford large, pale green crystals of $(\eta^5\text{-}C_5Me_5)_2ZrBr_2$ (3.22 g, 93%). An analytical sample was prepared by recrystallization from toluene. ^1H NMR (C_6D_6) δ 1.88 (s, 30H).

Anal. calcd. for $C_{20}H_{30}Br_2Zr$: C, 46.06; H, 5.80; Br, 30.63. Found: C, 46.24; H, 5.58; Br, 30.65.

Preparation of $(\eta^5\text{-}C_5Me_5)_2Zr(CH_3)Br$. Methylmagnesiumbromide (0.69 M in Et_2O, 6.0 mL, 4.14 mmol) was added via syringe to a stirred suspension of $(\eta^5\text{-}C_5Me_5)ZrBr_2$ (1.96 g, 3.76 mmol) in 25 mL Et_2O in a Schlenk tube. The mixture was diluted with 100 mL toluene. The volume of the mixture was reduced to 95-100 mL in vacuo. The pale green solution was stirred at 50°C for a period of 3 h, during which the color discharged and a fine white solid formed. The warm suspension was filtered through a medium porosity frit. The filtrate was stripped of solvent in vacuo to give a pale yellow powder. ^1H NMR analysis of this residue revealed $(\eta^5\text{-}C_5Me_5)_2Zr(CH_3)Br$ and $(\eta^5\text{-}C_5Me_5)_2Zr(CH_3)_2$ in the ratio 30:1. The product was dissolved in 35 mL THF and transferred, via a cannula tipped with filter

paper, into a second Schlenk tube and slowly cooled to -50°C. After 12 h at -50°C the supernatant was decanted and, after removal of residual solvent in vacuo, $(\eta^5\text{-}C_5Me_5)_2Zr(CH_3)Br$ was isolated as an analytically pure pale green crystalline solid (1.00 g, 58%). The supernatant was stripped of solvent in vacuo and the pale yellow, finely divided residue was washed 2 x 10 mL -50°C Et_2O and freed of residual solvent in vacuo to give an additional portion (600 mg, 35%) of product of sufficient purity for use in preparation of $(\eta^5\text{-}C_5Me_5)_2Zr(COCH_3)Br$. Combined yield, 93%. ^1H NMR (C_6D_6) δ -0.12 (s, 3H), 1.81 (s, 30H).

Anal. calcd. for $C_{21}H_{33}BrZr$: C, 55.24; H, 7.28; Br, 17.50. Found: C, 55.51; H, 7.32; Br, 17.02.

Preparation of $(\eta^5\text{-}C_5Me_5)_2Zr(COCH_3)Br$. $(\eta^5\text{-}C_5Me_5)_2Zr(CH_3Br)$ (1.50 g, 3.29 mmol) was dissolved in 25 mL THF in a Fischer-Porter bottle and stirred under 95 psi CO at room temperature for 1 h. The temperature was gradually reduced to -50°C over a 10 h period. The supernatant was removed via cannula and residual solvent was removed in vacuo at -50°C for 30 min, then at room temperature for 2 h to give analytically pure $(\eta^5\text{-}C_5Me_5)_2Zr(COCH_3)Br$ as large, pale yellow-green crystals (650 mg, 41%). The supernatant was reduced to 12 mL in vacuo at room temperature, stirred under 95 psi CO at room temperature for 1 h and slowly cooled to -50°C. A second crop of product was isolated as before (330 mg, 21%). Combined yield, 62%. The product slowly decarbonylates in C_6D_6 solution (< 10% after 20 min at room temperature). ^1H NMR (C_6D_6) δ 1.71 (s, 30H), 2.21 (s, 3H).

Anal. calcd. for $C_{22}H_{33}OBrZr$: C, 54.52; H, 6.86; Br, 16.49. Found: C, 54.79; H, 6.94; Br, 16.81.

Reaction of $(\eta^5\text{-}C_5Me_5)_2Zr(COCH_3)Br$ With $NaN(TMS)_2$ to Form $(\eta^5\text{-}C_5Me_5)_2Zr(OCCH_2)Br^-Na^+\cdot HN(TMS)_2$ (13). Acyl complex (25 mg, 0.052 mmol) and $NaN(TMS)_2$ (8 mg, 0.044 mmol) were combined in an NMR tube. Upon addition of 500 mL C_6D_6 and vigorous shaking, reaction occurred to give a clear, pale orange solution of 13.[51] ^1H NMR (C_6D_6) δ 0.09 (s, 18H), 1.86 (s, 30H), 4.01 (s, 1H), 5.01 (s, 1H). The amine H was not located.

Preparation of $(\eta^5\text{-}C_5Me_5)_2Zr(OCCH_2)(pyr)$ (14). A Schlenk tube was charged with $(\eta^5\text{-}C_5Me_5)_2Zr(COCH_3)Br$ (1.47 g, 3.04 mmol) and $NaN(TMS)_2$ (0.95 g, 5.19 mmol) (NOTE: A lower excess, ca. 10%, NaN(TMS) should be used to facilitate separation of product from unreacted base). THF (20 mL), was added and the mixture was stirred at room temperature for ca. 20 min. Upon addition of pyridine (400 μL, 4.7 mmol) the colorless solution turned pale yellow and a white solid precipitated. After 10 min the suspension was filtered on a medium porosity frit and the filtrate was stripped of solvent <u>in vacuo</u> to give a yellow solid. The residue was dissolved in 15 mL Et_2O and slowly cooled to -50:C. After standing for 12 h at -50°C the supernatant was removed <u>via</u> cannula and the yellow microcrystalline $(\eta^5\text{-}C_5Me_5)_2Zr(OCCH_2)(pyr)$ was washed 2 x 15 mL -50°C Et_2O and freed of residual solvent <u>in vacuo</u> (450 mg, 31%). ^1H NMR (THF-d_8) δ 1.60 (s, 30H), 3.51 (d, J = 1.6 Hz, 1H), 4.57 (d, J = 1.6 Hz, 1H), 7.56 (m, 2H), 7.91 (m, 1H), 8.43 (br, 1H), 9.26 (br, 1H); ^{13}C NMR (THF-d_8) δ 11.67 (q, $^1J_{CH}$ = 125 Hz, $C_5\underline{Me}_5$), 72.8 (dd, $^1J_{CH}$ = 148.4, 160.2 Hz, β-CH_2), 115.1 (s, $\underline{C}_5Me_5$), 124.6 (d, $^1J_{CH}$ = 164 Hz, pyr), 126.2 (d, $^1J_{CH}$ = 162 Hz, pyr), 139.1 (d, $^1J_{CH}$ = 166 Hz, pyr), 151.0 (d, $^1J_{CH}$ = 189 Hz, pyr), 153.0 (d, $^1J_{CH}$ = 182 Hz, pyr), 205.2 (pseudo-triplet, $^2J_{CH}$ = 8 Hz, α-C).

Reaction of 13 and 14 With H_2 to Give $(\eta^5\text{-}C_5Me_5)_2Zr(OCHCH_2)H$ (15). Pyridine adduct **14**, in C_6D_6 in an NMR tube, was treated with excess H_2. The yellow solution immediately discolored as enolate hydride **15** formed. ^1H NMR (C_6D_6) δ 1.94 (s, 30H), 3.95 (d, J = 5.9 Hz, 1H), 4.16 (d, J = 13.7 Hz, 1H), 6.14 (s, 1H), 6.80 (dd, J = 5.9, 13.7 Hz, 1H); ^{13}C NMR (C_6D_6) δ 11.8 (q, 126 Hz, CH_3), 89.4 (not resolved in gated spectrum, CH_2), 118.3 (s, $\underline{C}_5Me_5$), 154.2 (d, J = 171 Hz, CH). The same product was formed when **13**, generated <u>in situ</u>, was treated with H_2

Reaction of 13 and 14 With Ethylene to Give $(\eta^5\text{-}C_5Me_5)_2ZrOC(CH_2)CH_2CH_2$ (16). To a sample of **14** in C_6D_6 in an NMR tube was added 3 equiv of ethylene. The solution remained clear yellow as reaction occurred to produce cyclic enolate **16.** ^1H NMR (C_6D_6) δ 0.97 (t, J = 7.5 Hz, 2H), 1.82 (s, 30H), 3.35 (t, J = 7.5 Hz, 2H), 3.96 (s, br, 2H); ^{13}C (^1H) NMR (C_6D_6) δ 10.9 (CH_3), 43.6 ($-CH_2-$), 46.4 ($-CH_2-$), 81.4 (vinyl CH_2), 119.8 ($\underline{C}_5Me_5$), 170.2 (vinyl). The same product forms when **13**, generated <u>in situ</u> from $(\eta^5\text{-}C_5Me_5)_2Zr(COCH_3)Br$ and $NaN(TMS)_2$, is treated with ethylene.

Reaction of 13 and 14 With Acetylene to Give $(\eta^5\text{-}C_5Me_5)_2ZrOC(CH_2)CHCH$ (17). A sample of **14** in C_6D_6 in an NMR tube was treated with 4 equiv of acetylene and shaken. The solution remained yellow as reaction occurred to produce cyclic enolate **17.** ^1H NMR (C_6D_6) δ 1.80 (s, 30H), 4.07 (s, 1H), 4.22 (s, 1H), 6.83 (d, J = 11.7 Hz, 1H), 7.07 (d, J = 11.7 Hz, 1H); ^{13}C NMR (THF-d_8) δ 11.2 (q, 126 Hz, CH_3), 85.5 (pseudo-triplet, 156 Hz, vinyl CH_2), 120.8 (s, $\underline{C}_5Me_5$), 145.1 (d, 151 Hz, α-CH), 169.0 (not resolved in gated spectrum, vinyl), 198.5 (d, 129 Hz, β-CH). The same product is formed rapidly from <u>in situ</u>-generated **13.**

Reaction of 2a With (η^5-C_5Me_5)$TiCl_3$ to Form (Cp_2TiCl)-μ-η^2(C,O)-$OCCH_2$[(η^5-C_5Me_5)$TiCl_2$] (7). Ketene complex **2a** (11 mg, 0.050 mmol) and (η^5-C_5Me_5)$TiCl_3$ (13 mg, 0.045 mmol) were combined in an NMR tube. Upon addition of 400 µL C_6D_6 reaction occurred to produce an orange solution of μ-η^2(C,O) ketene complex **7**, previously characterized by K. Ott.[33] ^1H NMR (C_6D_6) w 1.99 (s, 30H), 4.83 (s, 1H), 4.90 (s, 1H), 6.21 (s, 10H).

Reaction of 2a With $CpTiCl_3$ to Form (Cp_2TiCl)-μ-η^2(C,O)-$OCCH_2$-($CpTiCl_2$) (8). Ketene complex **2a** (26 mg, 0.119 mmol) and $CpTiCl_3$ (21 mg, 0.095 mmol) were combined in an NMR tube. Upon addition of 400 µL C_6D_6 reaction occurred to give an orange solution of a single compound, identified as the bridging ketene complex **8** by ^1H NMR and by analogy with **7**. The product decomposed to give an unidentified dark solid in 1 h at room temperature. ^1H NMR (C_6D_6) w 4.67 (s, 1H), 4.87 (s, 1H), 6.11 (s, 10H), 6.20 (s, 10H).

Reaction of $Cp_2Zr(COCH_3)CH_3$ With CH_2PPh_3. $Cp_2Zr(COCH_3)CH_3$ (450 mg, 1.63 mmol) was dissolved in 10 mL Et_2O and immediately cooled to -50°C. A solution of CH_2PPh_3 (450 mg, 1.63 mmol) in 15 mL Et_2O (-60°C) was added. A voluminous white solid formed immediately. As the temperature was gradually raised to 25°C, the solid dissolved and a pale orange solution resulted. After filtration through a medium porosity glass frit, the solvent was removed in vacuo to give an orange oil. PPh_3 and CH_2PPh_3 were identified by NMR, along with two Cp-containing products (ratio 2:1). The major product is assigned as $Cp_2Zr[OC(CH_2)CH_3]CH_3$. ^1H NMR (C_6D_6) δ 0.35 (s, 3H), 1.63 (s, br, 3H), 3.87 (m, 2H), 5.81 (s, 10H). Resonances characteristic of Group IV metal enolates were observed in the

^{13}C NMR spectrum at δ 86.3 and 164.7. The minor product has not been identified.[43]

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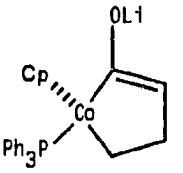

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