Synthesis and Reactivity of Transition Metal Homo- and Heterobinuclear Ketene Complexes

Thesis by

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To my parents

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ABSTRACT

The rearrangement of β-phenyltitanacyclobutane (1) to α-phenyltitanacyclobutane (2) is shown through labeling experiments to proceed by a stepwise mechanism. Ring opening of 1 to the metal-methylidene species followed by readdition of styrene affords both complexes 1 and 2.

The reaction of titanacyclobutanes with oxidizing agents produces cyclopropanes in good yield. The stereochemistry of this reaction has been investigated using cis-2,3-dimethyltitanacyclobutane and trans-2-deutero-3-phenyltitanacyclobutane. By the use of ^2H NMR, the stereochemistry of each step of the reaction has been determined.

The crystal and molecular structure of zirconaenolate anion $Cp_2Zr(\eta^2\text{-}OCCH_2\text{-}O,C)CH_3Na\cdot 2$ THF prepared by deprotonation of the corresponding acyl complex has been determined. The reactivity of this anion with electrophilic reagents is studied. Reaction with alkyl halides leads to C-substituted acyl complexes. Reaction with metal chlorides $L_2M(CH_3)Cl$ leads to binuclear ketene complexes $(Cp_2ZrCH_3)(\mu\text{-}\eta^2\text{-}OCCH_2\text{-}O,C)\text{-}(MCH_3L_2)$ (M = Zr, Pt; L = Cp, phosphines). The mechanism for the formation of these complexes and their reactivities are discussed in detail.

The interaction of phosphonium and sulfoxonium ylides with acyl complexes of titanium and zirconium is examined. Reaction of $Cp_2Zr(COR)R'$ (R,R' = alkyl, aryl) with $CH_2P\phi_3$ and $CH_2SO(CH_3)_2$ gives enolate complex $Cp_2Zr(OCR{=}CH_2)R'$. Treatment of titanocene chloro acyls

with $CH_2SO(CH_3)_2$ affords ketene complexes which react with excess ylides to give titanaoxacyclobutanes. The structure of titanaoxacyclobutane is determined by Dynamic NMR techniques. The zirconium chloro acyls react with $CH_2SO(CH_3)_2$ to give mixtures of ketene and enolate complexes. Both react further with the ylides to yield zirconaoxacyclobutanes.

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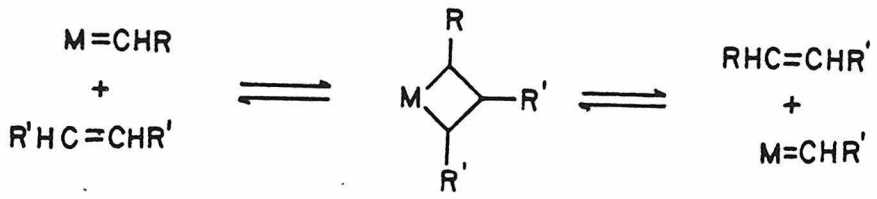
A. Mechanism of Rearrangement of Titanacyclobutane

Introduction

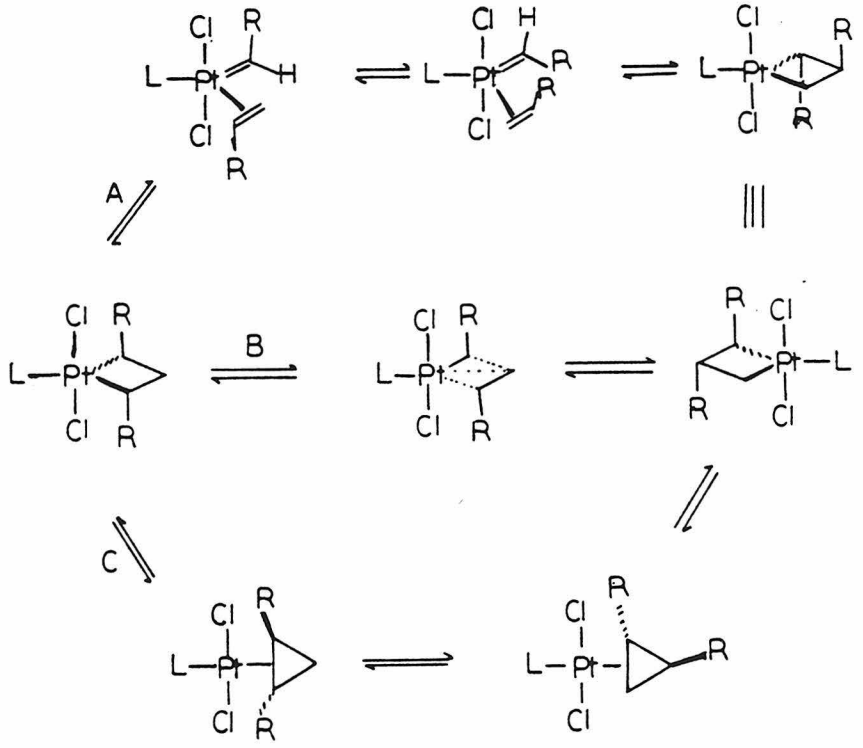
It is now generally accepted that the olefin metathesis reaction proceeds by a stepwise mechanism with alternating metallacarbene and metallacyclobutane intermediates.[1,2] The intermediacy of metallacarbene



has been documented by the isolation of metal alkylidene complexes and their reactions with alkenes.[3-5] Well-characterized metallacyclobutanes, however, are few and generally lack of metathetical activities.[6] Reaction of one metallacyclobutane that can possibly proceed by a mechanism related to olefin metathesis is the thermal rearrangement of platinacyclobutanes. Labeling and cross-over studies by Puddephatt and Casey demonstrate a concerted intramolecular rearrangement for the isomerization of α- to β-substituted platinacyclobutanes.[7,8] Three possible mechanisms have been suggested (Scheme I). In mechanism A, the proposed intermediate is a carbene-olefin complex that undergoes rotations of both the carbene and olefin ligands in the opposite directions. Mechanism B also suggests an intermediate resembling a carbene-olefin complex from increased interaction of platinum with the β-carbon by puckering of the metallacycle ring.

Stable titanacyclobutanes isolated from an olefin metathesis system have been reported by our laboratory.[9] We will address the mechanism of the isomerization of β-phenyltitanacyclobutane to α-phenyltitanacyclobutane for comparison to the corresponding platinum reactions. The results of this study have been communicated.[10]

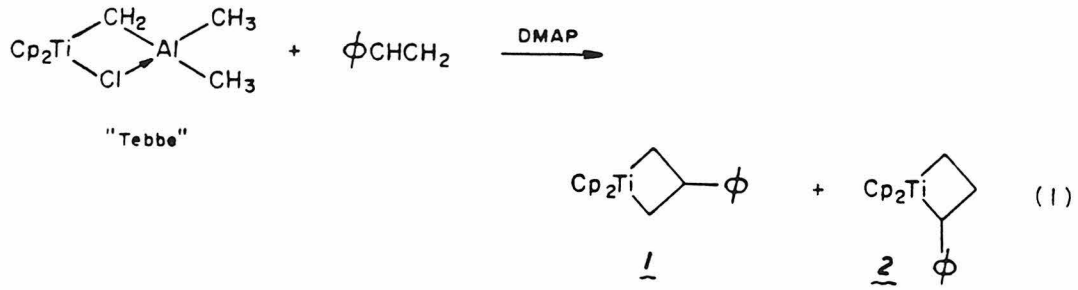
Scheme I



Results and Discussion

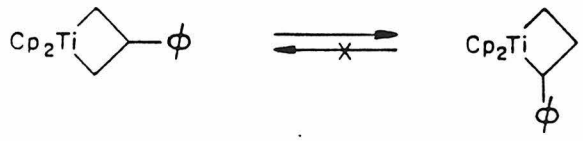
As reported previously, the reaction of the "Tebbe" reagent with styrene in toluene solution containing dimethylaminopyridine (DMAP) gives a

1:2.5 mixture of the β-isomer (1) and the α-isomer (2), The ratio of α- to β-isomer is probaly a factor of steric effect rather than electronic effect, since reactions of methyl and methoxy substituted styrenes give similar isomer ratios as styrene. Complexes 1 and 2 are easily separated due to their widely different solubilities (eq. 1). The β-isomer precipitates as an orange



(1)

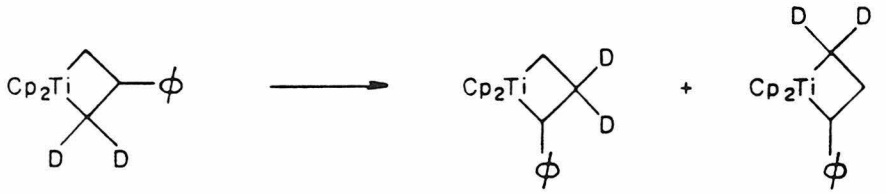
solid from the reaction mixture. The α-isomer is obtained from extraction of the reaction residue with n-hexane. Solutions of complex 1 in toluene readily isomerize to the α-isomer (2) at room temperature (eq. 2). The α-isomer is unreactive under the isomerization conditions, even with the added styrene.



(2)

By monitoring the disappearance of the β-isomer and the appearance of the α-isomer resonances in the ^1H NMR spectrum, the isomerization reaction is characterized by first order kinetics with $k = 3.0 \times 10^{-4}$ s^{-1} at

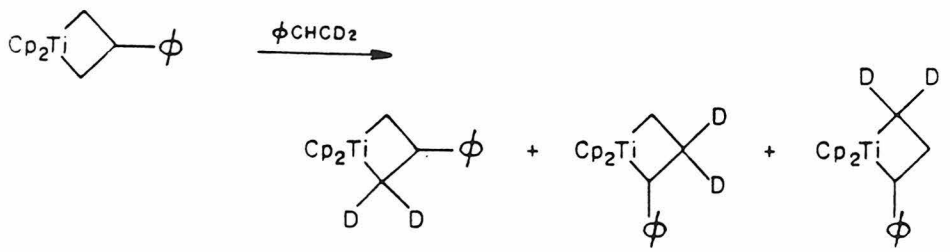
25°C.[12] Addition of styrene (2-10 equiv) does not affect the rate of isomerization. By comparison with the results of other titanacyclobutane reactions investigated in the group, the rate-determining step in the isomerization of 1 is considered to be the ring-opening of the titanacyclobutane to the titanium methylidene-olefin complex or the free titanium-carbene species.[9c] The detailed mechanism of the isomerization is further probed using isotopically labeled 1 and ^2H NMR.[13] The results are summarized in Table I. 2,2-d_2-1 isomerizes in toluene at room temperature to give 3,3-d_2-2 and 4,4-d_2-2 in a 1.6:1 ratio which is consistent with a secondary deuterium isotope effect (eq. 3). The unusually large secondary



(3)

2,2-d_2-1 3,3-d_2-2 4,4-d_2-2

isotope effect of 1.6 for titanacyclobutanes has been discussed earlier.[9c] Isomerization reaction of 1 in the presence of $\phi CHCD_2$ gives 3,3-d_2-2 as the major product (75%). 4,4-d_2-2 and 2,2-d_2-1 are also detected in 9 and 15% yields respectively (eq. 4). Since 4,4-d_2-2 can only be formed from reaction



(4)

2,2-d_2-1 3,3-d_2-2 4,4-d_2-2

Table I

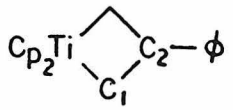
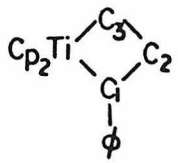
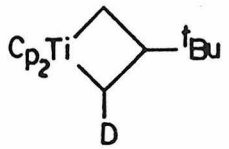
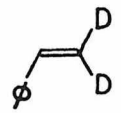
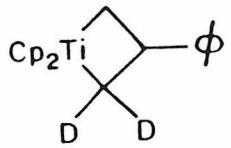
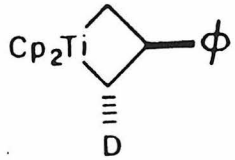
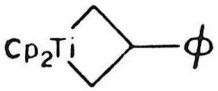
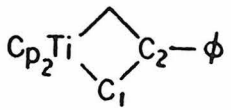
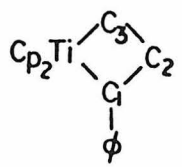
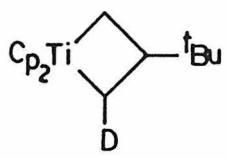
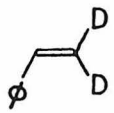
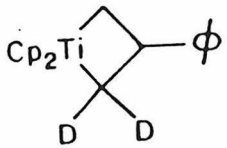
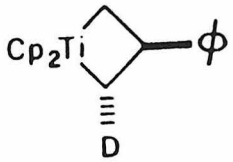
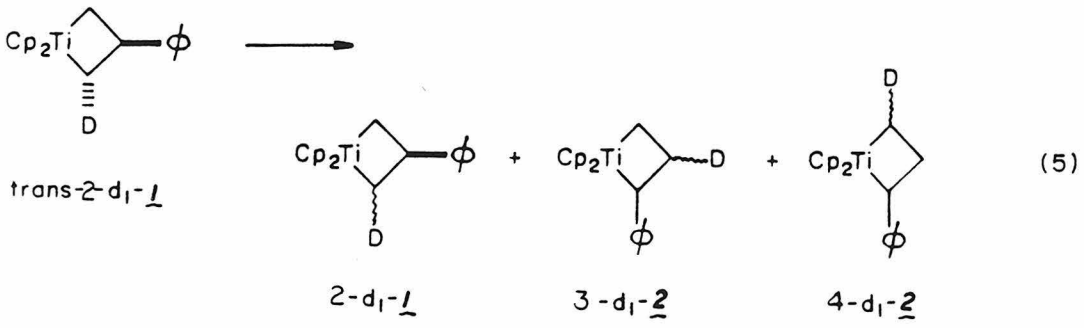
Reactant/ Condition	^2H Chemical Shift[a] / Relative Ratio									
		D-C_1		D-C_3		D-C_2[b]				
		cis	trans	cis	trans		cis	trans	cis	trans[c]
		2.24	2.66	2.89	2.97	0.06	5.52	4.92	1.75	2.07
1	 RT, 105 min, toluene	0.71	0.71	1.0		1.58	0.13	0.13	--	--
2	 RT, 240 min, toluene	0.14	0.29	1.0		1.40	0.04	0.05	--	--
3	 RT, 105 min, toluene	0.86	0.86	1.0		8.30	--	--	--	--
	$PhHC{=}CD_2$									

Table I. Continued

Reactant/ Condition		^{2}H Chemical Shift[a] / Relative Ratio									
			D-C_1		D-C_3		D-C_2[b]				
			cis	trans	cis	trans		cis	trans	cis	trans[c]
			2.24	2.66	2.89	2.97	0.06	5.52	4.92	1.75	2.07
4	 PhHC=CH_2	RT, 105 min, toluene	0.50	0.50	1.0		0.19	1.56	1.56	--	--
5	 t-BuHC=CH_2	Rt, 70 min, toluene	0	2.17	1.0		1.25	0	1.75	0.58	0.58

[a]Deuterium chemical shift relative to toluene methyl CH_2D at 1.95; [b]Signals of deuterium cis or trans to phenyl cannot be resolved. [c]Cis or trans to phenyl or t-butyl groups.

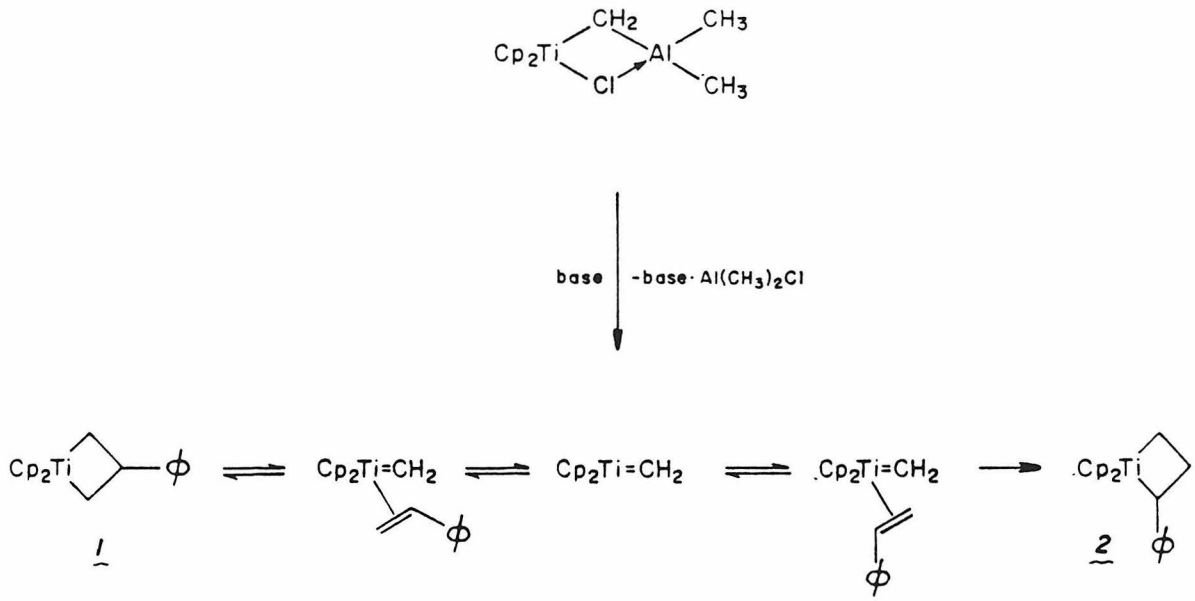
of 2,2-d_2-1, the above result indicates that olefin exchange reaction has occurred to give both the α- and β-isomer in 75:(9+15) or 3:1 ratio. In the absence of free olefins, isomerization can occur <u>via</u> carbene or olefin rotation in the metal-carbene-olefin complex. High rotation barrier of the carbene rule out the first. Schrock has estimated the free energy of activation ($\Delta G^{\ddagger}$) for the rotation of a tantalum alkylidene complex as 25 kcal/mol.[14] Theoretical studies by Mintz and Hehre suggest the torsional barrier for $Cp_2Ti{=}CH_2$ to be 36-52 kcal/mol.[15] To address the possibility of olefin rotation, we employed stereospecifically labeled <u>trans</u>-2-d_1-1, since rotation of olefin should define the relative stereochemistry of the α-isomer to be either <u>trans</u>-3-d_1-2 or <u>cis</u>-4-d_1-2. Isomerization of <u>trans</u>-2-d_1-1 in toluene without added styrene, however, gives all possible stereoisomers of 2 (eq. 5). Equal amounts of <u>cis</u>- and <u>trans</u>-4-d_1-2 are present as are the



(5)

scrambled β-isomers, 2-d_1-1 and d_1-styrene. We therefore rule out olefin rotation as a major isomerization pathway. From the kinetics and labeling experiments, we conclude that the apparent isomerization of 3-phenyltitanacyclobutane (1) is due to ring-opening of the titanacyclobutane followed by readdition of olefins to the titanium methylidene species

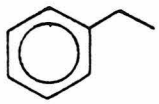
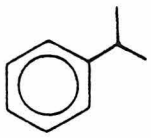
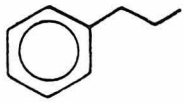
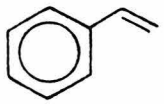
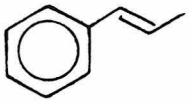
Scheme II



(Scheme II).

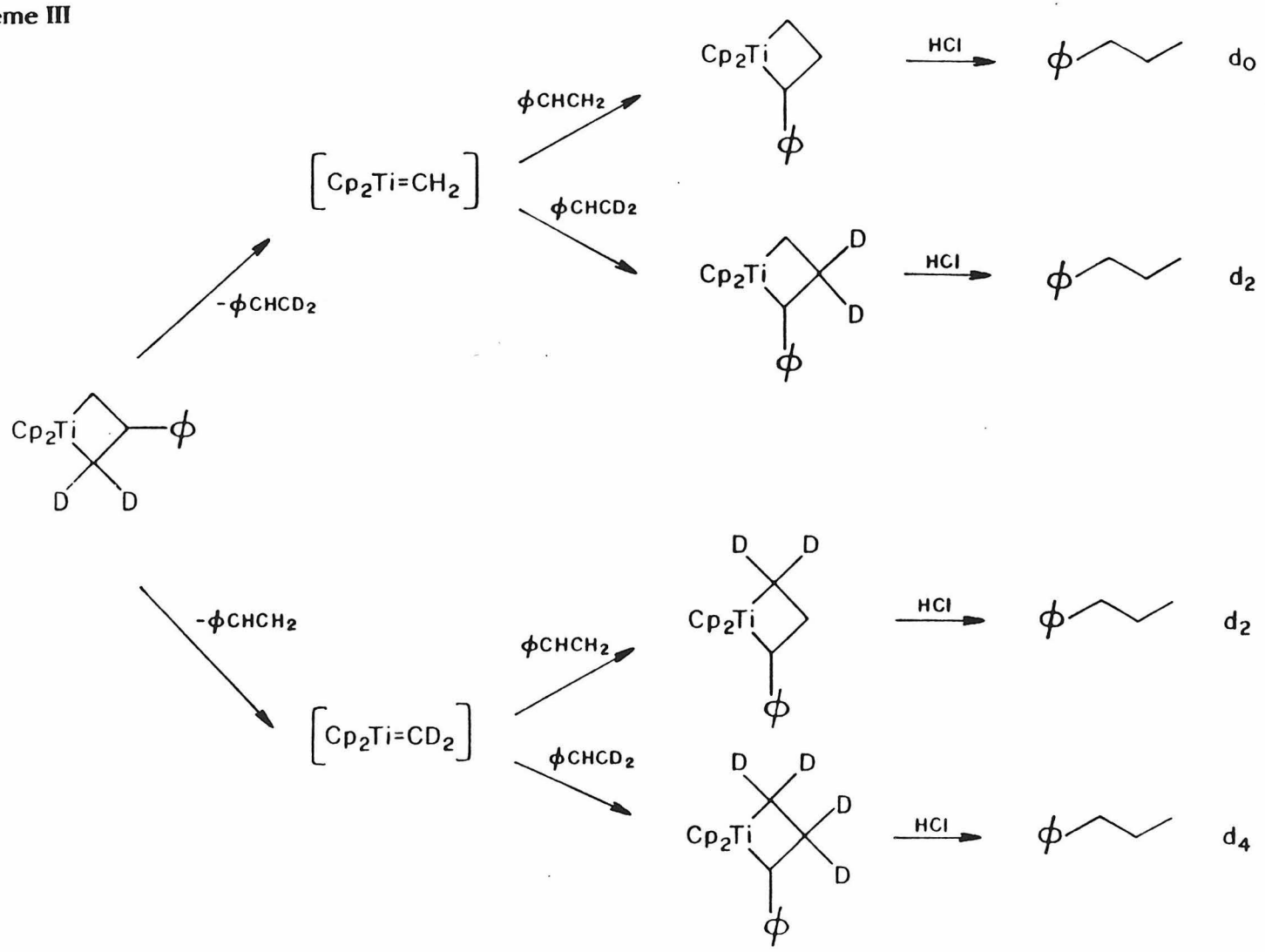
The intermolecular process is further supported by the following observations. A solution of 2,2-d_2-**1** in toluene is allowed to equilibrate at room temperature for 1 h before hydrolysis with anhydrous hydrogen chloride. The organic products are isolated and analyzed by gas chromatography and mass spectrometry. The results are summarized in Table II. Isopropyl benzene is mostly d_2 as expected from unreacted 2,2-d_2-**1**. The n-propyl benzene, from hydrolysis of **2**, containes molecules containing from d_0 to d_5 deuteria. The ratio of d_0:d_2:d_4 n-propyl benzene is approximately 1:2.5:1.1 (from 13:34:15), or that approaching a statistical olefin exchange (Scheme III). In the case where large excess of a 1:1 mixture of styrene-d_0 and d_2 is present in the reaction, the kinetic ratio of n-propylbenzene d_0:d_2:d_4 should

Table II.

Products	Yield (by GC)	d_n* (M ion, %)					
		d_0	d_1	d_2	d_3	d_4	d_5
	2.8	32.3	12.9	15.4	21.5	14.4	3.5
	54.0	8.4	6.0	76.4	1.9	7.3	--
	16.7	13.4	14.3	34.1	18.5	15.0	4.6
	10.0	39.1	2.0	58.8	--	--	--
	15.8	6.5	32.3	31.7	6.7	14.0	--

*The % of d_n was calcd based on intensities of the molecular ion peaks after corrections for isotopic abundance and fragmentation of M-1, M-2 peaks and normalized over a range of scans.

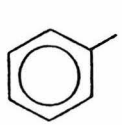
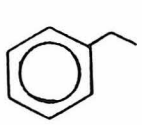
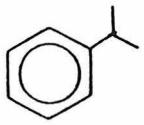
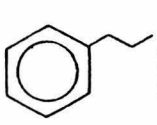
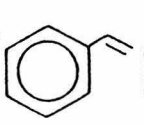
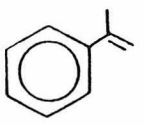
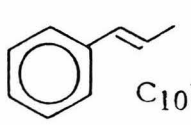
Scheme III


Cp2Ti
D
D
-φCHCD2
-φCHCH2
[Cp2Ti=CH2]
[Cp2Ti=CD2]
φCHCH2
φCHCD2
φCHCH2
φCHCD2
Cp2Ti
HCl
HCl
HCl
HCl
d0
d2
d2
d4

be 1.6 : (1.6+1) : 1 or 1.6 : 2.6: 1. However, under our reaction condition with no added styrene, both the olefin-d_0/d_2 and carbene-d_0/d_2 concentrations are controlled by the isotope effect (1.6). The predicted kinetic ratio from a statistical olefin exchange is therefore 1.6: $(1^2+1.6^2)$: 1.6 or 1:2.2:1. Since multiple olefin exchanges are possible, neither of these situations can apply directly. The presence of odd-numbered deuterium atoms in the n-propyl benzenes is rationalized in terms of reactions involving titanium hydrides or deuterides that are generated from the decomposition of **1**. Decomposition[16] is evident from the presence of significant amounts of ethyl benzene, styrene, and β-methyl styrene that show deuterium scrambling as well (Table III).

In contrast to the rearrangement of platinacyclobutanes where a concerted mechanism is suggested, titanacyclobutane isomerizations proceed through a metal-cabene intermediate. This result provides an important step for olefin metathesis in the form of olefin exchange reaction. If the α-isomer could then ring-open to give a substituted metal alkylidene[17] such as $Cp_2Ti{=}CH\phi$, a complete metathesis system would then be generated.

Table III

Thermodecomposition Products								$C_{10}H_{12}$*
$\xrightarrow[30\ min]{80^oC}$	1.5	15.7	17.6	7.5	--	48.3	6.2	3.2
solid state								
$\xrightarrow[2.5\ h]{52^oC}$	--	12.4	5.0	43.0	17.3	1.2	21.0	--
solid state								
$\xrightarrow[1\ h]{40^oC}$ benzene	3.8	31.5	2.5	32.8	1.1	1.4	25.3	--
solution								

*By GC-MS.

B. An Alternate Path to Reductive Elimination for Group IVB Metals: Mechanism of Cyclopropane Formation from Titanacyclobutane

Introduction

Reductive elimination of alkanes from dialkyl transition metal complexes is a key step in numerous catalytic and stoichiometric reactions. The formation of carbon-carbon bonds by reductive elimination is potentially an important reaction for metal-mediated synthesis of complex organic molecules. In many cases, this reaction is accelerated by prior oxidation of the metal complexes.[18,19] The few well-documented mechanistic studies of reductive elimination reactions address mainly middle and late-transition metals, such as d^6 complexes of Mn(I), Fe(I), and Co(III) and d^8 complexes of Ni(II), Pd(II), Pt(II), and Au(III), that have accessible higher oxidation states.[19,20] We now report a clean example of alkane elimination from an early transition metal dialkyl, a d^0 Ti(IV) complex, and describe the stereochemistry of formation and reaction of an observed intermediate. The results of this work have appeared.[21]

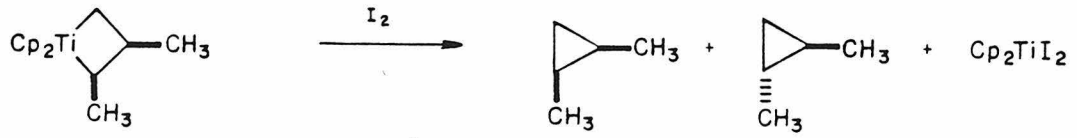
Results and Discussion

Reactions of iodine with readily available titanacyclobutanes produce cyclopropanes cleanly and in good yield (eq. 6).[9,22] Initial stereochemical studies of these iodinations were puzzling. cis-2,3-Dimethyltitanacyclobutane (3) gave mostly retention, favoring the less stable dimethylcyclopropane(9:1 cis/trans).[23] In contrast, trans-2-deutero-3-

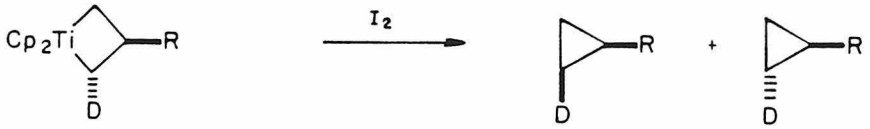
(6)

Cp ≡ η^5-C_5H_5, R ≡ alkyl

phenyltitanacyclobutane (trans-2-d_1-1),[13] which was expected to show even greater stereospecificity, gave an essentially nonstereospecific mixture of deuterated phenylcyclopropanes (7) under similar conditions (eqs. 7, 8).[24] The lack of stereospecificity of 7 was shown by integration of the 500 MHz ^{1}H NMR spectrum. The ratio of hydrogens trans to phenyl (δ 0.69) to hydrogens cis to phenyl (δ 0.52) was 1.1:1.0.[8]



3 9 : 1 (7)



(8)

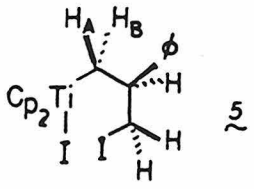
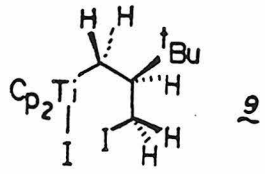
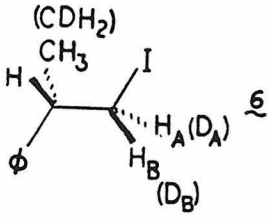
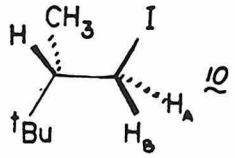
trans-2-d-1 R = ϕ

trans-2-d-8 R = ^{t}Bu

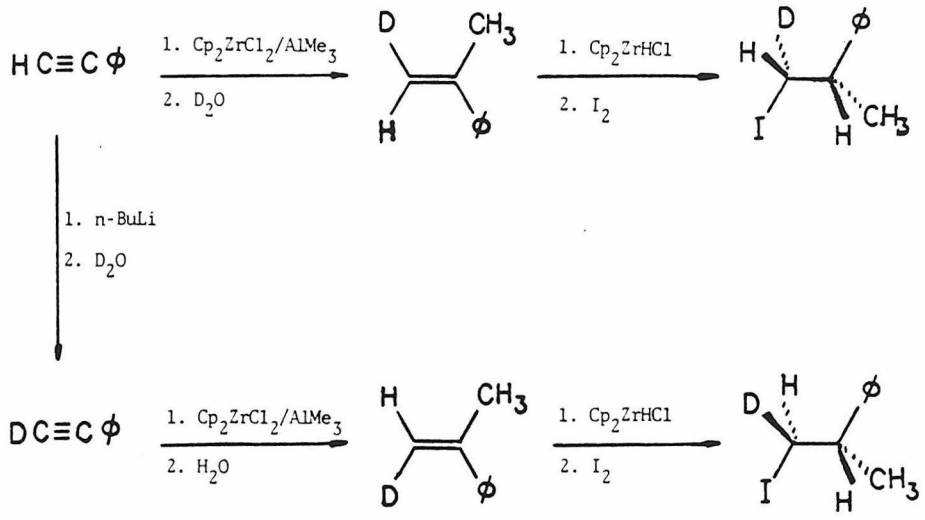
1 : 1

To resolve this apparent contradiction, a methylene chloride solution of trans-2-d_1-1 was treated with one equivalent of I_2 at -50°C. An intermediate was observed which upon warming formed a mixture of deuterated phenylcyclopropanes. The thermal instability of intermediate (5-d) precluded its isolation and necessitated spectroscopic and chemical characterizations. The ^1H NMR spectrum of intermediate 5 generated in situ at -70°C shows two singlets for the cyclopentadienyl protons (δ 5.91, 5.70) and two sets of doublets of doublets for the diastereotopic Ti-CH_2 protons at δ 1.28 and 0.31 with characteristic coupling constants. ^1H NMR spectrum of intermediate 9 is also assigned (Table IV). A similar intermediate has been postulated in reaction of Cp_2ZrHCl with allylic chlorides to give cyclopropanes.[25] Treatment of a solution of 5-d with gaseous HCl at -78°C produced a 1:1 mixture of 1-d-6 and 3-d-6. By comparison with the ^2H NMR spectra of two authentic threo and erythro-1-d-6 diastereomers prepared independently (Scheme IV),[26] 1-d-6 was shown to be exclusively the threo isomer (Scheme V). Similar results were obtained from hydrolysis of 9-d. 1-d-10 was assigned as the threo isomer base on coupling constants and deuterium chemical shift (δ 3.21) (Table IV). These results demonstrate (a) that there is no isotope effect in cleavage of 1 (or 8) to the diiodide 5 (or 9) and (b) that this Ti-C bond cleavage proceeds with retention of stereochemistry. Bromination of zirconocene alkyl chlorides, the only other stereochemical study of metal-carbon bond cleavage in a d^0 complex also proceeds with retention at the carbon center.[13] An oxidative reaction pathway is excluded for our

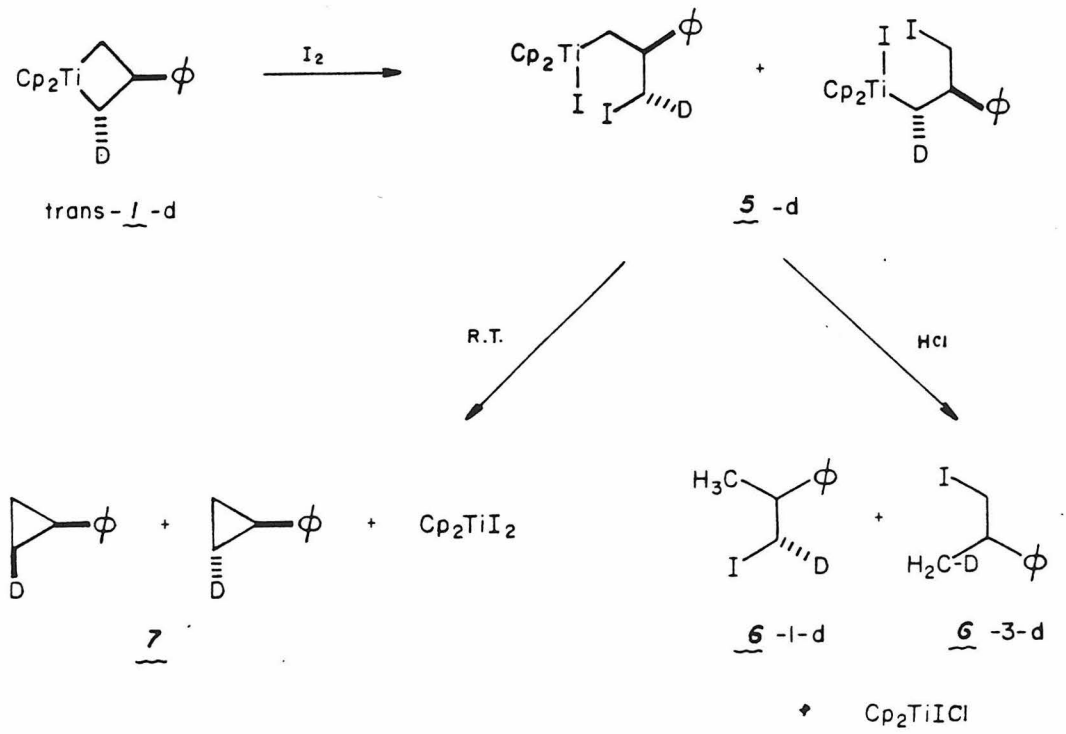
Table IV.

Compounds	Solvent Temp	^{1}H Chemical Shift	Assignment
 5	C_7D_8 -20°C	6.75-7.10 (m, 5H)	phenyl
		5.91 (s, 5H)	Cp
		5.70 (s, 5H)	Cp
		2.65-3.10 (m, 2h)	CH_2I and $CH\phi$
		1.28 (dd, J=10, 2.0 Hz, 1H)	H_A
		0.31 (dd, J=10, 7.5 Hz, 1H)	H_B
 9	C_7D_8 -20°C	5.96 (s, 5H)	Cp
		5.89 (s, 5H)	Cp
		3.09 (dd, J=4.0, 10 Hz, 1H)	CH_2I
		2.85 (dd, J=4.0, 10 Hz, 1H)	
		2.08 (d, J=10 Hz, 1H)	$TiCH_2$
		1.87 (d, J=10 Hz, 1H)	
		0.79 (s, 9H)	
		methine proton not located	
 6	C_6D_6 RT	6.70-7.10 (m, 5H)	ϕ
		2.53-3.10 (m, 3H)	CH_2, CH
		1.07 (d, J=6.3 Hz, 3H)	CH_3
	C_6H_6 RT	^{2}H δ 2.94 D_A	(erythro isomer)
		2.82 D_B	(threo isomer)
		1.05	CH_2D
 10	C_6D_6 RT	3.24 (dd, J=2.0, 9.3 Hz, 1H)	H_B
		2.47 (dd, J=11, 9.3 Hz, 1H)	H_A
		0.91 (d, J=6.3 Hz, 3H)	CH_3
		0.58 (s, 9H)	t-Bu

Scheme IV



Scheme V

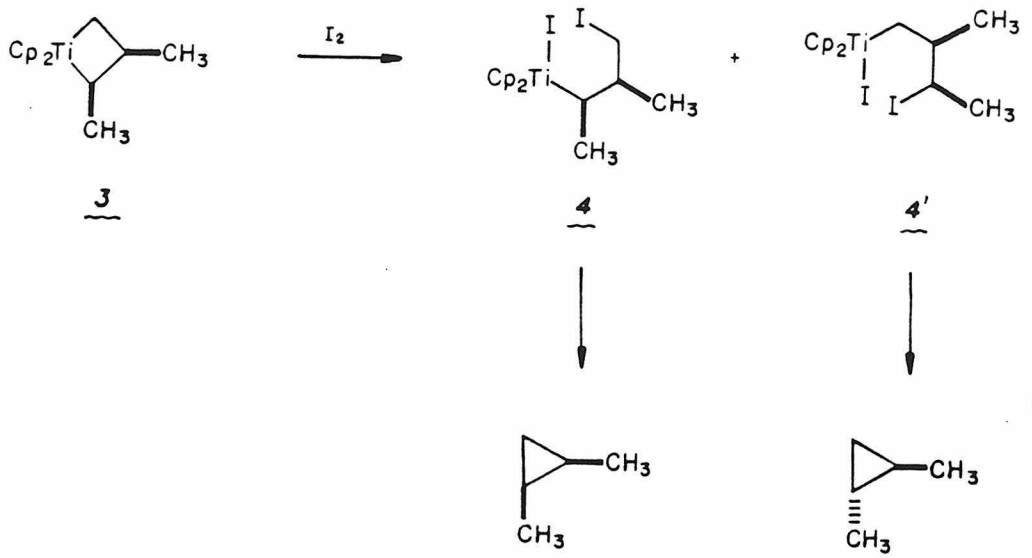


iodination reactions due to the inaccessibility to higher oxidation states of Ti(IV). The electron deficient (16 e⁻) metal favors a four-centered close transition state and results in the front side attack at the carbon to give retention of stereochemistry.

Formation of a 1:1 mixture of cyclopropane isomers from intermediates 5-d, suggests two possible reaction pathways: (a) complete scrambling occurs at both the α and γ-carbon of 5 before extrusion of cyclopropane; (b) the reaction of 5 proceeds with retention at the α-carbon and inversion at the γ-carbon (or vice versa). Scrambling at only one carbon center would give diastereomeric cyclopropanes in a 3:1 ratio. We have ruled out scrambling of the products from the control experiment which shows no epimerization of trans-(2-deutero-1-methylcyclopropyl)benzene (12) under the iodination reaction conditions. To test for racemization at the γ-carbon of 5, a solution of 5-d was allowed to react on warming to < 50% completion, then quenched with anhydrous HCl. The 1-d-6 recovered from the reaction was shown by ^2H NMR analysis to have retained the threo stereochemistry.

Since the second Ti-C bond cleavage appears to proceed without prior scrambling of the γ-carbon, (b) is the most likely mechanism of formation of cyclopropane from 5-d and 9-d. Mechanism (b) is also consistent with our initial observation in the cis-2,3-dimethyltitanacyclobutane (3) system. Here, it is likely that intermediate 4 is favored over 4' due to preferential attack of iodine on the less hindered Ti-C bond. Formation of cyclopropane from 4 by an intramolecular S_Ni process, with retention at α- and inversion at

Scheme VI



to the ease of nucleophilic displacement at primary halides, and **4'** would be preferentially scavenged by iodine to give $C_5H_{10}I_2$ products.[27]

We have shown that elimination of cyclopropane from reaction of titanacyclobutane and iodine occurs with sequential, stereospecific Ti-C bond cleavages.[28] This process provides an alternate path to simple oxidation and reductive elimination, a sequence which is highly unfavorable in these d^0 metal complexes.

Experimental Section

$AlMe_3$ was purchased as a 2 M solution in toluene from Aldrich. Zirconocene dichloride was purchased from Boulder Scientific. $LiAlD_4$ was purchased from Merck, Sharp and Dohme. $Li(O\text{-}\underline{t}\text{-}Bu)_3AlH$ was purchased from Aldrich. Cp_2ZrHCl and Cp_2ZrDCl were prepared by literature methods.[29] Phenylacetylene was purchased from Aldrich. $\underline{t}$-Butylacetylene was purchased from Farchan. Phenylacetylene-d_1 was prepared by deprotonation of phenylacetylene with $\underline{n}$-BuLi followed by deuterolysis with D_2O. All acetylenes were distilled before use. Styrene-d_1 and 3,3-dimethylbutene-d_1 were prepared by hydrozirconation reactions of appropriate acetylenes followed by hydrolysis (H_2O) or deuterolysis (D_2O).[13] $Cp_2TiCH_2AlMe_2Cl$, $Cp_2TiCH_2CMe_2CH_2$, and $Cp_2TiCH_2CH(\underline{t}\text{-}Bu)CH_2$ were prepared by known methods.[3,9] Deuterium labeled titanacyclobutanes were prepared similarly using deuterated olefins.

Dichloromethane was stirred over P_2O_5 and degassed. Pentane and hexane were stirred over concentrated H_2SO_4, then sodium-benzophenone ketyl. Benzene, diethyl ether, toluene, and tetrahydrofuran were stirred over CaH_2 then sodium-benzophenone ketyl. Solvents thus dried and deoxygenated were vacuum transferred into flasks sealed with teflon screw valves and stored under argon. Benzene-d_6 and toluene-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 line and dry box techniques. 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), a JEOL FX-90Q (89.60 MHz ^1H, 13.76 MHz ^2H) or a Brucker WM-500 (500.13 MHz ^1H, 76.76 MHz ^2H). Gas chromatographic analysis was performed on a Varian 1400 flame ionization instrument equipped with a Spectra-Physics System I computing integrator using 5' 19% FFAP for aromatic hydrocarbons and 5' 5% SE-30 on chrom W for alkyl iodides.

Preparation of 1-Deutero-ethynlbenzene. To 5 mL (45 mmol) of freshly distilled ethynlbenzene in 5 mL of hexane was added dropwise 40 mL of 1.6 M n-butyllithium in hexane at 0°C. The reaction mixture was warmed to room temperature and continued to stir for 10 min then quenched with 3 mL of D_2O. White solids precipitated and were filtered and washed with ether. The combined ether solution was dried ($MgSO_4$) and vacuum distilled to yield 3.7 g (80%) of product. ^1H NMR showed >95% deuterium incorporation.

Preparation of styrene-1-d. This is a general procedure for cis- and trans-styrene-1-d and styrene-2-d. Slight excess of Cp_2ZrHCl (or Cp_2ZrDCl) and ethynlbenzene (d_0 or d_1) were stirred in benzene until all solids were dissolved. All volatiles were removed under vacuum. The residue was taken up in ether and quenched with D_2O (or H_2O). The white precipitates were removed by filtration and washed with ether. The combined ether solution was dried ($MgSO_4$) then vacuum distilled. The yields are typically 70%.

Preparation of 3-Phenyltitanacyclobutane (1). A) From Tebbe Reagent. A homogeneous mixture of 1.5 g (5.3 mmol) "Tebbe" regent, two-fold excess of styrene and 0.7 g (5.8 mmol) DMAP in 10 mL of toluene was

stirred at -10°C for 1 h. Orange solids precipitated and were collected by filtration and washed with cold toluene and pentane. Recrystallization from THF-pentane with slow cooling to -50°C afford product in long needles in 35% yield: ^{1}H NMR (90 MHz, C_6D_6) δ6.99-7.40(m,5H),5.52(s,5H),5.40(s, 5H), 2.84 (dd, J = 10.8, 8.6 Hz, 2H), 2.39 (dd, J = 8.6 Hz, 8.6 Hz, 2H), 0.33 (m, 1H).

B) From 3,3-Dimethyltitanacyclobutane. A solution of 0.14 g (0.57 mmol) of titanacyclobutane, 0.15 mL (1.3 mmol) of styrene in 1 mL of toluene was stirred at 0°C 2 h, concentrated to half of its original volume, and diluted with 10 mL of pentane. After stirring for 20 min the solids were collected by filtration, washed with pentane and dried under vacuum.

Preparation of 2-Phenyltitanacyclobutane (2). A) From Tebbe Reagent. After separating the 3-phenyltitanacyclobutane from the reaction mixture, the filtrate was concentrated and extracted with n-hexane. The hexane extract was concentrated to give a dark red solid.

B) From 3,3-Dimethyltitanacyclobutane. The filtrate was concentrated under vacuum. The residual solids were recrystallized from toluene-pentane. ^{1}H NMR (90 MHz, C_6D_6) δ 6.71-7.35 (m, 5H), 5.31 (s, 5H), 5.08 (s, 5H), 4.74 (t, J = 9 Hz, 1H), 3.12 (m, 2H), 0.42 (m, 2H).

Isomerization of 3-Phenyltitanacyclobutane (1). A) ^{2}H NMR Analysis. In a typical reaction, the deuterium labeled 3-phenyltitanacyclobutane was loaded in a NMR sample tube. Protio toluene (0.4 mL) was added via syringe. In some cases, large excess of olefin was also added via syringe. The progress

of the reaction was monitored by ^2H NMR. A summary of the results are presented in Table I.

B) GC/MS Analysis. A solution of 20 mg 2,2-d_2-**1** in 1 mL benzene was stirred at room temperature for 1 h. All volatile components were removed under vacuum. The residue was redissolved in 1 mL of benzene, then hydrolyzed with anhydrous HCl. The volatile products were vacuum distilled and analyzed by GC/MS. Results are presented in Table II.

Thermolysis of 1 and 2. Solid state decomposition: recrystallized titanacyclobutane **1** or **2** was heated under vacuum at 80°C for 30 min during which time the red solids turned black. Volatile products were vacuum distilled and dissolved in benzene. n-Butylbenzene was added to the benzene solution as internal standard for quantitative GC analysis. Solution decomposition: a benzene solution of **1** was heated at 40°C for 1 h. Solvent and all volatile products were vacuum distilled and analyzed by GC.

Iodination reactions of 3-Phenyltitanacyclobutane (1). A). To a solution of 64 mg (0.22 mmol) of **1** in 3 mL of CH_2Cl_2 was added 0.6 mL of 0.39 M solution of iodine in CH_2Cl_2 (0.23 mmol) at -20°C. Reaction mixture was warmed to room temperature and continue to stirred for 1 h. The reaction mixture was washed with aqueous $Na_2S_2O_3$, dried over $MgSO_4$. Solvent was removed on rotovap. The residue was extracted with pentane. Concentration of the pentane solution under vacuum yield cyclopropylbenzene in 60%.

B) Formation of Titanocene 3-Iodo-2-phenylpropyl Iodide (5). Compound **1** (12 mg) was loaded in a NMR sample tube fitted with a septum.

Toluene-d_8 (0.4 mL) was added via syringe. A solution of iodine (10 mg, 1 equiv) in 0.2 mL toluene-d_8 was added to the NMR tube in thirds at -20°C. An intermediate was observed by ^1H NMR: δ5.83(s,5H),5.62(s,5H),3.10-2.70 (m, 2H), 1.28 (dd, J = 10, 2 Hz, 1H), 0.31 (dd, J = 10, 7.5 Hz, 1H), 0.6 (m, 1H).

C) Formation of 1-Iodo-2-iodomethyl-2-phenylpropane (14). Two equivalents of iodine in CH_2Cl_2 were added to the red solution of **1** at room temperature. Solvent was removed from the black reaction mixture on rotovap and the black residue was extracted three times with pentane. The combined pentane solution was filtered through charcoal then was evaporated under vacuum to yield a yellow liquid. ^1H NMR (90 MHz, C_6D_6) δ 6.63-7.10 (m, 5H), 2.50-3.20 (m, 5H).

Iodination Reaction of 3-t-Butyltitanacyclobutane (8). **A)** Same procedure for **1** was used to give t-butyl cyclopropane. ^1H NMR (C_7D_8) δ 0.83 (s, 9H), 0.1-0.3 (m, 4H), the methine proton is buried under the t-butyl proton resonances.

B) Formation of Titanocene 2-Iodomethyl-3,3-dimethylbutyl Iodide (9). Same procedure as **5**. The intermediate observed at -20°C has an ^1H NMR spectrum (C_7D_8, 90 MHz) δ 5.96 (s, 5H), 5.89 (s, 5H), 3.01 (dd, J = 10, 4 Hz, 1H), 2.85 (dd, J = 10, 4Hz, 1H), 2.08 (d, J = 10 Hz, 1H), 1.87 (d, J = 10 Hz, 1H), 0.79 (s, 9H), methine proton is not located.

C) Formation of 1-Iodo-2-iodomethyl-3,3-dimethyl Butane (15). Same procedure as formation of **14** from **1**. ^1H NMR (C_6D_6, 90 MHz) δ 3.21 (dd, J = 10, 4 Hz, 2H), 2.88 (dd, J = 10, 7 Hz, 2H), 0.58 (s, 9H), methine

proton was not located.

Hydrolysis of Titanocene 3-Iodo-1-phenylpropyl Iodide (5). One equiv. of iodide dissolved in CH_2Cl_2 was added slowly to **1** in CH_2Cl_2 at -20°C. Excess anhydrous HCl gas was added via a syringe to the reaction mixture. Solution turned from red to black. Dichloromethane was removed on rotovap and the black residue was extracted with pentane three times. Pentane was removed under vacuum to yield **6** as a yellow liquid which turned pink on standing. GC analysis showed >95% purity. ^1H NMR (90 MHz, C_6D_6) δ 6.74-7.12 (m, 5H), 2.49-3.01 (m, 3H), 1.09 (d, J_{HH} = 6.8 Hz, 3H); ^2H NMR (77 MHz, C_6D_6) δ 1.05 (CH_2D), 2.82 (CHD). The black residue showed an ^1H NMR spectrum (90 MHz, $CDCl_3$) δ 6.58 (s), 6.70 (s), 6.83 (s) in 1:2:1 ratio corresponding to Cp_2TiI_2, Cp_2TiICl, and Cp_2TiCl_2.

Hydrolysis of Titanocene 2-(Iodomethyl)-3,3-dimethyl-butyl Iodide 7. Employing the same procedure as the hydrolysis of **5** yielded 1-iodo-2,3,3-trimethyl butane **10.** ^1H NMR (C_6D_6, 90 MHz) δ 3.24 (dd, J = 9.3, 2.0 Hz, 1H), 2.47 (dd, J = 9.3, 11 Hz, 1H), 1.36 (m, 1H), 0.91 (d, J = 6.8 Hz, 3H), 0.58 (s, 9H).

Preparation of Cis- and Trans-2-methylstyrene-1-d. A solution of Cp_2ZrCl_2 (4.09 g, 13.7 mmol), 1.50 mL (13.6 mmol) of ethynlbenzene (d_0 or d_1) and 14.0 mL of 2 M $Al(CH_3)_3$-toluene (28.0 mmol) in 20 mL of CH_2Cl_2 was stirred at room temperature for 15 h. All volatiles were removed under vacuum. The residue was dissolved in 15 mL of ether and 1.5 mL of D_2O (or H_2O) was added dropwise. The white precipitates were removed by filtration and washed with ether. The combined ether solution was dried ($MgSO_4$) then vacuum distilled to yield the product in 70%.

Preparation of Threo- and Erythro-1-iodo-2-phenylpropane-1-d (1-d-6). A suspension of Cp_2ZrHCl (0.4 g, 1.5 mmol) and 0.15 mL of d_1-α-methylstyrene (cis or trans) in 4 mL benzene was stirred at room temperature for 4 h. The reaction mixture was filtered. To the filtrate was added a solution of 0.29 g (1.16 mmol) of iodine in 4 mL of benzene at 10°C. The residue remaining after evaporation of the benzene was extracted with pentane (3 x 5 mL). The combined pentane fractions were filtered through charcoal and concentrated to a colorless liquid which turned pink upon standing. ^2H NMR (77 MHz, C_6D_6) δ 2.97 (erythro isomer), 2.82 (threo isomer).

Preparation of Trans-(2-deutero-1-methylcyclopropyl)benzene (12). Cis-2-methylstyrene-1-d (0.65 g, 5.5 mmol), 2.3 mL of $CHCl_3$, 3 mL of 50% aqueous NaOH solution and 50 mg of $\phi CH_2N(CH_2CH_3)_3Cl$ were stirred at 50°C for 4 h. The reaction was diluted with water and extracted with CH_2Cl_2. The combined organic layers were dried and solvent was removed under vacuum to yield a 1:2 mixture of starting material and trans-(2,2-dichloro-3-duetero-1-methylcyclopropyl)benzene (**13**). Column chromatography (silica gel, pet. ether) separation yielded 300 mg of **13** (27%). ^1H NMR ($CDCl_3$, 90 MHz) δ 7.32 (m, 5H), 1.90 (s, 1H), 1.67 (s, 3H). A mixture of 4.5 mL CH_3OH and 0.15 mL of H_2O and small pieces of Na (0.8 g) were added over 1 h to a solution of **13** in 5 mL of ether at 0°C. The reaction was warmed to room temperature and stirred overnight before the addition of H_2O (4 mL). The aqueous layer was separated, acidified with aqueous HCl, and extracted twice with ether. After drying over $MgSO_4$, the ether was

removed to yield 150 mg of a clear yellow liquid. Kugelrohr distillation yielded 120 mg of colorless liquid (60% yield). ^1H NMR (C_6D_6, 500 MHz) δ 7.14 (m, 5H), 1.25 (s, 3H), 0.77 (s, 2H), 0.59 (s, 1H).

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(12) E_a = 25.5 kcal/mol. First order reaction was observed for at least 2.5 half lives. Other trapping agents such as acetylenes and olefins react more rapidly. For example, cyclopentene yields the corresponding metallacyclobutane with $k = 4.4 \times 10^{-4}$ s^{-1}.

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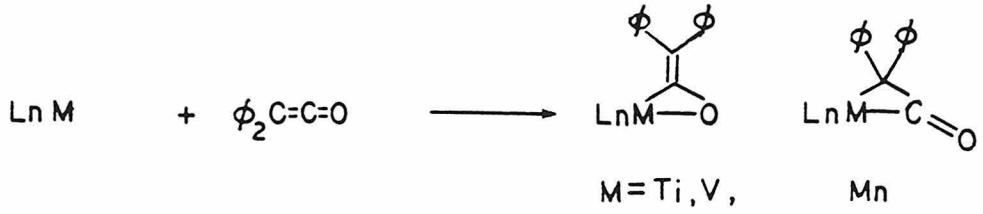
CHAPTER II

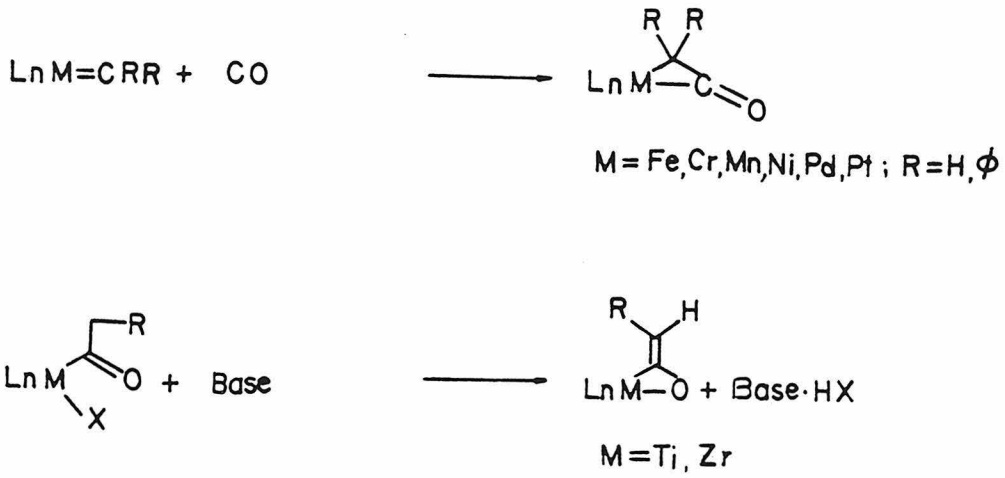
Synthesis and Reactivities of Transition Metal Homo- and Heterobinuclear Ketene Complexes

Introduction

Transition metal ketene complexes are proposed as key intermediates in the stoichiometric[1] and catalytic[2] reductions of carbon monoxide. Many stable metal ketene species have now been isolated and serve as models in the mechanistic investigations of CO hydrogenations. Recent studies have also demonstrated the potentials of using ketene complexes in the syntheses of large organic molecules.[3]

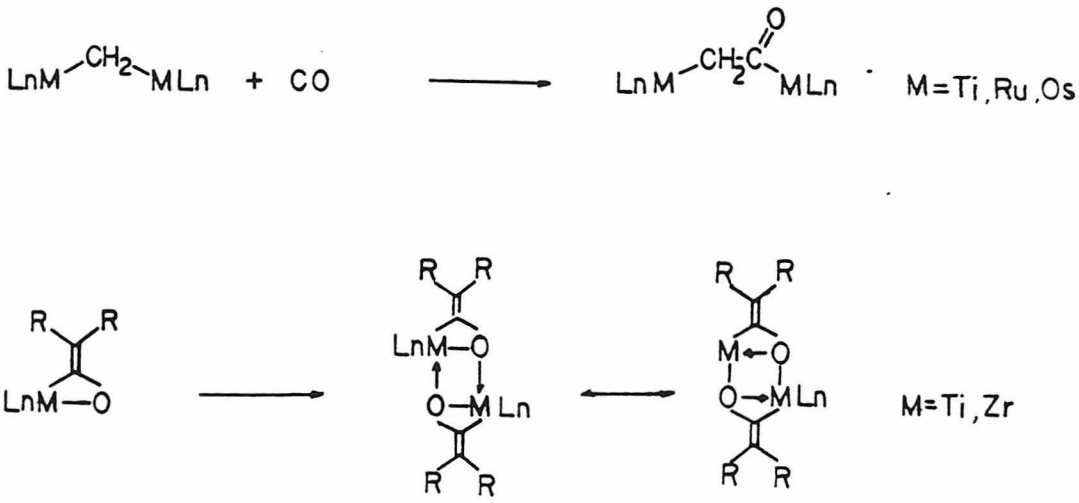
Mononuclear ketene complexes are generally obtained by one of the following methods. Direct reactions of stabilized diphenyl ketene with coordinatively unsaturated metals have been employed in the synthesis of $CpTi(CO)_2(\eta^2\text{-}OCC\phi_2\text{-}O,C)$,[4] $Cp_2V(\eta^2\text{-}OCC\phi_2\text{-}O,C)$,[5] $Cp_2Mn(\eta^2\text{-}OCC\phi_2\text{-}O,C)$,[6] and $(P\phi_3)_2Pt(\eta^2\text{-}OCC\phi_2\text{-}C,C)$.[7] Carbonylations of metal alkylidenes also successfully generate ketene complexes of Cr,[3b] Mn,[8] Fe,[9] Ni, Pd, and Pt.[1d] Deprotonation of early transition metal acyls of Ti and Zr by strong non-nucleophilic bases is another convenient route into metal ketene systems.[10] Other novel syntheses of neutral mononuclear ketenes include carbonylation of titanacyclobutene[11] and zirconocene dialkyls.[12] Casey has observed intramoleclar coupling of cyclopentadienyl and CO ligands to form ketene in the reaction of $CpRu(CO)(NO)CH_3$ with $P(CH_3)_3$.[13]



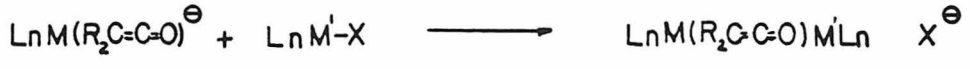


For metal catalyzed heterogeneous CO reduction (e.g., the Fischer-Tropsch process), coupling of surface bound methylene with carbon monoxide to form ketene may be relevant to the mechanism of hydrocarbon chain homologation.[14] A binuclear ketene complex is therefore a more accurate description of the intermediate which may still be bound to the metal surface. Complexes with ketene bridge have been proposed in the reactions of $(NEt_4)_2Fe_2(CO)_9$ with $CHCl_2C(O)Cl$ and the formation of $(Cp^*Co)_2(\mu\text{-}CH_2,\mu\text{-}CO)$. A few well-characterized bimetallic ketenes have so far been reported.[17-20] The preparations involve mostly reactions of bridging methylene complexes[21] with carbon monoxide. Certain dimeric ketene complexes are also under the catagory of binuclear compounds.[4,10a,12] The above synthetic procedures, however, lack of versatility

in forming hetero-bimetallic ketenes. Many mixed-metal bridging methylenes are known but their reactivities toward CO are not encouraging.[21] Dimerization of different mononuclear ketenes could result in satistical mixture of homo and hetero-bimetallic complexes.

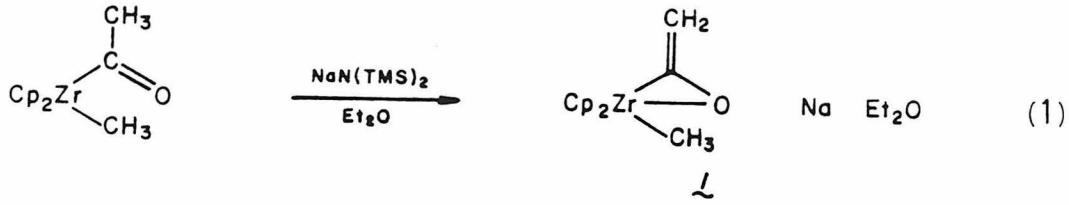


We have explored a different approach to the syntheses of bimetallic complexes using a reactive metal ketene complex to transfer the ketene fragment onto a second metal center. If successful, this method can potentially provide entries to a variety of mix-metal binuclear ketene complexes. A preliminary account of this work has appeared.[22]



Results and Discussion

The highly reactive ketene complex of choice was the zirconaenolate (ketene) anion $Cp_2Zr(\eta^2\text{-}OCCH_2\text{-}O,C)CH_3Na$ (1) prepared from reaction of $Na[N(Si(CH_3)_3)_2]$ and $Cp_2Zr(COCH_3)CH_3$ in ether at -30°C (eq. 1). The product precipitated as the etherate complex $1 \cdot Et_2O$ which ignited



(1)

spontaneously in dry air. It was also light sensitive and thermally unstable. The complex was insoluble in hydrocarbons and ether as expected for an ionic complex, but dissolved readily in THF to form $1 \cdot 2$ THF. Recrystallization by slow cooling of a pentane-THF solution of $1 \cdot Et_2O$ yielded benzene soluble crystals of $1 \cdot 2$ THF suitable for X-ray analysis. The molecular structure was solved by J. Armentrout and W. P. Schaefer. Complex $1 \cdot 2$ THF crystallizes in the space group $P\bar{1}$ with: a = 10.745(5) Å, b = 11.449(5) Å, c = 12.060(4) Å, α = 119.40(3)°, β = 91.26(4)°, γ = 114.83(4)°, v = 1123(1) Å^3, Z = 2. The molecular structure is shown in Figure 1 and the geometry of the planar $Zr(COCH_2)CH_3$ moiety is presented in Figure. 2. The location of the negative charge density of the complex is not clear from structural data. The C(1)-O and C(1)-C(2) bond lengths are typical of single and double bonds respectively. The $OCCH_2$ moiety strongly resembles that in the neutral

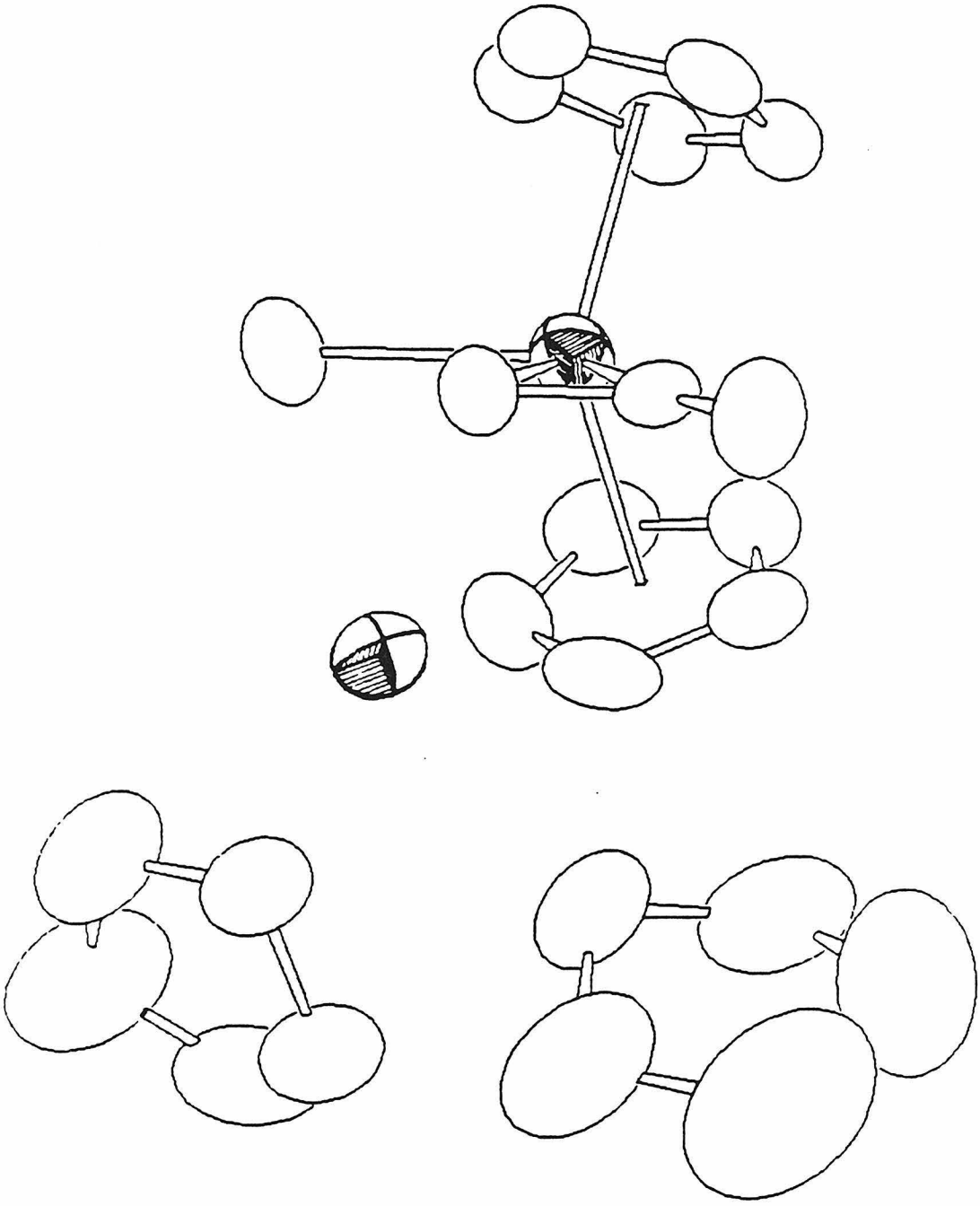


Figure 1. Molecular structure of 1·2 THF.

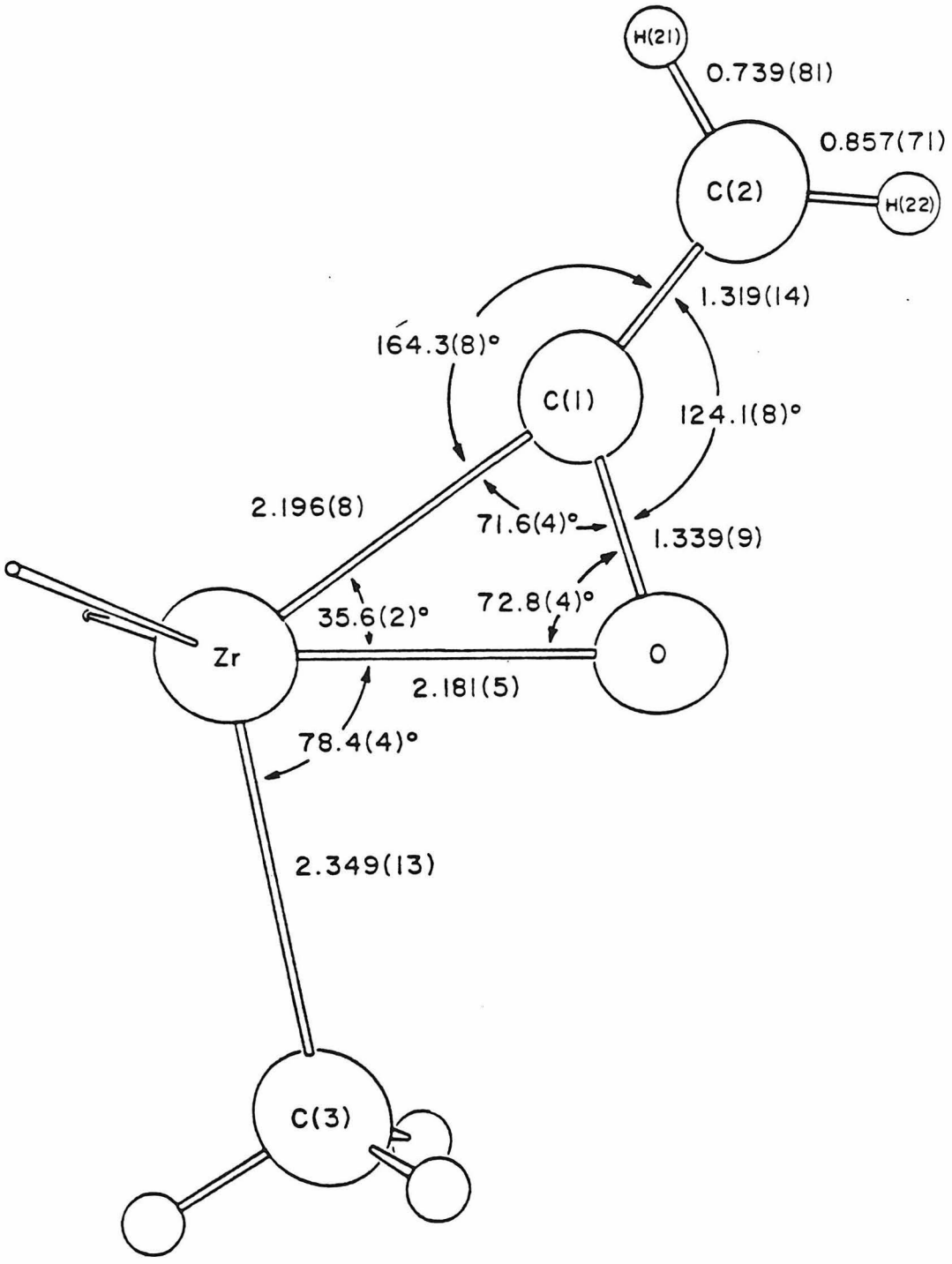


Figure 2. Molecular geometry of the equatorial ligands in 1·2 THF.

ketene complex $(\eta^5\text{-}C_5Me_5)_2Zr(\eta^2\text{-}OCCH_2\text{-}O,C)\cdot$pyridine[10b] except for the slightly shorter Zr-O bond in the latter (2.126(6) Å) which may reflect the greater donor ability of CH_3 versus pyridine ligand. The Zr-C(3) bond length is similar to the $Zr\text{-}CH_3$ distance in $Cp_2Zr(COCH_3)CH_3$ (2.336(7) Å). The counter ion Na is coordinated in a tetrahedral fashion by four oxygen atoms of the two THF solvent molecules and two ketene moieties (Table I). Complex 1·2 THF was the first structurally characterized metallaenolate anion.[24]

Table I. Coordination around Na for $Na(Cp_2Zr(COCH_2)(CH_3))\cdot 2$ THF.

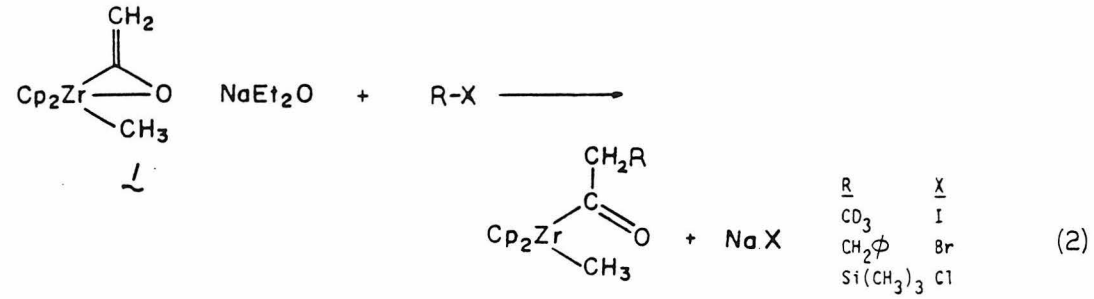
Distance		Å	
Na	O1	2.334	(6)
Na	O3	2.377	(7)
Na	O4	2.423	(9)
Na	O1'	2.311	(6)

where O1 is at X, Y, Z and O1' is at 1-X, 1-Y, 1-Z

Angles		deg	
O1	Na O3	118.8	(2)
O1	Na O4	123.6	(3)
O1	Na O1'	86.8	(2)
O3	Na O4	83.2	(3)
O3	Na O1'	97.5	(2)
O4	Na O1'	145.1	(3)

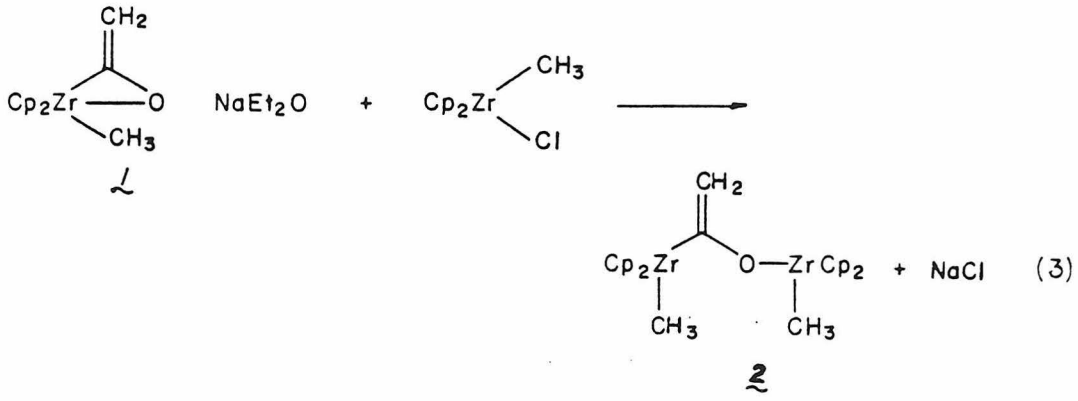
The reactivity of 1 was demonstrated by its reactions with organic halides (eq. 2). Treatment of 1 with CD_3I yielded $Cp_2Zr(COCH_2CD_3)CH_3$ quantitatively (^1H NMR). Reactions of 1 with ϕCH_2Br and $(CH_3)_3SiCl$

gave $Cp_2Zr(COCH_2CH_2\phi)CH_3$ and $Cp_2Zr(COCH_2Si(CH_3)_3)CH_3$, respectively. In all three cases, alkylations occurred at the C(2) carbon and no o-alkylation products were observed. This is especially interesting for $(CH_3)_3SiCl$ which is known to alkylate at oxygen in organic enolate reactions.[25] We attribute this to the stronger oxophilicity of zirconium versus silicon.



(2)

The reaction of 1 with transition metal halides of Ti(IV) and Zr(IV) were examined first. Cp_2MCH_3Cl (M = Ti and Zr) type complexes were chosen as substrates to minimize product isomers for ease of analysis. Treatment of 1·2 THF with Cp_2TiCH_3Cl in C_6D_6 gave a dark green solution with broad ^1H NMR signals that were uninterpretable. A mixture of $Cp_2Zr(CH_3)_2$ and $(Cp_2ZrCH_3)_2(\mu\text{-}\eta^2\text{-}OCCH_2\text{-}O,C)$ (2) was obtained from reaction of $1\cdot Et_2O$ and Cp_2ZrCH_3Cl (Et_2O/THF, -30°C) (eq. 3). Complex 2



(3)

2

was isolated in 65% yield and has been characterized by ^{1}H, ^{13}C NMR, IR and elemental analysis. Based on spectroscopic data, the structure of **2** was assigned as shown which differed from the bridging acyl type structures of Ru[18] and Os(u-η^2-OCCH$_2$-C,C)[19] complexes (Fig. 3). The ^{1}H NMR spectrum of **2** exhibited two inequivalent methylene protons with chemical shifts (4.61, 4.23 ppm) similar to a vinyl ether. The ^{13}C NMR shift of the α-carbon (208.9 ppm) also resembled that of zirconium enolates[26] (~170 ppm) rather than zirconium acyl (~300 ppm) complexes.[23a] The C-H couplings for the β-carbon (92.7 ppm) were 159 and 148 Hz, typical for sp^2 hybridized carbons.

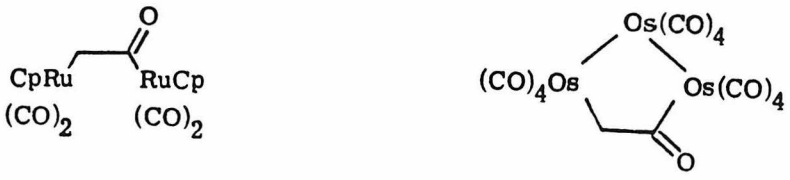
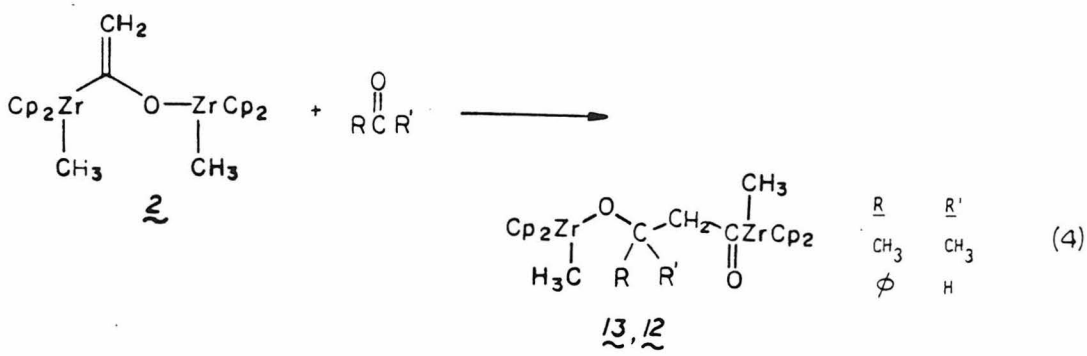


Figure 3

The metallaenolate nature of **2** was further confirmed by its reactivities toward organic carbonyls. Aldol type condensations were observed from reactions of **2** with benzaldehyde and acetone (eq. 4). Bridging acyl complexes of $(Cp_2ZrCH_3)_2(\mu\text{-}OCH\phi CH_2CO\text{-}O,C)$ (**12**) and $(Cp_2ZrCH_3)_2$-$(\mu\text{-}OC(CH_3)_2CH_2CO\text{-}O,C)$ (**13**) were formed quantitatively and have been characterized spectroscopically (Table IV). The metallaenolate

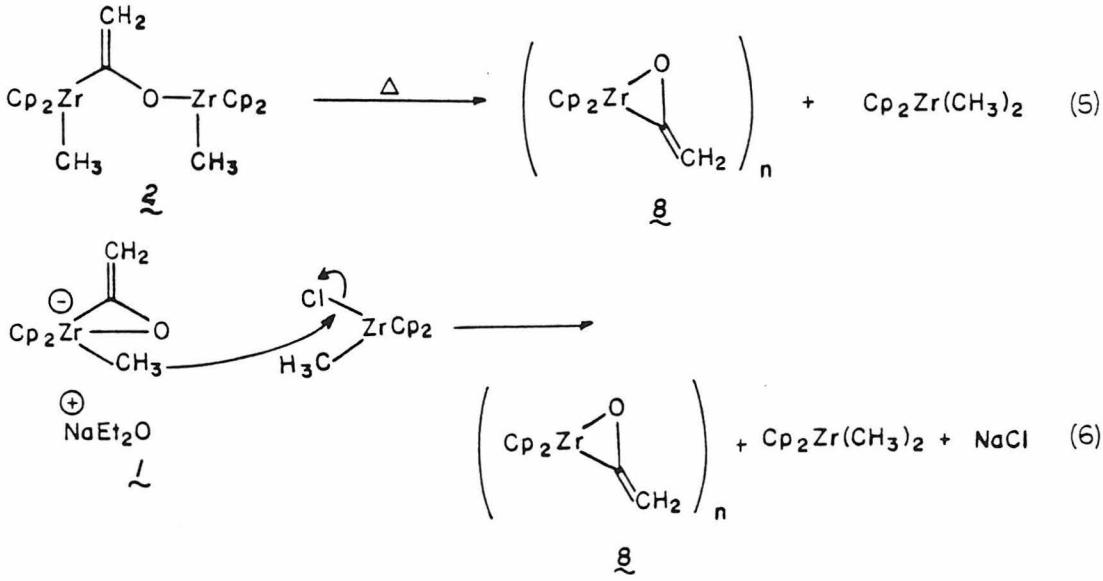


R	R'
CH_3	CH_3
ϕ	H

(4)

structure of 2 is probably a consequence of the oxophilicity of zirconium. Definite structural characterization by X-ray analysis would be desirable; however, repeated attempts to obtain X-ray quality crystals of 2 have been unsuccessful.[27]

Although 2 was stable in the solid state under an inert atmosphere, it decomposed in solution at room temperature overnight to $Cp_2Zr(CH_3)_2$ and $Cp_2Zr(\eta^2\text{-}OCCH_2\text{-}O,C)$ (8), identified by comparison to an authentic sample[28] (eq. 5). Since no decomposition was observed at -30°C, the presence of $Cp_2Zr(CH_3)_2$ in the initial product mixture was considered the result of direct methyl zirconation of 1 (eq. 6). The ^1H NMR spectrum of the



(5)

(6)

reaction of 1·2 THF and Cp_2ZrCH_3Cl at -30°C showed a mixture of 2 and $Cp_2Zr(CH_3)_2$ in a 2.5:1 ratio. Only a small amount of the byproduct $Cp_2Zr(\eta^2\text{-}OCCH_2\text{-}O,C)$ (8) is observed due to its low solubility. This second reaction pathway also accounts for the low yield of 2.

The thermal decomposition of 2 was also investigated. Kinetic data were obtained for the reaction at various concentrations and temperatures. The reaction exhibited second-order kinetics and fitted the rate law of $d[2]/dt = k_{obs}[2]^2$. The second-order plots were linear for 2.5 half lives. No significant change in rate constant was observed in the presence of added strong donor ligands such as pyridine and trimethyl phosphine (Table II). Activation parameters derived from kinetics data obtained at 46, 55, 65 and 75°C are listed in Table III. Entropy of activation was found to be 11.6 eu, low for a decomposition reaction. This is rationalized by the molecularity of the reaction which requires aggregation of two molecules of 2 or four zirconium atoms prior to decomposition in the transition state.

Reactions of 1 with other Cp_2ZrRCl (R = OCH_3, Cl, H) complexes were also studied. A similar binuclear ketene complex was obtained by treatment of 1 with Cp_2ZrOCH_3Cl (eq. 7). $(Cp_2ZrOCH_3)(\mu\text{-}\eta^2\text{-}OCCH_2\text{-}C,O)(Cp_2ZrCH_3)$ (3) was isolated in 55% yield and was fully characterized. The structure of 3 was assigned based on spectroscopic evidence. The only Zr-CH_3 signal in the ^1H NMR spectrum appeared at -0.12 ppm, which was closer to the methyl chemical shift of $Cp_2Zr(CH_3)_2$ (-0.13 ppm) than that of zirconium enolate $Cp_2Zr(OCCH_3CH_2)CH_3$ (0.32 ppm). Decomposition of 3 in C_6D_6 at room

Table II. Kinetics Data for the Decomposition of $Cp_2ZrCH_3)_2$-$(\eta^2\text{-}\mu\text{-}OCCH_2)$ 2 in C_6D_6 at 52°C.

2 t=0	L t=0	$k_{obs} \times 10^2$ M^{-1} s^{-1}
0.082 M	--	1.13 ± 0.02
0.092 M	0.093 M pyridine	1.33 ± 0.07
0.11 M	0.21 M PMe_3	1.19 ± 0.06

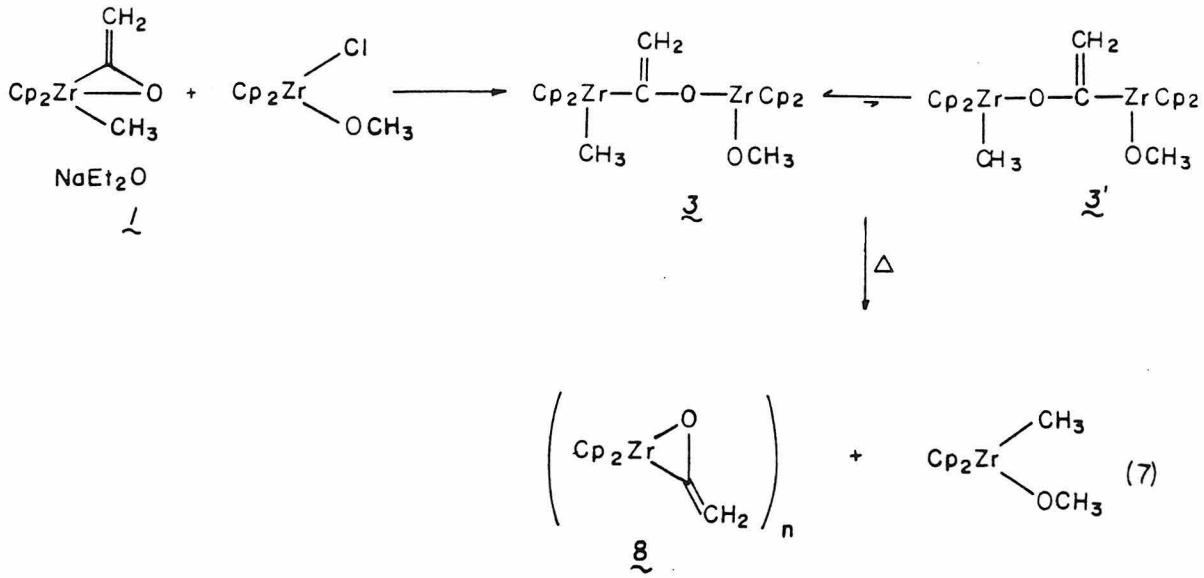
Table III. Activation parameter for the decomposition of 2 in C_6D_6.

T (°C)	$k_{obs} \times 10^2$ M^{-1} s^{-1}
46	0.363 ± 0.008
55	1.12 ± 0.02
65	4.18 ± 0.17
75	11.6 ± 0.7

$\Delta H^{\ddagger}$ = 26.0 ± 1.0 kcal/mol

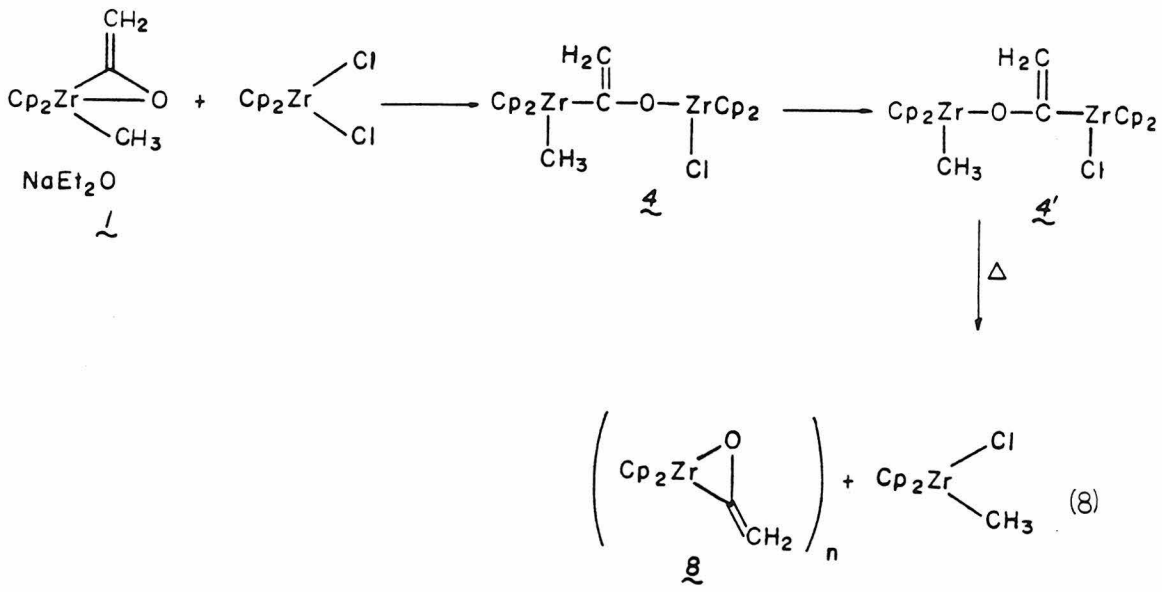
$\Delta G^{\ddagger}_{319}$ = 22.3 + 0.5 kcal/mol

$\Delta S^{\ddagger}$ = 11.6 ± 3.1 eu



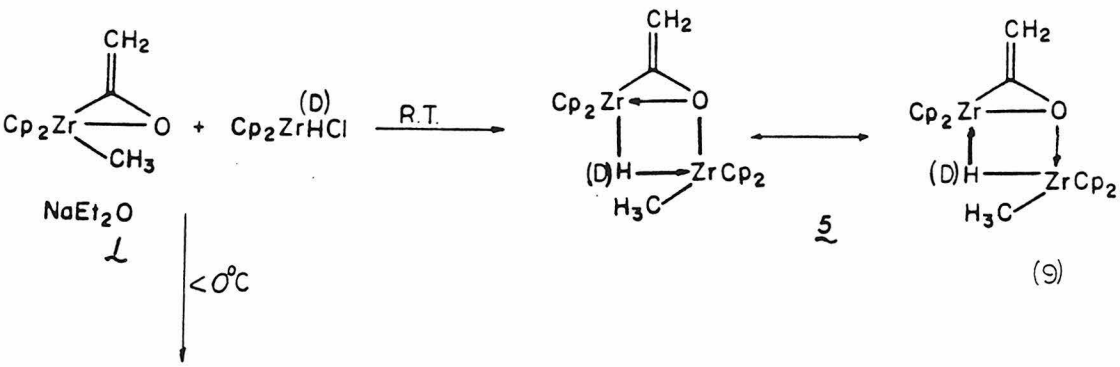
temperature as monitored by ^1H NMR revealed the presence of a transient species (**3'**) with $Zr-CH_3$ resonance at 0.29 ppm. After standing overnight at room temperature, only $Cp_2Zr(OCH_3)CH_3$ was present in solution.

Under similar reaction conditions, treatment of **1** with Cp_2ZrCl_2 yielded complex **4'** formulated as $(Cp_2ZrCH_3)(\mu\text{-}\eta^2\text{-}OCCH_2\text{-}O,C)(Cp_2ZrCl)$ from the chemical shift of the $Zr-CH_3$ signal (0.59 ppm). However, complex **4'** was not the initial product formed in the reaction. The ^1H NMR signals that appeared upon mixing of **1** and Cp_2ZrCl_2 at -20°C in toluene-d_8 differed from those of **4'**. The $Zr-CH_3$ shift (0.13 ppm) suggested a structure such as **4**. Complex **4** isomerized cleanly to **4'** in 3 h at -20°C. Compound **4'** was not isolated in pure form as it darkened even in the solid state at room temperature to give Cp_2ZrCH_3Cl and $Cp_2Zr(\eta^2\text{-}OCCH_2\text{-}O,C)$ (^1H NMR) (eq. 8).



Reaction of 1 with Cp_2ZrHCl afforded some unusual results. Two completely dissimilar products were isolated under different reaction conditions. The hydride analog, $(Cp_2ZrCH_3)(\mu\text{-}\eta^2\text{-}OCCH_2\text{-}O,C)(Cp_2ZrH)$ (5) was obtained by treatment of 1 with Cp_2ZrHCl in toluene at room temperature (eq. 9). The ^1H NMR spectrum of 5 resembled the bridging ketene complexes described previously with the exception that the Zr-CH_3 signal (0.56 ppm) appeared as a doublet with H-H coupling of 1 Hz, and the hydride resonance appeared as a broad singlet (0.19 ppm). The assignments were confirmed using Cp_2ZrDCl in the reaction. The Zr-CH_3 chemical shift suggested that the oxygen atom was attached to the same zirconium as the methyl group. The hydride and methyl couplings were also indicative of a strong interaction between Zr-H and Zr-CH_3 moieties. This type of coupling

has previously been observed in a similar system where a hydride ligand was crystallographically located to occupy a bridging position.[31d] Complex **5** reacted readily with CH_3I to yield CH_4 and (Cp_2ZrCH_3)-$(\mu$-η^2-$OCCH_2$-$O,C)(Cp_2ZrI)$ (6).



When **1** and Cp_2ZrHCl were allowed to react in THF-ether at -40°C, an unexpected product **7** was isolated (eq. 10). From ^1H and ^{13}C NMR data, **7** was formulated as the oxo complex $(Cp_2ZrCH_3)(Cp_2ZrCHCH_2)O$. Substituting Cp_2ZrDCl for Cp_2ZrHCl in the reaction incorporated deuterium in the α-position of the Zr-vinyl group. Hydrolysis of **7** with anhydrous HCl gas yielded CH_4, C_2H_4, and $(Cp_2ZrCl)_2O$. Complex **7** is the only example in all of our investigations where a C-O bond cleavage is observed. This reaction can serve as an excellent model for the final step in CO reduction

Table IV. NMR[a] and IR[b] Spectroscopic Data.

Compound	IR	NMR (Chemical Shift, Multiplicity, Coupling Constants in Hz) ^1H	NMR (Chemical Shift, Multiplicity, Coupling Constants in Hz) ^{13}C	Assignment
$Cp_2Zr(\eta^2\text{-}OCCH_2\text{-}O,C)CH_3Na\cdot Et_2O$[c]		δ 5.43 s		Cp
		4.55 d J = ?		CH_2
1·Et_2O		3.64 d J = ?		CH_2
		-0.68 s		$ZrCH_3$
$Cp_2Zr(\eta^2\text{-}OCCH_2\text{-}O,C)CH_3Na\cdot 2THF$		δ 5.70 s		Cp
		5.18 s		CH_2
1·2THF		4.37 s		CH_2
		-0.23 s		$ZrCH_3$
$(Cp_2ZrCH_3)_2(\mu\text{-}\eta^2\text{-}OCCH_2\text{-}O,C)$	1594 ($\nu_{C=C}$)		δ 208.9 dd J = 10	C
	1538 ($\nu_{C=C}$)	5.82 s	113.1 dm J = 172, 7	Cp
2		5.65 s	107.1 dm J = 172, 7	Cp
		4.61 s	92.7 dd J = 159, 148	CH_2
		4.23 s		CH_2
		0.43 s	33.0 q J = 119	$ZrCH_3$
		-0.17 s	18.8 q J = 117	$ZrCH_3$

Table IV. Continued.

Compound	IR	NMR (Chemical Shift, Multiplicity, Coupling Constants in Hz) ^1H	NMR (Chemical Shift, Multiplicity, Coupling Constants in Hz) ^{13}C	Assignment
$(Cp_2ZrOCH_3)(\mu\text{-}\eta^2\text{-}OCCH_2\text{-}O,C)(Cp_2ZrCH_3)$				
3	1592 $\nu_{C=C}$)		δ 206.4 dd J = 9	C
	1536 $\nu_{C=C}$)	δ 5.93 s	112.4 dm J = 172, 7	Cp
		5.68 s	106.6 dm J = 172, 7	Cp
		4.79 s	90.9 dd J = 146, 160	CH_2
		4.53 s		CH_2
		3.85 s	63.6 q J = 141	OCH_3
		-0.12 s	17.5 q J = 117	$ZrCH_3$
$(Cp_2ZrCH_3)(\mu\text{-}\eta^2\text{-}OCCH_2\text{-}O,C)(Cp_2ZrOCH_3)$		δ 5.87 s		Cp
3'		5.84 s		Cp
		4.86 s		CH_2
		4.18 s		CH_2
		3.40 s		OCH_3
		0.29 s		$ZrCH_3$
$(Cp_2ZrCl)(\mu\text{-}\eta^2\text{-}OCCH_2\text{-}O,C)(Cp_2ZrCH_3)$[d]		δ 6.01 s		Cp
4		5.84 s		Cp
		4.36 s		CH_2
		3.87 s		CH_2
		0.13 s		$ZrCH_3$

Table IV. Continued.

Compound	IR	NMR (Chemical Shift, Multiplicity, Coupling Constants in Hz) ^1H	^{13}C	Assignment
$(Cp_2ZrCH_3)(\mu\text{-}\eta^2\text{-}OCCH_2\text{-}O,C)(Cp_2ZrCl)$			δ 219.0	C
		δ 5.92 s	112.3	Cp
4'		5.77 s	109.5	Cp
		4.92 d J = 1	90.8	CH_2
		4.33 d J = 1		
		0.59	36.4	$ZrCH_3$
$(Cp_2ZrCH_3)(\mu\text{-}\eta^2\text{-}OCCH_2\text{-}O,C)(Cp_2ZrH)$			δ 191.8	C
5	1603 ($\nu_{C=C}$)	δ 5.60 s	109.7	Cp
	1540 ($\nu_{C=C}$)	5.50 s	104.3	Cp
		5.40 s	88.2	CH_2
		4.72 s		CH_2
		0.56 d J = 1	21.7	$ZrCH_3$
		0.19 broad s		ZrH
$(Cp_2ZrCH_3)(\mu\text{-}\eta^2\text{-}OCCH_2\text{-}O,C)(Cp_2ZrI)$				
6	1602 ($\nu_{C=C}$)	δ 5.93 s		Cp
	1555 ($\nu_{C=C}$)	5.76 s		Cp
		4.76 d J = 1		CH_2
		4.28 d J = 1		CH_2
		0.60 s		$ZrCH_3$

Table IV. Continued.

Compound	IR	NMR (Chemical Shift, Multiplicity, Coupling Constants in Hz) ^1H	^{13}C	Assignment
(Cp_2ZrCH_3) $(Cp_2ZrCHCH_2)O$		δ 7.56 dd J = 20, 15	δ 167.3	CH
		6.57 dd J = 15, 4.4	128.4	CH_2
7		5.77 dd J = 20, 4.4		CH_2
		5.80 s	115.4	Cp
		5.75 s	115.1	Cp
		0.26 s	47.4	$ZrCH_3$
$Cp_2Zr(\eta^2\text{-}OCCH_2\text{-}O,C)$[e]	1596 $\nu_{C=C}$		(CDCl$_3$)	
	1534 $\nu_{C=C}$	(CDCl$_3$)	δ 211.4	C
8		δ 5.84 s 5.03 s	109.1	Cp
		5.26 4.84 s	86.1	CH_2
		4.40 s 4.00 s		CH_2
$Z\text{-}Cp_2Zr(\eta^2\text{-}OCCHCH_3\text{-}O,C)CH_3Na\cdot Et_2O$[f]		δ 5.42 s		Cp
		5.03 q J = 6.8		CH
Z-9·Et_2O		1.81 d J = 6.8		CH_3
		-0.72 s		$ZrCH_3$
E-9·Et_2O[f]		δ 5.38 s		Cp
		3.94 q J = 6.8		CH
		1.62 q J = 6.8		CH_3
		-0.75 s 3H		$ZrCH_3$

Table IV. Continued.

Compound	IR	NMR (Chemical Shift, Multiplicity, Coupling Constants in Hz) ^1H	^{13}C	Assignment
Z-$Cp_2Zr(\eta^2$-OCCHCH$_3$-O,C)CH$_3$K·THF[f]		δ 5.48 s		Cp
		5.00 q J = 6.0		CH
Z-**10**·THF		1.90 d J = 6.0		CH_3
		-0.63 s		$ZrCH_3$
E-**10**·THF[f]		δ 5.44 s		Cp
		4.00 q J = 6.0		CH
		1.70 d J = 6.0		CH_3
		-0.65		$ZrCH_3$
Z-$(Cp_2ZrCH_3)_2(\mu$-η^2-OCCH$_2$-O,C)			δ 199.1 dd J = 7.8	C
	1602 ($\nu_{C=C}$)	δ 5.74 s	111.4 dm J = 172, 7	Cp
11		5.60 s	106.5 dm J = 172, 7	Cp
		5.11 q J = 6.3	101.0 d J = 150	CH
		0.39 s	34.2 q J = 119	$ZrCH_3$
		-0.23 s	17.2 q J = 117	$ZrCH_3$
		1.89 d J = 6.3	15.0 q J = 105	CH_3

Table IV. Continued.

Compound	IR	NMR (Chemical Shift, Multiplicity, Coupling Constants in Hz)		
		^1H	^{13}C	Assignment
$(Cp_2ZrCH_3)_2(OCH\phi CH_2CO)$			δ 322.1	CO
		δ 5.76 s	110.8	Cp
12		5.70 s	110.7	Cp
		5.89 s	106.8	Cp
		5.24 s	106.6	Cp
			80.4	CH
		3.26 m	59.4	CH_2
		0.53 s	20.5	$ZrCH_3$
		0.29 s	15.5	$ZrCH_3$
$(Cp_2ZrCH_3)_2[OC(CH_3)_2CHCO]$			δ 323.6	CO
		δ 5.81 s	110.4	Cp
13		5.43 s	106.6	Cp
			78.3	C
		3.00 s	59.3	CH_2
		1.23 s	30.7	$(CH_3)_2$
		0.54 s	19.0	$ZrCH_3$
		0.31 s	15.7	$ZrCH_3$

Table IV. Continued.

Compound	IR	NMR (Chemical Shift, Multiplicity, Coupling Constants in Hz) ^1H	^{13}C	Assignment
$(Cp_2ZrCH_3)_2(OC(CH_3)_2CHCH_3O)$			δ 325.9	CO
		δ 5.81	110.6	Cp
14		5.44 s	106.8	Cp
			80.3	C
		2.76 q J = 7	63.1	CH
		1.23 s	31.0	$OCCH_3$
		1.13 s	26.8	$OC\underline{C}H_3$
		0.59 s	19.4	$ZrCH_3$
		0.29 s	15.9	$ZrCH_3$
		1.20 d J = 7	11.8	$CH\underline{C}H_3$
Erythro-$(Cp_2ZrCH_3)_2(OCH\phi CHCH_3CO)$			δ 325.4	CO
		δ 5.74, 5.70 s	110.7	Cp
Erythro-**15**		5.42, 5.19 s	106.6	Cp
		5.44 d J = 4.8	85.4	OCH
		2.90 dq J = 4.8, 7.0	61.0	CH
		0.58 s	21.2	$ZrCH_3$
		0.34 s	15.3	$ZrCH_3$
		1.31 d J = 7.0	12.7	CH_3

Table IV. Continued.

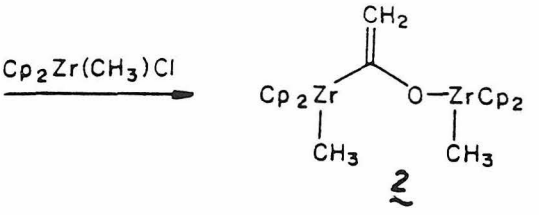
Compound	IR	NMR (Chemical Shift, Multiplicity, Coupling Constants in Hz) ^1H	^{13}C	Assignment
Threo-$(Cp_2ZrCH_3)_2(OCH\phi CHCH_3CO)$			δ 323.9	CO
		δ 5.73, 5.68 s	110.9	Cp
Threo-15		5.40, 5.20 s	106.9	Cp
		5.25 d J = 7.0	84.8	OCH
		3.19 dq J = 7.0, 7.0	60.0	CH
		0.55 s	21.0	$ZrCH_3$
		0.29 s	15.3	$ZrCH_3$
		1.23 d J = 7.0	11.8	CH_3

a ^1H (90 MHz) and ^{13}C (22.5 MHz) NMR spectra taken in benzene-d_6 at ambient temperatures unless otherwise noted. Chemical shifts are reported in δ relative to residue protons and carbons in the solvent. Coupling constants are reported in Hz. b IR spectra obtained in KBr unless otherwise indicated. c ^1H NMR taken in THF-d_8. d ^1H NMR recorded in toluene-d_8 at -20°C. e ^1H NMR taken in C_6D_6 and $CDCl_3$. f ^1H NMR obtained in THF-d_8 at 500 MHz.

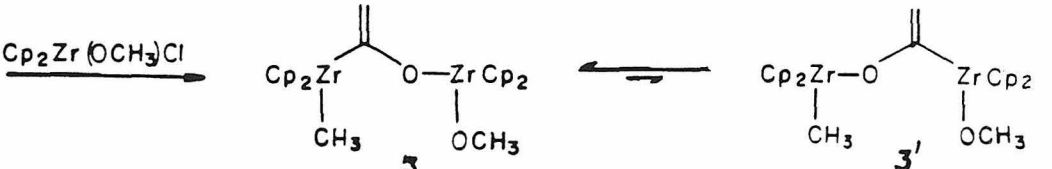
mediated by transition metals.[29] Particularly noteworthy is the mild condition (-40°C) under which C-O bond cleavage is observed.

A summary of the reactions of 1 with Cp_2ZrRCl (R = CH_3, OCH_3, Cl, H) is presented in Figure 4.

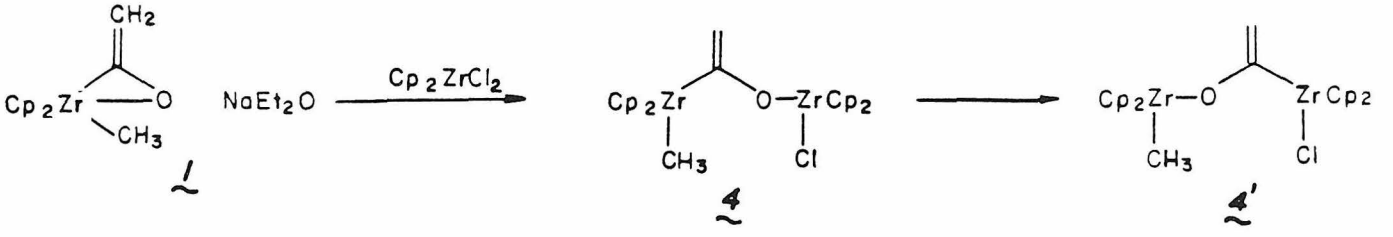
Before commenting on the mechanism of C-O bond cleavage reaction, we will discuss the pathway for the formations of homobinuclear ketene complexes from 1 and Cp_2ZrRCl (R = CH_3, OCH_3, Cl, and H). Three possible mechanisms seem plausible (Scheme I). Mechanism I is the simplest in that it requires no skeletal rearrangement. Direct oxygen addition of 1 to Cp_2ZrRCl affords ketene isomer A. Although o-alkylation was not observed in the reactions of 1 with organic halides, the known oxophilicity of zirconium make this pathway worthy of consideration. Mechanism II is based on the demonstrated nucleophilicity observed for the terminal carbon in reactions of 1 with organic alkylating reagents. Nucleophilic attack of Zr-Cl by the terminal carbon would produce a transient acyl intermediate. Early transition metal acyls are known to be highly oxophilic and adopt η^2 configuration via bonding of the lone pair electrons of the acyl oxygens with the metal atoms. Since there are two metal atoms present in the proposed acyl intermediate, interaction of the acyl oxygen with the second zirconium atom could result in rapid rearrangement by 1.3 shift to ketene isomer A (mechanism II). Alternatively, strong interaction of the η^2-acyl with the first Zr atom could enhance oxy carbene character of the acyl intermediate. Isomerization of this oxy carbene by 1.2 shift would then afford ketene isomer B (mechanism III). Rearrangements of this type have


$Cp_2Zr(CH_3)Cl$
CH_2
Cp_2Zr
O—$ZrCp_2$
CH_3
CH_3

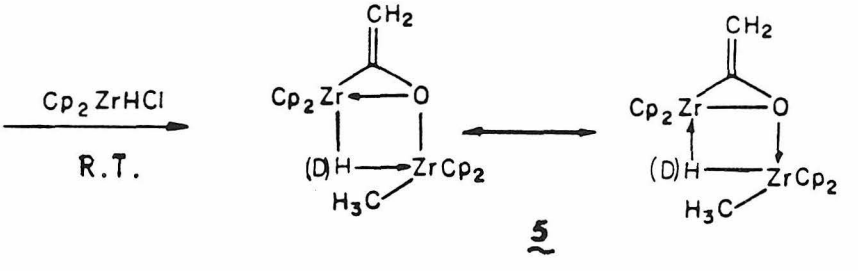
2


$Cp_2Zr(OCH_3)Cl$
Cp_2Zr
O—$ZrCp_2$
CH_3
OCH_3
Cp_2Zr—O
$ZrCp_2$
CH_3
OCH_3

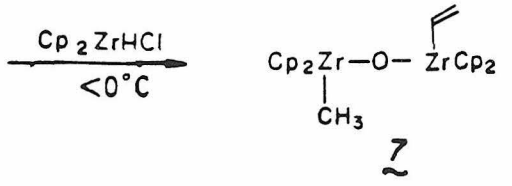
3 3'


CH_2
Cp_2Zr
O
CH_3
$NaEt_2O$
Cp_2ZrCl_2
Cp_2Zr
O—$ZrCp_2$
CH_3
Cl
Cp_2Zr—O
$ZrCp_2$
CH_3
Cl

1 4 4'

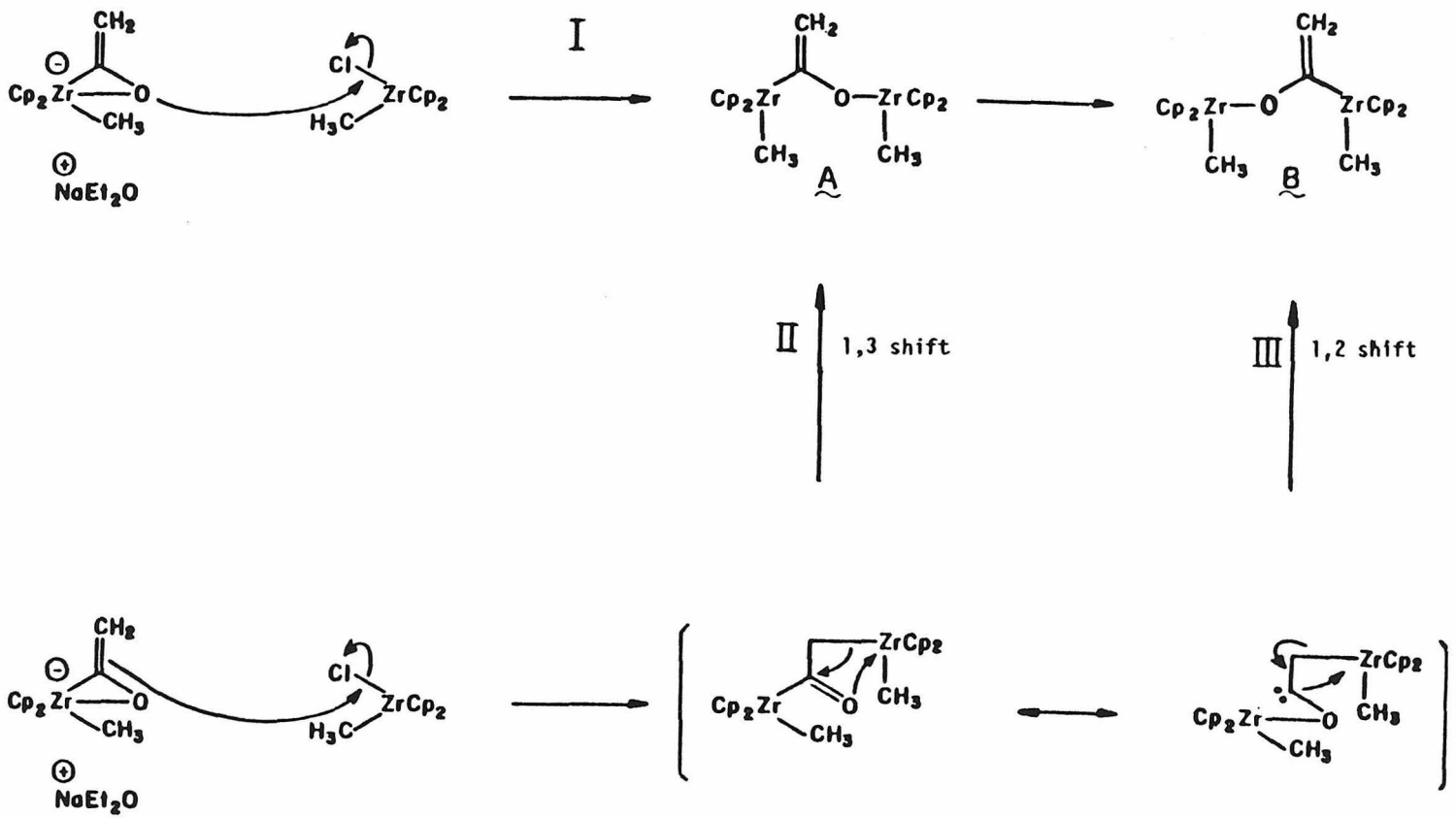

Cp_2ZrHCl
R.T.
CH_2
Cp_2Zr
O
(D)H
$ZrCp_2$
H_3C
CH_2
Cp_2Zr
O
(D)H
$ZrCp_2$
H_3C

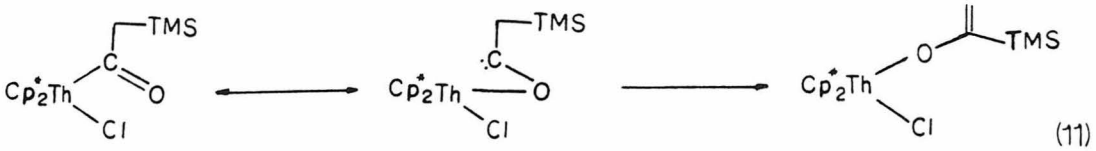
5


Cp_2ZrHCl
<0°C
Cp_2Zr—O—
$ZrCp_2$
CH_3

7

Scheme I

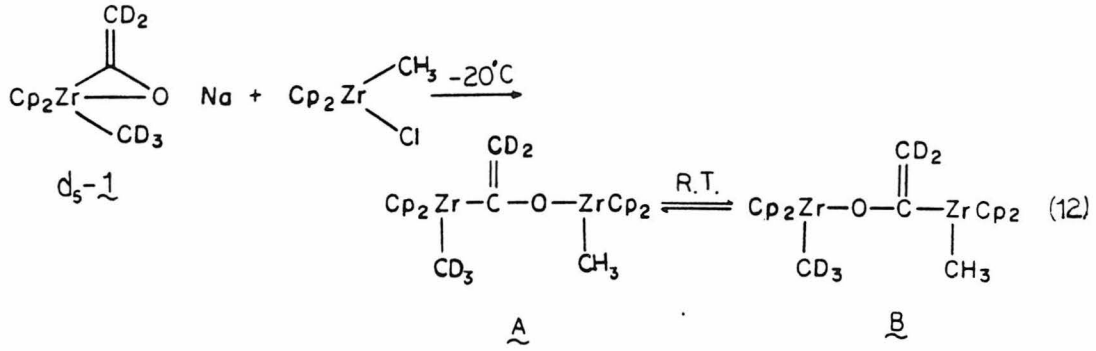




(11)

been observed for $Cp^*_2Th(COCH_2Si(CH_3)_3)Cl$ which thermally isomerizes to $Cp^*_2Th(OCSi(CH_3)_3)=CH_2$[30] (eq. 11).

Among the three mechanisms, III can be ruled out for the following reasons. The initial products (**3** and **4**) observed in the reactions of **1** with Cp_2ZrOCH_3Cl and Cp_2ZrCl_2 were both in the form of isomer A suggesting mechanism III was not in operation. Additional evidence that excluded possible methoxy and chloride ligand participation in the process was obtained from reaction of $Cp_2Zr(\eta^2\text{-}OCCD_2)CD_3\text{-}Na\cdot 2$ THF (**1**-d_5-2 THF) with Cp_2ZrCH_3Cl at -20°C (eq. 12). ^1H NMR spectrum of the reaction



d_5-**1**

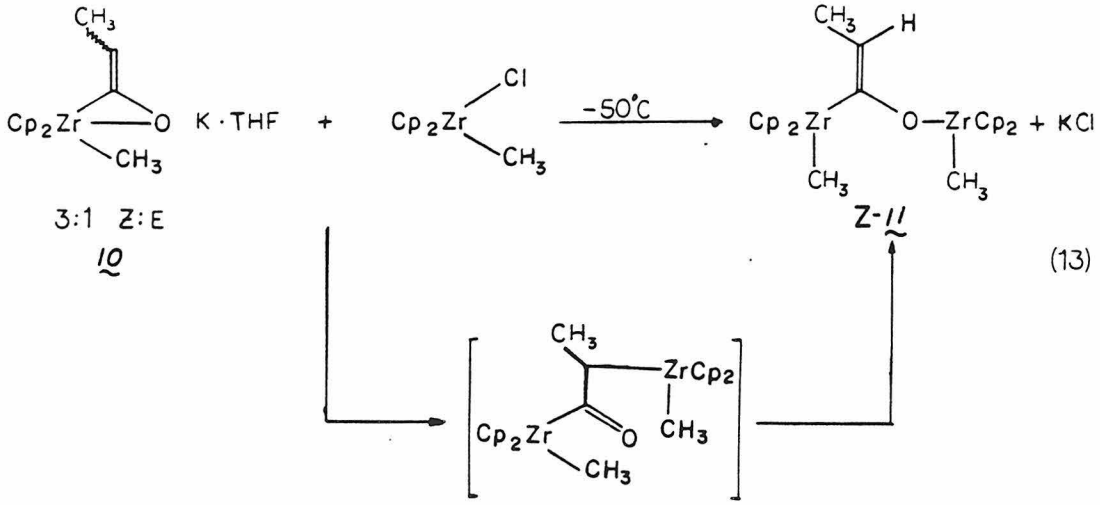
A **B**

(12)

recorded at this temperature revealed that the ketene complex **2** formed contains only one Zr-CH_3 signal at 0.4 ppm which was consistent with isomer A. Upon warming to room temperature, two Zr-CH_3 resonances correspond-

ing to both isomer A and B were observed in the ratio of 1:1 (1.5 H each).

In order to distinguish between the remaining two mechanisms (I and II), the alkyl substituted analog of metallaenolate anion was prepared. Deprotonation of $Cp_2Zr(\eta^2\text{-}OCCHCH_3\text{-}O,C)CH_3$ by K·H in THF yielded a 3:1 mixture of Z,E-$Cp_2Zr(COCHCH_3)CH_3K\cdot THF$ (Z,E-10·THF). The geometries of the double bonds were assigned based on the ^1H chemical shift of the vinyl protons (5.00 ppm, Z-10; 4.00 ppm E-10). Treatment of this 3:1 mixture of Z,E-10·THF with Cp_2ZrCH_3Cl in THF-d_8 at -50°C resulted in the formation of a single isomer of $(Cp_2ZrCH_3)_2(\mu\text{-}\eta^2\text{-}OCCHCH_3\text{-}C,O)$ (11) (eq. 13). No further isomerization of 11 was observed by ^1H NMR upon warming to room temperature. Analytically pure 11 has been isolated on preparative scale reaction in 77% yield. Complex 11 was assigned to be the Z isomer by ^1H NOE experiments. Irradiation of the downfield Cp resonance (5.74 ppm) resulted in enhancement of the vinyl (5.11 ppm) and the Zr-CH_3 (0.39 ppm) signals. Alternatively, irradiation of the Cp at 5.60 ppm induced enhancement of the allyl and zirconium methyl protons (1.89 and -0.23 ppm). Since

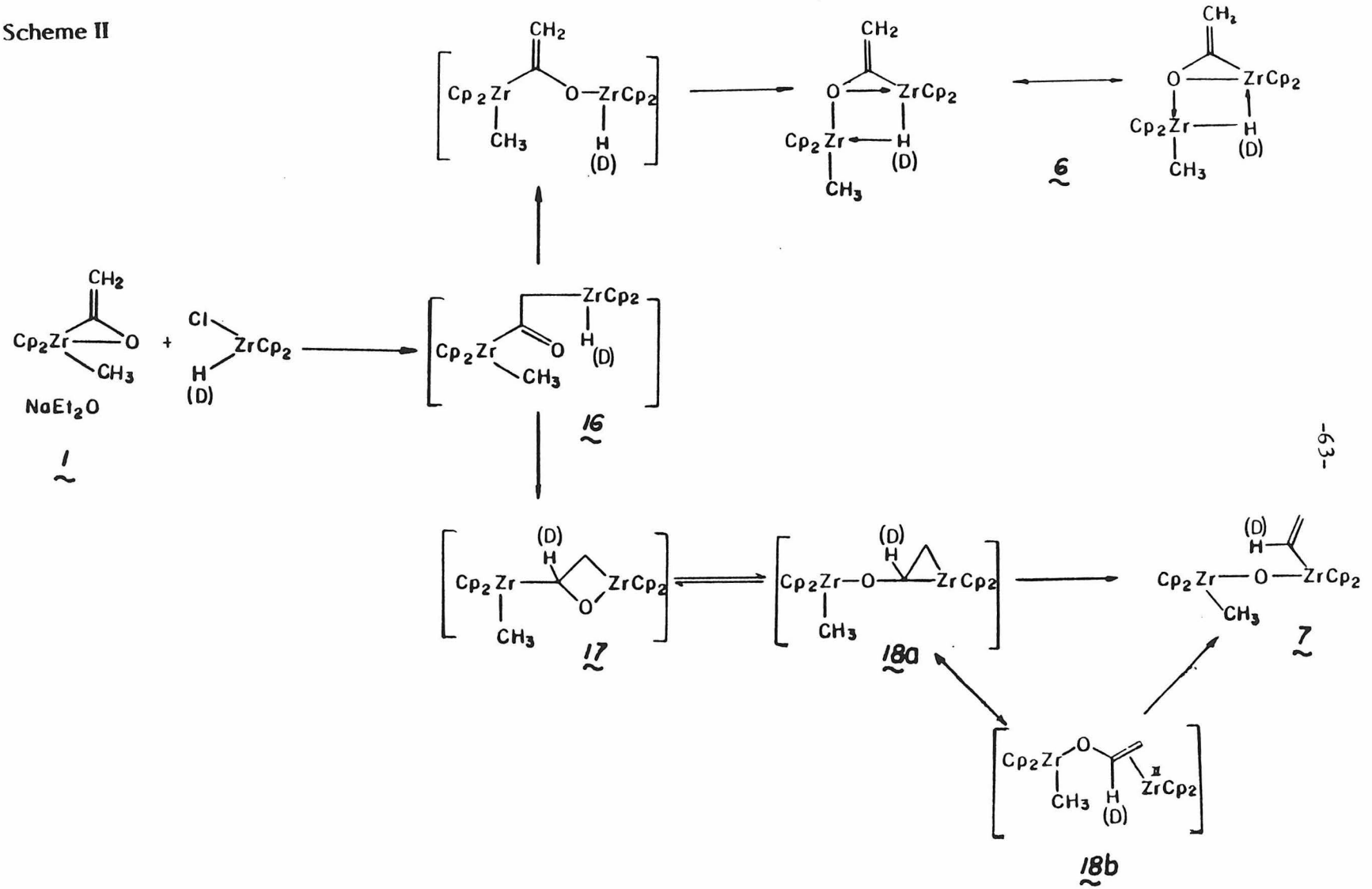


(13)

only Z-11 was observed in the above reaction, we disfavored mechanism I. In direct o-zirconation, the double bond of metallaenolate anion was not involved in the nucleophilic addition, and its geometry should therefore be conserved. Reaction using a mixture of Z,E-10 should then give a mixture of 11 in the same Z,E ratio. This is, however, not the case. In mechanism II, interaction of Cp_2ZrCH_3Cl with either Z or E-10 resulted in a common acyl intermediate which could subsequently rearrange to either Z or E-11. Presumably, Z-11 represents the thermodynamically more stable isomer and thus is formed exclusively. From the outcome of the deuterium and alkyl labeling experiments, we propose that mechanism II is the most likely reaction pathway for the formation of our neutral homobinuclear zirconium ketene complexes.

Mechanism II can also account for the product variations in the reaction of 1 with Cp_2ZrHCl (Scheme II). Recall that complex 5 was formed only when the reaction was carried out at room temperature, conditions under which thermal rearrangement between ketene isomer A and B has been observed in other bridging ketene complexes (e.g., 3'→ 3, 4'→ 4). It is likely that the initially formed ketene isomer A rearranges spontaneously to isomer B (5 in this case) under the reaction conditions and is therefore not observed. The reverse reaction (B→ A) is unfavorable, since complex 5 with bridging hydride is the thermodynamically more stable isomer. Bridging oxo complex 7, the second product was obtained when the reaction mixture was kept at a temperature when rearrangement of the acyl intermediate to isomer A was slow enough

Scheme II



for an alternate reaction to take place. We propose addition of Zr-H across the acyl C=O bond to yield an metallaoxacyclobutane type complex 17. Closer examination of 17 reveals that it has a metallated bridging aldehyde structure. The bridging aldehyde complex $(Cp_2ZrCl)_2(\mu-\eta^2-OCCH_2,-O,C)$ and its related compounds have been shown to undergo rapid dyotropic rearrangement[31] (Fig. 5). Following the same principle, 17 can isomerize to 18 which can be viewed as either a metallacyclopropane or a coordinated enolate complex. Rearrangement of 18 by either 1,3 shift or oxidative addition of zirconium enolate to Zr(II) would then give the observed oxo complex 7.

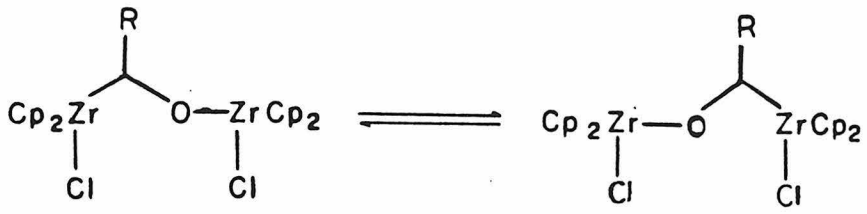
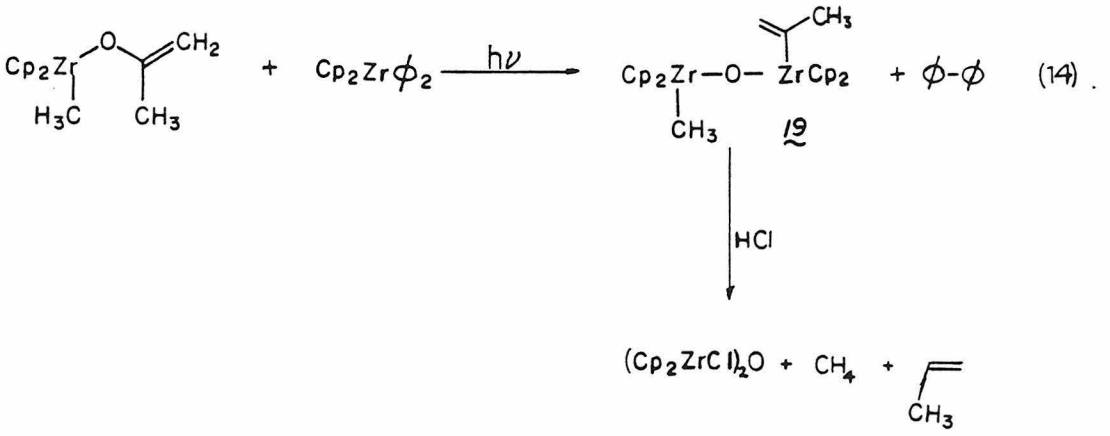


Figure 5

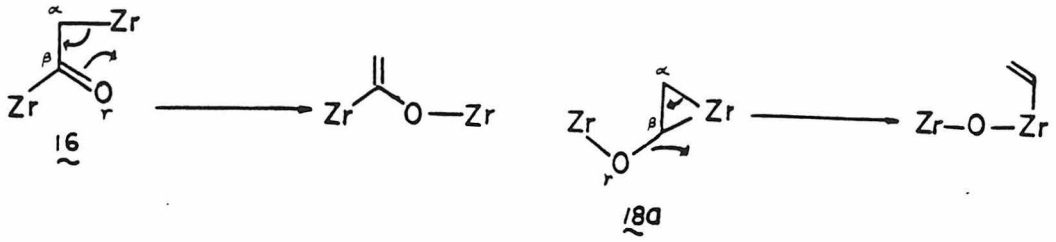
Since there have been no literature precedents for the final transformations in our Scheme, model studies were carried out to examine the viability of these steps. Complex 7-d_1 prepared from reaction of 1 and Cp_2ZrDCl showed deuterium incorporated in the α-position of the vinyl group which was consistent with our proposed mechanism. The oxidative addition of Zr enolate to Zr(II) was demonstrated by reaction of independently generated starting material. $Cp_2Zr\phi_2$ is known to form $Cp_2Zr(II)$ cleanly

upon UV photolysis[32] and $Cp_2Zr(OCCH_3{=}CH_2)CH_3$ can be isolated in pure form.[26] Upon mixing $Cp_2Zr\phi_2$ and $Cp_2Zr(OCCH_3{=}CH_2)CH_3$ in a sealed pyrex NMR tube no reaction was observed. However, after UV irradiation of the mixture for 2.5 h, its ^1H NMR spectrum revealed a new set of resonances at δ 5.81 (Cp), 4.77 (Cp), 2.08 (allyl methyl), and 0.26 ($Zr-CH_3$). The vinyl protons were obscured by impurities in the Cp region. Integration of the allyl methyl signal versus internal standard suggested a yield of 60%. Hydrolysis of the reaction mixture with anhydrous HCl gas afforded methane, propene,

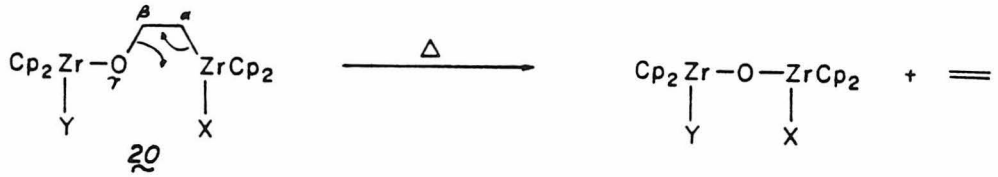


and $(Cp_2ZrCl)_2O$. From the above data, we formulated the reaction product to be $(Cp_2ZrCH_3)O(Cp_2ZrCCH_3{=}CH_2)$ (**19**) (eq. 14).

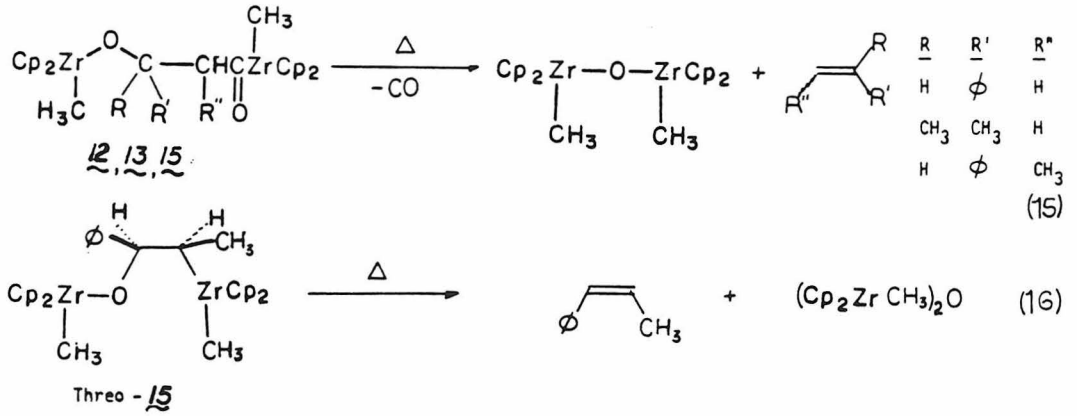
Rearrangement via a 1,3 shift has been proposed before (Scheme I). In both situations (**16** in Scheme I and **18** in Scheme II) the proposed intermediates contain oxygen atoms γ to the metal and the driving force for the rearrangements is the formation of strong Zr-O bonds. Our model studies



therefore center primarily on the formation and thermal reactions of complexes with the basic structure of **20**. Since decarbonylation[23a] in $Cp_2Zr(COR)R'$ (R',R = alkyl) type complexes is facile and proceeds with retention of stereochemistry, the aldol condensation products **12, 13** (or **15**)

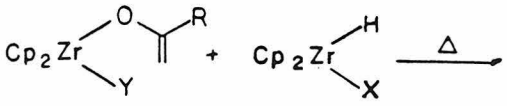


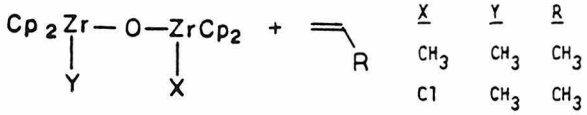
from reactions of **2** (or **11**) with acetone and ϕCHO are ideal precursors to complexes like **20**. A C_6D_6 solution of **12** (or **13**) yielded styrene (or isobutane) and $(Cp_2ZrCH_3)_2O$[23b] cleanly overnight at room temperature (eq. 15). At 70°C, the reaction was complete in less than 5 min. Although no intermediates were observed in the course of decomposition, the products obtained were still consistent with our proposed 1,3 shift mechanism. An



interesting observation which might help to address the stereochemical consequence of the rearrangement came from the decomposition of a diastereomeric mixture of **15**. Heating of a 3:2 mixture of erythro and threo-**15** generated from reaction of **11** and ϕCHO yielded both trans and cis β-methyl styrene in the same (3:2) ratio.[33] The retention of product stereochemistry can be rationalized as the result of a four-centered (2+2) transition state (eq. 16).

A different approach to generate **20** by hydrozirconation of enolates has also been explored. Heating mixtures of zirconium enolates[26,34] and excess Cp_2ZrHR (R = CH_3, Cl) in C_6D_6 at 70°C for 1 min cleanly afforded oxo complexes and zirconium alkyl derivatives (from hydrozirconation of olefins produced) (eq. 17). Again, no intermediates were observed. Although





X	Y	R
CH_3	CH_3	CH_3
Cl	CH_3	CH_3

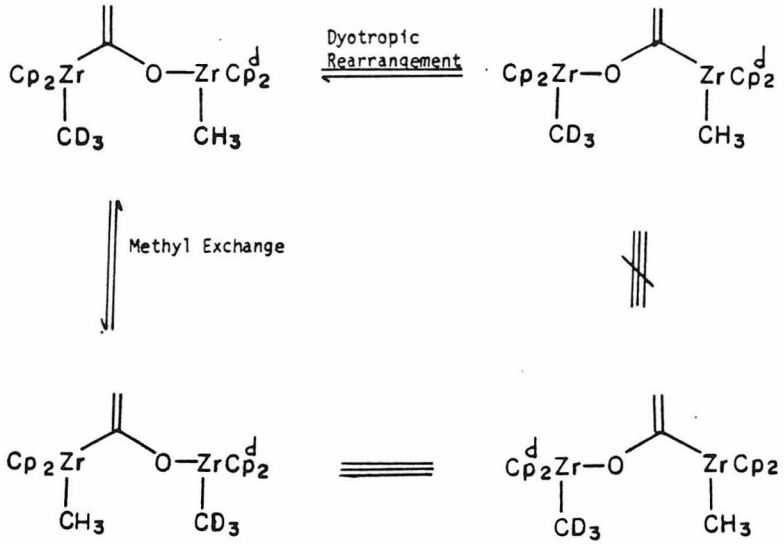
(17)

there is no direct evidence for **20** in these reactions, we can infer its existence by the known dicarbonylation and hydrozirconation mechanisms and the final decomposition products. The above results establish the viability of the last step in our proposed mechanism (**18a** or **18b** → **7**, Scheme II). The outcome of the reactions of Zr enolates with Zr hydrides and with Zr(II)

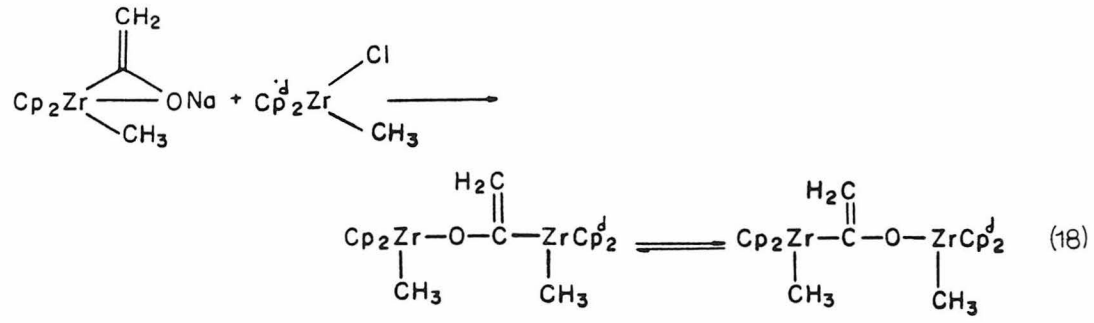
species also suggest some novel deoxygenation processes for the overall reduction of ketones (precursor to enolates) to olefins. Any potential applications of these reactions in organic synthesis are currently being investigated.[35]

So far, we have examined in detail the mechanism (II in Scheme I) of the formation of bridging ketene complexes. This mechanism is consistent with all initial ketene products observed and can be expanded to accommodate C-O cleavage reaction (Scheme II). The only aspect of the mechanism that has not been addressed is the rearrangement of isomer A to B (see Scheme I). In our investigation of this process, we chose the degenerate isomerization of $(Cp_2ZrCH_3)_2(\mu\text{-}\eta^2\text{-}OCCH_2\text{-}O,C)$ (2). In contrast to hetero-atom substituted systems **3** → **3'** and **4** → **4'**, **2** has no thermodynamic preference for either isomers. As mentioned before, reaction of 1-d_5·2 THF with Cp_2ZrCH_3Cl generated only isomer A of **2** which subsequently rearranged to isomer B (eq. 12). This result can be attributed to either a mechanism of Zr-methyl redistribution or to dyotropic ketene rearrangement (Scheme III). Many Zr(IV) alkyl complexes have been shown to disproportionate under thermal or photolytic conditions[36] and dyotropic isomerization is common for bridging aldehyde complexes of zirconium[31] (Fig. 5). In order to differentiate these two possible mechanisms, we prepared $Cp^d_2ZrCH_3Cl$ with deuterium labeled Cp's. If Zr-methyl exchanges were in operation, the Cp's on the two zirconium atoms would remain distinct and no scrambling would be observed, whereas dyotropic ketene rearrangement would result in complete scrambling of the cyclopentadienyl ligands (Scheme III).

Scheme III



The ^1H NMR spectrum of the reaction of 1·2 THF and $Cp_2^dZrCH_3Cl$ in THF-d_8 at -20°C indicated only one Cp signal (5.65 ppm) corresponding to isomer A of **2**. Upon warming to 24°C, its intensity decreased as a new Cp resonance (5.80 ppm) grew in and an equilibrium was reached in 20 min (eq. 18). Within experimental error, the rate of cyclopentadienyl ligand exchange ($4.54 \pm 0.33 \times 10^{-4}$ s^{-1}, 17°C) is identical to the Zr-CH_3, CD_3 scrambling



(18)

($5.07 \pm 0.39 \times 10^{-4}$ s^{-1}, 17°C) obtained before (eq. 12), suggesting only one isomerization process is responsible for both observations. Kinetic data on the isomerization of doubly labeled **2** (from 1-d_5·2 THF and $Cp_2{}^dZrCH_3Cl$) also showed the same rate constants for both Cp and methyl scramblings. Similar phenomenon was also observed in the reaction of $(Cp_2Zr(\mu\text{-}\eta^2\text{-}OCCHCH_3\text{-}O,C)CH_3Na\cdot Et_2O$ (**9**·Et_2O) and $Cp_2{}^dZrCH_3Cl$ to form **11**. In this case, isomerization was slow and complete scrambling was achieved after one day at room temperature. From the labeling experiments, we conclude that the isomerization of zirconium bridging ketene complexes is the result of dyotropic rearrangement of the ketene moiety. Kinetic data were obtained from the isomerization of deuterated **2** at various temperatures. The reaction exhibited a first-order reversible kinetics as expected. Activation parameters derived from the Eyring plot are listed in Table V. The negative entropy of activation ($\Delta S^{\ddagger}$ = -9.5 eu) suggests a highly organized

Table V. Activation parameters of the isomerization of **2** in toluene-d_8.

T (°C)	$k_{obs} \times 10^4$ s^{-1}
10	2.35 ± 0.15
15	4.44 ± 0.30
24	10.7 ± 0.1

$\Delta H^{\ddagger}$ = 18.6 ± 0.5 kcal/mol

$\Delta G^{\ddagger}_{297}$ = 21.4 + 0.3 kcal/mol

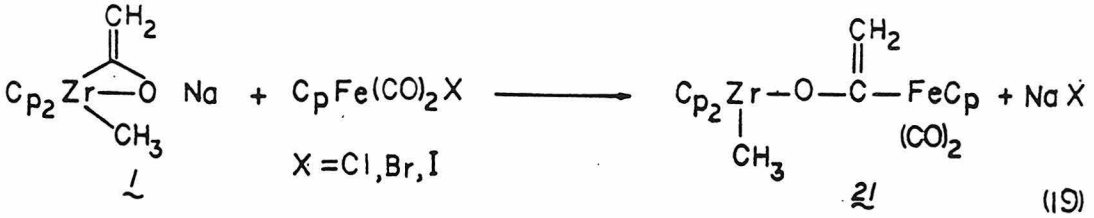
$\Delta S^{\ddagger}$ = -9.5 ± 1.7 eu

transition state (Fig. 6). The $\Delta S^{\ddagger}$ is in agreement with that calculated for formaldehyde complex $(Cp_2ZrCl)_2(\mu\text{-}OCCH_2\text{-}O,C)$ (-5.0 eu).[31] It is also in the range of concerted organic rearrangement processes with rigid cyclic transition state (e.g., $\Delta S^{\ddagger} \sim -14$ eu for Cope[37] and ~ -8 eu for Claisen rearrangements).[38]

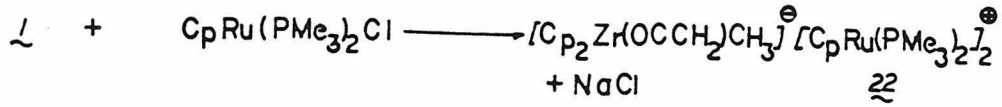
Figure 6

A survey of reactions of 1 with other transition metal halides show some promising results. $CpFe(CO)_2X$ (X = Cl, Br, I) reacted with 1 to yield one major product assigned as $(Cp_2ZrCH_3)(\mu\text{-}\eta^2\text{-}OCCH_2O,C)(CpFe(CO)_2)$ (21) by its ^1H NMR (δ 5.89, Cp; 4.35, CH; 4.26, Cp; 4.02, CH; 0.43, $ZrCH_3$) (eq. 19). Isolation and purification of 21 were difficult due to the presence of $(CpFe(CO)_2)_2$ impurity. Treatment of 1 with $CpRu(PMe_3)_2Cl$ in C_6D_6 afforded yellow precipitates. ^1H NMR of this yellow solid in THF-d_8 revealed a complex, containing one Cp_2Zr and two CpRu moieties. Based on its solubility property and ^1H NMR data (δ 5.42 (10H), 4.39 (10H), 1.48 (36H), -0.71 (3H)), a ionic structure of $(Cp_2Zr(OCCH_2)CH_3)^-(CpRu(PMe_3))_2Cl)^+$ (22) was proposed (eq. 20).

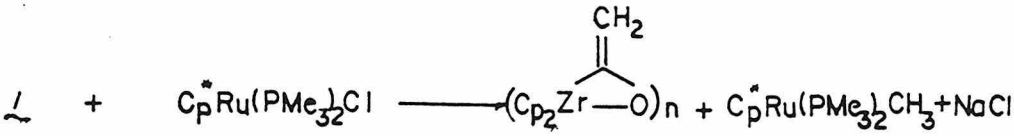
Replacing Cp with more electron rich C_5Me_3 on Ru resulted in the transfer of Zr-CH_3 to Ru (eq. 21). Only Pt(II) chlorides reacted cleanly with 1·2 THF



(19)

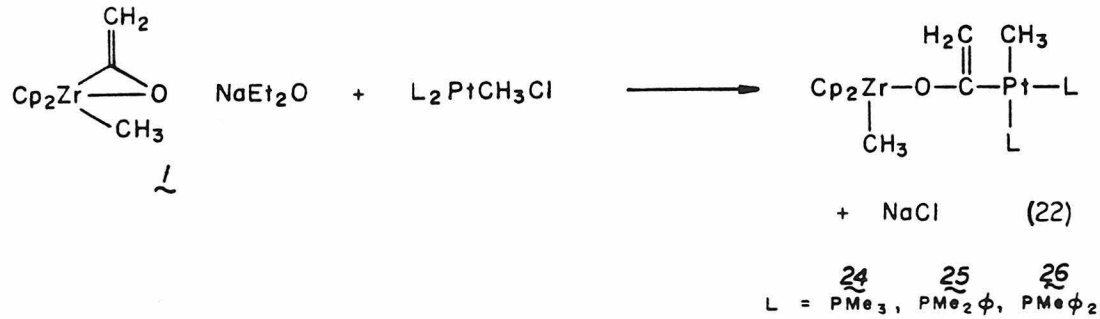


(20)

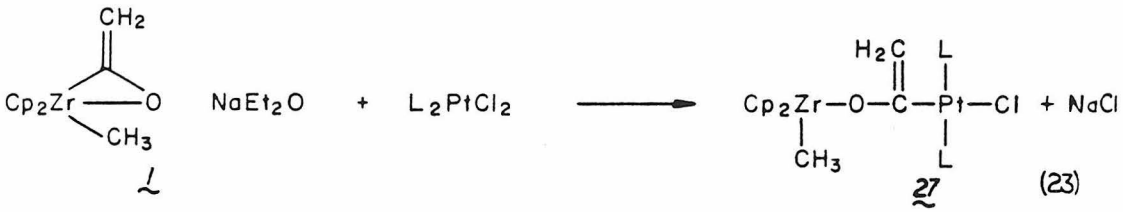


(21)

to yield complexes of $(Cp_2ZrCH_3)(\mu\text{-}\eta^2\text{-}OCCH_2\text{-}O,C)(PtL_2X)$ (X = CH_3, Cl; L = phosphines) quantitative by NMR (based on internal standard, 2 THF) (eqs. 22-23). Their structure assignments are supported by the ^1H, ^{13}C, ^{31}P NMR

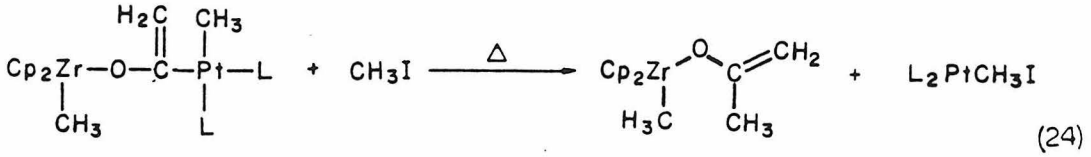


(22)



1 $NaEt_2O$ + L_2PtCl_2 → 27 + NaCl (23)

L = $PMe_2\phi$



24 + CH_3I $\xrightarrow{\Delta}$ $Cp_2Zr(OCCH_3{=}CH_2)CH_3$ + L_2PtCH_3I (24)

spectroscopic data (Table VI). The inequivalence of the phosphine ligands and the different J_{HP} and J_{PPt} values establishes cis orientation about Pt in **24**, **25**, and **26**. Complex **27**, however, adopts trans configuration around pt with equivalent phosphine ligands. Heating of a mixture of methyliodide and **24** results in the oxidative addition of CH_3I to Pt(II), followed by reductive elimination to yield $Cp_2Zr(OCCH_3{=}CH_2)CH_3$ and L_2PtCH_3I (eq. 24).

Table VI. ^{1}H, ^{31}P NMR Spectroscopic Data.

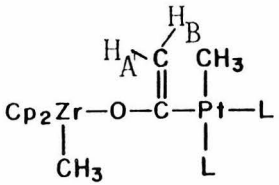
Compound	NMR (Chemical Shift, Multiplicity, Coupling Constants in Hz)				Assignment
	^{31}P		^{1}H		
 **24**	δ -29.3 d J_{P-P} = 12.2		δ 6.00 s		Cp
		J_{P-Pt} = 1354	5.06 ddd	J_{H-H} = 1.9 J_{H-P} = 12.7, 2.9 J_{H-Pt} = 90.8	H_A
	25.0 d J_{P-P} = 12.2				
		J_{P-Pt} = 1578	4.00 ddd	J_{H-H} = 1.9 J_{H-P} = 2.9, 2.9 J_{H-Pt} = 31.2	H_B
			1.20 d	J_{H-P} = 8.5 J_{H-Pt} = 21.7	$P(CH_3)_3$
L = PMe_3			1.04 dd	J_{H-P} = 6.8, 9.8 J_{H-Pt} = 69.6	$PtCH_3$
			0.93 d	J_{H-P} = 7.8 J_{H-Pt} = 19.4	$P(CH_3)_3$
			0.39 s		$ZrCH_3$

Table VI. Continued.

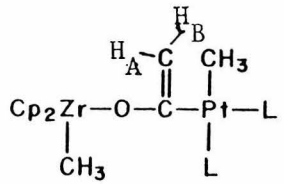
Compound		NMR (Chemical Shift, Multiplicity, Coupling Constants in Hz)			
		^{31}P	^{1}H		Assignment
		δ -16.9 d J_{P-P} = 12.2	δ 6.09 s		Cp
		J_{P-Pt} = 1550	5.08 ddd	J_{H-H} = 1.9 J_{H-P} = 13.2, 2.9 J_{H-Pt} = 94.8	H_A
		-13.2 d J_{P-P} = 12.8			
		J_{P-Pt} = 1914	4.21 ddd	J_{H-H} = 1.9 J_{H-P} = 2.4, 2.4 J_{H-Pt} = 32.2	H_B
			1.42 d	J_{H-P} = 8.3 J_{H-Pt} = 22.4	$P(CH_3)_2$
L = $PMe_2\phi$	25		1.20 dd	J_{H-P} = 7.3, 10.2 J_{H-Pt} = 70.4	$PtCH_3$
			1.02 d	J_{H-P} = 7.8 J_{H-Pt} = 18.6	$P(CH_3)_2$
			0.48 s		$ZrCH_3$

Table VI. Continued.

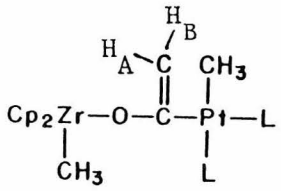
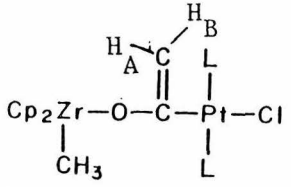
Compound	NMR (Chemical Shift, Multiplicity, Coupling Constants in Hz)				
	^{31}P		^{1}H		Assignment
	δ 0.81 d	J_{P-P} = 12.2	δ 6.01 s		Cp
		J_{P-Pt} = 1670	4.98 ddd	J_{H-H} = 1.97 J_{H-P} = 12.9, 2.9 J_{H-Pt} = 97.6	H_A
	3.50 d	J_{P-P} = 12.1 J_{P-Pt} = 1948	4.10 ddd	J_{H-H} = 1.9 J_{H-P} = 2.4, 2.4 J_{H-Pt} = 33.2	H_B
L = $PMe\phi_2$ **26**			2.05 d	J_{H-P} = 8.8 J_{H-Pt} = 25.4	PCH_3
			1.28 d	J_{H-P} = 6.8 J_{H-Pt} = 17.6	PCH_3
			1.18 dd	J_{H-P} = 6.8, 9.8 J_{H-Pt} = 76.2	$PtCH_3$
			0.50 s		$ZrCH_3$

Table VI. Continued.

Compound	NMR (Chemical Shift, Multiplicity, Coupling Constants in Hz)			
	^{31}P	^{1}H		Assignment
	δ -17.8 s J_{P-Pt} = 1758	δ 6.14 s		Cp
		5.02 dd	J_{H-H} = 1.9 J_{H-P} = 9.3 J_{H-Pt} = 92.8	H_A
		4.05 dt	J_{H-H} = 1.9 J_{H-P} = 2.5 J_{H-Pt} = 33.2	H_B
27		1.28 d	J_{H-P} = 8.5 J_{H-Pt} = 22.4	PCH_3
L = $PMe_2\phi$		0.50 s		$ZrCH_3$

[a] ^{1}H (500 MHz) and ^{31}P (36.2 MHz) NMR spectra taken at ambient temperature. ^{1}H chemical shifts are reported in δ relative to residue protons of solvent. ^{31}P chemical shift are reported relative to external H_3PO_4. Coupling constants are reported in Hz.

Experimental Section

Zirconocene dichloride purchased from Boulder Scientific was used without purification. $Cp_2Zr(CH_3)_2$, $Cp_2Zr(CD_3)_2$,[39] Cp_2ZrCH_3Cl,[40] Cp_2ZrHCl, Cp_2ZrDCl,[41] $Cp_2Zr\phi_2$,[39] and $Cp_2Zr(COCH_3)CH_3$[23a] were synthesized by known methods. $NaN(Si(CH_3)_3)_2$ was prepared by deprotonation of $HN(Si(CH_3)_2)_2$ with NaH. Enolate complex of $Cp_2Zr(OC(CH_3)=CH_2)CH_3$ was obtained from reaction of $Cp_2Zr(COCH_3)CH_3$ and $(CH_3)_2SOCH_2$.[26] L_2PtCl_2 and L_2PtCH_3Cl (L = phosphine) were prepared by literature method.[41,42]

Dichloromethane was stirred over P_2O_5 and degassed. Pentane and hexane were stirred over concentrated H_2SO_4, then sodium-benzophenone ketyl. Benzene, diethyl ether, toluene, and tetrahydrofuran were stirred over CaH_2 then sodium-benzophenone ketyl. Solvents thus dried and deoxygenated were vacuum transferred into flask sealed with teflon screw valves and stored under argon. 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 line and dry box techniques. 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), a JEOL FX-90Q (89.6 MHz ^1H, 13.7 MHz ^2H, 36.2 MHz ^{31}P, 22.5 MHz ^{13}C) or a Brucker WM-500 (500.13 MHz ^1H, 76.76 MHz ^2H, 125 MHz ^{13}C). Kinetics by ^1H NMR spectroscopy were obtained in automated mode on the JEOL FX-90Q.

Temperatures were determined by measuring $\Delta\nu$ MeOH and were constant to within ±0.1°C. Difference NOE's were measured on the Brucker WM-500. Infrared spectra were obtained on a Beckman IR-4240 spectrophotometer. Elemental analyses were performed by Dornis and Kolbe of West Germany.

Preparation of $[Cp_2Zr(\eta^2\text{-}OCCH_2\text{-}C,O)CH_3]Na\cdot Et_2O$ ($1\cdot Et_2O$). To a suspension of 1.0 g (3.6 mmol) of $Cp_2Zr(COCH_3)CH_3$ in 40 mL of ether at -40°C was added a solution of 0.67 g (3.6 mmol) $NaN[Si(CH_3)_3]_2$ in 10 mL of ether. A fine white powder precipitated after stirring for 1 h. The supernatant was removed by cannulation and the solid was washed with cold ether then dried under vacuum to give 1.16 g, 90% yield of the desired product. The compound is moderately light sensitive, pyrophoric in air and thermally unstable. For long term storage, **1** is kept at -40°C. Recrystallization by slow cooling of a 1:1 pentane-THF solution of $1\cdot Et_2O$ to -50°C afforded crystalline $1\cdot 2$ THF suitable for X-ray structural analysis. $1\cdot Et_2O$: ^1H NMR (THF-d8, 90 MHz) δ 5.43(s,10H),4.55(d,J =2 Hz, 1H), 3.64 (d, J = 2 Hz, 1H), -0.68 (s, 3H). $1\cdot 2$ THF: ^1H NMR (C_6D_6, 90 MHz) δ 5.70 (s, 10H), 5.18 (s, 1H), 4.37 (s, 1H), 3.47 (m, 8H), 1.31 (m, 8H), -0.23 (s, 3H).

Reactions of 1 with CD_3I, ϕCH_2Br and $(CH_3)_3SiCl$. To a 5 mm NMR tube was loaded 12-14 mg of $1\cdot 2$ THF and 0.4 mL of C_6D_6. One equiv of the alkyl halides was added via syringe and the solution turned yellow immediately. The ^1H NMR spectra of the reactions recorded showed formation of acyl complexes. $Cp_2Zr(COCH_2CD_3)CH_3$: ^1H NMR δ 5.32 (s, 10H), 2.55 (broad s, 2H), 0.53 (s, 3H).

$Cp_2Zr(COCH_2CH_2\phi)Br$: ^1H NMR δ 7.07 (m, 5H), 5.23 (s, 10H), 2.87 (m, AA'BB', 4H), 0.85 (s, 3H). $Cp_2Zr(COCH_2Si(CH_3)_3)Cl$: ^1H NMR δ 5.42 (s, 10H), 2.84 (broad s, 2H), 0.52 (s, 3H), 0.00 (s, 9H).

Preparation of $(Cp_2Zr(\eta^2\text{-}OCCHCH_3\text{-}C,O)CH_3)Na\cdot Et_2O$ (9·Et_2O). To a suspension of $Cp_2Zr(COCH_3)CH_3$ (1.0 g, 3.6 mmol) in 40 mL ether at -40°C was added 0.75 g (4.1 mmol) of $NaN(Si(CH_3)_3)_2$ in 10 mL ether. After stirring at -40°C for 20 min, solvent was removed via cannulation and the remaining white solid was washed with ether (3 x 10 mL), then dissolved in 10 mL of THF and cooled to 0°C. Methyl iodide (0.25 mL, 4.0 mmol) was added via syringe dropwise. Reaction mixture was warmed to room temperature for 5 min. THF was removed under vacuum and the yellow residue was extracted with 50 mL of ether and filtered. To the ether extract was added a solution of 0.65 g (3.5 mmol) of $NaN(Si(CH_3)_3)_2$ in 10 mL of ether at 0°C. After stirring for 20 min, a white solid was isolated by filtration and washed with ether and dried to yield 0.77 g (55%). By ^1H NMR, the Z and E isomers are present in 3:1 ratio. **Z-9**: ^1H NMR (THF-d_8, 500 MHz) δ 5.42 (s, 10H), 5.03 (q, J = 6.8 Hz, 1H), 1.81 (d, J = 6.8 Hz, 3H), -0.72 (s, 3H). **E-9**: ^1H NMR (THF-d_8, 500 MHz) δ 5.38 (s, 10H), 3.94 (q, J = 6.8 Hz, 1H), 1.62 (d, J = 6.8 Hz, 3H), -0.75 (s, 3H).

Preparation of $(Cp_2Zr(\eta^2\text{-}OCCHCH_3\text{-}C,O)CH_3)K\cdot THF$ (10·THF). A suspension of 0.50 g (1.8 mmol) of $Cp_2Zr(COCH_2CH_3)CH_3$[22] and 0.72 g (18 mmol) of KH in 40 mL of THF was stirred overnight at room temperature. The mixture was filtered through a pad of celite on a medium glass frit. Solvent was then removed under vacuum to give 0.50 g (71%) of beige

powder. By ^1H NMR the Z and E isomers are present in 2.4:1 ratio. **Z-10:** ^1H NMR (THF-d_8, 500 MHz) δ 5.48 (s, 10H), 5.00 (q, J = 6.0 Hz, 1H), 1.90 (d, J = 6.0 Hz, 3H), -0.63 (s, 3H). **E-10:** ^1H NMR (THF-d_8, 500 MHz) δ 5.44 (s, 10H), 4.00 (q, J = 6.0 Hz, 1H), 1.70 (d, J = 6.0 Hz, 3H), -0.65 (s, 3H).

Preparation of $Cp_2Zr(OCH_3)Cl$. To a solution of 0.60 g (2.2 mmol) of Cp_2ZrCH_3Cl in THF was added 0.089 mL (0.071 g, 2.2 mmol) of anhydrous CH_3OH. Solvent was removed under vacuum to yield a white solid which can be purified by sublimation (10^{-4} torr, 100°C). ^1H NMR (C_6D_6, 90 MHz δ 5.91 (s, 10H), 3.64 (s, 3H); ^{13}C NMR (C_6D_6, 22.5 MHz δ 113.3, 85.3.

Preparation of $(Cp_2ZrCH_3)(\mu\text{-}\eta^2\text{-}OCCHR\text{-}O,C)(Cp_2ZrX)$ (R = H, X = CH_3, (2); R = H, X = OCH_3 (3); R = CH_3, X = CH_3 (11)). This is a general procedure for the synthesis of **2**, **3** and **11**. To a suspension of $1{\cdot}Et_2O$ or $9Et_2O$ and 1 equiv of Cp_2ZrXCl (X = CH_3, OCH_3) in Et_2O at -20°C was added THF until reaction mixture became cloudy (approximately a 2:1 mixture of ether/THF). The mixture was stirred for 30 min at -20°C then filtered through a pad of celite on a medium glass frit. The filtrate was concentrated under vacuum to give a solid which was washed with cold ether three times and dried under vacuum. **2:** ^1H NMR (C_6D_6, 90 MHz) δ 5.82 (s, 10H), 5.65 (s, 10H), 4.61 (s, 1H), 4.23 (s, 1H), 0.40 (s, 3H), -0.17 (s, 3H); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 208.9 (pseudo t, J = 10 Hz), 113.1 (dm, J = 172, 7 Hz), 107.1 (dm, J = 172, 7 Hz), 92.7 (dd, J = 159, 148 Hz), 33.0 (q, J = 119 Hz), 18.8 (q, J = 117 Hz); IR (KBr) 1594, 1538 cm^{-1}

($\nu_{C=C}$). Yield: 65%. Anal. calcd. for $C_{24}H_{28}OZr_2$: C, 55.98; H, 5.48. Found: C, 55.80; H, 5.41. **3**: ^1H NMR (C_6D_6, 90 MHz) δ 5.93 (s, 10H), 5.68 (s, 10H), 4.79 (s, 1H), 4.53 (s, 1H), 3.85 (s, 3H), -0.12 (s, 3H); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 206.4 (pseudot, J = 9 Hz), 112.4 (dm, J = 172, 7 Hz), 106.6 (dm, J = 172, 7 Hz), 90.9 (dd, J = 146, 160 Hz), 63.6 (q, J = 141 Hz), 17.5 (q, J = 117 Hz); IR (KBr) 1592, 1536 cm^{-1} ($\nu_{C=C}$). Yield: 55%. Anal. calcd. for $C_{24}H_{28}O_2Zr_2$: C, 54.30; H, 5.32. Found: C, 54.26; H, 5.44. **11**: ^1H NMR (C_6D_6, 90 MHz) δ 5.74 (s, 10H), 5.60 (s, 10H), 5.11 (q, J = 6.3 Hz, 1H), 1.89 (d, J = 6.3 Hz, 3H), 0.39 (s, 3H), -0.23 (s, 3H); ^{13}C (C_6D_6, 22.5 MHz) δ 199.1 (d, J = 8 Hz), 111.4 (dm, J = 172, 7 Hz), 106.5 (dm, J = 172, 7 Hz), 101.0 (d, J = 150 Hz), 34.2 (q, J = 119 Hz), 17.2 (q, J = 117 Hz), 15.0 (q, J = 125 Hz); IR (KBr) 1602 cm^{-1} ($\nu_{C=C}$). Yield: 77%. Anal. calcd. for $C_{25}H_{30}OZr_2$: C, 56.77; H, 5.72. Found: C, 56.54; H, 5.62.

Reactions of 2 with ϕCHO and CH_3COCH_3. To a NMR sample tube fitted with a septum was loaded 53 mg (0.10 mmol) of 2 and 0.4 mL of C_6D_6. Organic carbonyl compounds were added via microsyringe. Freshly distilled ϕCHO (10 uL, 1 equiv) reacted immediately to give quantitative $(Cp_2ZrCH_3)_2(u\text{-}OCH\phi CH_2CO\text{-}C,O)$ (**12**): ^1H NMR (C_6D_6, 90 MHz) δ 7.00-7.56 (m, 5H), 5.76 (s, 5H), 5.70 (s, 5H), 5.39 (s, 5H), 5.24 (s, 5H), 3.26 (m, 2H), 0.53 (s, 3H), 0.29 (s, 3H), methine proton was not located; ^{13}C NMR (C_6D_6, 22.5 MHz) δ 322.1, 146.2, 128.6, 127.6, 126.4, 110.8, 110.7, 106.8, 106.6, 80.4, 59.4, 20.5, 15.1. Reaction of **2** with acetone (7 uL, 1 equiv) was complete in 8 h to yield

$(Cp_2ZrCH_3)_2(\mu\text{-}OC(CH_3)_2CH_2CO\text{-}C,O)$ (13) in 80%. ^1H NMR (C_6D_6, 90 MHz) δ 5.81 (s, 10H), 5.43 (s, 10H), 3.00 (s, 2H), 0.54 (s, 3H), 0.31 (s, 3H), 1.23 (s, 6H); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 323.6 (s), 110.4 (dm, J = 171, 7 Hz), 106.6 (dm, J = 173, 7 Hz), 78.3 (s), 59.3 (t, J = 127 Hz), 30.7 (q, J = 129 Hz), 19.0 (q, J = 120 Hz), 15.7 (q, J = 117 Hz). $Cp_2Zr(CH_3)_2$, decomposition of product of **2**, was observed in 20%.

Reactions of 11 with ϕCHO and CH_3COCH_3. To a solution of 50 mg (0.095 mmol) of **11** in 5 mL of THF at -78°C was added 15 µL (> 1 equiv) of freshly distilled ϕCHO. The reaction was stirred at -78°C for 1 h then warmed to room temperature slowly. Solvent was removed under vacuum to yield a yellowish solid of $(Cp_2ZrCH_3)_2(\mu\text{-}OCH\phi CHCH_3CO\text{-}C,O)$ (**15**) as a 3:2 mixture of erythro and threo diastereomers. **Erythro-15:** ^1H NMR (C_6D_6, 500 MHz) δ 7.00-7.36(m,5H),5.74(s,5H),5.70 (s, 5H), 5.42 (s, 5H), 5.19 (s, 5H), 2.90 (dq, J = 7.0, 4.8 Hz, 1H), 5.44 (d, J = 4.8 Hz, 1H), 0.58 (s, 3H),0.34 (s, 3H), 1.31 (d, J = 7.0 Hz, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 325.4, 110.7, 106.6, 85.4, 61.0 21.2, 15.3, 12.7. **Threo-15:** ^1H NMR (C_6D_6, 500 MHz) δ 7.00-7.36 (m, 5H), 5.73 (s, 5H), 5.68 (s, 5H), 5.40 (s, 5H), 5.20 (s, 5H), 3.19 (dq, J = 7.0, 7.0 Hz, 1H), 5.25 (d, J = 7.0 Hz, 1H), 0.55 (s, 3H), 0.29 (s, 3H), 1.23 (d, J = 7.0 Hz, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 323.9, 110.9, 106.9, 84.8, 60.0, 21.0, 15.3, 11.8.

To a NMR sample tube loaded with 24 mg (0.45 mmol) of **11** in 0.4 mL C_6D_6 was added 3.5 µL (1 equiv) of acetone. Reaction was complete overnight at room temperature to give quantitative $(Cp_2ZrCH_3)_2$-$(\mu\text{-}OC(CH_3)_2CHCH_3\text{-}C,O)$ (**14**): ^1H NMR (C_6D_6, 90 MHz) δ 5.81 (s,

10H), 5.44 (s, 10H), 2.76 (q, J = 7.0 Hz, 1H), 1.23 (s, 3H), 1.20 (d, J = 7.0 Hz, 3H), 1.13 (s, 3H), 0.59 (s, 3H), 0.25 (s, 3H); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 325.9, 110.6, 106.8, 80.3, 63.1, 31.0, 26.8, 19.4, 15.9, 11.8.

Decompositions of 2, 3, and 11. To a NMR sample tube was loaded 10-12 mg of 2 (3 or 11) dissolved in 0.4 mL C_6D_6. The reaction was allowed to stand at room temperature and monitored periodically by ^1H NMR. Decomposition of 2 at room temperature afforded $Cp_2Zr(CH_3)_2$ and $Cp_2Zr(\eta^2\text{-}OCCH_2\text{-}O,C)$ (8). Decomposition of 3 at room temperature yielded $Cp_2Zr(OCH_3)CH_3$ and 8. Decomposition of 11 gave $Cp_2Zr(CH_3)_2$ and $Cp_2Zr(\eta^2\text{-}OCCHCH_3\text{-}O,C)$.

Kinetics of the Decomposition of 2. In a 5 mm NMR sample tube was loaded 2 (22-28 mg) and 0.4 mL of C_6D_6, then capped with a septum. Toluene (5 μL, 4.33 mg, 0.0470 mmol) was added via syringe to serve as the internal standard. Initial concentration of 2 was calculated by integrating the C_5H_5 or $Zr\text{-}CH_3$ resonances of 2 against toluene methyl signal in the ^1H NMR spectrum at room temperature. The sample was then placed in the probe of the JEOL FX-900 maintained at 46°C and spectra were obtained at regular intervals. The effective concentration of 2 was obtained from the relative integrals of $Zr\text{-}CH_3$ of 2 and toluene methyl. Least square analysis of second-order plots of $1/(2)\text{-}1/(2)_0$ vs. time yielded the rate constants. The procedure was repeated for various concentrations of 2 at different temperatures. In some cases, pyridine and $P(CH_3)_3$ were added to the reaction mixture. Activation parameters were obtained from least square analysis of $\ln k/T$ vs. $1/T$ plots.

Reaction of 1·2 THF with Cp_2ZrCl_2. In a 5 mm NMR tube was loaded 20 mg of 1·2 THF and 1 equiv Cp_2ZrCl_2. The tube was capped with a septum and 0.4 mL of toluene-d_8 was added via syringe at -78°C. ^1H NMR spectrum recorded at -20°C showed one clean product (4): δ 6.01 (s, 10H), 5.84 (s, 10H), 4.36 (s, 1H), 3.87 (s, 1H), 0.13 (s, 3H). The reaction mixture was kept at -20°C overnight. A new isomer (4') was observed. ^1H NMR δ 5.92 (s, 10H), 5.77 (s, 10H), 4.92 (d, J = 1 Hz, 1H), 4.33 (d, J = 1 Hz, 1H), 0.59 (s, 3H); ^{13}C NMR δ 291.0, 112.3, 109.5, 90.8, 36.4. The light yellow solution of the new isomer darkened upon standing at room temperature to give Cp_2ZrCH_3Cl and $Cp_2Zr(\eta^2\text{-}OCCH_2\text{-}C,O)$.

Preparation of $(Cp_2ZrCH_3)(\mu\text{-}\eta^2\text{-}OCCH_2\text{-}O,C)(Cp_2ZrH)$ (5). A suspension of 0.75 g (2.0 mmol) 1·Et_2O and 0.60 g (2.0 mmol) Cp_2ZrHCl in 40 mL toluene was stirred at room temperature for 1 h. The reaction mixture was filtered through a medium frit filter packed with 2 cm celite. The filtrate was concentrated under vacuum. The resulting solid was washed three times (10 mL each) with ether then dried under vacuum to yield 0.40 g (40%) of 5. ^1H NMR (C_6D_6, 90 MHz) δ 5.60 (s, 10H), 5.50 (s, 10H), 5.44 (s, 1H), 4.72 (s, 1H), 0.56 (d, J = 1 Hz, 1H), 0.19 (broad s, 1H); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 191.8, 109.7, 104.3, 88.2, 21.7; IR (nujol) 1603, 1540 cm^{-1} ($\nu_{C=C}$).

Reaction of $(Cp_2ZrCH_3)(\mu\text{-}\eta^2\text{-}OCCH_2\text{-}O,C)(Cp_2ZrH)$ (5) with CH_3I. To a NMR sample tube containing 11 mg (0.022 mmol) of 5 in 0.4 mL C_6D_6 was added 10 μL (large excess) of CH_3I via syringe. An intermediate was observed upon mixing of the reagents: ^1H NMR δ 6.07 (s, 10H), 5.98 (s, 10H),

4.09 (s, 1H), 3.55 (s, 1H), 0.14 (s, 3H). After standing at room temperature for 20 min, only a new isomer (6) was present with ^{1}H NMR δ 5.93 (s, 10H), 5.76 (s, 10H), 4.79 (d, J = 1.5 Hz, 1H), 4.28 (d, J = 1.5 Hz, 1H), 0.60 (s, 3H). The final product was unstable at room temperature and decomposed to Cp_2ZrCH_3I and $Cp_2Zr(\eta^2\text{-}OCCH_2\text{-}O,C)$ (8).

Preparation of $(Cp_2ZrCH_3)(Cp_2ZrCHCH_2)(\mu\text{-}O)$ (7). To a suspension of 0.38 g (1.0 mmol) 1·Et_2O and 0.30 g (1.2 mmol) Cp_2ZrHCl in 20 mL Et_2O at -40°C was added 20 mL of THF. The reaction mixture was stirred at -40°C for 3 h then 0°C for 2 h before filtering through a medium frit packed with 2 cm celite. The filtrate was concentrated under vacuum to give a solid which was washed with ether to yield 0.30 g (60%) of 7. ^{1}H NMR (C_6D_6, 90 MHz) δ 7.56 (dd, J = 20, 15 Hz, 1H), 6.57 (dd, J = 15, 4.4 Hz, 1H), 5.77 (dd, J = 20, 4.4 Hz, 1H), 5.80 (s, 10H), 5.75 (s, 10H), 0.26 (s, 3H); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 167.3, 128.4, 115.4, 115.1, 47.4; IR (nujol) 738 cm^{-1} (ν Zr-O-Zr).

Reaction of Z,E-10 with Cp_2ZrCH_3Cl. To a 5 mm NMR sample tube was loaded 12 mg (0.030 mmol) of Z,E-10 (in 3:1 ratio) and 8 mg (1 equiv) of Cp_2ZrCH_3Cl. The sample tube was capped and kept in liquid N_2. THF-d_8 (0.4 mL) was added via syringe. The frozen solvent was thawed and the sample was stored at -50°C. ^{1}H NMR spectrum of the reaction was recorded at this temperature. ^{1}H NMR δ 6.18 (s, 10H), 5.68 (s, 10H), 5.18 (q, J = 6.3 Hz, 3H), 1.80 (d, J = 6.3 Hz, 3H), 0.15 (s, 3H), -0.67 (s, 3H). The same spectrum was obtained at room temperature. Difference ^{1}H NOE spectroscopy: irradiation of the downfield Cp resonance enhanced vinylic resonance

at δ 5.18 and Zr-CH_3 at δ 0.15. Irradiation of Cp resonance at δ 5.68 resulted in enhancement of methyl protons at δ 1.80 and Z-CH_3 at δ -0.67.

Photolysis of $Cp_2Zr\phi_2$ and $Cp_2Zr(OC(CH_3)=CH_2)CH_3$[26] (28). To a pyrex NMR sample tube fitted with a septum cap was loaded 35 mg (0.09 mmol) of $Cp_2Zr\phi_2$ and 0.5 equiv of **28** dissolved in 0.5 mL C_6D_6. The tube was irradiated under UV for 2.5 h. ^1H NMR showed complete disappearance of the enolate and appearance of $(Cp_2ZrCH_3)(Cp_2ZrC(CH_3)=CH_2)O$ in 60%. ^1H NMR (C_6D_6, 90 MHz) δ 5.81 (s, 10H), 5.78 (s, 10H), 2.09 (broad s, 3H), 0.27 (s, 3H), vinyl protons were not located. Excess anhydrous HCl gas was introduced to the NMR tube via syringe. ^1H NMR of the hydrolysis reaction showed resonances due to propene, methane and $(Cp_2ZrCl)_2O$.

Thermolysis of 12, 13, and 15. Compounds **12**, **13**, and **15** were generated <u>in situ</u> from reactions of **2** or **11** with ϕCHO and acetone in C_6D_6. Compound **12** was heated at 70°C for 5 min. ^1H NMR showed a clean reaction producing stvrene and $(Cp_2ZrCH_3)_2O$. ^1H NMR δ 5.74 (s, 20H), 0.24 (s, 6H). Compound **13** was heated at 75°C for 4 h. ^1H NMR showed clean decomposition to isobutylene and $(Cp_2ZrCH_3)_2O$. Compound **15** was heated at 75°C for 10 min. ^1H NMR of volatile products collected by vacuum transfer showed a 2:1 mixture of trans:cis β-methyl styrene. The ^1H NMR of the residue shows resonances due to $(Cp_2ZrCH_3)_2O$.

Reaction of Cp_2ZrHX with $Cp_2Zr(O(CH_3)=CH)CH_3$ (28) (X = CH_3, Cl).

Compound **28** and excess Cp_2ZrHX were placed in a 5 mm NMR sample tube along with 0.4 mL of C_6D_6. The tube was capped and heated to 70°C for 1 min. ^1H NMR spectrum showed a clean reaction that yielded two products, $(Cp_2ZrCH_3)(Cp_2ZrX)O$ and $Cp_2Zr(CH_2CH_2CH_3)CH_3$. (Cp_2ZrCH_3)-$(Cp_2ZrCl)O$: ^1H NMR δ 5.93 (s, 10H), 5.82 (s, 10H), 0.31 (s, 3H).

Preparation of $Cp_2^dZrCH_3Cl$. A mixture of 90 mL freshly distilled C_5H_6, 10 mL Et_2O, 50 mL of D_2O and a small amount of Na metal was stirred at room temperature for 2 days. The organic layer was separated and dried over $MgSO_4$. Ether and monomeric CpH(D) were separated form high boiling material by distillation. Additional CpH(D) was obtained from heating the residue at 100°C. The combined ether and CpH(D) was again stirred with D_2O (25 mL)and small amount of Na. The procedures of deuterium exchange, separation and distillation were repeated four times. The final ether mixture was allowed to stand at RT for a week to achieve maximum dimerization of CpH(D). After removing ether by distillation, the residue was heated at 100°C to yield 14.0 mL of CpD. ^1H NMR shows 77% deuterium incorporation.

To a suspension of 5.4 g (0.22 mol) of NaH in 80 mL THF at 0°C was added a solution of 14.0 mL (17.3 g, 0.17 mmol) of freshly distilled CpD in 20 mL THF. After gas evolution, the purple reaction mixture was stirred at room temperature for 30 min and solvent was removed under vacuum. The residue was recrystallized from cooling a THF-pentane solution to -20°C. The pink solid was collected by filtration, washed with pentane and dried under vacuum to yield 13.8 g (92%) of $NaCp^d$.

Preparation of $Cp_2^dZrCl_2$ was achieved by closely following a known method.[43] To a solution of 11.5 g (0.049 mol) of $ZrCl_4$ in 50 mL benzene was added 8.8 g (0.10 mol) of $NaCp^d$ in THF dropwise at 0°C. The reaction mixture was stirred at room temperature for 3 h then refluxed for 10 min. After the solvent was removed under vacuum the residue was extracted with 250 mL of CH_2Cl_2 and filtered. The filtrate was concentrated on rotovap to yield 5.3 g (37%) of $Cp_2^dZrCl_2$.

$Cp_2^dZrCl_2$ was treated with H_2O and ϕNH_2 to yield $(Cp_2^dZrCl)_2O$ in 97% yield. $Cp_2^dZrCH_3Cl$ was obtained from reaction of $(Cp_2^dZrCl)O$ with $Al(CH_3)_3$ in 58% yield. Both conversions followed published procedures.[40,41]

Kinetics of the Isomerization of 2. A 5 mm NMR sample tube was loaded 22 mg (0.050 mmol) of **1·2** THF and 14 mg (0.051 mmol) of $Cp_2^dZrCH_3Cl$ and capped with a septum. The tube was placed in liquid N_2 and 0.4 mL of toluene-d_8 was slowly added via syringe. The sample was thawed and agitated briefly to allow formation of **2** at -20°C. The sample was then placed in the NMR probe at 10°C and spectra were obtained at regular intervals. The effective concentration of each isomer was calculated from the relative integrals of the two C_5H_5 signals. Least square analysis of first order plots of $\ln(X_e-X)$ vs. time yielded the rate constants. The procedure was repeated and activation parameters were derived from additional rate constants recorded at 15 and 24°C.

Reactions of 1·2 THF with L_2PtR_3Cl (R = CH_3, Cl; L = PMe_3, $PMe_2\phi$, $PMe\phi_2$). A 5 mm NMR tube was loaded with **1·2** THF (~20 mg), 1 equiv of L_2PtR_2Cl and 0.4 mL of C_6D_6. The sample tube was

capped, shaken and centrifuged. Using 2 THF as internal standard, the ^{1}H NMR spectrum showed quantitative formation of one product. ^{1}H, ^{31}P NMR data and proposed structure of the products are shown in Table VI.

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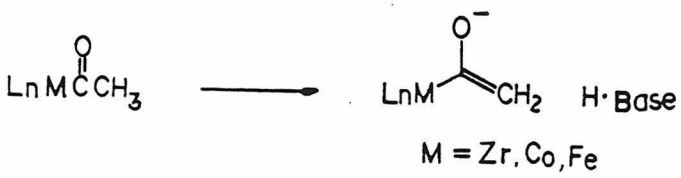
CHAPTER III

The Reactions of Phosphonium and Sulfoxonium Ylides With Acyl Derivatives of Titanocene and Zirconocene

Introduction

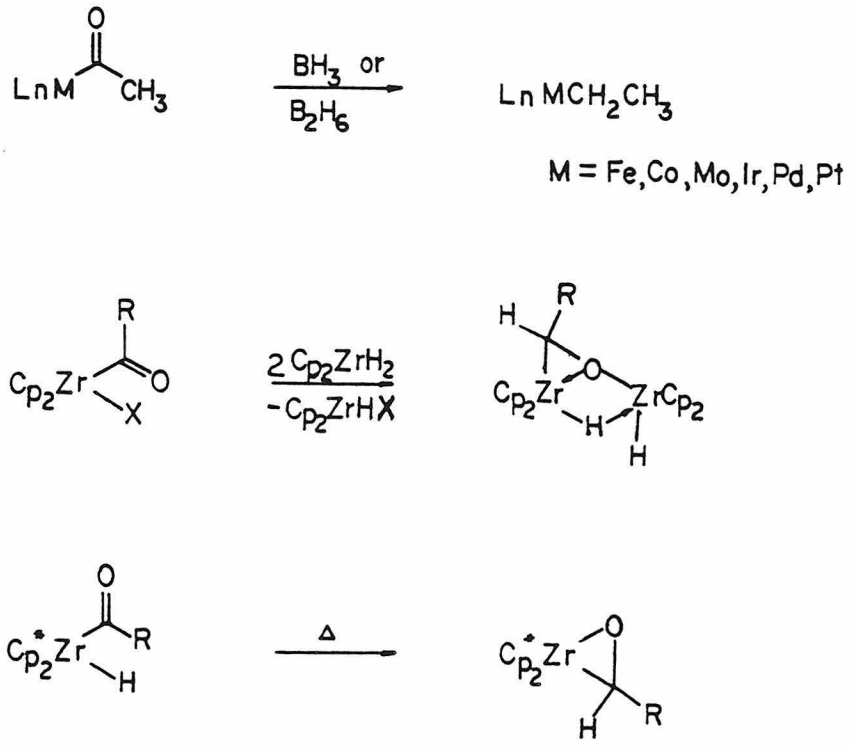
The importance of transition metal acyl complexes in stoichiometric and catalytic transformations has now been widely accepted. Metal acyl derivatives have been prepared by oxidative-addition of acyl halides, carboxylic anhydrides or by insertion reactions.[1]

Based on the known reactivities of the acyls in the literature, similarities between transition metal acyl complexes and their organic carbonyl analogs (ketone, ester and aldehyde) have emerged. Enolates have long been used in the C-C bond formation in organic synthesis. Deprotonation of the acyl ligands with bulky non-nuclophilic base to form the corresponding metallaenolates has been recently reported.[2-4,5c] These reactive species have shown activities comparable to the organic enolates in alkylation and aldol condensation reactions. Furthermore, reactions of chiral ironenolates exhibit high asymmetric induction which is potentially useful for the enantiomeric synthesis of organic molecules.[3b]



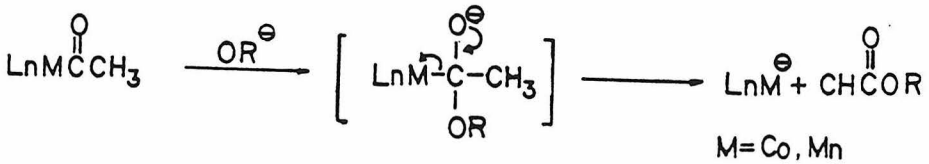
The reactivities of acyls towards nucleophiles, however, are not well understood. Examples are limited to mostly metal hydride reactions. Iron and ruthenium acyls of $CpM(CO)(PR_3)(COCH_3)$ have been reduced to metal alkyls by BH_3/THF. Initial coordination of the Lewis acid BH_3 to acyl

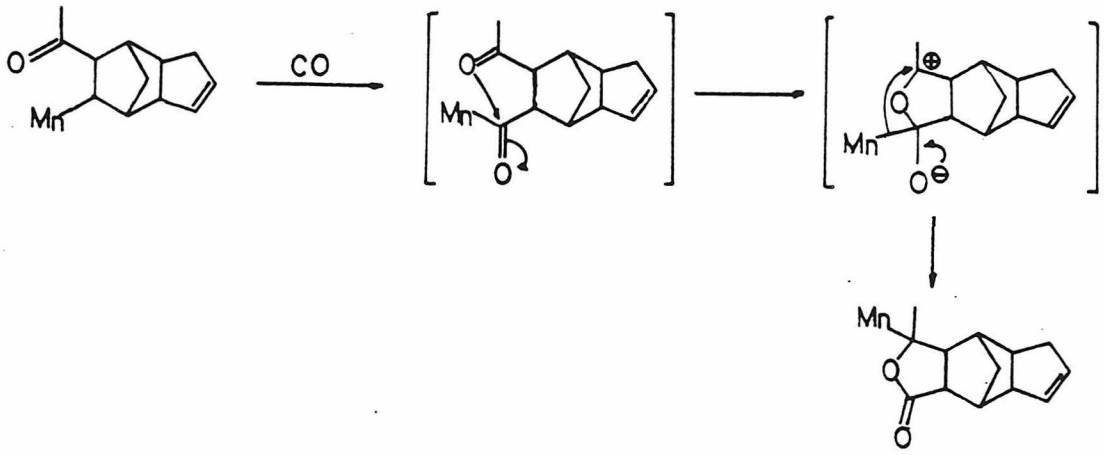
oxygen followed by hydride addition and elimination are proposed. Similar reductions were also observed between reactions of diborane and acyl complexes of Co, Mo, Ir, Pd, an Pt.[6] Intra- and intermolecular additions of hydride to acyl carbonyl have been demonstrated for the formation of metal aldehyde complexes of Zr.[7,8,16]



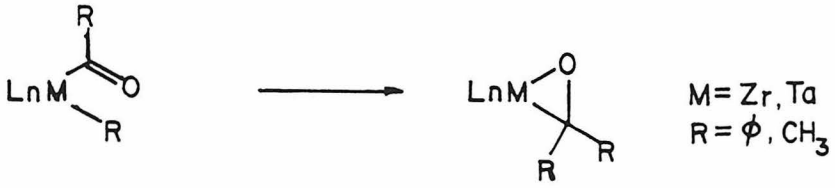
Reactions of alkoxy nucleophiles with metal acyls often show cleavage of the metal-carbon bonds and formation of carboxylic acid derivatives presumably by addition of OR^- to acyl carbonyl followed by elimination of the metal fragment.[9] The analogous sequence is also proposed for the lactone formation from carbonylation of a Mn alkyl. complex.[10] In this case, the oxygen atom of an existing carbonyl functions as the nucleophile.

Unfortunately, reactions between carbon nucleophiles and acyl complexes are rare. Treatment of metal acyls with alkyl lithium reagents often leads to products not involving the carbonyl sites.[11] Although no direct

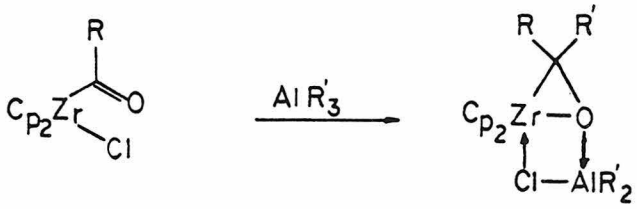




evidence has been suggested, intramolecular addition of metal alkyl to acyl. has been in the formation of ketone complexes of Zr and Ta.[12,13] This process is also proposed in the carbonylations of titanacyclobutene,[14] titanacyclopentane,[15] zirconacyclopentene,[16] and Cr Fischer carbene-alkyne adduct[17] to yield Ti vinyl ketenes, cyclopentanone, Zr ketones and Cr ketene complexes, respectively.



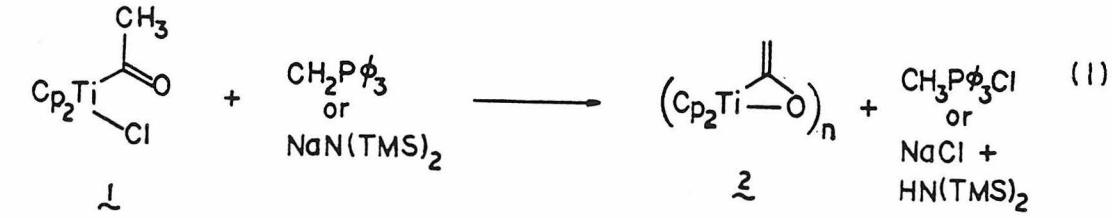
Recently, we have discovered a Lewis acid ($AlMe_3$) catalyzed formation of Zr ketone complexes from acyls in our laboratories.[18] The exact nature of the reaction is currently under investigation. Two mechanistic possibilities are (1) addition of Al-alkyl to carbonyl followed by halide elimination, (2) formation of Zr-alkyl by metathesis reaction and subsequent intramolecular alkyl addition to aryl.



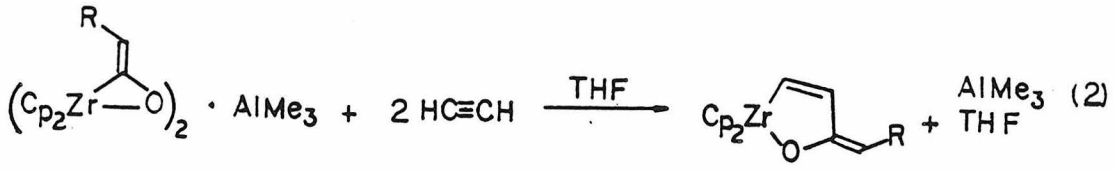
In this chapter, we will examine the interactions of metal acyl complexes of Ti and Zr with neutral carbon nucleophiles of phosphonium and sulfoxonium ylides.[19]

Results and Discussion

It has been shown that reactions of th Ti chloro acyl complexes (1) with CH_2PPh_3 afford ketene complexes (2) via dehydrohalogenation. The same products were also obtained when strong non-nucleophilic bases (e.g., $NaN(TMS)_2$) were used in the reactions presumably by the same mechanism[5a] (eq. 1). This methodology has been extended to the Zr series. The substituted Zr ketone analogs are of interest for their ease in preparation and handling. More importantly, Lewis acid activated Zr ketenes have been demonstrated to react cleanly with olefinic substrates to yield cyclic

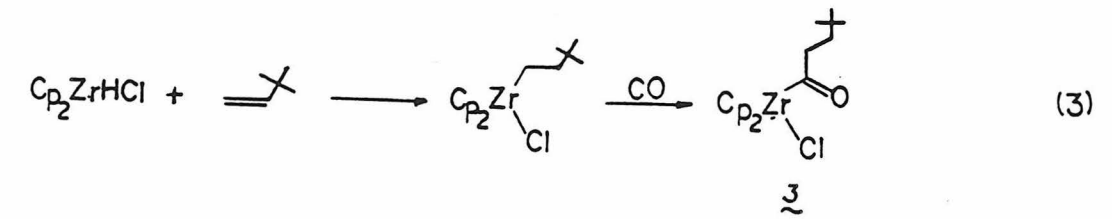


(1)

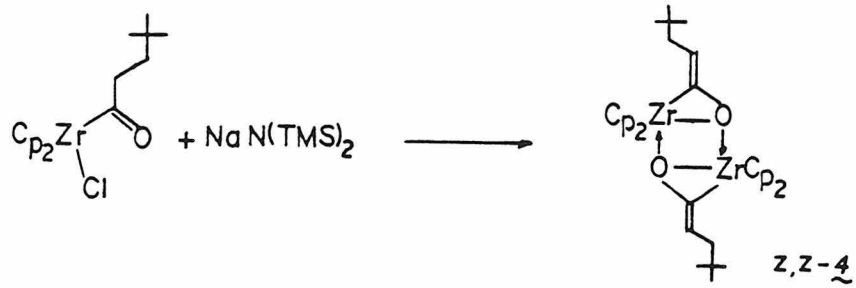


(2)

enolates that are potentially useful in the synthesis of large organic molecules[20] (eq. 2). The Zr chloro acyls, precursors to the ketene complexes, can be easily prepared from hydrozirconation of alkenes followed by carbonylation reaction[1d] (eq. 3). As previously reported,[5a] treatment of complex **3** with $NaN(TMS)_2$ gave Zr ketene dimer **4** in high yield (80%) (eq. 4). A minor product was also observed. Complex **4** was assigned as th Z,Z-isomer by comparison of its vinyl proton shift (5.68 ppm) with a structurally characterized Z,Z-**4**-$AlMe_3$ adduct (6.05 ppm).[20] The minor product contained one vinyl proton at 4.61 ppm and was assumed to be the isomeric dimer Z,E-**4**.[21]



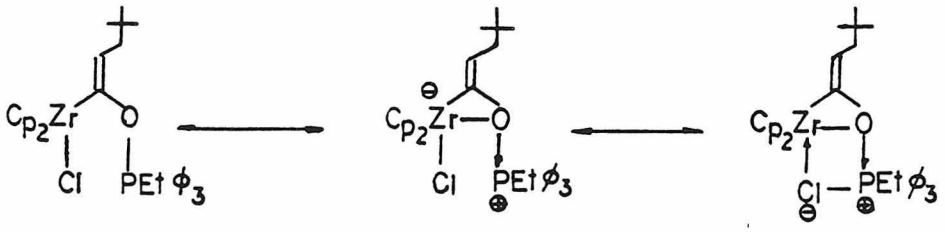
(3)



Z,Z-4 (4)

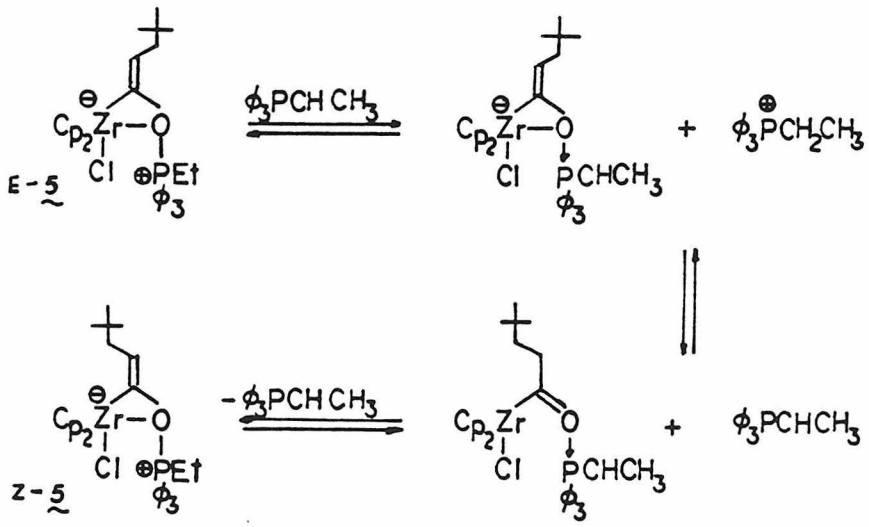
It is not clear whether the Z isomer of the Zr ketene complex is the kinetic or thermodynamic product of the reaction. For steric reasons, the strong bulky base $NaN(TMS)_2$ seems to favor front side deprotonation and the formation of the Z isomer. No further isomerization to the E-isomer has yet been observed. Deprotonation of **3** using bulky but less basic phosphorous ylide $CH_3CHP\phi_3$ has enabled us to observe an intermediate at low temperature. Mixing of **3** and $CH_3CHP\phi_3$ in toluene at -20°C gave a homogeneous orange solution. Addition of pentane to the reaction precipitated a yellow solid. Isolation of the solid was impractical for its low melting point (<RT). The identity of the yellow precipitate was deduced from its ^1H, ^{13}C, and ^{31}P NMR data (Table I) to be a $CH_3CH_2P\phi_3^+Cl^-$ adduct of Zr ketene (**5**). The lack of C-P coupling at the quartenary carbon suggests that the P is coordinated to the oxygen and the chemical shift of the vinyl proton (4.71 ppm) implies a trans double bond geometry for the ketene complex. Although the solubility of **5** in toluene resembles that of a neutral complex, the ^{31}P NMR signal (26.1 ppm) suggests a cationic rather than a penta coordinated phosphorous.[22] The true form of E-**5** is probably an average of the three resonance structures shown in

Scheme I

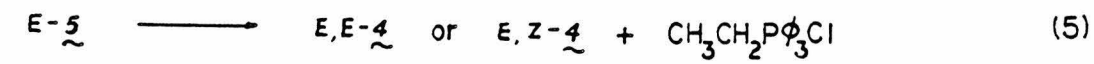


Scheme I. After warming a toluene solution of E-5 to 0°C, a second product was observed. This new complex was assigned to be th Z isomer of 5 (Z-5) based on its vinyl proton shift (5.41 ppm). The rate of the isomerization varied from hours to days at 0°C. A possible mechanism is shown in Scheme II suggesting isomerization via proton exchange as catalyzed by the excess ylide present in the reaction mixture. After overnight at room temperature, the solution of E-5 afforded $CH_3CH_3P\phi_3^+Cl^-$ and ketene

Scheme II

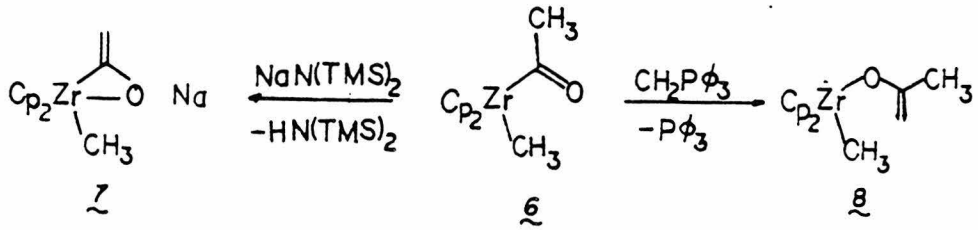


dimers of E,E-4 or E,Z-4 (eq. 5). The ratio of E,E-4 to E,Z-4 is depended on the rate of isomerization of E-5. Only a small amount of Z,Z-4 was observed. The above results demonstrate that the stereochemistry of substituted Zr ketene complexes can be controlled by employing different bases for the dehydrohalogenation of the chloro acyl complexes.



(5)

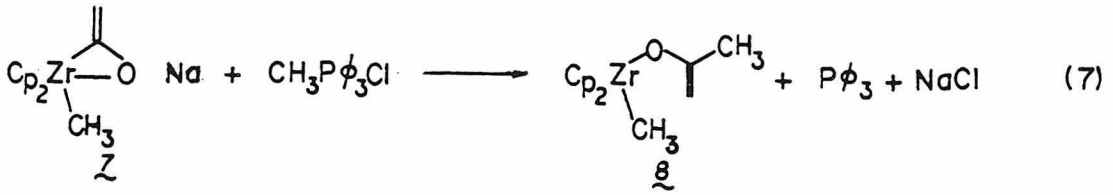
Replacing the halide leaving group with a alkyl ligand, the Zr acyl complex $Cp_2Zr(COCH_3)CH_3$ (6) when treated with $NaN(TMS)_2$ and $CH_2P\phi_3$ gave the ketene anion 7 and enolate 8,[23] respectively[5c,23] (eq. 6). It appears



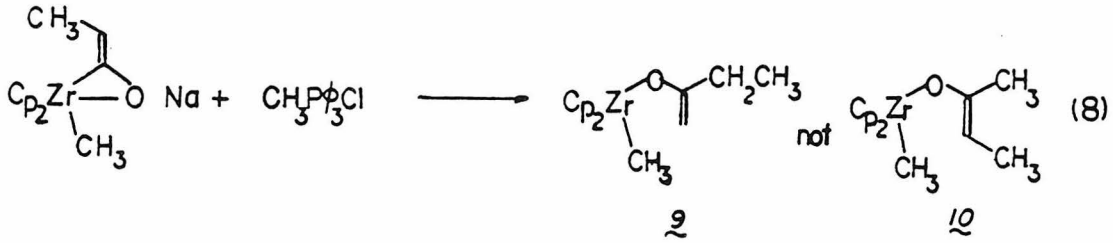
(6)

that the methyl ligand decreases the α-proton acidity of the acyl complex. Instead of serving as a base in the reaction, the phosphorous ylide reacts as a nucleophile transferring the methylene group to the acyl complex. Enolate 8 was also obtained from reaction between anion 7 and $CH_3P\phi_3^+Cl^-$ (eq. 7). There are two probable mechanisms that can account for the observation. First, we exclude the possibility of enolate formation by direct alkylation of 7 at the quarternary carbon based on alkyl labeling

experiment. Treatment of methyl substituted anion with $CH_3P\phi_3^+Cl^-$ cleanly afforded enolate 9 (eq. 8). No direct alkylation product 10 was observed. The alternative mechanism suggests that anion 7



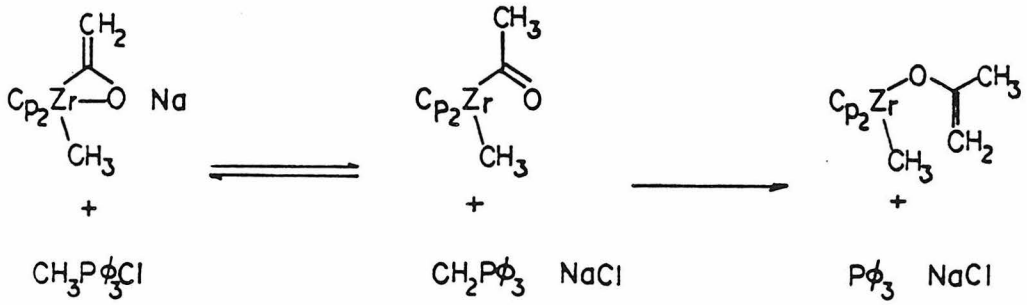
(7)



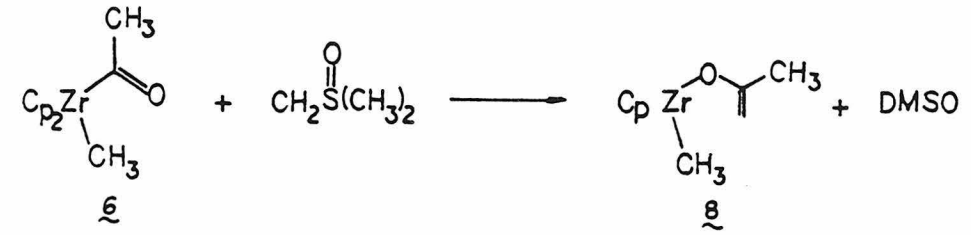
(8)

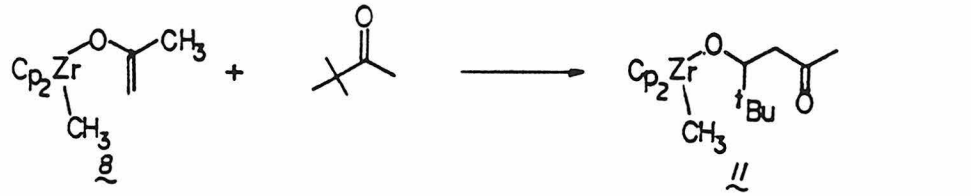
deprotonates $CH_3P\phi_3^+Cl^-$ to form $CH_2P\phi_3$ and the acyl complex 6. Although the relative basicity between $CH_2P\phi_3$ and anion 7 is not known, the equilibrium is shifted to the right by the irreversible formation of enolate 8 from $CH_2P\phi_3$ and the acyl complex (Scheme III). The phosphonium ylide is

Scheme III

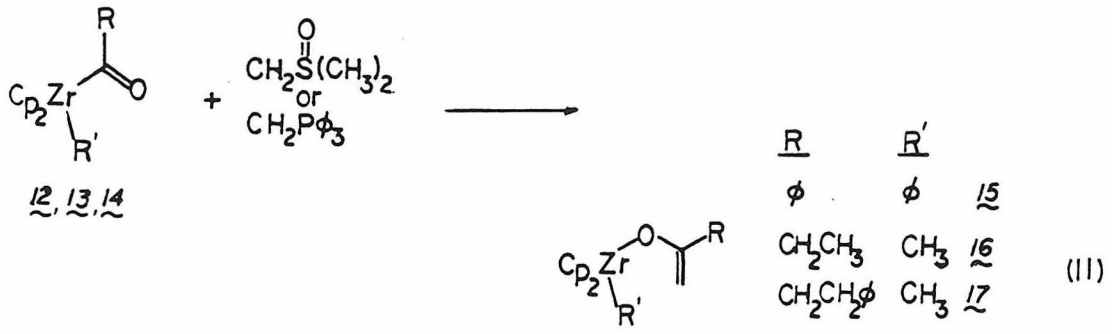


not the only reagent that can transform acyls into enolates. Treatment of **6** with the less basic sulfoxonium ylide $CH_2SO(CH_3)_2$ resulted in clean and higher yield of **8** (eq. 9). Complex **8** was isolated and purified by vacuum distillation (60°C, 10^{-4} torr). Contrary to most transition metal organometallic complexes, **8** is a colorless liquid at room temperature (a crystalline white solid at -40°). Complex **8** was characterized by IR, ^1H, ^{13}C NMR, and elemental analysis. The enolate nature of **8** was confirmed by its reaction with organic carbonyls. Pivalaldehyde reacts with **8** instantly to give the aldol product of $Cp_2Zr(OCH^tBuCH_2COCH_3)CH_3$ (**11**) (eq. 10).





The transformation of Zr alkyl acyls appears to be general. Complexes of $Cp_2Zr(CO\phi)\phi$ (**12**), $Cp_2Zr(COCH_2CH_3)(CH_3)$ (**13**), and $Cp_2Zr(COCH_2CH_2\phi)CH_3$ (**14**) were also converted to their corresponding enolates $Cp_2Zr(OC\phi{=}CH_2)\phi$ (**15**), $Cp_2Zr(OCCH_2CH_3{=}CH_2)CH_3$ (**16**), and $Cp_2Zr(OCCH_2CH_2\phi{=}CH_2)CH_3$ (**17**) by $CH_2P\phi_3$ and $CH_2SO(CH_3)_2$ (eq. 11). Attempts to prepare enolates from substituted phosphorous ylides were not successful. Reaction of **6** with $CH_3CHP\phi_3$ gave a mixture of unidentified

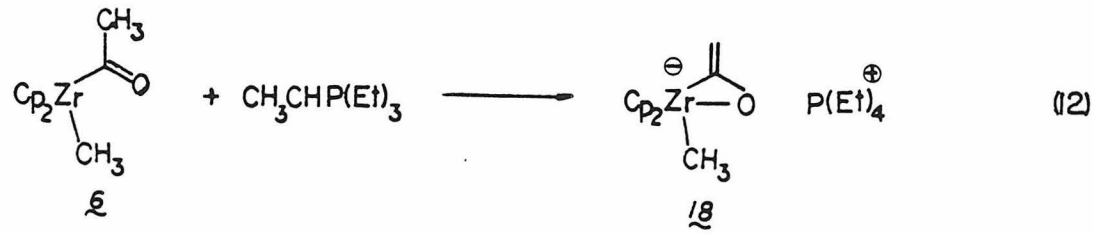


12, 13, 14

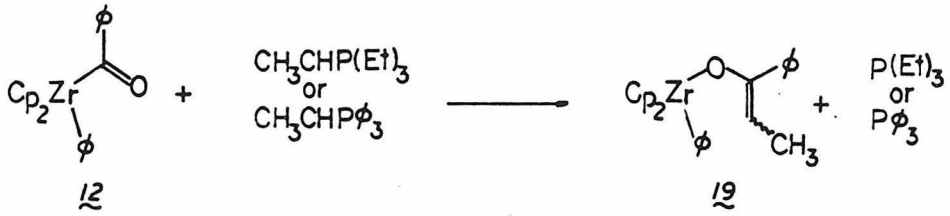
R	R′	
φ	φ	15
CH_2CH_3	CH_3	16
$CH_2CH_2\phi$	CH_3	17

(11)

products that contained no enolate or ketene anion (^1H NMR). Triethyl phosphonium ethylide $CH_3CHP(CH_2H_3)_3$ reacted as a base when treated with 6 to give anion $Cp_2Zr(OCCH_2)CH_3^-$ with PEt_4^+ as the counterion (18) (eq. 12). Without any acidic protons, $Cp_2Zr(CO\phi)\phi$ (12) reacted with either $CH_3CHP\phi_3$ or $CH_3CHP(Et)_3$ cleanly to give $Cp_2Zr(OC\phi{=}CHCH_3)\phi$ (19) (eq. 13). The ^1H NMR spectrum of complex 19 showed two vinyl proton signals (quartets at 4.92 and 4.93 ppm) and two methyl resonances (doublets at 1.71 and 1.72 ppm) in a ratio of 3:2. Since only one Cp resonance was observed and the difference in the vinyl proton shifts was small (0.01 ppm) for configuration isomers, we therefore considered complex 19 existed as a mixture of conformers (or rotamers). The double bond



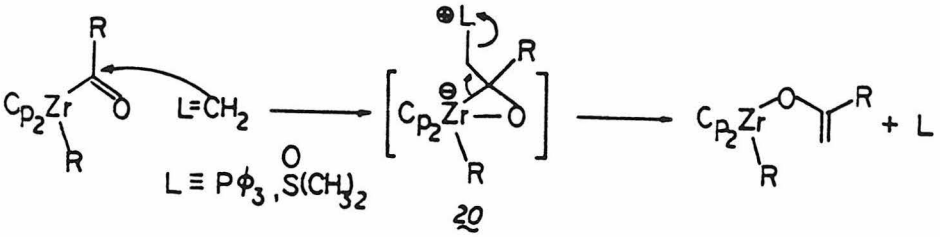
6 18 (12)



geometry of **19** is not known.

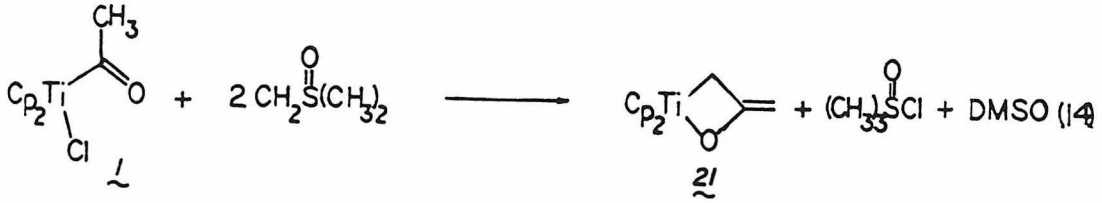
One plausible mechanism for the formation of enolates from acyls and ylides is shown in Scheme IV. Addition of the neutral ylide to th C=O of the acyl complex generates a zwitterion intermediate **20** which can subsequently rearrange and eliminate $P\phi_3$ or DMSO to form the enolate complex.

Scheme IV



Recall that chloro acyl complexes of Ti(1) reacted with phosphonium ylides to form neutral ketene complexes (2) (eq. 1). The possibility of enolate formation from the same complexes with less basic sulfoxonium ylides was examined. Treatment of a yellow suspension of acyl complex **1** with excess

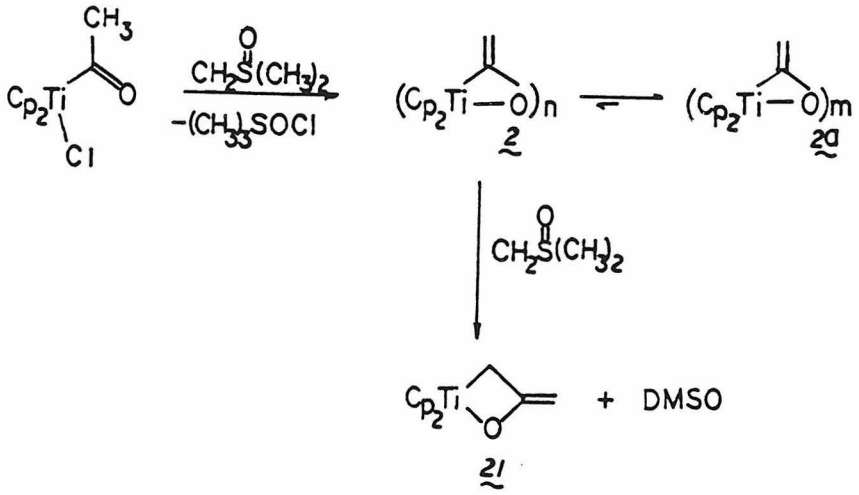
$CH_2SO(CH_3)_2$ (toluene, RT) resulted in a homogeneous solution from which a red solid **21** was isolate (72%) (eq. 14). The product **21** is moderately air sensitive and is stable in solid state at room temperature under inert atmosphere indefinitely. Complex **21** is not soluble in pentane and ether, but readily dissolves in other organic solvents. Unlike the oligomeric ketene complex **2** obtained from reaction of **1** and $CH_2P\phi_3$ (eq. 1), elemental analysis and spectral data (Table I) of **21** suggest a cyclic structure. Cryoscopic molecular determination revealed a monomeric **21** in solution (mol. wt. calcd., 234; found, 230).



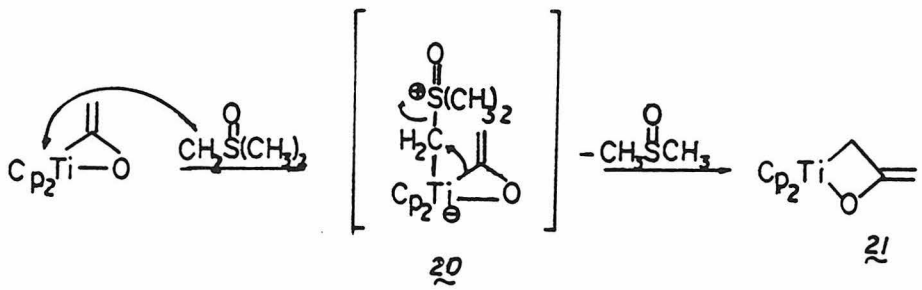
The carbon and hydrogen compositions of **21** and the reaction by-products $(CH_3)_2SOCl$ and $(CH_3)_2SO$, suggest that two succeeding reactions are involved in the generation of **21** from **1** and $CH_2SO(CH_3)_2$. The first step is thought to be the formation of ketene **2** and $(CH_3)_3SOCl$. The ketene complex reacts further with ylide to give **21** and DMSO. This hypothesis was examined by treatment of **2** prepared independently[5a] with $CH_2SO(CH_3)_2$. The red ketene isomer of **2** reacted instantly to give **21**. The same product **21** was also obtained from the isomeric yellow ketene **2a**, but much slower. This is consistent with previous observation that complex **2** is the kinetic and

reactive ketene oligomers and an equilibrium exists between 2 and 2a in solution in favor of 2a (1:10)[5a] (Scheme V). The coupling of the ylide CH_2 and the ketene complex is rationalized to proceed by an ionic intermediate 22 (resembled 20 in Scheme IV) generated by ylide coordination to the metal. Rearrangement of intermediate 22 and elimination of DMSO would then give the product observed (Scheme VI).

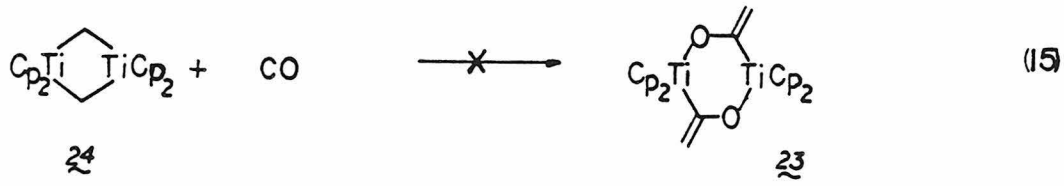
Scheme V



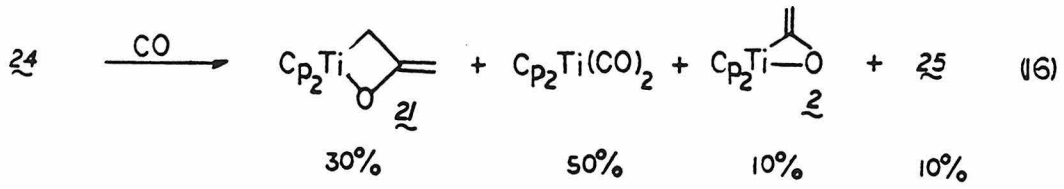
SchemeVI



Although misinterpreted as $(Cp_2TiOCCH_2)_2$ (23), complex 21 has been observed before in the reaction of $(Cp_2TiCH_2)_2$ (24) with CO[24] (eq. 15). The carbonylation of 22 was repeated and monitored by ^1H NMR. The signals corresponding to 21 an $Cp_2Ti(CO)_2$ increased with time at the expense of starting dimer 24. Red ketene 2 and an unidentified product 25 were also present in small but constant amount throughout the reaction. Bridging methylene complex 24 was completely consumed under 1 atm of CO after 22.5 h at room temperature. $Cp_2Ti(CO)_2$ and 21 were present in 50 and 30% based on internal standard (eq. 16). Many possible reaction pathways have been considered, but no attempts were made to elucidate the mechanism.



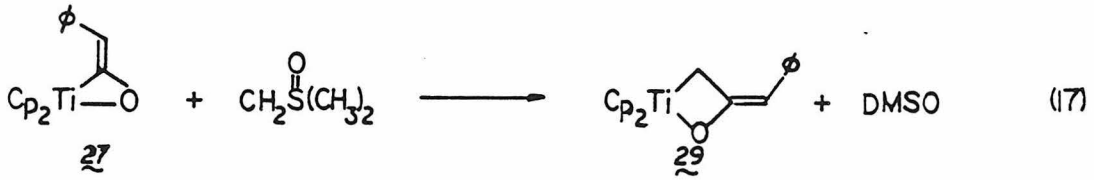
(15)



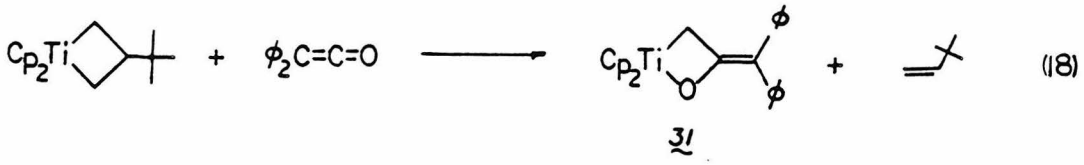
(16)

The sulfoxonium ylide $CH_2SO(CH_3)_2$ also reacts with mono-substituted Ti ketenes. Complex $Cp_2Ti(\eta^2\text{-}OCCH\phi\text{-}O,C)$ (27) was prepared by deprotonation of $Cp_2Ti(COCH_2\phi)Cl$ (26) with $NaN(TMS)_2$. Only one isomer of 27 was obtained. ^1H NOE experiments performed using 27 and its

ethylene insertion product titanaoxacyclopentane $Cp_2TiOCCH_2CH_2{=}CH\phi$ (28), however, failed to establish the doubled bond geometry of 27. The complex was tentatively assigned as the Z isomer based on possible steric interaction between th bulky base ($NaN(TMS)_2$) and the acyl complex. The Zr ketene complex 4 prepared in a similar manner as 27, also has Z double bond. The Ti ketene complex 27 reacted slowly with $CH_2SO(CH_3)_2$ ($t_{1/2}$ ~ 2 h) to yield $Cp_2TiOCCH_2{=}CH\phi$ (29) (CH_2Cl_2, RT, eq. 17). Complex 29 was characterized spectroscopically (^1H, ^{13}C NMR, Table I) for it decomposed in solution to unidentified products.



Disubstituted ketene complex $Cp_2Ti(\eta^2\text{-}OCC\phi_2\text{-}O,C)$[25] (30) reacted with $CH_2SO(CH_3)_2$ to give intractable products (no ^1H NMR signals). The diphenyl analog of 21, however, can be achieved by a complete different method of synthesis. Heating a toluene solution of 3-t-butyltitanacyclobutane[26] (a source of titanocene methylidene "$Cp_2Ti{=}CH_2$") and excess diphenylketene (70°C, 10 min) afforded analytically pure crystalline precipitates of 31 in 71% yield[27] (eq. 18). Complex 31 was characterized by both spectroscopic and chemical means. ^1H, ^{13}C NMR, and IR data of 31 are listed in Table I. Hydrolysis reaction of 31 using anhydrous HCl gas gave Cp_2TiCl_2 and $\phi_2CHCOCH_3$ (^1H NMR). Attempts to prepare 21 from "Cp_2TiCH_2" and CH_2CCO were unsuccessful, since free ketene dimerizes rapidly under reaction conditions.



31

Metallaoxacyclobutanes (e.g., **21**, **29**, **31**) have been proposed as intermediates in the transition metal catalyzed olefin epoxidations[28] and conversion of carbonyls to alkenes by metal alkylidenes.[29] The analogous complexes have been observed in the olefin oxidation by SO_3,[30] as well as in "Wittig" transformations[31,22] (Figure 1). Besides complex **21**, **29**, and **31**, only three other metallaoxacyclobutanes have been reported. Preparations of these complexes involved treatment of high valent, electron rich transition metals (Ir(I), Rh(I), and Pt(0)) with tetracyano oxiranes (eq. 19). The platinaoxacyclobutane has been structurally characterized to show a puckered ring system.[32]

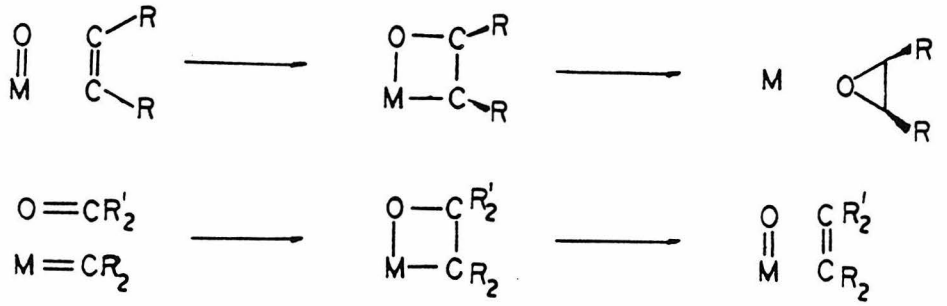
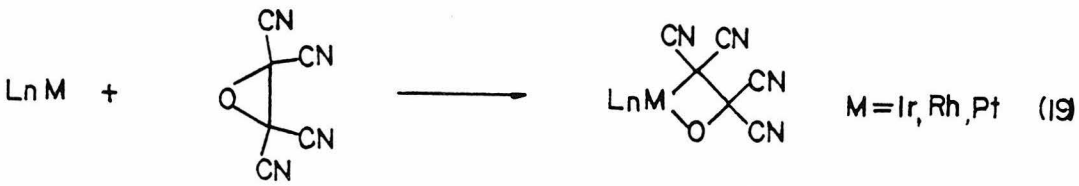


Figure 1



Recrystallization of **21** and **31** from a variety of solvents failed to yield crystals suitable for X-ray analysis. The solution structures of the titanoxacyclobutanes were examined using Dynamic NMR techniques. At room temperature, the ^1H NMR spectrum of **21** exhibited one sharp singlet for the two Cp ligands and a broad lump for the Ti-CH_2 protons. The methylene signal sharpened with increased temperature characteristic of an exchange process. After cooling a CD_2Cl_2 solution of **21** to -40°C, the methylene signal resolved into two doublets (2.23 and 1.24 ppm, $\Delta\nu$ = 87 Hz) with geminal coupling of 10 Hz. AT -60°C, the Cp's also appeared as two singlets ($\Delta\nu$ = 2 Hz) (Fig. 2). The above results strongly suggest a puckered ring for **21** at low temperature. Interconversion of the two degenerated puckered conformers by ring flip is rapid at room temperature. The free energy of activation ($\Delta G^{\ddagger}$) for the exchange process was calculated to be 13.0 ± 0.2 kcal. Similar ring inversion was also observed for **29** with $\Delta G^{\ddagger}$ = 12.9 ± 2.2 kcal (Fig. 3). Unlike **21** and **29**, complex **31** is puckered at room temperature (two Cp's and two Cp_2TiCH_2 signals, Table I). Coalescence of the Cp resonances was achieved at 100°C and $\Delta G^{\ddagger}$ for the ring flip was calculated to be 19.2 ± 0.2 kcal (Fig. 4). It appears that in the puckered conformation of titanaoxacyclobutane, the back donation from the lone pair of electrons of the oxygen atom to the metal and orbital is maximized (Fig. 5). Similar argument for the π-donation of an alkoxy ligand to Ti(IV) has been used to rationalize the lengthening of Ti-Cl bond in $Cp_2Ti(OCH_2CH_3)Cl$.[33] The large difference observed in the $\Delta G^{\ddagger}$'s of **21** and

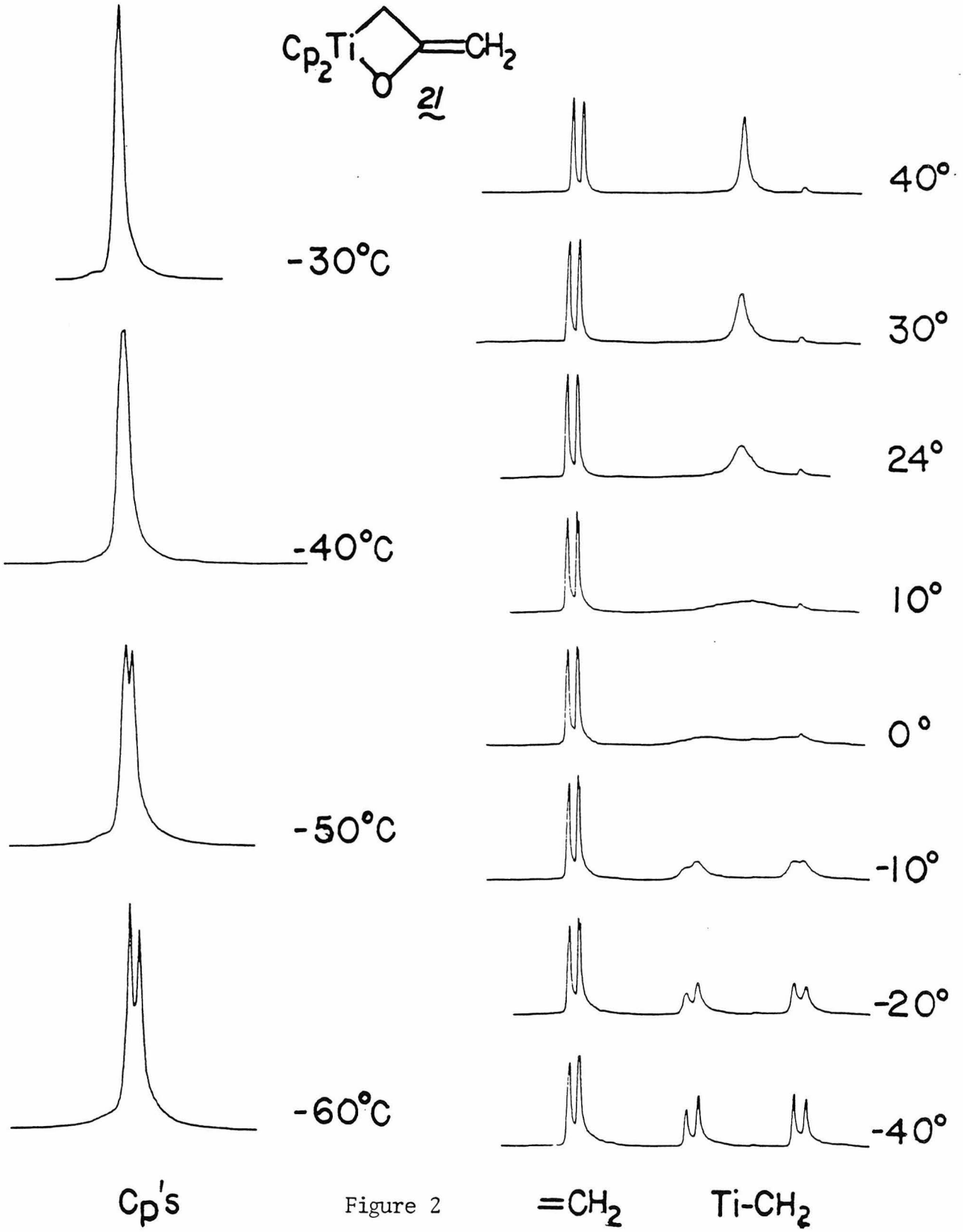
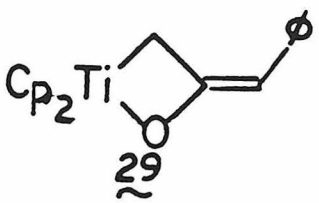
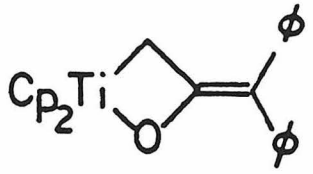


Figure 2



29



31

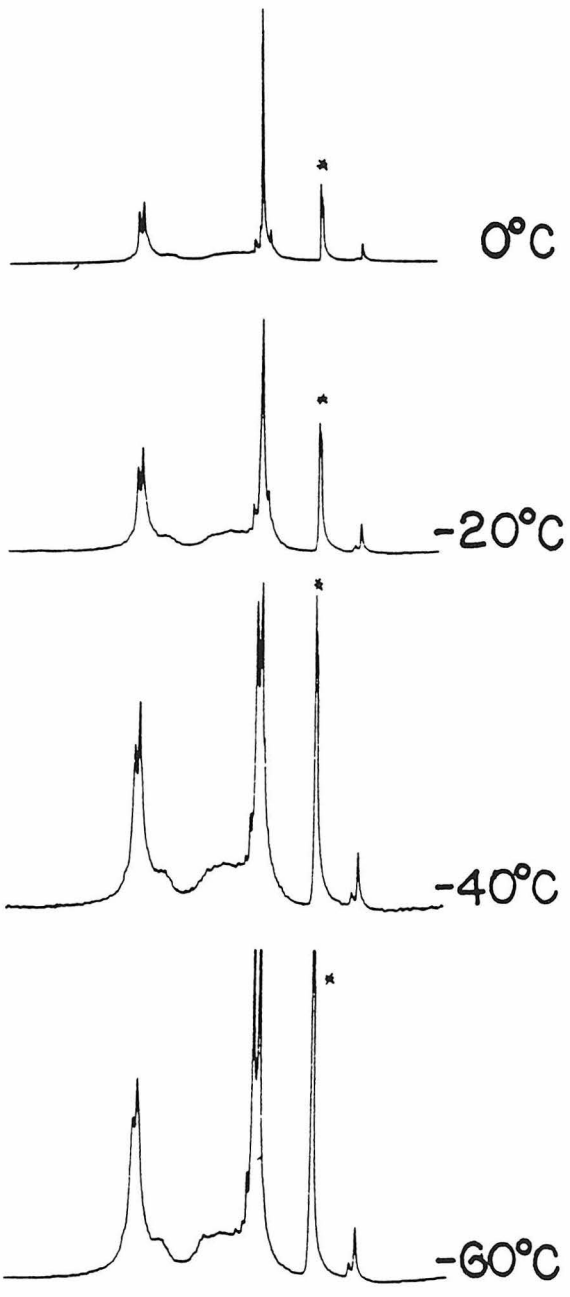


Figure 3

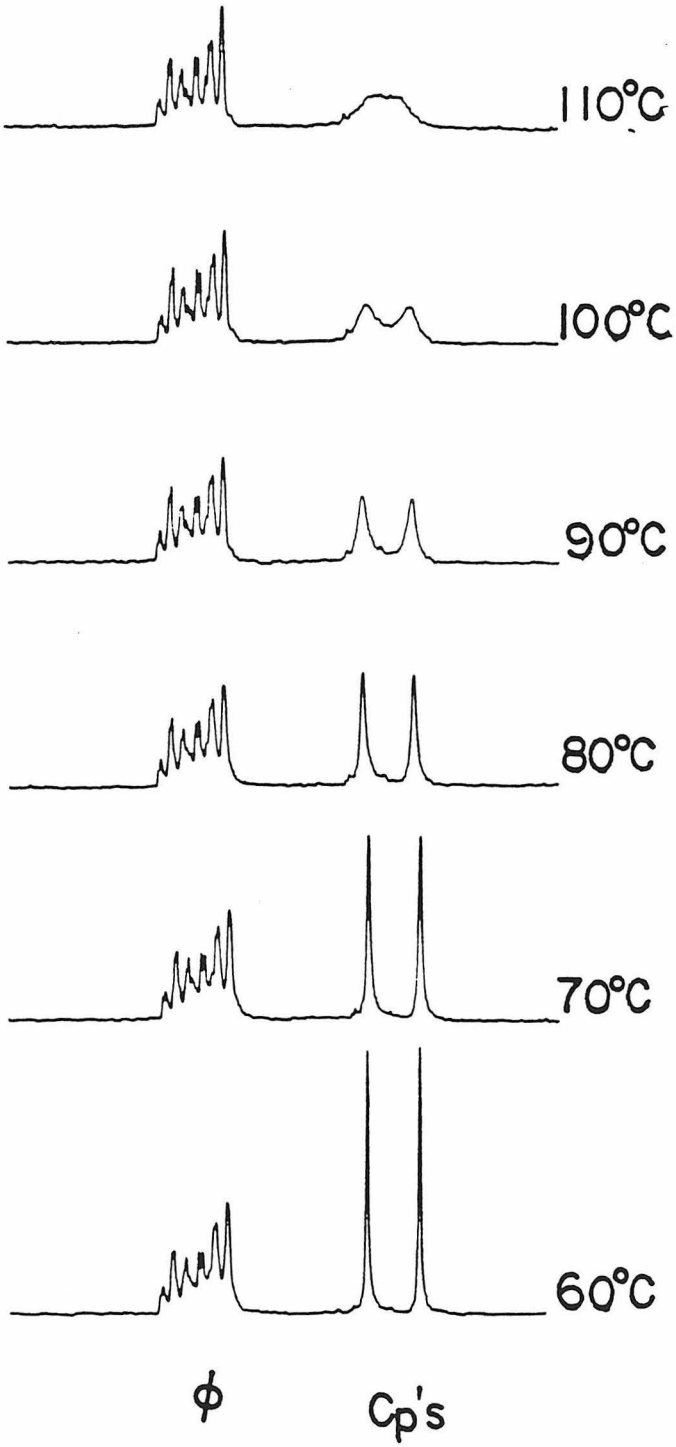
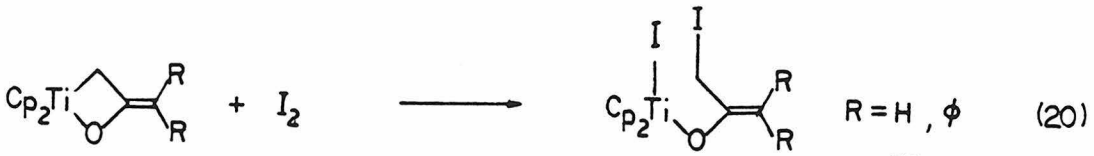


Figure 4

Figure 5

31 is attributed to the additional stabilization for 31 achieved by delocalization of the second lone pair of electrons on the oxygen through the exo double bond to the aryl group. The same stabilization, however, is not present for mono-phenyl 29 ($\Delta G^{\ddagger}$: 31 > 21 ~ 29). This is rationalized as the phenyl ring is out of conjugation by free rotation. In complex 31, for steric and electronic reasons, one of the two phenyl rings is forced to be in conjugation with the exo double bond.

Complex 21 and 31 are unreactive toward ethylene and CO. Hydrolysis reaction of 21 and 31 with anhydrous HCl gave acetone and $\phi_2CHCOCH_2$, respectively. Treatment of 21 with one equivalent of iodine resulted in the cleavage of the Ti-C bond to form α-iodo enolate 32. Iodine also reacted with 31 to give the corresponding enolate 33 (eq. 20). Both complex 32 and 33 have been characterized by ^1H and ^{13}C NMR (Table I). Metal enolate complex of this type has never been observed directly. α-Halo-



R = H , ϕ (20)

32 . 33

genated Zn enolates are implied in the synthesis of 1,4-diketones from α,α'-dibromoketones mediated by Zn/Cu couple.[34] Noyori has also suggested the reactive intermediates in the iron carbonyls catalyzed coupling reactions between α,α'-polybromoketones and olefin substrates as α-bromoenolates of iron.[35] Elimination of the bromide ion forms an oxyallyl cation which can undergo cycloaddition reaction with 1,3-diene to yield seven-membered ring

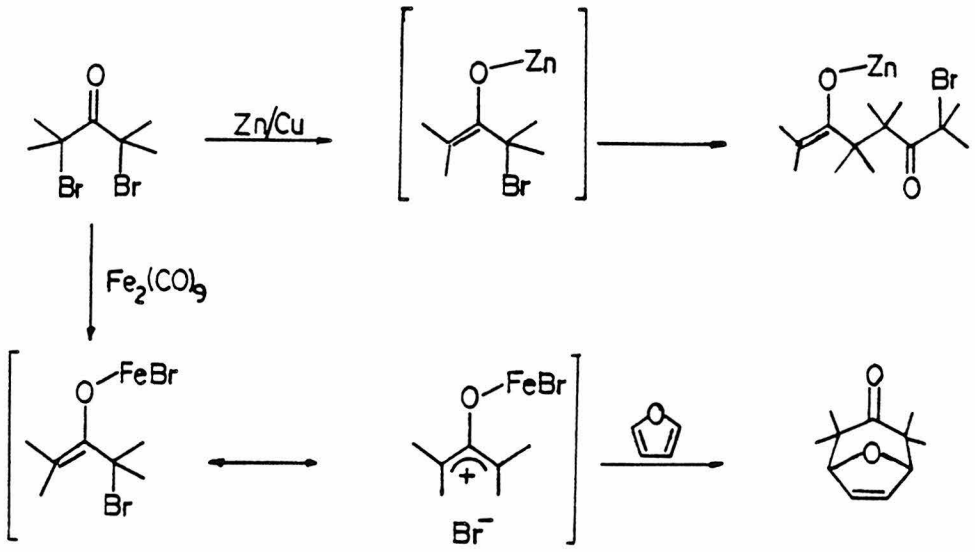
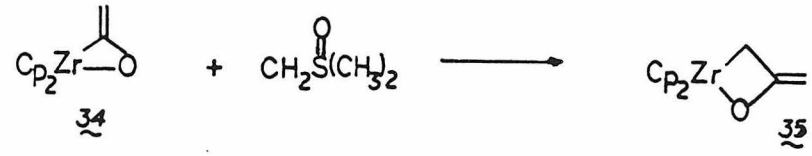


Figure 6

ketone (Fig. 6). Unfortunately, the α-iodoenolates of Ti (**32** and **33**) were unreactive toward furan. This is not surprising since both **32** and **33** are stable organometallic species whereas α-bromo Fe enolate is proposed as reactive intermediate. Furthermore, formation of an oxyallyl cation is less likely for an electron deficient d^0, Ti(IV), complex than d^6 Fe(II) species (Fig. 7).

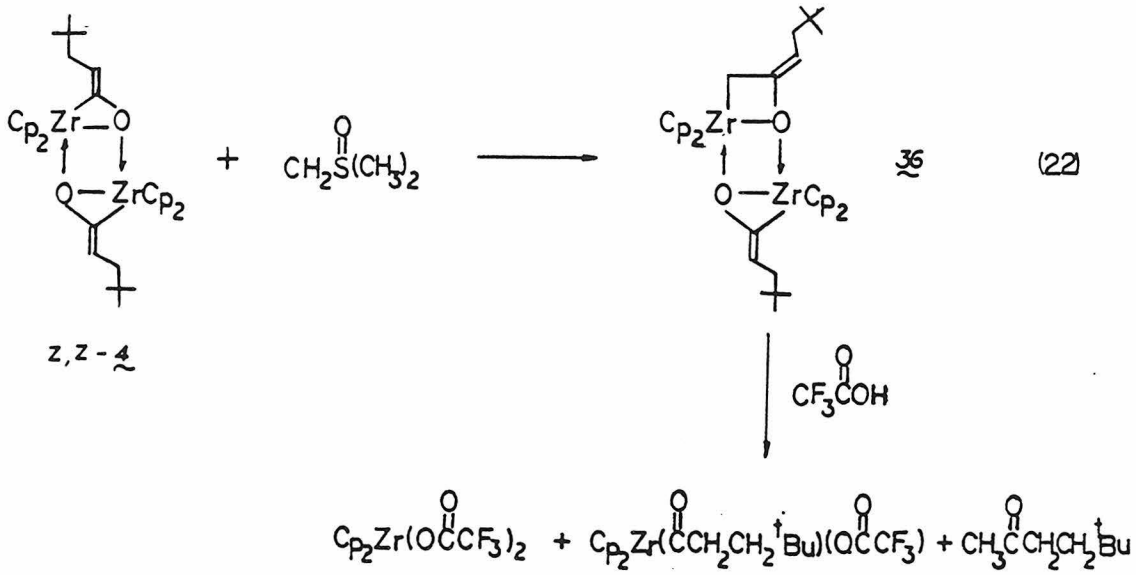
Figure 7

We have also investigated interactions of Zr ketenes with $CH_2SO(CH_3)_2$. Unlike its Ti counterpart, the $Cp_2Zr(\eta^2\text{-}OCCH_2\text{-}O,C)$ (**34**) complex reacted slowly even with large excess of ylide. After 30 h at room temperature, the ^1H NMR spectrum of the reaction mixture revealed a small but new set of Cp (6.11 ppm) and vinyl (3.98, 3.91 ppm) resonances in 10:1:1 ratio. Since the chemical shifts of the vinyl protons resembled the exo-methylene of **21**, the new species was assigned as $Cp_2\overline{ZrOCCH_2}=CH_2$ (**35**) (eq. 21). Reaction of the highly soluble Zr ketene Z,Z-**4** with excess $CH_2SO(CH_3)_2$ required heating(70°C overnight) for complete



(21)

consumption of the starting ketene complex. Spectral data and subsequent hydrolysis reaction suggested a dimer like complex (**36**) (eq. 22). Two sets of signals in equal intensities were observed with one correspond-

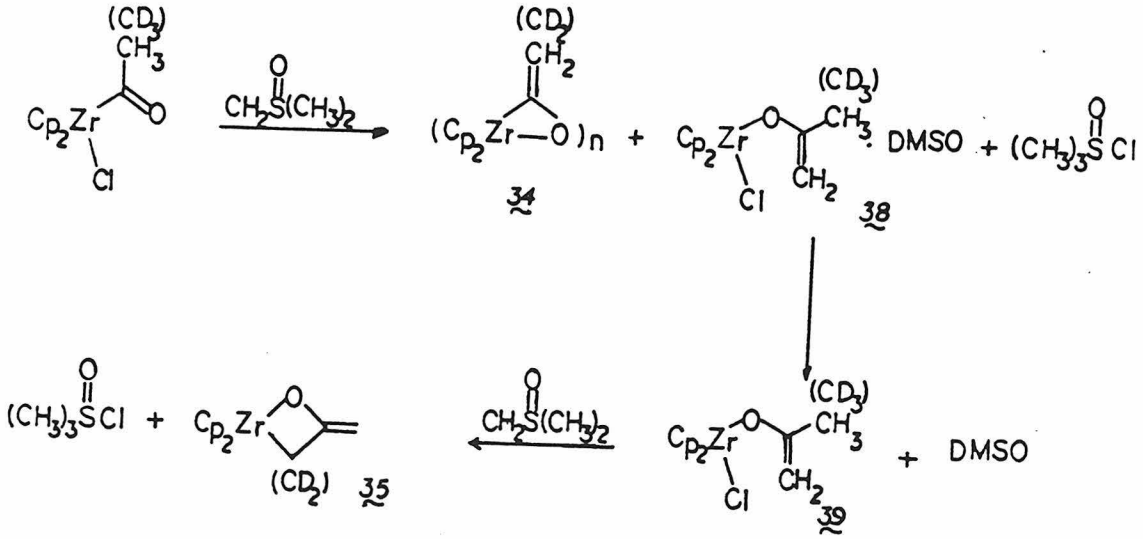


ing to the ketene part of **36**. The new upfield vinyl signal (4.16 ppm, triplet) was not due to the isomerization of ketene double bond (E,E-**4** has vinyl signal at 4.60 ppm), but from a zirconaoxacyclobutane. Hydrolysis of the reaction mixture confirmed the assignment.

Recall that our original objective was to examine enolate formation from coupling of sulfoxonium ylide with chloro acyl complex. We have shown that reactions of Ti acyls and $CH_2SO(CH_3)_2$ afford ketene complexes which react further with excess ylide to yield titanaoxacyclobutanes. Treatment of Zr chloro acyl $Cp_2Zr(COCH_3)Cl$ (**37**) with $CH_2SO(CH_3)_2$, however, gave a mixture of two products **34** and **38** at -20°C. Complex **34** was identified by comparison with an authentic sample. Based on the ^1H NMR data, complex **38** was considered as the DMSO adduct of the desired enolate (δ 6.17, Cp; 3.93, 3.81, CH_2; 1.75, CH_3; 1.68, DMSO). After warming the mixture to room temperature, the ^1H NMR of the reaction showed a decreasing **34**, presumably by formation of insoluble oligomers. The resonances corresponding to **38** were replaced by a new set of signals (5.98, Cp; 3.86, 3.83, CH_2; 1.68,

CH_3; 1.75, DMSO). We attribute this new species as the uncoordinate enolate **39** (Scheme VII). Treatment of complex **39** with excess $CH_2SO(CH_3)_2$ for two days (RT) resulted in the formation of another new species. It has the same ^1H NMR as complex **34** in the Cp and vinyl regions. Using deuterium labeled acyl $Cp_2Zr(COCD_3)Cl$ (d_3-**37**) in the reaction, the fate of the acyl methyl was monitored by ^2H NMR. The results are presented in Scheme VII. The Zr-methylene protons of **35** that were obscured by the DMSO signal in the ^1H NMR were located at δ 1.75 from the ^2H NMR spectrum of d_2-**35**. Reaction products **34** and **38** demonstrate that sulfoxonium ylides are capable of reacting with Zr chloro acyl complexes in both acid-base and nucleophilic fashions. The mechanism for the formation of zirconaoxacyclobutane from **39** is thought to proceed by deprotonation of the enolate methyl proton followed by intramolecular nucleophilic displacement of chloride.

Scheme VII



From the results obtained above, it appears that reactions of metal acyls with phosphonium and sulfoxonium ylides yield ketene or enolate complexes, depending on the metal and the ancillary ligands. More importantly, we have shown that coupling of neutral Ti and Zr ketene complexes with sulfoxonium ylides afford metallaoxacyclobutanes, a class of compounds that have been speculated on but seldom observed. The absence of these metallaoxacyclobutane species is probably due to the lack of synthetic routes, rather than their inherent instabilities. The corresponding carbon analog (metallacyclobutane) and the higher and lower homologs (metallaoxacyclopentane and metallaoxirane) are known for various transition metals. Metallaoxiranes are metal complexes of aldehydes, ketones and ketenes. Reactions of these complexes (especially Ti, Zr) with alkenes (and alkynes) have been shown to form metallaoxacyclopentanes (and -pentenes). Based on our observations in the coupling of ylides and metal ketenes, a general method may be in hand for the synthesis of other metallaoxacyclobutanes from metal aldehyde and ketone complexes. An alternate synthetic entry will be the deprotonation of chloro enolate complex (e.g., 39), followed by internal chloride displacement.

Figure 8

Table I. Spectroscopic Data.

Compound	NMR[a] (Chemical Shift, Multiplicity, Coupling Constants in Hz)			Others (IR or ^{31}P NMR)
	^1H	^{13}C	Assignment	
Z,E-4[b]		δ 187.8	C	
		186.0	C	
	δ 5.91 s	109.3	Cp	
	5.84 s	109.1	Cp	
	5.66 t J = 7.3	99.9	CH	
	4.60 t J = 7.3	99.4	CH	
	2.16 d J = 7.3	44.5	CH_2	
	1.24 d J = 7.3	43.9	CH_2	
	1.18 s	30.1	t-Bu	
	1.16 s	30.0	t-Bu	
		31.9	C	
		31.5	C	
E,E-4[b]		δ 186.0	C	
	δ 5.87	109.3	Cp	
	4.59 t J = 7.3	99.4	CH	
	2.13 d J = 7.3	43.9	CH_2	
	1.16 s	30.1	t-Bu	
		31.9	C	

Table I. Continued.

Compound	NMR[a] (Chemical Shift, Multiplicity, Coupling Constants in Hz) ^1H	^{13}C		Assignment	Others (IR or ^{31}P NMR)
E-5[c]		δ 193.1		C	^{31}P NMR[d] (C_7D_8, -20°C)
	δ 6.82-7.87 m			ϕ	δ 26.1
	5.96 s	107.0		Cp	
	4.70 t J = 6.8	86.4		CH	
	3.94 dq J = 6.8,11.7	16.0	J = 4.9	PCH_2	
	2.44 d J = 6.8	45.4		CH_2	
	1.22 s	30.4		t-Bu	
	1.18 t J = 6.8	6.9	J = 5.0	$PCH_2\underline{CH_3}$	
		33.0		C	
Z-5[c]		δ 194.5		C	
	δ 6.82-7.87 m			ϕ	
	5.98 s	107.1		Cp	
	5.41 t J = 6.8	84.4		CH	
	3.94 dq J = 6.8, 11.7	16.3	J = 49	$P\underline{CH_2}CH_3$	
	2.62 d J = 6.8	47.0		$\underline{CH_2}$	
	1.35 s	30.1		t-Bu	
	1.18 t J = 6.8	5.6	J = 5.0	$PCH_2\underline{CH_3}$	
		32.1		C	

Table I. Continued.

Compound	NMR[a] (Chemical Shift, Multiplicity, Coupling Constants in Hz) ^1H	^{13}C	Assignment	Others (IR or ^{31}P NMR)
$Cp_2Zr(OCCH_3=CH_2)CH_3$ **8**		δ 164.8	C	
	δ 5.80 s	110.9	Cp	
	3.82 m	86.2	CH_2	
	1.61 s	22.9	CH_3	
	0.32 s	21.4	$ZrCH_3$	
$Cp_2Zr(OCH^tBuCH_2COCH_3)CH_3$ **11**				
	δ 5.86 s		Cp	
	5.65 s		Cp	
	4.02 dd J = 6.3, 5.4		OCH	
	2.07 d J = 6.3		CH	
	2.06 d J = 5.4		CH	
	1.08 s		$COCH_3$	
	0.73 s		t-Bu	
	0.26 s		$ZrCH_3$	
$Cp_2Zr(OC\phi=CH_2)\phi$ **15**		δ 179.1	C	
			φ	
	δ 5.85 s	112.3	Cp	
	4.69 s	88.0	CH_2	
	4.24 s		CH_2	

Table I. Continued.

Compound	NMR[a] (Chemical Shift, Multiplicity, Coupling Constants in Hz) ^1H	^{13}C	Assignment	Others (IR or ^{31}P NMR)
$Cp_2Zr(OCCH_2CH_3{=}CH_2)CH_3$ **16**		δ 169.8	C	
	δ 5.78 s	110.8	Cp	
	3.88 s	84.6	$=CH_2$	
	3.81 s		$=CH_2$	
	1.92 q J = 7.0	30.0	CH_2	
	0.98 t J = 7.0	12.1	CH_3	
	0.35 s	21.5	$ZrCH_3$	
$Cp_2Zr(OCCH_2CH_2\phi{=}CH_2)CH_3$ **17**				
	δ 7.07 m		ϕ	
	5.80 s		Cp	
	3.69 s		$=CH_2$	
	3.66 s		$=CH_2$	
	obscured by sulfur ylide		$CH_2CH_2\phi$	
	0.44 s		$ZrCH_3$	
$[Cp_2Zr(\eta^2\text{-}OCCH_2\text{-}O,C)CH_3]^-PEt_4^+$ **18**[e]				
		δ 202.4 d	C	^{31}P NMR
	δ 5.36 s	104.8 dm J = 168	Cp	δ 39.0
	4.36 d J = 2.0	71.0 t J = 150	$=CH_2$	
	3.45 d J = 2.0		$=CH_2$	

Table I. Continued.

Compound	NMR[a] (Chemical Shift, Multiplicity, Coupling Constants in Hz) ^1H	^{13}C	Assignment	Others (IR or ^{31}P NMR)
18 continued	δ 2.37 dq J = 7.8, 13.7	δ 12.0 dt J = 159, 130	PCH_2CH_3	
	1.19 dt J = 7.8, 18.0	6.1 dq J = 6, 129	PCH_2CH_3	
	-0.61 s	10.6 2q J = 118	$ZrCH_3$	
$Cp_2Zr(OC\phi=CHCH_3)\phi$ 19	δ 7.00-7.61 m		φ	
	5.83 s		Cp	
	4.93 q J = 7.3		CH	
	4.92 q J = 7.3		CH_3	
	1.72 d J = 7.3		CH_3	
	1.71 d J = 7.3		CH_3	
$Cp_2\overline{TiOC}\overline{CH_2=CH_2}$ 21				IR (KBr)
		δ 182.6 t J = 5	C	$\nu_{C=C}$ 1588 cm^{-1}
	δ 5.70 s	113.2 dm J = 174.6	Cp	
	3.73 broad s	79.0 dd J = 155	$=CH_2$	
	3.64 d J = 1		$=CH_2$	
	1.80 broad s	55.4 dt J = 129.8	$TiCH_2$	
	(CD_2Cl_2, -20°C)			
	5.86 s		C	
	5.84 s		Cp	
	3.38 broad s		$=CH_2$	

Table I. Continued.

Compound	NMR[a] (Chemical Shift, Multiplicity, Coupling Constants in Hz) ^1H	^{13}C	Assignment	Others (IR or ^{31}P NMR)
21 continued	δ 3.28 d J = 1		$=CH_2$	
	2.23 d J = 10		$TiCH_2$	
	1.24 d J = 10		$TiCH_2$	
$Cp_2Ti(\eta^2\text{-}OCCH\phi\text{-}O,C)$ **27**	δ 7.63-6.98 m		φ	
	6.63 s		CH	
	5.66 s		Cp	
$Cp_2\overline{TiOCCH_2CH_2}=CH\phi$ **28**	δ 7.34 m		φ	
	5.79 s		Cp	
	5.14 broad s		CH	
	3.65 t J = 7.3		$TiCH_2$	
	1.96 t J = 7.3		CH_2	
$Cp_2\overline{TiOCC}H_2=CH\phi$ **29**[f]		δ 180.7	C	
	δ 7.26 m	128.6, 128.1, 126.4, 123.0	φ	
	5.96 s	113.3	Cp	
	4.90 s	97.8	CH	
	2.25 broad s	obscured by solvent	$TiCH_2$	

Table I. Continued.

Compound	NMR[a] (Chemical Shift, Multiplicity, Coupling Constants in Hz) ^1H	^{13}C	Assignment	Others (IR or ^{31}P NMR)
$Cp\overline{TiOCCH_2}=C\phi_2$ **31**		δ 178.0	C	
	δ 7.26 m	145.9, 144.4, 133.2 131.5, 125.3, 124.8	φ	
	5.89 s	113.4	Cp	
	4.44 s	113.3	Cp	
	2.54 d J = 10	108.6	$=CH_2$	
	1.91 d J = 10	55.1	$TiCH_2$	
$Cp_2Ti(OCCH_2I=CH_2)I$ **32**		δ 169.0	C	
	δ 6.00 s	116.2	Cp	
	4.24 s	89.1	$=CH_2$	
	4.06 s		$=CH_2$	
	3.37 s	7.8	CH_2I	
$Cp_2Ti(OCCH_2I=C\phi_2)I$ **33**		δ 164.0	C	
	δ 7.10 m	141.3, 141.8, 130.6, 128.7, 126.2, 125.5	φ	
		117.9	$C\phi_2$	
	5.92 s	116.7	Cp	
	4.29 s	8.6	CH_2I	

Table I. Continued.

Compound	NMR[a] (Chemical Shift, Multiplicity, Coupling Constants in Hz)			Others (IR or ^{31}P NMR)
	^{1}H	^{13}C	Assignment	
$Cp_2\overline{ZrOCCH_2}=CH_2$ **35**	δ 6.11 s			
	3.98 s			
	3.91 s			
	1.75 s (by ^{2}H NMR)			
$Cp_2Zr(\eta^2\text{-}OCCHCH_2{}^tBu\text{-}O,C)\cdot Cp_2ZrOCCH_2=CHCH_2{}^tBu$ **36**				
	δ 5.79 s		Cp	
	4.16 t J = 7.8		CH	
	2.23 d J = 7.8		CH_2	
	1.20 s		^tBu	
	obscured by DMSO		$ZrCH_2$	
	5.87 s		Cp	
	5.67 t J = 7.8		CH	
	2.17 d J = 7.8		CH_2	
	1.16 s		^tBu	
$Cp_2Zr(OCCH_3=CH_2)Cl\cdot(CH_3)_2SO$ **38**[g] (toluene-d_8, -20°C)				
	δ 6.17 s		Cp	
	3.93 s		CH_2	
	3.81 s		CH_2	

Table I. Continued.

Compound	NMR[a] (Chemical Shift, Multiplicity, Coupling Constants in Hz) ^1H	^{13}C	Assignment	Others (IR or ^{31}P NMR)
38 continued	δ 1.75 s		CH_3	
	1.68 s		$(CH_3)_2SO$	
$Cp_2Zr(OCCH_3{=}CH_2)Cl$ 39[h] (toluene-d_8, RT)				
	δ 5.98 s		Cp	
	3.86 s		$=CH_2$	
	3.83 s		$=CH_2$	
	1.68 s		CH_3	

[a] ^1H (90 MHz) and ^{13}C (22.5 MHz) NMR spectra taken in benzene-d_6 at ambient temperature unless otherwise noted. Chemical shifts are reported in δ relative to residue protons and carbons in the solvent. Coupling constants are reported in Hz. [b] ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra taken in toluene-d_8. [c] ^1H (400 MHz) and ^{13}C (22.5 MHz) NMR spectra recorded at -20°C in toluene-d_8. [d] ^{31}P NMR (33.6 MHz) spectrum obtained at -20°C in toluene-d_8 using H_3PO_4 as external reference. [e] ^1H (90 MHz), ^{13}C (22.5 MHz) and ^{31}P (33.6 MHz) NMR spectrum recorded in THF-d_8. [f]Spectra taken in CD_2Cl_2. [g] ^1H (90 MHz) NMR recorded at -20°C in toluene-d_8. [h] ^1H NMR taken in toluene-d_8.

Experimental Section

Salt free phosphorous ylides, $CH_2P\phi_3$ and $CH_3CHP\phi_3$, were prepared by Koster's method.[36] Sulfoxonium ylides were prepared by literature method[37] and stored in neat form at -40°C. Acyl complexes of Ti and Zr were prepared by carbonylation[38] of the corresponding alkyl compounds.[39] 3-^{t}Butyltitanacyclobutane[26] and $(Cp_2TiCH_2)_2$[40] were synthesized by known methods. Ketene and diphenyl ketene were prepared following established procedures.[41]

Dichloromethane was stirred over P_2O_5 and degassed. Pentane, hexane were stirred over concentrated H_2SO_4, then sodium-benzophenone ketyl. Benzene, diethyl ester, toluene and tetrahydrofuran were stirred over CaH_2 then sodium benzophenone ketyl. Solvents thus dried and deoxygenated were vacuum transferred into flask sealed with teflon screw valves and stored under argon. 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 line and dry box techniques. Argon used for Schlenk work was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. NMR spectra were recorded on a Varian EM-390 (90 MHz ^1H), a JEOL FX-900 (89.60 MHz ^1H, 13.76 MHz ^2H, 22.5 MHz ^{13}C, 36.2 MHz, ^{31}P), or a Brucker WM-500 (500.13 MHz ^1H, 76.76 MHz ^2H, 125 MHz ^{13}C). Variable temperature ^1H NMR experiments were performed on the JEOL FX-900. Infrared spectra were obtained on a Beckman IR 4240 spectrophotometer.

Elemental analyses were performed by Dornis and Kolbe of West Germany.

Reaction of $Cp_2Zr(COCH_2CH_2{}^tBu)Cl$ (3) with $\phi_3P{=}CHCH_3$. To a 5 mm NMR tube was loaded 18 mg (0.049 mmol) of $Cp_2Zr(COCH_2CH_2{}^tBu)Cl$ and 19 mg (1.3 equiv) of ϕ_3P-$CHCH_3$. The sample tube was cooled to -78°C and 0.4 mL of toluene-d_8 was added via syringe. The tube was agitated briefly at -20°C to give a homogeneous orange solution. **E-5:** ^1H NMR (0°C, 90 MHz) δ 6.82-7.87 (m, 15H), 5.96 (s, 10H), 4.70 (t, J = 6.8 Hz, 1H), 3.94 (dq, J = 6.8, 11.7 Hz, 2H), 2.44 (d, J = 6.8 Hz, 2H), 1.22 (broad s, 9H), 1.18 (t, J = 6.8 Hz, 3H); ^{13}C NMR (-10°C, 100 MHz) δ 193.1, 107.0, 86.4, 45.4, 33.0, 30.4, 16.0 (J_{C-P} = 49 Hz), 6.94 (J_{C-P} = 4.4 Hz); ^{31}P (-20°C, 36.2 MHz) δ 26.1. The reaction mixture was allowed to stand at 0°C (for hours or days) and a new set of signals appeared in the ^1H NMR spectrum. **Z-5:** δ 5.98 (s, 10H), 5.41 (t, J = 6.8 Hz, 1H), 2.62 (d, J = 6.8 Hz, 2H), 1.35 (broad s, 9H). After standing overnight at RT, white precipitates formed and the ^1H NMR of the pale yellow solution showed a mixture of Z,Z-, Z,E-, E,E-$[Cp_2Zr(\eta^2\text{-}COCHCH_2{}^tBu\text{-}C,O)]_2$.

Reaction of $Cp_2Zr(COCHCH_3)CH_3{\cdot}Na$[42] with $(CH_3)_3SOCl$. To a solution of 0.43 g (0.96 mmol) of 7·Et_2O[47] in THF at -40°C as added 0.10 mL (1.6 mmol) of MeI. The reaction was stirred at -40°C for 30 min then solvent was removed under vacuum at -20°C. The residue was redissolved in ether and was added 1 equiv of $NaN(TMS)_2$ in ether at -40°C. $SO(CH_3)_3Cl$ (1 equiv) was added and the reaction warmed to room temperature. The reaction mixture was filtered and ether was removed under vacuum to yield a liquid mixture of enolate and acyl complexes. ^1H NMR (C_6D_6, 90 MHz) δ 5.78 (s,

10H), 3.91 (broad s, 1H), 3.83 (s, 1H), 1.94 (q, J = 7.3 Hz, 2H), 0.99 (t, J = 7.3 Hz, 3H), 0.38 (s, 3H); δ 5.74 (s, 10H), 1.41 (q, J = 7.3 Hz, 2H), 0.76 (t, J = 7.3 Hz, 3H), 0.24 (s, 3H).

Preparation of $Cp_2Zr(OCCH_3{=}CH_2)CH_3$ (8). A solution of 0.25 g (1.0 mmol) of $Cp_2Zr(CH_3)_2$ and 0.11 mL (1.1 mmol) of $(CH_3)_2SOCH_2$ in 20 mL of toluene was stirred under 1 atm of CO for 30 min. Toluene and $(CH_3)_2SO$ were removed under vacuum overnight. The residue was distilled (60°C, 10^{-4} torr) to yield a clear liquid: ^1H NMR (C_6D_6, 90 MHz) δ 5.80 (s, 10H), 3.82 (m, 2H), 1.61 (s, 3H), 0.32 (s, 3H); ^{13}C NMR (C_6D_6, 90 MHz) δ 164.8, 110.9, 86.2, 22.9, 21.5.

Anal. calcd. for $C_{14}H_{18}OZr$: C, 57.29; H, 6.18. Found: C, 57.37; H, 6.25.

Reaction of $Cp_2Zr(COR)R'$ with ϕ_3PCH_2 or $(CH_3)_2SOCH_2$ (R = R' = φ, 12, R = CH_2CH_3, R' = CH_3, 13, R = $CH_2CH_2\phi$, R' = CH_3, 14). In a 5 mm NMR tube was loaded 20-25 mg of **12**, **13** or **14**, 1 equiv of ϕ_3PCH_2 (or $(CH_3)_2SOCH_2$) and 0.4 mL C_6D_6. The NMR spectra of the resulting solutions were recorded (Table I).

Reaction of $Cp_2Zr(COCH_3)CH_3$ (6) with $(CH_3CH_2)_3P{=}CHCH_3$. A solution of 0.26 g (1.0 mmol) of $Cp_2Zr(CH_3)_2$ and 0.1 mL (1.0 mmol) of neat $(CH_3CH_2)_3P{=}CHCH_3$ in 20 mL of benzene was stirred under 1 atm of CO. Pale yellow solids precipitated in 2 min. After 30 min at room temperature, the supernatant was removed via cannulation and the solids were washed twice with pentane (1.5 mL each) and dried under vacuum to yield **18**. ^1H NMR (THF-d_8, 90 MHz) δ 5.36 (s, 10H), 4.36 (d, J = 2 Hz, 1H), 3.45 (d, J = 2

Hz, 1H), 2.37 (dq, J = 7.8, 13.7, 8 Hz), 1.19 (dt, J = 7.8, 18.0 Hz, 12H), -0.61 (s, 3H). ^{13}C NMR (THF-d_8, 22.5 Hz) δ 202.4, 104.8 (dm, J = 168, 7.2 Hz), 71.0 (t, J = 150 Hz), 12.0 (dt, J = 159, 130 Hz), 10.6 (q, J = 118 Hz), 6.1 (dq, J = 6, 129 Hz). ^{31}P NMR (THF-d_8, 36.2 MHz) δ 39.0.

Reaction of $Cp_2Zr(CO\phi)\phi$ (12) with $Et_3P{=}CHCH_3$ and $\phi_3P{=}CHCH_3$. To a solution of 62 mg (0.15 mmol) of $Cp_2Zr(CO\phi)\phi$ in 5 mL of benzene was added 20 μL (0.20 mmol) of neat phosphorane via syringe. The reaction was stirred for 10 min at room temperature. Volatile material was removed under vacuum. The residue was extracted with ether. After the removal of ether under vacuum, the second residue was further extracted with pentane. Concentration of the pentane solution yield an oil (**19**): ^1H NMR (C_6D_6, 90 MHz) δ 7.00-7.61 (m, 10H), 5.83 (s, 10H), 4.92 and 4.93 (q, J = 6.3 Hz, 1H), 1.72 and 1.74 (d, J = 6.3 Hz, 3H).

To a 5 mm NMR sample tube was loaded with 21 mg (0.056 mmol) $Cp_2Zr\phi_2$, 17 mg (0.059 mmol) $\phi_3P{=}CHCH_3$, and 0.4 mL C_6D_6. The tube was capped with rubber septum and CO was introduced via syringe. The tube was shaken briefly and the ^1H NMR for the reaction was recorded. A similar spectrum as above was obtained.

Preparation of $Cp_2\overline{TiOCCH_2{=}CH_2}$ (21). To a suspension of **1** (1.0 g, 3.9 mmol) in 20 mL of benzene was added 0.79 g (8.6 mmol) of neat sulfoxonium methylide by syringe. Reaction mixture turned red and heat was generated. The resulting solution was filtered through a medium frit packed with celite (2 cm), then evaporated under vacuum to yield brick red solids. The solids were washed with pentane and cold ether, then dried under

vacuum overnight to yield 0.66 (77%) product: mp 145-148°C decomp; ^{1}H NMR (C_6D_6, 90 MHz, 20°C) δ 5.70 (s, 10H), 3.73 (broad s, 1H), 3.64 (d, J = 1 Hz, 1H), 1.80 (broad s, 2H); ^{1}H NMR (CD_2Cl_2, 90 MHz, -60°C) δ 5.86 (s, 5H), 5.84 (s, 5H), 3.38 (broad s, 1H), 3.28 (d, J = 1 Hz, 1H), 2.23 (d, J = 10 Hz, 1H), 1.24 (d, J = 10 Hz, 1H); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 182.6 (pseudo t, ^{2}J = 5 Hz), 113.2 (dm, ^{1}J = 174 Hz, ^{3}J = 6 Hz), 79.0 (dd, J = 155 Hz), 55.4 (dt, ^{1}J = 129 Hz, ^{3}J = 8 Hz); IR (nujol) 1588 (C=C) cm^{-1}. Mol. wt. 240 (calcd. 234).

Anal. calcd. for $C_{13}H_{14}OTi$: C, 66.68; H, 6.03. Found: C, 66.65; H, 5.98.

Reaction of $(Cp_2TiCH_2)_2$ (24) with CO. A 5 mm NMR sample tube loaded with 12 mg of $(Cp_2TiCH_2)_2$ and 0.4 mL C_6D_6 was sealed under 1 atm of CO. The reaction was monitored periodically by ^{1}H NMR.

Preparation of $Cp_2Ti(\eta^2$-OCCHφ-O,C) (27). A solution of $Cp_2Ti(COCH_2\phi)Cl$ (1.0 g, 3.0 mmol) $NaN(Si(CH_3)_3)_2$ (0.6 g, 3.3 mmol) in 30 mL of toluene was stirred at -30°C for 30 min. The reaction mixture was warmed to room temperature and solvent was removed under vacuum. The concentrated mixture was allowed to stand overnight. The yellow precipitates were collected by filtration and washed with pentane, ether and dried under vacuum to yield 0.8 g (include 3.0 mmol of NaCl, 69%) of product: ^{1}H NMR (C_6D_6, 90 MHz) δ 7.63-6.98 (m, 5H), 6.63 (s, 1H), 5.66 (s, 10H). Complex **27** is sparingly soluble in aromatic solvents. In the presence of $P(CH_3)_3$, **1** is solubilized to give ^{1}H NMR (C_6D_6) δ 7.48 (m, 10H), 6.97 (s, 1H), 5.18 (s, 10H).

Reaction of 27 with $(CH_3)_2SOCH_2$. To a 5 mm NMR sample was loaded a mixture of **27** and NaCl in 0.4 mL CD_2Cl_2. $(CH_3)_2SOCH_2$ (5 μL, 1.3 equiv) was added via syringe. ^1H NMR spectra of the reaction were recorded periodically. Reaction reached 90% completion after 7 h at room temperature. ^1H NMR (90 MHz) δ 7.27 (m, 5H), 5.96 (s, 10H), 4.91 (s, 1H), 2.26 (broad s, 2H). Preparative scale reaction was carried under similar condition (400 mg of 4:1 mixture of **27** and NaCl, 0.13 mL $(CH_3)_2SO{=}CH_2$ in 10 mL CH_2Cl). Solvent $CHCl_2$ was removed under vacuum and the residue was washed with ether. The residue (containing NaCl) was redissolved in CH_2Cl_2 and filtered through a pad of celite on a medium glass frit. The filtrate was concentrated to a dark red solid which was washed with pentane and dried under vacuum. The product decomposed in solution overnight to unidentified material. ^1H NMR spectrum of the solid is the same as above. ^{13}C NMR (CD_2Cl_2, 22.5 MHz) δ 180.7, 128.6, 128.1, 126.1, 123.0, 113.3, 97.8.

Reaction of 27 with C_2H_4. Ethylene gas was introduced via syringe to a 5 mm NMR sample tube loaded with 10 mg of **27** in 0.4 mL C_6D_6 and capped with a septum. Reaction turned from yellow to deep green. ^1H NMR (90 MHz) δ 7.34 (m, 5H), 5.79 (s, 10H), 5.14 (broad s, 1H), 3.65 (broad t, J = 7.3 Hz, 2H), 1.96 (t, J = 7.3 Hz, 2H).

Preparation of $Cp_2\overline{TiOCCH_2{=}C\Phi_2}$ (31). A. From ^{t}Bu-titanacyclobutane. A solution of 0.55 g (2.0 mmol) of titanacyclobutane, 0.39 g (4.0 mmol) of diphenyl ketene in 4 mL of toluene was heated at 80°C for 10 min. Purplish red solids precipitated. The dark green supernatant was removed by cannulation. The solids were washed with pentane and ether then

dried under vacuum overnight (71% yield). Recrystallization from ether dichloromethane or toluene yielded thin plates: mp 186-189°C decomp; ^{1}H NMR (C_6D_6, 90 MHz) δ 7.26 (m, 10H), 5.89 (s, 5H), 5.44 (s, 5H), 2.54 (d, J = 10 Hz, 1H), 1.91 (d, J = 10 Hz, 1H); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 55.1, 108.6, 113.3, 113.4, 124.8, 125.3, 131.5, 133.2, 144.4, 145.9, 178.0.

Anal. calcd. for $C_{25}H_{22}OTi$: C, 77.72; H, 5.74. Found: C, 77.69; H, 5.76.

Reaction of 21 and 31 with I_2. To a 5 mm NMR sample tube loaded 10-12 mg of **21** (or **31**) dissolved in 0.4 mL of C_6D_6 was added a solution of 1 equiv of I_2 in 0.2 mL of C_6D_6 via syringe. **21** + I_2: ^{1}H NMR (C_6D_6, 90 MHz) δ 6.00 (s, 10H), 4.24 (broad s, 1H), 4.06 (s, 1H), 3.37 (s, 2H); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 169.0, 116.2, 89.1, 7.82. **31** + I_2: ^{1}H NMR (C_6D_6, 90 MHz) δ 7.10 (m, 10H), 5.92 (s, 10H), 4.29 (s, 2H); ^{13}C NMR (C_6D_6, 22.5 MHz) δ 164.0, 141.3, 141.8, 130.6, 128.7, 126.2, 125.5, 117.9, 116.7, 8.56.

Reaction of $Cp_2Zr(\eta^2$-OCCH$_2$-O,C) (34) with $(CH_3)_2SOCH_2$. To a NMR sample tube was loaded with ~15 mg **34**, NaCl mixture, large excess $(CH_3)_2SOCH_2$ and 0.4 mL C_6D_6. The reaction tube was capped with a spectrum and monitored periodically by ^{1}H NMR. After 30 h at room temperature, a new set of signals appeared in the ^{1}H NMR spectrum: δ 6.11 (s, 10H), 3.99 (s, 1H), 3.92 (s, 1H).

Reaction of Z,Z-4 with $(CH_3)_2SOCH_2$. To a 5 mm NMR sample tube was added 12 mg of Z,Z-**4**, 2 equiv of $(CH_3)_2SOCH_2$ and 0.4 mL C_6D_6. The tube was capped with a septum and heated to 80°C overnight. ^{1}H NMR (90 MHz) δ 5.87 (s, 10H), 5.79 (s, 10H), 4.16 (t, J = 7.8 Hz, 1H), 2.25 (d, J = 7.8

Hz, 2H), 2.17 (d, J = 7.8 Hz, 2H), 1.20 (s, 9H), 1.16 (s, 9H).

Reaction of $Cp_2Zr(COCH_3)Cl$ (37) with $(CH_3)_2SOCH_2$. To a 5 mm NMR sample tube was loaded 15 mg of $Cp_2Zr(COCH_3)Cl$ and 0.4 mL toluene-d_8. The tube was capped with rubber septum and cooled to -20°C. One equiv (4.2 μL) of $(CH_3)_2SOCH_2$ was added via micro-syringe and white solids precipitated. ^1H NMR spectrum of the reaction mixture at -20°C showed: δ 5.83 (s, 10H), 5.33 (s, 1H), 4.53 (s, 1H), 6.17 (s, 10H), 3.93 (s, 1H), 3.81 (s, 1H), 1.75 (s, 3H), 1.67 (s, 6H, DMSO). The reaction was warmed to room temperature. After 1 h ^1H NMR of the reaction revealed a different set of signals: δ 5.98 (s, 10H), 3.86 (s, 1H), 3.83 (s, 1H), 1.76 (s, 6H), DMSO), 1.68 (broad s, 3H). The same spectrum was obtained after 12 h at room temperature. Large excess of $(CH_3)_2SOCH_2$ (10-20 equiv) was added to the reaction mixture. After two days at room temperature, the ^1H NMR spectrum reaction mixture exhibited signals at δ 6.11 (s, 10H), 3.98 (s, 1H), 3.91 (s, 1H), as the major product and 5.80 (s, 10H), 3.81 (s, 1H), 3.66 (s, 1H) as the minor product.

References and Notes

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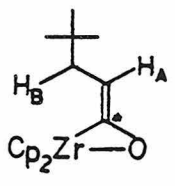
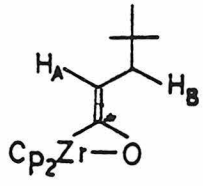
($^3J_{C-H}$).



$J_{C^*-H_A}$ = 8.8 Hz
$J_{C^*-H_B}$ = 7.3 Hz

Z isomer



$J_{C^*-H_A}$ = 11.2Hz
$J_{C^*-H_B}$ = 5.5Hz

E isomer

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